

Novel Polymeric Surfactants to Stabilise Emulsions

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Submitted in partial fulfilment of the requirements for the
degree of *Doctor of Philosophy*

Declaration of Originality

I hereby declare that this PhD thesis is my work. Any information that is not belonging to my work is appropriately referenced.

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ABSTRACT

This PhD project aims to synthesise polymeric surfactants, characterise their aqueous solution properties and emulsifying abilities, and obtain a structure-property relationship. In this study, different polymeric surfactants were synthesised using Group Transfer Polymerisation (GTP) method.

The first project of this PhD thesis includes the synthesis of two series of diblock copolymers and the characterisation of their aqueous solution properties and emulsifying abilities. In order to make a comparison between the two-polymer series, the molar mass (MM), composition and hydrophobic monomer kept the same, whereas different hydrophilic monomer used for each polymer series. Thus, in both series, ethyl methacrylate (EtMA) was used as a hydrophobic monomer, and poly(ethylene glycol) methyl ether methacrylate (PEGMA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) was used as a hydrophilic monomer in Polymer series 1 and 2, respectively.

The second project of this PhD thesis includes the synthesis of triblock copolymers using the same monomers studied in the previous project; PEGMA, EtMA and DMAEMA. The architecture of the linear triblock copolymers is ABC (A is PEGMA, B is EtMA, and C is DMAEMA), and it kept the same in the whole project. Moreover, the MM and composition of the copolymers kept the same as with the previous chapter to observe the effects of diblock and triblock copolymers on their properties.

The third project of this PhD thesis includes the synthesis of seven different architecture of copolymers varying from statistical to gradient, diblock, triblock copolymers. The copolymers were based on hydrophilic DMAEMA and hydrophobic *n*-butyl methacrylate units. The MM and composition kept constant to observe the effect of architecture on the emulsifying and aqueous solution properties.

It was found that the all the polymers were successfully synthesised and the effective pK_a (if any), cloud points, critical micelle concentrations (CMC) and hydrophile-lipophile balance (HLB) values, and hydrodynamic diameters were affected by the structure of the polymers, such as composition and MM. Most importantly, all polymeric surfactants were found to emulsify methyl laurate in water, and the stability of the emulsions was found to strongly depend on the architecture, composition and MM of the polymers.

ACKNOWLEDGEMENTS

Firstly, I want to thank Dr Theoni K. Georgiou for allowing me to do a PhD and giving me advice, help, guidance and encouragement throughout my PhD. In addition to this, I am incredibly thankful for her understanding and support.

I would like to thank the Department of Materials, Imperial College London, to fund my PhD project.

I want to thank my colleagues, Joana and Thanos, for having fun at lunch. Thanks for handling my negative mood and opening a Birsen Support Group on Whatsapp. Hopefully, after submitting my thesis, I will be a happier person. Thanks to my colleague Xinmo, who started to PhD journey same time as me. I will miss taking selfies together in the lab and miss the incredible and unique presentation we had in our second year. Also, I would like to thank John Natan for his support, sending me funny videos and bringing me to very nice restaurants.

Also, I would like to thank my flatmate Berke for his patience and always being there for me when I need a hug. Also, thank you for making me laugh every day. I would like to thank to the funniest and cutest couple, Ulker and Hacu for their endless support. I would like to thank my crazy friend, Bebeksu (Ismo), for making me smile every time I talk to him. Thank you for going out with me and helping me to forget my problems with your positive energy. I am feeling very lucky to have a friend like you. I hope you will always be in my life Bebeksu.

I want to thank my cousin Ipek for encouraging me to do a PhD and my auntie Zulfiye for her love, delicious food and endless support. In addition to this, I would like to thank my cousin Cansu for listening to me and supporting me throughout my PhD.

I want to thank David Poussin for sharing his knowledge, helping me understand how to use most machines (especially UV-VIS) throughout my PhD. I am sorry for asking you many questions about microscopy. You were always kind and patient to me! Also, I have really appreciated your support and motivational speech during the last months of my PhD.

I want to thank my best friend, sister, Bebisim (Dr Anna Constantinou). In four years, I had many up and down, and you were always next to me, supporting and giving me strength with your presence bebisim. You are a truly wonderful friend, and I think there is no word to explain how much I appreciate your friendship. Thank you so much for making lab and polymerisations fun. I will miss our dancing to Cypriot songs, very loud laughs and having communication with our eyes. I had a perfect time in Crete. Thank you so much for making it memorable and for

your patience in taking me hundreds of photos. I hope we can go again to one of the Greek islands, Bebisim. I will leave Imperial, but I will always be with you, Bebisim, even if we live in different countries.

Finally, I would like to thank to my family for their infinite love and support. Firstly, I would like to thank my grandmother, Yuksel and grandfather, Cafer, for their endless love. I promise I will make you proud. Next, I would like to thank my father, Hasan, who always supported me in my studies since I moved to the UK. Hopefully, you will have a chance to come to my graduation and visit London for the millionth time. I would like to thank my brother, Halit, for his endless love, advice, encouragement and for believing me more than I believe in myself. I promise I will do what you wanted me to do after I finish my PhD and I will always be by your side. Finally, I would like to thank the woman of my life, my idol, my mum, Filiz. There are no words how to express my appreciation and love to you. I couldn't have come so far without your support. I love you, mum, and thank you so much for being an amazing mother.

PUBLICATIONS AND PRESENTATIONS

The information below shows the publications and presentations I did during my PhD studies.

Somuncuoğlu, B.; Lee, Y.L.; Constantinou, A.P.; Poussin, D.L.M.; Georgiou, T.K. “[Ethyl Methacrylate Diblock Copolymers as Polymeric Surfactants: Effect of Molar Mass and Composition](#)” *Eur. Polym. J.* **2021**, 154, 1-11. DOI: 10.1016/j.eurpolymj.2021.110537

Constantinou, A.P.; Zhang, K.; Somuncuoğlu, B.; Feng, B.; Georgiou, T.K.; “[PEG-based methacrylate tetrablock terpolymers: how does the architecture control the gelation?](#)” *Macromolecules.* **2021**, X, XXX-XXX. ISSN: 0024-9297

Constantinou, A.P.; Patias, G.; **Somuncuoğlu, B.**; Brock, T.; Lester, D.W.; Haddleton, D.M.; Georgiou, T.K. “[Homo- and co-polymerisation of di\(propylene glycol\) methyl ether methacrylate – a new monomer](#)” *Polym. Chem.* **2021**, X, XXX-XXX. DOI: 10.1039/D1PY00444A

Poster Presentations

Somuncuoğlu, B.; Georgiou, T.K. “Novel Polymeric Surfactants to Stabilise Emulsions”, European Polymer Congress (EPF 2019), Creta Maris Convention Centre and Beach Resort, Hersonissos Heraklion Crete, Greece, June 2019.

Somuncuoğlu, B.; Georgiou, T.K. “Fabrication of Particles using Block copolymers by Emulsion Templating Method”, 2nd NSFC-RSC Symposium Novel Polymer Synthesis to Solve Tomorrow’s Problems, University of Warwick, Coventry, United Kingdom, December 2018.

Somuncuoğlu, B.; Georgiou, T.K. “Fabrication of Particles using Block copolymers by Emulsion Templating Method”, 4th London Polymer Group Symposium, Dental Institute, King’s College London, United Kingdom, November 2018.

Somuncuoğlu, B.; Georgiou, T.K. “Fabrication of Particles using Block copolymers by Emulsion Templating Method”, Postgraduate Research Day, Imperial College London, United Kingdom, March 2018.

Somuncuoğlu, B.; Longbottom B, Bon S.A.F. “Synthesis of Surface-Textured Polymer Colloids”, Warwick Polymer Conference 2016, University of Warwick, Coventry, United Kingdom, July 2016.

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LIST OF ABBREVIATIONS

AA: Acrylic acid

APG1: Alkyl polyglycoside

ATRP: Atom transfer radical polymerisation

BuMA: Butyl methacrylate

CaH₂: Calcium hydride

C₁₂E₃: Polyoxyethylene 3-lauryl ether

CDCl₃: Deuterated chloroform

CMC: Critical micelle concentration

Cryo-TEM: Cryogenic transmission electron microscopy

D₂O: Deuterium oxide

DI: Deionised

DLS: Dynamic light scattering

DMAEMA: 2-(Dimethylamino) ethyl methacrylate

DPPH: 2,2-diphenyl-1-picrylhydrazyl hydrate

EC: Emulsifiable concrete

EOR: Enhanced oil recovery

Et₃N: Triethylamine

EtMA: Ethyl methacrylate

GPC: Gel permeation chromatography

GTP: Group transfer polymerisation

HeMA: Hexyl methacrylate

HEMAGI: 2-(D-glucosamin-2-N-yl)carboylethyl methacrylate

HEUR: Ethoxylated urethanes

HLB: Hydrophilic-lipophilic balance

HMPAM: Hydrophobically modified polyacrylamides

^1H NMR: Proton nuclear magnetic resonance spectroscopy

KCNS: Potassium thiocyanate

$\text{K}_2\text{S}_2\text{O}_8$: Potassium per sulfate

LMA: Lauryl methacrylate

MC: Microcapsule

ME: Microemulsions

MM: Molas mass

MMA: Methyl methacrylate

MMD: Molar mass distribution

MTS: Methyl trimethylsilyl dimethylketene acetal

NMP: Nitroxide-mediated polymerisation

O/W/O: Oil-in-water-in-oil emulsion

O/W: Oil-in-water emulsion

PAA: Polyacrylic acid

PDI: Polydispersity

PDMS: Poly(dimethyl siloxane)

PEG: Poly(ethylene glycol)

PEGA: Poly(ethylene glycol) methyl ether acrylate

PEGMA: Penta(ethylene glycol) methyl ether methacrylate

PEO: Poly(ethylene oxide)

PFG: Pulsed field gradient

PMMA: Poly(methyl methacrylate)

PS: Poly(styrene)

PTFE: Polytetrafluoroethylene

PVP: Polyvinylpyrrolidone

RAFT: Reversible addition-fragmentation chain-transfer polymerisation

RDRP: Reversible-deactivation radical polymerisation

SANS: Small-angle neutron scattering

SAXS: Small-angle x-ray scattering

SC: Suspension concrete

SDS: Sodium dodecyl sulfate

TBABB: Tetrabutylammonium bibenzoate

TBCs: Tapered block copolymers

TMAEMA: Quaternized trimethyl-amino ethyl methacrylate

THF: Tetrahydrofuran

VOCs: Volatile organic compounds

W/O/W: Water-in-oil-in-water emulsion

W/O: Water-in-oil emulsion

WP: Wettable power

$c(\infty)$: is the solubility of the bulk

$c(r)$: Solubility of the particle

$\bar{D}$: Dispersity indices

r : Radius of the drop

R : Molar gas constant

T : Temperature

V_m : Molar volume of the dispersed phase

η_0 : Newtonian shear viscosity

ρ : Density of the dispersed phase

ρ_0 : is the density of the continuous phase

d_{hs} : Hydrodynamic diameter

W_h : weight fraction of the hydrophilic component

W_l : weight fraction of the hydrophilic component

ϕ cream: Volume fraction of the cream phase

Dedicated to my mother, father and brother

CHAPTER 1: INTRODUCTION

Colloids are playing an important role in biological systems, nanomedicines, nanotechnology and many other different fields that we use in our everyday lives.¹ The origin of colloids borrowed a century ago from the Greek word "kolla" meaning glue-like.² Colloids are a two-phase system, one of the phase is discrete particles, and they are dispersed in the continuous phase. The continuous phase and dispersed particles could be solid, liquid and gas. An example of colloid dispersions that we come across in everyday life includes milk, mayonnaise, butter, cosmetic and pharmaceutical lotions, toothpaste, coffee creamers, polystyrene foam, stained glass, beer head, inks and many more.²⁻⁴ For instance, mayonnaise, milk, cosmetic and pharmaceutical lotions are examples of dispersion of liquid in the liquid medium, whereas ink is an example of dispersion of solid particles in the liquid medium.

1.1 Emulsions

An emulsion is a subclass of colloids used in pharmaceuticals, food, cosmetics, healthcare and agricultural systems.⁵ Specifically, an emulsion is a heterogenous system consisting of two immiscible liquids such as oil and water. One liquid is dispersed in the other liquid (called continuous phases) as a microscopic droplet or colloidal size.⁶ The appearance of emulsion (or macroemulsions) is opaque and the radius of the particle size distribution ranges between 1 and 100 μm .^{7,8} In most situations, one of the phase is water or an aqueous solution and the other phase is an organic liquid.^{9,10} In the literature, the organic phase is often referred to as the "oil" phase and hydrocarbons are one of the most commonly used oil phases.

Emulsions are divided into two main types (see **Figure 1.1**): 1) oil-in-water (o/w) and 2) water-in-oil (w/o).⁹ In oil-in-water emulsions, the oil phase is dispersed as a small droplet in the water (continuous) phase whereas, in water-in-oil emulsions, the water phase is dispersed as a small droplet in the oil (continuous) phase. Oil-in-oil emulsions,^{7,5} water-in-water emulsions¹¹ and multiple emulsions such as o/w/o and w/o/w¹² (oil-in-water-in-oil and water-in-oil-in-water) have also been reported in the literature even though they are not that common. Multiple emulsions are made of large droplets that are dispersed in the continuous phases but this large droplets are consisted of smaller/tiny droplets.¹³ For instance, water-in-oil-in-water emulsion consists of water droplets suspended in larger oil droplets that are suspended in a continuous water phase. Depending on the size and the stability of droplets, emulsions are classified into three categories; 1) macroemulsions (classical emulsions, 1-100 μm), microemulsions (10-100 nm) and nanoemulsions (20-500 nm).⁸ The shape of the droplets is spherical for all three types

of emulsions, and microemulsions have an extra lamellar shape. This PhD thesis is focused on the macroemulsions.

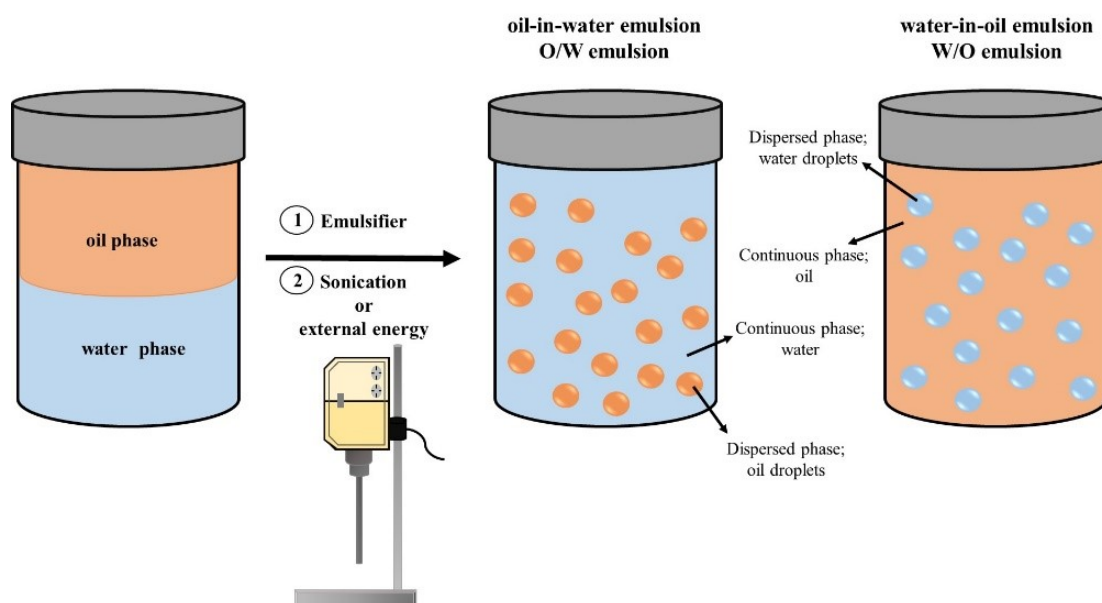


Figure 1.1. Schematic representation of oil-in-water (O/W) and water-in-oil (W/O) emulsion. In O/W emulsion, the oil droplets (orange) are dispersed in the continuous phase, which is the water phase. In W/O emulsion, the water droplets (blue) are dispersed in the continuous phase, which is the oil phase.

1.1.1 Stability of Emulsions

Emulsions are kinetically stable systems and they have tendency to break.¹⁴ If the emulsion system is stable, there is no detectable change in the spatial arrangement, number as well size-distribution of the drops within the experimental timescale.¹⁵ Depending on the conditions, the experimental timescale can change from seconds or years.⁶ Emulsions are thermodynamically unstable systems, and droplets rearrange themselves to separate to form two bulk phases to decrease the interfacial tension.^{16,17} The well-known and studied mechanisms that are responsible for emulsion destabilisation, shown in **Figure 1.2**, are: flocculation, Ostwald ripening, creaming, sedimentation as well as coalescence. Each destabilisation mechanisms involves various surface forces, which makes the analysis more complicated.¹⁸ Those destabilisation mechanisms occur either simultaneously or consecutively depending on the conditions and makes the analysis more complicated. In reality, those destabilisation mechanisms occur in combination, which means that one mechanism promotes or enhance the other. However, one of those destabilisation processes is enough to make the emulsion system

unstable.¹⁵

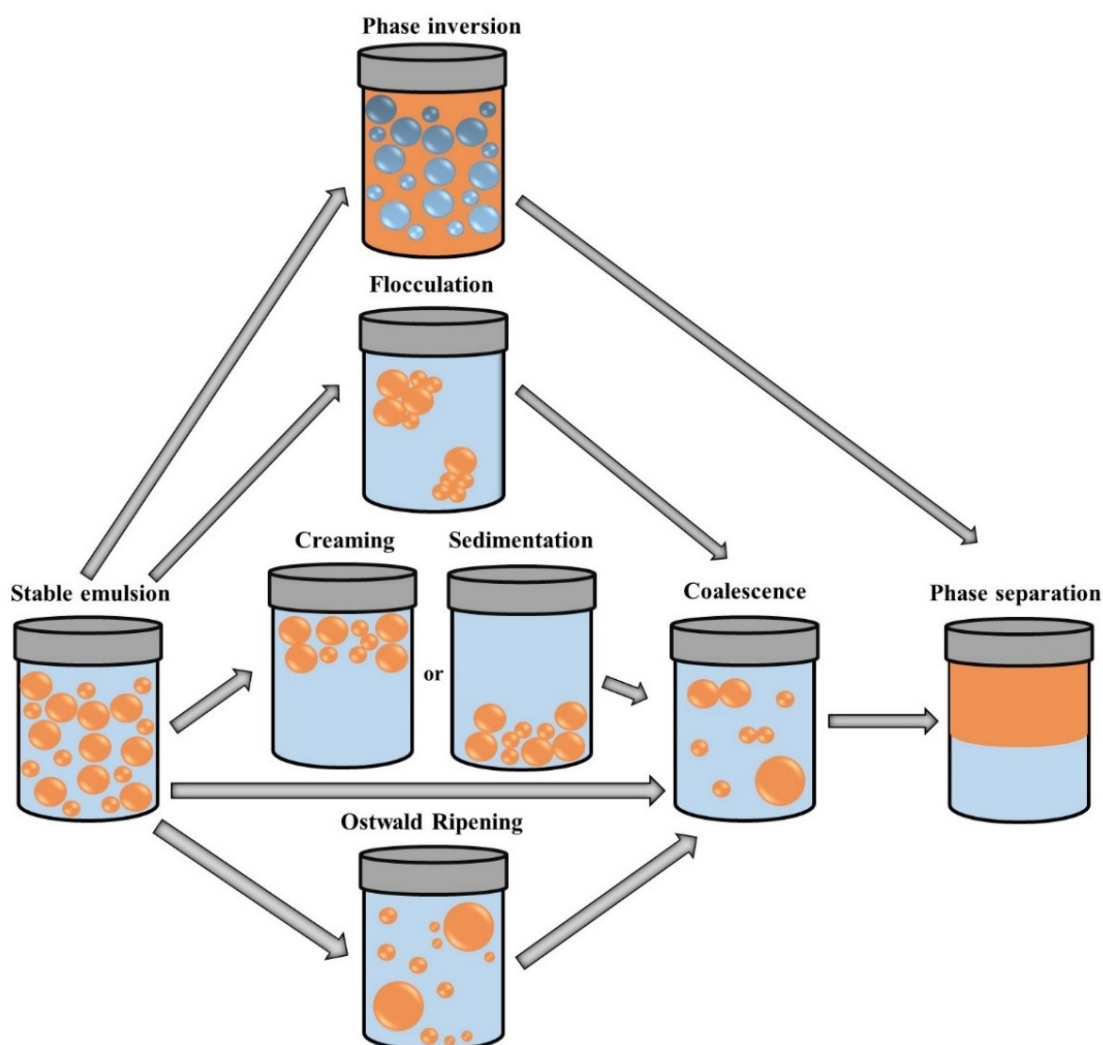


Figure 1.2. The schematic representation of instability mechanisms of emulsions. The orange and blue colour represent the oil phase and water phase, respectively.

Before discussing each instability mechanism, it is important to give some brief information on what happens when two emulsion droplets are close to each other. When two emulsion droplets start to approach each other, the interstitial film or thin lamellar film of the continuous phase will form between the emulsion droplets.¹⁹ The film starts to get thicker, and when it reaches its critical thickness, solvent molecules and adsorbed emulsifier molecules starts to squeeze out.¹⁹ If the emulsifier is not sufficiently adsorbed on the surface of the emulsion droplet, it will desorb, and the interfacial concentration decreases which results lowering the stabilizing effect and results merging two droplets each other.¹⁹ On the other hand, if the emulsifier adsorbs strongly on the interface, the osmotic forces play a vital role. It will bring solvent molecules as well as counter ions back to the interstitial region, and this will prevent

droplets from merging. The different destabilisation mechanisms of emulsions are explained in the following section in more detail.

1.1.1.1 Creaming and Sedimentation

In an emulsion system, there are external forces such as centrifugal and gravitational forces. When these forces are higher than the Brownian motion of droplets, the concentration gradient increases and droplets move to the bottom if their density is bigger than the medium. This phenomenon is called sedimentation. On the other hand, if droplets move rapidly to the top under gravity, it means that the density of droplets are smaller than the medium, and this is called creaming.¹⁸ Note that, in both processes, there is no change in the size of the emulsion droplets.⁶ The creaming speed of isolated spherical drop (v_s) moving through in the continuous phase is given by Stokes' Law (see **equation 1.1**).¹⁵ Please note that this equation is valid for diluted emulsions in the absence of flocculation. The creaming or sedimentation of the diluted emulsion system could be inhibited by: 1) choosing the density-matched bulk phases or choosing phases with small density difference 2) reducing the size of the average droplets 3) increasing the viscosity of the continuous phase.^{15,18} Emulsion drops less than a micron in diameter could be achieved by applying high energy to the system using a homogeniser. The density of the dispersed and continuous phase could be matched by adding sugar or ethanol to the water phase. The viscosity of the emulsion system could be modified by adding starches or gums to thicken the continuous phase.

$$v_s = \frac{2r^2 (\rho_0 - \rho)g}{9\eta_0} \quad \text{Equation 1.1}$$

where r is the radius of the drop, ρ is the density of the dispersed phase and ρ_0 is the density of the continuous phase, g is the acceleration because of the gravity and η_0 is the Newtonian shear viscosity of the continuous phase.

1.1.1.2 Flocculation

Flocculation is the aggregation of droplets into larger units due to the presence of the van der Waals attraction between the emulsion droplets without change in droplet size distribution.^{6,18} The van der Waals attraction is inversely proportional to the distance between the two droplets (h). When there is no sufficient repulsion between the two droplets to keep them apart, the aggregation happens, and it may be strong (not easily reversible) or weak (reversible) depending on the strength of the attractive energy existing.²⁰ The formation of the flocs increases the chance of formation of the creaming because flocs rise faster compared to the

individual drops due to the larger effective radius.¹⁵ The flocculation can be overcome by: 1) the addition of ionic surfactants, which provide an electrical double layer between the two droplets, hence the formation of repulsive energy between the droplets and 2) the addition of non-ionic surfactants.

1.1.1.3 Ostwald ripening

In a polydisperse system, Ostwald ripening takes place due to the solubility difference between the small and large droplets.¹⁸ The small droplets have a higher solubility than the large droplets due to the effect of the Laplace pressure on small droplets.²⁰ The Laplace pressure causes an increase of the pressure inside the droplet and results in diffusion of the molecules from the high-pressure region to low-pressure regions.⁷ This results to the tiny droplets dissolving, diffusing through the continuous phase and being deposited on the larger droplets. The solubility of spherical particles increases with a decrease in size, and the relationship is given by Kelvin equation:¹⁵

$$c(r) = c(\infty) \exp\left(\frac{2\gamma V_m}{rRT}\right) \quad \text{Equation 1.2}$$

Where $c(\infty)$ is the solubility of the bulk (only a planar interface), $c(r)$ is the solubility of the surrounding a particle of radius r , γ is the interfacial tension between the continuous and dispersed phase, V_m is the molar volume of the dispersed phase, R is the gas constant, and T is the absolute temperature. Therefore, the high solubility of droplets due to their small radius, dissolved and diffuse through the aqueous phase and deposited on the larger droplets. In theory, Ostwald ripening should be completed by the formation of one single drop due to the merging of all droplets into one drop. However, in real-time, this does not happen because the rate of droplet growth decreases when droplet size increases. Finally, the size distribution of the emulsion drops increases.¹⁸ The size growth could be inhibited by the addition of a third component that has extremely low solubility in the continuous phase whereas soluble in the dispersed phase.⁷

1.1.1.4 Coalescence

Coalescence is the most crucial destabilisation mechanism of emulsions and it attracts scientific attention by both academic and industrial research.¹⁹ Coalescence is an irreversible process; it occurs when two or more droplets fuse to form a single large droplet.¹⁵ The driving force for the formation of coalescence is thinning and disruption of the film of the continuous phase that separate two droplets.^{15,20} When two droplets are separated with approximately 1 μm distance,

interfaces of droplets interacts and deformation begins. The film rupture is dependent on the mechanical properties of the film and fluctuations of the thickness of the film and when they approached each other the van der Waals forces dominate, and fusion of droplets takes place. The overall stability of the emulsion is determined by the rate of the thinning film and its strength against the rupture.

1.1.1.5 Phase Inversion

This process occurs when the dispersed phase exchange with the continuous phase.²⁰ For instance, if an oil-in-water (O/W) type of emulsion with time or change in the conditions inverts to a water-in-oil (W/O) emulsion. Until phase inversion takes place, multiple emulsions are formed.

In addition to these, other external factors affect the stability of an emulsion.¹⁹ The external factors include the presence of bacteria as well as other microorganisms. They affect the stability of emulsions by changing the characteristics of the system.¹⁹

1.1.2 Formation of Emulsions

1.1.2.1 Principles of Homogenization

Emulsions are prepared by using two different emulsification methods; low-energy emulsifying process and high energy emulsifying process.²¹ In high energy methods, intense mechanical energy is applied to break the macroscopic phases into smaller droplets.²² On the other hand, in low energy methods emulsions are formed spontaneously due to the changes in interfacial properties by changing the temperature (phase inversion temperature method) or composition (phase inversion composition method).²¹ To achieve small size droplets, a significant energy input is required.²³ High energy emulsification methods use mechanical devices (homogenizers) such as high-intensity ultrasonic homogenizers, membrane homogenizers, colloid mills, micro fluidization, high-pressure homogenizers and high shear mixers.^{22,24,25} The suitable mechanical device is chosen by considering the cost of the process, the volume of materials, nature of the dispersed and continuous phase, and the desired physiochemical properties of the final emulsion.²⁵

A high-intensity ultrasound device is a popular emulsification method used in many applications because is easy to clean and operate and provides good emulsion stability and high energy efficiency. The ultrasound devices create acoustic cavitation, and it generates air bubbles in the system. The acoustic cavitation air bubbles collapse and oscillates, hence

generate physical effects. collapses the air bubbles in the system. These physical effects include; high temperature and pressure, turbulence, a high-speed liquid jet, shock waves as well as intense physical shearing in the medium.²⁶ The continuous intense physical shearing break down large droplets into smaller droplets and leads to formation of stable O/W emulsions.²⁵ The mechanism of ultrasound emulsification is schematically represented in **Figure 1.3**.

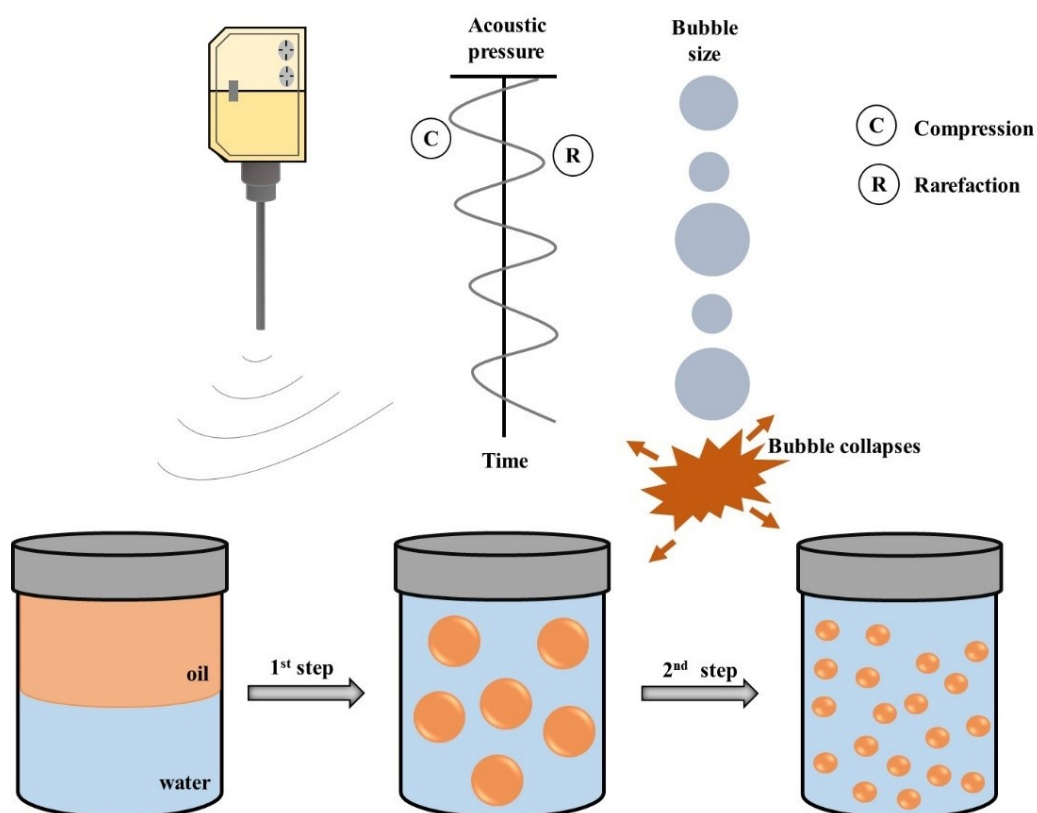


Figure 1.3. The schematic representation of applying acoustic pressure in order to form emulsion from two immiscible phases.

The sonication power, ultrasound amplitude as well as ultrasonic emulsification time have an important role in the size of the emulsion droplets.²⁴ Increasing the sonication power of ultrasound increases the acoustic power and this results to a reduction of the size of the emulsion droplets, hence enhancing the stability of the emulsion.^{25,27} Furthermore, it was reported that the ultrasound amplitude has more important role in reduction of droplet size compared to the emulsification time. On the other hand, the size of the emulsion droplets is also affected by over-processing, which means that the size of the emulsion droplets increases

due to the temperature rise which is the result of friction loss created by high pressure of homogenizers.²⁴ The size of the emulsion droplets increases because the emulsifier is losing its functionality by: 1) unfolding polymer chains or 2) dehydration of surfactant head groups or/and 3) depolymerization of biopolymer chains.

1.1.2.2 Role of Emulsifier

The emulsifier is usually dissolved in the water phase however, it is not always the case. There are studies available that emulsifier dissolves in the oil phase. Once the emulsifier is dissolved in the water phase, the oil phase is added into the system and high energy mixer was applied that leads to the formation of a coarse emulsion.²⁴ Once the coarse emulsion is fragmented into smaller droplets due to the existence of disruptive forces, emulsifiers adsorb on the surfaces of the emulsion droplets hence decreasing the interfacial tension and this increases the production of the fine droplets.²⁴

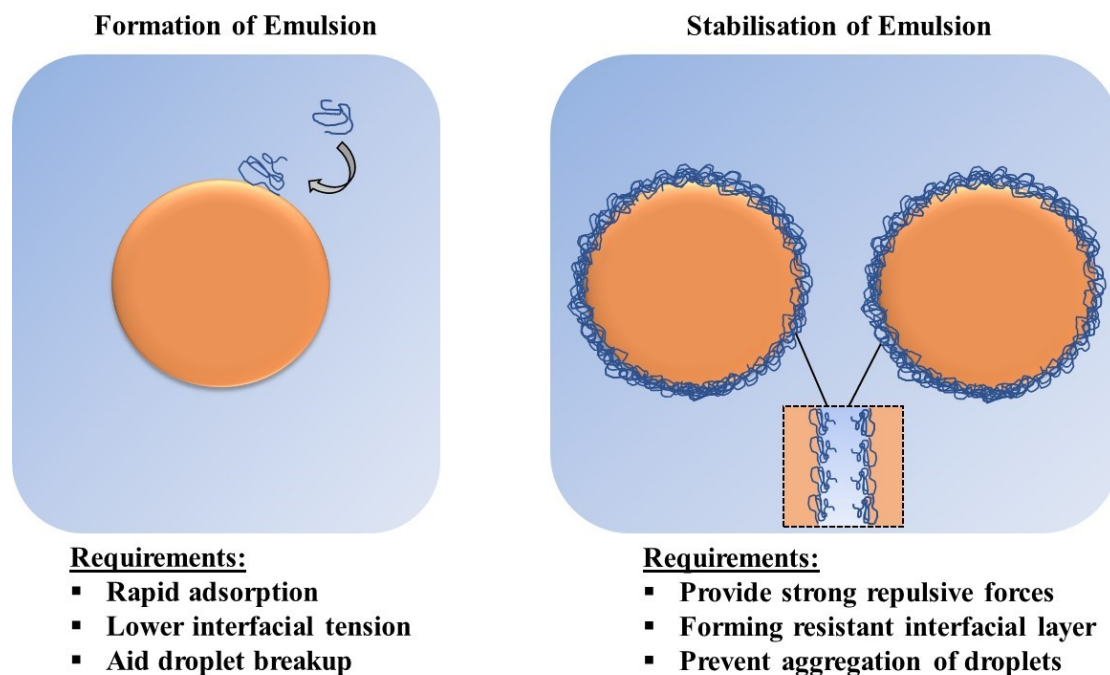


Figure 1.4. The role of emulsifiers represented schematically. Firstly, emulsifiers help formation of emulsion droplets (left) and secondly in providing stability to the emulsion droplets (right).

If the emulsifier has good emulsifying ability, it leads to the generation of smaller emulsion droplets because it enhances the decrease of the interfacial tension. Another important property of emulsifier during the droplet fragmentation is its rate of adsorption on the surface of the emulsion droplets.

The rate of adsorption should be faster than the droplet fragmentation (see **Figure 1.5**). The reason for this is that if the emulsifier molecules are not fully adsorb on the surface of the droplets, they can't reduce the interfacial tension, which will lead to the formation of bigger droplets sizes because the emulsifiers are not able to generate a protective layer to prevent coalescence.²⁴ In summary, the fast adsorption of emulsifiers leads to stabilisation of droplets and smaller droplets size. In contrast, slow adsorption leads to bigger emulsion droplets and droplets merging (see **Figure 1.5**).

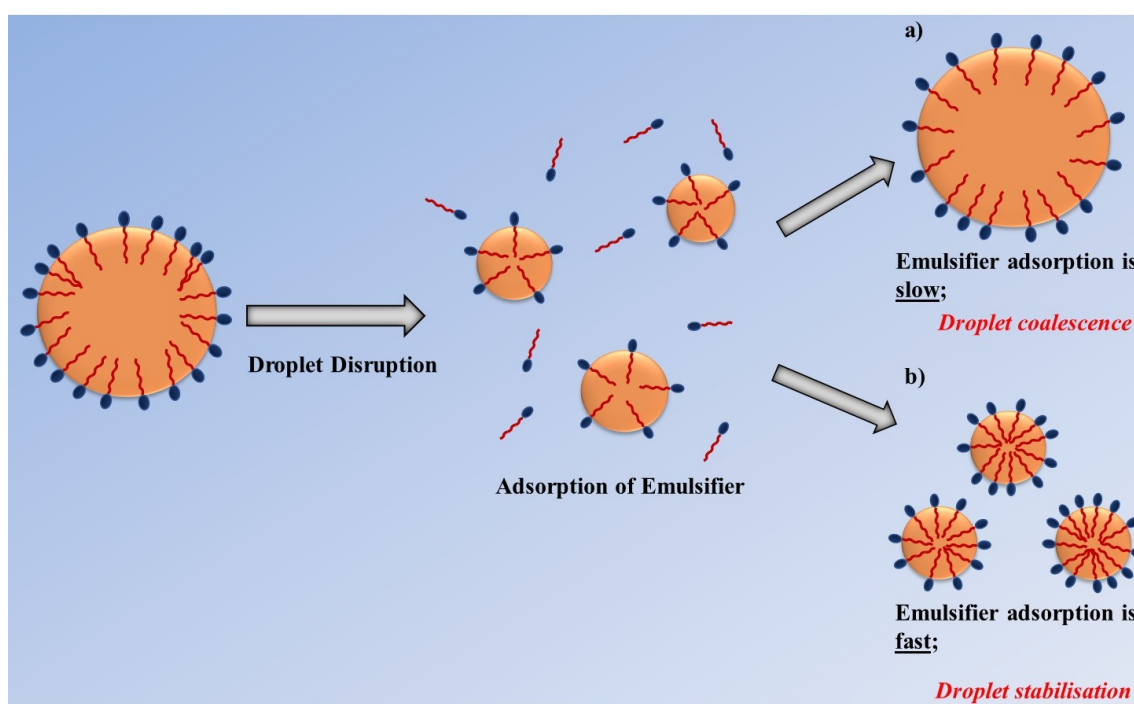


Figure 1.5. The schematic representation physicochemical processes occur during the formation of droplets using the homogenizer.

As mentioned before, the power and amplitude of ultrasound affects the mean droplet diameter of the emulsion.²⁵ The concentration and type of emulsifier also affects the size of the emulsion droplets. Therefore, when the size of emulsion droplets is considered, all those variables should be taking into account.²⁴ Addition of excess emulsifier into the system will decrease the size of the emulsion droplets. At some point, it reaches the upper limit, and the size of the emulsion droplets is not decreased anymore. On the other hand, when limited amount of emulsifier was added into the system, the surface of the emulsion droplets could not be covered, therefore droplets merge together.

1.2 Emulsifying Agents

As mentioned in the previous section, to have a stable emulsion, a third component, an emulsifier, is needed to provide long-term stability. Emulsifiers are divided into three general classes of materials: 1) colloidal particles, 2) surfactants and 3) polymers.²⁸ A brief description and examples for each type of emulsifier will be discussed in the following section. These three types of emulsifiers are known as "true" emulsifiers because they have better adsorption efficiency on the O/W interface. However, in the literature, inorganic electrolytes are also present as an additive for stabilising the emulsion.¹⁹ They are not classified under emulsifiers because they have been the least effective additives and have limited utility. An example of inorganic electrolytes includes potassium thiocyanate (KCNS). The adsorption of anionic species on oil-water interface is weak therefore, there is slight electrical effect and provides short-term stability of emulsion droplets. The adsorption of all different types of emulsifiers on a droplet is shown in **Figure 1.6**.

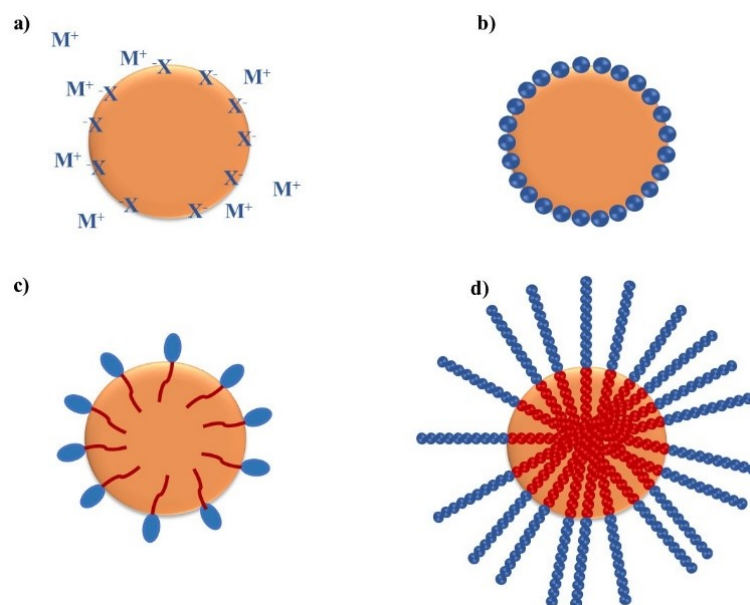


Figure 1.6. Emulsion droplets stabilised using four different emulsifiers. The emulsion droplets stabilised by a) ionic inorganic electrolytes b) colloidal particles c) surfactants and d) polymers.

1.2.1 Colloidal Particles

Particles have been extensively used to adsorb at oil/water interface in order to reduce the interfacial area between the two immiscible liquids.²⁹ Particles provide steric barrier between the droplets to prevent the coalescence by volume exclusion as well as steric hinderance.³⁰ Stabilisation of oil or water droplets by solid particles are called Pickering emulsions.^{31,32} The wettability of the solid particle is an important parameter that determines the type of the emulsion. For instance, when one of the liquids wets the solid poorly, it becomes the dispersed phase and the one that wets the solid more, becomes the continuous phase. Therefore, hydrophilic particles wetted by the aqueous phase favour the formation of o/w emulsions whereas hydrophobic particles wetted by the oil phase favour the formation of w/o emulsions.^{29,33,34,35} The stability of emulsions stabilised by solid particles is effected by: 1) size of the particle, 2) shape, 3) concentration, 4) wettability, 5) zeta potential and 6) interaction between the particles.³⁰ According to previous studies, smaller particles (larger than 1 nm) provide high stability against the coalescence and Ostwald ripening.^{30,36} In the literature, most of the Pickering emulsions are stabilised by spherical particles. Recently however, there is an increasing interest in anisotropic particles³⁷ (such as Janus dumbbells³⁸, peanuts³⁹ and cubes³⁹), ellipsoids^{40,41}, sphereocylinders⁴², carbon nanotubes⁴³, rods⁴⁴, disc-like⁴⁵, fibrous-

like ⁴⁶ and others. Pickering emulsions are stabilised by variety of particles such as metallic particles, clay, polymeric particles, natural stabilizers; starch, protein, cellulose and others.^{47,48} In the literature, calcium carbonate, silica and titania are the most popular inorganic particles used as Pickering emulsifiers for past decades.⁴⁹

1.2.2 Surfactants

Surfactants are one of the most versatile chemicals used in everyday life. They are used in various applications such as detergents and cleaning, food chemistry, pharmaceuticals, oil recovery, nanotechnology and many more.^{50,51} Surfactants are also called **surface-active agents**, originate its name from their capability to adsorb at interfaces of two immiscible phases and modify the physical properties of those interfaces. The term interface describes the boundary in liquid/gas, liquid/liquid and solid/liquid systems.

Surfactants are organic and amphiphilic molecules. The origin of amphiphile comes from Greek; amphi means "both" and phil means "like", which means that surfactant molecule likes both polar and apolar environments. Therefore, all surfactants have at least one hydrophilic head group that is covalently bonded to at least one hydrophobic tail group. Consequently, these incompatible units linked together in one structure give different behaviours and properties in aqueous solutions and dispersions.^{50,10,52} Schematic representation of the conventional surfactant is shown in **Figure 1.7**. In addition to conventional surfactants, different architectures of surfactant molecules are also present, and they are schematically illustrated in Figure 1.7.⁵³ Gemini surfactants are also called dimeric surfactants and they have two surfactant molecules that are connected head to head by a spacer group. On the other hand, in bolaform surfactants, two surfactant molecules that are connected tail to tail by the spacer group. Trimeric surfactant contains three surfactant molecules that connected to each other, and if the surfactant molecules increase and become four and many surfactant molecules, they are called tetra- and polymeric surfactants, respectively (see **Figure 1.7**).

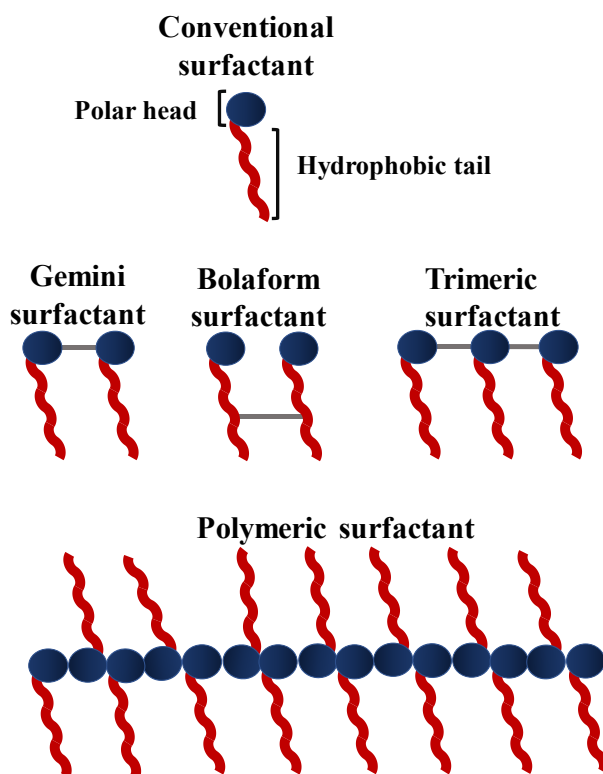


Figure 1.7. The schematic representation of conventional surfactant, gemini surfactant, bolaform surfactant, trimeric surfactant and polymeric surfactant molecule. The polar head group and hydrophobic tail are represented by red and blue, respectively.

Using different head and tail group of the surfactant leads to formation of variety of surfactants.⁵¹ The surfactants are divided into four basic classes due to the nature of the head group type. Those four basic classes of surfactants are: 1) anionic, 2) cationic, 3) non-ionic, and 4) zwitterionic (or amphoteric). Anionic surfactants consist of negatively charged polar head groups such as sulfate, phosphate, sulfonate as well as carboxylate.^{50,51,54} Cationic surfactants have positively charged polar head groups and an example include ammonium residue. Non-ionic surfactants have non-charged and highly polar head group, examples include polyethylene oxides and polyols. The zwitterionic surfactants have both positive and negative charges, but the total charge of the surfactant molecule is zero, examples include betaines and sulfobetaines. The tail group of the surfactant could be double or single bond, branched or single hydrocarbon chain. In addition to this, siloxane, fluorocarbon or aromatic groups are present.

In an aqueous solution, there is strong network between the water molecules.⁵⁰ Addition of apolar molecule into an aqueous solution will perturb the network and interaction energy reduced. Therefore, a layer of water molecules is formed, in which the water molecules are

facing directly the apolar species and provide shielding for other solvent molecules. Thus, the entropy decreases because interfacial water molecules are frozen around the apolar molecule and their freedom decreases. If the apolar molecules self-assemble and the interfacial water molecules re-enter to the bulk phase and regain its freedom, hence increasing the entropy in the system. This mechanism is called the "hydrophobic effect" and it enhances the polymer self-assembly and the formation of micelles. The formation of micelles is illustrated schematically in **Figure 1.8**. The Gibbs free energy of micellization is given in **Equation 1.1**, below.⁵³ In the equation, R is the ideal gas constant, T is temperature and CMC is critical micelle concentration of amphiphilic molecule.

$$\Delta G_{\text{micelle}} = RT \ln(\text{CMC}) \quad \text{Equation 1.1}$$

Both hydrophilic and hydrophobic moieties in the surfactant molecules interact differently with the "selective" solvent.⁵⁰ For instance, if the selective solvent is water and anionic surfactant such as low concentration of sodium dodecyl sulphate (SDS) molecules added, they dissolve as individual ions.⁵³ Due to its amphiphilic nature, they adsorb at the air water interface; the hydrophobic chain is exposed to air and the hydrophilic part is exposed to the water phase shown in step 2 (**Figure 1.8**). The presence of surfactant molecules at air-water interface disrupts the cohesive energy of the surface which decreases the surface tension.⁵⁵ When the concentration of surfactant molecules increases, more amphiphilic molecules are on the surface of water, leading to the surface tension to decrease even more (step 3, **Figure 1.8**). As shown in step 4 (in **Figure 1.8**), increasing the concentration of surfactant molecules even more, results to the complete coverage of interface by amphiphilic molecules. At this point the surface tension does not decrease further and the amphiphilic molecules start forming a micelles or aggregates. The concentration at which this occurs is called critical aggregate concentration (CAC) or critical micelle concentration (CMC).⁵⁵ The effect of concentration on surface tension is shown in **Figure 1.9**.

When the concentration of the surfactant molecules is higher than their CMC, the equilibrium of three states are present which are; 1) free unimers in the solution, 2) adsorbed monomolecular layer and 3) aggregation of surfactants molecules into micelles.⁵¹ On the other hand, below CMC, the surfactant molecules continuously leave and enter the surface.

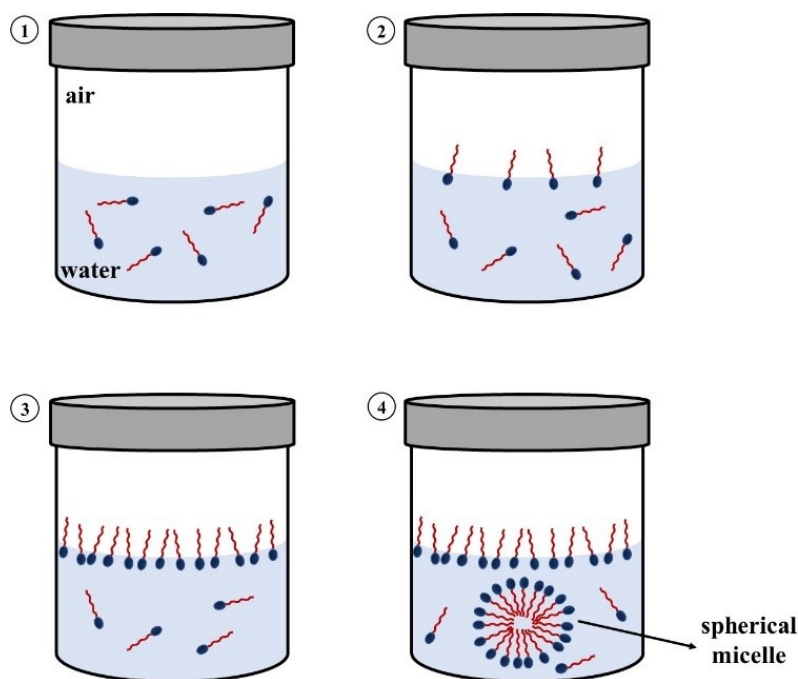


Figure 1.8. The schematic illustration of: Step 1, addition of surfactant molecules into water. Step 2 and 3, the concentration of surfactant molecules increases, and they adsorb at air-water interface. Step 4, the surfactant molecules aggregate to form micelles.

Micelles are dynamic species and they contain approximately 50-200 surfactant molecules.⁵¹ There is continuous interchange between formation and dissociation of micelles, and it happens in microsecond timescale. The formation and dissociation of the micelles dependent on the balance between interactions such as; 1) hydrocarbon-hydrocarbon chains, 2) polar head groups-head groups and 3) hydrocarbon chain-water molecules and 4) solvation of the polar head group. When two polar head groups approach each other, they start to repel each other and opposes the aggregation.⁵³ The repulsion originates from the steric effects and the dehydration of the head groups, leads to hydration repulsion. Furthermore, electrostatic repulsion is also present between the equally charged polar head groups. Therefore, the CMC values of ionic surfactants are higher than the non-ionic surfactants due to electrostatic repulsion between the charged groups.

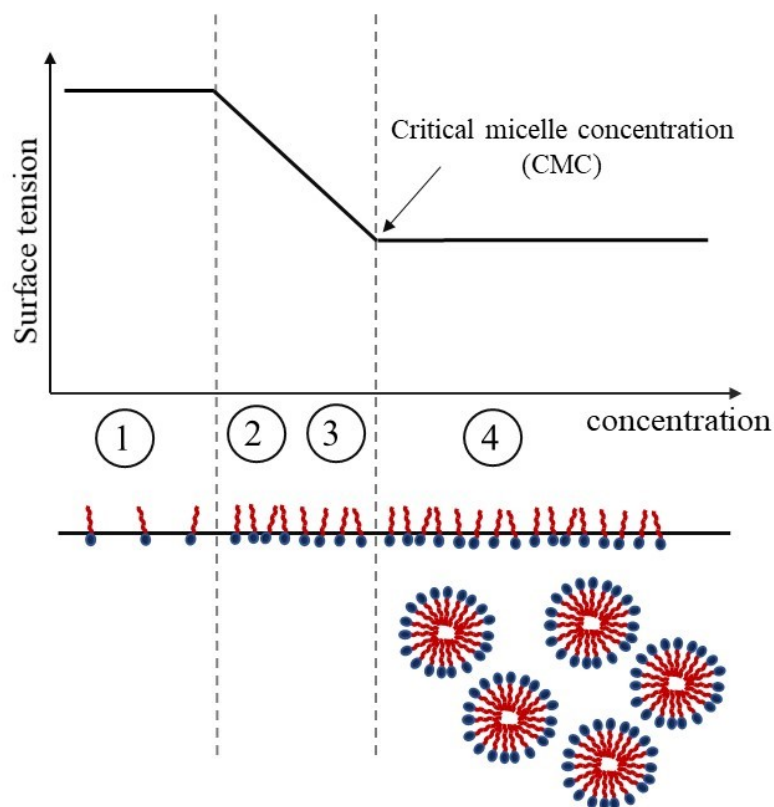


Figure 1.9. The effect of concentration on surface tension. The concentration point where there is no decrease in the surface tension is the critical micelle concentration (CMC) of the amphiphilic molecule.

The size of the micelles can be determined using light scattering methods,^{56,57} cryogenic transmission electron microscopy (cryo-TEM),^{58–60} small-angle neutron scattering (SANS)^{59,61} and small-angle X-ray scattering (SAXS).^{53,59} In this thesis, the size of the self-assembled structures was determined using dynamic light scattering as it was the easiest and readily available method to use.

The CMC of the amphiphilic molecules can be determined using various methods such as surface tension,^{62,63} light scattering,^{64,65} turbidity,⁶⁶ use of fluorescent probe,^{67,68,69} osmotic pressure,⁶⁶ and conductivity.^{63,70}

In the literature, there are various surfactants available and they are widely used a plethora of applications. An important parameter that can be used to choose the correct emulsifier for the specific application is the hydrophilic-lipophilic balance (HLB) introduced by Griffin in 1949.^{28,71} The chemical structures of surfactant molecules taken into account and HLB value are determined using the **Equation 3.11**.^{52,4}

The HLB value is in the range of between 0 and 20. It predicts whether surfactants will stabilise O/W or W/O type emulsions.^{72,73} When the HLB value of surfactant is higher than 10, it means that the surfactant is hydrophilic and stabilises O/W type emulsions. However, when the HLB value is lower than 10, the surfactant is hydrophobic and stabilised W/O type emulsions.⁷² The relationship between the HLB value of surfactants and the application is given in **Table 1.1**. The HLB concept was verified by the empirical Bancroft's rule that states that water soluble surfactants will stabilise O/W emulsions, whereas oil soluble surfactants will stabilise W/O emulsions.^{10,74} The HLB value concept was mainly applied for the small molecule surfactants.⁷⁵ Consequently, the type of emulsifier affects the type of the emulsions formed. The type of the formed emulsion was also affected by the volume ratio of the phases present in the system.¹⁹

The emulsion type can be determined using electron microscopy which gives detailed information about the emulsion structure.⁵³ However, this technique is expensive, and it requires complicated sample preparation and time. There are available techniques that are quicker and do not need sample preparation. Measuring the electrical conductivity of the emulsion is one of the methods that determines the type of emulsion. For instance, the O/W type emulsion has higher conductivity because the continuous phase is water and has higher conductivity than the oil phase. Another technique to determine type of emulsion is addition of optically visible dye. If the colour of the emulsion changes, it means that the dye is dissolved and in the continuous phase. The drop test is another method used to determine the type of emulsion, which was performed in this project. More detailed information is given in the experimental section.

Table 1.1. The relationship of HLB range of surfactants with suitable applications.⁵²

HLB range	Applications
1-3	mixing different oils together
4-6	W/O emulsifier
7-9	wetting agents
8-1	O/W emulsifier
13-15	detergents
13-18	solubilizers

1.2.3 Polymeric Surfactants

Polymeric surfactants or 'macrosurfactants' are known to be macromolecule with amphiphilic structure, that contain both hydrophobic and hydrophilic units.^{76,77} In the literature, they are also known as micellar polymers, amphiphilic polymers as well as hydrophobically modified water-soluble polymers.⁷⁸ They are one of the most crucial components in disperse systems and widely used in many industrial applications such as detergents, agrochemicals, paper coatings, personal care products, inks, pharmaceuticals, optoelectronics, dyestuffs, biotechnology, water-purification, nanotechnology, enhanced oil recovery and ceramics.^{79,52} Oil-in-water (O/W), water-in-oil (W/O) emulsions and suspensions are the most vital applications of polymeric surfactants.⁸⁰ Polymeric surfactants have also been reported to be efficient dispersers,^{81,82} rheology modifiers,⁸³ and efficiency boosters in microemulsions.⁸⁴

In recent years, there is an interest in using polymeric surfactants compared to the low molar mass (MM) surfactants.⁸⁵ The reason is, they have a well-defined structure, and the MM, composition, could be varied which provide great opportunities such as functionality, flexibility as well as diversity which tailors the stability of emulsions by providing electrostatic and steric stabilisation.^{86,87,88} Furthermore, polymeric surfactants have lower diffusion coefficients as well as CMC compared to their low MW surfactants.⁷⁷ The low mobility property of polymeric surfactants provide advantage in the coating industry because mobile polymeric surfactants cause formation of weak polymer film properties. In addition to this, a small quantity is needed for emulsification which makes it more cost-effective compared to the traditional low MM surfactants.⁸⁹

The polymeric surfactant with good emulsifying ability should have four following properties: 1) droplets should be completely covered by the polymeric surfactant, because any bare areas without surfactant will lead to flocculation due to the Van der Waals attraction, 2) the adsorbed layer should be thick enough to prevent the flocculation 3) the surfactant should adsorb strongly on the surface of the droplet, 4) the stabilising chain should have strong solvation so that it can provide good steric stabilisation.⁸⁰

Polymers of different architectures, specifically, linear diblock and triblock copolymers, star copolymers, comb-like polymers and graft copolymers have been studied as emulsifiers.⁸⁵

1.2.3.1 Homopolymers

A homopolymer is a polymer that its structure is consisted of a single type of repeat unit.⁹⁰ The single repeat unit can contain one or more than one species of monomer unit. The schematic representation of homopolymer is shown in **Figure 1.10**. Each red sphere shown in **Figure 1.10**, represent the repeat unit of the homopolymer. An example to homopolymer is poly(ethylene glycol) (PEG) also called poly(ethylenxe oxide) (PEO), and it is consisted of repeating units ethylene oxide.⁸⁰ This is one example of the homopolymer used as a polymeric surfactant. In addition to this, poly(vinyl pyrrolidone) (PVP) is another example of polymeric surfactant used in pharmaceutical formulations. Both PEG and PVP have small surface activity to O/W interface therefore they are not the best dispersants or emulsifiers.^{79,80}

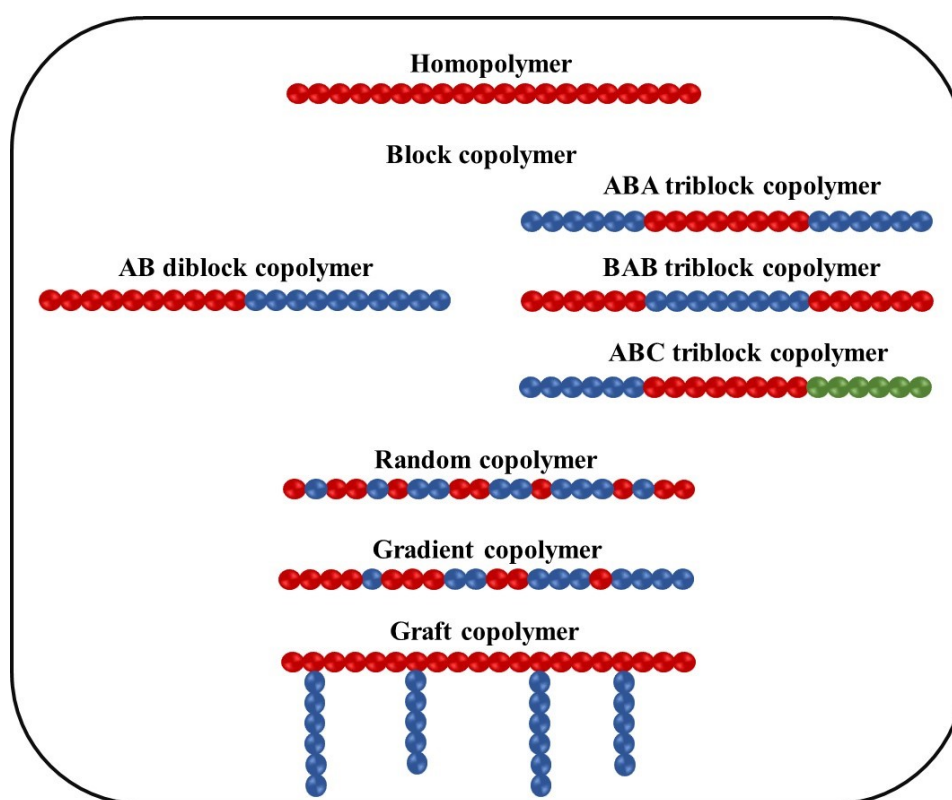


Figure 1.10. Schematic representation of polymers with different architectures. The red spheres represent the repeating unit of monomer A and blue spheres represent the repeating unit with monomer B. A and B are different types of monomer.

1.2.3.2 Copolymers

A copolymer is a polymer which contains two or more different species of repeating unit.⁹⁰ According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), if a copolymer contains two, three or four different monomer species, is named a bipolymer, terpolymer or quaterpolymer, respectively.⁹¹ The types of copolymers are divided into different categories according to the arrangement of repeating units along the polymer chain.⁹⁰ The categories of copolymers are divided into: 1) statistical copolymers, 2) random copolymers, 3) alternating copolymers, 4) block copolymers, and 5) graft copolymers. The schematic representation of different types of copolymers are shown in **Figure 1.10**. The statistical copolymer is defined as copolymer, the repeating units of monomer is sequentially distributed according to the statistical laws along the polymer chain. The alternating copolymer is copolymer that consists of two types of repeat units which is alternated along the polymer chain. This thesis is not focused on alternating and statistical copolymers, therefore only definition explained. Other types of copolymers, random, block and graft copolymers will be discussed in more detail in the following section.

Block Copolymers

Block copolymers are copolymers that consist of at least two different species and the same type of repeating units are distributed in long sequences or blocks.^{90,1} The **Figure 1.10** shows the schematic representation of most common block copolymers, which are AB diblock copolymers and ABA triblock copolymers. The monomer A and B is represented in red and blue, respectively. Block copolymers are the most commonly used polymeric surfactants due to having a simple topology.⁹²

Amphiphilic block copolymers used as a polymeric surfactant in many fields such as cosmetics, enhanced oil recovery, delivery systems, water purification, coatings, electronics.⁹² In recent years, amphiphilic block copolymers are preferred more compared to the small molecule surfactants. This is because amphiphilic polymers provide flexibility, diversity and functionality to the structure by changing macromolecular parameter such as architecture, MM, composition as well as the chemistry of the monomers.

Amphiphilic block copolymers with well-defined structures also self-assemble into aggregates in order to minimize the water-hydrophobic interactions which is energetically unfavourable.⁹³ The amphiphilic block copolymers self-assemble in aqueous solution so the hydrophobic blocks are in the core of the self-assembled structure (micelle) and the hydrophilic blocks form

the corona (shell) of the structure which "protects" and stabilise the micelles.^{94,95} This self-assembly occurs due to the hydrophobic effect, i.e. the entropy of the water.⁵¹ Reverse micelles can be formed when hydrophilic block forms the core and hydrophobic block forms the corona (shell), in non-hydrophobic media.⁹⁶ Micelles are often spherical but other morphologies can also be formed like cylinders (or rods or worms), bicontinuous structures, vesicles, lamellae and many more.^{95,97-99} The final morphology of the aggregates is dependent on the packing parameter: $p = v/a_0l_c$. The a_0 is the contact area of the hydrophilic block, v is the volume of the hydrophobic block and l_c is the length of the hydrophobic block.⁹⁸ Spheres are formed when $p < 1/3$, cylindrical micelles or hexagonally packed cylinders are formed when $1/3 < p < 1/2$, vesicles or modulated lamellae are formed when $1/2 < p < 1$, and multi-layered lamellae or planar bilayers are formed when $p = 1$.^{98,95}

The amphiphilic block copolymers self-assemble into aggregates when they reach to their critical micelle concentration (CMC). The CMC is dependent on the temperature, ionic strength, pH and the chemical structure of the amphiphile.⁵⁰ The CMC of block copolymers is the order of 10^{-5} g mL⁻¹ or smaller and it is much lower compared to the surfactants.⁸⁰ Therefore, the formation of micelle is thermodynamically more favourable than the low MM surfactants.⁸⁰

The aggregates that are formed from polymers have better stability and durability compared to the small-molecule aggregates.⁹⁷ The reason for this is the physical and mechanical properties of the polymers. Therefore, due to this property of amphiphilic block copolymers, they received more attentions for the possible applications. There are many researches available for diblock copolymers including micellization, their stimuli responsive in aqueous solutions, emulsion stabilization.⁷⁸

According to Tharwat Tadros, block copolymers are one of the most effective polymeric surfactants.⁸⁰ In the literature, block copolymers especially, diblock and triblock copolymers are the most commonly used polymeric surfactants.⁷⁸ An example of the most widely and longest used polymeric surfactants are the ABA triblock copolymer (A-B-A) polaxomers, known with the commercial names Pluronics (BASF, from Germany), and Synperonic PE (ICI, U.K.), which are consisted of PEG/PEO as a hydrophilic monomer (A block) and poly(propylene oxide) (PPO) as a hydrophobic monomer (B Block).^{78, 79} They contain one block of PPO which adsorb at hydrophobic surface and two blocks of PEO (PEO-*b*-PPO-*b*-PEO) and they are dangling in an aqueous solution and provide steric stabilisation.⁷⁹ The adsorption of PPO chains are not strong therefore they are not ideal polymeric emulsifiers.¹⁰⁰

However, those type of polymeric surfactants are widely used in different fields such as printing inks, detergents, paints, agrochemicals and coatings.⁷⁹

Random Copolymers

Random copolymers are copolymers and its structure is consisted of randomly distributed repeating units along the polymer chain.⁹⁰ The schematic representation of random copolymers are shown in **Figure 1.10**. As an example, the red spheres represent repeating unit with monomer A, and blue spheres represent repeating unit with monomer B. Random copolymers are used as a polymeric surfactant to stabilise the emulsion droplets.⁸⁰ An example of a polymeric surfactant that has a random copolymer architecture includes, the poly(vinyl alcohol), PVA. This is because it contains some vinyl acetate groups which is the residue from the partial hydrolysis of poly(vinyl acetate) that is hydrophobic and vinyl alcohol groups that is hydrophilic, which gives the molecule an amphiphilic character. The hydrophobic acetate groups preferably attach to the hydrophobic surface of styrene and vinyl alcohol groups dangling in the aqueous medium. Therefore, the block distribution of the acetate groups along the backbone of the PVA, provide effective adsorption on the o/w emulsion droplets. Another example to random copolymer is (PS-*co*-PAA) which is consisted of styrene and acrylic acid.¹⁰¹ It is commercially available copolymer which is used as a polymeric surfactant in industry.

Graft Copolymers

Graft copolymers are branched polymers, where the chemical structure of the main chain is different to that of its branches.⁹⁰ The schematic representation of simplest form of graft copolymer is shown in **Figure 1.10**. A graft copolymer is also referred "comb" stabiliser when it consists polymeric backbone B and some chains of A ("teeth").⁸⁰ When a comparison is made between block and graft copolymer, the latter offers more parameters that could systematically be varied such as graft length, backbone length and graft (side chain) density and it has additional architectural flexibility.¹⁰² That is why in the last decades graft copolymers are widely used in emulsion polymerisation.

An interesting example are, polysaccharides based graft copolymers like inulin with the commercial name INUTEC® N25 that has been used to disperse systems.⁸⁰

Gradient Copolymers

In last decades gradient copolymers, also called tapered copolymers have attracted interest due to their unique chain microstructure.¹⁰³ They contain at least one segment along the copolymer chain in which the composition is changing gradually from predominantly one monomer to second monomer.^{103–105} A special class of gradient copolymers are tapered block copolymers (TBCs) which contains a gradient (or taper) region in the middle of the two distinct blocks.^{105,106} The schematic representation gradient copolymer is shown in **Figure 1.10**. Due to unique chain microstructure of gradient copolymers, they experience lower inter- and intra-chain repulsion compared to the block and statistical copolymers.¹⁰³ In addition to this, they also show different properties, such as: thermal properties, behaviour at interfaces as well as properties in solution.¹⁰³ Amphiphilic gradient copolymers is another class of gradient copolymers with unique chain microstructure. As an example, they consist gradual change of monomers from hydrophobic to hydrophilic along the polymer chain. Hence, their unique structure makes them to respond to temperature, pH and type of solvent which affects their self-assembly in solution.^{107–110} Due to those properties, they are attracted by pharmaceutical and biomedical applications.^{111,112} The properties of gradient copolymers can be optimised by varying the degree of the gradient region as well as taper length and this makes it very attractive for the industrial research.^{103,106} Shull and co-workers studied the behaviour of gradient poly(styrene-*grad*-acrylic acid) copolymer at liquid/liquid interface and compared it to the diblock copolymers with same monomers, similar MM and overall composition.¹¹³ They observed that, gradient copolymers are more effective interfacial modifiers compared to the diblock copolymers. The reason for this was, gradient copolymers extended along the interface, hence they have many junction points which results more "parallel" structure. On the other hand, the junction point of diblock copolymers are placed at the oil/water interface. The schematic representation of gradient copolymers and diblock copolymers at oil/water interface is shown in **Figure 1.11**. In the literature, there are various examples for gradient copolymers.¹⁰³ The most common monomer used in synthesis of gradient copolymers includes styrene and the synthesis were performed by controlled living polymerisation techniques which will be discussed in the following section. In the literature, there is very limited research that uses gradient copolymers as stabilizers in emulsion and dispersion.¹¹⁴

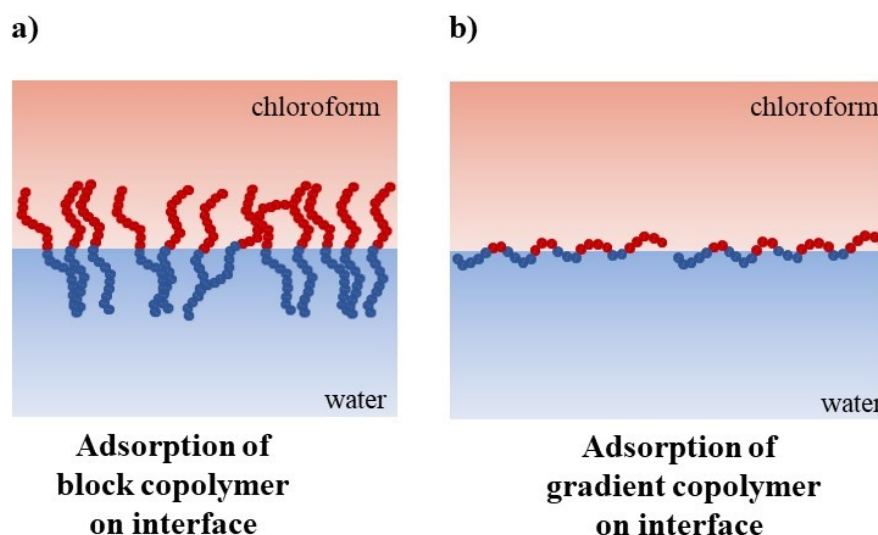


Figure 1.11. The schematic representation of adsorption of **a)** block copolymer on interface, **b)** gradient copolymer on interface.

1.2.4 Natural Emulsifiers

Phospholipids are one class of natural emulsifiers, that can be found in microorganism cell walls, plants as well as animals.²⁴ The most common commercial product using a phospholipid-based emulsifier is called lecithin. The structure of lecithin contains hydrophilic head groups of phospholipids which is either anionic or zwitterionic. The tail group of phospholipids contains two fatty acids which are non-polar, and the number of carbon atoms and double bonds are varied. Other common examples of polysaccharide based polymeric surfactants include emulsan and chitosan.⁵⁵ A second class of natural emulsifiers are biosurfactants.²⁴ An example of biosurfactants are Saponins which are natural small molecule surfactants and obtained from the bark of the tree called *Quillaja Saponaria*. Saponins have an amphiphilic structure and they self-assemble into micelles in water which lead to formation and stability of O/W emulsions. The commercial name of saponin is Q-Naturale and it is used as an emulsifier in food industry. Biopolymers including proteins are third class of natural emulsifiers. Proteins consist of strings of amino acids that are covalently linked with peptide bonds. The proteins have polar and non-polar amino acids that makes the whole structure amphiphilic and thus able to stabilise the emulsion by absorbing on the oil-water interface. In addition, proteins contain amino acids that are mixtures of anionic, cationic or neutral depending on to the pH conditions. Caseins and whey proteins are most common proteins used as food emulsifiers. Egg proteins and gelatins are another example for proteins that are

frequently used as food emulsifiers. Proteins are less able to lower the interfacial tension compared to the synthetic emulsifiers, however they provide better stability for emulsions.¹¹⁵ A fourth class of natural emulsifiers includes colloidal particles that are used to stabilise emulsions through Pickering stabilisation mechanism.²⁴ Examples of colloidal particles used as food emulsifiers include, soy protein, chitin, starch, pea protein and cocoa particles.

In recent years, protein-polysaccharides electrostatic complexes are used polymeric surfactants in order to prepare products for the food industry.^{115,116} They were using both protein and polysaccharides together in order to combine the advantages. The role of the protein was to provide repulsive and electrostatic repulsion forming a viscoelastic adsorbed layer onto the emulsion droplets and the polysaccharide's role was to increase the viscosity and delay the formation of coalescence, creaming and sedimentation.¹¹⁵ An example of protein-polysaccharide complex includes β -lactoglobulin-gum arabic, which is used to stabilise O/W emulsions.¹¹⁵ **Figure 1.12** shows the schematic representations of adsorption of different natural emulsifiers on the interface.

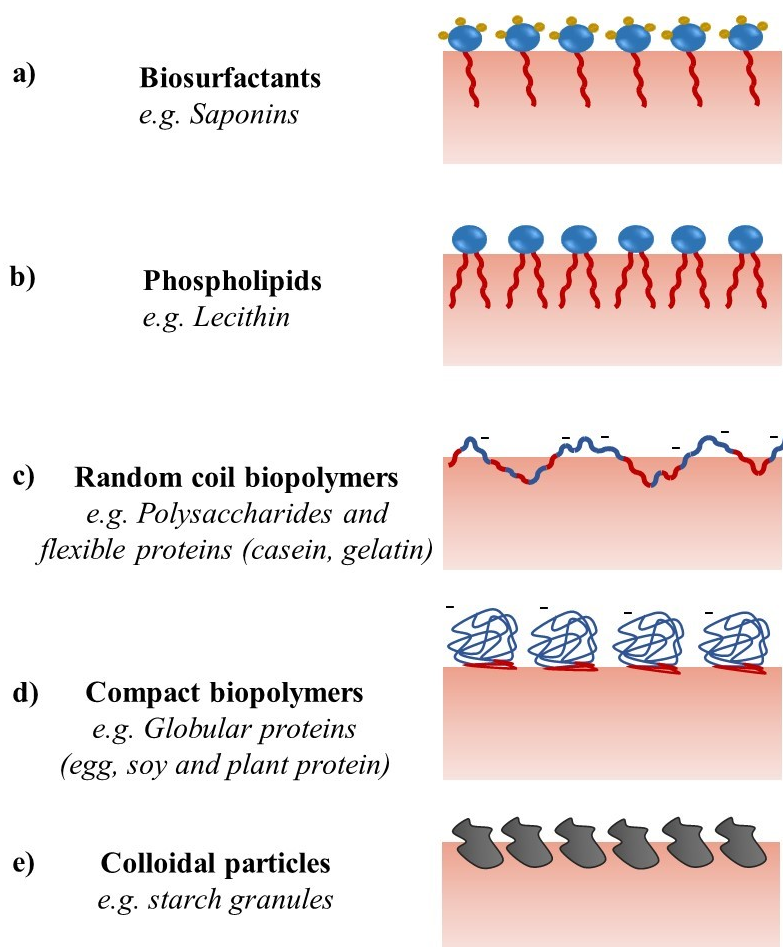


Figure 1.12. The adsorption behaviour of different types of emulsifiers on the interface.

1.3 Synthesis of Polymeric Surfactants

As mentioned previously, due to the flexibility, functionality and diversity of polymeric surfactants, they are preferable compared to the traditional surfactants.⁸⁵ Therefore, polymeric surfactants with better emulsifying properties can be synthesised because they are easy to tailor. The following section discusses the different polymerisation techniques that well-defined amphiphilic copolymers that can be used as an emulsifier can be synthesised with.

1.3.1 Living-Controlled Polymerisation Methods

Copolymers and homopolymers with well-defined structure, composition and molecular weight can only be synthesised using living or controlled/living polymerisation techniques.¹¹⁷ A living polymerisation is a chain growth polymerisation that takes place without any chain transfer reaction and chain termination.¹¹⁸

The first living polymerisation method was discovered by Michael Szwarc in 1956.¹¹⁹ He fabricated block copolymers based on butadiene and styrene with living anionic polymerisation using sodium naphthalide and THF as the polymerisation initiator and solvent, respectively.¹¹⁸ Szwarc named those polymers as '*living polymers*' because when additional monomer is supplied, the polymers continue to propagate and grow in the absence of chain transfer and chain termination.¹²⁰

After the original discovery of living anionic polymerisation method, cationic, coordination and ring opening polymerisation were developed as living polymerisation methods.¹²¹ In addition to these methods, reversible deactivation radical polymerisation (RDRP) methods were developed. RDRPs include three types of radical polymerisation methods such as nitroxide-mediated polymerisation (NMP)^{122–124}, reversible addition-fragmentation chain transfer radical polymerisation (RAFT)^{125–128} as well as atom transfer radical polymerisation catalysed using transition metal complex (ATRP).^{129–133} RDRP even though they are free radical polymerisation methods control the kinetics of the polymerisation as such so well-defined polymers, i.e. polymers of narrow MM distribution (MMD), controlled MM, composition and architecture can be synthesised.

1.3.1.1 Group Transfer Polymerisation (GTP)

The group transfer polymerisation (GTP) is living anionic polymerisation method and discovered in 1983 under DuPont's exploratory research projects by Webster and his co-workers.^{134,135} They undertook the synthesis of alkyl methacrylate by GTP using silyl ketene acetal as an initiator. The monomers used to polymerised using GTP method include α,β unsaturated ketones, carboxamides, nitriles and esters.¹³⁴ It is an ideal method to synthesise polymethacrylates.⁹⁰ The propagation step includes, transferring of silyl group to the monomer by Michael addition, hence producing a new terminal silyl ketene acetal group. The GTP method can take place at room temperature and is catalysed using nucleophilic anions or Lewis acid catalyst.¹³⁶ The mechanism of GTP is dependent on the nucleophilicity of the catalyst used.^{136,137} In the propagation step, the nucleophilic catalyst can react with the active species in two different ways: 1) associative mechanism and 2) dissociative mechanism.

In the associative mechanism a nucleophilic anion activates the trimethylsilyl group, and there is an intramolecular transfer of trimethylsilyl group to the monomer with a concerted reaction.^{137,138} The schematic representation of associative mechanism is shown in **Figure 1.13**. In propagation step, the ketene acetal double bond act as a propagation centre, and there is nucleophilic addition of π - electrons to the monomer. The main step that differentiates the associative mechanism from dissociative is the initiation step which is the concerted addition of methyl trimethylsilyl group to the monomer (see **Figure 1.13**).⁹⁰

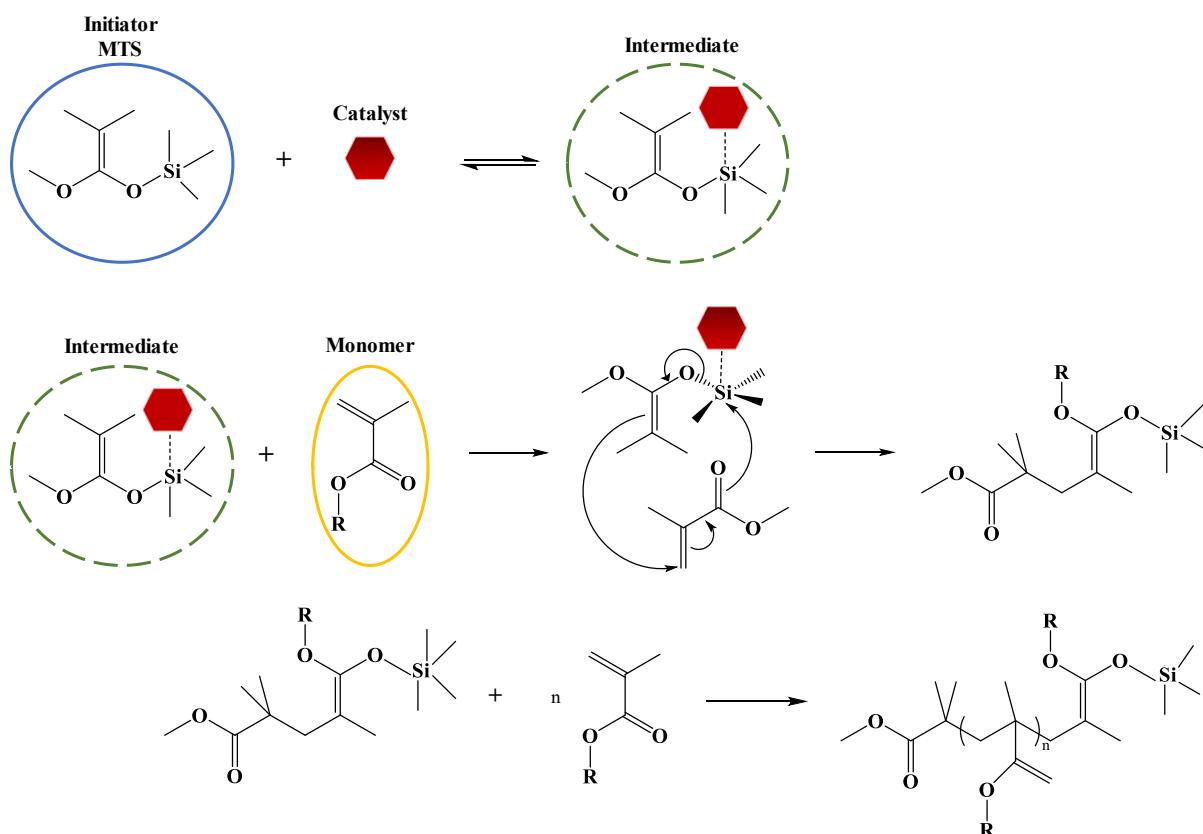


Figure 1.13 The associative mechanism of GTP method. The initiator molecule, MTS is circled by blue and the catalyst is shown in red square.

In the dissociative mechanism, the catalyst react with the trimethylsilyl group and produces ester enolate anion and trimethylsilyl-nucleophile compound.¹³⁶ The intermediate active ester enolate reacts with the monomer and it is shown in **Figure 1.14**. Recent findings have shown that when a nucleophilic catalyst is used, the reaction proceeds through the dissociative mechanism. In this study, the polymers that are produced by GTP method was proceed through the dissociative mechanism.

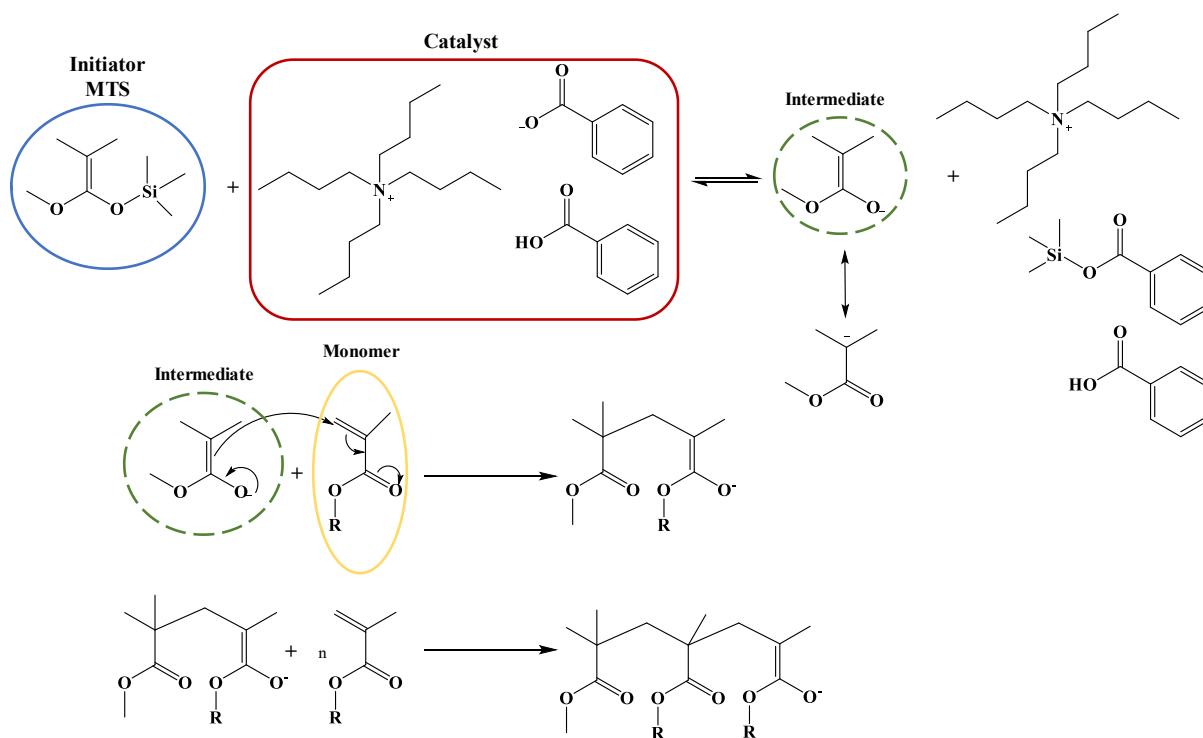


Figure 1.14. The dissociative mechanism of GTP method. The initiator molecule (MTS) is circled by blue and the catalyst is shown in red square.

The advantage of GTP is that it works at ambient temperatures and it gives products with quantitative yield with a good control of over molar mass as well dispersities.^{134,139} Compared to anionic polymerisation and other living polymerisation methods, it is cost-effective, works at higher concentrations, easy to scale up and quicker.¹⁴⁰ The polymerisation of each block takes approximately 15 minutes to be completed at room temperature.^{85,141,140} Furthermore, the conversion of monomer to polymer is 100% and it doesn't require any intermediate purification steps thus sequential polymerisation to produce block copolymer can be easily be carried out in an one-pot reactor. GTP has plenty of solvent options, however THF and toluene is the most popular solvent used in this method.¹³⁸ As it was mentioned previously, the GTP works best for the synthesis of methacrylate polymers. Due to the similar reactivities of most methacrylate monomers, GTP allows synthesis of topological isomers such as ABC, BAC, ACB and A-*b*-(B-*co*-C) terpolymers just by changing the order of monomer additions.¹³⁶ Synthesis of complex architectures such as multiple block copolymers, macromonomers, network, star-like, comb-like, gradient and homogenous gels are also possible.^{136,139} Finally, multiple polymers can be synthesised on the same day, with a variation of structural parameters, such as molar mass, composition and architecture in a controlled way.¹⁴⁰

A drawback of GTP is that it is very sensitive technique, thus the presence of any active hydrogen compound leads to termination of the active chain molecules.⁹⁰ Therefore, the polymerisation should be performed under dry conditions and reactants/solvents should be perfectly purified and dried. It was original believe that the maximum MM that could be obtained by GTP was 30,000 g mol⁻¹.¹³⁸ However recent studies by our group have fabricated polymers up to 100,000 g mol⁻¹. Finally, the main drawback of GTP is that is limited to (meth)acrylic monomers.¹³⁹

1.4 Characterisation Techniques of Emulsions

The gravitational separation such as sedimentation and creaming are one of the vital instability mechanisms that take place in cosmetics, pharmaceuticals, agrochemicals, petrochemicals as well as foods.¹⁴² Therefore, in order to inhibit or prevent the instability of emulsion, it is important to determine the what factors cause the emulsion system to be unstable. As discussed previously, the instability of the emulsion system is affected by: the density difference between dispersed and continuous phase, the viscosity of the continuous phase, the electrical charge on the droplets, the interactions between droplets and the size of the droplets.¹⁴²

Once an emulsion system becomes unstable, there is a change in the appearance and it can be seen by naked human eye.²³ Therefore visual observation of emulsions without any analytical instrument is one of the easiest, fastest as well as inexpensive method to evaluate the gravitational separation mechanism. As discussed in section 1.1.1, sedimentation occurs when density of dispersed phase is higher than the continuous phase, which cause droplets to move downward and formation of thick separated layer at the bottom of the vial. On the other hand, creaming occurs when density of dispersed phase is lower than the continuous phase, which cause droplets to move upwards, hence forming thick layer at the top.

One of the method that monitors the sedimentation and creaming is: collecting samples from different heights within an emulsion and then measuring the droplet concentration.¹⁴³ This could be performed by measuring density or evaporating the water phase. However, this method causes the emulsion system to be destroyed, therefore it is not a useful method to observe the sedimentation and creaming. The extent of creaming and sedimentation can be determined by measuring the thickness of the sedimentation and creaming layer with naked human eye, and this was the preferred method in this thesis. However, other instability mechanisms such as Ostwald ripening, flocculation and coalescence could not be determined by visual observation. In addition to this, emulsion system that contain droplet sizes less than

100 μm could not be observed by naked human eye, therefore droplet size distribution is required in order to have more information about the instability phenomena.

The size of the emulsion droplets could be determined by performing various methods such as; conductivity measurements¹⁴⁴, light scattering^{145,146}, laser diffraction technique^{147,148}, confocal and optical microscopy²³, ultrasonic spectroscopy^{149,150} and nuclear magnetic resonance (NMR).^{144,151} Light scattering is destructive technique because emulsion should be diluted before any measurements performed and do not measure the true particle size.^{144,145} Pulsed field gradient (PFG) NMR is another technique that determines the droplet size distribution of the emulsions.^{144,152} The advantage of this technique is; non-invasive, measurement could be performed for opaque concentrated emulsions, little sample preparation is required. However, it is expensive for routine measurements and time consuming.

Optical transmission spectroscopy is one of the most commonly used techniques to characterise the size and shape of the emulsion droplets, it is one of the techniques used in this study. The reason why it is a common technique is; comparatively inexpensive and easy to use.²³ The absence of flocculation is observed when the emulsion droplets relatively small and distributed homogeneously in the image. On the other hand, the presence of flocculation in the emulsion system is determined when bigger-sized droplets come closer to each other without merging into bigger droplets. The Ostwald ripening can be observed by observing the growth of droplet size and size distribution over time.⁷² Coalescence observed in the presence of big and small droplets at the same time.

Other microscopy techniques are available to study the instability phenomena; electron, atomic force, and confocal fluorescent microscopy. The limitations of optical microscopy are that: 1) slide-spreading is required which may cause changes in the structure of the original emulsions, 2) mostly only spherical droplets are observed, 3) resolution is low due to the similar refractive index values of dispersed and continuous phase, 4) results are subjective, and 5) multiple images are needed on different section of the sample to obtain reliable results. Therefore, optical microscopy alone is not enough technique to determine the emulsion system's size droplets or instability mechanism. Analytical sources such as surface charge or particle size analysis are required with optical microscopy to obtain an accurate instability mechanism of emulsions.

1.5 Applications of Emulsions Stabilised by Polymeric Surfactants

As already mentioned in previous sections, polymeric surfactants are versatile, and they are widely used in different applications. This section discusses recent examples of polymeric surfactants used in various applications that are related to emulsions. Please note that, the role of polymeric surfactants on each application is described briefly.

1.5.1. Emulsion Polymerisation

Emulsion polymerisation is one of the main applications of polymeric surfactants.^{78,101,153} In emulsion polymerisation, water is used as non-solvent, water soluble initiator (e.g potassium persulphate, $K_2S_2O_8$) used to initiate the reaction and the monomer (e.g methyl methacrylate or styrene) is emulsified in water in the presence of ionic surfactant or non-ionic polymeric surfactants.⁸⁰ The main role of polymeric surfactants is to decrease the interfacial tension and stabilise the emulsion droplets by providing steric repulsion which prevents the formation of coalescence and Ostwald ripening.⁷⁸ In addition to this, they have an effect on the number of droplets formed.⁸⁰

Polymeric surfactants attracted interest compared to low MM surfactants because they have lower CMCs and diffusion coefficient values and they provide numerous advantages on the properties of the final synthesised latex particles which are also called emulsion polymers.^{80,154} In addition to this, the most important advantage of polymeric surfactants is that the MM, composition and architecture can be changed in order to optimise their stabilising properties for emulsion polymerisation.⁷⁷

The most commonly used polymeric emulsifiers in emulsion polymerisation are non-ionic amphiphilic block copolymers that is based on PEG/PEO.⁷⁷ For example, poly(styrene-*b*-ethylene oxide) diblock copolymer was used as an emulsifier for the emulsion polymerisation of styrene. This well-defined amphiphilic block copolymer was suitable as an emulsifier because it adsorbed on the surface of the styrene and formed a good anchor chain while the PEO chains were stabilising chains that were dangling in the aqueous medium and provide steric stabilisation. In another example, the amphiphilic diblock copolymer poly(methyl methacrylate-*b*-ethylene oxide) was used as polymeric surfactants for synthesis of PMMA latexes by emulsion polymerisation. In order to identify structure-property relationships, a systematic study was carried out where ten diblock copolymers with different MM and compositions were synthesised and investigated. The MM of the PMMA block was varied between 400 and 2500 g mol⁻¹ and the MM of the PEO block was varied between 750 and 5000

g mol⁻¹. According to the results, the best emulsifying ability of block copolymer was when PEO block was 2000 g mol⁻¹ and PMMA block was 800 g mol⁻¹. In order to observe the effect of hydrophilicity on the size and number of the particles, the MM of PEO block was increased to 5000 g mol⁻¹ while MM of PMMA block was kept constant (800 g mol⁻¹). Results show that when hydrophilicity increased, the average diameter of the particles increased, the number of particles decreased, and rate of conversion decreased. In addition to this, increasing the overall MM of diblock copolymer to 6200 g mol⁻¹ also resulted in increasing the size of particles and decreasing of both the conversion rate as well as the number of particles. Consequently, the MM and the hydrophilicity of the block copolymer play important role in latex production.⁸⁰ Another example of diblock copolymer used as a polymeric surfactant in emulsion polymerisation of PMMA latex is (DMAEMA₁₀-*b*-MMA₁₄).¹⁵⁵

In another study, to investigate the architecture effect of block copolymers on emulsion polymerisation of MMA, a triblock copolymer poly(MMA-*b*-PEO-*b*-MMA) was synthesised and compared with a diblock copolymer poly(MMA-*b*-PEO). The MM of PMMA kept constant and the MM of PEO was 10 000 g mol⁻¹. The rate of the emulsion polymerisation was the same when the diblock or triblock copolymer was used as the emulsifier. However, when the diblock copolymer was used, the size of particles was smaller and larger number of particles were produced compared to the triblock copolymer. As a result, diblock copolymers show higher efficacy than triblock copolymers. Recently, block-random copolymers were used as a polymeric surfactants in emulsion polymerisation.¹⁰¹ Example to random-block copolymer includes PS-*b*-(PS-*co*-PAA) which is successfully used as a stabiliser in emulsion polymerisation of styrene.

In a work by another group, high MM block copolymers were used as a polymeric surfactants and hairy particles of styrene with core-shell structure were synthesised.¹⁵⁶ The polymeric surfactant used was brush-type block copolymer, specifically PS₄₀-*b*-PPEGMA₇₀. A similar study was performed by same research group where MMA was polymerised instead of styrene while keeping the brush-type block copolymer same. Results showed that, growing latex (PMMA) is incompatible with hydrophobic PS segment therefore irregular morphology of particles obtained.¹⁵⁴ Another example of polymeric surfactant used in the synthesis of hairy particles is asymmetric block copolymer, PS₄₆-*b*-PAA₁₄₂.¹⁵⁷ Successful emulsion polymerisation of cross-linked and non-cross linked hairy poly(butyl acrylate) latex particles were synthesised and application of mechanical forces lead to selective cleavage of the "hairs" from the surface.

Finally, graft copolymers have also been used as a polymeric surfactant. An example includes poly(p-methylstyrene-*graft*-ethylene oxide).⁸⁰

Recent interesting studies use polymeric surfactants with antimicrobial properties were used for the synthesis of particles in emulsion polymerisation for the coating industry.¹⁵⁸ In an example the antimicrobial polymeric surfactant consisting of a hydrophobic butyl methacrylate block and statistical hydrophilic 2-(D-glucosamin-2-N-yl)carboylethyl methacrylate (HEMAGI) and quaternized trimethyl-amino ethyl methacrylate (TMAEMA) glycomonomers blocks. These block copolymers were used a polymeric surfactant to fabricate butyl methacrylate particles using emulsion polymerisation. According to their findings increasing the hydrophilicity of polymeric surfactants lead to decrease in the surface properties which is also observed in previous studies when diblock copolymer was used.^{80,158}

1.5.2 Enhanced Oil Recovery

Approximately 80% of the worldwide exploited crude oils are in the form of an emulsion. Specifically in the petroleum sector normally the oil is in an O/W type emulsion.^{159–162} The crude oil emulsions contains resins and asphaltenes which are surface-active components and make crude oil emulsions stable for hours or days.¹⁶² Enhanced oil recovery (EOR) is a method that aim to maximise production of the oil in the reservoir.¹⁶³ The chemical methods of EOR includes displacing fluid that is injected in oil reservoirs, which ease the mobilisation of the crude oil that is trapped between the porous rocks.⁷⁶ The most widely used displacing fluid is water and it is consisted of additives such as polymeric surfactants, traditional surfactants, polymer or inorganic base that are either used in alone or combination of three.^{76,164,165} One of the main aims of EOR is to decrease the interfacial tension at oil/water interfaces so that the trapped crude oil can mobilise.¹³ Therefore, surfactants injected in order to decrease the interfacial tension between displacing water and crude oil trapped between the porous rocks due to the capillary forces.¹⁶⁵ In addition to this, they alter the wettability of the porous rock surface from oil wet to water wet and control the mobility with the purpose of increasing the amount of oil from reservoir. The role of polymers in EOR is to increase the viscosity of the water and inorganic base (e.g. sodium hydroxide or carbonate) reacts with the organic acid components of the acidic crude oil and forms surfactants in situ.^{76,166} Using polymeric surfactants as an additive in EOR is a good option since it combines the i) role of surfactant which reduces the interfacial tension of oil/water interface and ii) role of polymer for enhancing the viscosity of aqueous solution that affects the capillary number positively, is not a new method.^{76,78,167} The rheology of the solution was changed by varying the amount of the

hydrophobic moiety of the polymeric surfactant which provides multiple options to use in EOR applications.¹⁶⁸ In addition to this, the advantages of using polymeric surfactant instead of surfactant-polymer mixture in EOR are: i) they prevent selective adsorption on the porous rocks, ii) they avoid the unwanted chemical interactions and chromatographic separations in the porous system, and iii) they prevent surfactants to be solubilised in the oil.^{76,169} However, there are only few studies reported that consider of the salt effects, viscosity and surface properties of polymeric surfactants used in EOR. One of the first published work on EOR that studied both interfacial properties and viscosity behaviour is poly(1-alkene-*co*-maleic anhydride).^{76,170}

Furthermore, hydrophobically modified polyacrylamides (HMPAM) are also used as polymeric surfactants in EOR.¹⁶⁹ According to the results, they showed good interface/surface activities and they showed good solution thickener properties. Furthermore, polyesters¹⁷¹ and polysaccharides¹⁷² are used as a polymeric surfactants in EOR. Raffa *et. al.* and his co-workers synthesised polystyrene-*b*-poly(sodium methacrylate), and the hydrophilic block contains randomly distributed poly(ethylene glycol) methyl ether acrylate (PEGA) comonomer.^{76,169} Results show that incorporation of PEGA macromonomer moiety to the block copolymer, enables decreasing the surface tension of the water. Examples of patented polymeric surfactants in EOR applications are⁷⁶: i) tapered copolymer containing vinyl acetate and acrylic acid ii) a block copolymer of styrene, acrylic acid and ethyl acrylate iii) acrylamide based polymers that are partially hydrolysed and containing neutral or charged hydrophobic monomers iv) a surfactant mixed with polymeric co-surfactants (patented by BASF). The polymeric co-surfactants have architecture of comb, star, multiblock containing hydrophilic units such as PPO, vinyl alcohol, allyl alcohol, vinylpyrrolidone, PEO, (meth)acrylic acid, maleic anhydride and hydrophobic units containing α -olefins. Lately, methyl ester sulfonate that is obtained from natural oils is grafted into the polymer chain which is acrylamide and it is a promising candidate for EOR applications.¹⁶³

1.5.3 Pesticide Formulations

Worldwide, the most widely used method to protect plants from insects, fungi, pathogenic bacteria, weeds and other pests is the use of pesticides.^{173,174} However, chemical pesticides are carrying potential risks for human health and environment due to containing volatile organic compounds (VOCs) such as xylene.²¹ Therefore, there is an increasing attention for developing pesticides that are eco-friendly, sustainable and controlled method to apply it to the plants (e.g. sprays).^{21,173} The effectiveness of the pesticides are determined by its storage stability and

application performance onto the crops and it must be developed during the formulation stage.¹⁷⁵

Recently, variety of pesticide delivery systems were developed and they include microcapsule (MC), wettable power (WP), suspensions concrete (SC), emulsifiable concrete (EC), microemulsions (ME), nanoemulsions.^{174,176,177} One of the carries for pesticide formulations includes, and environmentally friendly formulations.¹⁷⁸ The pesticide oil-in-water (O/W) emulsion (EW) is preferred compared to the emulsion concrete (EC) and microemulsions due to containing a large number of organic compounds such as dimethylbenzene as a solvent that is not environmentally friendly.^{174,179} The EW has small-sized liquid droplets containing water-insoluble pesticides or organic solvents containing pesticides, and those liquid droplets are dispersed in the water phase.¹⁷⁹ The EW is considered to be a safe and environmentally friendly formulation. The disadvantages of EW is the generation of large droplets sizes such as 0.5-3.5 μm , and it may cause unwanted toxicity.¹⁷⁴ Therefore, nanoemulsions are used as a carrier for the agrochemical application.^{21,177} Using nanoemulsions provides many advantages such as: i) good physical characteristics and long shelf life, ii) small sizes of droplets (20-200 nm) produced and they can uniformly deposited on to plant leaves and iii) lower amount of surfactants are required compared to the microemulsions.^{21,174} An example to nanoemulsion formulations contains β -cypermethrin as a pesticides, alkyl polyglycoside (APG) and polyoxyethylene 3-lauryl ether (C_{12}E_3) as mixed surfactants and methyl laurate as an oil phase.¹⁷⁷ Another example of nanoemulsion system includes polyoxyethylene non-ionic surfactant that stabilises the β -cypermethrin in methyl decanoate droplets. This nanoemulsion system is ideal candidate for pesticides delivery for the plant leaves.¹⁸⁰

1.5.4 Cosmetics and Personal care formulations

Emulsions such as O/W, W/O and multiple emulsions (W/O/W) are also used in cosmetic formulations.¹⁸¹ All three components, emulsifier, water phase and oil phase are important. Depending on the cosmetic product, the oil phase may include perfumes, pigments, minerals or vegetable oils whereas water phase may include natural or synthetic water-soluble polymers, vitamins, minerals and proteins. Commonly used oil phases used in cosmetic formulations are, linolin, silicone and paraffin oils. The role of oil phase in this application is to form a barrier and prevent the loss of water from the skin.

In addition to cosmetic emulsions, nanoemulsions and microemulsions are also available.¹⁸¹ Microemulsions are used in perfume gels, sunscreen gels, hair styling gels etc. due to their

transparency. When microemulsion is prepared, large amount of surfactant is required compared to the macroemulsions and nanoemulsions which gives disadvantage because it may cause to skin irritation. On the other hand, nanoemulsions consist small size droplets (50-200 nm) which can easily enter to rough surface of the skin and they enhance penetration of antioxidants, vitamins etc. into the skin.

The physicochemical characteristic of cosmetic emulsions such as droplet size distribution is important parameter in formulation because it affects the rheology and stability of emulsion which affects the self-life of the cosmetic product.¹⁸¹ Most cosmetic emulsions shelf life stability is varying between 3-5 years therefore accelerated storage stability testing should be performed which is a challenge for formulation scientist. An example to cosmetic emulsions is skin creams which contains non-ionic or polymeric surfactants as an active ingredient for preparation or emulsifier for the stabilisation.

In cosmetics and personal care applications, the second largest class of ingredients is polymeric surfactants. They are used in cosmetics and personal care formulations as a rheology modifier, emulsifier, stabilizer, destabilizer, thickener, film former, conditioner and many more.⁵² The main advantage of using polymeric surfactants in cosmetic formulations is because they are high molecular weight materials which cannot penetrate the skin (beyond the stratum corneum) therefore they do not cause harm when applied.¹⁸¹ In addition to this, polymeric surfactants have low irritation, toxicity and sensitization potentials. An example of neutral emulsifiers used in cosmetic formulations is proteins. They are chosen because they can stabilise emulsions by adsorbing strongly onto the oil/water interfaces. Other examples of natural ingredients include high molecular weight polymeric surfactants such as xanthan gum and hydroxyethyl cellulose widely used in the cosmetic industry. They can be used as a stabiliser in emulsions/ suspensions which prevent formation of destabilisation and they can act as rheology modifiers in order to change the consistency of the product. The most widely used polymeric surfactant in cosmetic formulations is block copolymer with ABA architecture, where block B is PPO and block A is PEO which is commercially available as Pluronic.

In the cosmetic industry, silicone-based materials are also frequently used polymeric surfactants. These materials consist of poly(dimethyl siloxane), (PDMS) and they are combined with specific groups according to the specific applications. For instance, dimethicone copolyol is PDMS, and polyoxyalkylene ether was incorporated as a specific group for the special application. The polyether-modified silicones containing polyglucoside or alkyl groups

are used as emulsifiers for water-silicone emulsions. In addition to this, they are also used to prevent skin irritation and act as defoamers, but this role depends on the type and modification degree of glycol. Furthermore, amino-functional silicones enhance the properties of hair-conditioning products.

When polymers are used as rheology modifiers in cosmetic formulations, they are normally synthetic. These are based on monomers like: ethylene oxide, allyl, acrylic and vinyl. The polymeric surfactants show thickening properties due to the formation of the chain entanglement.^{52,181} An example of polymeric surfactant used as a thickener is hydrophobically-modified carbomers such as acrylates/C₁₀₋₃₀ alkyl acrylate cross polymer which acts as emulsifier and rheology modifier. In addition to this, ethyl acrylate, ethoxylated long-chain alkyl acrylates and methacrylic acid co-polymers are used as alkali swellable thickeners. The thickening effect is created by the addition of alkali (such as triethanolamine) to neutralise lightly cross-linked poly(acrylic acid) which cause charged carboxylate groups to extend in the solution and lead to the formation of a "gel" due to the double layer repulsion.¹⁸¹ Polymeric surfactants are also used for both, to stabilise and thicken the emulsion, such as acryloyl taurate/vinyl pyrrolidone containing alpha and beta hydroxy acids.⁵² Having a N-acryloyl taurate moiety provides comb-like architecture that enhances the emulsifying and thickening properties and clarity. Furthermore, gradient copolymers are also used for skin hydration and formulation additives in anti-wrinkling creams.¹⁰⁴ In addition to this, gradient copolymers containing isobornyl methacrylate and various acrylate comonomers are also used in make up applications.

The effective styling hair product should; give glossy hair, increase hair volume, provide non-sticky feeling and many more.⁵² Polymeric surfactants provide these properties of hair styling products. The volatile organic compounds such as ethanol in aerosol sprays are replaced with water by using polymeric surfactants. They act as a film former by forming a non-hydroscopic film hence give a hair fixed style. The typical polymeric surfactants used as a film former have an architecture of block and graft because they contain distinct blocks which leads to segregative phase separation. The polymer gained mechanical rigidity and shock-absorbing properties due to the segregations. Furthermore, amphiphilic gradient copolymers such as styrene/acrylic acid (AA) are also used as hair fixatives, adhesives and toughening agents.¹⁰⁴ For instance, gradient copolymers such as styrene/acrylate/methacrylic acid are used by L'Oréal due to having low dispersity which prevents the phase separation and able to use in

nail varnish due to having good adhesion and mechanical properties, and good spray ability for aerosol compositions.

Finally, polymers can also use in hair dyes. An example is the hydrophobically modified ethoxylated urethanes (HEUR) is a triblock copolymer with ABA architecture and A block is hydrophobic and B block is hydrophilic.⁵² The HEUR polymeric surfactant is used in hair-colour dye to enhance the colour of the hair.

1.6 References

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CHAPTER 2: AIM OF THESIS

One of the most important classes of polymeric surfactants is amphiphilic block copolymers.¹ Specifically, di- and triblock are the most commonly used polymeric surfactants, and they are used as emulsion stabilisers in many different applications.

This study aims to synthesise a series of copolymers and observe how the polymer characteristics affect the emulsifying abilities of emulsions and establish a structure-property relationship. Firstly, we wanted to systematically explore the effect of MM and composition on the emulsifying abilities of copolymers. Therefore, the first study aims to synthesise two series of amphiphilic well-defined diblock copolymers. The first polymer series consists non-ionic and hydrophilic penta(ethylene glycol) methyl ether methacrylate (PEGMA, PEG) unit, and the second polymer series consists of ionic and hydrophilic, 2-(dimethyl amino) ethyl methacrylate (DMAEMA). Both polymer series is sharing the same hydrophobic unit, ethyl methacrylate (EtMA). The MM of the copolymers was targeted to 9000 g mol⁻¹, 6000 g mol⁻¹ and 3000 g mol⁻¹ and composition were targeted to 75-25, 60-40 and 50-50 hydrophilic-hydrophobic w/w%.

The second study of this PhD thesis aims to investigate if combining the three comonomers (PEGMA, EtMA and DMAEMA) to make triblock copolymers will improve the emulsifying abilities. The architecture of the triblock copolymers was kept constant, and ABC architecture was chosen due to providing better emulsifying properties.² In ABC architecture, B is the hydrophobic unit (EtMA), A and C are the hydrophilic units (PEGMA and DMAEMA). In order to make a comparison between the diblock copolymer series, the MM was targeted to 9000 g mol⁻¹, 6000 g mol⁻¹ and 3000 g mol⁻¹. The composition was targeted to 30-35-35, 30-30-40 and 30-25-45 w/w/w% of PEGMA-EtMA-DMAEMA. The composition of the PEGMA was kept constant, and the ratio of DMAEMA was increased.

The third study aims to investigate the effect of architecture on the emulsifying properties of copolymers. In this part of the study, seven different architectures of copolymers were synthesised. The MM of the copolymers were kept constant to 9000 g mol⁻¹. However, the composition of the hydrophilic component was varied to 75 wt% and 50 wt%. In this study, ionic DMAEMA was used as a hydrophilic unit, and *n*-butyl methacrylate was used as a hydrophobic unit.

The structural properties of all synthesised copolymers were determined, and their aqueous solution properties such as cloud points (CPs) effective pK_a s, critical micelle concentration (CMC) and hydrodynamic diameter (d_{hs}) values were determined.

Finally, emulsifying abilities of copolymers were determined by observing the volume fraction of the cream phase (Φ_{cream}) of each emulsion over a month. In addition to this, the size of the emulsion droplets was observed for a specific period.

CHAPTER 3: EXPERIMENTAL

3.1. Materials and Methods

Materials

Monomers were purchased from Sigma Aldrich Co Ltd., Irvine, United Kingdom. These monomers were; *n*-butyl methacrylate (BuMA, MM:142.20 g mol⁻¹ 99%), ethyl methacrylate (EtMA, MM: 114.14 g mol⁻¹, 99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, MM: 157.21 g mol⁻¹, 98%) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, MM: 300 g mol⁻¹, 94%), methyl methacrylate (MMA, MM:100.12 g mol⁻¹, 99%), *n*-hexyl methacrylate (HeMA, MM: 170.25 g mol⁻¹, 98%) and lauryl methacrylate (LMA, MM:254.41 g mol⁻¹ 96%). Compounds used for purification of monomers; calcium hydride (CaH₂, ≥ 90%) and basic aluminium oxide (Al₂O₃.KOH) were also purchased from Sigma Aldrich Co Ltd., Irvine, United Kingdom. Furthermore, compounds used for characterisation of polymers includes; deuterated chloroform used as NMR solvent (CDCl₃, 99.8 %), tetrahydrofuran used as polymerisation solvent (THF, HPLC grade, ≥ 99.9%), triethylamine (Et₃N, HPLC grade) used as additive for mobile phase in gel permeation chromatography, the initiator methyltrimethylsilyl dimethylketene acetal (MTS, 95%), were also purchased Sigma Aldrich Co Ltd., Irvine, United Kingdom. Moreover, sodium hydroxide pellets (NaOH, 97%), hydrochloric acid solution (volumetric, 1M), concentrated hydrochloric acid (HCl, ACS reagent, 37%) and the free-radical inhibitor 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) were also purchased from Sigma Aldrich Co Ltd., Irvine, UK. The PTFE hydrophilic syringe filters (pore size: 0.45 µm, diameter: 25 mm), Nylon syringe filters (pore size: 0.45 µm, diameter: 25 mm), and *n*-hexane were purchased from Fisher Scientific UK Ltd., Loughborough, UK. For the calibration of GPC, poly(methyl methacrylate) (PMMA) standard samples were used and they were purchased from Fluka, Sigma Aldrich Co Ltd., Irvine, UK. The mobile phase used in gel permeation chromatography (GPC) was tetrahydrofuran (not stabilised, HPLC grade) and PTFE syringe filters (pore size: 0.45 µm, diameter: 13 mm) were purchased from WR International Ltd., Lutterworth, UK. The oil phase, which is methyl laurate (> 98%) was purchased from Tokyo Chemical Industry UK Ltd., Oxford, UK.

Methods

The purification of low molar mass (MM) monomers (MMA, EtMA, BuMA, HeMA and DMAEMA) which are commercially available were prepared by following three steps; 1) the removal of any acidic impurities such as traces of free-radical inhibitor monomethyl ether hydroquinone and methacrylic acid were removed by passing the monomer twice through activated basic alumina 2) free-radical inhibitor (DPPH) was added to the monomer flask in order to prevent unwanted polymerisation, 3) Approximately 1g of drying agent (CaH_2) was added to the monomer flask and stirred for minimum 2 hours. The low MM monomers; DMAEMA, MMA, EtMA, BuMA and HeMA were distilled under vacuum just one day before the polymerisation in order to remove the CaH_2 , $\text{Ca}(\text{OH})_2$ and DPPH. In addition to this, MTS was also distilled under vacuum one day before the polymerisation. The high MM PEGMA was mixed with freshly purified 50 vol% THF, and passed from basic alumina twice, followed by mixing with CaH_2 for 2 hours. Unlike low MM monomers, DPPH was not added to PEGMA flask because it is high MM monomer and cannot be distilled. Instead PEGMA was purified according to Vamvakaki et al.¹ The catalyst, TBABB, was stayed under vacuum for overnight before polymerisation in order to provide moisture free environment. Freshly purified THF (polymerisation solvent) was collected using solvent purification system on the same day as polymerisation performed, which consists of activated alumina column (Pure SolvTM Micro 100 Liter solvent purification system, obtained from Sigma Aldrich). The polymerisation flasks and solvent flasks were hydrophobised using 250 μl and 1000 μl of dichlorodimethylsilane, respectively. It was followed by washing with ethanol and then acetone. All glassware was placed into an oven (140 °C) for overnight before distillation and polymerisation. The glassware was assembled under the vacuum when they were hot, and a heat gun was also used to provide a moisture-free environment.

3.2 Catalyst Synthesis

The synthesis of catalyst, TBABB, was synthesised by following the same procedure done by Dicker and co-workers.² Tetrabutyl ammonium solution (80 mL, 40% in water) and benzoic acid (10 g) were added into 250 mL round bottom and stirred until the mixture is homogenous. The mixture (aqueous phase) was transferred into the separation funnel, and the organic phase, which is chloroform (75 mL), was added. The organic phase was extracted three times and collected in a beaker, and it was followed by adding 10g of benzoic acid. Filtration was carried

out after the addition of magnesium sulphate, which acts as a desiccant in order to remove $\text{MgSO}_4/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. A rotary evaporator was used to remove chloroform. The white solid form of a product was collected and dissolved in warm THF (100 mL). Dried diethyl ether (70 mL) was added for recrystallisation of the product. Finally, a vacuum oven was used to dry the product.

3.3 Polymer Synthesis and Recovery

3.3.1 Block Copolymer Synthesis

The block copolymers are synthesised using the one-pot group transfer polymerisation (GTP) method, a living anionic polymerisation technique with the sequential addition of monomers to the polymerisation flask after the addition of catalyst, solvent, and initiator.^{3–5} Similar studies were performed by Vamvakaki and Patrikios previously.^{6–11} In addition to this, our group also synthesised block copolymers using GTP.^{12–17} In this PhD project, the synthesis of block copolymers followed the same procedure, except the order of addition of monomers was different and different monomers used. In addition to this, the amount of chemicals was also varied, amounts of ingredients for every polymer synthesis is available in the Appendix. Before adding ingredients, vacuum and argon cycles were applied to the 250 mL round bottom flask in order to ensure moisture-free environment. Approximately 10 mg of catalyst (TBABB) was added into the polymerisation flask and closed with rubber septum and it was purged with argon. An example of synthesis of P-A5 with theoretical polymer structure $\text{PEGMA}_{12}\text{-}b\text{-EtMA}_{21}$ is described. Firstly, the polymerisation solvent THF (44mL) and then initiator, MTS (0.6 mL, 0.51g, 0.003mmol) were syringed into the polymerisation flask under stirring. It was followed by syringing (20.3 mL, 10.6 g, 0.035 mmol) PEGMA. The PEGMA was syringed through PTFE filter (pore size, 0.45 μm) to the polymerisation flask in order to prevent CaH_2 to pass through. After addition of PEGMA, reaction let to stirring for 15 min in order to make sure that all monomer reacts. The temperature of the reaction increased from 24 to 34 °C which is an exothermic reaction. Once 15 min was completed, approximately 1 mL of sample was taken from the polymerisation flask for characterisation using GPC and ^1H NMR. The second monomer EtMA (7.73 mL, 7.09 g, 0.062 mmol) was syringed to the polymerisation flask and exothermic reaction was observed (26.0 to 31.0 °C). Once polymerisation was completed, the sample was syringed for characterisation for GPC and ^1H NMR. Finally, 2-3 drops of methanol

were added for all GPC and ^1H NMR samples and polymerisation flask in order to make sure that polymerisation was terminated.

3.3.2 Gradient Copolymer Synthesis

Gradient copolymers were synthesised via one-pot GTP method with addition of two monomers simultaneously at a controlled rate. An example of synthesis of P-D7 with theoretical polymer structure $\text{BuMA}_7\text{-}b\text{-(BuMA}_{13}\text{-}grad\text{-DMAEMA}_{13})\text{-}b\text{-DMAEMA}_6$ is described. Like other polymer synthesis, before adding ingredients into the polymerisation flask, the vacuum-argon cycles were applied three times. The TBABB (10 mg) was added into the polymerisation flask and closed with rubber septum and it was purged with argon. The THF (77.1 mL) was syringed into the polymerisation flask and it was followed by syringing the MTS (0.65 mL, 0.56 g, 0.003 mmol). Monomer, BuMA (3.58 mL, 3.2 g, 0.02 mmol) was syringed into the polymerisation flask, the temperature increased to 25.3 to 28.0 °C and once monomer fully reacted, samples were taken for GPC and ^1H NMR analysis. BuMA (7.16 mL, 6.4 g, 0.04 mmol) and DMAEMA (6.86 mL, 6.4 g, 0.04 mmol) were syringed into the polymerisation flask simultaneously at different rates. The temperature of the reaction increased rapidly from 26.0 to 38.0 °C and in order to prevent the uncontrollable exotherm reaction, polymerisation flask was placed inside the water bath. Approximately 1 mL of samples were taken for GPC and ^1H NMR analysis. Finally, DMAEMA (3.43 mL, 3.2 g, 0.02 mmol) was syringed to the polymerisation flask and the temperature increased from 25.1 to 28.9 °C and samples were taken for GPC and ^1H NMR analysis. Finally, 2-3 drops of methanol were added for all GPC and ^1H NMR samples and polymerisation flask to terminate the active polymer chains.

3.3.3 Triblock Copolymer with a statistical middle block

Triblock copolymers with a statistical copolymer as a middle block were synthesised using GTP. The middle block of the copolymer was synthesised by syringing the two monomers simultaneously at a controlled rate. An example of synthesis of P-D6 with theoretical polymer structure $\text{BuMA}_7\text{-}b\text{-(BuMA}_4\text{-}co\text{-DMAEMA}_{22})\text{-}b\text{-DMAEMA}_6$ is described. Before adding the ingredients, the vacuum-argon cycles were applied to the polymerisation flask. The TBABB (10 mg) was added and closed with rubber septum and it was purged using argon. The THF (77.3 mL) was syringed into the polymerisation flask and it was followed by syringing the MTS (0.65 mL, 0.56 g, 0.003 mmol). BuMA (3.58 mL, 3.2g, 0.022 mmol) was syringed, and

the temperature increased from 25.3 to 29.7 °C. When monomer is fully reacted, the sample (~ 1 mL) was taken from polymerisation flask for GPC and ^1H NMR analysis. Addition of BuMA (1.8 mL, 1.6 g, 0.011 mmol) and DMAEMA (12 mL, 11.2 g, 0.07 mmol) was occurred at the same time with a controlled rate and the temperature increased from 26.0 to 34.0 °C. The water bath was applied to prevent the uncontrollable reaction. After all monomers were added and polymerised (as indicated by the temperature decreasing), a sample was taken for GPC and ^1H NMR analysis. Lastly, DMAEMA (3.43 mL, 3.2 g, 0.02 mmol) was added and the temperature increased from 26 to 29.7 °C. The sample was taken for GPC and ^1H NMR analysis. Finally, 2-3 drops of methanol were added for all GPC and ^1H NMR samples and polymerisation flask in order to make sure that polymerisation had terminated.

3.3.4 Statistical Copolymer Synthesis

Statistical copolymers were also synthesised using the GTP method. In statistical copolymer synthesis, monomers were added simultaneously instead of sequentially. An example of synthesis of P-A7 with theoretical polymer structure $\text{PEGMA}_{12}\text{-co-EtMA}_{21}$ is described. Before adding catalyst into the polymerisation flask, vacuum-argon cycles were applied. The TBABB (10 mg) was added and closed with rubber septum and it was purged with argon. Firstly, the polymerisation solvent THF (44 mL) was syringed and then the two monomers, PEGMA (20.25 mL, 10.63 g, 0.035 mmol) and EtMA (7.73 mL, 7.09 g, 0.062 mmol), were syringed simultaneously into the polymerisation flask. Once all monomers were syringed, initiator MTS (0.60 mL, 20.25 g, 0.003 mmol) was syringed and reaction initiated. The temperature of the reaction increased from 24 to 39 °C. In first polymer series, the water bath was not needed, but in other polymer series water bath was used in order to prevent uncontrollable exothermic reaction. When 15 min was completed, approximately 1 mL of sample was taken from the polymerisation flask for GPC and ^1H NMR analysis. Finally, 2-3 drops of methanol were added to terminate the polymerisation.

3.3.5 Polymer Recovery

Firstly, a rotary evaporator was used to remove the THF partially and then the viscous polymer solution was precipitated in *n*-hexane (400 mL) under stirring. The precipitated polymers were placed into the freezer for 30 mins in order to enhance the precipitation. The *n*-hexane was removed, and precipitated polymers were placed into the vacuum oven for a week in order to make sure that *n*-hexane and THF was fully evaporated.

3.4 Polymer Characterisation

3.4.1 Characterisation in Organic Solvents

3.4.1.1 Proton Nuclear Magnetic Resonance (^1H NMR) Spectroscopy

A 400-MHz Avance Bruker NMR spectrometer (Bruker, UK Ltd., Coventry, UK), was used to acquire the chemical composition of the final copolymers and their linear precursors. As an NMR solvent, deuterated chloroform (CDCl_3) was used and TMS was used as a reference. A 650 μl of CDCl_3 was added to the samples.

The analysis of the ^1H NMR spectra was performed using Mastrenova software programme in order to calculate the experimental chemical composition of the copolymers. The **Table 3.1** shows the distinctive peaks that was used for calculation of experimental chemical composition of the copolymers.

Table 3.1. The distinctive peaks, and type/number of protons that is used to identify the monomer.

Monomer name	Type of protons	No of protons	Distinctive peak (ppm)
PEGMA	three methoxy protons	3	3.35
DMAEMA	protons of two methyl groups next to nitrogen atom	6	2.25
MMA	three methoxy protons	3	3.6
EtMA	three methyl protons	3	1.3
BuMA	two methylene protons close to ester	2	3.9
HeMA	two methylene protons	2	3.9
LMA	two methylene protons next to methyl group	2	1.29

3.4.1.2 Gel Permeation Chromatography (GPC)

The molar mass (MM) and molar mass distributions (MMD) of the final copolymers and their linear precursors were determined using GPC which is purchased from Agilent technologies UK Ltd., Shropshire, UK. The GPC system includes 1) Agilent SECurity, 2) a “1260 Iso” isocratic pump, 3) Analytical linear M column (SDA083005LIM), 4) refractive index (RI) detector (Agilent 1250) 5) a Polymer Standard Service (PSS) SDV. Two different mobile phases were pumped; 1) 5 vol% Et₃N in a THF solvent, 2) pure THF. During the analysis, the mobile phase flow rate was 1 mL min⁻¹. Before running any measurements, approximately 1 mL of mobile phase was added to the sample and it was filtered using PTFE syringe filters with a pore size 0.45 µm. In addition to this, prior to the measurements, the GPC machine was calibrated with PMMA standards and it is based on six narrow MM; 2000, 4000, 8000, 20 000, 50 000 and 100 000 g mol⁻¹.

As can be seen from polymerisation tables (see **Table 4.1**), there are two different MM values for each polymer. The MM stands for the experimental, which is obtained from GPC and MM^{theor.} stands for theoretical MM which is a value calculated using the **equation 3.1** below.

$$MM^{\text{theor.}} \text{ (g mol}^{-1}\text{)} = (\sum_i MM_i \times DP_i) + 100 \quad \text{Equation 3.1}$$

As shown in **equation 3.1** above, the theoretical MM was calculated by multiplying the degree of polymerisation (DP_i) of each monomer with MM of each monomer. In theoretical MM calculations, 100 g mol⁻¹ was included in the result due to the presence of initiator (MTS) at the end of the polymer chain.

3.4.2 Characterisation in Aqueous Solutions

All aqueous copolymer solutions were prepared using deionised water, DI from a Milli-Q system (Millipore) and all the experiments were performed at room temperature.

3.4.2.1 Dynamic Light Scattering

A 1 w/w% water-soluble polymer solutions were prepared using fresh DI water. Zetasizer Nano ZSP (Malvern Instruments Ltd., Malvern, UK) was used in order to determine the hydrodynamic diameter (d_{hs}) of copolymers. Polymers that were not soluble in water and have DMAEMA unit which is ionisable, their pH was adjusted to pH 5 and 7. Once polymers are fully soluble, they are passed from Nylon syringe filters with a pore size 0.45 µm in order to

remove dust particles as well as large aggregates. Before running any measurements, filtered polymer solutions were allowed to settle for 30 minutes in order to let if there are any air bubbles to escape. Three measurements were performed for each sample and the mean values were calculated which is the maximum of the peak by intensity that corresponds to hydrodynamic diameter. Measurements were performed at 25 °C and the scattered light at a backscatter angle was 173 °C. In this PhD project, two values were reported as a hydrodynamic diameter d_{hs} ; 1) experimental d_{hs} , which is the value obtained from DLS 2) theoretical d_{hs} , it is a calculated hydrodynamic diameter which is a theoretical model and dependent on architecture of the copolymer. The theoretical hydrodynamic diameter calculations were based on two models. In first model, it was assumed that block copolymer architectures form spherical micelles and in second model, statistical copolymers are assumed to form random coil configuration. For instance, diblock copolymers assembles to spherical micelles (core-shell) and it was assumed that hydrophobic (B) repeated units fully overlaps in order to prevent contact with water and hydrophilic (A and/or C) repeated units fully extended in water. In this PhD project, most of the copolymers assembles to form core-shell micelles however there are other architectures present that assembles to flower-type micelles.

The architectures with different micelles structures will be more discussed in the corresponding results and discussion chapters.

As can be seen from **Table 3.2**, for every copolymer with a specific architecture, has different equation to calculate the theoretical hydrodynamic diameter. The DP represents the experimental degree of polymerisation which is calculated using experimental MM (after precipitation) and composition. In theoretical hydrodynamic diameter equations, 0.254 nm is used as a projected length of one methacrylate unit for calculations of block copolymers that assembles to micelles.

Table 3.2. The equation of theoretical hydrodynamic diameters for block and statistical copolymers with different architectures.

Architecture of copolymer	General Structure		Theoretical hydrodynamic diameter equation (nm)	Equation No.
	Full	Abbr.		
Diblock copolymer	A-b-B	AB	$d_h = (DP_A + 2 \times DP_B) \times 0.254$	3.2
Triblock copolymer	A-b-B-b-C	ABC	For $DP_A < DP_C$ $d_h = (DP_B + 2 \times DP_C) \times 0.254$	3.3
			For $DP_A > DP_C$ $d_h = (DP_B + 2 \times DP_A) \times 0.254$	3.4
	A-b-B-b-A	ABA	$d_h = (DP_B + 2 \times DP_A) \times 0.254$	3.5
	B-b-A-b-B	BAB	$d_h = (DP_B + DP_A) \times 0.254$	3.6
	A-b-(A-co-B)-b-B	A-b-(A-stat-B)-b-B	i) $d_h = [DP_B + 2 \times (DP_R + DP_A)] \times 0.254$ ii) $d_h = [(DP_B + 2 \times DP_A + DP_R)] \times 0.254$	3.7 3.8
Tetrablock copolymer	A-b-B-b-A-b-B	ABAB	$d_h = (DP_B + DP_A) \times 0.254$	3.9
Gradient copolymer	A-b-(A-grad-B)-b-B	A-b-(A-grad-B)-b-B	i) $d_h = [DP_B + 2 \times (DP_G + DP_A)] \times 0.254$ ii) $d_h = [(DP_B + 2 \times DP_A + DP_G)] \times 0.254$	3.7 3.8
Statistical copolymer	A-co-B	A-stat-B	$d_h = 2 \times [2.20 \times 2 \times (DP_A + DP_B)/3]^{1/2} \times 0.154$	3.10

^IDP represents degree of polymerisation. The experimental DP is calculated by using experimental MM and composition from GPC and ¹H NMR analysis.

^{II} d_h represents the diameter of gyration, which is obtained by DLS.

^{III}0.254 nm is the projected length of one methacrylate unit.

^{IIII}A represents the hydrophilic B represents the hydrophobic repeated units. The presence of second hydrophilic repeated unit is represented by C. Stat and grad represents the statistical and gradient parts respectively.

3.4.2.2 Potentiometric Titrations

Aqueous polymer solutions containing DMAEMA units were prepared with a concentration of 1 w/w%. The HI98103 pH-checker (Hanna instruments Ltd., Leighton Buzzard, UK) was used to perform the titrations. The initial pH of the polymer solutions was recorded, and they were titrated from pH 2 to pH 12 by adding 0.246 M NaOH solution. For each polymer, titration curves were plotted, and the half-equivalence point was determined as a pK_a value. The pK_a value is the pH at which 50% of DMAEMA units are protonated.

3.4.2.3 Cloud Point

A 1 w/w% of aqueous polymer solutions were prepared for all water-soluble polymers. For polymers that are insoluble in water, they were protonated by 10% and their behaviour was observed. Polymer solutions were placed inside the water bath and temperature of the water bath increased from 25 to 80 °C, by increasing 1 °C and the behaviour of the polymer solutions observed visually. In this experiment, IKA RCT stirrer hot plate was used to heat the water bath and IKA ETS-D5 was used to control the temperature. The temperature at which the polymer solution turned to cloudy was recorded as a cloud point.

3.4.2.4 Critical Micelle Concentration (CMC)

Aqueous polymer solutions with 13 different concentrations; 0.0001, 0.00025, 0.0005, 0.001, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.25, 0.5 and 1.0 w/w% were prepared for each polymer. The aqueous polymer solutions were filtered five times using the 0.45 µm pore size PTFE filters in order to remove large aggregates and dust particles. DLS was used to measure the kilo count per second (kcps) per sample and 10 kcps values were recorded and average taken for each sample. The attenuation, position and type of cuvette kept same for all measurements. The graphs of kcps versus concentration graphs were plotted for each sample and tangent line was drawn and CMC values were determined for each polymer.

3.5 Stabilisation of Emulsions using Polymeric Surfactants

3.5.1 Hydrophile-Lipophile Balance (HLB)

The theoretical hydrophile-lipophile balance (HLB) of polymeric surfactants were calculated using the **Equation 3.11** which is introduced by Griffin.^{18,19} The formula consists the weight fraction of the lyophilic (W_l), and weight fraction of the hydrophilic (W_h) components.

$$HLB = \frac{W_h}{W_h + W_l} \times 20 \quad \text{Equation 3.11}$$

3.5.2 Preparation of Emulsions

In this project, emulsions of methyl laurate and water was obtained by using in house synthesised polymeric surfactants. The polymeric surfactants were dissolved in the methyl laurate phase and it was followed by addition of DI water. The concentration of polymeric surfactant in total emulsion was 1 w/w% and the weight ratio of methyl laurate and water phase was 1:1. Once all ingredients were added together, Hielscher UP050H Ultrasonic Processor (1 full cycle and 100% amplitude) was used for 1 minute for emulsification.

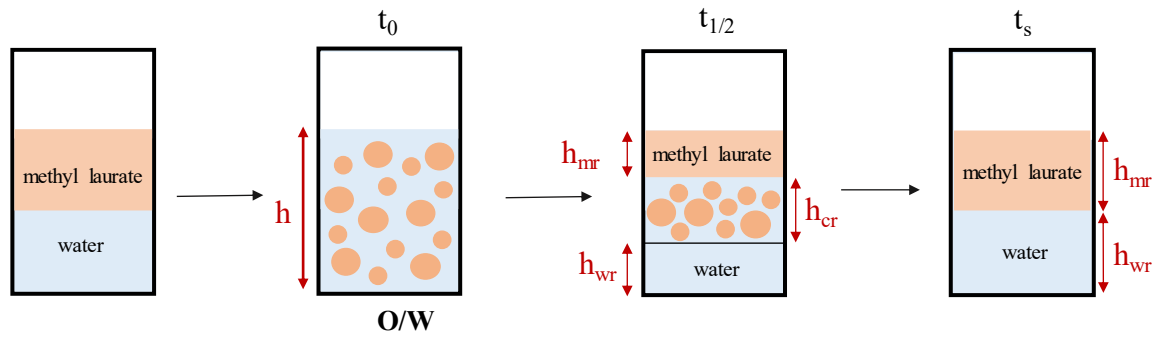
3.5.3 Characterisation of Emulsions

3.5.3.1 Type of Emulsions

The type of emulsions (O/W or W/O) was determined by performing drop tests. The freshly prepared emulsions (2 drops) were added into approximately 3 mL of DI water and 3 mL of methyl laurate separately. If the emulsion is O/W, the emulsion drops uniformly distributed in the water phase, whereas they precipitate in the form of coagulated spherical drops in the methyl laurate. On the other hand, if emulsion is W/O, emulsion drops uniformly distributed in the methyl laurate, whereas precipitates in the form of coagulated spherical drops in the water phase.

3.5.3.2 Visual Observations of Emulsions

After emulsions were produced, the glass vials were placed immediately in front of the stand with a black background. The distance between the emulsion and camera kept constant throughout the experiment. The photographs of emulsions were taken using Apple iPhone 7 with a 12-megapixel camera. The photographs of emulsions were taken at regular times, and the thickness of the cream layer measured, and volume fraction of the cream layer was measured using **Equation 3.12** (see **Figure 3.1**).



$$\phi_{\text{cream}} = h_{\text{cr}}/h$$

Equation 3.12

$$t_0 \phi_{\text{emulsion}} = 1 \text{ and } \phi_{\text{water}} = \phi_{\text{methyl laurate}} = 0$$

$$t_{1/2} \phi_{\text{emulsion}} = 1/2 \text{ and } 0 < \phi_{\text{water}}, \phi_{\text{methyl laurate}} < 1$$

$$t_s \phi_{\text{emulsion}} = 0 \text{ and } \phi_{\text{water}} = \phi_{\text{methyl laurate}} = 1$$

Figure 3.1. The schematic representation of visual observation to determine the volume fraction of the cream phase (ϕ_{cream}).

3.5.3.3 Microscopy Observations of Emulsions

The size of the emulsion droplets was determined by using Olympus BX51 Optical Transmission Spectroscopy with a 12-bit Olympus camera (DP070). A drop of freshly made emulsion was placed on a microscopy slide and covered with a coverslip, and they were observed under the microscopy as soon as emulsification finished. The size of the emulsion droplets observed after emulsification and a week to see the change in the size of emulsion droplets. The size of the emulsion droplets was analysed using a software program called Image J.

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CHAPTER 4: CHARACTERISATION OF DIBLOCK COPOLYMERS AS POLYMERIC SURFACTANTS

This chapter of my PhD thesis has been already published and can be found:

B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

Please note that section 4.4.2.2 is not included in the paper.

In the last decades, tailor-made polymeric surfactants, such as amphiphilic block copolymers, have attracted great interest due to providing more significant opportunity than traditional low MW surfactants.¹ Patrickios and co-workers systematically investigated the emulsifying ability of diblock copolymers.² In their work, they used benzyl methacrylate (BzMA) and non-ionic methoxy hexa(ethylene glycol) methacrylate (HEGMA) as a hydrophobic and hydrophilic block, respectively. According to the results, the low MM polymeric surfactants (2500 and 5000 g mol⁻¹) provide better emulsifying ability than the higher MM (10 000 g mol⁻¹) diblock copolymers and their homopolymers. On the other hand, Georgiou and co-workers performed a systematic study of the emulsifying ability of diblock copolymers that are based on non-ionic poly(ethylene glycol) methacrylate (PEGMA) and *n*-hexyl methacrylate (HEMA). They observed that diblock copolymers with the highest MM (9000 g mol⁻¹) and HEMA (50 wt%) content show better emulsifying ability.

Therefore, this study aims to systematically investigate the emulsifying ability of diblock copolymers and the effect of MM and composition on their properties. The first part of the thesis includes the syntheses of two well-defined amphiphilic diblock copolymer series and the corresponding statistical copolymers, which are named **polymer series 1** and **polymer series 2**. The characterisation of Polymer series 1&2 in aqueous and organic solvents is also discussed. The **polymer series 1** is based on PEGMA, a non-ionic, hydrophilic monomer, while in **polymer series 2**, DMAEMA was used as the hydrophilic comonomer that is pH responsive. Both series share the same hydrophobic component, EtMA, and in both polymer series, the MM and the composition were systematically varied to observe how these affect the properties of copolymers. The composition of copolymers was targeted to 50-50, 60-40 and 75-25 hydrophilic-hydrophobic w/w%. The MM of copolymers was targeted to 3000 g mol⁻¹, 6000 g mol⁻¹ and 9000 g mol⁻¹. The chemical structure and names of monomers used in this chapter is shown in **Figure 4.1**.

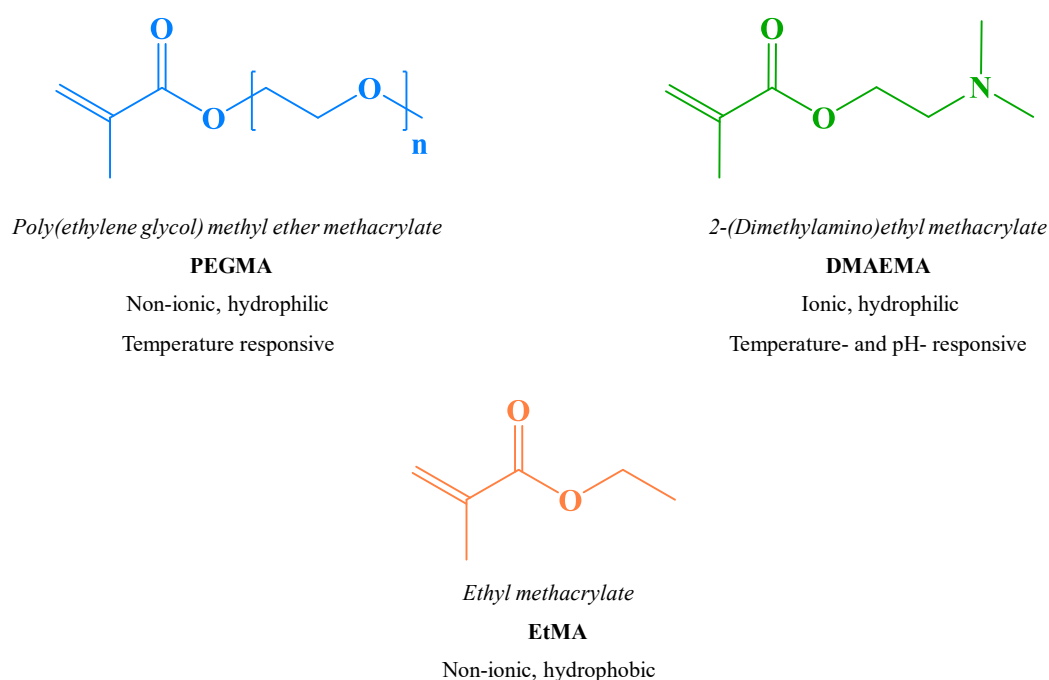


Figure 4.1. The chemical structures, names and abbreviations of monomers used to synthesise polymer series 1 and 2.

4.1. Synthesis of Diblock and Statistical copolymers

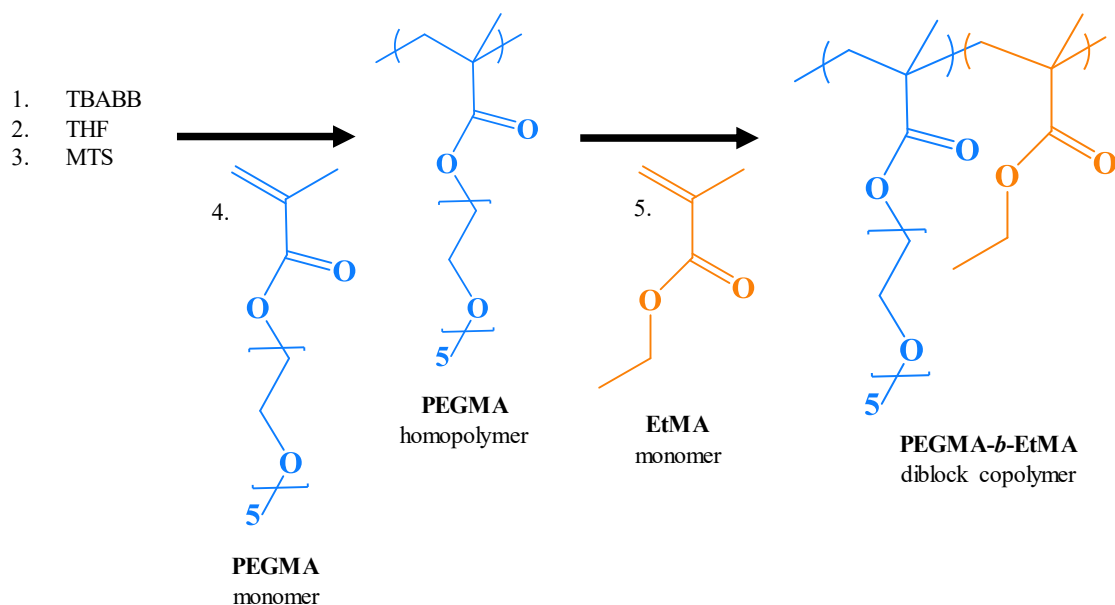
All block and statistical copolymers were synthesised via the one-pot GTP method, which is an anionic polymerisation technique. Two different general synthetic routes were followed, depending on the desired polymer. In **polymer series 1**, route A was followed; catalyst (TBABB), GTP solvent (THF) and monofunctional initiator (MTS) were added into the polymerisation flask, respectively, and it was followed by sequential addition of the monomers. PEGMA was added first and the EtMA monomer second, as shown in **Figure 4.2**. The PEGMA monomer was used as a first monomer because it is less reactive compared to EtMA monomer, and it is more difficult to polymerise as a second block.

The **polymer series 2** was polymerised following the same route as the **polymer series 1**; the only difference is the order and chemical nature of the hydrophilic monomer (see **Figure 4.2**). Specifically, the EtMA monomer was used as a first monomer instead of DMAEMA monomer. The reason for this is because DMAEMA is more reactive than EtMA.

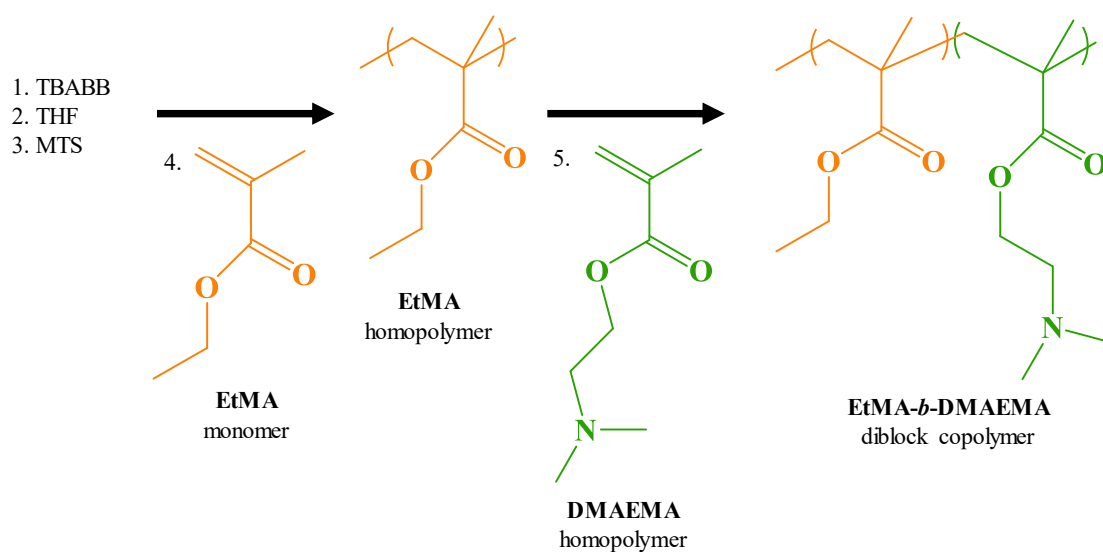
The synthesis of statistical copolymers was polymerised by following the second route (**Figure 4.2**). Like in the synthesis of block copolymers, catalyst (TBABB) and polymerisation solvent (THF) were added into the polymerisation flask. It was followed by adding monomers and as

a final step, initiator (MTS) was added into the polymerisation flask to initiate the reaction. All statistical copolymers were synthesised in the same way; the only variables were the amounts and the chemistry of the monomers.

A) Synthesis of diblock copolymers (Polymer Series 1):



B) Synthesis of diblock copolymers (Polymer Series 2):



C) Synthesis of statistical copolymer:

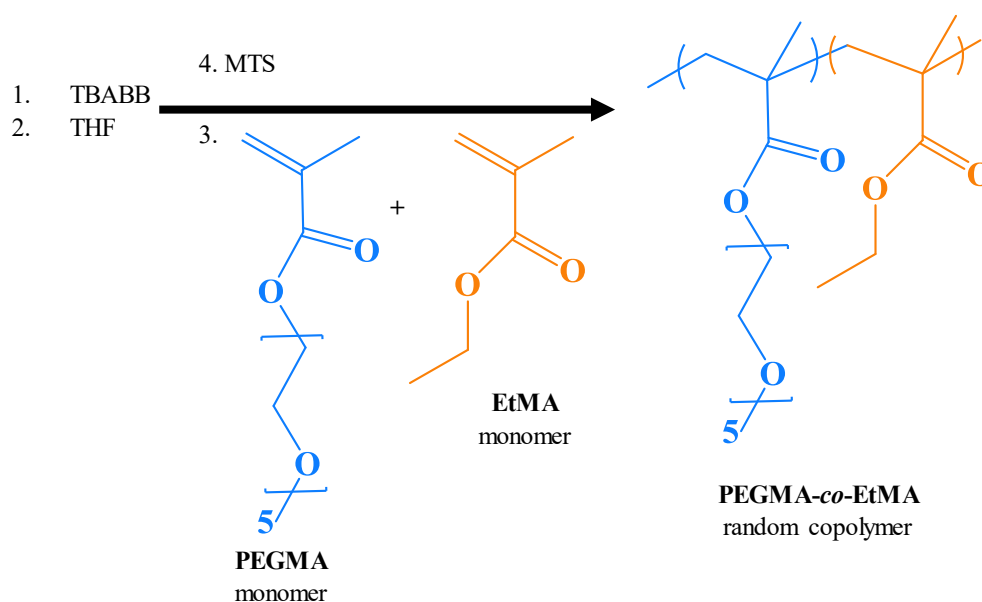


Figure 4.2. The schematic diagram of; **A)** and **B)** sequential addition of monomers (PEGMA, EtMA and DMAEMA) after addition of catalyst (TBABB), polymerisation solvent (THF) and initiator (MTS) **C)** The simultaneous addition of monomers, before addition of MTS.

In this study, eleven copolymers for **polymer series 1**, were successfully synthesised, specifically, nine well-defined diblock copolymers (P-A1-6 and P-A8-10) and two statistical copolymers (P-A7 and P-A11). The structures of the copolymers are schematically represented in **Figure 4.3**. Furthermore, for **polymer series 2**, nine well-defined diblock copolymers (P-B1-9) and one statistical copolymer (P-B10) were successfully synthesised and are schematically represented in **Figure 4.3**. In both polymer series, the composition was varied from 50-50%, to 60-40% and 75-25% w /w, of hydrophilic-hydrophobic, and the MM from 3000, to 6000 and 9000 g mol⁻¹.

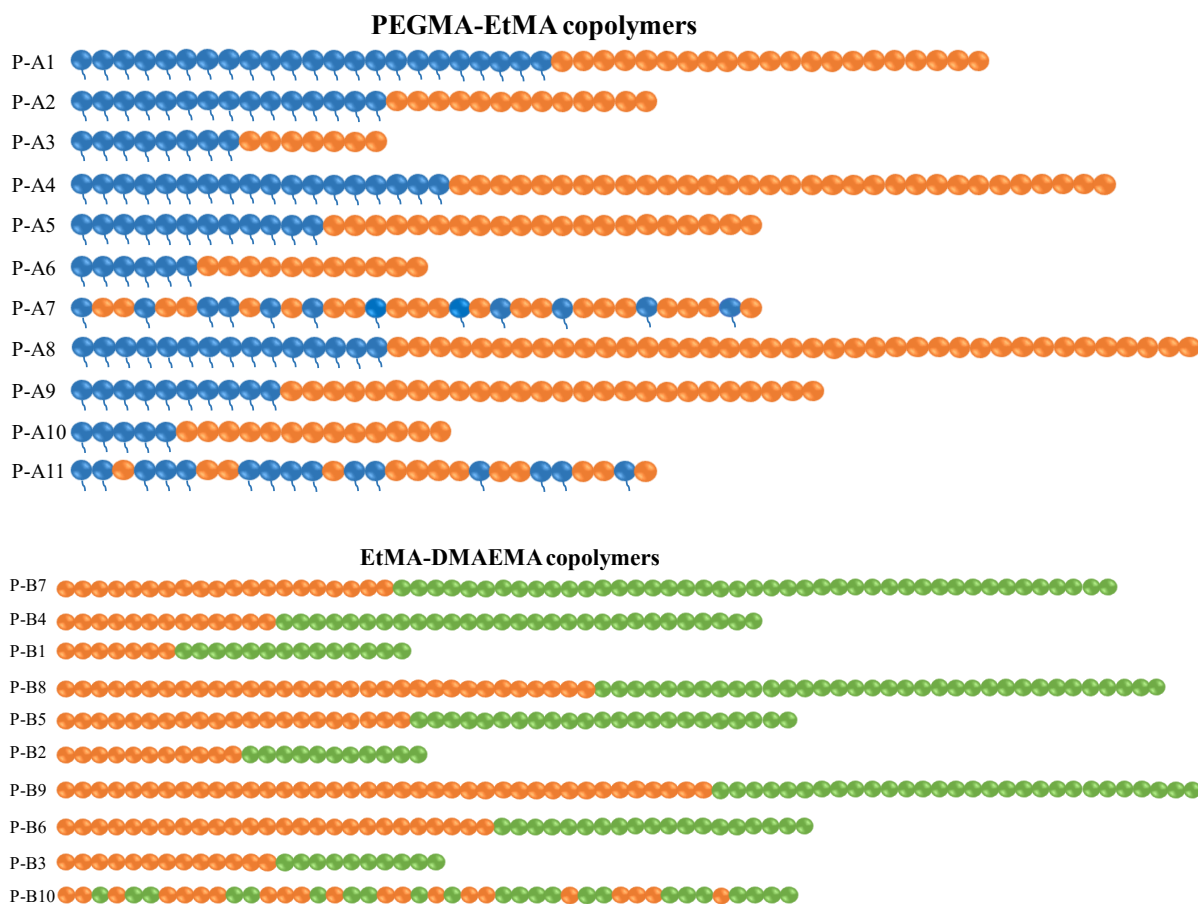


Figure 4.3. Schematic representations of all synthesised PEGMA-EtMA (**polymer series 1**) and EtMA-DMAEMA based (**polymer series 2**) copolymers. The hydrophobic EtMA units are shown in orange spheres and hydrophilic PEGMA and DMAEMA units are shown in blue and green spheres, respectively. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

4.2 Structural Properties

The theoretical and experimentally determined MMs, MMDs (dispersity indices, $\bar{D}$), theoretical and experimentally determined composition for both **polymer series 1** and **2** are discussed in the following section. Specifically, the structural properties of **polymer series 1** and **2** are tabulated in **Table 4.1**.

4.2.1 Molar Mass and Molar Mass Distribution

The experimental MMDs and MMs of all diblock copolymers and their homopolymers as well as statistical copolymers were determined using GPC. An example of a GPC chromatogram, specifically of P-A5 is shown in **Figure 4.4**. As can be seen the GPC traces of the homopolymer (PEGMA₁₂) and the diblock copolymer (PEGMA₁₂-*b*-EtMA₂₁) are represented by blue and orange, respectively. The MM peak of PEGMA₁₂-*b*-EtMA₂₁ appears after the PEGMA₁₂, which confirms that chain extension occurred due to the addition of EtMA monomer and that the MM increased. Thus, this proves a successful sequential GTP. In addition to this, the absence of unreacted monomer peak indicates that complete consumption of monomer hence 100% conversion of the monomer to polymer observed. Similar chromatogram profiles were observed for other copolymers in **polymer series 1**. The GPC chromatogram of all the copolymers from polymer series 1 can be found in Appendix section. These results are similar to previous studies on diblock copolymers prepared *via* GTP.^{2,3}

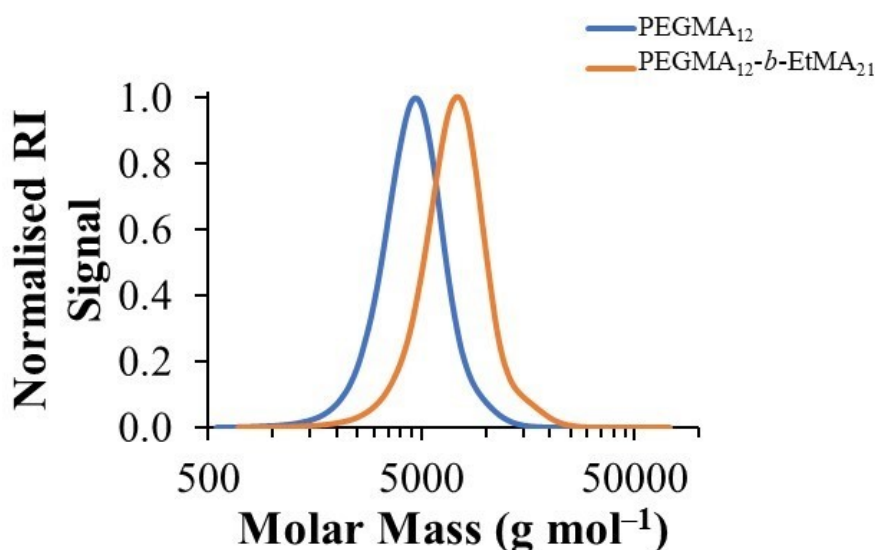


Figure 4.4. The GPC chromatogram of P-A5: PEGMA₁₂-*b*-EtMA₂₁. The blue and orange lines represent the PEGMA homopolymer and the diblock copolymer, PEGMA₁₂-*b*-EtMA₂₁, respectively. Reproduced, with permission, from “B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

Table 4.1 shows the theoretical chemical structures, the theoretical MMs, the number average MMs (M_n), the dispersity indices ($\bar{D}$ values), theoretical and experimental composition for all copolymers from **polymer series 1** and their precursors. The final M_n s of diblock copolymers vary between 3830 and 11,700 g mol⁻¹, which is in good agreement with theoretical MMs. When comparing the theoretical with the corresponding experimental M_n values, M_n values are slightly higher than the theoretical. This was expected and observed before in several GTP studies.⁴⁻⁸ One of the reasons for this is the presence of moisture and protic impurities in the reaction vessel which causes initiator molecules to terminate and thus less initiation sites are active that results in higher MM. As can be seen from **Table 4.1**, the $\bar{D}$ values for **polymer series 1** was found to be 1.11-1.18. The $\bar{D}$ values are quite low, close to 1, which confirms a successful “living” polymerisation.

Table 4.1. The theoretical polymer structure, theoretical molar mass ($MM^{\text{theor.}}$), number-average MM, M_n , dispersity index ($\mathcal{D}$) and composition of the diblock copolymers, and their homopolymer precursor.

	No.	Theoretical Polymer Structure ^a	$MM^{\text{theor. b}}$ (g mol ⁻¹)	M_n^c (g mol ⁻¹)	$\mathcal{D}^d$	w/w% PEGMA-EtMA	
						Theoretical	¹ H NMR
Polymer Series 1	P-A1	PEGMA ₂₃	6850	8580	1.13	100-00	100-00
		PEGMA ₂₃ - <i>b</i> -EtMA ₂₀	9100	11700	1.16	75-25	74-26
	P-A2	PEGMA ₁₅	4600	6410	1.11	100-00	100-00
		PEGMA ₁₅ - <i>b</i> -EtMA ₁₃	6100	8180	1.12	75-25	74-26
	P-A3	PEGMA ₈	2350	3160	1.13	100-00	100-00
		PEGMA ₈ - <i>b</i> -EtMA ₇	3100	4150	1.11	75-25	73-27
	P-A4	PEGMA ₁₈	5500	5859	1.17	100-00	100-00
		PEGMA ₁₈ - <i>b</i> -EtMA ₃₂	9100	10765	1.13	60-40	59-41
	P-A5	PEGMA ₁₂	3700	4290	1.13	100-00	100-00
		PEGMA ₁₂ - <i>b</i> -EtMA ₂₁	6100	6700	1.13	60-40	59-41
	P-A6	PEGMA ₆	1900	2550	1.18	100-00	100-00
		PEGMA ₆ - <i>b</i> -EtMA ₁₁	3100	4130	1.15	60-40	58-42
Polymer Series 2	P-A7	PEGMA ₁₂ - <i>co</i> -EtMA ₂₁	6100	6560	1.15	60-40	58-42
	P-A8	PEGMA ₁₅	4600	5244	1.15	100-00	100-00
		PEGMA ₁₅ - <i>b</i> -EtMA ₃₉	9100	10596	1.13	50-50	50-50
	P-A9	PEGMA ₁₀	3100	3970	1.13	100-00	100-00
		PEGMA ₁₀ - <i>b</i> -EtMA ₂₆	6100	7100	1.13	50-50	48-52
	P-A10	PEGMA ₅	1600	2270	1.17	100-00	100-00
		PEGMA ₅ - <i>b</i> -EtMA ₁₃	3100	3830	1.15	50-50	55-45
	P-A11	PEGMA ₁₅ - <i>co</i> -EtMA ₁₃	6100	7350	1.16	75-25	73-27
						w/w% DMAEMA-EtMA	
	P-B7	EtMA ₂₀	2350	3080	1.11	100-00	100-00
		EtMA ₂₀ - <i>b</i> -DMAEMA ₄₃	9100	11000	1.09	75-25	73-27
Polymer Series 2	P-B4	EtMA ₁₃	1600	1990	1.12	100-00	100-00
		EtMA ₁₃ - <i>b</i> -DMAEMA ₂₉	6100	6490	1.09	75-25	73-27
	P-B1	EtMA ₇	850	1180	1.15	100-00	100-00
		EtMA ₇ - <i>b</i> -DMAEMA ₁₄	3100	3650	1.10	75-25	73-27
	P-B8	EtMA ₃₂	3700	5090	1.08	100-00	100-00
		EtMA ₃₂ - <i>b</i> -DMAEMA ₃₄	9100	11200	1.08	60-40	59-41
	P-B5	EtMA ₂₁	2500	3480	1.10	100-00	100-00
		EtMA ₂₁ - <i>b</i> -DMAEMA ₂₃	6100	7860	1.08	60-40	58-42
	P-B2	EtMA ₁₁	1300	1760	1.13	100-00	100-00
		EtMA ₁₁ - <i>b</i> -DMAEMA ₁₁	3100	3600	1.10	60-40	58-42
Polymer Series 2	P-B9	EtMA ₃₉	4600	6670	1.08	100-00	100-00
		EtMA ₃₉ - <i>b</i> -DMAEMA ₂₉	9100	10500	1.11	50-50	48-52
	P-B6	EtMA ₂₆	3100	4120	1.09	100-00	100-00
		EtMA ₂₆ - <i>b</i> -DMAEMA ₁₉	6100	7110	1.09	50-50	49-51
	P-B3	EtMA ₁₃	1600	2180	1.11	100-00	100-00
		EtMA ₁₃ - <i>b</i> -DMAEMA ₁₀	3100	3850	1.11	50-50	49-51
P-B10		EtMA ₂₁ <i>co</i> - DMAEMA ₂₃	6100	7200	1.09	60-40	58-42

^a PEGMA is the abbreviation of poly(ethylene glycol) methyl ether methacrylate, EtMA is the abbreviation of ethyl methacrylate and DMAEMA is the abbreviation of 2-(dimethylamino) ethyl methacrylate. ^b The theoretical MM ($MM^{\text{theor.}}$) was calculated using the equation: $MM^{\text{theor.}} (\text{g mol}^{-1}) = (\sum_i MM_i \times DP_i) + 100$. ^d The dispersity index ($\bar{D}$) and the number average molar mass (M_n) were determined using Gel Permeation Chromatography (GPC). The GPC was calibrated using six poly methyl methacrylate) (PMMA) standard samples; 2000,4000,8000, 20 000 and 50 000 g mol^{-1} .

The GPC traces of P-B5 from **polymer series 2**: the homopolymer (EtMA_{21}) and diblock copolymer ($\text{EtMA}_{21}\text{-}b\text{-DMAEMA}_{23}$) that are represented by orange and green, respectively are shown in **Figure 4.5**. The same observations of full conversion of the monomer to the polymer and the homopolymer to the diblock copolymer can be made as in **polymer series 1**, and previous GTP studies, suggesting a successful sequential GTP. The same observations can be made for all the **polymers in series 2** for which their GPC traces can be found in the Appendix.

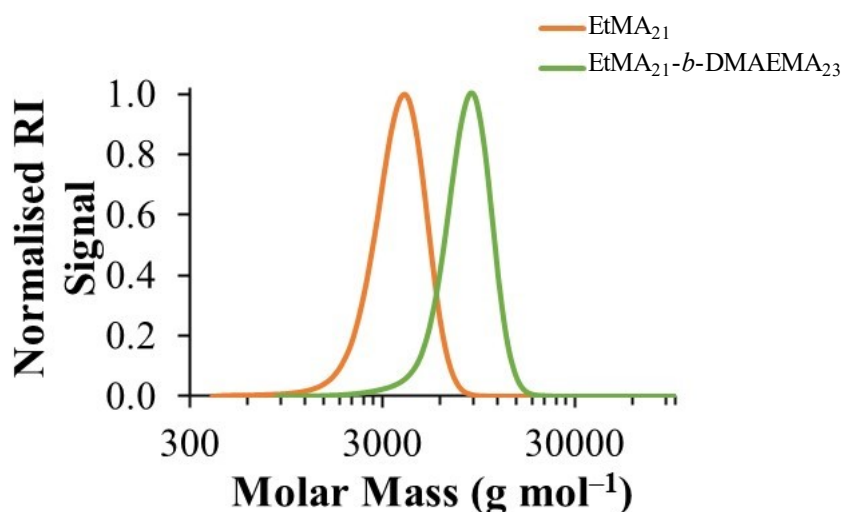


Figure 4.5. The GPC chromatogram of P-B5: $\text{EtMA}_{21}\text{-}b\text{-DMAEMA}_{23}$. The orange and green lines represent the EtMA homopolymer and $\text{EtMA}_{21}\text{-}b\text{-DMAEMA}_{23}$, respectively. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

As can be seen from **Table 4.1**, the experimental M_n values of the final copolymers are varying between 3600 and 11000 g mol⁻¹ which is reasonably close to the targeted MM. The experimental M_n values are slightly higher than the theoretical MMs, due to the partial deactivation of initiator as it was discussed for **polymer series 1** and similarly to previous published GTP studies.^{3,5,9-12} The $\bar{D}$ values are found between 1.08 and 1.15, so very close to 1, which is ideal value for successful “living” GTP method, which is similar to previously reported studies.¹³⁻¹⁶

When comparing the two-polymer series, **polymer series 1** has higher $\bar{D}$ values compared to **polymer series 2**. This is due to the presence of PEGMA which is a macromonomer with an average MM which means that it has a wider MMD. This has been previously reported in many PEG-based macromonomer GTP studies.^{6,1} In addition to this, the PEGMA macromonomer is not distilled prior to polymerisation, which means that the impurities were present, and this causes deactivation in the polymerisation, hence higher MM. Finally, in “living” polymerisation techniques such as GTP, it is expected that the $\bar{D}$ values decrease when the MM of the copolymers increases, which is a case for both polymer series.

4.2.2 Polymer Composition

The experimental composition of **polymer series 1** and **2** were obtained by using ¹H NMR spectroscopy. The weight percentages of diblock copolymers and their precursors were calculated by taking the integral of the distinctive peaks that belongs to the representative units of copolymer. The ¹H NMR spectra of P-A2: PEGMA₁₅-*b*-EtMA₁₃ and its precursor PEGMA₁₅ are shown in **Figure 4.6** (b) (in orange), and (a) (in blue), respectively as an example. The expected peaks are observed for PEGMA homopolymer, and additional peaks that belong to EtMA unit are observed for the diblock copolymer. The composition is calculated by taking integral of the distinctive peak of the PEGMA block at 3.35 ppm, which belongs to the three methoxy protons which is ‘e’ protons (**Figure 4.6**). The second distinct peak that appears at 1.25 ppm belongs to EtMA with methyl group which is ‘g’ protons.

The ¹H NMR spectrum of P-B1: EtMA₇-*b*-DMAEMA₁₄ and its precursor EtMA₇ are shown in **Figure 4.7** (b) in orange and (a) in green, respectively. The composition of DMAEMA was calculated by using the peak at 2.25 ppm is used belongs to the six methyl protons ‘g’ which is next to the amine group. As can be seen from **Table 4.4**, there is a good agreement between experimental and theoretical composition of final copolymers and their precursors including

the experimental error of the NMR spectrometer. Furthermore, no peaks were observed corresponding the protons of the double bonds of the monomers, which confirms full conversion of monomers to polymers and a successful polymerisation.

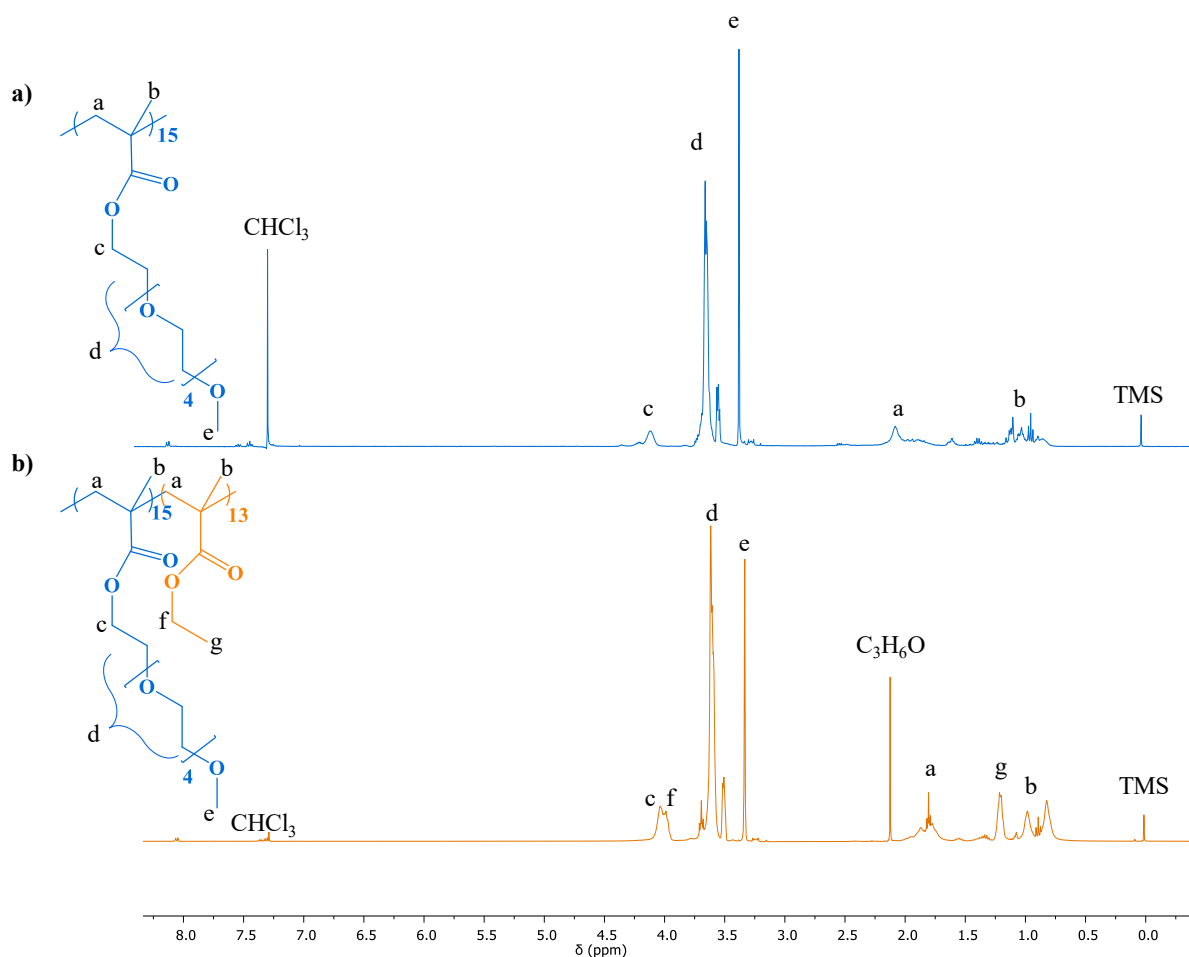


Figure 4.6. The ^1H NMR spectra of (a) PEGMA homopolymer and (b) diblock copolymer, P-A2: PEGMA₁₅-b-EtMA₁₃ shown in blue and orange, respectively. The chemical structures of PEGMA and EtMA are also coloured in blue and orange, respectively. Reproduced, with permission, from “B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

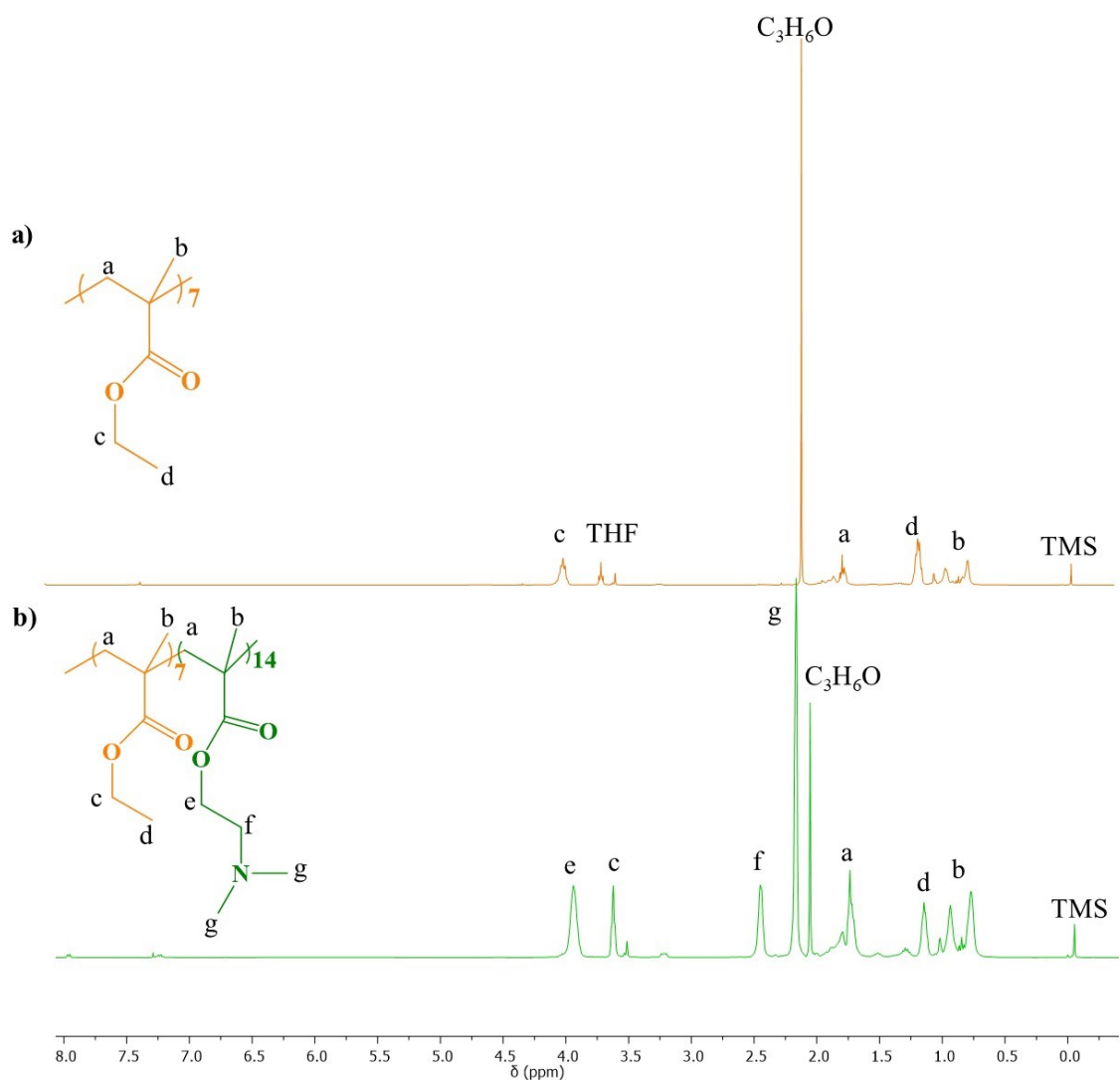


Figure 4.7. The ^1H NMR spectra of (a) EtMA homopolymer and (b) diblock copolymer, P-B1: EtMA₇-*b*-DMAEMA₁₄ shown in blue and orange, respectively. The chemical structures of PEGMA and EtMA are also coloured in orange and green, respectively. Reproduced, with permission, from “B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

4.3 Aqueous Solution Properties

All the following properties were analysed using 1 w/w% aqueous polymer solutions. Please note that P-A4, P-A7, P-A8 and P-A9 from the PEGMA-EtMA polymer series are not well water-soluble as well as P-B5, P-B6, P-B8, P-B9 and P-B10 for the EtMA-DMAEMA polymer series. These are polymers with higher hydrophobic content and MM, and thus is expected that their aqueous solubility will be poor. Therefore, the aqueous characterisation for these polymers would not be discussed.

4.3.1 Cloud Points

The cloud points of the 1 w/w% of copolymer solutions in DI water was determined by visual tests. When the temperature increases, the polymer solution turn from a colourless to cloudy solution due to the precipitation of the polymer.¹⁷ According to the previous studies, the MM,^{4,1,18–20} architecture,^{2,5,9,17} and composition^{4,8,17,20} of the polymer can affect the cloud point as well as the solvent^{21,22} and the pH^{18,19} and ionic strength^{23–25} of the solution.

In this chapter, the effect of composition and MM of the polymer will be discussed. **Table 4.2** shows the cloud point values for **Polymer series 1**. The cloud points cannot be determined for P-A4, P-A7, P-A8 and P-A9 because, as mentioned above, they were not soluble in water. As can be seen from the results, for similar MM, the cloud points decrease when the composition of EtMA units increases. This was expected and observed before.^{5,7,13,26} Increase in EtMA units affects the micellization in two ways: (i) increase in EtMA unit results longer hydrophobic blocks which means that larger micellar hydrophobic core with bigger interfacial area between water and core will form (ii) lower number of hydrophilic units that results to shorter hydrophilic blocks forming the shell hence the steric stabilisation of the micelles in water is less efficient. When keeping the composition constant and comparing polymers of different MM, the cloud points increased when increasing MM as expected and observed.

The cloud point values of **Polymer series 2** is summarised in **Table 4.2** and same trend observed with **Polymer series 1**. When the wt% of EtMA content increases, the cloud point decreases. At similar overall MM ($M_n = 3600, 3650, 3850 \text{ g mol}^{-1}$), an increase in the EtMA composition and decrease in DMAEMA composition leads to a decrease in the cloud point. This trend was observed due to the same reasons of **Polymer series 1**, which is explained previously. The cloud points for P-B5, P-B6, P-B8, P-B9 and P-B10 could not be determined because they are not soluble in water.

Therefore, visual tests were performed for copolymers with no protonation (initial pH ~ 7.8-8.8) and at 10% protonation of the DMAEMA units. The cloud point for statistical copolymer (P-B10) cannot be determined because it was insoluble in water even after protonation (pH~7). According to the results, 10% protonation of DMAEMA units does not show any cloud points in the range of 23-80°C, which means that protonation of the amino groups has a robust effect on the thermoresponsive behaviour of the copolymers at low concentrations. The reason for this is that 10% protonation cause the formation of a more hydrophilic structure. The positive charges on amino groups cause electrostatic repulsion, hence preventing the aggregation of the micelles, hence preventing the precipitation resulting in higher cloud points. Other studies have similar results with the effect of protonation of DMAEMA units on its thermoresponsive characteristics.²⁷

As discussed, the composition effect of EtMA was same for both polymer series; increasing wt% of EtMA results decrease in cloud point values. On the other hand, increasing MM of polymers show an opposite effect on the cloud points of two polymer series. As shown in **Figure 4.8A**, for non-ionic PEGMA based copolymers, the cloud points increase when MM increases. However, for ionic DMAEMA based copolymers when MM increases, the cloud points decreases (see **Figure 4.8B**) which was previously observed from other studies.⁷ In addition to this, PEGMA homopolymers also showed same trend as DMAEMA based copolymers.¹¹ However, for PEGMA based copolymers, the opposite trend was observed.^{1,28} This can be explained by comb-like structures of PEGMA based copolymers that self-assemble differently due to the long side groups. In addition to this, in DMAEMA based copolymers, the DP has higher strength on affecting cloud point values. Therefore, when MM of copolymers increases, the cloud point values decrease. However, this is not the case in PEGMA based copolymers.

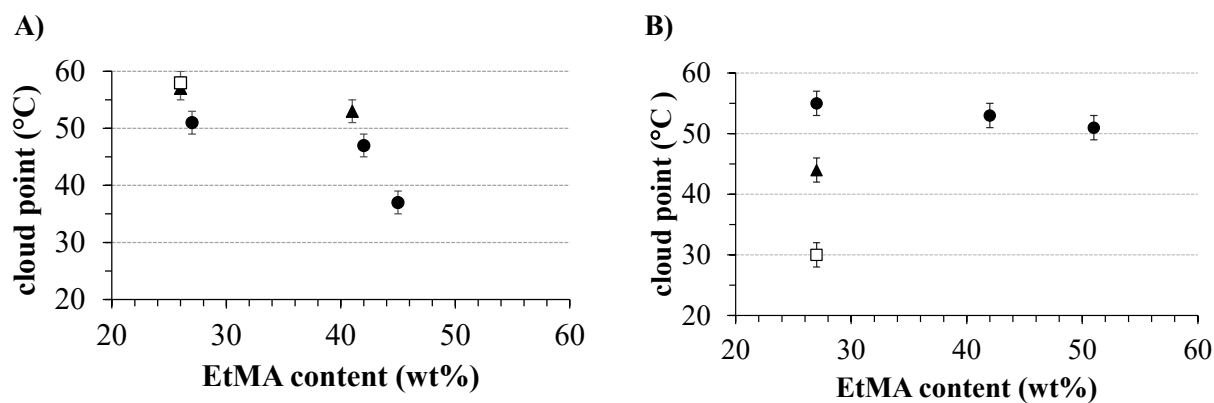


Figure 4.8. The effect of experimental ethyl methacrylate (EtMA) content on the cloud point of **A) Polymer series 1**, PEGMA-EtMA based copolymers and **B) Polymer series 2**, EtMA-DMAEMA based copolymers. The circle (●), triangle (▲) and square (◻) represents polymers with different MMs; 3000, 6000 and 9000 g mol⁻¹, respectively. Reproduced, with permission, from “B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

Table 4.2. Theoretical polymer structure, calculated and experimental hydrodynamic diameters (d_{hs}), polydispersity indices (PDI) and cloud points of 1 w/w% aqueous solutions of polymers.

No.	Theoretical Polymer Structure ^a	EtMA wt % by NMR	MM ^{theor.} (g mol ⁻¹)	Hydrodynamic diameter (<i>d</i> _h , nm)			PDI	p <i>K</i> _a s ± 0.1	Cloud Points ± 2 °C		HLB ^e	CMC ^f x10 ⁻⁵
				Theo. ^b	Exp. ± 0.5 ^c	Exp. ± 0.5 ^d			0% H ⁺	10% H ⁺		mol L ⁻¹
P-A1	P ₂₃ - <i>b</i> -E ₂₀	26	9100	20.8	21.0	78.8	0.260	-	58	-	14.8	0.85
P-A2	P ₁₅ - <i>b</i> -E ₁₃	26	6100	17.0	11.7	15.7	0.034	-	57	-	14.8	3.06
P-A3	P ₈ - <i>b</i> -E ₇	27	3100	7.4	5.6	8.7	0.068	-	51	-	14.6	24.1
P-A4	P ₁₈ - <i>b</i> -E ₃₂	41	9100	23.8	NS ^g	NS	NS	-	NS	-	11.8	NS
P-A5	P ₁₂ - <i>b</i> -E ₂₁	41	6100	15.6	13.5	18.2	0.071	-	53	-	11.8	3.73
P-A6	P ₆ - <i>b</i> -E ₁₁	42	3100	8.3	8.7	11.7	0.031	-	47	-	11.6	12.1
P-A7	P ₁₂ - <i>co</i> -E ₂₁	42	6100	2.6	NS	NS	NS	-	NS	-	11.6	NS
P-A8	P ₁₅ - <i>b</i> -E ₃₉	50	9100	23.8	NS	NS	NS	-	NS	-	10	NS
P-A9	P ₁₀ - <i>b</i> -E ₂₆	52	6100	16.6	NS	NS	NS	-	NS	-	9.6	NS
P-A10	P ₅ - <i>b</i> -E ₁₃	45	3100	8.2	10.1	15.7	0.137	-	37	-	11	6.53
PA-11	P ₁₅ - <i>co</i> -E ₁₃	27	6100	2.4	5.43	5.9	0.298	-	35	-	14.6	NS
P-B7	E ₂₀ - <i>b</i> -D ₄₃	27	9100	33.2	15.7	24.4	0.076	6.9	30	No CP	14.6	0.23
P-B4	E ₁₃ - <i>b</i> -D ₂₉	27	6100	20.8	8.7	11.7	0.068	7.1	44	No CP	14.6	7.70
P-B1	E ₇ - <i>b</i> -D ₁₄	27	3100	11.9	5.6	8.7	0.065	7.1	55	No CP	14.6	13.7
P-B8	E ₃₂ - <i>b</i> -D ₃₄	41	9100	31.5	NS	NS	NS	6.7	NS	No CP	11.8	NS
P-B5	E ₂₁ - <i>b</i> -D ₂₃	41	6100	22.1	NS	NS	NS	6.9	NS	No CP	11.6	NS
P-B2	E ₁₁ - <i>b</i> -D ₁₁	42	3100	11.4	5.6	8.7	0.066	6.6	53	No CP	11.6	27.8
P-B9	E ₃₉ - <i>b</i> -D ₂₉	48	9100	30.8	NS	NS	NS	6.6	NS	No CP	9.6	NS
P-B6	E ₂₆ - <i>b</i> -D ₁₉	48	6100	20.7	NS	NS	NS	6.7	NS	No CP	9.8	NS
P-B3	E ₁₃ - <i>b</i> -D ₁₀	49	3100	10.3	6.5	28.2	0.199	6.6	51	No CP	9.8	2.60
P-B10	E ₂₁ - <i>co</i> -D ₂₃	42	6100	3.0	NS	NS	NS	6.8	NS	No CP	9.6	NS

^a P represents poly(ethylene glycol) methyl ether methacrylate (PEGMA), E represents ethyl methacrylate (EtMA) and D represents 2-(dimethylamino) ethyl methacrylate (DMAEMA).

^b Theoretical hydrodynamic diameter values based on the experimental degree of polymerisations (DPs) of PEGMA, EtMA and DMAEMA units. The DPs were calculated using the MM of copolymers after precipitation using GPC and the experimental composition using ¹H NMR. The equation used to calculate the theoretical hydrodynamic diameter of block copolymers is $d_h = (DP_{EtMA} + 2 \times DP_{PEGMA/DMAEMA}) \times 0.254$ nm. The equation used to calculate the hydrodynamic diameter of statistical copolymer is $d_h = 2 \times [2.20 \times 2 \times (DP_A + DP_B)/3]^{1/2} \times 0.154$. ^c Experimental hydrodynamic diameter values are given by number and it is obtained using DLS. ^d Experimental hydrodynamic diameter is given by intensity and it is obtained using DLS. ^e Hydrophile-lipophile balance (HLB) was calculated using this equation by Griffin; $HLB = (W_h/W_h + W_l) \times 20$. The weight fraction of the hydrophile and lipophile unit is calculated using the experimental composition obtained from ¹H NMR. ^f CMC represents the critical micelle concentration of the polymer. ^g NS stands for non-soluble as the polymer was not soluble to perform the experiment.

4.3.2 Effective pK_a s

Hydrogen ion titration were performed to determine the effective pK_a s of **polymer series 2**, and as can be seen from **Table 4.2**, the effective pK_a values are varying between 6.6 and 7.1. The pK_a values are similar to the previously reported DMAEMA based containing polymers.^{3,6,7,27,28} According to the previous studies, increasing the hydrophobicity of the copolymer and/or hydrophobic content results decrease in the pK_a values due to decrease in dielectric constant with an increase of hydrophobicity, causing ionisation to be more difficult.^{6,7,13,29} As can be seen from **Table 4.2**, the pK_a values are decreasing by increasing the hydrophobic EtMA content for all diblock copolymers, within the experimental error, therefore there is a good agreement with the previous studies. For instance, for polymers P-B7, P- B8 and P-B9, with similar MM (10 500, 11 000 and 11 200 g mol⁻¹), the pK_a decreases from 7.1 to 6.6, by increasing the hydrophobic content from 27 to 52 wt%. Similar decrease in pK_a values with increase in hydrophobic content is also observed in other polymers in this series and it is shown in **Figure 4.9**. The lowest pK_a was expected and observed in P-B9, it is the most hydrophobic copolymer in the polymer series hence low pK_a value. Generally, statistical copolymers are more insoluble compared to the block copolymers, this is because they cannot form traditional core-corona micelles and they form aggregates.²⁷ It is observed in P-B10 which is the least soluble polymer in this series, and it precipitates at higher pH values. The DMAEMA units are weaker due to the steric hinderance and the surrounding hydrophobic EtMA units, which makes the protonation harder, hence decrease the pK_a value compared to most of the polymers. Therefore, it was observed that the polymers that have more DMAEMA units and less steric hinderance, easier to protonate, hence stronger base which results higher pK_a values.

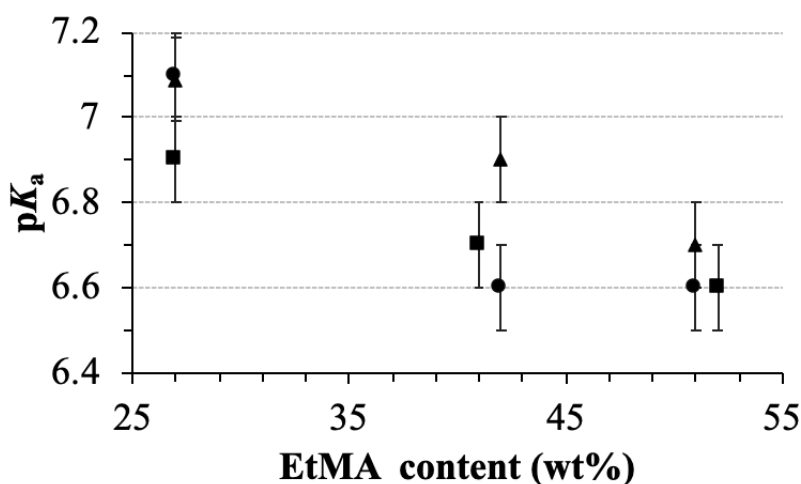


Figure 4.9. Effect of experimental ethyl methacrylate (EtMA) weight content on the pK_a s. The circle (●), triangle (▲) and square (■) represents polymers of different MMs; 3000, 6000 and 9000 g mol⁻¹, respectively. Reproduced, with permission, from “B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

4.3.3 Hydrodynamic diameters

The theoretical hydrodynamic diameter (calculated) values of all amphiphilic diblock as well as statistical copolymers of **polymer series 1** and **2** in an aqueous solution were calculated and they are listed in **Table 4.2**. The theoretical hydrodynamic diameters were calculated by assuming that the diblock copolymers self-assemble into spherical (core-shell) micelles, with hydrophobic EtMA units being core of the micelles and hydrophilic PEGMA units is the shell of the micelle shown in (a) **Figure 4.10**. When theoretical hydrodynamic diameter was calculated for **polymer series 2**, it was also assumed that diblock copolymers self-assemble into core-shell micelles, the hydrophilic DMAEMA units are form the shell, and hydrophobic EtMA units form the core of the micelles as it is schematically shown in (c) **Figure 4.10**. However, for statistical copolymers, a random coil configuration was assumed in both polymer series (see (b) and (d) **Figure 4.10**). The theoretical hydrodynamic diameter of diblock copolymers for both **polymer series 1** and **2** were calculated by using an equation $d_h = (DP_{EtMA} + 2 \times DP_{Hydrophilic\ unit}) \times 0.254\text{ nm}$, where in **polymer series 1** and **2**, PEGMA and DMAEMA

used respectively. These theoretical calculations assume that the polymer chains are fully stretched.

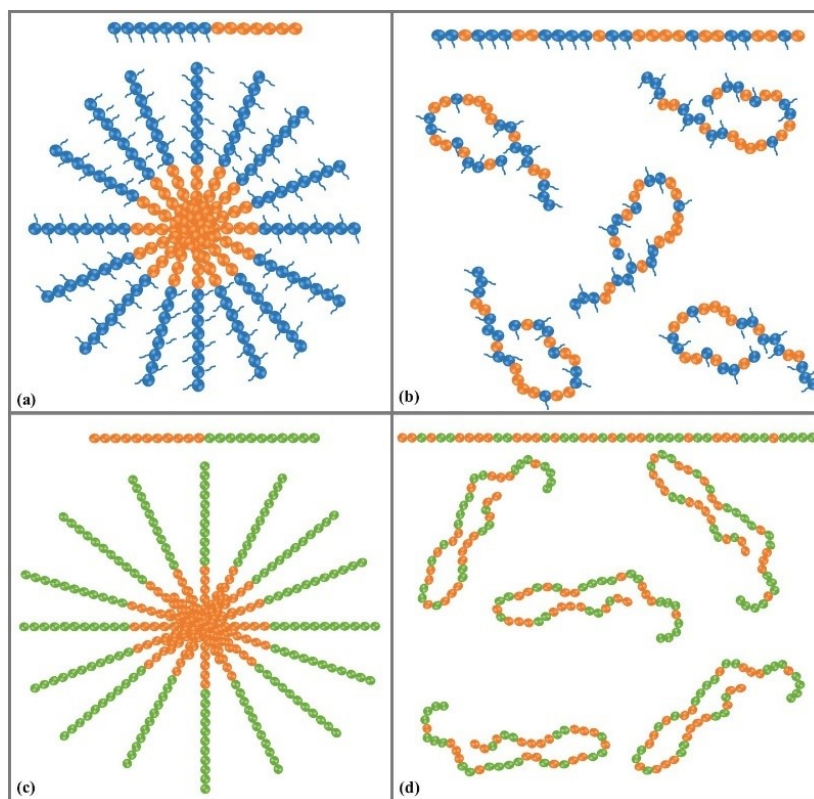


Figure 4.10. The schematic structures of; **(a)** and **(c)** spherical core-shell micelles adopted by the diblock copolymers (P-A1-6 and P-A8-10), (P-B1-P-B9) and **(b)** and **(d)** random coil configuration adopted by statistical copolymers (P-A7 and P-A11) and P-B10. The hydrophilic PEGMA and DMAEMA are coloured blue and green, respectively, while hydrophobic EtMA units are coloured in orange. Reproduced, with permission, from “B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

The experimental hydrodynamic diameter values and polydispersity indices (PDI) were determined by DLS and compared with theoretical hydrodynamic diameter values (see **Table 4.2**). The experimental hydrodynamic diameter values were reported by taking the maximum peak of the intensity. According to the DLS histograms, the peak that was observed corresponds to the micelles which are observed in most of the copolymers. In some of the histograms two to three peaks were observed. Peaks that correspond to are below 3 nm

normally correspond to unimers (nonself-assembled polymers), then intermediate size peaks (5 to 22nm) to micelles and bigger size peaks to bigger aggregates, as expected and observed before for block-based polymers.¹ The histograms of copolymers for both **polymers series 1&2** can be found in Appendix.

As can be seen from **Table 4.2**, the theoretical and experimentally determined hydrodynamic diameter values increase as the MM increases. In addition, in most cases the experimental hydrodynamic diameter values were smaller than the theoretical diameter values as expected since the theoretical model assumes a fully stretched chain and observed in previous studies.^{27,28} In two cases, the experimentally determined diameter is slightly bigger, and this is due to the presence of PEGMA. PEGMA has long side chains, and when the theoretical hydrodynamic diameter was calculated, the length of side chains was not included. Therefore, the experimental hydrodynamic diameters of micelles were higher than it was calculated.

In **polymer series 2**, the self-assembly behaviour of polymers was investigated in their initial pH (~ 8.4-9.2). As shown, the size of the micelles is decreased when the MM of the copolymer decreased. When comparison was made between the micelle size of PEGMA-based diblock and DMAEMA-based diblock copolymers, the PEGMA-based copolymers has bigger micelle size. This is expected because the bulkier PEGMA units, i.e. presence of the long side chains of the PEGMA units compared to DMAEMA units.

For the statistical copolymers of both series, it is assumed that it is in a random coil configuration and the diameter was calculated using the equation; $\langle d_g^2 \rangle^{1/2} = 2 \times [2 \times 2.20 \times (DP_{\text{PEGMA or DMAEMA}} + DP_{\text{EtMA}})/3]^{1/2} \times 0.154 \text{ nm}$. Only one statistical copolymer was soluble P-A11 and the experimental diameter is higher than the theoretical random coil configuration because some minor aggregation may happen due to the long hydrophilic PEG side chains and also because the theoretical calculation does not take into account these chains. This has been observed before for PEGMA based statistical copolymers when TEM was used to confirm no micelles are formed.²⁷

4.3.4 Critical Micelle Concentration

The critical micelle concentration (CMC) of soluble diblock copolymers in **Polymer series 1** and **2** were determined using DLS and listed in **Table 4.2**. For each polymer, thirteen different concentrations prepared in DI water and intensity kilo counts per second measured. The CMC of PEGMA based copolymers were found to be between 0.86 to $24.1 \times 10^{-5} \text{ mol L}^{-1}$, and DMAEMA based copolymers were found to be between 0.23 to $27.8 \times 10^{-5} \text{ mol L}^{-1}$. Patrickios and co-workers were studied methacrylate-based diblock copolymers and observed similar CMC ($10^{-5} \text{ mol L}^{-1}$) values.² The CMC graph of PEGMA- based and DMAEMA based diblock copolymers are available in Appendix.

4.4 Diblock Copolymers and Statistical Copolymers as Polymeric Emulsifiers

The methyl laurate-water emulsions were prepared using 1.0 w/w% polymeric surfactants. An ultrasonic processor was used to emulsify equal weights of methyl laurate and water phases for 1 minute.

4.4.1 Type of Emulsions

The type of emulsions (O/W or W/O) were determined experimentally by performing drop tests, and theoretically determined by calculating their HLB values. According to the drop test experiments, all polymeric surfactants stabilise O/W type emulsions. This was determined by uniform distribution of emulsion droplets in the water phase whereas precipitation in the form of coagulated spherical drops in the methyl laurate.

The O/W type emulsion is also confirmed by HLB values which is introduced by Griffin (see **Equation 3.11** in Experimental). As can be seen from **Table 4.2**, the HLB values of polymeric surfactants in **Polymer series 1** and **2** are varied between 9.6-14.8 and 9.6-14.6, respectively. According to Griffin, HLB values higher than ~6 indicates that they are water-soluble and stabilises O/W type emulsions. Consequently, high HLB values indicate that they form O/W type emulsions.

4.4.2 Emulsion Stability

4.4.2.1 Visual Observations

The stability of the emulsions is observed visually, and images of emulsions are taken at eight different times; 1 min, 2 hours, 4 hours, one day, two days, three days, one week, two weeks, three weeks and a month after emulsification performed. As shown in **Figures 6 and 9** in the Appendix, all polymeric surfactants can emulsify water and methyl laurate phases and form O/W emulsions. As can be seen from the images, within two hours that emulsification performed, there is no change in the appearance of the emulsions. However, one day after emulsification completed, the clear aqueous phase separates and appear at the bottom of the vial, and the cream phase appears as a top layer. The volume fraction of the cream phase (ϕ_{cream}) was determined by measuring the thickness of the cream phase and using **Equation 3.12** in the experimental section. The graph of ϕ_{cream} phase versus time was plotted and shown in **Figures 8 and 10** in the Appendix. As it was expected, due to emulsions nature, the stability of the emulsion decreases over time.

When comparing two different polymer series, in **polymer series 1** (PEGMA-EtMA), the ϕ_{cream} phase is varied between 0.570 and 0.672. On the other hand, in **polymer series 2** (EtMA-DMAEMA), the ϕ_{cream} is varied between 0.615-0.702. Therefore, the higher ϕ_{cream} phase, the better emulsifying ability of polymeric surfactants, hence better stabilisation of emulsion droplets and resists gravitational separation. The ϕ_{cream} values of all emulsions stabilised by polymeric surfactants are summarised and available in the Appendix (**Tables 3 and 4**).

As shown from the emulsion images, there is no noticeable difference observed when polymeric surfactants with different MM and composition used. Graphs A and C in **Figure 4.11** shows the ϕ_{cream} versus MM of **polymer series 1** and **2**, respectively. As seen from graphs, different trends observed for each polymer series. For **polymer series 2**, the highest ϕ_{cream} phase is observed when MM is 7000 g mol⁻¹ which seems optimum and maximum MM. On the other hand, for **polymer series 1**, the optimum MM cannot be observed, and the trend changes when the composition is varied. For instance, when the composition of PEGMA-EtMA is 75-25 w/w %, the MM does not affect the stability of the emulsions. On the other hand, when the composition of PEGMA-EtMA is 60-40 w/w%, the stability of emulsions decreases when MM increases. Increasing hydrophobicity of PEGMA-EtMA to 50-50 w/w% has a slight decrease in stability when MM increases.

The statistical copolymers (7000 g mol⁻¹) have the emulsifying ability and able to form emulsions. In a previous study performed by Georgiou and co-workers, PEGMA based statistical copolymer PEGMA_{6.5}-*co*-HeMA_{11.5} could not efficiently stabilise the emulsion, where the hydrophobic monomer used was *n*-hexyl methacrylate (HeMA).¹ However, in their work, tetradecane was used as an oil phase that may affect polymeric surfactant's emulsifying ability; hence, a direct comparison between polymeric surfactants in both work could not be made. In contrast, previously reported studies observed that comb-like PEGMA based statistical copolymers can stabilise emulsions. However, in their research, tetradecane and 1-bromo decane were used as an oil phase.^{30,31}

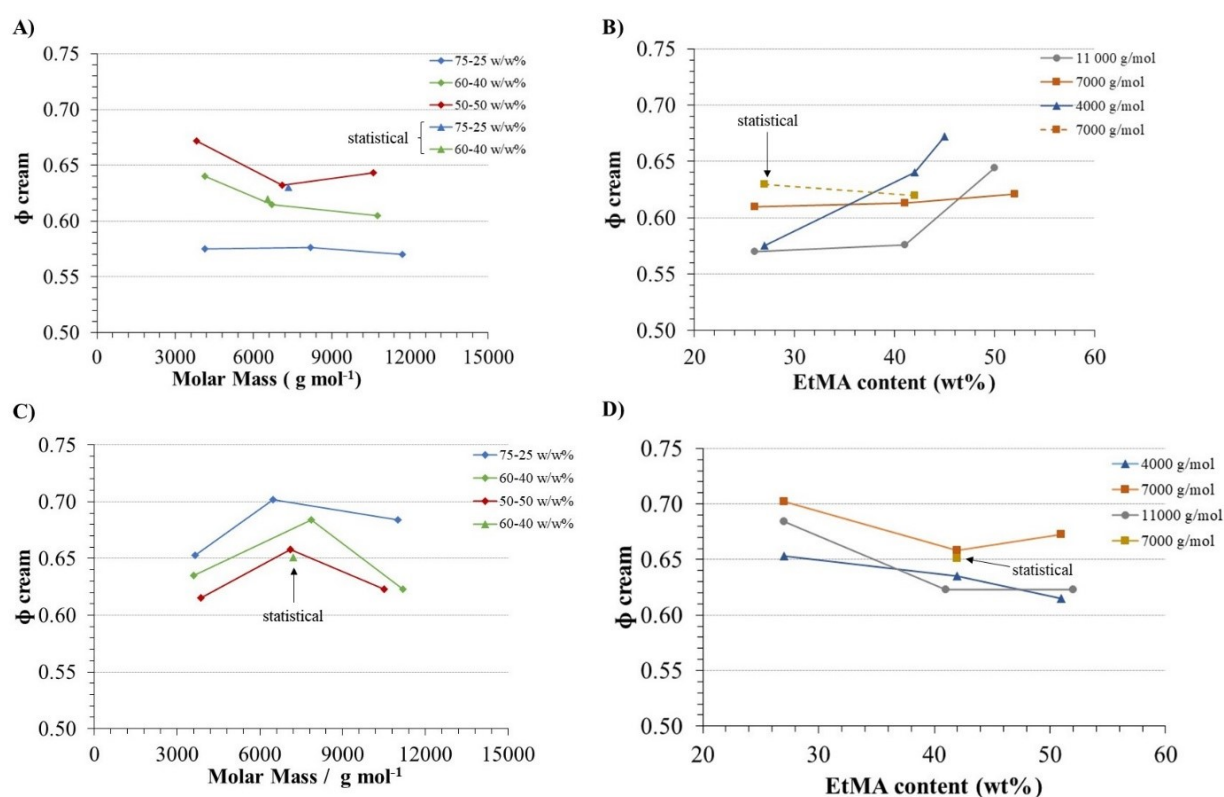


Figure 4.11. A and C) The effect of copolymers' molar mass on the fraction of the cream phase resolved. The cream phase fraction for **polymer series 1** and **2** is represented as A and C, respectively. **B and D)** The effect of weight percentage of EtMA on the fraction of the cream phase resolved. The cream phase fraction for **polymer series 1** and **2** is represented B and D, respectively. In graphs **A** and **C**, diblock copolymers are represented by a circle (●), and statistical copolymers are represented by a triangle (▲). In graphs **B** and **D**, the diblock copolymers are represented by grey, orange and navy. The statistical copolymers are represented by dark yellow. Reproduced, with permission, from "B. Somuncuoğlu, Y. Lin Lee,

A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

To observe the effect of composition on the stability of emulsions, the ϕ_{cream} phase versus EtMA content is plotted, and **polymer series 1** and **2** is shown in **Figure 4.11**, B and D, respectively. As shown in the graph, two opposite trends are observed for both polymer series. Increasing the EtMA content in **polymer series 1** (non-ionic, PEGMA based) increases emulsions stability. On the other hand, increasing the EtMA content in **Polymer series 2** (ionic, DMAEMA based) decreases the emulsion stability. Consequently, the DMAEMA unit has a more dominant factor than the non-ionic PEGMA due to the presence of charged groups on DMAEMA providing electrostatic repulsion between the emulsion droplets, hence enhancing the stability of emulsion and prevents the formation of coalescence.

Despite its convenience, the visual observation method does not give any information about other instability mechanisms such as Ostwald ripening, coalescence and flocculation. Therefore, another technique should be used to have more details about the instability mechanism.

4.4.2.2 Microscopy Observations

The droplet size and distribution of the emulsion droplets is essential in determining the stability of emulsions. Therefore, optical transmission spectroscopy is performed to determine the size and distribution of the emulsion droplets, thus instability mechanism. In this study, the size of the emulsion droplets was observed immediately after emulsification performed. An example of emulsions using polymeric surfactants, P-A8, P-A9 and P-A10 are shown in **Figure 4.12 a-c**. As seen from the micrographs, the emulsion system contains tiny droplets. The emulsion was very concentrated and placing a coverslip on the emulsion drop may disturb the droplets or packed very close to each other.

The size of the emulsion droplets was observed after a week of emulsification performed. The micrographs of emulsions using polymeric surfactants, P-A8, P-A9 and P-A10, are shown in **Figure 4.12 d-f**. As shown and as expected, the size of the emulsion droplets increases over time, and the stability decreased, which is observed visually.

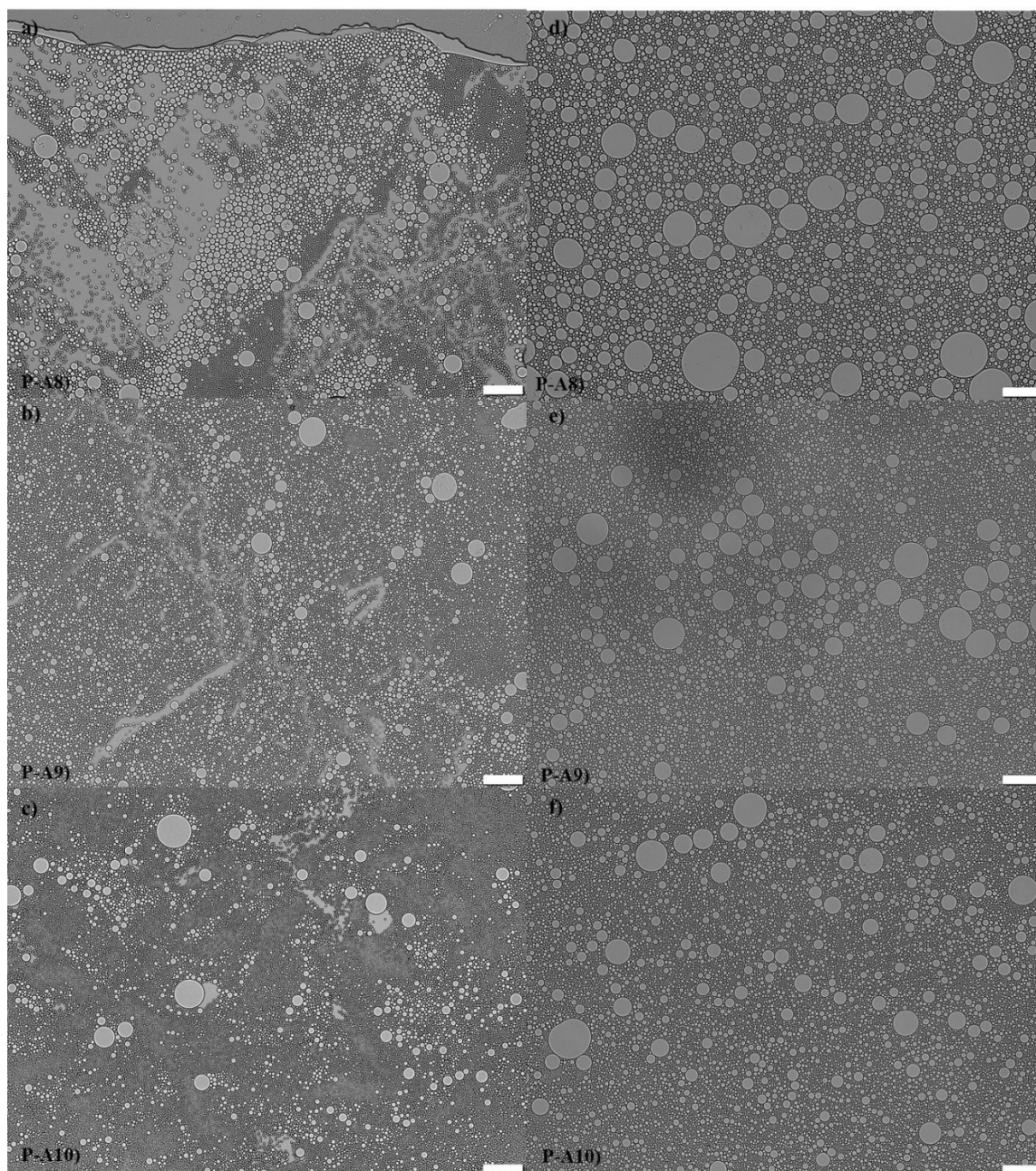


Figure 4.12. The optical micrographs of O/W emulsions stabilised using polymeric surfactants in Polymer series 1 (P-A8, P-A9 and P-A10). The micrographs are taken; a-c) immediately after emulsification performed and d-f) after seven days. The scale bar is equal to 50 μm .

The size of the emulsion droplets immediately after emulsification and a week was observed for **polymer series 2**. As can be seen from the optical micrographs (**Figure 4.13**), the size of the emulsion droplets increases over time. According to Saunders and co-workers, the size of the emulsion droplets stabilised by polymeric surfactants is about 10 μm .³¹ For **polymer series 1**, the size of the emulsion droplets after emulsification is measured to be 7.1-9.9 μm , and for **polymer series 2**, it is 6.8-8.2 μm .

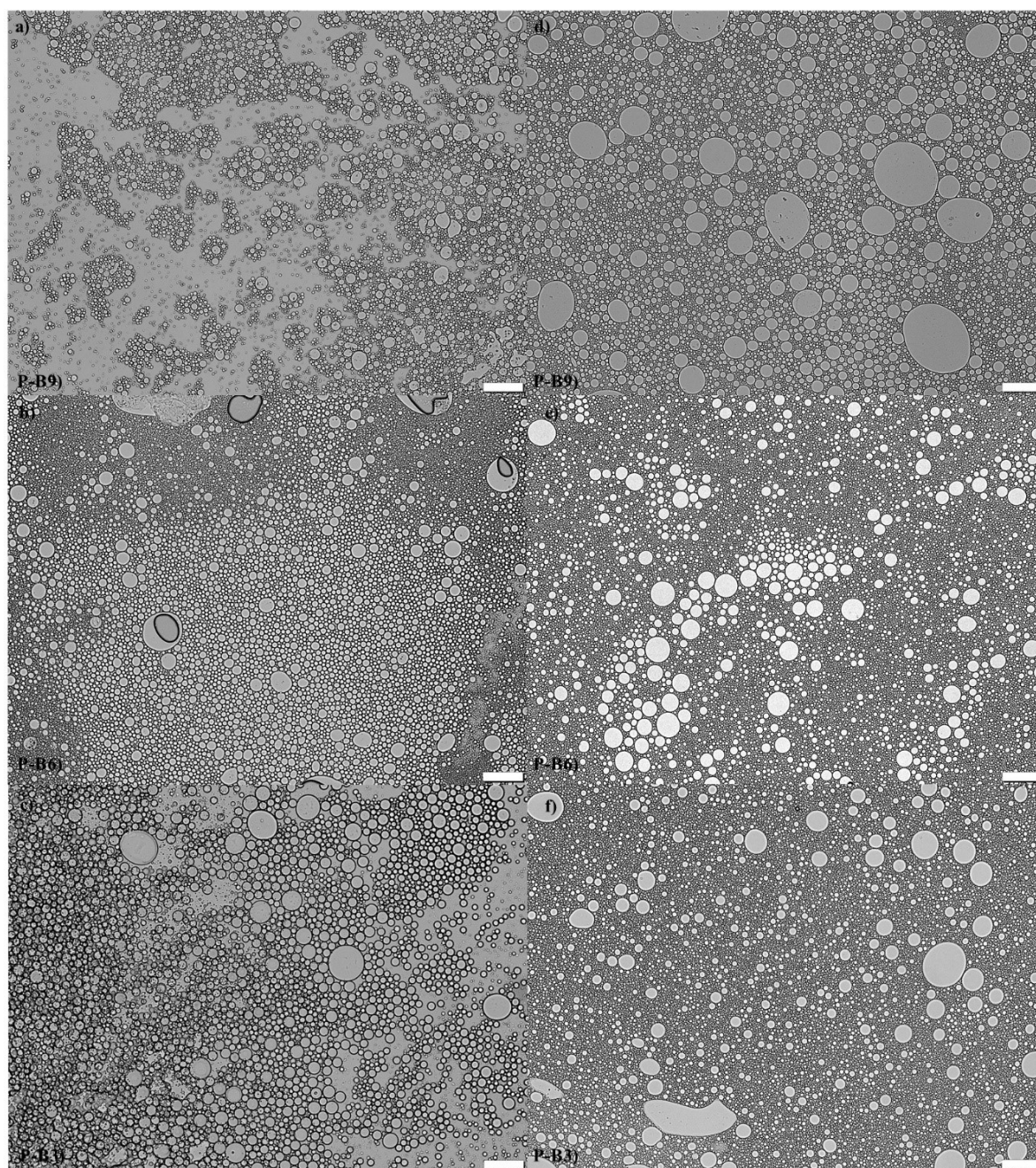


Figure 4.13. The optical micrographs of O/W emulsions stabilised by using polymeric surfactants in **polymer series 2** (P-B9, P-B6 and P-B3). The micrographs are taken; a-c)

immediately after emulsification performed and d-f) after seven days. The scale bar is equal to 50 μm .

The size of the droplets is measured for all emulsions. The diameter of emulsion droplet versus polymeric surfactants is shown in **Figure 11** in the Appendix. As seen from the graphs, no trends observed with polymer and the size of the emulsion droplet. Furthermore, when a comparison made in the sizes of the emulsion droplets after emulsification and a week, there is no considerable change in the size of the emulsion droplets, which shows that they are stable.

The size of the emulsion droplets is varied in each sample. For instance, **Figure 4.14** shows the optical micrographs of P-A9 sample, but each image belongs to a different drop of emulsion stabilised by P-A9. Therefore, to have an accurate droplet size distribution, multiple drops from the same sample should be taken and measured.

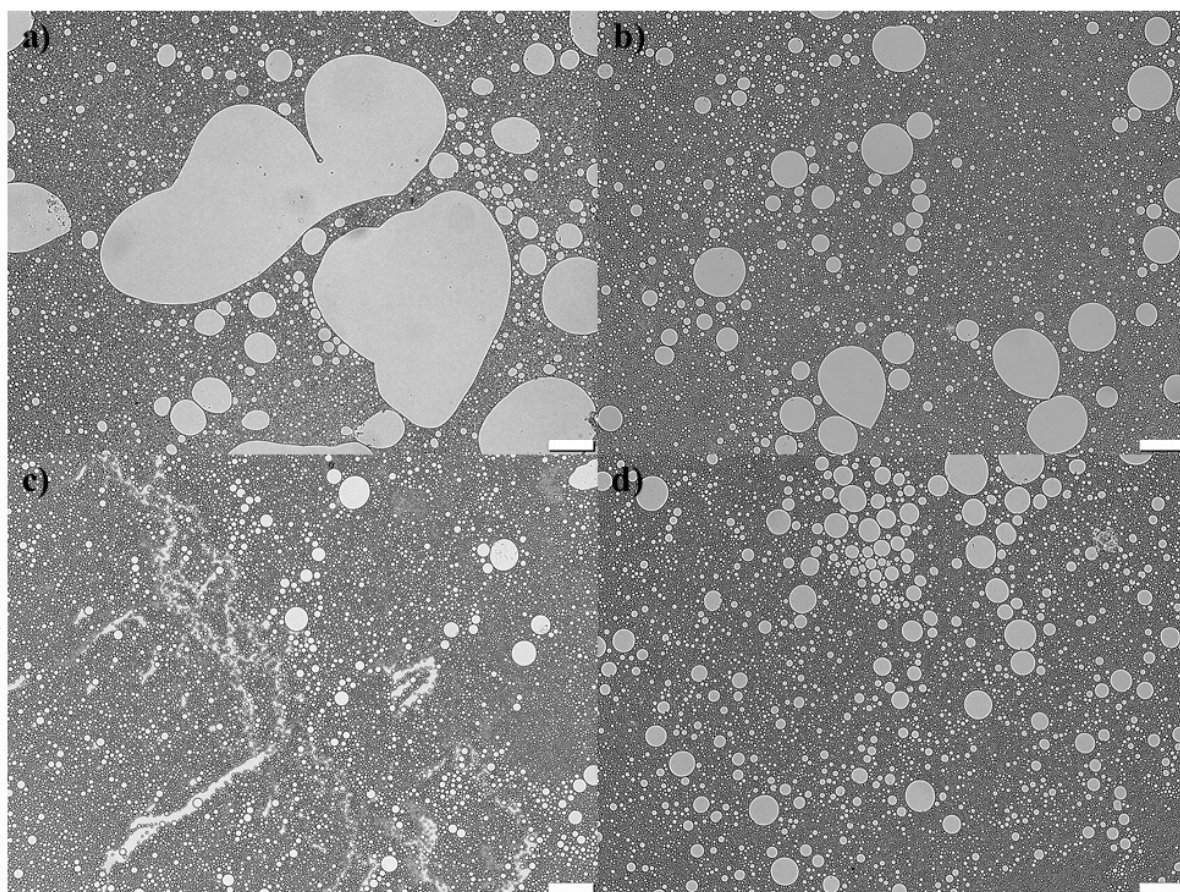


Figure 4.14. The optical micrographs of O/W emulsions stabilised by P-A9 (PEGMA₁₀-*b*-EtMA₂₆). The micrographs are taken directly after emulsification was performed. Each micrograph shows different drops of freshly made O/W emulsions. The scale bar is equal to 50 μm .

4.5 Conclusions

This chapter of PhD thesis includes synthesis of two polymer series; **Polymer series 1** and **2**. **Polymer series 1** is consisted of nine well-defined diblock copolymers and two statistical copolymers and they are based on PEGMA-EtMA units. **Polymer series 2** is consisted of nine well-defined diblock copolymers and one statistical copolymer, and they are based on DMAEMA-EtMA units. The aqueous solution properties such as hydrodynamic diameter, CMC, effective pK_a s, cloud point values were determined. In addition to this, the emulsifying properties of synthesised polymeric surfactants are evaluated. The key findings in this chapter are:

- The M_n values of synthesised PEGMA-EtMA (**Polymer series 1**) based copolymers are varied between 3830 and 11700 g mol⁻¹ and the MMDs are varied between 1.11 and 1.16. Furthermore, M_n values of DMAEMA-EtMA (**Polymer series 2**) based copolymers are varied between 3600 and 11200 g mol⁻¹ and the MMDs are varied between 1.08 and 1.11. The experimental compositions of diblock and statistical copolymers is close to their targeted compositions: 75-25, 60-40 and 50-50 w/w/% of PEGMA-EtMA and DMAEMA-EtMA.
- The cloud points of **Polymer series 1** were varied between 35 and 58°C and the cloud points of **Polymer series 1** increases when the MM increases. An opposite trend was observed for **Polymer series 2**. When the MM increases, the cloud point decreases. The cloud point values of **Polymer series 2** is varied between 30 and 55 °C.
- The effective pK_a values of **Polymer series 2** is varied between 6.6 and 7.1. The effective pK_a values of copolymers decreased when MM increased.
- All diblock copolymers self-assemble to form spherical core-shell corona micelles and statistical copolymers adopt to random coil configuration. The hydrodynamic diameter values of **Polymer series 1** was determined, and the values are varied between 5.6 and 21 nm. The values of **Polymer series 2** are varied between 5.6 and 15.7 nm. For both polymer series, sizes of the spherical micelles decrease when the MM of the diblock copolymer decreases.
- The CMC values of **Polymer series 1** were determined and it was range between 0.86 to 24.1x10⁻⁵ mol L⁻¹. Furthermore, the CMC values of **Polymer series 2** were found to be between 0.23 to 27.8x10⁻⁵ mol L⁻¹.
- The HLB values of **Polymer series 1** and **2**, range between 9.6-14.8, and 9.6-14.6, respectively. Therefore, they are water-soluble and stabilise the O/W type emulsions.

- All synthesised diblock and statistical copolymers (polymeric surfactants) able to stabilise methyl laurate in water emulsions. Drop tests were performed, and all polymeric surfactants able to form O/W type emulsions.
- Visual observations of emulsions were observed for a month, and the cream layer thickness measured. It was observed that the thickness of the cream layer decreases, which means that the stability decreases over time.

4.6 References

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CHAPTER 5: CHARACTERISATION OF TRIBLOCK COPOLYMERS AS POLYMERIC SURFACTANTS

The synthesis of triblock copolymers as a polymeric surfactant has been extensively studied and reported before. In the literature, triblock copolymers based on hydrophilic poly(ethylene oxide) (PEO) moieties are the most popular and studied polymeric surfactants.¹ They are based on PEO and the hydrophobic monomer is varied to poly(propylene oxide), poly(butylene oxide) or less often styrene.¹⁻³ Those type of polymeric surfactants are commercially available as Pluronic, Synperonic, Poloxamers with different molecular weights and compositions depending on their applications.⁴ Another example of triblock copolymer used as polymeric surfactants includes PMMA-*b*-PEO-*b*-PMMA and PEO-*b*-PS-*b*-PEO. However, they have limited commercial availability.^{4,5} Apart from commercially available triblock copolymers, there are other triblock copolymers used as a polymeric surfactants to stabilise emulsions. The effect of architecture of polymeric surfactants on the stability of emulsions were observed by Patrickios and co-workers.⁶ They studied linear amphiphilic four isomeric terpolymers (ABC, ACB, BAC and statistical copolymer) based on DMAEMA, methoxyhexa(ethylene glycol) methacrylate (HEGMA) and benzyl methacrylate (BzMA). The DMAEMA and HEGMA are hydrophilic monomers and BzMA is the hydrophobic monomer. According to the results, ABC architecture, where hydrophobic BzMA is the middle block forms more stable emulsions, while the statistical copolymer is forming the least stable emulsions. To the best of our knowledge, there is no systematic study performed for polymeric surfactants with ABC architecture.

In the previous chapter, it was concluded that neither PEGMA-EtMA nor DMAEMA-EtMA diblock copolymers were able to stabilise emulsions for long periods. In this chapter, we want to investigate if combining the three comonomers to make ABC triblock copolymers will improve their emulsifying properties. The ABC architecture was chosen because, according to the previous studies, the presence of a hydrophobic unit as a middle block provides better surfactant properties.⁶ Thus, triblock copolymers with ABC structure were synthesised via the one-pot GTP method, where A, B and C is PEGMA, EtMA and DMAEMA, respectively. The chemical structures of monomers used in this study is shown in **Figure 5.1**. In order to have a comparison between the properties of triblock copolymers and diblock copolymers, similar MMs and compositions were used. Specifically, three different MMs were targeted 3000, 6000 and 9000 g mol⁻¹, and the targeted PEGMA-EtMA-DMAEMA compositions were 30-35-35,

30-30-40 and 30-25-45 w/w/w% where the composition of PEGMA kept constant and the DMAEMA/EtMA ratio was increased.

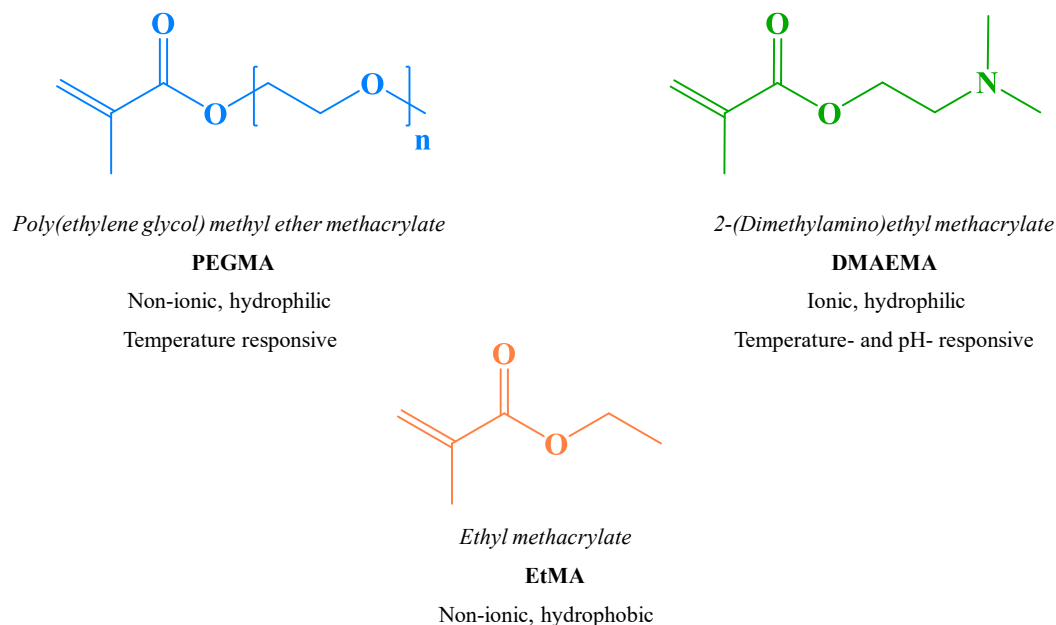


Figure 5.1. The chemical structures, names and abbreviations of monomers used in this study.

5.1. Synthesis of Triblock and Statistical Copolymer

The ABC structured triblock copolymers and statistical copolymer were synthesised *via* the one-pot GTP method. The synthesis of triblock copolymer was performed by following the route which is shown in **Figure 5.2**. Firstly, the catalyst (TBABB) followed by polymerisation solvent (THF) and then monofunctional initiator (MTS) were added into polymerisation flask. The additions of PEGMA, EtMA and DMAEMA were followed sequentially. The reason why PEGMA was added as the first monomer is because of its lower reactivity compared to other monomers and more difficult to polymerise as a second block.

Synthesis of triblock copolymers

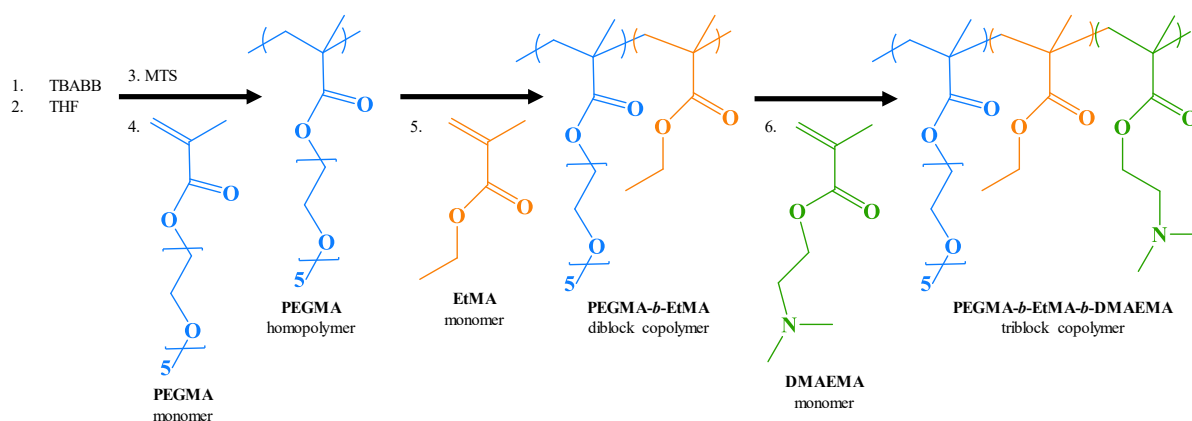


Figure 5.2. The schematic diagram of sequential addition of monomers (1) PEGMA, 2) EtMA, and 3) DMAEMA after the additions of the catalyst (TBABB), polymerisation solvent (THF) and monofunctional initiator (MTS).

In this study, nine well-defined triblock copolymers (P-C1 to P-C9) and one statistical copolymer (P-C10) were successfully synthesised *via* the one-pot GTP method. The structures of nine triblock copolymers and a statistical copolymer are schematically illustrated in **Figure 5.3**.

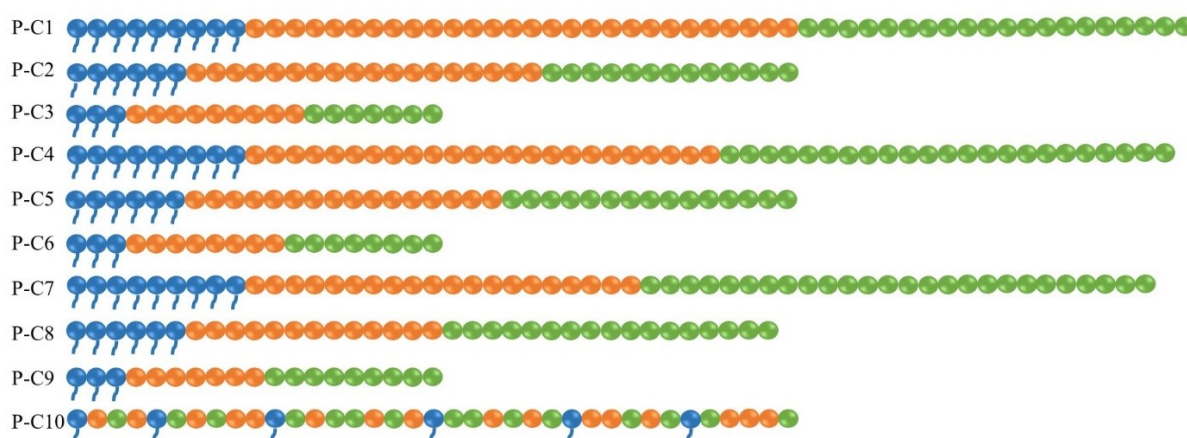


Figure 5.3. Schematic representations of nine triblock copolymers (P-C1 to P-C9) and one statistical copolymer (P-C10) studied in this chapter. The hydrophilic PEGMA, hydrophobic EtMA and hydrophilic DMAEMA units are represented by blue, orange and green, respectively.

5.2 Structural Properties

The structural properties of all copolymers and their homopolymers such as theoretical MMs, experimental MMs, MMDs (dispersity indices, $\bar{D}$) as well as theoretical/experimental compositions are summarised and discussed in the following sections. The GPC chromatograms and ^1H NMR spectra of the triblock copolymer and its precursors are also presented and discussed.

5.2.1 Molar Mass and Molar Mass Distributions

The number average MM (M_n) and MMDs ($\bar{D}$) of triblock copolymers and their linear precursors were determined using GPC. The example of the GPC chromatogram of P-C8 was shown in **Figure 5.4**. The GPC traces of the PEGMA homopolymer (PEGMA₆), the diblock copolymer (PEGMA₆-*b*-EtMA₁₃) and the final triblock copolymer (PEGMA₆-*b*-EtMA₁₃-*b*-DMAEMA₁₇) are represented in blue, orange and green, respectively. The GPC chromatogram confirms a successful sequential GTP. Specifically, the peaks of the diblock copolymers appeared after the peak of the PEGMA homopolymers, and subsequently, the peak that corresponds to the triblock (PEGMA₆-*b*-EtMA₁₃-*b*-DMAEMA₁₇) appeared after the diblock peak. This means that chain extension occurred as the polymerisation progresses, hence an increase in the MM from the homopolymer to the diblock and triblock. In addition to this, there is no peak that belongs to unreacted monomers, partial deactivation of polymer chains or unsuccessful addition of the monomers, which means that all monomer is fully reacted, hence 100% conversion of monomer to polymer. A similar GPC chromatogram profile was observed for other polymers, and they can be found in the Appendix section.

The theoretical chemical structure, theoretical MMs, number average MMs (M_n) as well as dispersity indices of final copolymers and their linear precursors are summarised and shown in **Table 5.1** along with the theoretical and experimentally determined compositions. The M_n s of the final copolymers vary between 3650 and 12 000 g mol⁻¹, and they are reasonably close to the targeted MMs and comparable with the copolymers from the previous chapter. According to the results, the experimental M_n values are consistently higher than the theoretical MM, as expected and observed in other published GTP studies. One of the reasons for higher M_n values is the partial deactivation of the initiator (MTS), which is caused by the presence of any protic impurities or humidity in the system that leads to initiator molecules to terminate.

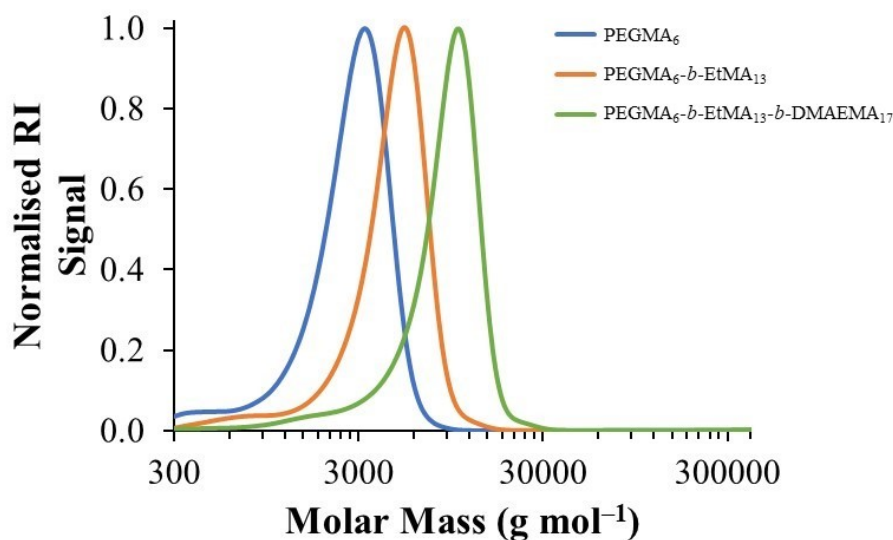


Figure 5.4. The GPC chromatograms of P-C8: PEGMA₆-*b*-EtMA₁₃-*b*-DMAEMA₁₇ and its precursors. The PEGMA₆ homopolymer, the diblock copolymer PEGMA₆-*b*-EtMA₁₃ and the final triblock copolymer PEGMA₆-*b*-EtMA₁₃-*b*-DMAEMA₁₇ and they are coloured in blue, orange and green, respectively.

The $\bar{D}$ values of copolymers ranged between 1.18-1.22, which is satisfactory low to confirm a successful living polymerisation method. The $\bar{D}$ values are similar to other previous studies where PEGMA based copolymers were synthesised using GTP.⁷ As it was mentioned in Chapter 5, PEGMA is macromonomer which means that it has average MM which leads to broader MMDs for the copolymers. In addition to this, it cannot be purified *via* distillation therefore it provides impurities to the polymerisation, results higher $\bar{D}$ values. Furthermore, the $\bar{D}$ values are slightly higher (~ 1.22) for low MWs copolymers, and it decrease with increasing MWs of the copolymers, which is expected to observe with living polymerisation techniques.⁸ The statistical copolymer, P-C10, has lower $\bar{D}$ values compared to the most of the copolymers in this series because all monomers were added into the polymerisation flask at the same time and initiator was added later, providing water bath in order to provide cooling of the system, to prevent the overheating of the flask. This led to more controlled polymerisation, hence obtaining polymer with having narrower MMD.

It was expected triblock copolymers will have higher $\bar{D}$ values compared to the diblock copolymers (**polymer series 1 and 2**). This is because, when triblock copolymers were synthesised, one more addition of monomer was performed compared to synthesis to diblock

copolymer. This allows humidity into the system which causes deactivation of the polymer chains and hence gives broader MMDs.

Table 5.1. The theoretical polymer structure, theoretical molar mass ($MM^{\text{theor.}}$), number-average MM, M_n , dispersity index ($\bar{D}$) and composition of the triblock copolymers, and their precursors.

No.	Theoretical Polymer Structure ^a	$MM^{\text{theor. b}}$ (g mol ⁻¹)	M_n^c (g mol ⁻¹)	$\bar{D}^d$	% w/w PEGMA- <i>b</i> -EtMA- <i>b</i> -DMAEMA	
					Theoretical	¹ H NMR
P-C1	PEGMA ₉	2800	3080	1.23	100-0-0	100-0-0
	PEGMA ₉ - <i>b</i> -EtMA ₂₈	5950	7120	1.22	46-54-0	46-54-0
	PEGMA ₉ - <i>b</i> -EtMA ₂₈ - <i>b</i> -DMAEMA ₂₀	9100	11300	1.19	30-35-35	30-37-34
P-C2	PEGMA ₆	1900	2450	1.17	100-0-0	100-0-0
	PEGMA ₆ - <i>b</i> -EtMA ₁₈	4000	5150	1.16	46-54-0	46-54-0
	PEGMA ₆ - <i>b</i> -EtMA ₁₈ - <i>b</i> -DMAEMA ₁₃	6100	7640	1.18	30-35-35	29-37-35
P-C3	PEGMA ₃	1000	1500	1.21	100-0-0	100-0-0
	PEGMA ₃ - <i>b</i> -EtMA ₉	2050	2640	1.18	46-54-0	46-54-0
	PEGMA ₃ - <i>b</i> -EtMA ₉ - <i>b</i> -DMAEMA ₇	3100	3850	1.22	30-35-35	29-38-34
P-C4	PEGMA ₉	2800	3220	1.18	100-0-0	10-0-0
	PEGMA ₉ - <i>b</i> -EtMA ₂₄	5500	6720	1.17	50-50-0	39-61-0
	PEGMA ₉ - <i>b</i> -EtMA ₂₄ - <i>b</i> -DMAEMA ₂₃	9100	10800	1.21	30-30-40	29-32-39
P-C5	PEGMA ₆	1900	2370	1.19	100-0-0	100-0-0
	PEGMA ₆ - <i>b</i> -EtMA ₁₆	3700	4450	1.20	50-50-0	47-53-0
	PEGMA ₆ - <i>b</i> -EtMA ₁₆ - <i>b</i> -DMAEMA ₁₅	6100	7270	1.22	30-30-40	28-32-40
P-C6	PEGMA ₃	1000	1200	1.34	100-0-0	100-0-0
	PEGMA ₃ - <i>b</i> -EtMA ₈	1900	2410	1.16	50-50-0	47-53-0
	PEGMA ₃ - <i>b</i> -EtMA ₈ - <i>b</i> -DMAEMA ₈	3100	3650	1.20	30-30-40	27-32-41
P-C7	PEGMA ₉	2800	4228	1.14	100-0-0	100-0-0
	PEGMA ₉ - <i>b</i> -EtMA ₂₀	4150	7677	1.13	55-45-0	53-47-0
	PEGMA ₉ - <i>b</i> -EtMA ₂₀ - <i>b</i> -DMAEMA ₂₆	9100	12000	1.32	30-25-45	29-26-45
P-C8	PEGMA ₆	1900	2420	1.24	100-0-0	100-0-0
	PEGMA ₆ - <i>b</i> -EtMA ₁₃	3400	4200	1.19	55-45-0	51-49-0
	PEGMA ₆ - <i>b</i> -EtMA ₁₃ - <i>b</i> -DMAEMA ₁₇	6100	8310	1.16	30-25-45	32-24-44
P-C9	PEGMA ₃	1000	1580	1.21	100-0-0	100-0-0
	PEGMA ₃ - <i>b</i> -EtMA ₇	1750	2420	1.21	55-45-0	56-44-0
	PEGMA ₃ - <i>b</i> -EtMA ₇ - <i>b</i> -DMAEMA ₉	3100	3940	1.22	30-25-45	28-28-44
P-C10	PEGMA ₆ - <i>co</i> -EtMA ₁₆ - <i>co</i> -DMAEMA ₁₅	6100	8640	1.20	30-30-40	30-32-39

^a PEGMA, EtMA and DMAEMA are abbreviations of poly(ethylene glycol) methyl ether methacrylate, ethyl methacrylate and 2-(dimethylamino)ethyl methacrylate, respectively. ^b The theoretical MM ($MM^{\text{theor.}}$) was calculated using the equation: $MM^{\text{theor.}}$ (g/mol) = ($\sum_i MM_i \times DP_i$) + 100. ^c The number average molar mass (M_n) and ^d dispersity ($\bar{D}$) were determined using Gel Permeation Chromatography (GPC). The experimental composition The GPC was calibrated using six poly (methyl methacrylate) (PMMA) standard samples; 2000, 4000, 8000, 20 000 and 50 000 g mol⁻¹.

5.2.2 Polymer Composition

The experimental compositions of the final copolymers and their linear precursors were determined using the ^1H NMR and they are in good agreement with the theoretical expected composition, as summarised in **Table 5.1**. The ^1H NMR spectra of c) P-C8: PEGMA₆-*b*-EtMA₁₃-*b*-DMAEMA₁₇ (in green) and its precursors: a) homopolymer, PEGMA₆ (in blue) and b) diblock, PEGMA₆-*b*-EtMA₁₃ (in orange) are shown in **Figure 5.5**. As can be seen additional peaks are present in (b) and (c) which belong to EtMA and DMAEMA units respectively. This and the fact there are no unreacted monomer peaks in the ^1H NMR spectra which suggests there is 100% conversion of the monomer to the polymer confirms a successful sequential polymerisation of triblock copolymers. The experimental weight percentages of polymers were calculated by using the integral of the distinctive peaks that belongs to the repeated units of each polymer. The distinctive peak of; a) PEGMA unit is at 3.35 ppm and it belongs to the three methoxy protons labelled with 'e' b) EtMA unit is at 1.25 ppm and it belongs to methyl protons labelled with 'g' c) DMAEMA unit is at 2.25 ppm and it belongs to six methyl protons that is next to amine group and it is labelled with 'j'.

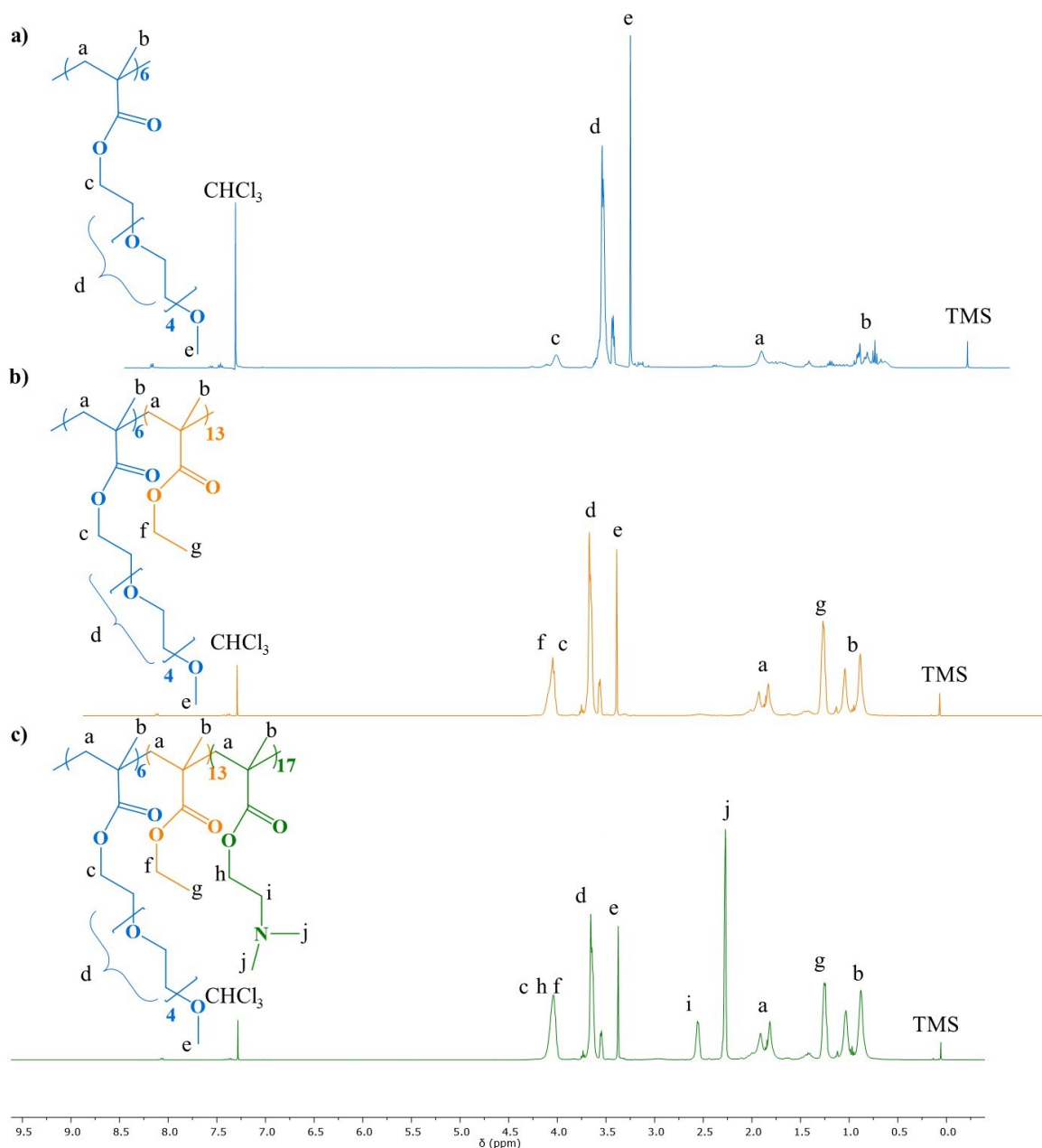


Figure 5.5. The ^1H NMR spectra of the a) PEGMA₆ homopolymer, b) PEGMA₆-*b*-EtMA₁₃ diblock copolymer and c) PEGMA₆-*b*-EtMA₁₃-*b*-DMAEMA₁₇ triblock copolymer shown in blue, orange and green, respectively. The chemical structures of the repeated units of PEGMA, EtMA and DMAEMA are also shown in blue, orange and green, respectively.

5.3 Aqueous Solution Properties

5.3.1 Cloud Points

The cloud points of 1 w/w% aqueous copolymer solutions in DI water was determined by observing visually at a temperature range from 25 °C and 80 °C. The cloud points of triblock copolymers are listed on **Table 5.2**. All copolymer solutions were soluble at pH ~ 8.2-9.2, where DMAEMA units were not protonated. The cloud point for statistical copolymer could not be determined because it was not soluble. The composition, MM, solution of the pH and ionic strength are one of the factors that strongly influence the thermoresponsive properties.^{9,10} In these terpolymers the thermoresponsive behaviour can be attributed to both the DMAEMA and PEGMA units. According to the previous studies, the cloud points of the PEGMA-based copolymers are strongly influenced by the side chain length of the PEGMA based methacrylate unit and the % composition in the case of copolymers. In this polymer series, the length of the side group and the wt% PEGMA was kept constant, so the differences in the cloud points between the polymers can only attributed to the change of the DMAEMA/EtMA ratio and the overall MM of the polymer. The cloud point of a DMAEMA homopolymer (when DP ~ 20), is around 43 °C, which is similar with polymers, P-C1 and P-C4. As can be seen from **Table 5.2**, when the composition was kept constant, and the MM was increased, the cloud point decreased, as was observed in the previous chapter and previously published studies.^{8,11}

When keeping the MM, the same and changing the DMAEMA/ratio, the cloud point was not affected significantly and was the same within experimental error. This was not surprising since it was mentioned above that the differences in degree of polymerisation are not significant and the micellar sizes are very similar as well.

5.3.2 Effective pK_a s

Hydrogen ion titrations were performed in order to determine the effective pK_a values of triblock copolymers. The effective pK_a values of DMAEMA units are listed in **Table 5.2**. The effective pK_a values of all triblock copolymers ranged between 6.8-7.2, which is similar with previously reported DMAEMA-based polymers.^{9,10,12} According to the previous studies, the pK_a is strongly affected by the hydrophobic content or/and hydrophobicity of the polymer. The pK_a s of the polymer decreases with increase of hydrophobicity and/or hydrophobic content of copolymer. Thus, as expected this was observed in this study too as seen in **Figure 5.6**. However, there is only small change in the EtMA content, therefore there is not big difference in pK_a values.

Interestingly, it can also be observed that the pK_a values of copolymers increase when decreasing the MM of the copolymer while keeping the composition constant. Specifically, the pK_a values increased from 6.9 to 7.0 to 7.1 by decreasing the MM from 10 800 to 7270 to 3650 g mol^{-1} . The trend is not as pronounced and the differences are small (almost within the experimental error) but it can be easily explained since smaller polymers are easily to dissolve and form smaller micelles which results to easier access to the DMAEMA groups to be protonated, i.e. less acid is needed, and consequently higher pK_a is observed. The appearance of the aqueous solutions did not change, and colourless solutions were observed between pH 2 and 12.

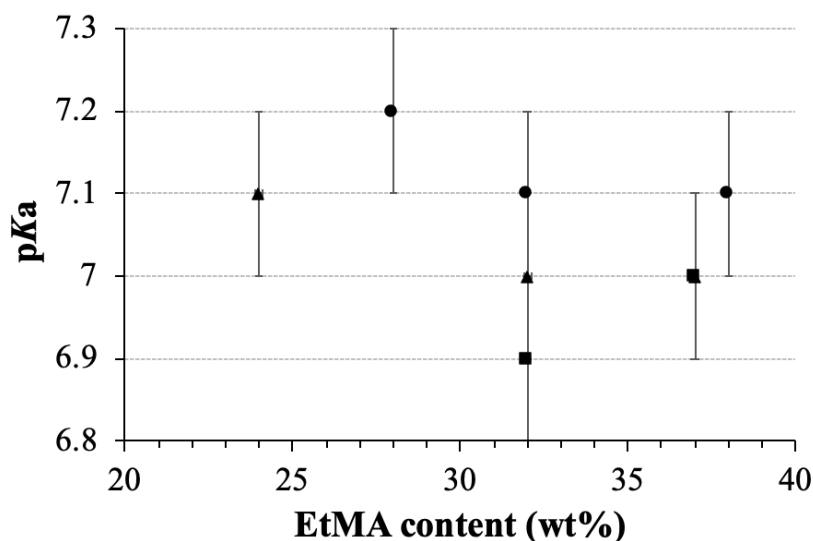


Figure 5.6. The effect of experimental ethyl methacrylate (EtMA) content on pK_a values. With circle (●), triangle (▲) and square (■) polymers of different MMs; 3000, 6000 and 9000 g mol^{-1} are represented, respectively.

Table 5.2. The theoretical polymer structure, experimental (d_{hs}) and theoretical (calculated) hydrodynamic diameters, polydispersity indices (PDI), cloud points and effective pK_{as} of 1 w/w% aqueous polymer solutions.

No.	Theoretical Polymer Structure ^a	EtMA wt % by NMR	MM ^{theor.} g mol ⁻¹	Hydrodynamic diameter, <i>d</i> _{hs} (nm)			PDI		Cloud Points ± 2 °C	HLB ^d	p <i>K</i> _a s ± 0.1	CMC x10 ⁻⁵ mol L ⁻¹ ^e
				Theo. ^b	Experimental ± 0.5							
					pH 7 ^c	pH ⁱ ^c	pH 7	pH ⁱ				
P-1C	P ₉ - <i>b</i> -E ₂₈ - <i>b</i> -D ₂₀	37	9100	23.6	6.5	15.7	0.272	0.039	49	12.8	7.0	2.21
P-2C	P ₆ - <i>b</i> -E ₁₈ - <i>b</i> -D ₁₃	37	6100	18.6	4.9	11.7	0.264	0.026	51	12.8	7.0	6.54
P-3C	P ₃ - <i>b</i> -E ₉ - <i>b</i> -D ₇	38	3100	9.3	5.6	8.7	0.240	0.035	52	12.6	7.1	13.0
P-4C	P ₉ - <i>b</i> -E ₂₄ - <i>b</i> -D ₂₃	32	9100	24.0	18.2	15.7	0.381	0.018	49	13.6	6.9	4.63
P-5C	P ₆ - <i>b</i> -E ₁₆ - <i>b</i> -D ₁₅	32	6100	16.6	10.1	11.7	0.332	0.091	51	13.6	7.0	13.8
P-6C	P ₃ - <i>b</i> -E ₈ - <i>b</i> -D ₈	32	3100	8.1	7.5	7.5	0.305	0.096	55	13.6	7.1	68.0
P-7C	P ₉ - <i>b</i> -E ₂₀ - <i>b</i> -D ₂₆	26	9100	19.5	18.2	18.2	0.489	0.088	40	14.8	6.8	2.08
P-8C	P ₆ - <i>b</i> -E ₁₃ - <i>b</i> -D ₁₇	24	6100	17.0	11.7	10.1	0.343	0.071	52	15.2	7.1	3.01
P-9C	P ₃ - <i>b</i> -E ₇ - <i>b</i> -D ₉	28	3100	10.1	7.5	6.5	0.303	0.089	57	14.4	7.2	0.64
P-10C	P ₆ - <i>co</i> -E ₁₆ - <i>co</i> -D ₁₅	32	6100	2.8	1.74	NS ^f	0.868	-	NS	13.8	7.0	NS

^a P represents poly(ethylene glycol) methyl ether methacrylate (PEGMA), E represents ethyl methacrylate (EtMA) and D represents 2-(dimethylamino)ethyl methacrylate (DMAEMA).

^b Theoretical hydrodynamic diameter values based on experimental degree of polymerisations (DPs) of EtMA, PEGMA and DMAEMA units. The DPs were calculated by using the MM of copolymers after precipitation and the experimental composition which are obtained using GPC and ¹H NMR. The equation used to calculate the theoretical hydrodynamic diameter is $d_h = (DP_{EtMA} + 2 \times DP_{DMAEMA}) \times 0.254$ nm. ^c Experimental hydrodynamic diameter values are given by intensity, and it is obtained using DLS. ^d Hydrophile-lipophile balance (HLB) was calculated using this equation by Griffin; $HLB = (W_h/W_h + W_l) \times 20$. ^e CMC stands for critical micelle concentration of copolymer. ^f NS stands for insoluble polymer, so the experiments were unable to be performed.

5.3.3 Hydrodynamic Diameters

The theoretical (upper limits) diameter values of triblock and statistical copolymer were calculated assuming formation of spherical micelles with fully stretched polymer chains of triblock copolymers and formation of random coil configuration by statistical copolymers. It was assumed that the hydrophobic EtMA-based block will form the core of the micelle and hydrophilic DMAEMA and PEGMA-based blocks orientate towards to water, i.e. form the shell of the micelle, which is schematically represented in (a) **Figure 5.7**. The theoretical values of triblock copolymers are calculated by using the degree of polymerisation of EtMA hydrophobic block plus twice degree of polymerisation of the longest hydrophilic block and it is multiplied by the projected length of the one repeated of methacrylate unit.

In calculations, degree of polymerisation of DMAEMA was used because it has longer blocks compared to PEGMA, and it was assumed that the overall size of the micelle affected by the longest hydrophilic block and not PEGMA blocks. The theoretical hydrodynamic diameters of all copolymers are listed on **Table 5.2**.

The hydrodynamic diameter of triblock copolymers in aqueous solution was determined using DLS. Their self-assembly behaviour of copolymers was observed in their initial pH (8.6-9.2) and pH 7 and it is summarised in **Table 5.2**. According to the hydrodynamic diameters, it was confirmed that all triblock copolymers self-assemble to form spherical micelles. In addition to this, the theoretically predicted hydrodynamic diameter values shows the same trend with the experimental values. Furthermore, the experimental hydrodynamic diameter for all triblock copolymers are lower than the theoretical hydrodynamic diameters at their initial pH. This result is expected and also observed in previously with ABC triblock copolymer studies.¹¹ The reason why theoretical values are bigger than the experimental ones both the, hydrophobic as well as hydrophilic blocks of the polymer chains are assumed to be fully extended. However, in reality the hydrophobic EtMA blocks will be in a collapsed state therefore the size of the micelles will be smaller than it is theoretically calculated. The variation of MM/length as well as composition of polymer results in change in the micelle size. The size of the micelles decreased when the MM of the copolymer was decreased, as expected, and observed before. Specifically, the bigger micelle sizes are observed for polymers P-C1, P-C4 and P-C7, which they have targeted MM 9000 g mol⁻¹. In terms of the effect of the composition of the polymer on the hydrodynamic diameter no clear trend is observed. In particular for polymers of the similar MM even if the composition was changed because the change in degree of

polymerisation was so small the hydrodynamic diameters were of similar size within the experimental error.

When comparison was made between the micelle sizes of copolymers at their initial and pH 7 two different trends are observed. Specifically, at pH 7, polymers P-C1, P-C2, P-C3 and P-C5 that more EtMA than DMAEMA units have smaller micelle size compared to their initial pH due to the protonation of some DMAEMA units that makes the polymer more hydrophilic and less aggregation is observed. However, when the EtMA are less than the DMAEMA units (P-C4, P-C7, P-C8 and P-C9), and the micelles have a bigger shell (corona) than core, bigger micelles are observed in the lower pH because the electrostatic repulsion of the cationic DMAEMA groups extend the DMAEMA blocks, force the shell of the micelle to swell and thus the whole micelle structure expands.

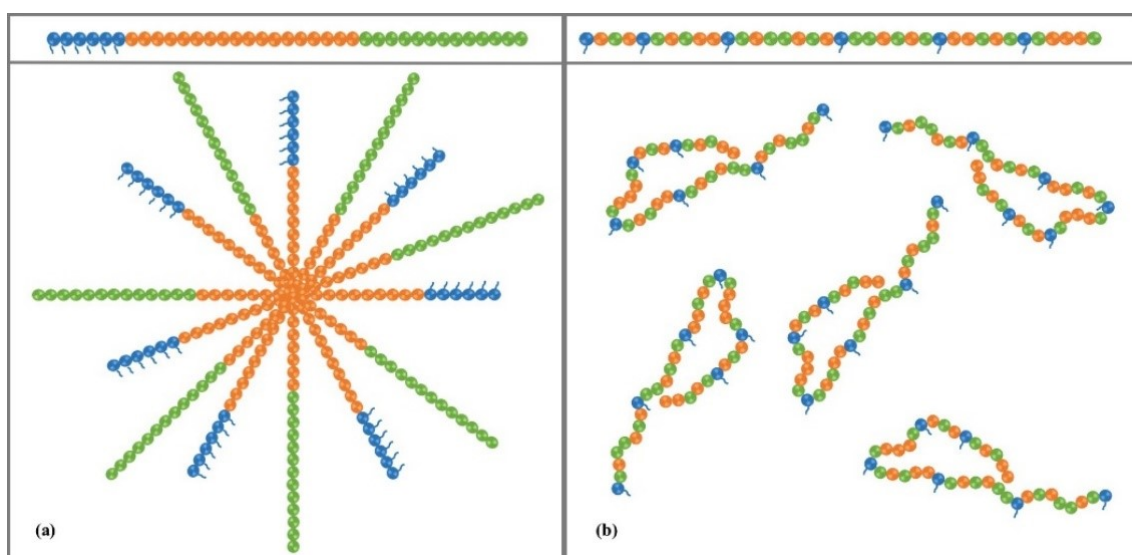


Figure 5.7. The schematic representation of a) P-C1 that self-assemble to micelles b) P-C10 that forms random coil configuration. The PEGMA, EtMA and DMAEMA units are shown in blue, orange and green, respectively.

5.3.4 Critical Micelle Concentration

Thirteen different concentrations of triblock copolymers in DI water were prepared, and their CMC values were determined using DLS. The CMC value of statistical copolymer (P-C10) could not be investigated because it has poor solubility in water. The CMC values of all triblock copolymers were determined, and they are listed in **Table 5.2**. The CMC values of triblock copolymers were between 0.64 to $68 \times 10^{-5} \text{ mol L}^{-1}$. The CMC graphs of all copolymers are shown in **Figure 14** in Appendix.

As shown in **Table 5.2**, in this study, it was also observed that triblock copolymers have higher CMC values than the diblock copolymers. On the other hand, Broekhuis and co-workers also observed that triblock copolymers have lower CMC values than diblock copolymers.¹

5.4 Triblock and Statistical Copolymers as Polymeric Emulsifiers

The methyl laurate-water emulsions were prepared using $1.0 \text{ w/w\%}$ polymeric surfactants. An ultrasonic processor was used to emulsify equal weights of methyl laurate and water phases for 1 minute.

5.4.1 Type of Emulsions

The type of emulsions (O/W or W/O) was determined by performing drop tests for the freshly prepared emulsions. According to the drop test results, all polymeric surfactants forms O/W type emulsions. This was determined by observing a coagulated spherical drop of emulsions in the methyl laurate, whereas the uniform distribution of emulsion drops in the water. The type of the emulsions was also confirmed by calculating the hydrophile-lipophile balance of polymeric surfactants using the Griffin equation (see **equation 3.11** in the Experimental section). According to Griffin, HLB values higher than ~ 6 indicates that polymeric surfactants are water-soluble, and they stabilise O/W emulsions. As summarised in **Table 5.2**, the HLB values of polymeric surfactants are varied between 12.6 and 15.2 , which confirms that they stabilise O/W type emulsions.

5.4.2 Stability of Emulsions

5.4.2.1 Visual Observation

The stability of the emulsions is observed visually, and images of emulsions are taken at eight different times; 1 min, 2 hours, 4 hours, one day, two days, three days, one week, two weeks, three weeks and a month after emulsification performed. As shown in **Figure 16** in Appendix, all polymeric surfactants can emulsify water and methyl laurate phases and form opaque O/W emulsions. The emulsions stabilised by polymeric surfactants are stable for a month, and complete phase separation into oil and water did not happen for any of the emulsion. In order to obtain a clearer idea of the effect of composition and MM of polymeric surfactants on the stability of the emulsion, the volume fraction of the cream phase (ϕ_{cream}) was determined by measuring the thickness of the cream (opaque) layer. The ϕ_{cream} values of all emulsions stabilised by in-house synthesised polymeric surfactants are summarised and available in Appendix (see **Table 6**). According to the results, the ϕ_{cream} phase of emulsion decreases over time (see **Figure 15** in Appendix). This is expected and observed in the previous study using diblock copolymers.

The effect of MM on the emulsifying ability of the polymeric surfactant was observed by plotting ϕ_{cream} phase versus MM of polymeric surfactants. Please note that the composition of triblock copolymers is represented in the order of PEGMA-EtMA-DMAEMA. As shown in **Figure 5.8**, the same trend observed for the most hydrophobic (30-35-35 w/w%) and intermediate (30-30-40 w/w%); increasing MM of the polymeric surfactants lead to a decrease in the ϕ_{cream} phase, which results in a less stable emulsion. On the other hand, when more hydrophilic polymeric surfactant (30-25-45 w/w%) is used, the emulsion stability increases when MM increases. Therefore, for the least hydrophilic and intermediate polymeric surfactant, the maximum MM to obtain stable emulsion is 4000 g mol^{-1} , whereas for most hydrophilic surfactant maximum MM to obtain stable emulsion is $11\,000 \text{ g mol}^{-1}$.

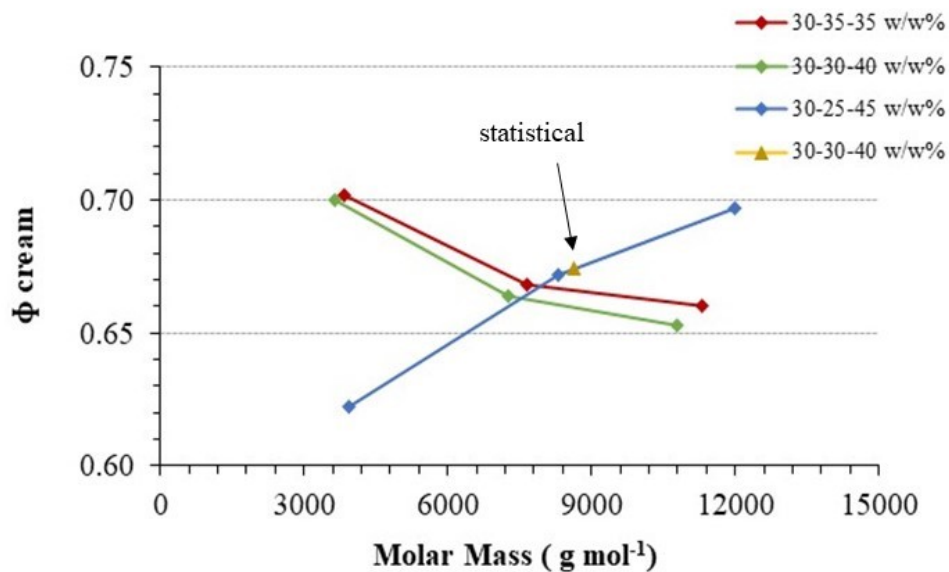


Figure 5.8. The effect of copolymers molar mass on the volume fraction of the cream phase. The triblock copolymers are represented by rhombus (◆), and the statistical copolymer is represented by a triangle (▲). The composition of the triblock copolymers is represented in the order of PEGMA-EtMA-DMAEMA w/w%.

In order to observe the effect of composition of polymeric surfactants on stability of emulsions, ϕ_{cream} phase versus composition of EtMA and DMAEMA are plotted, and it is shown in **Figure 5.9 A and B** respectively. As shown in graph, opposite effect observed for polymeric surfactants with different MMs. Polymeric surfactants with high MMs showed increase in stability of emulsions when the EtMA content increases. The polymeric surfactant with a MMs, 4000 g mol^{-1} and 28 wt% of EtMA content forms the least stable emulsion compared to other polymeric surfactants. Increasing the EtMA content by 4 wt%, lead to increase in the ϕ_{cream} from 0.622 to 0.7. However, increasing the EtMA content even more does not make any more stable emulsions. On the other hand, polymeric surfactants with MMs $11\,000 \text{ g mol}^{-1}$ shows decrease in the stability of emulsion ($\phi_{\text{cream}} = 0.69$ to 0.65) when composition of EtMA increases from 26 to 32 wt%. Increasing composition of EtMA from 32 to 37 wt%, does not affect the stability of the emulsion. The polymeric surfactants with intermediate MMs (8000 g mol^{-1}) shows slight change in the stability of the emulsion. The ϕ_{cream} phase changed from 0.668 to 0.672 when composition of EtMA increased to 24 to 37 wt%.

Finally, the most stable emulsion is formed when polymeric surfactant with highest EtMA content (38 wt%) and lowest MM used and least stable emulsion is formed when lowest content of EtMA with lowest MM used.

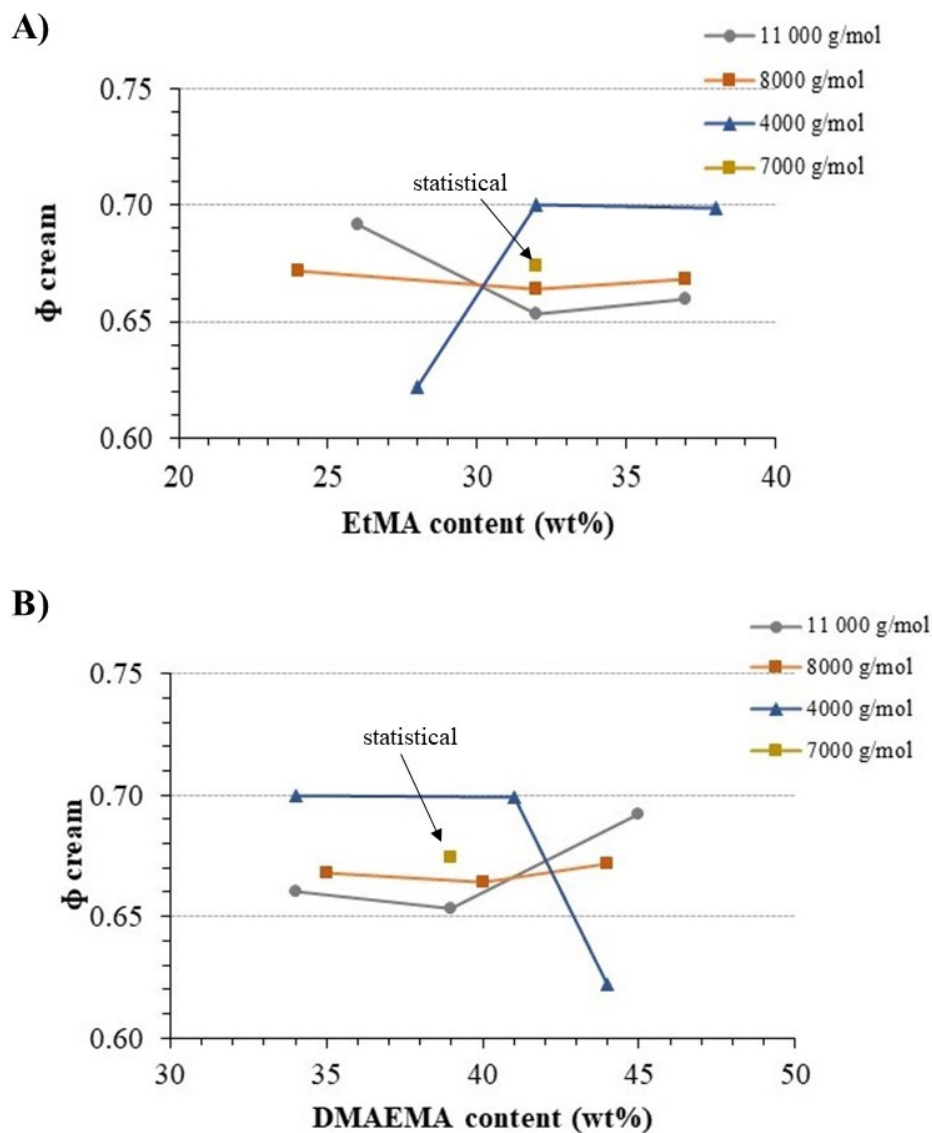


Figure 5.9. The effect of weight percentage of: a) EtMA and b) DMAEMA on the volume fraction of the cream ϕ_{cream} phase. The MMs of polymeric surfactants are 11 000, 8000 and 4000 g mol⁻¹ and represented in grey, orange and navy, respectively. The statistical copolymer is represented in yellow.

5.4.2.2 Microscopy Observation

Optical transmission spectroscopy was performed in order to obtain information about the size of emulsion droplets and understand the instability mechanism. The size of the emulsion droplets was observed directly after the emulsification performed, after two days and a week in order to see the change in the size of emulsion droplets over time. The size of the emulsion droplets was measured after emulsification performed and they were varied between 6.1-7.9 μm and after a week they were varied between 6.5-7.6 μm . When comparison made between the size of droplets on the same day and after a week, the sizes of droplets are close to each other. This indicates that the emulsions stabilised by triblock copolymers are quite stable.

The optical micrographs of P-C7 are shown in **Figure 5.10**. As shown, over time, the size of the emulsion droplets gets bigger which is expected due to the unstable nature of emulsion system. The size of the emulsion droplets stabilised by triblock and statistical copolymers are summarised in **Table 7** in Appendix.

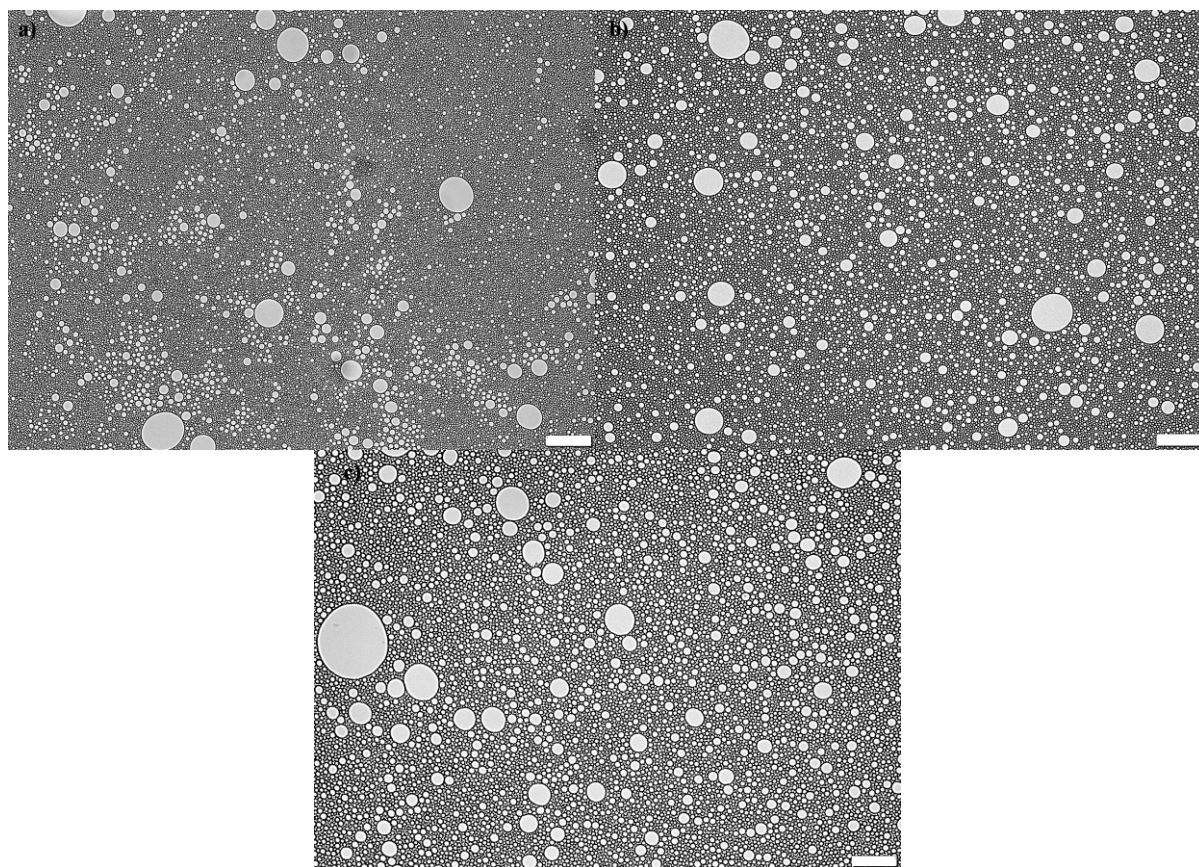


Figure 5.10. The optical micrographs of O/W emulsions stabilised by P-C7 The micrographs are taken; a) one day, b) a week and c) a month after emulsification performed. The scale bar is equal to 50 μm .

5.5 Conclusions

This chapter of PhD thesis includes the synthesis of nine well-defined triblock copolymers with ABC architecture (PEGMA-*b*-EtMA-*b*-DMAEMA) and one statistical copolymer *via* the one-pot GTP method. The aqueous solution properties such as hydrodynamic diameter, CMC, effective pK_a s, cloud point values were determined. In addition to this, the emulsifying properties of synthesised triblock copolymers are evaluated as polymeric surfactants. The key findings in this chapter are;

- The M_n values of all synthesised copolymers are varied between 3650 and 12000 g mol⁻¹ and they are satisfactorily close to the theoretical values. Furthermore, the MMDs are varied between 1.16 and 1.32 which is satisfactorily low. The experimental compositions of triblock copolymers are close to their targeted compositions: 30-35-35, 30-30-40 and 30-25-45 w/w/w% of PEGMA-EtMA-DMAEMA.
- The cloud points of triblock copolymers were varied between 40 and 55 °C, the cloud points of triblock increases when the MM decreases. The cloud point for statistical copolymer could not be investigated due to the poor solubility in water.
- The effective pK_a values are varied between 6.8 and 7.1.
- All triblock copolymers self-assemble to form spherical core-shell corona micelles. The hydrodynamic diameter values of triblock copolymers at their initial pH (8.6-9.2) were determined, and the values are varied between 6.5 and 18.2 nm. The size of the spherical micelles decreases when the MM of the triblock copolymer decreases.
- The CMC values of all triblock copolymers are varied between 0.64-68.0 x 10⁻⁵ mol L⁻¹.
- The HLB values of all copolymers range between 12.6-15.2, which means that they are water-soluble and stabilise the O/W type emulsions.
- All synthesised triblock and statistical copolymers (polymeric surfactants) able to stabilise methyl laurate in water emulsions. Drop tests were performed, and all polymeric surfactants able to form O/W type emulsions.
- Visual observations of emulsions were observed for a month, and the cream layer thickness measured. It was observed that the thickness of the cream layer decreases, which means that the stability decreases over time.

- The effect of MM and the composition of polymeric surfactants on the stability of emulsions were determined. According to the results, for compositions (30-35-35 and 30-30-40 w/w/w%, PEGMA-EtMA-DMAEMA), increasing MM results decrease in the ϕ_{cream} phase. On the other hand, when the composition of polymeric surfactant is 30-25-45 w/w/w%, an increase in MM results increase in ϕ_{cream} .
- The effect of the weight percentage of EtMA content on the stability of emulsions was measured. According to the results, for low MM (4000 g mol^{-1}) polymeric surfactants, an increase of EtMA content from 28 to 32 wt% forms more stable emulsions. On the other hand, the opposite trend was observed for polymeric surfactants with higher MMs (7000 and $11\,000 \text{ g mol}^{-1}$). When the composition of EtMA increased from 30 to 35 wt%, the ϕ_{cream} phase changed slightly.

5.6 References

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CHAPTER 6: CHARACTERISATION OF BUTYL METHACRYLATE BASED COMPLEX ARCHITECTURES OF COPOLYMERS AS POLYMERIC SURFACTANTS

In previous chapters, we systematically investigated the effect of composition and MM on the emulsifying properties of EtMA-based polymeric surfactants. This chapter is separated in two sections. The first section studies diblock copolymers of varying hydrophobic units in order to investigate the effect of the hydrophobic block on the stability of the emulsions, with DMAEMA-based diblock copolymers being able to be recovered upon precipitation and forming stable emulsions. Therefore, the second section investigates BuMA-based copolymers of varying architectures, such as statistical, gradient and block copolymers. To the best of our knowledge, this is the first study that the effect of architecture on the emulsifying properties of polymeric surfactants is compared. The studies are discussed in more detail below.

As previously mentioned, diblock copolymers with varying hydrophobic block were synthesised and investigated. The hydrophobic monomers used in the first part of this section are methyl methacrylate (MMA), *n*-butyl methacrylate (BuMA), hexyl methacrylate (HeMA) and lauryl methacrylate (LMA). As a hydrophilic block, DMAEMA was used so that the only variable is the hydrophobic block. The structures of hydrophobic monomers are shown in **Figure 6.1**. The synthesis of diblock copolymers was performed in the same way as discussed in Chapter 4, only orders of addition of monomers and their quantities varied. In order to have a comparison with EtMA-based diblock copolymers, same composition and MMs were targeted. The targeted MMs is 6000 g mol^{-1} , and composition was 60-40 w/w%, DMAEMA-EtMA. Finally, four different diblock copolymers were synthesised, and their properties and characterisation are followed in the next section.

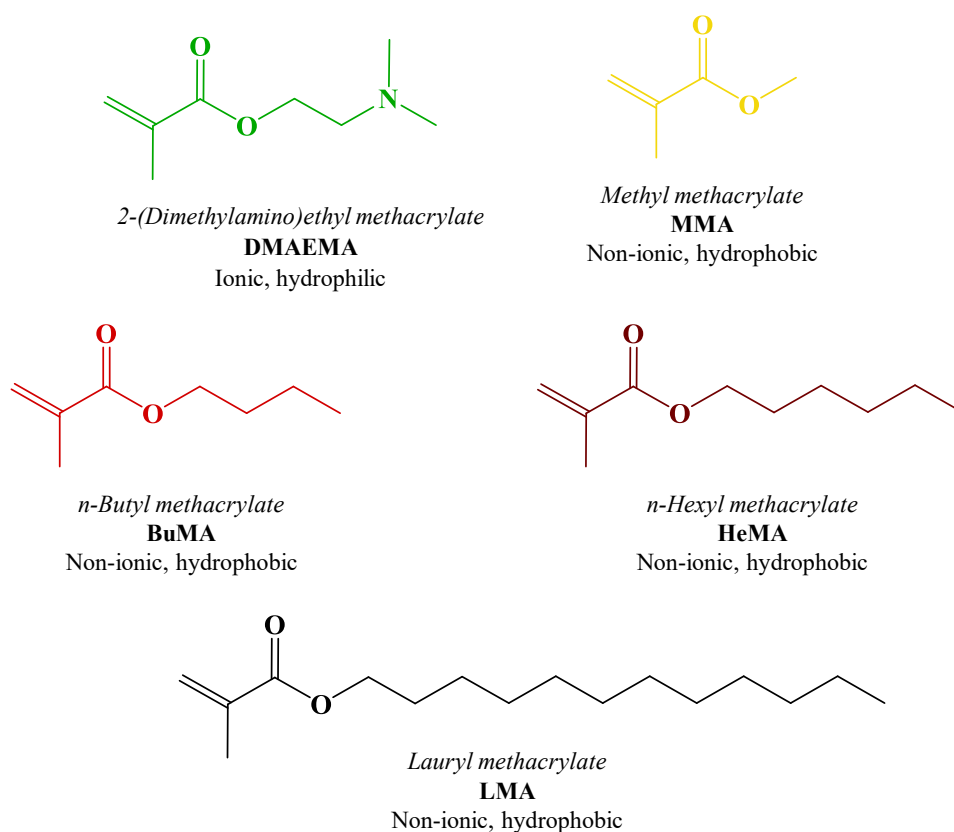


Figure 6.1. The chemical structures of hydrophobic monomers used in this study.

6.1 Structural Properties

The experimental composition, number-average MMs (M_n), and MMDs (dispersity indices, $\mathcal{D}$) of diblock copolymers and their linear precursors were determined and discussed in the following section. The experimental values of diblock copolymers and their linear precursors were compared with the theoretical values and summarised in **Table 6.1**.

6.1.1 Molar Mass and Molar Mass Distributions

The experimental MMs and MMDs values of all diblock copolymers and their linear precursors were determined using GPC and summarised in **Table 6.1**. The successful sequential polymerisation is confirmed by GPC chromatogram of P-H4, shown in **Figure 6.2**. The GPC traces of homopolymer (LMA₈) and diblock copolymer (LMA₈-*b*-DMAEMA₂₀) is represented in black and green, respectively. As shown, the MM peak of LMA₈-*b*-DMAEMA₂₀ appears after LMA₈, which means that the MM increases by the addition of DMAEMA units. Furthermore, there is no peak for unreacted monomer, which means that all monomers are converted to polymer. Similar GPC chromatograms observed for other diblock copolymers, and they are available in Appendix (see **Figure 17**).

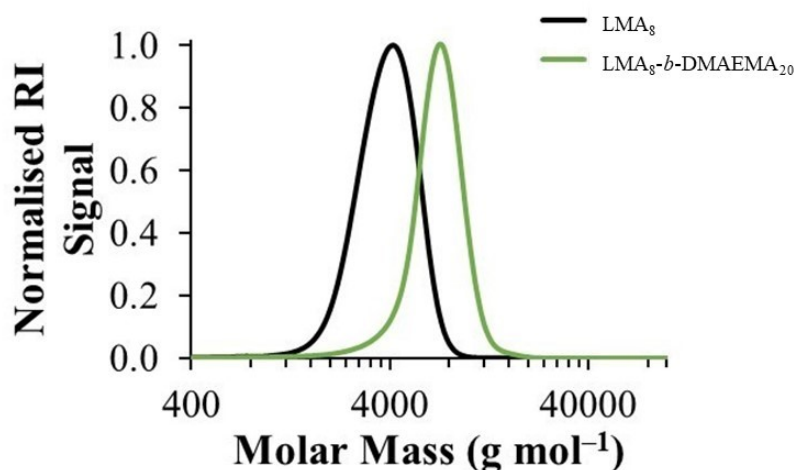


Figure 6.2. The GPC chromatogram of P-H4; The LMA₈ homopolymer, the diblock copolymer LMA₈-*b*-DMAEMA₂₀ and they are coloured in black and green, respectively.

As shown in **Table 6.1**, experimental M_n values are close to the targeted MMs and they are varied between 5900 and 7010 g mol⁻¹. Comparing experimental and theoretical values, P-H1 and P-H3 have higher experimental M_n values than their targeted MM. The reason is partial deactivation of the initiator (MTS) molecules due to impurities and humidity present in the system observed, which is also observed in previous chapters and previously reported GTP studies.¹⁻³ On the other hand, P-H2 and P-H3 have lower experimental M_n values than the theoretical ones.

The D values of copolymers and their linear precursors have narrow MWDs. They vary between 1.09 and 1.22, confirming the successful ‘living’ polymerisation, similar to previously reported GTP studies.^{4,5} As shown in **Table 6.1**, when the MM of the polymer increases, the D decreased, which is observed in living polymerisation methods.^{6,7,8}

6.1.2 Composition

The theoretical and experimental composition of diblock copolymers and their precursors were listed in **Table 6.1**. The ¹H NMR spectrum of the LMA-based diblock copolymer and its precursors can be found in **Figure 6.3**. The monomer composition of copolymers was determined by taking the integral of the representative peak. The peak for DMAEMA appears at 2.25 ppm, and it belongs to six methyl protons next to the amine group. In addition to this, the distinct peak of LMA is the methylene protons and it appears at 1.29 ppm.

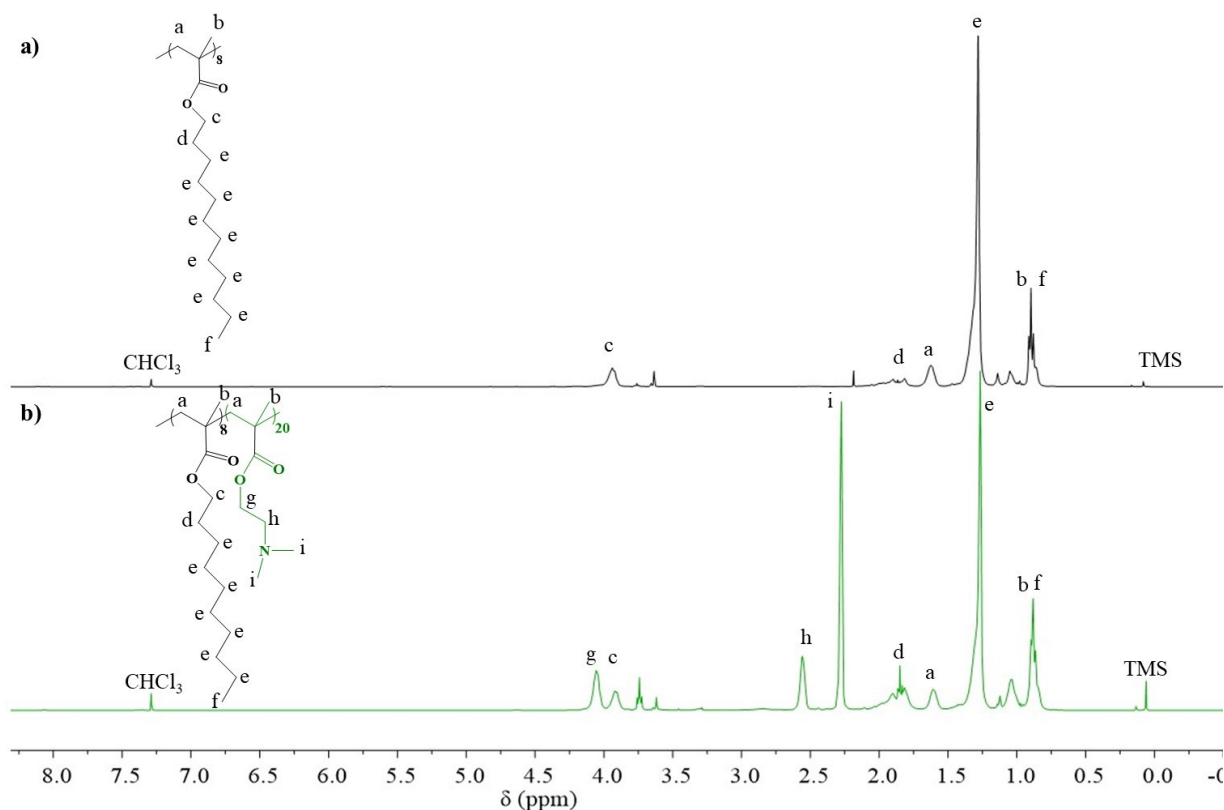


Figure 6.3. The ^1H NMR spectrum of a) homopolymer, LMA_8 and b) diblock copolymer, $\text{LMA}_8\text{-}b\text{-DMAEMA}_{20}$. The homopolymer and diblock copolymer were represented in black and green, respectively.

Table 6.1. The theoretical polymer structure, theoretical and experimental molar masses, molar mass distributions and compositions of the synthesised diblock copolymers and their precursors.

No.	Theoretical Polymer Structure ^a	$\text{MM}^{\text{theor. b}}$ (g mol^{-1})	M_n^c (g mol^{-1})	$\bar{D}^d$	% w/w H-DMAEMA ^c	
					Theoretical	^1H NMR
P-H1	DMAEMA_{24}	3600	3790	1.17	100-0	100-0
	$\text{DMAEMA}_{23}\text{-}b\text{-MMA}_{24}$	6100	7010	1.13	40-60	41-59
P-H2	BuMA_{17}	2400	2899	1.14	100-0	100-0
	$\text{BuMA}_{17}\text{-}b\text{-DMAEMA}_{23}$	6100	6020	1.22	40-60	38-62
P-H3	HeMA_{14}	2400	2960	1.15	100-0	100-0
	$\text{HeMA}_{14}\text{-}b\text{-DMAEMA}_{23}$	6100	5900	1.20	40-60	40-60
P-H4	LMA_8	2000	3618	1.11	100-0	100-0
	$\text{LMA}_8\text{-}b\text{-DMAEMA}_{20}$	5144	6600	1.09	39-61	40-60

^a DMAEMA, MMA, BuMA, HeMA and LMA stands for 2-(dimethylamino)ethyl methacrylate, *n*-butyl methacrylate, *n*-hexyl methacrylate and lauryl methacrylate. The theoretical MM was calculated using equation: $\text{MM}^{\text{theor.}} (\text{g mol}^{-1}) = (\sum_i \text{MM}_i \times \text{DP}_i) + 100$. ^c and ^d The number average molar mass (M_n) and dispersity index ($\bar{D}$) were determined using Gel Permeation Chromatography (GPC). The GPC was calibrated using six poly (methyl methacrylate) (PMMA) standard samples. Standard samples are; 2000,

4000, 8000, 20 000 and 50 000 g mol⁻¹. ^e H-DMAEMA represents the one of the hydrophobic monomers (MMA, BuMA, HeMA and LMA) that is polymerised with DMAEMA.

6.2 Aqueous Solution Properties

The aqueous solution properties such as hydrodynamic diameter and effective pK_a s are determined and discussed below. The cloud points and CMC values of diblock copolymers could not be investigated due to their poor solubility in water.

6.2.1 Effective pK_a s

The hydrogen ion titrations were performed to determine the effective pK_a values of diblock copolymers and they are shown in **Table 6.2**. The effective pK_a values of diblock copolymers were found to be between 6.4 and 7.0, and it is similar to the previously reported studies of DMAEMA based polymers.^{6,9,10} As shown in **Table 6.2**, when the hydrophobicity of the copolymer increases, the pK_a value decreases due to the decrease of the dielectric constant. The lowest pK_a value was observed for polymer with lauryl methacrylate because it is the most hydrophobic compared to others and has the lowest dielectric constant.

6.2.2 Hydrodynamic diameter

The experimental hydrodynamic diameter (d_h) of 1 w/w% polymers in DI water was determined using DLS and compared with their theoretical hydrodynamic diameter values (see **Table 6.2**). The diblock copolymers have poor solubility in water at their initial pH, therefore in order to enhance the solubility, the DMAEMA units are protonated and experiments performed at pH 7. The theoretical hydrodynamic diameter is calculated by assuming that the diblock copolymer self-assemble into spherical micelles. The hydrophilic DMAEMA units form the shell and hydrophobic units (MMA, BuMA, HeMA or LMA), forming the core of the spherical micelles.

As shown in **Table 6.2**, the experimental hydrodynamic diameter is lower than the theoretical ones, this is expected and previously published by other studies.^{5,11} The experimental hydrodynamic diameter of diblock are varied between 10.1 and 164 nm. Polymers, P-H2 and P-H3 have smaller experimental hydrodynamic diameter than their theoretical values. The reason for this is theoretical model assumes that: a) the hydrophobic part fully overlaps and b) both hydrophobic and hydrophilic part of the polymer chains fully extends and c) polymer chains self-assemble into spherical micelles.⁵ However, in real time experiments polymer chains might overlap in greater extent and hydrophobic part is in collapsed state which results smaller micelle sizes. On the other hand, the experimental hydrodynamic diameter values of

P-H1 and P-H4 are higher than the theoretical values. The reason for this could be: a) hydrophobic units might overlap in lesser extent and b) the repulsion between the hydrophilic DMAEMA units, and c) the hydrophobic interactions especially in P-H4 enhances the aggregation.

Table 6.2. Theoretical polymer structure, composition of hydrophobic component, theoretical molar mass, experimental and theoretical hydrodynamic diameter, and effective pK_a values of diblock copolymers.

No.	Theoretical Polymer Structure ^a	Hydrophobic wt% by NMR	MM ^{theor.} (g/mol)	Hydrodynamic Diameter (d_h , nm)		PDI	Cloud Points $\pm 2^\circ\text{C}$ 10 % H ⁺	HLB	$pK_{as} \pm 0.1$	CMC $\times 10^{-5}$ mol L ⁻¹
				Theo. ^b	Exp ± 0.5 ^c pH 7					
P-H1	D ₂₃ - <i>b</i> -M ₂₄	41	6100	20.7	37.8	0.259	-	8.2	7.0	NS ^d
P-H2	B ₁₇ - <i>b</i> -D ₂₃	38	6100	16.1	15.7	0.215	-	7.6	6.7	NS
P-H3	H ₁₄ - <i>b</i> -D ₂₃	40	6100	15.0	10.1	0.225	-	8.0	6.7	NS
P-H4	L ₈ - <i>b</i> -D ₂₀	40	5144	15.5	164	0.273	-	8.0	6.4	NS

^aD (DMAEMA), M (MMA), B (BuMA), H (HeMA) and L (LMA) stands 2-(dimethylamino)ethyl methacrylate, methyl methacrylate, *n*-butyl methacrylate, hexyl methacrylate and lauryl methacrylate, respectively. ^b Theoretical hydrodynamic diameter values were calculated using experimental degree of polymerisations (DPs) of DMAEMA, MMA, BuMA, HeMA and LMA. The DPs were calculated by using the MM of copolymers after precipitation and the experimental composition which are obtained using GPC and ¹H NMR, respectively. The equation used to calculate the theoretical hydrodynamic diameter is $d_h = (DP_{\text{Hydrophobic unit}} + 2 \times DP_{\text{DMAEMA}}) \times 0.254 \text{ nm}$. ^c Experimental hydrodynamic diameter values are given by intensity and it is obtained using DLS. The CMC and cloud points could not be investigated due to their poor solubility. ^d NS represents polymer is insoluble.

6.3 DMAEMA based Diblock Copolymers of varying hydrophobic block as Polymeric Emulsifiers

The methyl laurate-water emulsions were prepared using 1.0 w/w% polymeric surfactants. An ultrasonic processor was used to emulsify equal weights of methyl laurate and water phases for 1 minute. The type of emulsions and stability of emulsions were discussed in the following section.

6.3.1 Type of Emulsions

The type of emulsions was determined by performing drop tests for the freshly prepared emulsions. The drops of emulsion are added into methyl laurate and water containing vials. The drops of emulsion were uniformly distributed in the water whereas, they form a coagulated spherical drop in the methyl laurate thus, polymeric surfactants forms O/W type emulsions. The HLB value of diblock copolymers were determined and summarised in **Table 6.2**. As shown, the HLB values are varied between 7.6 and 8.2. The HLB values of polymeric surfactants higher than ~6 indicates that they will stabilise O/W type emulsions.³ The type of emulsions were agreed to each other both theoretically and experimentally. Compared to other diblock copolymers (**Polymer series 1** and **2**) and triblock copolymer series (**Polymer series 3**), these four diblock copolymers have lower HLB values due to the hydrophobic nature of diblock copolymers.

6.3.2 Stability of Emulsions

6.3.2.1 Visual Observations

The stability of the emulsions is observed visually, and images of emulsions are taken at four different times; 1 min, 2 hours, one day, two days and a week after emulsification performed. The thickness of the cream phase was measured for a week at specific times and ϕ_{cream} phase against time graph was plotted (see **Figure 6.4**). As it was observed in other diblock and triblock copolymer series, the stability of the emulsions decreases over time. As can be seen from the graph, the lowest ϕ_{cream} phase observed for P-H1 containing MMA as a hydrophobic block. The polymeric surfactants, P-H2, P-H3 and P-H4, show very similar values of ϕ_{cream} . BuMA was chosen as the hydrophobic unit in order to fabricate the polymers of varying architectures, as the stability of the emulsions formed by BuMA-based polymers is comparable to the ones of HeMA and LMA, and the BuMA-based polymers were easily recovered via simple precipitation.

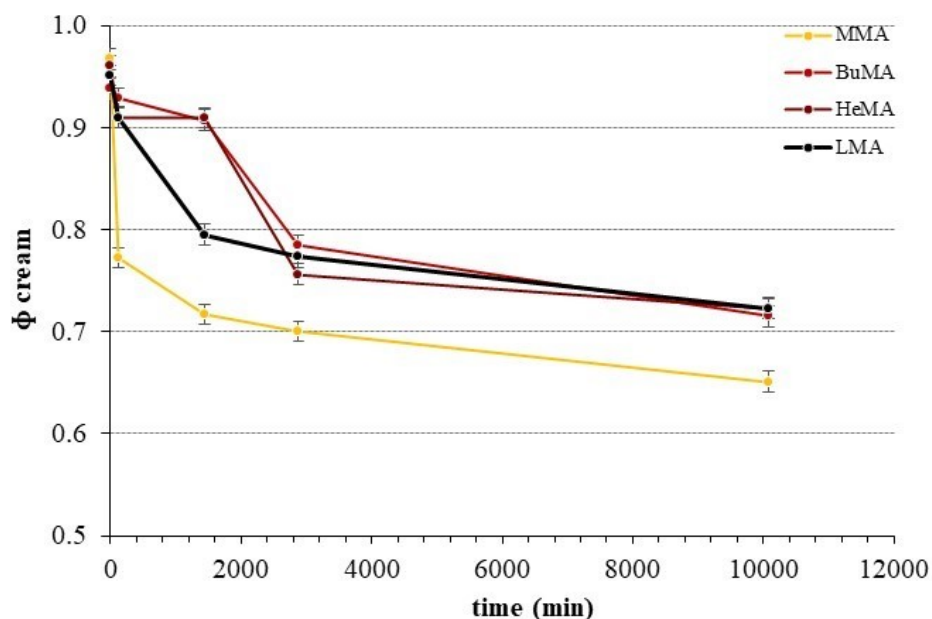


Figure 6.4. Graph shows the fraction of cream phase resolved for polymers with four different hydrophobic monomers over time.

6.4 Conclusions

In this section, four diblock copolymers based on DMAEMA and a hydrophobic monomer varying from MMA, BuMA, HeMA and LMA were synthesised and they were investigated with main focus on their emulsifying properties. It is concluded that:

- DMAEMA based diblock (P-H1-4) copolymers with different hydrophobic monomers such as MMA, BuMA, HeMA and LMA was successfully synthesised *via* GTP. The M_n values were varied between 5900 and 7010 g mol⁻¹ and they are satisfactorily close to their theoretical value. The MMDs were varied between 1.09 and 1.22, which is satisfactorily close to 1 and confirms successful “living” polymerisation.
- The cloud point and CMCs of DMAEMA based diblock copolymers (P-H1-4) could not be investigated due to their poor solubility in water. The effective pK_a values were varied between 6.4 and 7.0. The highest pK_a was observed for a diblock copolymer with MMA (least hydrophobic), and the lowest pK_a was observed for LMA (most hydrophobic).
- All diblock copolymers able to stabilise methyl laurate in water emulsions. All diblock copolymers able to form O/W type emulsions. Furthermore, HLB values were calculated, and they range between 7.6-8.2.
- The stability of emulsions observed for a week, and the ϕ_{cream} phase of emulsions were decreasing over time.

- The least stable emulsion was observed for a diblock copolymer, P-H1, containing MMA. The polymeric surfactants, P-H2, P-H3 and P-H4, show very similar values of ϕ_{cream} .

The second section of this chapter includes the synthesis of BuMA-based copolymers with complex architectures and their characterisation in organic and aqueous solutions. In addition to BuMA, DMAEMA was used as a hydrophilic, pH-responsive unit. The chemical structures of DMAEMA and BuMA are shown in **Figure 6.5**. This chapter includes seven different architectures of copolymers, and there are two families: **Family A** and **Family B**, where MM and architectures were constant between the two families and the only variable was composition. Specifically, in **Family A** and **B**, the hydrophilic component composition was 50 and 75wt%, respectively, while the MM of the copolymers was kept constant to 6000 g mol⁻¹.

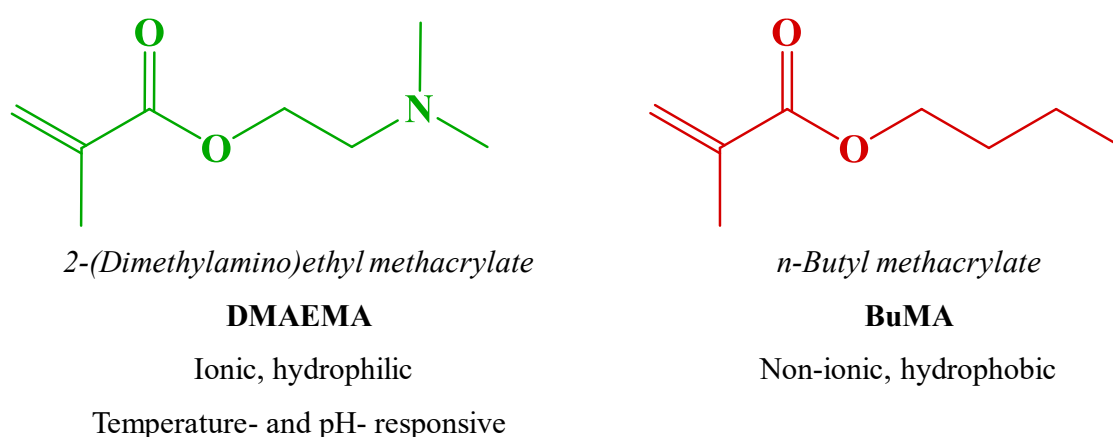


Figure 6.5. Names, abbreviations and chemical structures of monomers used in this study. The 2-(dimethylamino) ethyl methacrylate (DMAEMA) and *n*-butyl methacrylate (BuMA) are used as monomers for polymerisation.

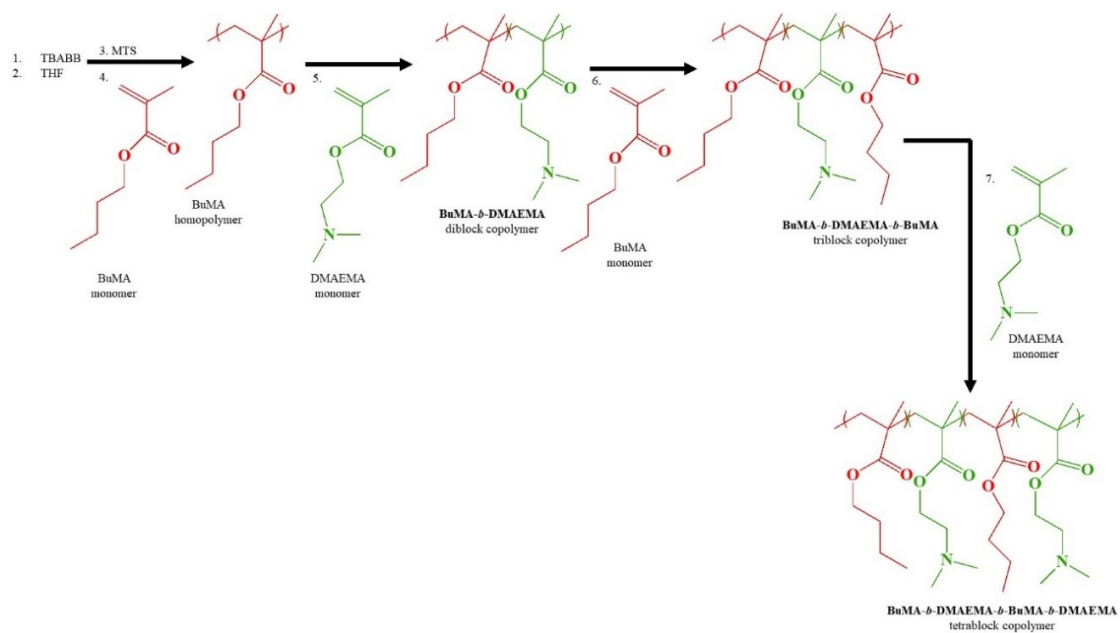
6.5 Synthesis of Copolymers with Complex Architectures

In this study, seven different architectures and two different compositions were successfully synthesised *via* one-pot GTP. The seven different architectures were: BA, BAB, ABA, BABA, B-*stat*-A, B-*b*-(B-*stat*-A)-*b*-A and B-*b*-(B-*grad*-A)-*b*-A, where B was the hydrophobic BuMA and A the hydrophilic DMAEMA block. The synthesis of tetrablock, triblock with a middle block as a statistical copolymer, and gradient copolymer are discussed and schematically illustrated in **Figure 6.6**. The synthesis of diblock and statistical copolymers were explained in Chapter 4. The tetrablock copolymer was synthesised by following **route A**, where catalyst (TBABB), polymerisation solvent (THF) and initiator (MTS) was added into the polymerisation flask, and it was followed by the addition of monomers sequentially. Compared

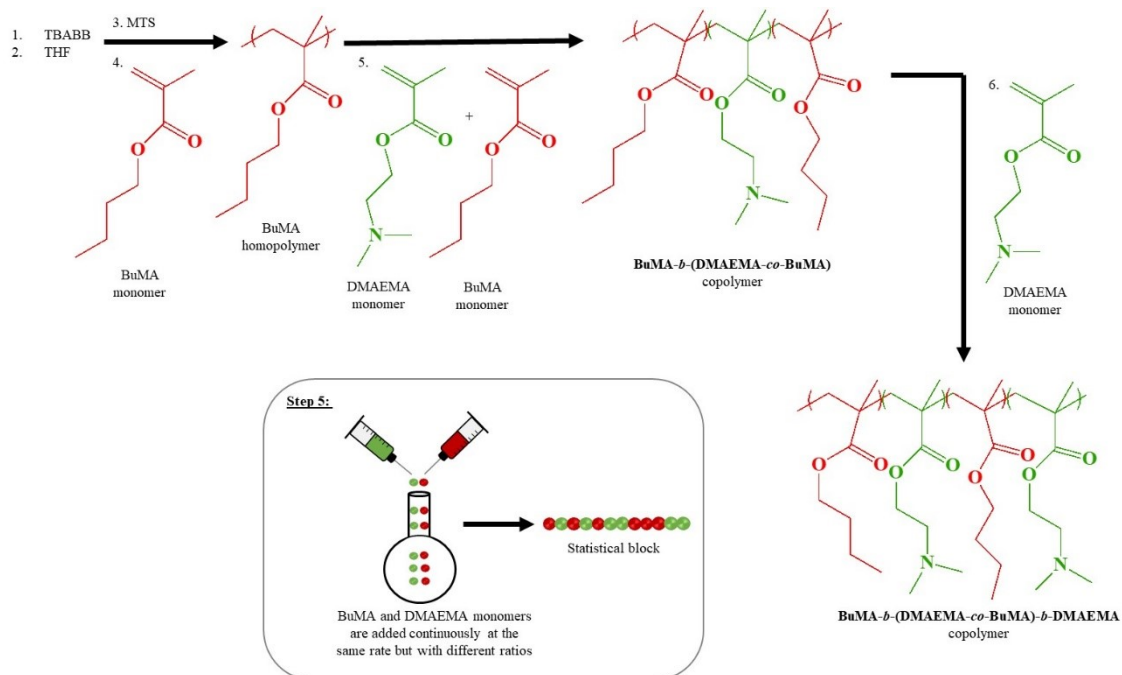
to triblock copolymers (see Chapter 5), the synthesis of tetrablock copolymer consists of one more step: the addition of the fourth monomer as a fourth block. The difference between **route A** and **B/C** is the synthesis of the middle statistical and gradient block.

The synthesis of triblock copolymer with a statistical block in the middle was synthesised following **route B**. **In route B**, the statistical middle block is synthesised by the simultaneous addition of different ratios of BuMA and DMAEMA but at the same rate and time. The triblock copolymer with gradient block in the middle was synthesised following **route C**. **In route C**, the middle gradient block was fabricated by the simultaneous addition of BuMA and DMAEMA at different rates and ratios. The synthesis of gradient copolymer in this way is the first study performed *via* the one-pot GTP method. Our group in the past has synthesised gradient copolymers by multiple monomer additions with a GTP method, however, high D value was observed.¹²

A) Synthesis of tetrablock copolymers:



B) Synthesis of triblock copolymer with a statistical middle block:



C) Synthesis of triblock copolymer with a gradient middle block:

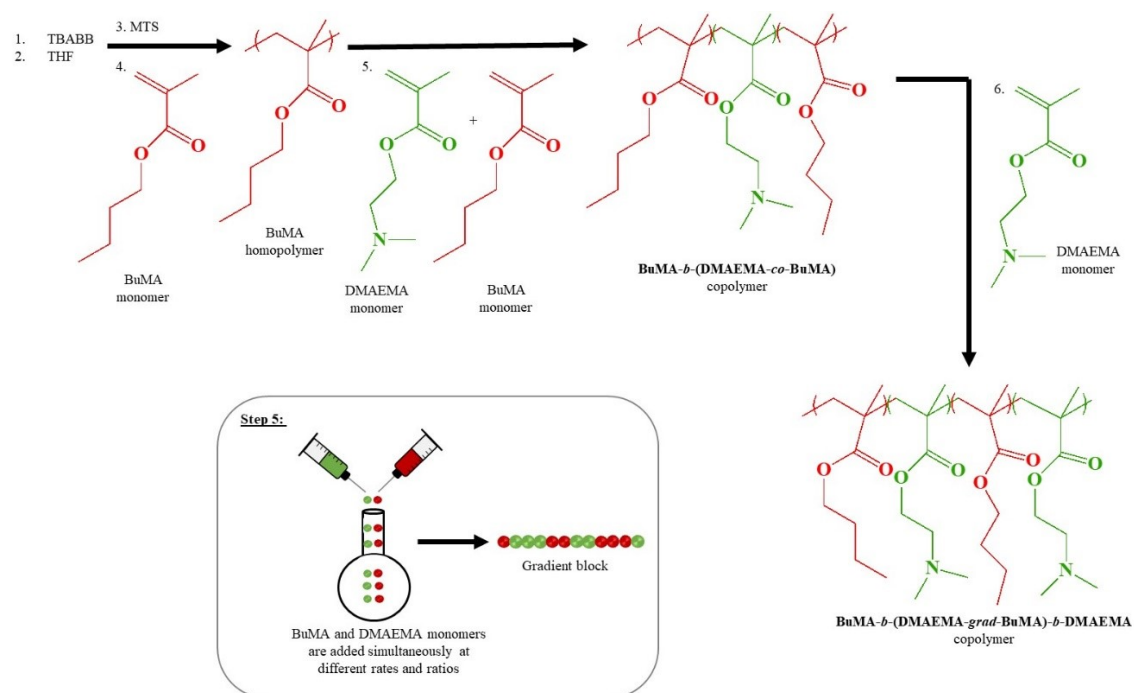


Figure 6.6. The schematic representation of synthetic routes of A) tetrablock copolymer, BuMA-*b*-DMAEMA-*b*-BuMA-*b*-DMAEMA, B) triblock copolymer with a statistical middle block, BuMA-*b*-(BuMA-*co*-DMAEMA)-*b*-DMAEMA, and C) triblock copolymer with a gradient middle block BuMA-*b*-(BuMA-*co*-DMAEMA)-*b*-DMAEMA.

In this study, fourteen copolymers with seven different architectures and two different compositions were successfully synthesised *via* one-pot GTP, and they are schematically represented in **Figure 6.7**. Family **A** consists of copolymers with a composition of 50-50 w/w% BuMA-DMAEMA, and **family B** consists of copolymers with a composition of 75-25 w/w% DMAEMA-BuMA. The DMAEMA and BuMA units are shown in green and red, respectively.

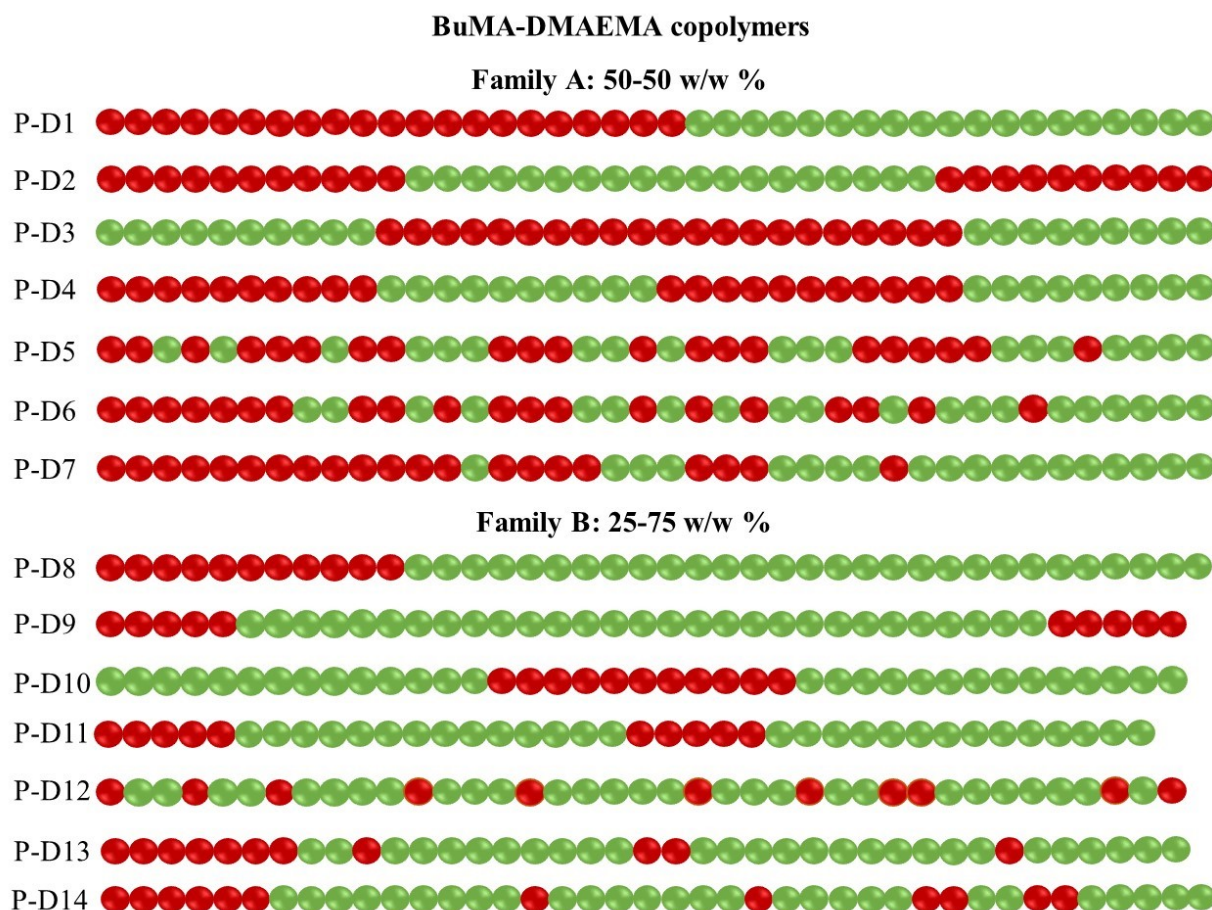


Figure 6.7. Schematic representation of all synthesised copolymers with different architectures. In **family A** and **family B** the copolymers have a 50 and 75 DMAEMA wt% composition. The red and green balls represent BuMA units and DMAEMA units, respectively.

6.6 Structural Properties

The structural properties such as MMs, experimental MMs and MMDs (dispersity indices, $\bar{D}$) of all fourteen copolymers and their homopolymers are summarised and discussed in the following section. The experimental and theoretical composition of all copolymers and their linear precursors are also summarised and discussed in the next section.

6.6.1 Molar Mass and Molar Mass Distribution

The theoretical MMs and experimental MMs of all copolymers and their linear precursors were determined using GPC. The successful polymerisation of copolymers was confirmed by the GPC chromatogram shown in **Figure 6.8** below. **Figure 6.8** shows the GPC traces of the BuMA₁₁-*b*-DMAEMA₁₀-*b*-BuMA₁₁-*b*-DMAEMA₁₀ (P-D4) shown in brown dotted line. The precursors BuMA₁₁, BuMA₁₁-*b*-DMAEMA₁₀ and BuMA₁₁-*b*-DMAEMA₁₀-*b*-BuMA₁₁ is represented by red, green and yellow dashed line, respectively. As can be seen from the GPC chromatogram, the peak shifts from right to the left, which indicates increase of MMs by addition of second, third and fourth monomers. There was absence of other peaks in GPC chromatogram, which means that polymerisation is free from 1) unsuccessful addition of second, third and fourth monomer, 2) unreacted monomer and 3) partial deactivation of the polymer chains, therefore there was complete consumption of monomer and 100% conversion of the monomers to the polymer. Similar GPC chromatograms were observed for other copolymers and they can be found in **Appendix**.

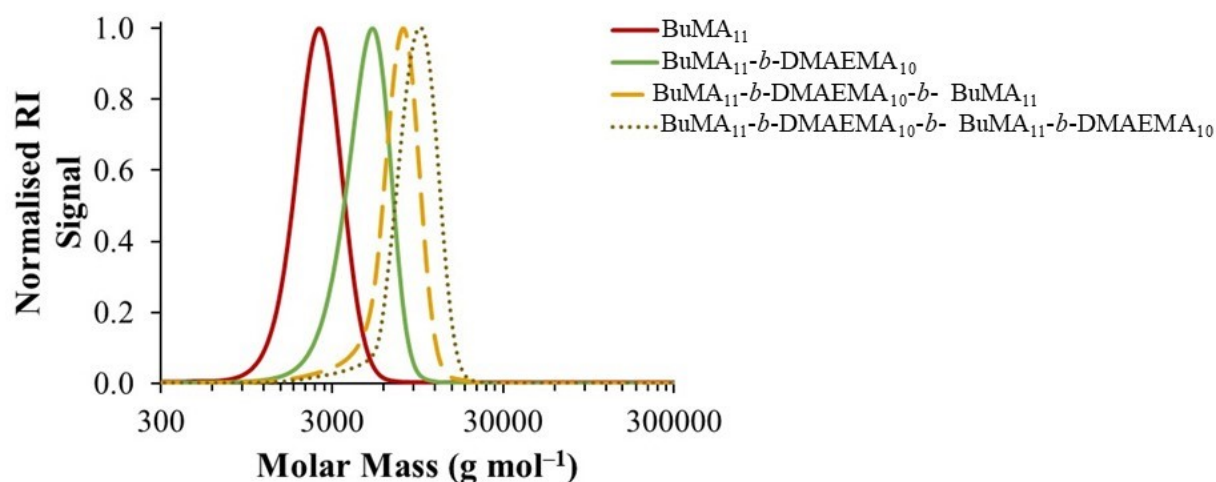


Figure 6.8. The GPC chromatogram of P-D4. The theoretical polymer structure is BuMA₁₁-*b*-DMAEMA₁₀-*b*-BuMA₁₁-*b*-DMAEMA₁₀. The homopolymer (BuMA₁₁), diblock (BuMA₁₁-*b*-DMAEMA₁₀), triblock (BuMA₁₁-*b*-DMAEMA₁₀-*b*-BuMA₁₁) and tetrablock (BuMA₁₀-*b*-DMAEMA₁₁-*b*-BuMA₁₀-DMAEMA₁₁) are represented by red, green, yellow and brown respectively.

The theoretical structure, theoretical and experimental MMs, MMDs (dispersity indices, $\bar{D}$), and composition of copolymers and their linear precursors were summarised and shown in **Table 6.3**. The experimental MM and MMDs of copolymers and their linear precursors were determined by GPC. The MMDs of copolymers were varying between 1.09 and 1.17 (close to 1) which confirms that successful sequential “living” polymerisation, similar to the previously reported GTP studies.^{11,13,14} As can be seen from **Table 6.3**, the $\bar{D}$ values of the copolymers decreased when the MM of the polymers increased. This is observed in previous studies with polymers synthesised by GTP and expected for living polymerisation techniques. When comparison was made between two families, **family A** has lower $\bar{D}$ values compared to **family B**. This can be attributed to the addition of higher amount of DMAEMA (**family B**), which leads to more exothermic reaction, hence higher $\bar{D}$ values. Another reason can be synthesis of polymers performed on different day which means that the humidity in the atmosphere was different. The highest $\bar{D}$ value was observed in P-D13 (BuMA₇-*b*-(DMAEMA₂₂-*co*-BuMA₄)-*b*-DMAEMA₆), it was expected because the monomers for the fabrication of the middle block were added on the same time and it was challenging to add them dropwise. So the flask overheated a bit during polymerisation that led to higher $\bar{D}$ values. Furthermore, the statistical copolymer (P-D12, BuMA₁₁-*co*-DMAEMA₂₉) has lower $\bar{D}$ values compared to other copolymers in **family B**, this was due to addition of all monomers to the polymerisation flask before addition of MTS and providing cooling system to the polymerisation flask with addition of water bath. Therefore, more controlled polymerisation performed which leads to lower $\bar{D}$ value. It should be noted that the $\bar{D}$ value for the gradient copolymers is quite low and significantly lower than previous studies on gradient polymers fabricated via GTP that have been reported in our group.

According to the results, the experimental MM values of final copolymers were varying between 7700 and 10,200 g mol⁻¹, which is close to or slightly higher than the targeted MMs. This was expected and also reported in previous chapters as well as previous studies.^{3,15–17} The first reason for higher experimental MMs is attributed to use of PMMA standard samples for calibration of GPC. The second reason is presence of protic impurities or humidity in the system, and this leads deactivation of the initiator molecules or active species hence higher experimental MMs obtained. This is common in GTP methods, and it was previously reported by other studies.^{6,18–21}

Table 6.3. The theoretical polymer structure, experimental molar mass (MM) (number average MM, M_n) and theoretical molar mass ($MM^{\text{theor.}}$), dispersity indices ($\bar{D}$) and composition of the copolymers and their homopolymers.

	No.	Theoretical Polymer Structure ^a	$MM^{\text{theor. b}}$ (g mol ⁻¹)	M_n^c (g mol ⁻¹)	$\bar{D}^d$	% w/w DMAEMA-BuMA	
						Theoretical	¹ H NMR
F A M I L Y A	P-D1	BuMA ₂₁	3100	3700	1.13	0-100	0-100
		BuMA ₂₁ - <i>b</i> -DMAEMA ₁₉	6100	8800	1.11	50-50	50-50
	P-D2	BuMA ₁₁	1600	2400	1.10	0-100	0-100
		BuMA ₁₁ - <i>b</i> -DMAEMA ₁₉	4600	6400	1.10	33-67	35-65
		BuMA ₁₁ - <i>b</i> -DMAEMA ₁₉ - <i>b</i> -BuMA ₁₁	6100	8900	1.06	50-50	50-50
	P-D3	DMAEMA ₁₀	1600	1910	1.15	100-0	100-0
		DMAEMA ₁₀ - <i>b</i> -BuMA ₂₁	4600	6400	1.10	33-67	32-68
		DMAEMA ₁₀ - <i>b</i> -BuMA ₂₁ - <i>b</i> -DMAEMA ₁₀	6100	8900	1.05	50-50	48-52
	P-D4	BuMA ₁₁	1600	2400	1.10	0-100	0-100
		BuMA ₁₁ - <i>b</i> -DMAEMA ₁₀	3100	4400	1.11	75-25	71-29
		BuMA ₁₁ - <i>b</i> -DMAEMA ₁₀ - <i>b</i> -BuMA ₁₁	4600	7000	1.10	67-33	68-32
		BuMA ₁₁ - <i>b</i> -DMAEMA ₁₀ - <i>b</i> -BuMA ₁₁ - <i>b</i> -DMAEMA ₁₀	6100	7700	1.09	50-50	50-50
	P-D5	BuMA ₂₁ - <i>co</i> -DMAEMA ₁₉	6100	9700	1.09	50-50	46-54
	P-D6	BuMA ₇	1100	1500	1.14	0-100	0-100
		BuMA ₇ - <i>b</i> -(BuMA ₁₃ - <i>co</i> -DMAEMA ₁₄)	5100	8100	1.06	60-40	60-40
		BuMA ₇ - <i>b</i> -(BuMA ₁₂ - <i>co</i> -DMAEMA ₁₄)- <i>b</i> -DMAEMA ₆	6100	9700	1.05	50-50	49-51
	P-D7	BuMA ₇	1100	1500	1.13	0-100	0-100
		BuMA ₇ - <i>b</i> -(BuMA ₁₄ - <i>grad</i> -DMAEMA ₁₃)	5100	7100	1.08	60-40	60-40
		BuMA ₇ - <i>b</i> -(BuMA ₁₃ - <i>grad</i> -DMAEMA ₁₃)- <i>b</i> -DMAEMA ₆	6100	8900	1.06	50-50	48-52

	No.	Theoretical Polymer Structure ^a	MM ^{theor. b} (g mol ⁻¹)	M _n ^c (g mol ⁻¹)	Đ ^d	% w/w DMAEMA-BuMA	
						Theoretical	¹ H NMR
F A M I L Y B	P-D8	BuMA ₁₁	1600	2200	1.13	100-0	100-0
		BuMA ₁₁ - <i>b</i> -DMAEMA ₂₉	6100	8110	1.12	75-25	74-26
	P-D9	BuMA ₅	850	1300	1.15	0-100	0-100
		BuMA ₅ - <i>b</i> -DMAEMA ₂₉	5350	8000	1.09	60-40	60-40
		BuMA ₅ - <i>b</i> -DMAEMA ₂₉ - <i>b</i> -BuMA ₅	6100	8200	1.11	75-25	73-27
	P-D10	DMAEMA ₁₄	2350	3500	1.13	100-0	100-0
		DMAEMA ₁₄ - <i>b</i> -BuMA ₁₁	3850	6000	1.12	60-40	60-40
		DMAEMA ₁₄ - <i>b</i> -BuMA ₁₁ - <i>b</i> -DMAEMA ₁₄	6100	9500	1.14	75-25	74-26
	P-D11	BuMA ₅	850	1200	1.17	0-100	0-100
		BuMA ₅ - <i>b</i> -DMAEMA ₁₄	3100	4300	1.15	25-75	23-77
		BuMA ₅ - <i>b</i> -DMAEMA ₁₄ - <i>b</i> -BuMA ₅	3850	5800	1.11	67-33	62-38
		BuMA ₅ - <i>b</i> -DMAEMA ₁₄ - <i>b</i> -BuMA ₅ - <i>b</i> -DMAEMA ₁₄	6100	8900	1.12	75-25	77-23
	P-D12	BuMA ₁₁ - <i>co</i> -DMAEMA ₂₉	6100	8500	1.10	75-25	72-28
	P-D13	BuMA ₇	1100	1600	1.15	0-100	0-100
		BuMA ₇ - <i>b</i> -(DMAEMA ₂₂ - <i>co</i> -BuMA ₄)	5100	7700	1.19	80-20	71-29
		BuMA ₇ - <i>b</i> -(DMAEMA ₂₂ - <i>co</i> -BuMA ₄)- <i>b</i> -DMAEMA ₆	6100	9400	1.17	75-25	74-26
	P-D14	BuMA ₆	900	960	1.13	0-100	0-100
		BuMA ₆ - <i>b</i> -(BuMA ₅ - <i>grad</i> -DMAEMA ₂₄)	4500	9300	1.10	67-33	68-32
		BuMA ₆ - <i>b</i> -(BuMA ₅ - <i>grad</i> -DMAEMA ₂₄)- <i>b</i> -DMAEMA ₅	6100	10200	1.10	75-25	75-25

^a DMAEMA and BuMA are abbreviations of 2-(dimethylamino) ethyl methacrylate and *n*-butyl methacrylate. ^b The theoretical MM (MM^{theor.}) was calculated using the equation: MM^{theo.} (g/mol) = (Σ_i MM_i x DP_i) + 100. ^c and ^d The number average molar mass (M_n) as well as dispersity index (Đ) were determined using Gel Permeation Chromatography (GPC). The experimental composition of diblock copolymers and their linear precursors were determined using ¹H NMR. The GPC was calibrated using six poly (methyl methacrylate) (PMMA) standard samples; 2000,4000,8000, 20 000 and 50 000 g/mol.

6.6.2 Polymer Composition

The experimental compositions of the final copolymers and their linear precursors were determined using ^1H NMR spectroscopy and they are summarised in **Table 6.3**. As can be seen from results, there is a good agreement between the experimental and theoretical weight percentages, that confirms the successful synthesis of polymers. The weight percentages of the final copolymers and their linear precursors were determined by taking the integral of the distinctive peaks that belongs to representative unit of the copolymer. As an example, the ^1H NMR spectrum of P-D4 with theoretical polymer structure $\text{BuMA}_{11}\text{-}b\text{-DMAEMA}_{10}$ is shown in **Figure 6.9**. The homopolymer BuMA_{11} is shown in red (a), the diblock $\text{BuMA}_{11}\text{-}b\text{-DMAEMA}_{10}$ shown in green (b), the triblock $\text{BuMA}_{11}\text{-}b\text{-DMAEMA}_{10}\text{-}b\text{-BuMA}_{11}$ shown in yellow (c) and tetrablock copolymer $\text{BuMA}_{11}\text{-}b\text{-DMAEMA}_{10}\text{-}b\text{-BuMA}_{11}\text{-}b\text{-DMAEMA}_{10}$ is shown in brown (d). The composition of the DMAEMA was calculated by taking the integral of the distinctive peak which is the one that appears at 2.25 ppm that belongs to six methyl protons ‘i’ which is next to the amine group. The composition of the BuMA was determined by taking the integral of the distinctive peak which is the one that appears at 3.9 ppm that belongs to two methylene protons ‘c’ that is closest to the ester.

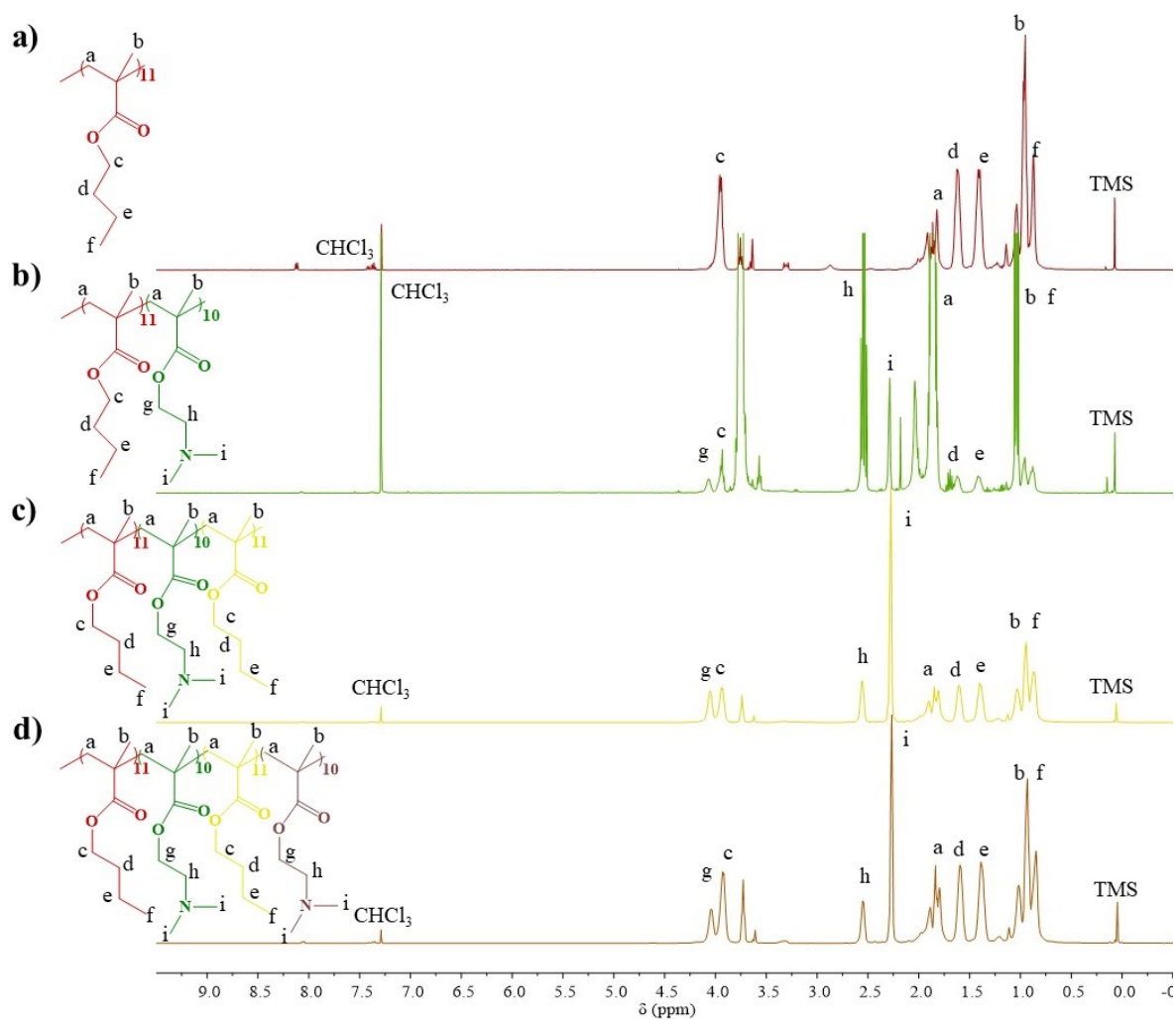


Figure 6.9. The ^1H NMR spectra of (a) BuMA homopolymer (BuMA₁₁) shown in red and (b) diblock copolymer, BuMA₁₁-*b*-DMAEMA₁₀ shown in green, (c) triblock copolymer, BuMA₁₁-*b*-DMAEMA₁₀-*b*-BuMA₁₁ shown in yellow and (d) tetrablock copolymer, BuMA₁₁-*b*-DMAEMA₁₀-*b*-BuMA₁₁-*b*-DMAEMA₁₀ shown in brown.

6.7 Aqueous Solution Properties

6.7.1 Cloud Points

The cloud points of 1 w/w % of aqueous copolymer solutions were determined by visual tests, and they are summarised in **Table 6.4**. In this chapter, thermoresponsive ability of the copolymer is attributed from the DMAEMA units only. Due to increase in the temperature the colourless solution turns into cloudy solution due to the precipitation of the copolymer. The factors that affects the cloud point of the polymer solutions are ionic strength, pH of the solution, MMs, composition and architecture of the polymer.^{13,15,5,22–24} In this chapter, the architecture and the composition of the copolymers two design factors; therefore, their effects on cloud points were observed. Regarding **family A**, the cloud points of copolymers at their initial pH were not able to be determined because they were not soluble in water. The DMAEMA units were protonated by 10% to enhance the solubility however, the polymer solutions did not show any cloud points within the temperature range tested (25-80 °C). The reason for this is, when pH of the solution decreases, the amino groups of the DMAEMA units are positively charged, which means that the hydrophilicity of the structure increases. For the **Family B**, the cloud points of copolymers were determined at their initial pH (8.7-9.1) and listed in **Table 6.4**. As can be seen from **Table 6.4**, cloud point was not determined for P-D9 and P-D12 because they were insoluble at their initial pH. When comparison was made between copolymers, it was observed that P-D8, BA has the highest cloud point. When comparison was made between two triblock copolymers, P-D10, ABA and P-D13, B-*b*-(B-*stat*-A)-*b*-A shows cloud points at 35 °C and 29 °C, respectively. As can be seen from results, the composition and MM of both copolymers are similar within the experimental error therefore the only parameter that affect the cloud point is architecture. The effect of architecture on cloud points were also observed by previous studies.^{13,14} The lower cloud point was observed for P-D13 because the in middle block DMAEMA units are randomly copolymerised between the BuMA units, therefore it stabilises itself lesser extent compared to P-D10, ABA. In addition to this, the size of the micelle of P-D13, B-*b*-(B-*stat*-A)-*b*-A is bigger (see **Table 6.4**) and it forms bigger aggregates, hence the aggregation is easier compared to P-D10, hence this results in lower cloud point. It is worth noting that, P-D10, ABA and P-D11, BABA shows similar clouds points at 35 °C and 36 °C, respectively even though they have different architecture. One of the reasons for showing similar cloud points is both copolymers form spherical micelles with similar size of micelle (see **Table 6.4**). The composition and MM for both polymer varies, therefore not only architecture plays role on cloud point values.

6.7.2 Effective pK_a

The effective pK_a values of DMAEMA units were determined and listed in **Table 6.4**. In **family A**, the pK_a values of copolymers were varied between 6.1 and 6.8. In **family A**, the lowest pK_a value was observed for a statistical copolymer, (P-D5) which is expected and observed in previous studies.¹⁴ The reason for lowest pK_a value is, due to its architecture, it cannot form a micelle hence it cannot stabilise itself in solvent which results in low solubility. In addition to this, DMAEMA units are randomly distributed around the hydrophobic BuMA units which results in steric hinderance hence it is harder to protonate the DMAEMA units results in lower pK_a value. As shown in **Figure 6.10**, there is no obvious difference between the pK_a values of the copolymers, which means that different polymer architectures do not affect the value of the pK_a . In previous studies, they studied the effect of architecture on polymeric networks, linear as well as star copolymers and it was observed that the architecture of the copolymer has no effect on pK_a value.⁵ The highest pK_a value was observed for diblock copolymer P-D1 and it was expected because it forms spherical micelles where DMAEMA units are more exposed to water therefore protonation is easier hence higher pK_a value. Polymers, P-D2 and P-D4 have lower pK_a value compared to P-D1, because they form flower-like micelles, where DMAEMA units are hindered between the hydrophobic BuMA units which prevents DMAEMA units to protonate, hence results in weaker base and lower pK_a value.

In **family B**, the pK_a values of all synthesised copolymers were found to be between 6.6 and 7.0 (see **Table 6.4**). There is a good agreement between previously reported studies with polymers containing DMAEMA units.^{14,24} As it was expected, **family B** has higher pK_a values compared to **family A**. This trend was expected because pK_a is strongly affected by hydrophobicity of the copolymers and it is also observed in previous chapters in this thesis as well as other studies.^{13,14} Therefore, due to the higher hydrophobic BuMA content of **family A**, the lower the pK_a value. This is explained by increase in the hydrophobicity results in decrease in the dielectric constant, which makes ionisation of DMAEMA units more difficult, hence lowering the pK_a value.^{17,5} In **family B**, it was observed that the P-D8 is the strongest base with higher pK_a value compared to other copolymers. This was expected because P-D8 is diblock copolymer and it forms core-corona micelles, where DMAEMA units are forming the corona of the micelle and DMAEMA units are exposed to water, therefore easy to protonate the DMAEMA units. Polymer, P-D9 forms flower-like micelles and compared to other copolymers (P-D8, P-D10 and P-D11), DMAEMA units are more sterically hindered and it is more harder to protonate DMAEMA units, therefore lower pH is needed hence lower pK_a value

compared to other copolymers. As can be seen from **Table 6.4** and **Figure 6.10**, the architecture does not play role in pK_a value.

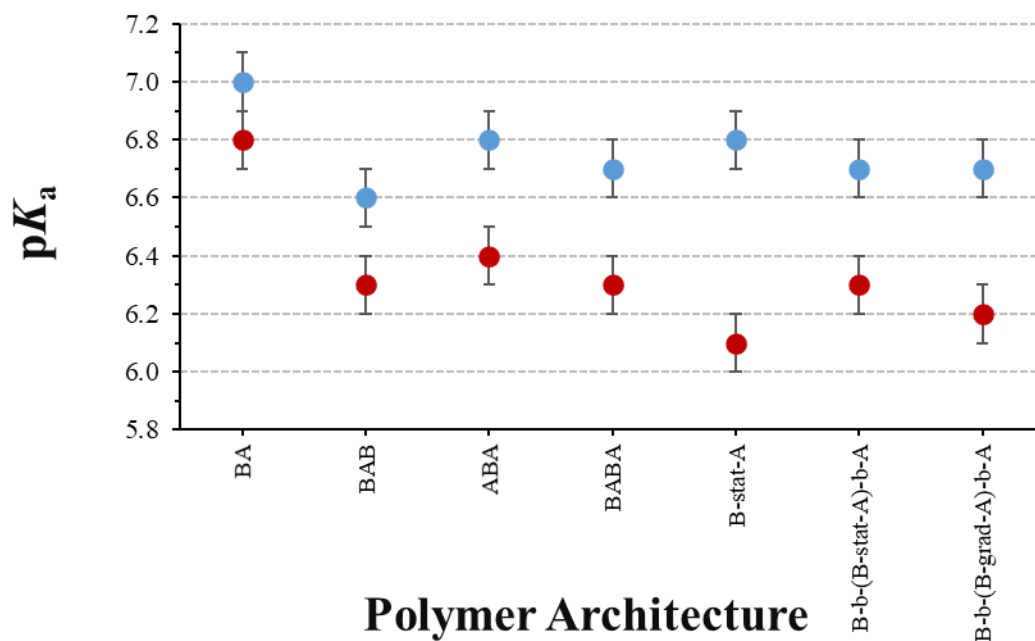


Figure 6.10. The effect of architecture of BuMA-DMAEMA based copolymers on the effective pK_a value. The targeted composition of **family A** (50-50 w/w %) and **family B** (25-75 w/w %) is represented in red and blue circles, respectively. Please note B-*stat*-A denotes that the two monomers are statistically distributed within the polymer chain. B and A represents, BuMA and DMAEMA, respectively.

Table 6.4. The polymer architecture, theoretical polymer architecture, theoretical and experimental hydrodynamic diameters (d_h s), polydispersity indices (PDI), cloud points, effective pK_a and critical micelle concentration (CMC) of aqueous copolymer solutions.

No.	Polymer Architecture ^a	Theoretical Polymer Structure	Hydrodynamic diameter (<i>d_h</i> , nm)								PDI			Cloud Points ±2 °C	p <i>K_a</i> s ± 0.1	HLB ^j	CMC ^k x10 ⁵ mol L ⁻¹
			Theo ^b	Exp ± 0.5 ^h						pH ⁱ	pH 5	pH 7	pH ⁱ				
				pH 5			pH 7										
				1 st	2 nd	3 rd	1 st	2 nd	3 rd								
	FAMILY A																
P-D1	BA	B ₂₁ - <i>b</i> -D ₁₉	24.3 ^c	-	10.1	-	-	32.7	-	NS	0.357	0.678	NS	NS	6.8	10	NS
P-D2	BAB	B ₁₁ - <i>b</i> -D ₁₉ - <i>b</i> -B ₁₁	16.0 ^d	-	-	255			91.3	NS	0.302	0.293	NS	NS	6.3	10	NS
P-D3	ABA	D ₁₀ - <i>b</i> -B ₂₁ - <i>b</i> -D ₁₀	20.3 ^c	-	10.1	255	-	-	164	NS	0.363	0.847	NS	NS	6.4	9.6	NS
P-D4	BABA	B ₁₁ - <i>b</i> -D ₁₀ - <i>b</i> -B ₁₁ - <i>b</i> -D ₁₀	16.3 ^d	-	11.7	-	-	-	190	NS	0.390	0.476	NS	NS	6.3	10	NS
P-D5	B- <i>stat</i> -A	B ₂₁ - <i>co</i> -D ₁₉	3.0 ^e	-	10.1	142	NS	NS	NS	NS	1.000	NS	NS	NS	6.1	9.2	NS
P-D6	B- <i>b</i> -(B- <i>stat</i> -A)- <i>b</i> -A	B ₇ - <i>b</i> -(B ₁₂ - <i>co</i> -D ₁₄)- <i>b</i> -D ₆	18.9 ^f 30.1 ^g	-	11.7	-	-	28.2	190	NS	0.330	0.328	NS	NS	6.3	9.8	NS
P-D7	B- <i>b</i> -(B- <i>grad</i> -A)- <i>b</i> -A	B ₇ - <i>b</i> -(B ₁₃ - <i>grad</i> -D ₁₃)- <i>b</i> -D ₆	17.9 ^f 20.4 ^g	-	15.7	-	-	-	164	NS	0.232	0.234	NS	NS	6.2	9.6	NS
	FAMILY B																
P-D8	BA	B ₁₁ - <i>b</i> -D ₂₉	27.3 ^c	-	28.2	-	-	18.2	-	21	0.140	0.205	0.040	41	7.0	14.8	6.2
P-D9	BAB	B ₅ - <i>b</i> -D ₂₉ - <i>b</i> -B ₅	15.7 ^d	-	24.4	-	-	10.1	220	NS	0.313	0.394	NS	NS	6.6	14.6	NS
P-D10	ABA	D ₁₄ - <i>b</i> -B ₁₁ - <i>b</i> -D ₁₄	28.5 ^c	-	18.2	-	-	13.5	-	13.5	0.201	0.327	0.038	35	6.8	14.8	10.5
P-D11	BABA	B ₅ - <i>b</i> -D ₁₄ - <i>b</i> -B ₅ - <i>b</i> -D ₁₄	15.5 ^d	-	18.2	220	1.12	11.7	255	11.7	1.000	0.420	0.069	36	6.7	15.4	11.2
P-D12	B- <i>stat</i> -A	B ₁₁ - <i>co</i> -D ₂₉	2.9 ^e	1.1	-	164	NS	NS	NS	NS	0.565	NS	NS	NS	6.8	14.4	NS
P-D13	B- <i>b</i> -(B- <i>stat</i> -A)- <i>b</i> -A	B ₇ - <i>b</i> -(B ₄ - <i>co</i> -D ₂₂)- <i>b</i> -D ₆	18.9 ^f 30.1 ^g	-	28.2	342	1.5	15.7	295	18.2	0.716	0.405	0.090	29	6.7	14.8	10.6
P-D14	B- <i>b</i> -(B- <i>grad</i> -A)- <i>b</i> -A	B ₆ - <i>b</i> -(B ₅ - <i>grad</i> -D ₂₄)- <i>b</i> -D ₅	17.9 ^f 20.4 ^g	1.1	21	255	1.29	11.7	190	NS	1.000	0.508	NS	27	6.7	15	NS

^a The architecture of the polymers, B represents the *n*-butyl methacrylate, BuMA (B) and A represents 2-dimethyl(aminoethyl) methacrylate, DMAEMA (D). B-*stat*-A denotes that the monomers are randomly distributed in this segment of the polymer chain. ^b The theoretical hydrodynamic diameter values are based on experimental degree of polymerisations (DPs) of BuMA (B) and DMAEMA (D) units. The DP was calculated by using the MM after the precipitation which is obtained using GPC and experimental composition was determined using ¹H NMR. ^c The BA and

ABA (P-D1, P-D10, P-D8 and P-D10) architectures forms core-shell spherical micelles and the equation used to calculate experimental hydrodynamic diameter is $d_h = (DP_{BuMA} + 2 \times DP_{DMAEMA}) \times 0.254 \text{ nm}$.^d The BAB and BABA (P-D2, P-D4, P-D9 and P-D11) architectures forms flower-like micelles and the equation used to calculate experimental hydrodynamic diameter is $d_h = (DP_{DMAEMA} + DP_{BuMA}) \times 0.254 \text{ nm}$.^e The B-*stat*-A statistical copolymer (P-D5 and P-D12) assumed to adopt random coil configuration and the equation used to calculate hydrodynamic diameter is $d_h = 2 \times [2.20 \times 2 \times (DP_{DMAEMA} + DP_{BuMA})/3]^{1/2}$. The B-*b*-(B-*stat*-A)-*b*-A and B-*b*-(B-*grad*-A)-*b*-A (P-D6, P-D7, P-D13 and P-D14) architectures assumed to form core-shell spherical micelle and two different equation is used to calculate the hydrodynamic diameter.^f If the gradient and random part of triblock copolymers B-*b*-(B-*stat*-A)-*b*-A and B-*b*-(B-*grad*-A)-*b*-A assumed to be hydrophobic; $d_h = [DP_{BuMA \text{ (block)}} + 2 \times (DP_{\text{statistical/gradient}} + DP_{DMAEMA \text{ (block)}})] \times 0.254 \text{ nm}$.^g If the triblock copolymers assumed to be hydrophilic; $d_h = [DP_{BuMA \text{ (block)}} + 2 \times DP_{DMAEMA \text{ (block)}} + DP_{\text{stat/grad}}] \times 0.254 \text{ nm}$.^h The experimental hydrodynamic diameter of aqueous polymer solutions were determined using DLS.^j The hydrophile-lipophile balance of copolymers were determined using the Griffin equation (see Experimental **Equation 3.11**).^k The CMC stands for critical micelle concentration of polymer.^l NS stands for an insoluble polymer; therefore, the experiment cannot be performed.

6.7.3 Hydrodynamic Diameter

The experimental hydrodynamic diameter, d_h , and PDI values of 1 w/w% aqueous polymer solutions were determined using DLS compared with theoretical (calculated) hydrodynamic diameter values. It is summarised in **Table 6.4**. In DLS measurements, the maximum of the peak by intensity was recorded as an experimental hydrodynamic diameter. As shown in **Table 6.4**, some polymers consist of three peaks, such as 1st, 2nd and 3rd peak, corresponding to unimers, micelles and aggregates. The number given in bold represents the peak with the highest intensity. The d_h values of copolymers were determined at three different aqueous solutions; i) initial pH (8.7-9.1), which is alkaline, ii) pH 7, and iii) acidic pH 5. Please note that in **family A** and **B**, the MM and composition kept constant and only the architecture of the copolymers varied. On the other hand, the composition of BuMA-DMAEMA units of **family A** and **B** is 50-50 w/w% and 75-25 w/w%, respectively.

The theoretical hydrodynamic diameter of copolymers was calculated by assuming that; i) all polymer chains are fully stretched, ii) the hydrophobic BuMA unit are forming the core and hydrophilic DMAEMA units forming the shell of the micelle iii) the hydrophobic BuMA units fully overlap, iv) methacrylate backbone is fully extended, v) the projected length of the methacrylate backbone is 0.254 nm and vi) polymer chains assemble to the structures shown in **Figure 6.11**. As can be seen from **Figure 6.11**, it is assumed that the diblock copolymers (P-D1 and P-D8) form core-shell spherical micelle; the hydrophobic BuMA units (shown in red spheres) forming the core of the micelle and the hydrophilic DMAEMA units (shown in green spheres) forming the shell of the micelle. In addition to this, triblock copolymers with ABA (P-D3 and P-D10) architectures where the hydrophobic block (BuMA) is in the middle block assumed to form spherical core-shell micelles. On the other hand, triblock copolymers with BAB architecture (P-D2 and P-D9), where the middle block is the hydrophilic DMAEMA assumed to form flower-like micelles. As can be seen from **Figure 6.11**, hydrophobic block BuMA is the core of the micelle and hydrophilic DMAEMA units are making a loop therefore each polymer chains forming the “petal” of the flower.²⁵ Furthermore, the flower-like micelles are assumed to form in polymers (P-D4, P-D11) with architectures of BABA. Triblock copolymers with a middle block are: statistical copolymer (P-D6) and gradient (P-D7) assumed to form a spherical core-shell micelle. However, when theoretical calculations made, it was assumed that polymers could self-assemble into two possible structures depending on whether gradient and statistical segment assumed to be hydrophilic or hydrophobic. If the gradient segment (P-D7) and statistical segment (P-D6) of the triblock copolymer were assumed to be

hydrophobic: it is assumed to form the structure shown in **a) Figure 6.11**, whereas if it is assumed to be hydrophilic, it is assumed to form the structure shown in **b) Figure 6.11**.

As shown in **Table 6.4**, the experimental hydrodynamic diameter of polymers in **Family A** (50-50 w/w% BuMA-DMAEMA) could not be investigated because they are insoluble in their initial pH. The protonation of DMAEMA units enhanced the solubility of polymers and their self-assembly behaviour observed at pH 7. According to the results, polymers P-D2, P-D3, P-D4, P-D6 and P-D7 forms large aggregates at pH 7 because they are still hydrophobic, and hydrophobicity enhances the aggregation.¹⁴ Therefore, to improve the solubility of polymers, the pH was adjusted to 5. At pH 5, the experimental hydrodynamic diameter of polymers, P-D1, P-D3, P-D4, P-D6 and P-D7 are varied between 10.1-15.7 nm, which shows that they assemble to form micelles. However, copolymers P-D2 and P-D5 forms aggregates, which is expected due to the architecture enhance the hydrophobicity, thus aggregation.

As shown in **Table 6.4**, both experimental and theoretical hydrodynamic diameter values are affected by the architecture of the copolymers. When comparing theoretical and experimental hydrodynamic diameter, it was observed that theoretical hydrodynamic diameter has higher values. This was expected and observed in previously reported studies.^{5,14,15,26} The reason for this is that the theoretical model assumes that the polymer chains are fully stretched, however, in real-time experiments, they are in the collapsed state or a coil. On the other hand, the experimental hydrodynamic diameter values are higher for some polymers than the theoretical ones. The reason is; i) the hydrophobic core overlap to a lesser extent, ii) the presence of positive charge on DMAEMA units leads to electrostatic repulsion, which results in a bigger size of micelle.

As shown in **Table 6.4**, all copolymers (P-D8, P-D10, P-D11 and P-D13) at their initial pH form a micelle, and the hydrodynamic diameter values vary between 11.7 and 21 nm. The MM and composition of copolymers were kept the same, so the only variable was architecture, and it was observed that the size of the micelle is strongly affected by architecture which is also observed in Family A.⁴ When comparison made between these three (P-D8, P-D10 and P-D11) and the diblock copolymer, P-D8 (AB) has higher d_h values. The reason for this is, in diblock copolymer (P-D8), the BuMA chains overlaps to a lesser extent, whereas in P-D10 and P-D11, BuMA chains overlap in bigger extent.

The experimental hydrodynamic diameter is also affected by the pH of the solution. When comparison made between initial pH and pH 7, the copolymers, P-D8 and P-D13 has lower experimental d_h at pH 7. The reason is protonation of DMAEMA units leads to more hydrophilic structure of copolymer whereas hydrophobicity enhances the aggregation. On the other hand, when pH of the solution changed from pH 7 to pH 5, the experimental hydrodynamic diameter values increased. This was expected because more DMAEMA units are protonated at pH 5, which means there is more electrostatic repulsion between positively charged units, thus bigger micelle size.

Consequently, **family B** contains smaller micelle sizes compared to **family A**. This is because **family A** contains more hydrophobic polymers, which enhances the hydrophobic interaction, hence aggregation, which is also observed in previous chapters. It is also observed that the pH plays an important role in the size of the micelles. At pH 5, the size of the micelles is bigger than the pH 7. Most importantly, it was observed that architecture affects the size of the micelles.

The PDI values of **family B** are varied between 0.038 and 0.090. at the initial pH values. Low PDI values and the presence of only one peak indicates that the sample is monodisperse. On the other hand, the PDI values of **family A** and **B** at pH 5 and 7 are higher for some polymers due to unimers, micelles, and large aggregates.

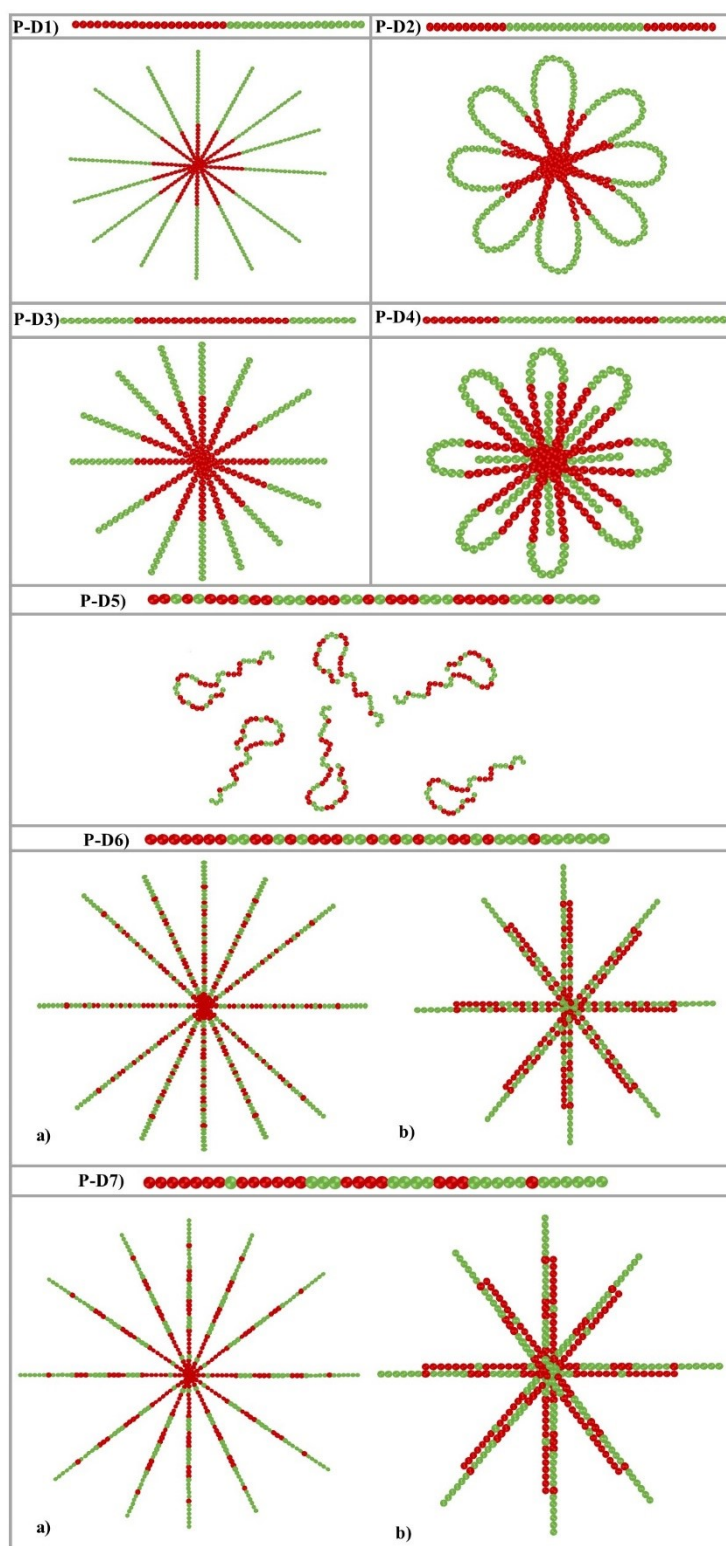


Figure 6.11. Schematic representation of the spherical (P-D1, P-D3, P-D6 and P-D7) flower-like micelles (P-D4 and P-D11) and random coil configuration (P-D5) formed by the different architecture of block copolymers of **family A**. The BuMA and DMAEMA units are represented by red and green, respectively.

6.7.4 Critical Micelle Concentration

The CMC of DMAEMA-BuMA based copolymers in DI water was determined using DLS. The copolymers from **Family A** have poor solubility in water. Therefore, their CMC values could not be investigated. In addition to this, from **Family B**, the CMC values of copolymers with P-D9, P-D12 and P-D14 could not be determined due to their poor solubility in water. On the other hand, the CMC values of copolymers; P-D8, P-D10, P-D11 and P-D13 were determined and listed on **Table 6.4**. The CMC of copolymers are varied between $6.2\text{--}11.2 \times 10^{-5} \text{ mol L}^{-1}$.

6.8 Complex Architectures of Copolymers as Polymeric Emulsifiers

The complex architectures of DMAEMA-BuMA based copolymers from **Family A** and **Family B** used to form emulsions, and they were evaluated as polymeric surfactants to stabilise methyl laurate/water emulsions. A 1 w/w% of polymeric surfactants were solubilised in methyl laurate, and water was added, followed by sonication for 1 minute. The ratio of water to methyl laurate phase was 1:1.

6.8.1 Type of Emulsions

The type of emulsions formed by polymeric surfactants was determined by performing drop tests experiments and theoretically determined by calculating the HLB value using **Equation 3.11** in the experimental section. The HLB values of polymeric surfactants are summarised in **Table 6.4**. As seen from the results, the HLB values of polymeric surfactants vary between 9.2-15. The HLB values higher than ~6 means that the polymeric surfactant is water-soluble; therefore, it stabilises the O/W emulsions.³ Thus, all synthesised polymeric surfactants should stabilise the O/W emulsions. The type of emulsion was also confirmed by performing drop tests experiments. Freshly prepared emulsion drops were added to the water phase, and they are uniformly distributed in the water phase. On the other hand, the addition of emulsion drops in methyl laurate leads to coagulation of drops spherical drops in the methyl laurate. Therefore, all synthesised polymeric surfactants form O/W type emulsions.

6.8.2 Stability of Emulsions

As mentioned in the introduction section, emulsion consists of two immiscible liquids, and one phase is dispersed as droplets in the other liquid phase. By their nature, they are unstable

systems, and by time, phase separation of two phases will occur. In this study, the stability of emulsions was observed by both visual and microscopy observations.

6.8.2.1 Visual Observation

The stability of the emulsions is observed visually, and images of emulsions are taken at eight different times. Specifically, at 1 min, 2 hours, 4 hours, one day, two days, five days, one week, two weeks, three weeks and a month after the emulsion was fabricated. The images of O/W emulsions stabilised by polymeric surfactants from **family A** and **family B** are shown in **Figure 21** and **23** in Appendix, respectively. As shown, all polymeric surfactants were able to emulsify water and methyl laurate phases and form opaque emulsions. Due to the nature of the emulsions, over time, the creaming occurred, and the emulsion phase (cream layer) appeared at the top of the vial, and the aqueous phase appeared at the bottom of the vial due to having a higher density than the methyl laurate. The depth of the emulsion phase or cream layer is dependent on the weight fraction of the methyl laurate. As expected, and observed in previous chapters, over time, the thickness of the cream phase started to decrease, and the thickness of the aqueous phase increases for both **family A** and **family B**. The ϕ_{cream} phase of Family A and B emulsions were determined at eight different times, and a graph, ϕ_{cream} versus time, was plotted. As shown in **Figures 22** and **24** in Appendix for all copolymers, the ϕ_{cream} phase decreases over time. Please note that the higher the ϕ_{cream} phase means, the more stable the emulsion is.

When comparing emulsions, **family A** has a cloudy aqueous phase, whereas **family B** has a colourless aqueous phase that appeared at the bottom of the vial. The reason is the more hydrophilic nature of the polymeric surfactants in **family B**.

As discussed in Chapter 4 and 5, the nature of the hydrophilic unit and weight percentage of both hydrophilic and hydrophobic unit is vital in determining the stability of emulsions. In this chapter, the effect of composition on the stability of the emulsions was also observed. **Figure 6.12** shows the ϕ_{cream} stabilised by the different architecture of polymeric surfactants. **Family A** (50-50 w/w%, DMAEMA-BuMA) and **family B** (75-25 w/w%, DMAEMA-BuMA) are represented in red and blue squares, respectively. As shown on the graph, polymeric surfactants belonging to **family B** have higher ϕ_{cream} for all architectures than **family A**.

The effect of architecture on the ϕ_{cream} phase was observed for a month and shown in **Figure 6.12**. As shown, both compositions show similar architecture trends on the emulsion stability except for statistical, gradient copolymers and triblock containing statistical middle block. For

family A, the lowest ϕ_{cream} phase was observed for gradient copolymer (P-D7), whereas for **family B**, the statistical copolymer (P-D5) has the lowest ϕ_{cream} phase. When comparing the architectures, BA, BAB and ABA, the most stable one is observed to be ABA (DMAEMA-*b*-BuMA-*b*-DMAEMA). Similar results were observed for Patrickios and co-workers.¹⁷ They studied the emulsifying abilities of triblock copolymers. They found out that the hydrophobic units forming the middle block have better emulsifying capabilities than the first or last block. This study observed that the least stable emulsion is created for both compositions when diblock copolymer (BuMA-*b*-DMAEMA) was used as polymeric surfactants.

The architecture effect is more dominant in polymeric surfactants with higher hydrophobicity. For instance, for hydrophobic polymeric surfactants (**family A**), the ϕ_{cream} phase increases from BA to BAB, and ABA is; 0.526 to 0.577 and 0.630. On the other hand, for hydrophilic polymeric surfactants (**family B**), the ϕ_{cream} phase increases from BA to BAB and ABA is; 0.625 to 0.641 and 0.659. For tetrablock copolymers, the composition does not have any effect on the stability of the emulsions.

When comparison made between four different architectures (BA, BAB, ABA and BABA) in **family B**, both BA and BABA show similar ϕ_{cream} phase whereas, triblock copolymers, BAB and ABA have better stability. On the other hand, for **family A**, the order of stability of emulsions is ABA (most stable), BABA, BAB and BA (least stable).

As shown and expected, for both compositions (**family A and B**), the least stable emulsion is observed when statistical copolymer (P-D5 and P-D12) was used as a polymeric surfactant. Furthermore, in **family B**, the triblock copolymer, B-*b*-(B-*stat*-A)-*b*-A with a statistical middle block, is more stable than the diblock, BA and other polymeric surfactants with different architectures. In both **family A and B**, the gradient copolymer, B-*b*-(B-*grad*-A)-*b*-A has a lower emulsifying ability than the B-*b*-(B-*stat*-A)-*b*-A.

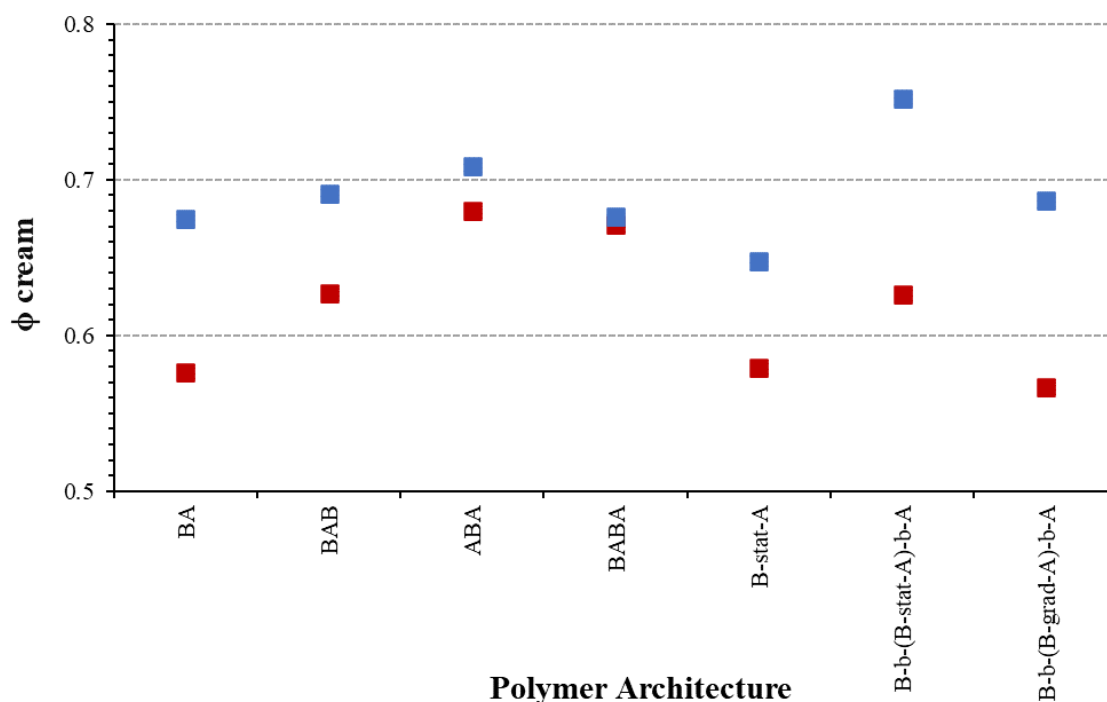


Figure 6.12. The volume fraction of cream phase against polymer architecture. The more hydrophilic polymeric surfactants (75-25 w/w%) and hydrophobic surfactants (50-50 w/w%) represented in blue and red squares, respectively. B and A represents, BuMA and DMAEMA, respectively.

6.8.2.2 Microscopy Observation

In order to have more information about the instability of emulsions, the droplet size distribution of emulsion droplets was determined using Optical Transmission Spectroscopy. The droplet size distribution of the emulsions was investigated directly after the emulsification and one day, a week and a month after the emulsification formed. An example of micrographs for an emulsion stabilised by P-D6 and P-D13 with an architecture of B-*b*-(B-*stat*-A)-*b*-A are shown in **Figure 6.13**, a-c) and d-f) respectively.

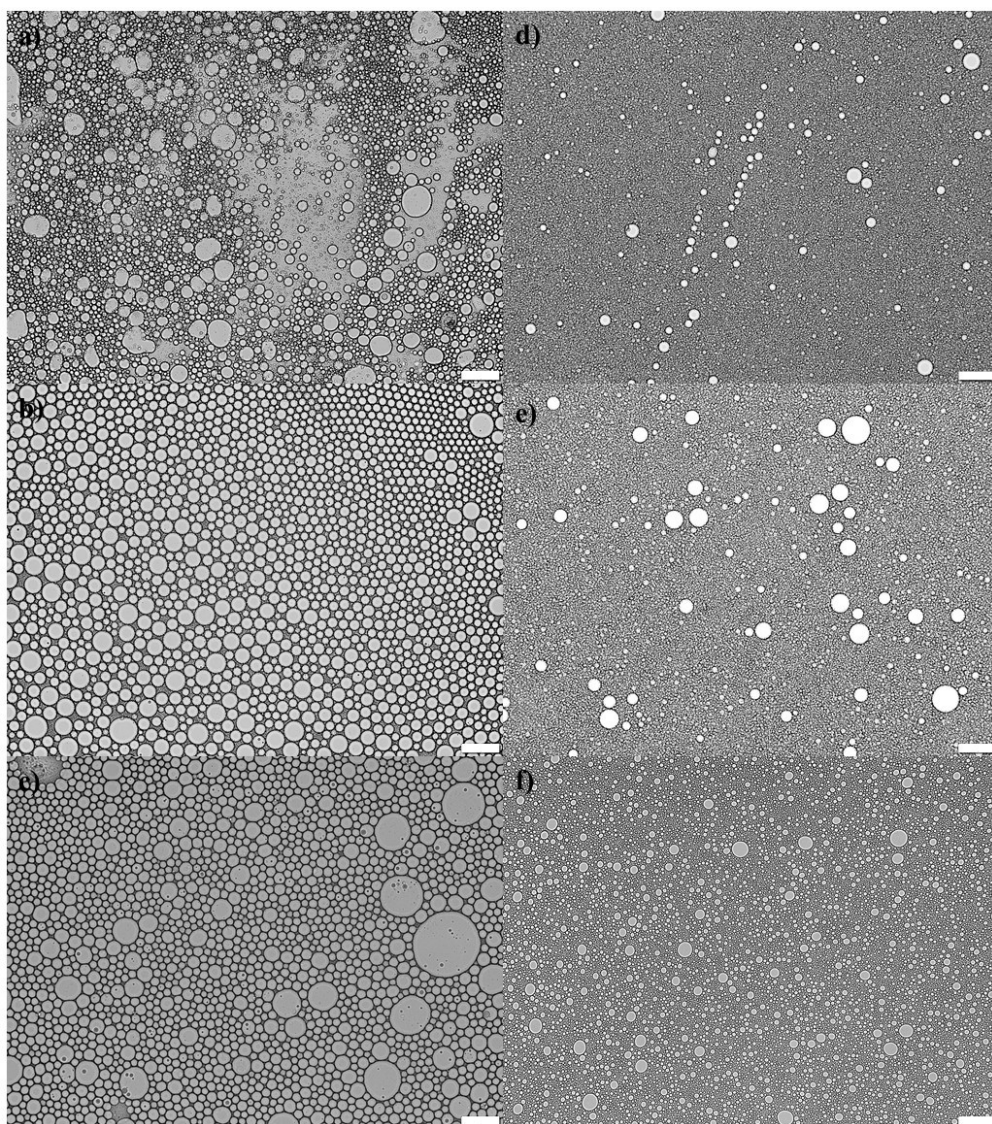


Figure 6.13. The optical micrographs of O/W emulsions stabilised by P-D6, BuMA₇-*b*-(BuMA₁₂-*co*-DMAEMA₁₄)-*b*-DMAEMA₆. The micrographs are taken; a) one day, b) a week and c) a month after emulsification performed. The optical micrographs of O/W emulsions stabilised by P-D13, BuMA₇-*b*-(BuMA₄-*co*-DMAEMA₂₂)-*b*-DMAEMA₆. The micrographs are taken; d) one day, e) a week and f) a month after emulsification performed. The scale bar is equal to 50 μm .

As shown, the size of the emulsion droplets is quite polydisperse, and the average diameter is calculated to be $7.79 \pm 0.11 \mu\text{m}$ after 1 day of emulsification performed. After a week, the average emulsion droplet diameter increased to $14.0 \pm 0.18 \mu\text{m}$. The size of the emulsion droplets is increased due to the presence of an instability mechanism, which is Ostwald ripening. The size of the emulsion droplets after a month of emulsification performed was $21.53 \pm 0.19 \mu\text{m}$, and it is also apparent from the micrograph c) in **Figure 6.13**.

The size of the emulsion droplets is also observed for P-D13 after one day, week and a month of emulsification performed, and they are shown in **Figure 6.13**. As can be seen from the images, the structural features of emulsion droplets of P-D13 are not clear, only for big droplets. The P-D13 forms stable emulsions with lots of droplets with a smaller diameter and when they are placed on the microscopy slide, they come very close to each other and hard to see using Optical microscopy. Over time, the structural features of droplets become clearer f) in **Figure 6.13** because the diameter of drops increases due to the instability of emulsion droplets.

As shown on the optical micrographs (see **Figure 6.13**, c and f), the size of drops are much bigger for P-D6 compared to the P-D13. This means that, P-D13 provides better steric stabilisation between the droplets therefore they have smaller droplet sizes, hence better stability.

The least stable emulsion was observed for P-D5, BuMA₂₁-*co*-DMAEMA₁₉, and the optical micrograph is taken after a month (see **Figure 6.14**). As can be seen from **Figure 6.14**, the emulsion droplets are polydisperse, and the presence of small droplets next to the big droplets indicates the Ostwald ripening instability mechanism.

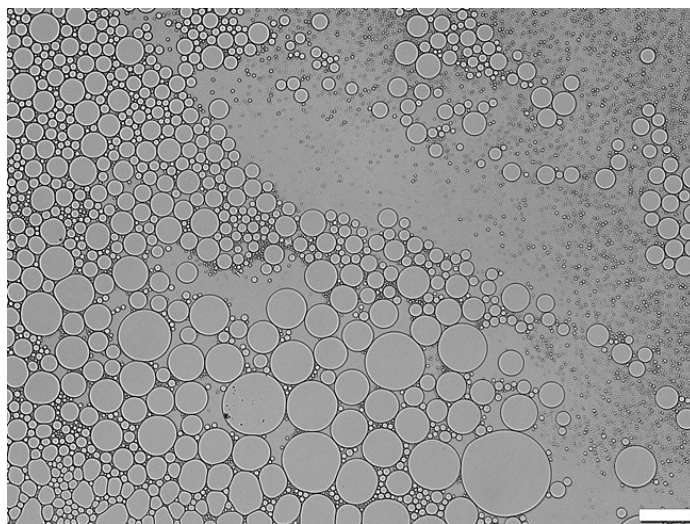


Figure 6.14. The optical micrograph of O/W emulsions stabilised by statistical copolymer, P-D5, BuMA₂₁-*co*-DMAEMA₁₉. The scale bar is equal to 50 μm .

6.9 Conclusions

In this section, two polymer series, **Family A** and **B**, based on DMAEMA and BuMA monomers, were successfully synthesised *via* GTP. Both **Family A** and **B** consisted of polymers with seven different architectures BA, BAB, ABA, BABA, B-*stat*-A, B-*b*-(B-*stat*-A)-*b*-A and B-*b*-(B-*grad*-A)-*b*-A. In **Family A**, the targeted composition was 50-50 w/w%, and in **Family B**, the targeted composition was 75-25 w/w% (DMAEMA-BuMA). The aqueous solution properties such as hydrodynamic diameter, CMC, effective pK_a s, cloud point values were determined. In addition to this, the emulsifying properties of synthesised polymeric surfactants are evaluated. The key findings in this chapter are;

- The M_n values of synthesised copolymers in **family A** were varied between 8800-9700 g mol⁻¹, and D values were varied between 1.06 and 1.11. Furthermore, M_n values of **family B** were varied between 8110-10200 g mol⁻¹ and D values were varied between 1.10-1.17.
- The CPs of **family A** at their initial pH could not be determined due to the poor solubility in water. On the other hand, the CPs for **family B** were found to be between 27 and 41°C. Finally, it was observed that architecture affects the cloud points of copolymers. The highest CP was observed for a copolymer with the architecture of BA, and the lowest was for B-*b*-(B-*grad*-A)-*b*-A.
- The effective pK_a values of copolymers in **family A** was varied between 6.1-6.8, and in **family B**, it was varied between 6.6 and 7.0. The lower pK_a values observed for Family A is because having higher hydrophobic content than **family B**.
- The CMC values of copolymers with architectures BA, ABA, BABA and B-*b*-(B-*stat*-A)-*b*-A were determined, and values are varied between $6.2-11.2 \times 10^{-5}$ mol L⁻¹.
- The HLB values of **family A** was calculated, and they range between 9.2-10. For **family B**, the HLB values were varied between 14.8-15.4.
- All synthesised copolymers able to stabilise methyl laurate in water emulsions. Drop tests were performed, and all polymeric surfactants able to form O/W type emulsions.
- The stability of emulsions observed for a month, and the ϕ_{cream} phase of emulsions were decreasing over time.
- The effect of composition on the stability of emulsions are studied, and it was observed that polymeric surfactants with targeted composition; 75-25 w/w% of DMAEMA-BuMA (**family B**) have better emulsifying ability than the 50-50 w/w% of DMAEMA-BuMA (**family A**).

- The effect of polymeric surfactant architecture on the stability of emulsions were studied, and the least stable emulsion was observed for a polymeric surfactant, P-D5 and P-D7, which are statistical and gradient copolymers.
- The most stable emulsion was observed for a hydrophilic polymeric surfactant (**family B**), P-D13, with the architecture of B-*b*-(B-*stat*-A)-*b*-A.

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CHAPTER 7: CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

In this PhD thesis, five different series of copolymers have been successfully synthesised *via* GTP and were evaluated in terms of the surface activity and emulsifying properties.

The first study includes the synthesis of two series of copolymers containing diblock and statistical copolymers. **Polymer series 1** is based on non-ionic, thermoresponsive PEGMA and **Polymer series 2** is based on ionic, pH- and temperature-responsive DMAEMA monomer. In both polymer series, EtMA was used as a hydrophobic monomer. In order to make a comparison between two polymer series, the composition and MM of the copolymer were systematically varied to observe how these affect the properties of copolymers. The composition of copolymers was targeted to 50-50, 60-40 and 75-25 hydrophilic-hydrophobic w/w%. The MM of the copolymers was targeted to 9000 g mol⁻¹, 6000 g mol⁻¹ and 3000 g mol⁻¹.

The second study focused on synthesising linear ABC triblock copolymers containing the three comonomers studied in the previous study: PEGMA, EtMA and DMAEMA. The aim was to observe if combining three comonomers will improve the emulsifying properties of copolymers. In order to have a comparison between the properties of triblock and diblock copolymers, similar MMs and compositions were used. The MM of copolymers was targeted to 9000 g mol⁻¹, 6000 g mol⁻¹ and 3000 g mol⁻¹. The targeted compositions of PEGMA-EtMA-DMAEMA were 30-35-35, 30-30-40 and 30-25-45 w/w/w% where the composition of PEGMA kept constant and DMAEMA/EtMA ratio increased.

The third study was focused on the synthesis of complex architectures, which consist of BuMA as a hydrophobic unit and DMAEMA as a hydrophilic unit. This study includes seven different architectures of copolymers, and there are two families: **family A** and **family B**, where MM and architectures were kept the same, and only the composition was varied. The composition of DMAEMA-BuMA was varied to 50-50 w/w% and 75-25 w/w%. The MM of the copolymers were kept constant to 6000 g mol⁻¹.

All the synthesised copolymers were characterised in both organic and aqueous solvents, and the main findings are listed below:

- Forty-nine well-defined copolymers, six statistical and forty-three block copolymers were successfully synthesised *via* GTP. The composition and MM of copolymers were determined using ^1H NMR and GPC, respectively.
- The experimental MM values of the copolymers were satisfactorily close to their targeted MM values. In addition to this, the MMDs of copolymers are satisfactorily low, and they are lower than 1.32.
- The CP values of copolymers are affected by both the MM and the composition of the copolymers. Increasing the hydrophobic content of copolymer results in decrease in the CP values. Increasing MM of the non-ionic copolymer leads to an increase in CPs. On the other hand, increasing MM of the ionic copolymer leads to a decrease in CPs.
- The effective pK_a values of copolymers were affected by the hydrophobic content, and the more hydrophobic the polymer is, the lower the pK_a value.
- The CMC values of all soluble copolymers were determined, and the values are ranged between 10^{-4} and 10^{-5} mol L $^{-1}$.
- All synthesised copolymers are able to stabilise methyl laurate in water emulsions.
- The HLB values of all copolymers were calculated, and it was observed that all copolymers stabilise O/W type emulsions. The type of emulsions was also confirmed by performing drop tests experiments.
- The stability of the emulsions decreases over time.
- The MM and composition of the copolymers affect the stability of the emulsion.
- For DMAEMA based series, it was observed that decreasing hydrophobic content leads to an increase in the stability of emulsions. On the other hand, for PEGMA based series, increasing hydrophobic content lead to an increase in the stability of emulsions.
- The polymer architecture affects the stability of the emulsions.

7.2 Future work

In scope of investigating additional architectures that could stabilise emulsions, graft or/and star copolymers could be synthesised and compared with the previously studied architectures .

The surface tension of the polymeric surfactants is one of the crucial parameters to determine the emulsifying properties.¹ Therefore, the surface tension of the polymeric surfactants could be determined. In addition to this, the rheological behaviour of the synthesised copolymers could be investigated, which is another important parameter of polymeric surfactants.

As mentioned in the Introduction section, Pluronics are the most widely used polymeric surfactants in various applications. Therefore, the best-performing polymeric surfactant could be chosen and be compared with the Pluronics to observe which one has the better emulsifying properties.

The best performing polymeric surfactants could be used to stabilise the emulsions for pesticide delivery applications. In a previously reported study, methyl laurate was used as an oil phase.² In addition to this, we observed that the in-house synthesised block copolymers could stabilise the methyl laurate in water emulsions in our study. Therefore, they could be a good candidate for pesticide formulations.

The synthesised polymeric surfactants could stabilise the emulsions and fabricate particles using an emulsion templating method.³ A series of synthesised copolymers could be used to investigate systematically the size of the particles fabricated using block copolymers.

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APPENDIX



Ethyl methacrylate diblock copolymers as polymeric surfactants: Effect of molar mass and composition

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Publication: European Polymer Journal

Publisher: Elsevier

Date: 5 July 2021

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Table 1. Densities and molar mass (MM) of ingredients used to synthesise polymers.

Ingredient	Role	Molar Mass (g mol⁻¹)	Density (g cm⁻³)
PEGMA	Monomer	300	1.05
DMAEMA	Monomer	157.21	0.933
MMA	Monomer	100.12	0.936
EtMA	Monomer	114.14	0.917
BuMA	Monomer	142.20	0.894
HeMA	Monomer	170.25	0.863
LMA	Monomer	254.41	0.868
MTS	Initiator	0.858	0.858

Table 2. The calculations of synthesised copolymers in this PhD study.

Equations used: DP= MM polymer/MM monomer DP= moles monomer/moles initiator						
Chapter 4.						
P-A1: PEGMA-<i>b</i>-EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	41.7					
MTS				0.40	0.3432	0.001969
PEGMA	0.75	6750	22.50	25.31	13.29	0.044
EtMA	0.25	2250	19.71	4.83	4.43	0.039
Target MM	9000	9000				

Chapter 4.						
P-A2: PEGMA-<i>b</i>-EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	42.2					
MTS				0.60	0.5148	0.002953
PEGMA	0.75	4500	15.00	25.5	13.29	0.044
EtMA	0.25	1500	13.14	4.83	4.43	0.039
Target MM	6000					

Chapter 4.						
P-A3: PEGMA-<i>b</i>-EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	29.1					
MTS				0.80	0.6864	0.003938
PEGMA	0.75	2250	7.50	16.88	8.86	0.030
EtMA	0.25	750	6.57	3.22	2.95	0.026
Target MM	3000	3000				

Chapter 4.						
P-A4: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	43.9					
MTS				0.40	0.3432	0.001969
PEGMA	0.6	5400	18.00	20.25	10.63	0.035
EtMA	0.4	3600	31.54	7.73	7.09	0.062
Target MM	9000	9000				

Chapter 4.						
P-A5: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	44.4					
MTS				0.60	0.5148	0.002953
PEGMA	0.6	3600	12.00	20.25	10.63	0.035
EtMA	0.4	2400	21.03	7.73	7.09	0.062
Target MM	6000	6000				

Chapter 4.						
P-A6: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	30.5					
MTS				0.80	0.6864	0.003938
PEGMA	0.6	1800	6.00	13.50	7.09	0.024
EtMA	0.4	1200	10.51	5.15	4.73	0.041
Target MM	3000	3000				

Chapter 4.						
P-A7: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	44.4					
MTS				0.60	0.5148	0.002953
PEGMA	0.6	3600	12.00	20	10.63	0.035
EtMA	0.4	2400	21.03	7.8	7.09	0.062
Target MM	6000	6000				

Chapter 4.						
P-A8: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	45.3					
MTS				0.40	0.3432	0.001969
PEGMA	0.5	4500	15.00	17	8.86	0.30
EtMA	0.5	4500	39.43	9.66	8.86	0.078
Target MM	9000	9000				

Chapter 4.						
P-A9: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	45.9					
MTS				0.60	0.5148	0.002953
PEGMA	0.5	3000	10.00	16.88	8.86	0.030
EtMA	0.5	3000	26.28	9.66	8.86	0.078
Target MM	6000	6000				

Chapter 4.						
P-A10: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	31.5					
MTS				0.80	0.6864	0.003938
PEGMA	0.5	1500	5.00	11.0	5.91	0.020
EtMA	0.5	1500	13.14	6.4	5.91	0.052
Target MM	3000	3000				

Chapter 4.						
P-A11: PEGMA- <i>b</i> -EtMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	44.4					
MTS				0.60	0.5148	0.002953
PEGMA	0.6	3600	12.00	20	10.63	0.035
EtMA	0.4	2400	21.03	7.8	7.09	0.062
Target MM	6000	6000				

Chapter 4.						
P-B1: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	49.0					
MTS				0.80	0.6864	0.003938
DMAEMA	0.75	2250	14.31	9.50	8.86	0.056
EtMA	0.25	750	6.57	3.22	2.95	0.026
Target MM	3000	3000				

Chapter 4.						
P-B2: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	48.9					
MTS				0.80	0.6864	0.003938
DMAEMA	0.6	1800	11.45	7.60	7.09	0.045
EtMA	0.4	1200	10.51	5.15	4.73	0.041
Target MM	3000	3000				

Chapter 4.						
P-B3: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	48.9					
MTS				0.80	0.6864	0.003938
DMAEMA	0.5	1500	9.54	6.33	5.91	0.038
EtMA	0.5	1500	13.14	6.44	5.91	0.052
Target MM	3000	3000				

Chapter 4.						
P-B4: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	71.5					
MTS				0.60	0.5148	0.002953
DMAEMA	0.75	4500	28.62	14.24	13.29	0.039
EtMA	0.25	1500	13.14	4.83	4.43	0.039
Target MM	6000	6000				

Chapter 4.						
P-B5: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	71.4					
MTS				0.60	0.5148	0.002953
DMAEMA	0.6	3600	22.90	11.40	10.63	0.068
EtMA	0.4	2400	21.03	7.73	7.09	0.062
Target MM	6000	6000				

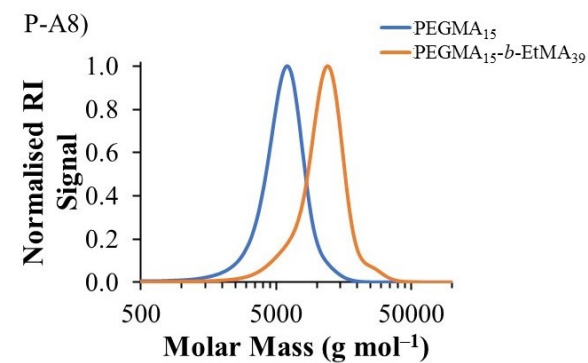
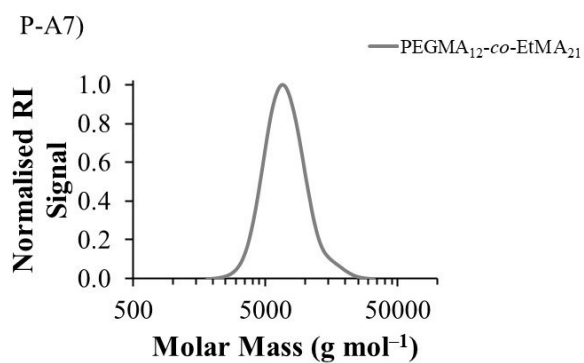
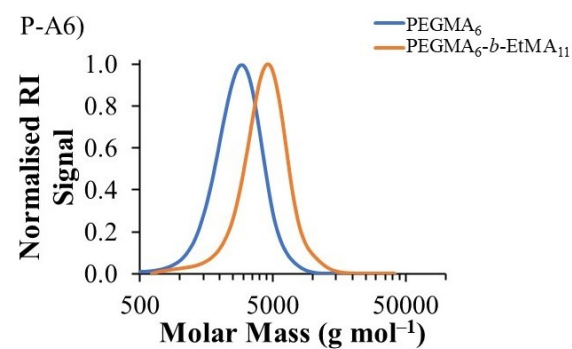
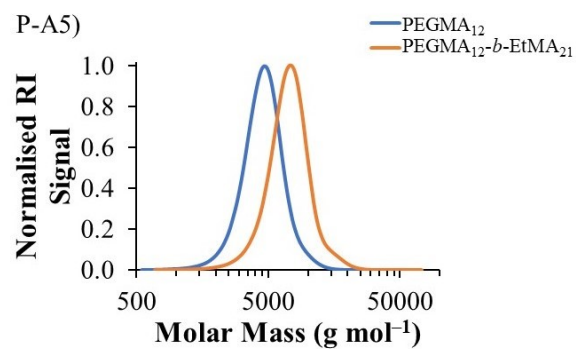
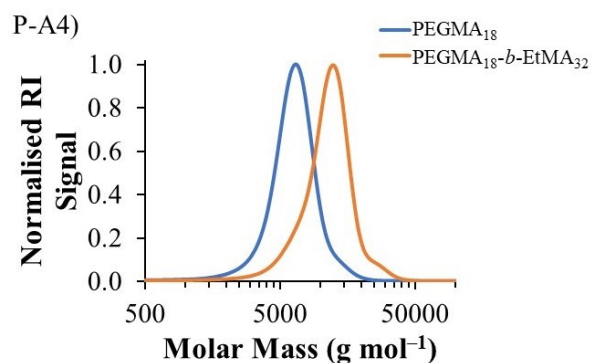
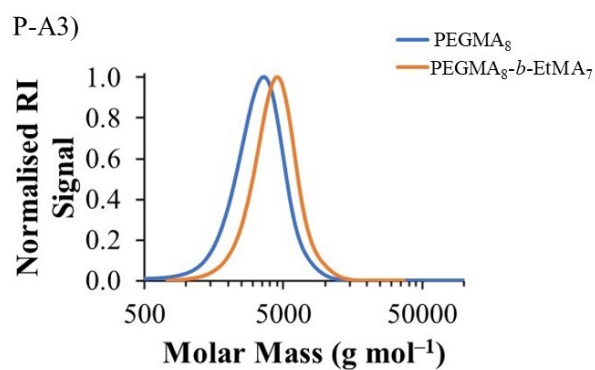
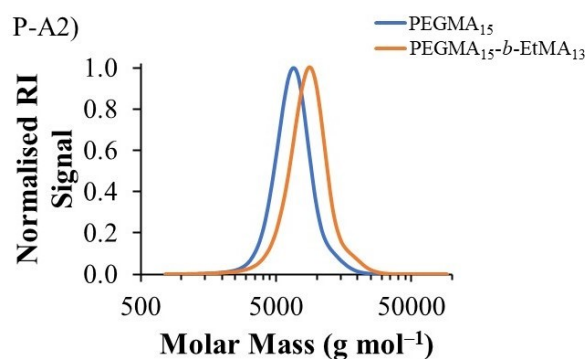
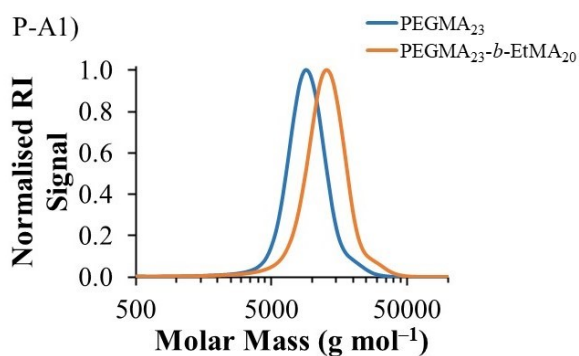
Chapter 4.						
P-B6: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	71.4					
MTS				0.60	0.5148	0.002953
DMAEMA	0.5	3000	19.08	9.50	8.86	0.056
EtMA	0.5	3000	26.28	9.66	8.86	0.028
Target MM	6000	6000				

Chapter 4.						
P-B7: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	70.8					
MTS				0.40	0.3432	0.001969
DMAEMA	0.75	2250	42.94	14.24	13.29	0.085
EtMA	0.25	2250	19.71	4.83	4.43	0.039
Target MM	9000	9000				

Chapter 4.						
P-B8: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	70.8					
MTS				0.40	0.3432	0.001969
DMAEMA	0.6	5400	34.35	11.40	10.63	0.068
EtMA	0.4	3600	31.54	7.73	7.09	0.062
Target MM	9000	9000				

Chapter 4.						
P-B9: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	70.8					
MTS				0.40	0.3432	0.00196
DMAEMA	0.5	4500	28.62	9.50	8.86	0.056
EtMA	0.5	4500	39.43	9.66	8.86	0.078
Target MM	9000	9000				

Chapter 4.						
P-B10: EtMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	71.4					
MTS				0.60	0.5148	0.00295
DMAEMA	0.6	3600	22.90	11.40	10.63	0.068
EtMA	0.4	2400	21.03	7.73	7.09	0.062
Target MM	6000	6000				



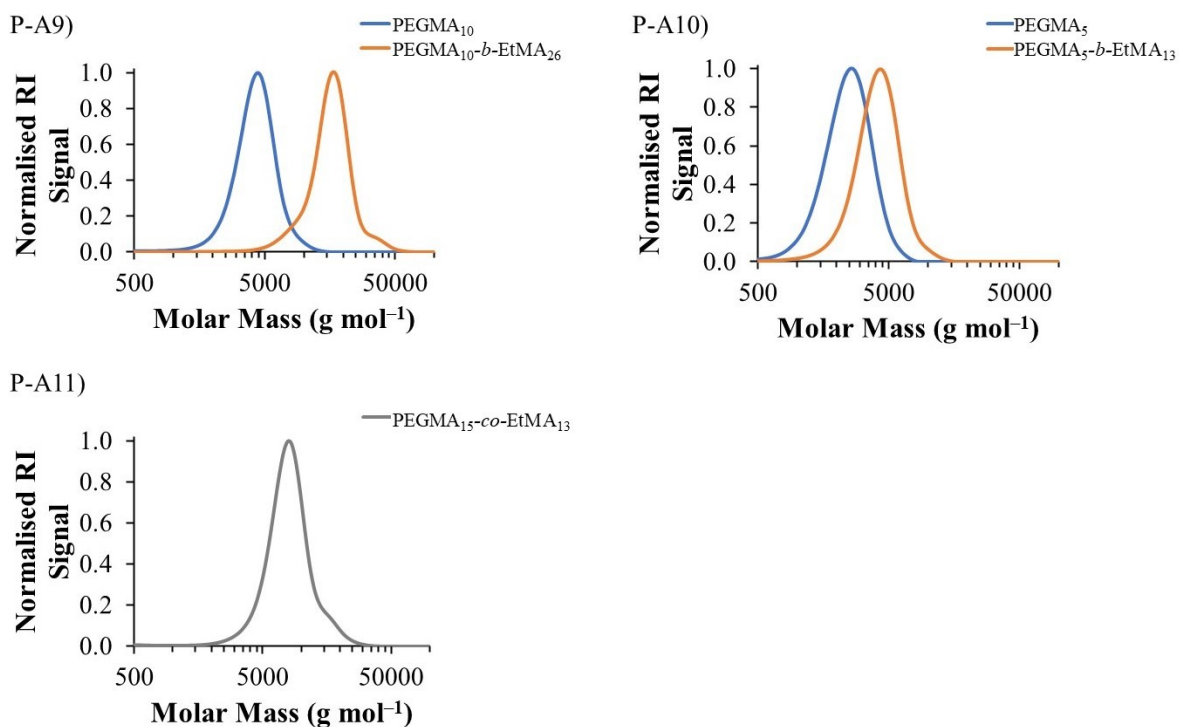
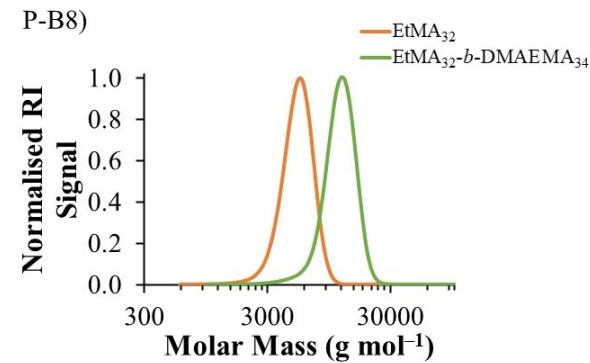
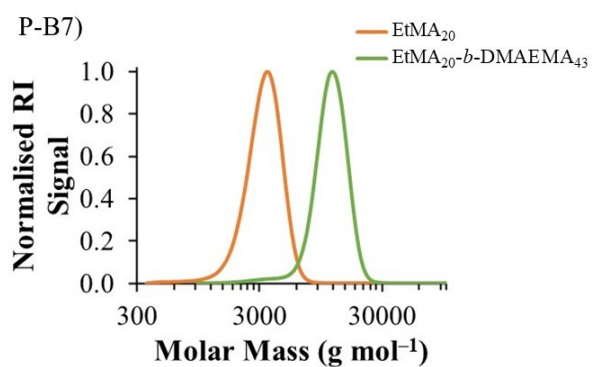
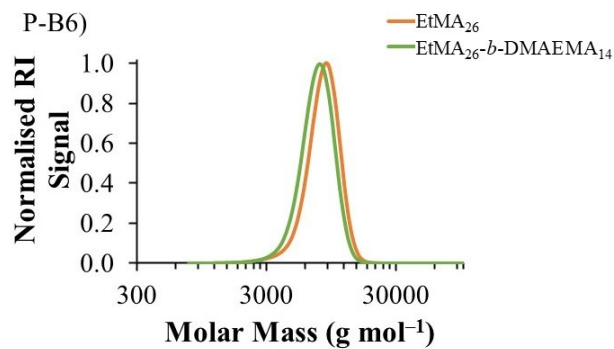
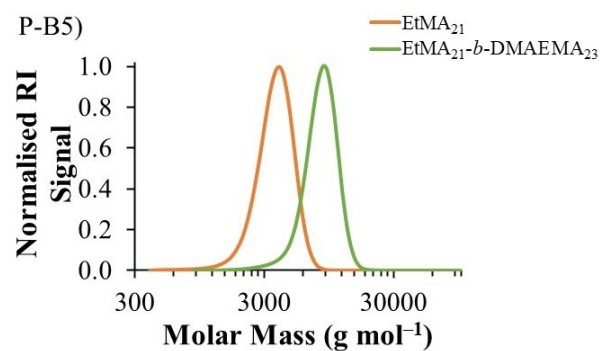
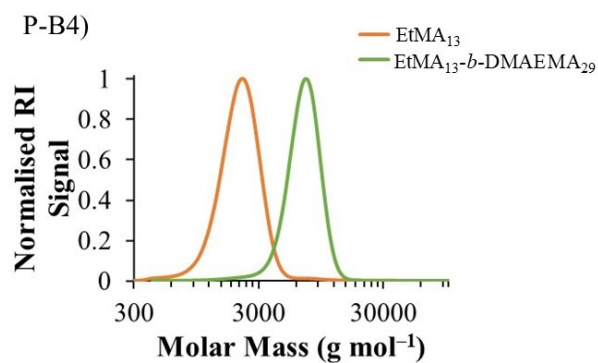
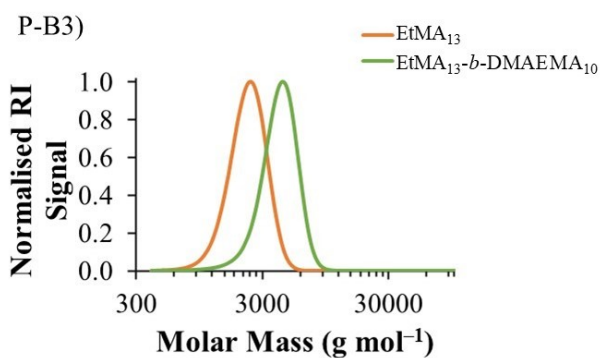
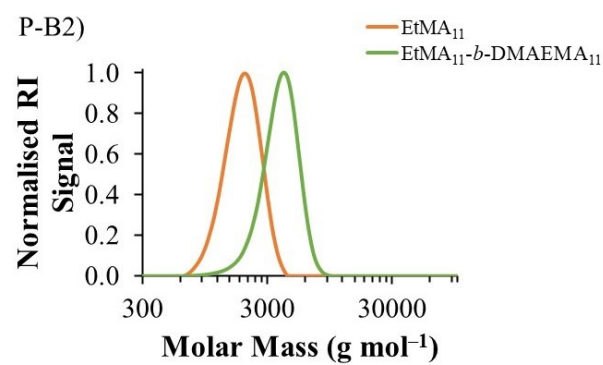
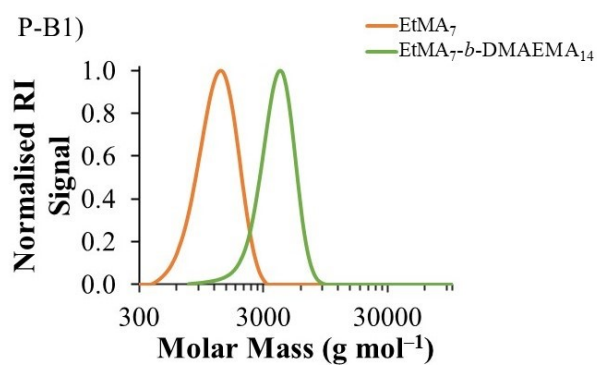


Figure 1. GPC histogram of PEGMA-EtMA based copolymers of Polymer series 1. The blue and orange lines represent the PEGMA homopolymer and the diblock copolymer, respectively. The grey lines represent statistical copolymer. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.



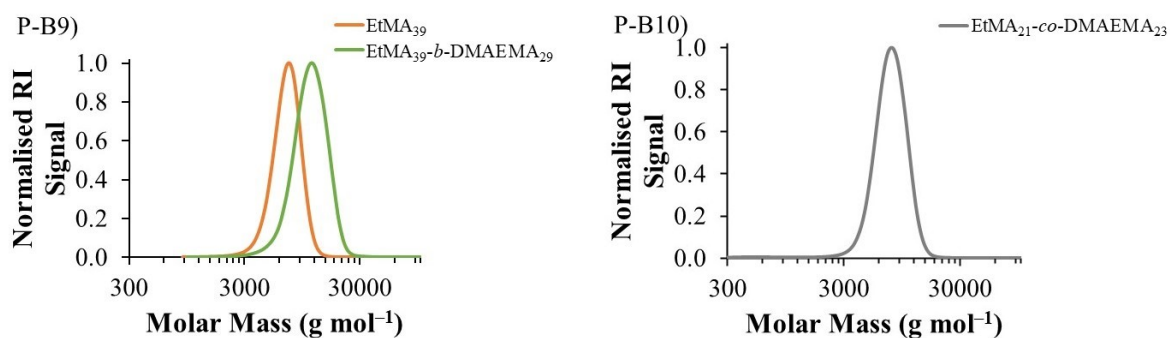


Figure 2. GPC histogram of EtMA-DMAEMA based copolymers of Polymer series 2. The orange and green lines represent the EtMA homopolymer and the diblock copolymer, respectively. The grey lines represent statistical copolymer. Reproduced, with permission, from “B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

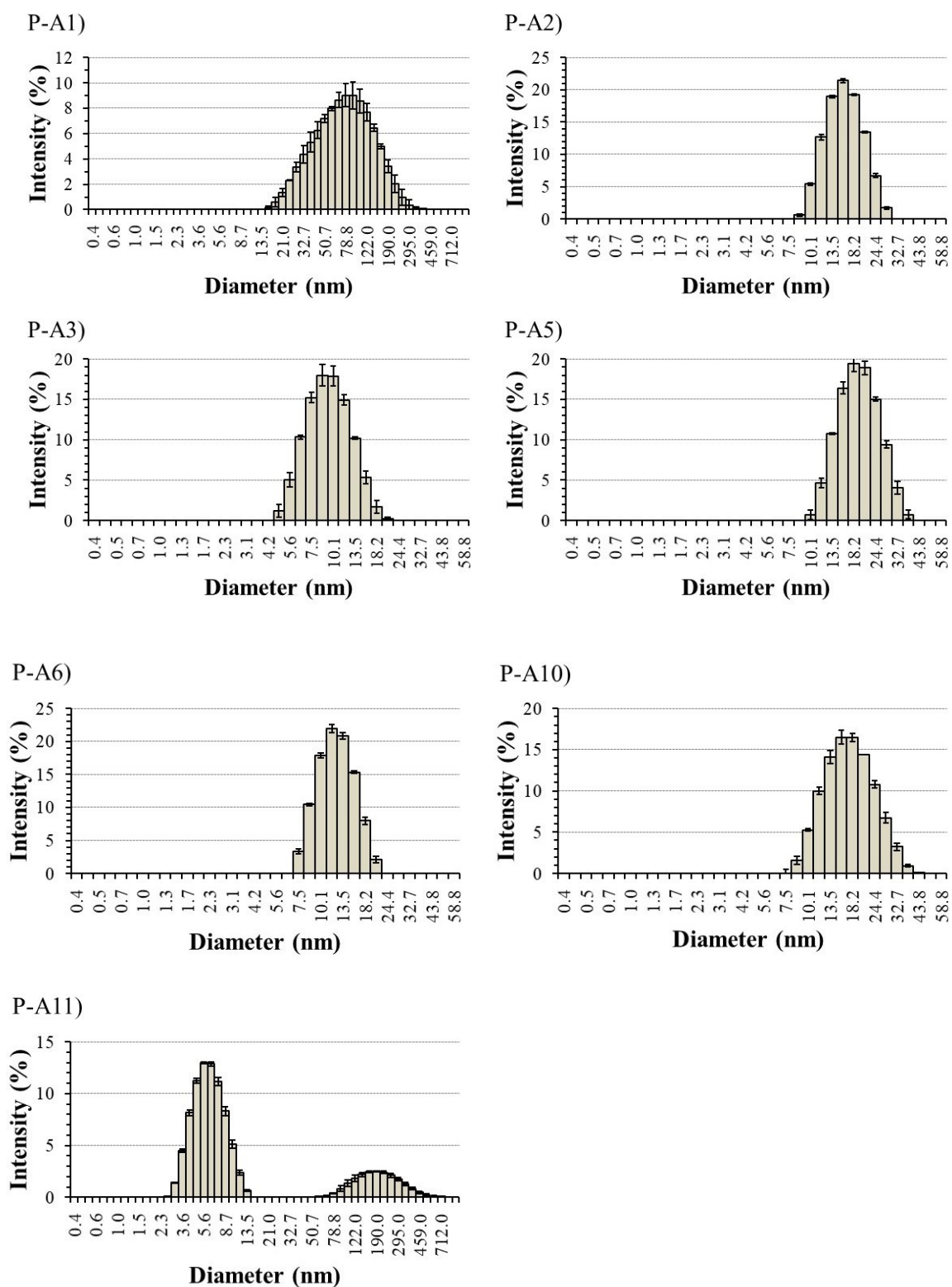


Figure 3. DLS histograms of PEGMA-*b*-EtMA based diblock copolymers of Polymer series 1. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

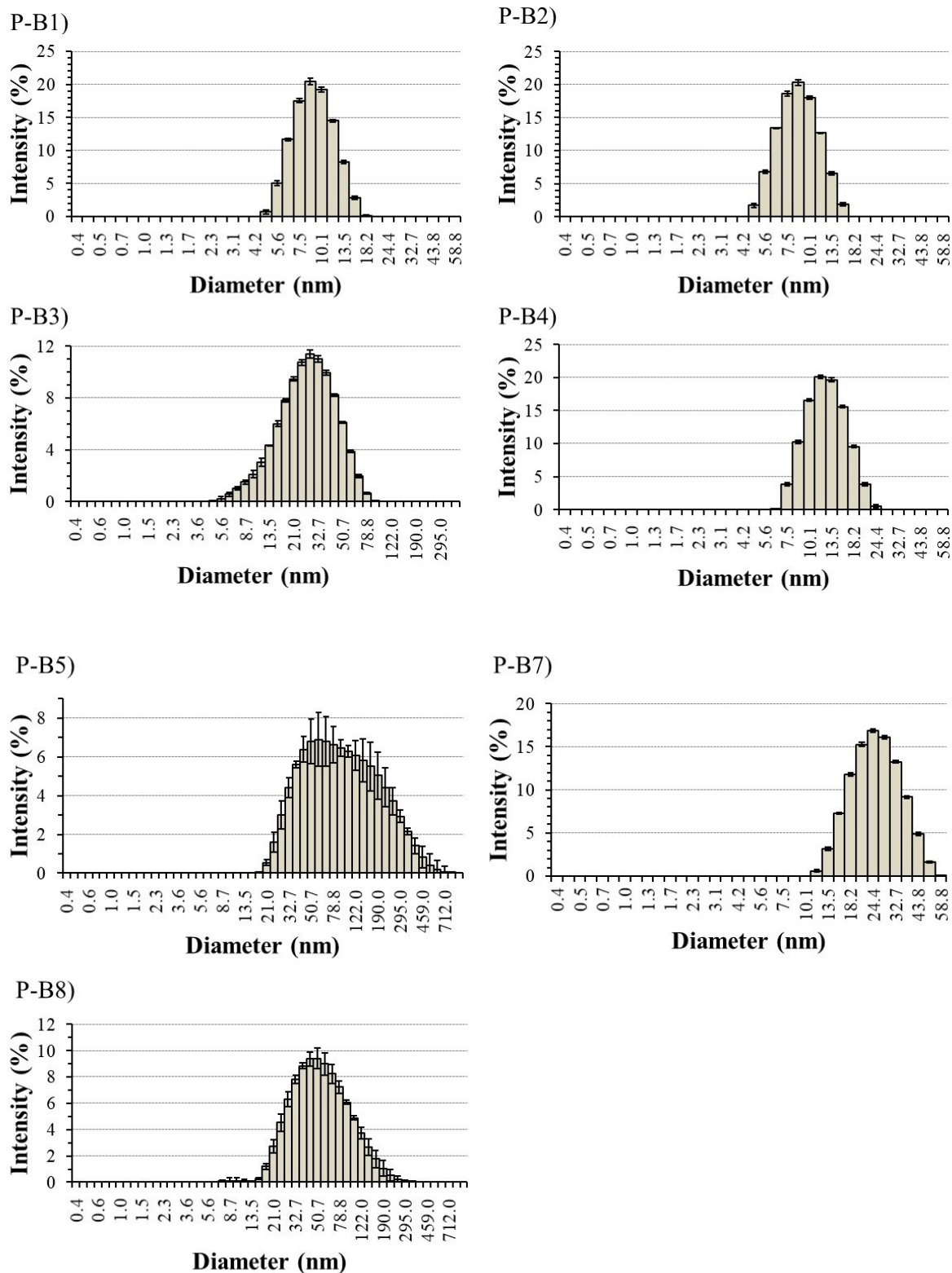


Figure 4. DLS histograms of EtMA-*b*-DMAEMA based diblock copolymers of Polymer series 2. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

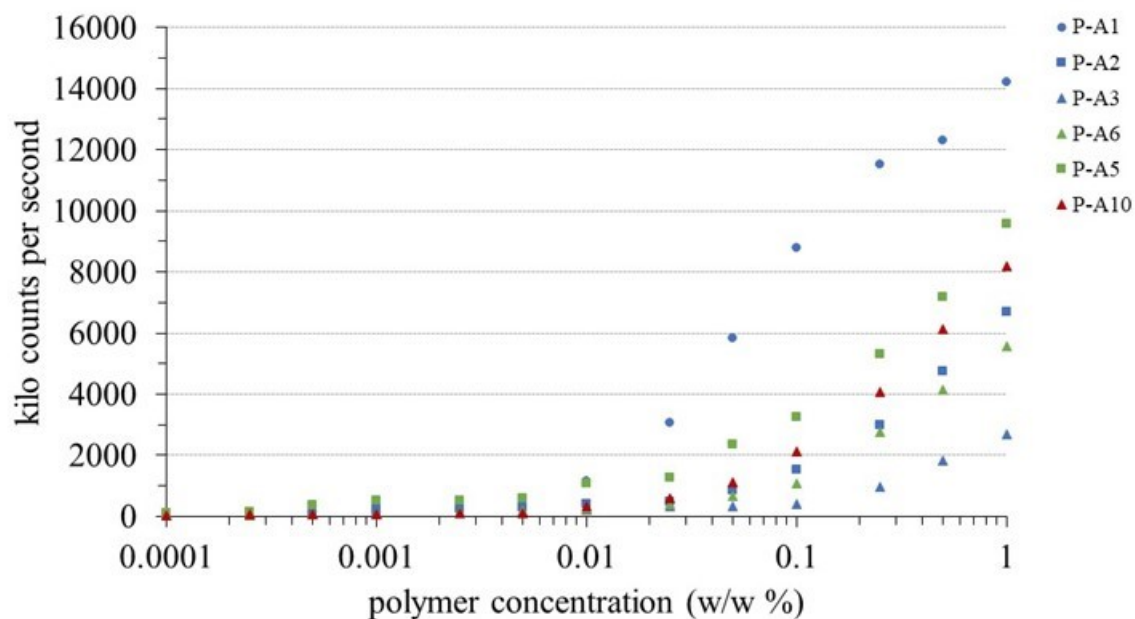


Figure 5. The graph shows the kilo counts per second versus polymer concentration. The targeted composition of diblock copolymers; 75-25, 60-40 and 50-50 w/w% are represented in blue, green and red, respectively. The circle (●), square (■) and triangle (▲) polymers of different MMs; 9000, 6000 and 3000 g mol⁻¹ are represented, respectively. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

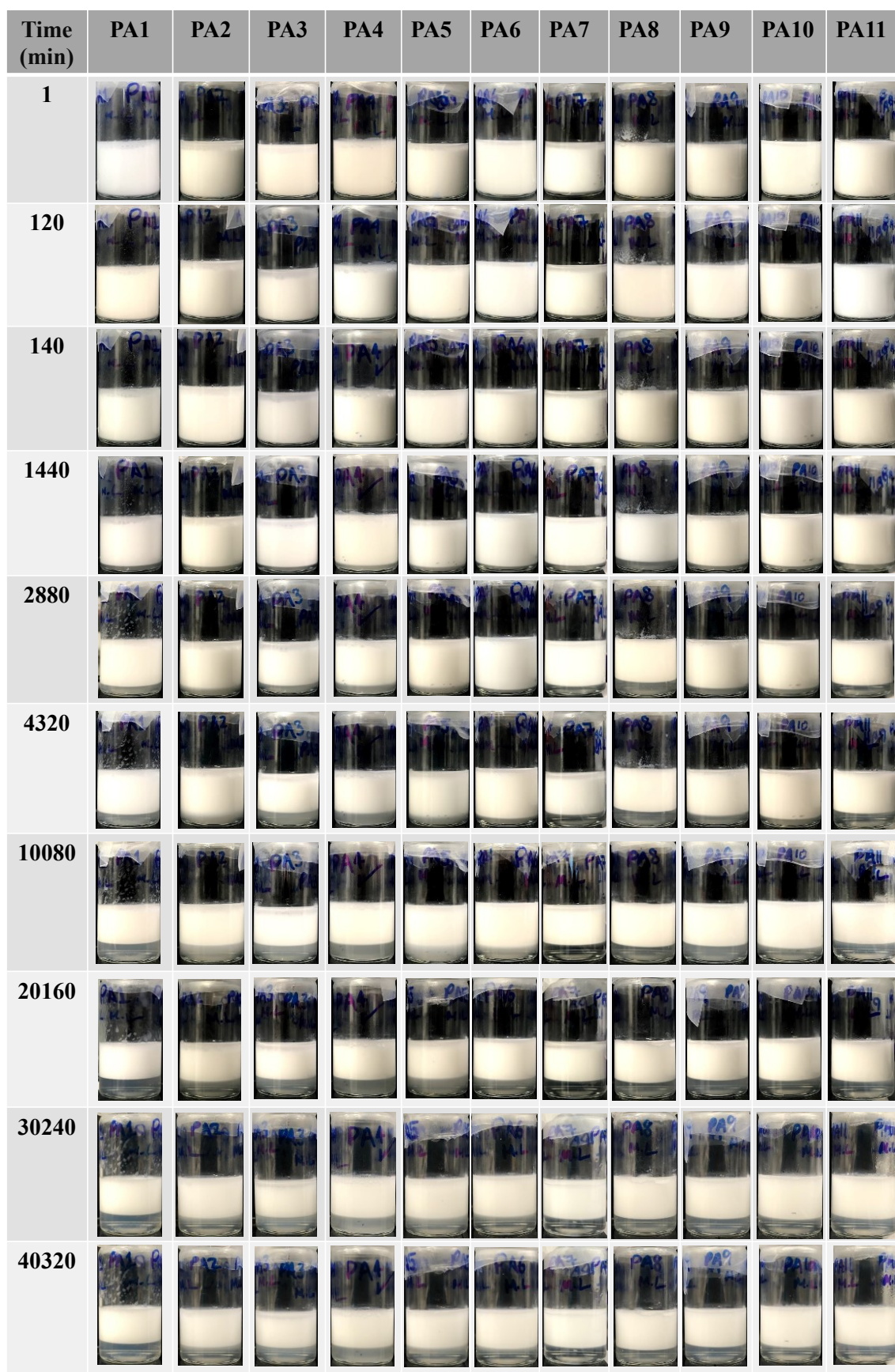


Figure 6. Images of emulsions taken at different time scales for Polymer series 1. A 1 w/w % copolymer was mixed with equal weights of methyl laurate and water.

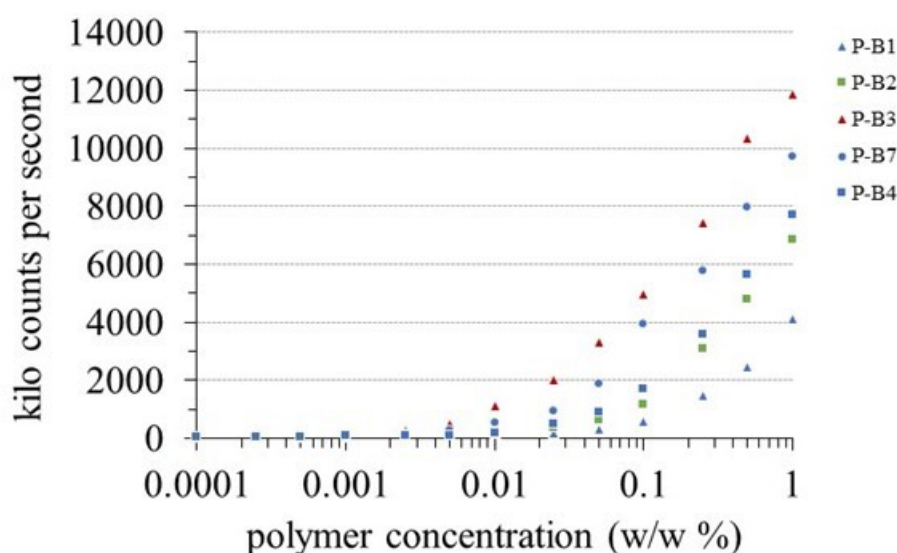


Figure 7. The graph shows the kilo counts per second versus polymer concentration. The targeted composition of diblock copolymers; 75-25, 60-40 and 50-50 w/w% are represented in blue, green and red, respectively. The circle (●), square (■) and triangle (▲) polymers of different MMs; 9000, 6000 and 3000 g mol⁻¹ are represented, respectively. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

Table 3. The fraction of the cream phase-resolved for Polymer series 1 at different times.

time (min)	ϕ cream										
	P-A1	P-A2	P-A3	P-A4	P-A5	P-A6	P-A7	P-A8	P-A9	P-A10	P-A11
1	0.831	0.845	0.86	0.922	0.879	0.926	0.820	0.941	0.924	0.903	0.934
120	0.817	0.835	0.851	0.880	0.874	0.924	0.816	0.915	0.901	0.903	0.921
240	0.811	0.817	0.840	0.865	0.852	0.914	0.812	0.895	0.897	0.893	0.915
1440	0.787	0.749	0.769	0.803	0.822	0.876	0.796	0.813	0.861	0.878	0.853
2880	0.758	0.713	0.699	0.751	0.788	0.865	0.742	0.783	0.833	0.838	0.833
4320	0.701	0.673	0.626	0.686	0.757	0.836	0.674	0.776	0.786	0.813	0.754
10080	0.616	0.612	0.601	0.637	0.641	0.761	0.626	0.694	0.700	0.794	0.713
20160	0.595	0.600	0.58	0.623	0.621	0.668	0.604	0.661	0.656	0.694	0.670
30240	0.579	0.597	0.576	0.611	0.615	0.648	0.603	0.657	0.644	0.676	0.670
40320	0.570	0.576	0.575	0.605	0.613	0.640	0.590	0.644	0.632	0.672	0.637

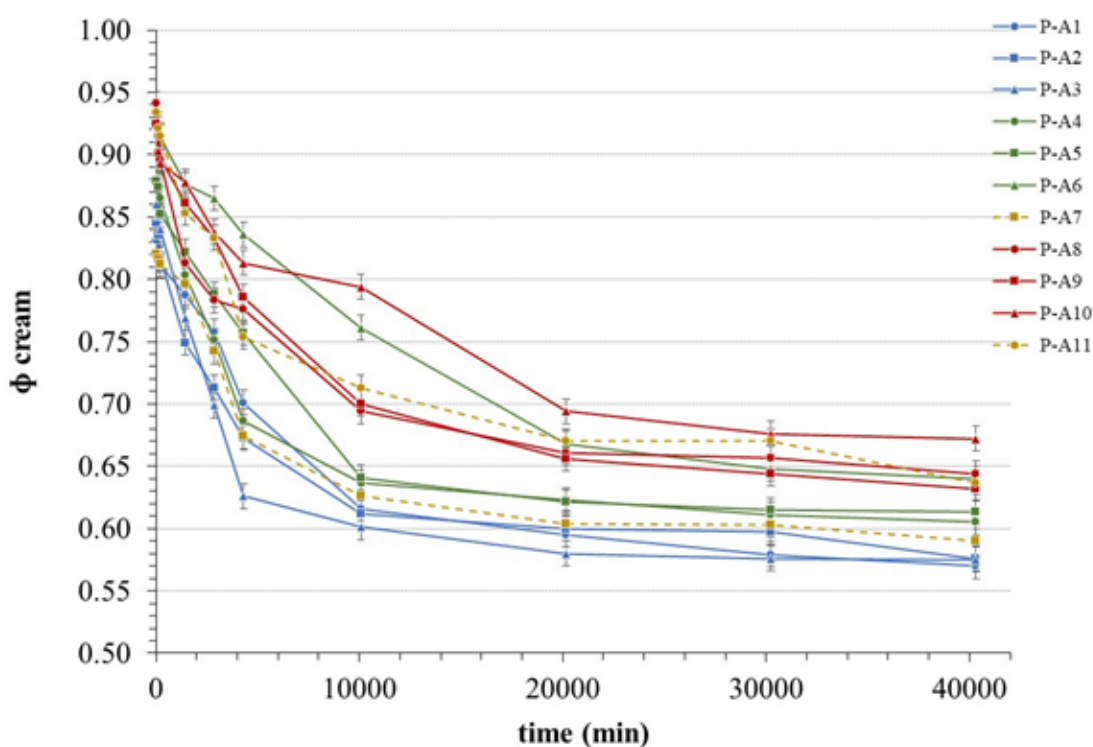


Figure 8. The graph shows the fraction of cream phase-resolved for Polymer series 1 over time. The targeted composition of diblock copolymers; 75-25, 60-40 and 50-50 w/w % are represented in blue, green and red, respectively. The random copolymers with composition 75-25 and 60-40 w/w % are represented in dark yellow. The circle (●), square (■) and triangle (▲) polymers of different MMs; 9000, 6000 and 3000 g mol⁻¹ are represented, respectively. Reproduced, with permission, from “ B. Somuncuoğlu, Y. Lin Lee, A. P. Constantinou, D. L. M. Poussin and T. K. Georgiou, *Eur. Polym. J.*, 2021, **154**, 110537, DOI: 10.1016/j.eurpolymj.2021.110537.

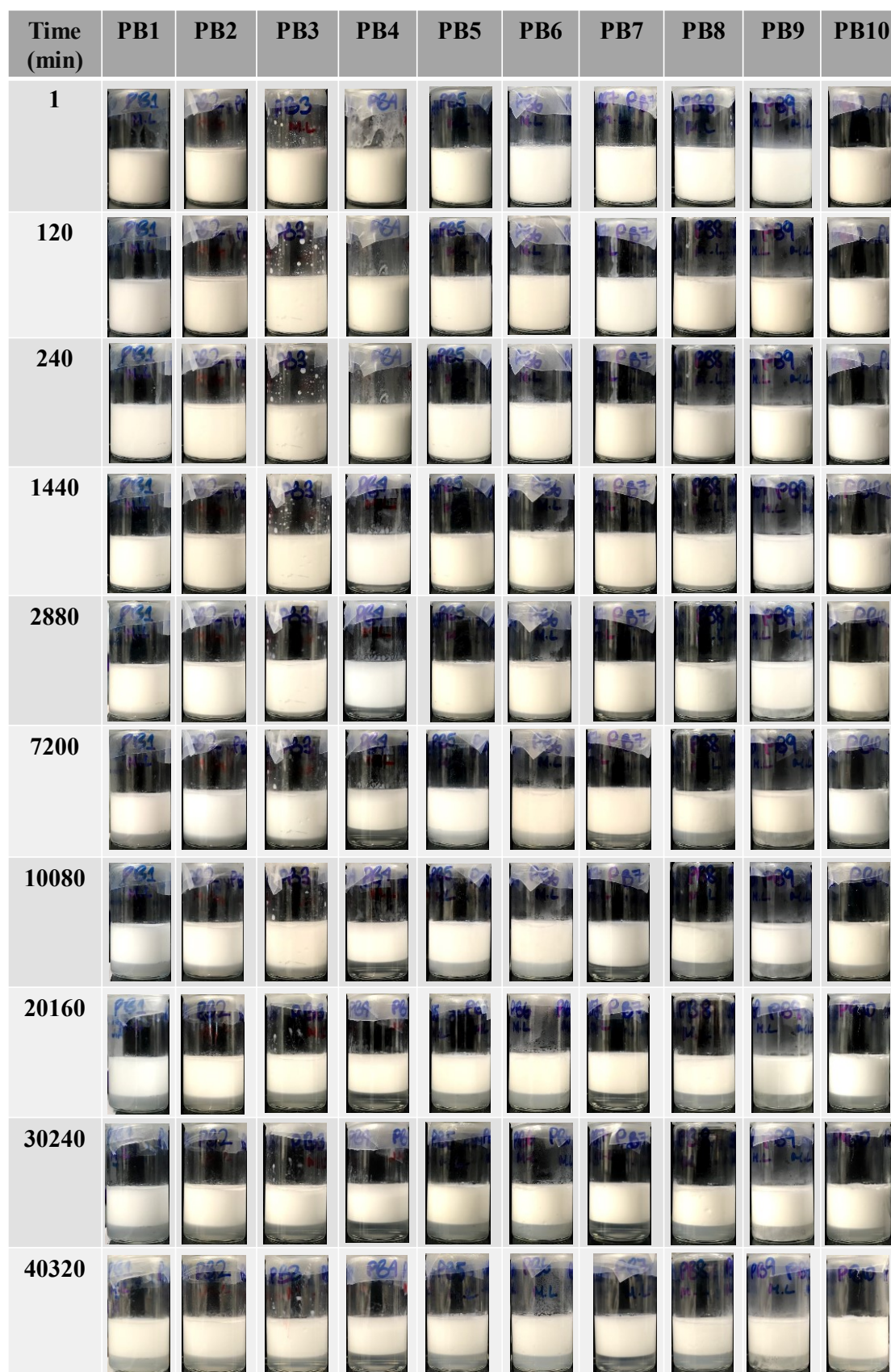


Figure 9. Images of emulsions taken at different time scales. A 1 w/w % copolymer was mixed with equal weights of methyl laurate and water.

Table 4. The fraction of the cream phase-resolved for Polymer series 2 at different times.

time (min)	ϕ cream									
	P-B1	P-B4	P-B7	P-B6	P-B8	P-B2	P-B3	P-B5	P-B9	P-B10
1	1.002	1.000	0.953	0.943	0.925	0.907	0.948	0.941	0.919	0.980
120	0.961	0.960	0.927	0.939	0.869	0.907	0.946	0.932	0.883	0.960
240	0.950	0.953	0.907	0.922	0.858	0.897	0.950	0.896	0.867	0.917
1440	0.895	0.885	0.900	0.823	0.848	0.878	0.890	0.865	0.779	0.888
2880	0.856	0.833	0.898	0.801	0.763	0.873	0.865	0.836	0.734	0.815
7200	0.700	0.726	0.763	0.686	0.639	0.731	0.821	0.694	0.645	0.811
10080	0.679	0.715	0.734	0.682	0.634	0.697	0.734	0.684	0.638	0.737
20160	0.676	0.712	0.700	0.675	0.634	0.677	0.644	0.680	0.636	0.693
30240	0.666	0.708	0.686	0.670	0.628	0.663	0.632	0.672	0.626	0.681
40320	0.653	0.702	0.684	0.658	0.623	0.635	0.615	0.658	0.623	0.679

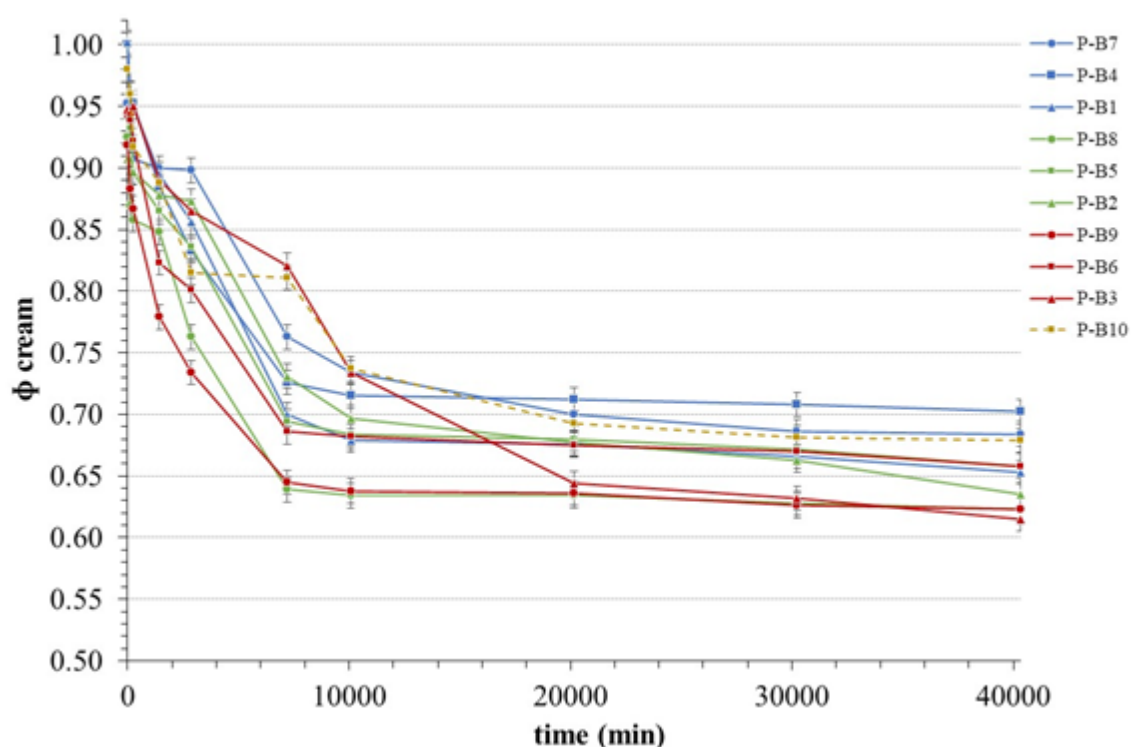


Figure 10. The graph shows the fraction of cream phase-resolved for Polymer series 2 over time. The targeted composition of diblock copolymers; 75-25, 60-40 and 50-50 w/w % are represented in blue, green and red, respectively. The random copolymers with composition 75-25 and 60-40 w/w % are represented in dark yellow. The circle (●), square (■) and triangle (▲) polymers of different MMs; 9000, 6000 and 3000 g mol⁻¹ are represented, respectively.

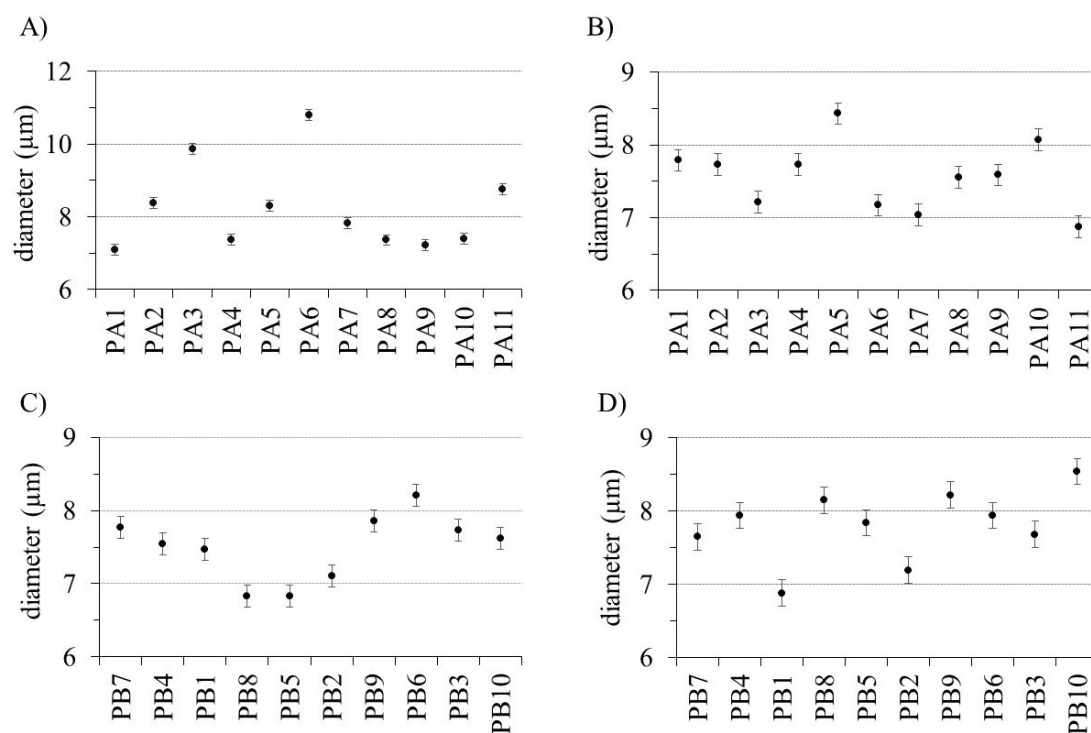


Figure 11. The diameter of emulsion droplets determined by Optical transmission microscopy. The size of the emulsion droplets of **Polymer series 1** is shown in graph A) and B), and **Polymer series 2** is shown in C) and D). The size of the emulsion droplets measured; A) and C) immediately after emulsification and B) and D) after one week.

APPENDIX- CHAPTER 5

Table 5. The calculations of synthesised copolymers in this PhD study.

Chapter 5						
P-C1: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				60.396		
MTS				0.5	0.429	0.0025
PEGMA	0.3	2700	9	12.657	6.6451	0.0222
EtMA	0.35	3150	27.598	8.4543	7.7526	0.0679
DMAEMA	0.35	3150	20.037	8.3093	7.7526	0.0493
Target MM	9000	9000				

Chapter 5.						
P-C2: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				56.937		
MTS				0.7	0.6006	0.0034
PEGMA	0.3	1800	6	11.813	6.2021	0.0207
EtMA	0.35	2100	18.398	7.8907	7.2357	0.0634
DMAEMA	0.35	2100	13.358	7.7553	7.2357	0.046
Target MM	6000	6000				

Chapter 5.						
P-C3: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				29.32		
MTS				0.7	0.6006	0.0034
PEGMA	0.3	900	3	5.9067	3.101	0.0103
EtMA	0.35	1050	9.1992	3.9453	3.6179	0.0317
DMAEMA	0.35	1050	6.679	3.8777	3.6179	0.023
Target MM	3000	3000				

Chapter 5.						
P-C4: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				60.417		
MTS				0.5	0.429	0.0025
PEGMA	0.3	2700	9	12.657	6.6451	0.0222
EtMA	0.3	2700	23.655	7.2465	6.6451	0.582
DMAEMA	0.4	3600	22.899	9.4963	8.8601	0.0564
Target MM	9000	9000				

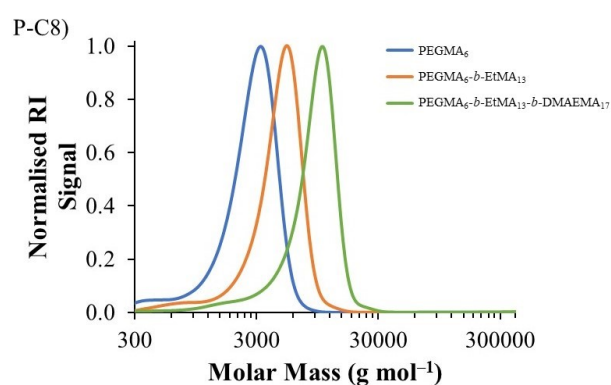
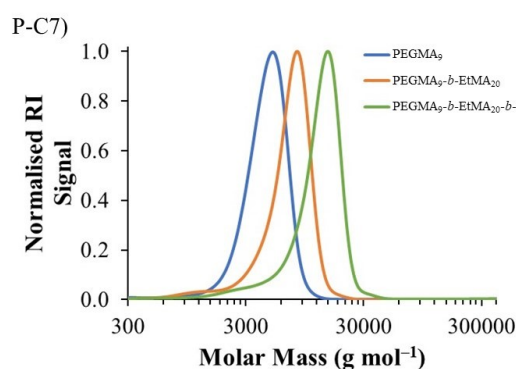
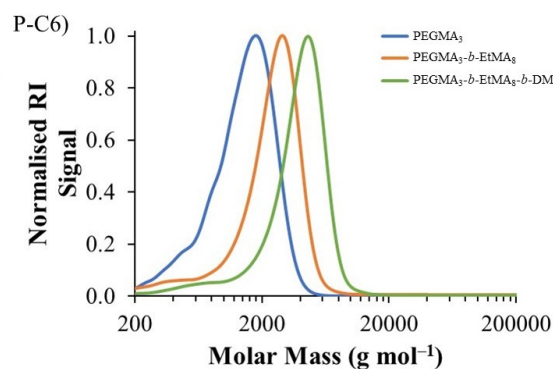
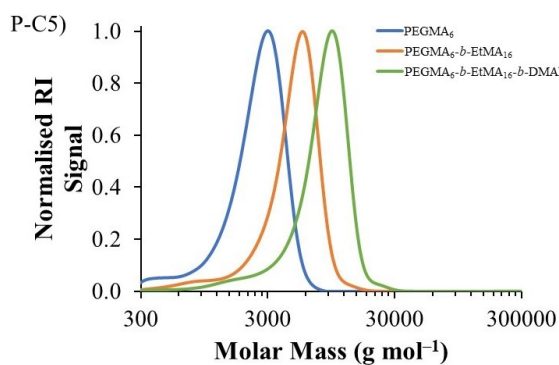
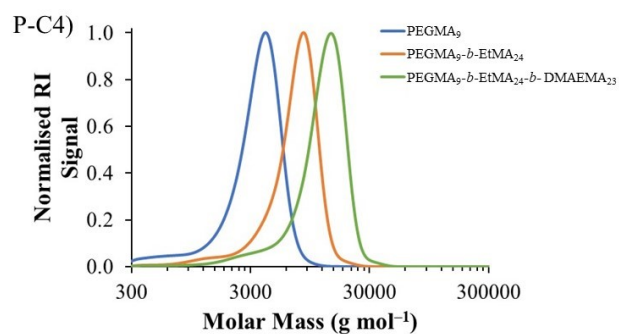
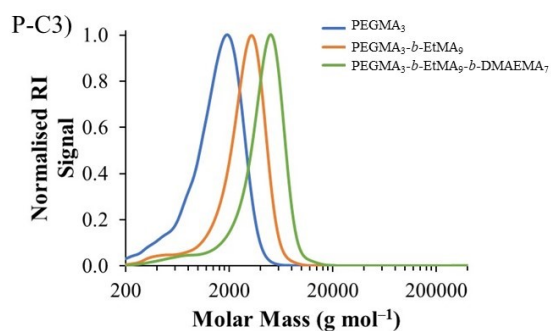
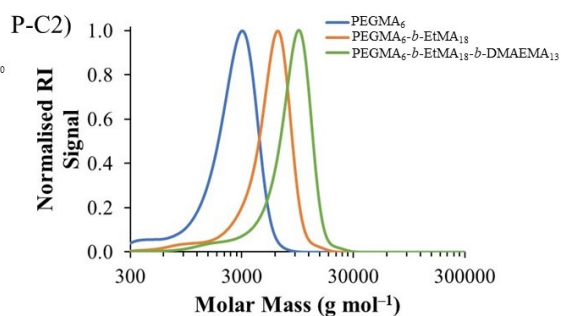
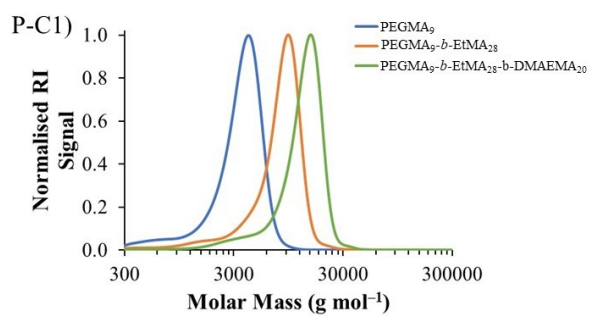
Chapter 5.						
P-C5: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				48.82		
MTS				0.6	0.5148	0.003
PEGMA	0.3	1800	6	10.126	5.316	0.0177
EtMA	0.3	1800	15.77	5.7972	5.316	0.0466
DMAEMA	0.4	2400	15.266	7.5971	7.0881	0.0451
Target MM	6000	6000				

Chapter 5.						
P-C6: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				29.329		
MTS				0.7	0.6006	0.0034
PEGMA	0.3	900	3	5.9067	3.101	0.0103
EtMA	0.3	900	7.8851	3.3817	3.101	0.0272
DMAEMA	0.4	1200	7.6331	4.4316	4.1347	0.0263
Target MM	3000	3000				

Chapter 5.						
P-C7: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF						
MTS				0.5	0.429	0.0025
PEGMA	0.3	2700	9	12.66	6.65	0.0222
EtMA	0.25	2250	19.713	6.04	5.54	0.0485
DMAEMA	0.45	4050	13.5	9.49	9.97	0.0332
Target MM	9000					

Chapter 5.						
P-C8: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				49.448		
MTS				0.6	0.5148	0.003
PEGMA	0.3	1800	6	10.126	5.316	0.0177
EtMA	0.25	1500	13.142	4.2191	4.43	0.0388
DMAEMA	0.45	2700	17.174	8.5467	7.9741	0.0507
Target MM	6000	6000				

Chapter 5.						
P-C9: PEGMA-EtMA-DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				29.339		
MTS				0.7	0.6006	0.0034
PEGMA	0.3	900	3	5.9067	3.101	0.0103
EtMA	0.25	750	6.5709	2.8181	2.5842	0.0226
DMAEMA	0.45	1350	8.5872	4.9856	4.6515	0.0296
Target MM	3000	3000				



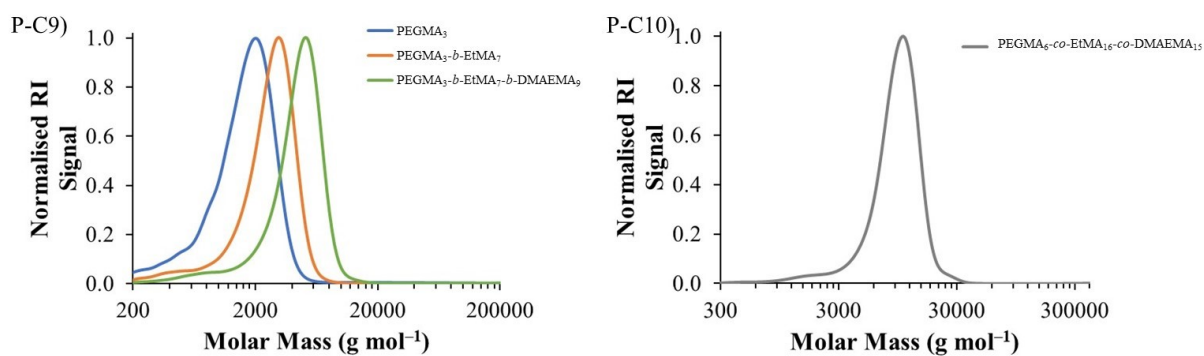
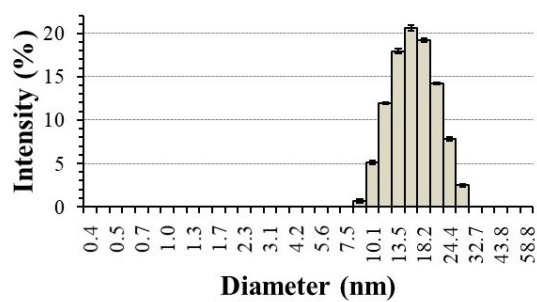
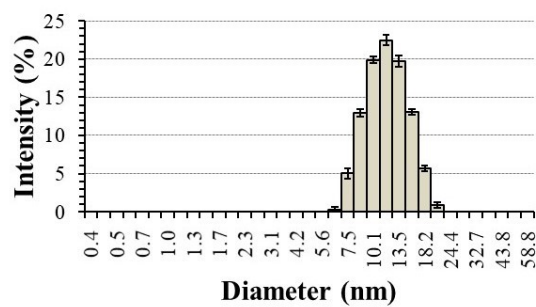


Figure 12. GPC histogram of PEGMA-EtMA-DMAEMA based copolymers of Polymer series 3. The blue, orange, and green lines represent the PEGMA homopolymer, diblock copolymer, and triblock copolymer, respectively. The grey lines represent statistical copolymer.

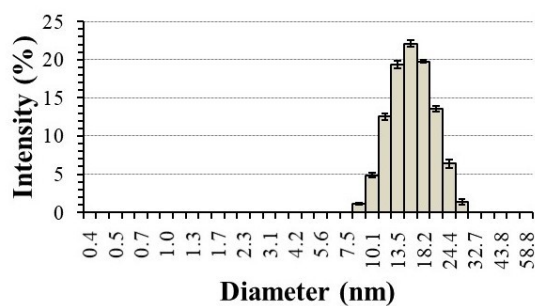
P-C1)



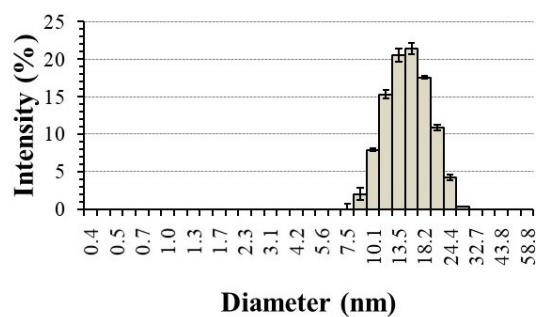
P-C2)



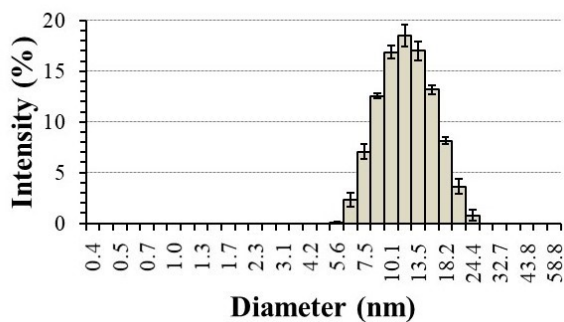
P-C3)



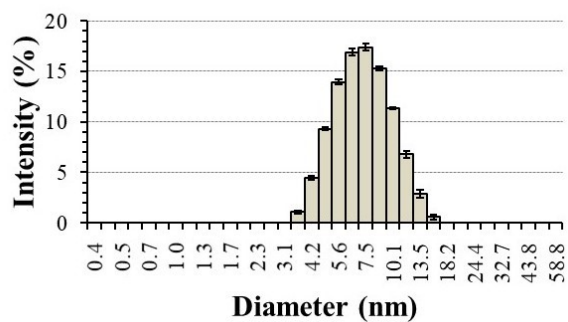
P-C4)



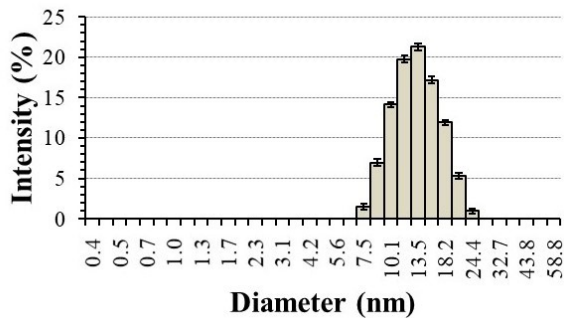
P-C5)



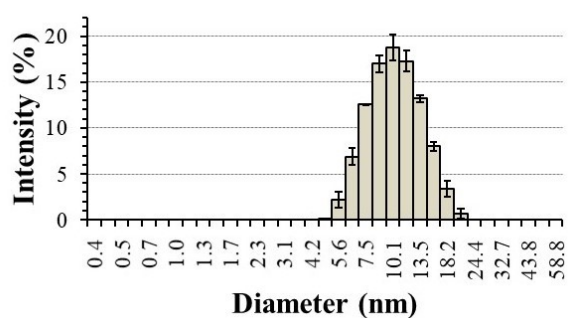
P-C6)



P-C7)



P-C8)



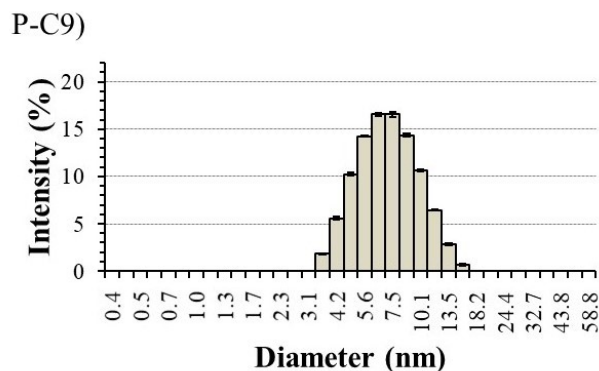


Figure 13. DLS histograms of PEGMA-*b*-EtMA-*b*-DMAEMA based triblock copolymers.

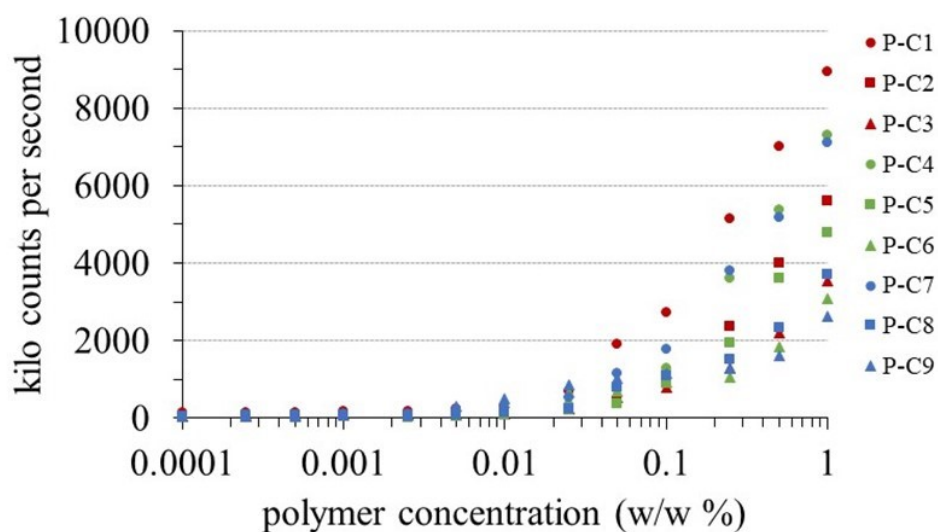


Figure 14. The graph shows the kilo counts per second versus polymer concentration. The targeted composition of triblock copolymers; 30-35-35, 30-30-40 and 30-25-45 w/w% are represented in red, green and blue, respectively. The circle (●), square (■) and triangle (▲) polymers of different MMs; 9000, 6000 and 3000 g mol⁻¹ are represented, respectively.

Table 6. The fraction of the cream phase-resolved for emulsions stabilised by PEGMA-b-EtMA-DMAEMA copolymers at different times.

PC1-PC10										
ϕ cream										
time (min)	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
1	0.948	0.948	0.942	0.939	0.965	0.962	0.951	0.907	0.910	0.953
120	0.915	0.926	0.948	0.918	0.922	0.962	0.921	0.907	0.893	0.942
240	0.909	0.912	0.949	0.917	0.904	0.949	0.923	0.902	0.891	0.936
720	0.865	0.888	0.922	0.881	0.878	0.914	0.884	0.867	0.712	0.882
2880	0.812	0.865	0.828	0.833	0.791	0.840	0.834	0.805	0.685	0.872
4320	0.766	0.746	0.762	0.764	0.757	0.808	0.78401	0.760	0.684	0.845
10080	0.735	0.700	0.721	0.684	0.687	0.742	0.718	0.69	0.641	0.737
20160	0.670	0.675	0.715	0.674	0.681	0.735	0.707	0.686	0.638	0.729
30240	0.668	0.669	0.709	0.668	0.669	0.722	0.699	0.682	0.630	0.678
40320	0.660	0.668	0.702	0.653	0.664	0.699	0.697	0.672	0.622	0.674

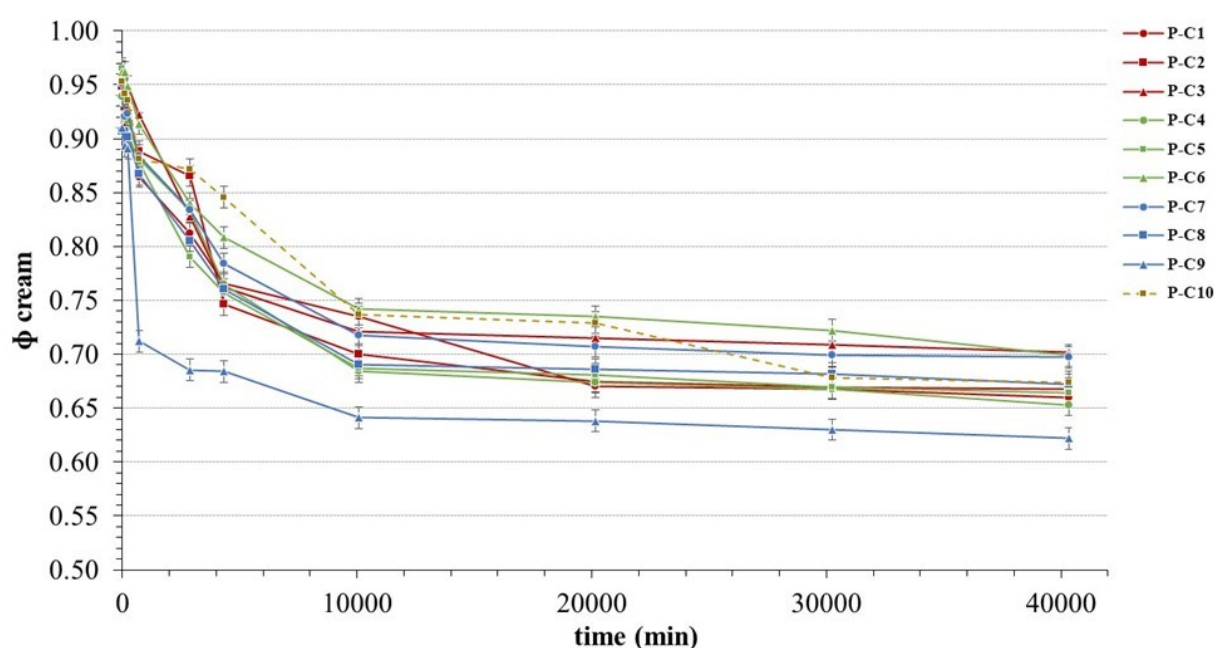


Figure 15. The graph shows the fraction of cream phase-resolved for PEGMA-EtMA-DMAEMA based copolymers over time. The targeted composition of diblock copolymers; 30-35-35, 30-30-40 and 30-25-45 w/w % are represented in red, green and blue, respectively. The statistical copolymer is represented in dark yellow. The circle (●), square (■) and triangle (▲) polymers of different MMs; 9000, 6000 and 3000 g mol⁻¹ are represented, respectively.

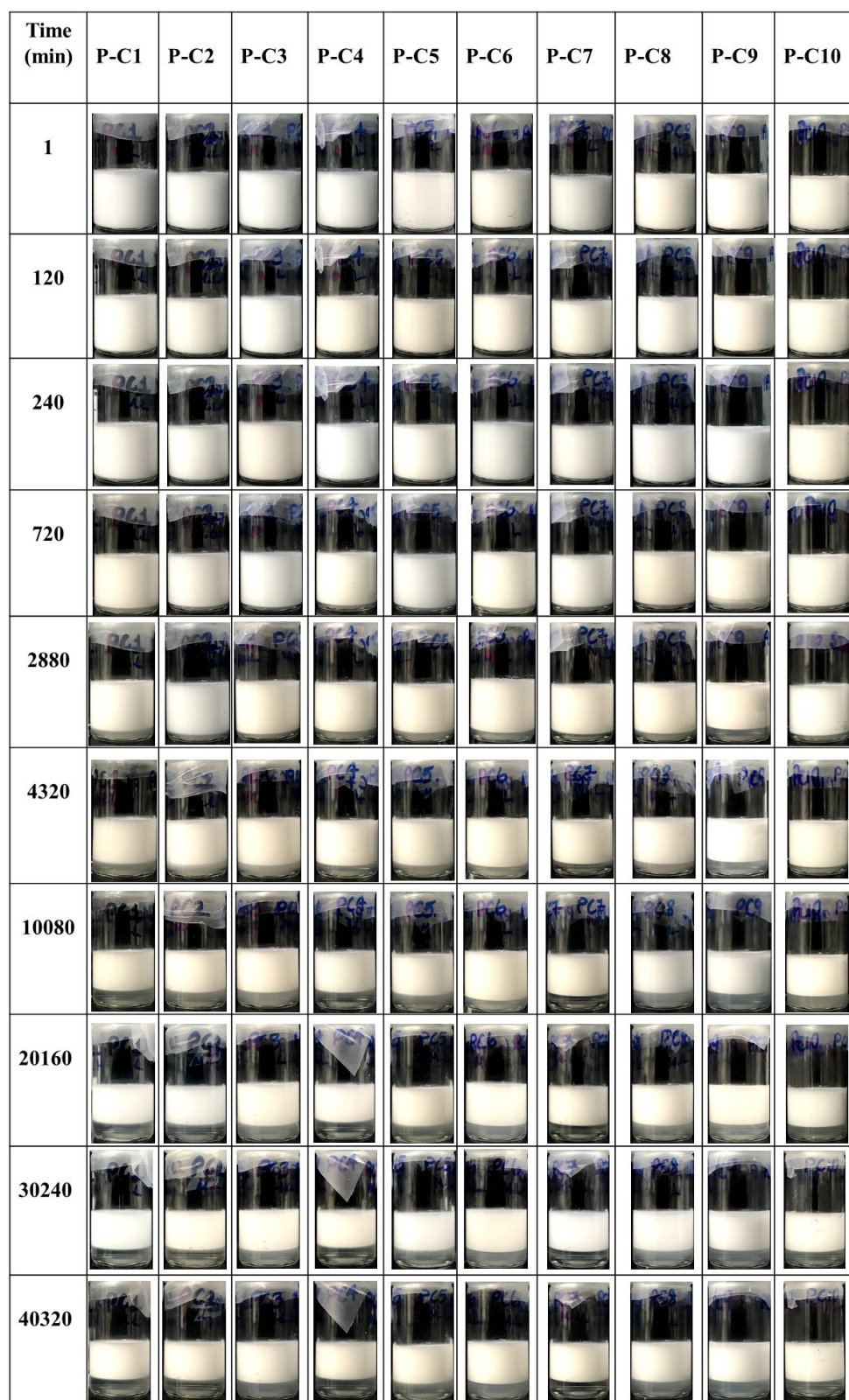


Figure 16. Images of emulsions taken at different time scales. A 1 w/w % copolymer was mixed with equal weights of methyl laurate and water.

Table 7. Size of the emulsion droplets for PEGMA-EtMA-DMAEMA based copolymers.

On the same day		
Polymer No.	Average diameter (μm)	Error (μm)
PC1	8.57	1.25
PC2	6.13	0.27
PC3	8.15	0.68
PC4	7.52	0.2
PC5	9.32	0.58
PC6	7.58	0.41
PC7	7.24	0.18
PC8	7.53	0.51
PC9	6.46	0.11
PC10	10.37	0.42

After 2 days		
Polymer No.	Average diameter (μm)	Error (μm)
PC1	7.18	0.1
PC2	7.75	0.24
PC3	7.74	0.15
PC4	7.6	0.15
PC5	6.66	0.21
PC6	6.9	0.15
PC7	7.51	0.13
PC8	6.93	0.1
PC9	7.19	0.1
PC10	5.81	0.25

After a week		
Polymer No.	Average diameter (μm)	Error (μm)
PC1	7.37	0.08
PC2	7.6	0.1
PC3	6.74	0.05
PC4	7.015	0.08
PC5	8.53	0.06
PC6	6.52	0.08
PC7	7.03	0.14
PC8	6.75	0.07
PC9	7.47	0.065
PC10	7.28	0.19

CHAPTER 6- APPENDIX

Chapter 6.						
P-H1: DMAEMA- <i>b</i> -MMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	53.4					
MTS				0.60	0.5148	0.002953
MMA	0.4	2400	23.97	7.52	7.09	0.071
DMAEMA	0.6	3600	22.90	11.40	10.63	0.068
Target MM	6000	6000				

Chapter 6.						
P-H2: BuMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	53.1					
MTS				0.60	0.5148	0.002953
BuMa	0.4	2400	16.78	7.88	7.09	0.050
DMAEMA	0.6	3600	22.90	11.40	10.63	0.068
Target MM	6000	6000				

Chapter 6.						
P-H3: HeMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF	52.7					
MTS				0.60	0.5148	0.002953
DMAEMA	0.6	3600	22.90	11.40	10.63	0.068
HexMA	0.4	2400	14.10	8.21	7.09	0.042
Target MM	6000	6000				

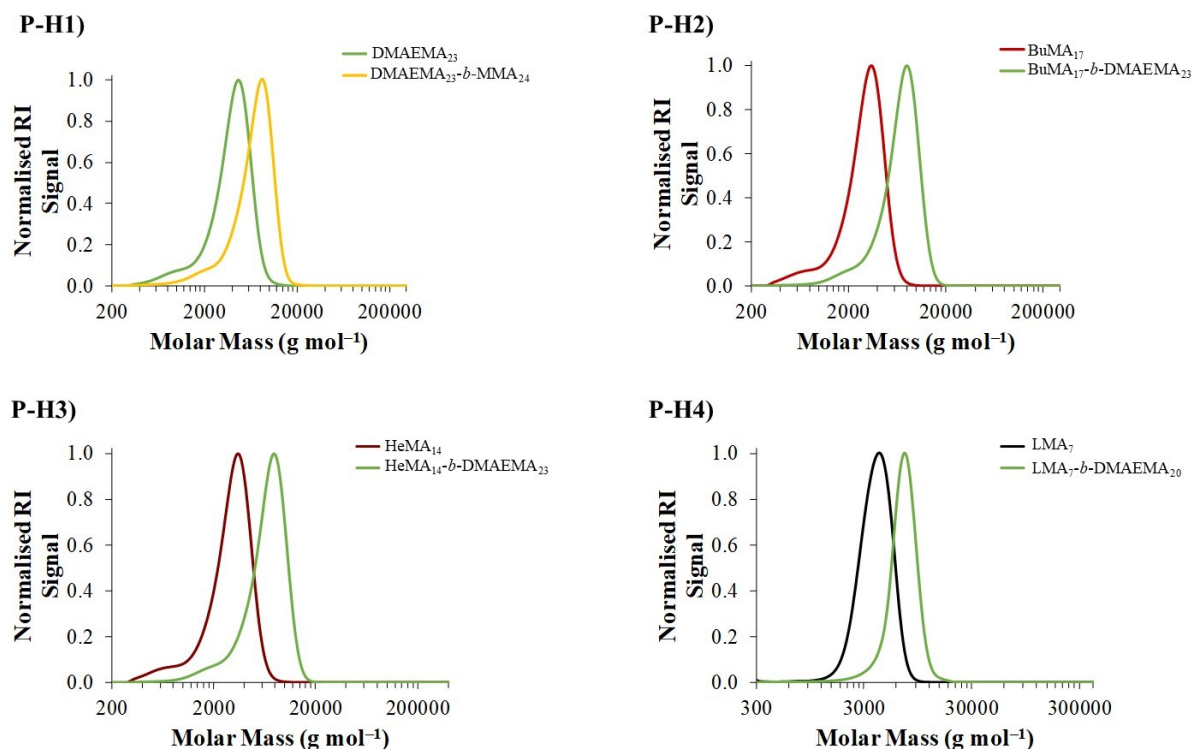


Figure 17. GPC histogram of DMAEMA based copolymers with different hydrophobic monomers. The hydrophobic monomers: MMA, BuMA, HeMA and LMA are represented in yellow, red, brown and black, respectively. The DMAEMA unit is represented in green.

Table 7. The fraction of the cream phase-resolved for DMAEMA based copolymers with different hydrophobic monomers. The P-H1, P-H2, P-H3 and P-H4 represents DMAEMA based copolymers with hydrophobic monomers: MMA, BuMA, HeMA and LMA, respectively.

time (min)	ϕ cream			
	P-H1	P-H2	P-H3	P-H4
1	0.967	0.938	0.96	0.951
120	0.772	0.929	0.91	0.91
1440	0.717	0.907	0.909	0.795
2880	0.7	0.785	0.756	0.773
10080	0.651	0.715	0.722	0.723

APPENDIX-CHAPTER 6

Table 8. The calculations of synthesised copolymers in this PhD study.

Chapter 6.						
P-D1: BuMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.1		
MTS				0.65	0.56	0.003
BuMA	0.5	3000	21.1	11	9.6	0.07
DMAEMA	0.5	3000	19.1	10.3	9.6	0.06
Target MM	6000	6000				

Chapter 6.						
P-D2: BuMA- <i>b</i> -DMAEMA- <i>b</i> -BuMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.1		
MTS				0.65	0.56	0.003
BuMA	0.25	1500	10.5	5.37	4.8	0.03
DMAEMA	0.5	3000	19.1	10.3	9.6	0.06
BuMA	0.25	1500	10.5	5.37	4.8	0.03
Target MM	6000	6000				
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.1		
MTS				0.65	0.56	0.003
DMAEMA	0.25	1500	9.54	5.14	4.8	0.03
BuMA	0.5	3000	21.1	10.7	9.6	0.07
DMAEMA	0.25	1500	9.54	5.14	4.8	0.03
Target MM	6000	6000				

Chapter 6.						
P-D4: BuMA- <i>b</i> -DMAEMA- <i>b</i> -BuMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.1		
MTS				0.65	0.56	0.003
BuMA	0.25	1500	10.5	5.37	4.8	0.03
DMAEMA	0.25	1500	9.5	5.14	4.8	0.03
BuMA	0.25	1500	10.5	5.37	4.8	0.03
DMAEMA	0.25	1500	9.5	5.14	4.8	0.03
Target MM		6000				

Chapter 6.

P-D5: BuMA- <i>co</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.1		
MTS				0.65	0.56	0.003
BuMA	0.5	3000	21.1	10.7	9.6	0.07
DMAEMA	0.5	3000	19.1	10.3	9.6	0.06
Target MM	6000	6000				

Chapter 6.						
P-D6: BuMA- <i>b</i> -(BuMA- <i>co</i> -DMAEMA)- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.1		
MTS				0.65	0.56	0.003
BuMA	0.17	1000	7.03	3.58	3.2	0.02
DMAEMA	0.33	2000	12.7	6.86	6.4	0.04
BuMA	0.33	2000	14.1	7.16	6.4	0.04
DMAEMA	0.17	1000	6.36	3.43	3.2	0.02
BuMA						
Target MM	6000	6000				

Chapter 6.						
P-D7: BuMA- <i>b</i> -(BuMA- <i>grad</i> -DMAEMA)- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.1		
MTS				0.65	0.56	0.003
BuMA	0.17	1000	7.03	3.58	3.2	0.02
DMAEMA	0.33	2000	12.7	6.86	6.4	0.04
BuMA	0.33	2000	14.1	7.16	6.4	0.04
DMAEMA	0.17	1000	6.36	3.43	3.2	0.02
Target MM		6000				

Chapter 6.						
P-D8: BuMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.3		
MTS				0.62	0.56	0.003
BuMA	0.25	1500	10.5	5.37	4.8	0.03
DMAEMA	0.75	4500	28.6	15.4	14.4	0.09
Target MM		6000				

Chapter 6.						
P-D9: BuMA- <i>b</i> -DMAEMA- <i>b</i> -BuMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.3		
MTS				0.62	0.56	0.003
BuMA	0.125	750	5.27	2.68	2.4	0.02
DMAEMA	0.75	4500	28.6	15.4	14.4	0.09
BuMA	0.125	750	5.27	2.68	2.4	0.02
Target MM		6000				

Chapter 6.						
P-D10: DMAEMA- <i>b</i> -BuMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.3		
MTS				0.62	0.56	0.003
DMAEMA	0.375	2250	14.3	7.72	7.2	0.05
BuMA	0.25	1500	10.5	5.37	4.8	0.03
DMAEMA	0.375	2250	14.3	7.72	7.2	0.05
Target MM		6000				

Chapter 6.						
P-D11: BuMA- <i>b</i> -DMAEMA- <i>b</i> -BuMA- <i>b</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.3		
MTS				0.62	0.56	0.003
BuMA	BuMA	0.125	750	5.27	2.68	2.4
DMAEMA	0.375	2250	14.3	7.72	7.2	0.05
BuMA	BuMA	0.125	750	5.27	2.68	2.4
DMAEMA	0.375	2250	14.3	7.72	7.2	0.05
Target MM		6000				

Chapter 6.						
P-D12: BuMA- <i>co</i> -DMAEMA						
Chemical Substance	Target wt%	MM block	DP	mL	g	Moles
THF				77.3		
MTS				0.62	0.56	0.003
BuMA	0.25	1500	10.5	5.37	4.8	0.03
DMAEMA	0.75	4500	28.6	15.4	14.4	0.09
Target MM		6000				

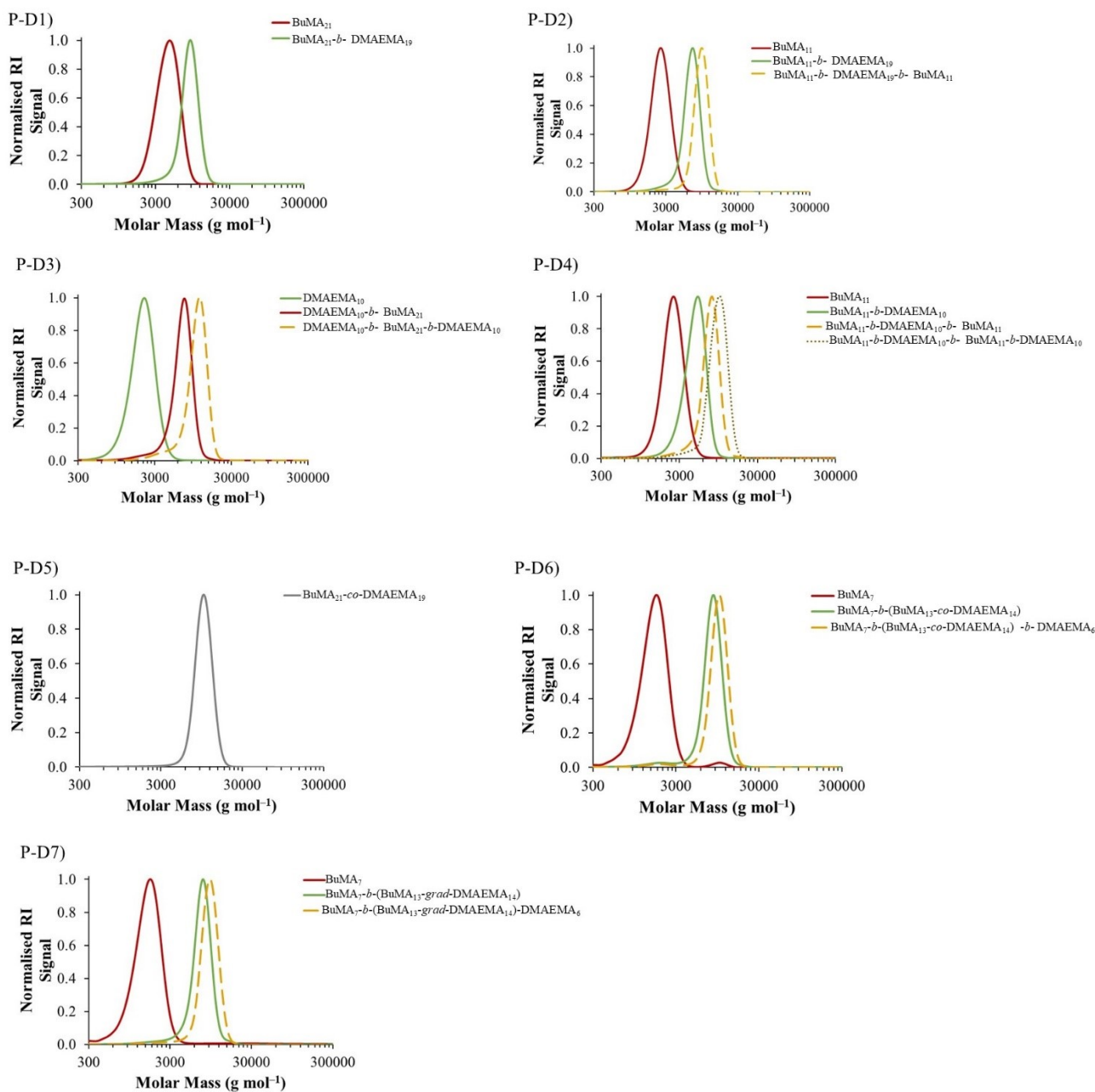


Figure 18. GPC histogram of DMAEMA-BuMA based copolymers of Family A.

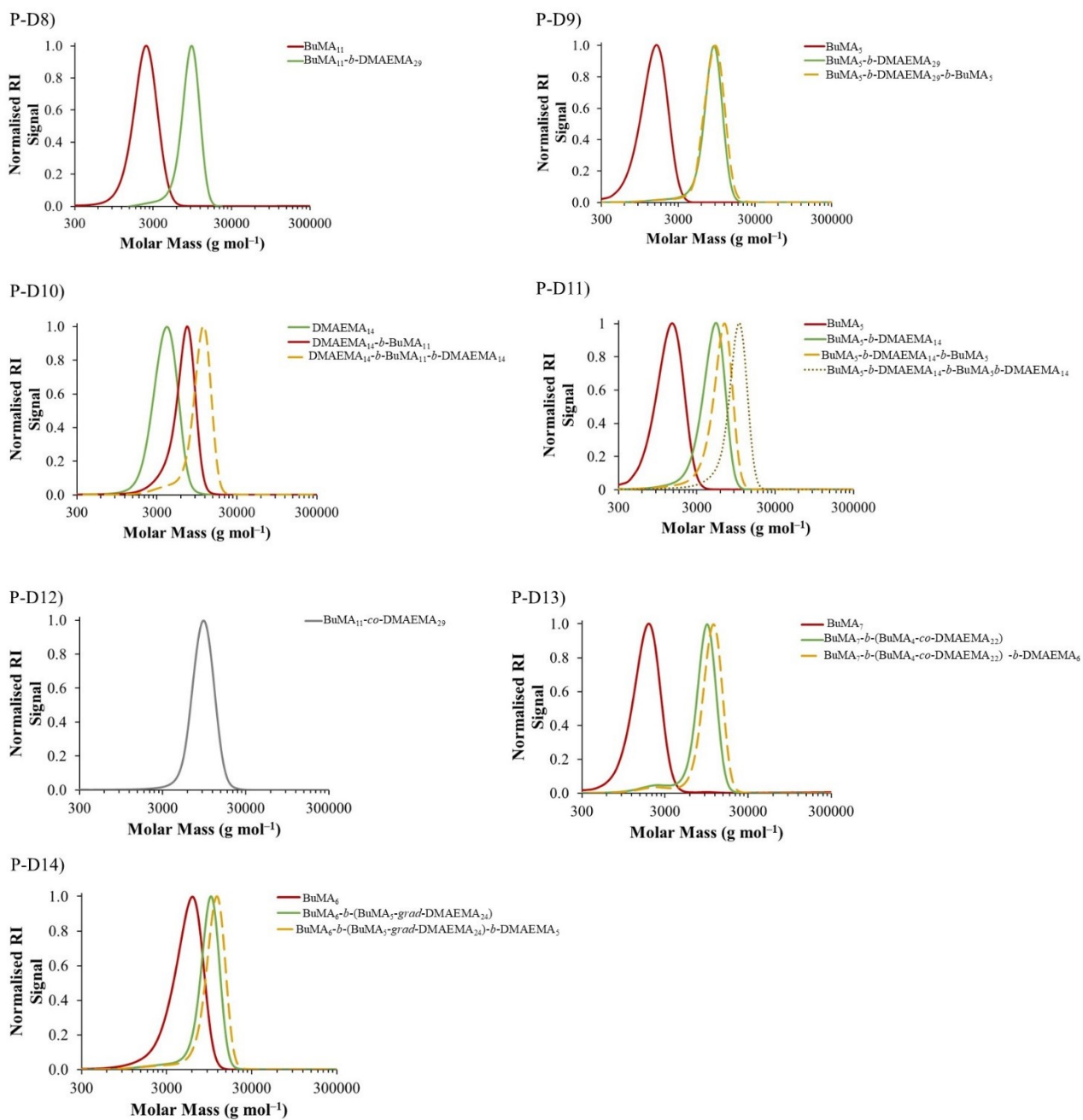


Figure 19. GPC histogram of DMAEMA-BuMA based copolymers of Family B.

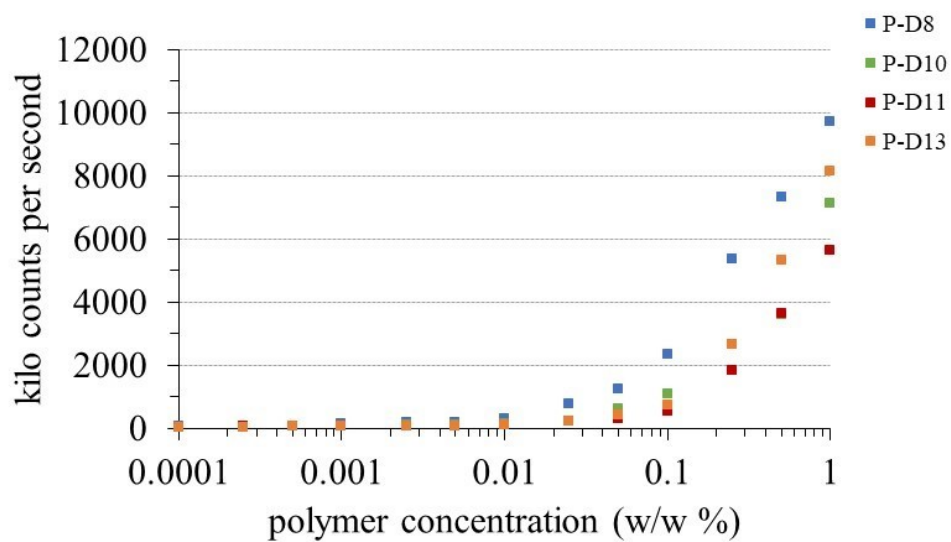


Figure 20. The CMC graph of BuMA-DMAEMA based copolymers with different architectures from Family B,

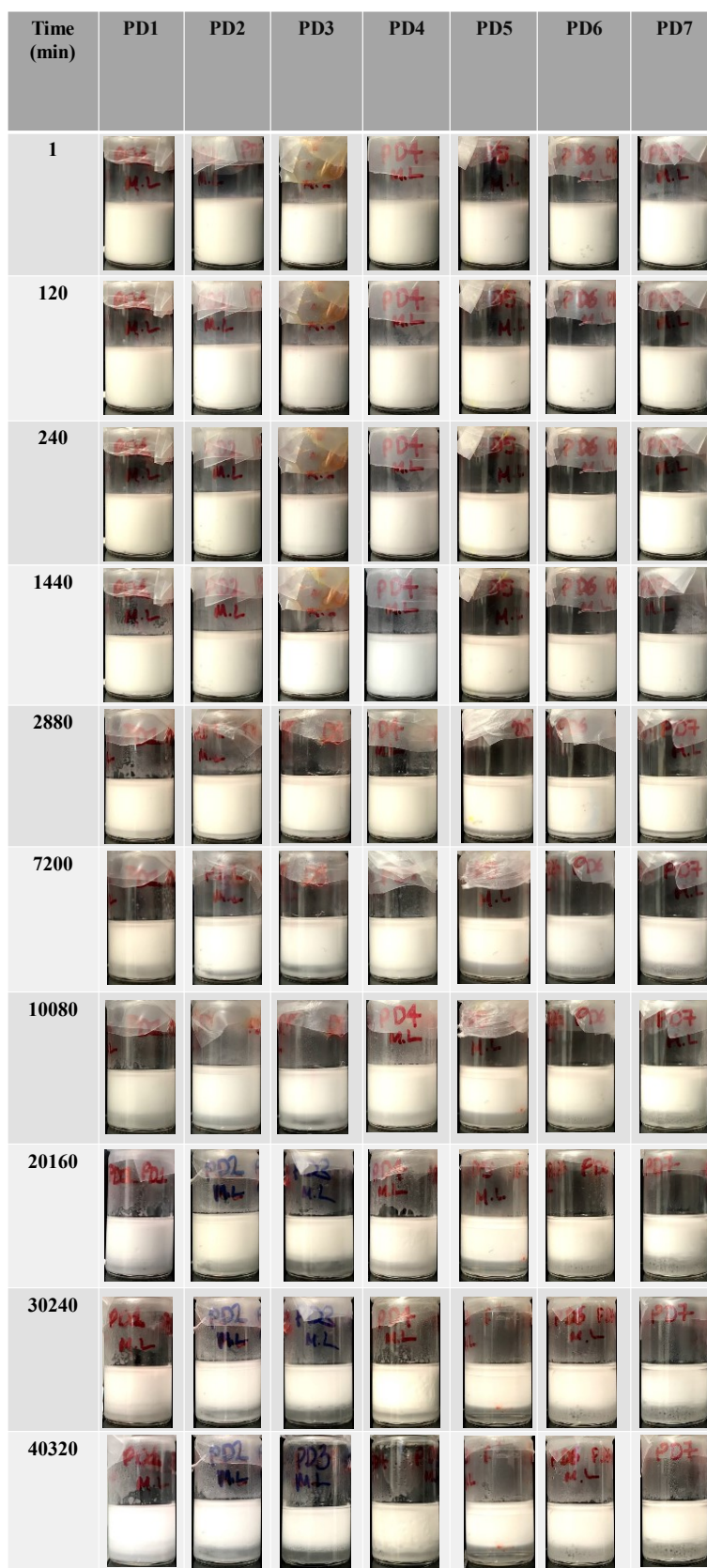


Figure 21. Images of emulsions taken at different time scales. A 1 w/w % copolymer was mixed with equal weights of methyl laurate and water.

Table 9. The fraction of the cream phase-resolved for BuMA-DMAEMA based copolymers (Family A) at different times.

PD1-PD7							
ϕ cream							
time (min)	D1	D2	D3	D4	D5	D6	D7
1	0.945	0.944	0.943	0.977	0.91	0.943	0.951
120	0.941	0.938	0.937	0.919	0.811	0.954	0.941
240	0.922	0.924	0.927	0.812	0.785	0.902	0.921
1440	0.809	0.864	0.784	0.802	0.773	0.80	0.803
2880	0.756	0.782	0.734	0.77	0.748	0.777	0.776
7200	0.675	0.703	0.639	0.718	0.580	0.622	0.640
10080	0.650	0.684	0.635	0.667	0.571	0.606	0.580
20160	0.607	0.654	0.635	0.641	0.550	0.591	0.537
30240	0.552	0.592	0.633	0.624	0.54	0.583	0.531
40320	0.526	0.577	0.630	0.621	0.529	0.576	0.517

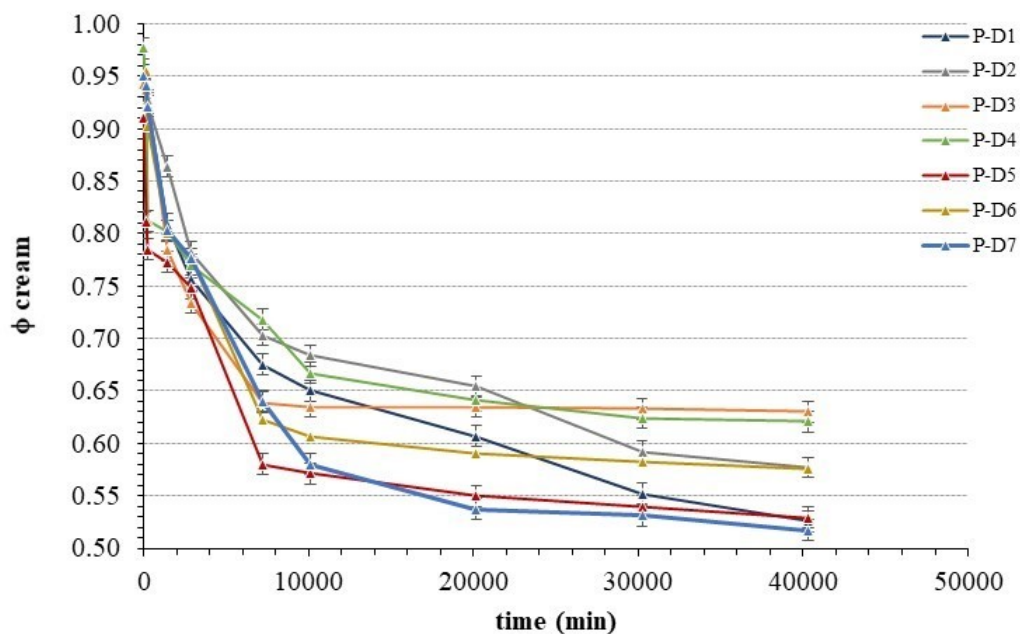


Figure 22. The graph shows the fraction of cream phase-resolved for BuMA-DMAEMA based polymers (Family A) over time.

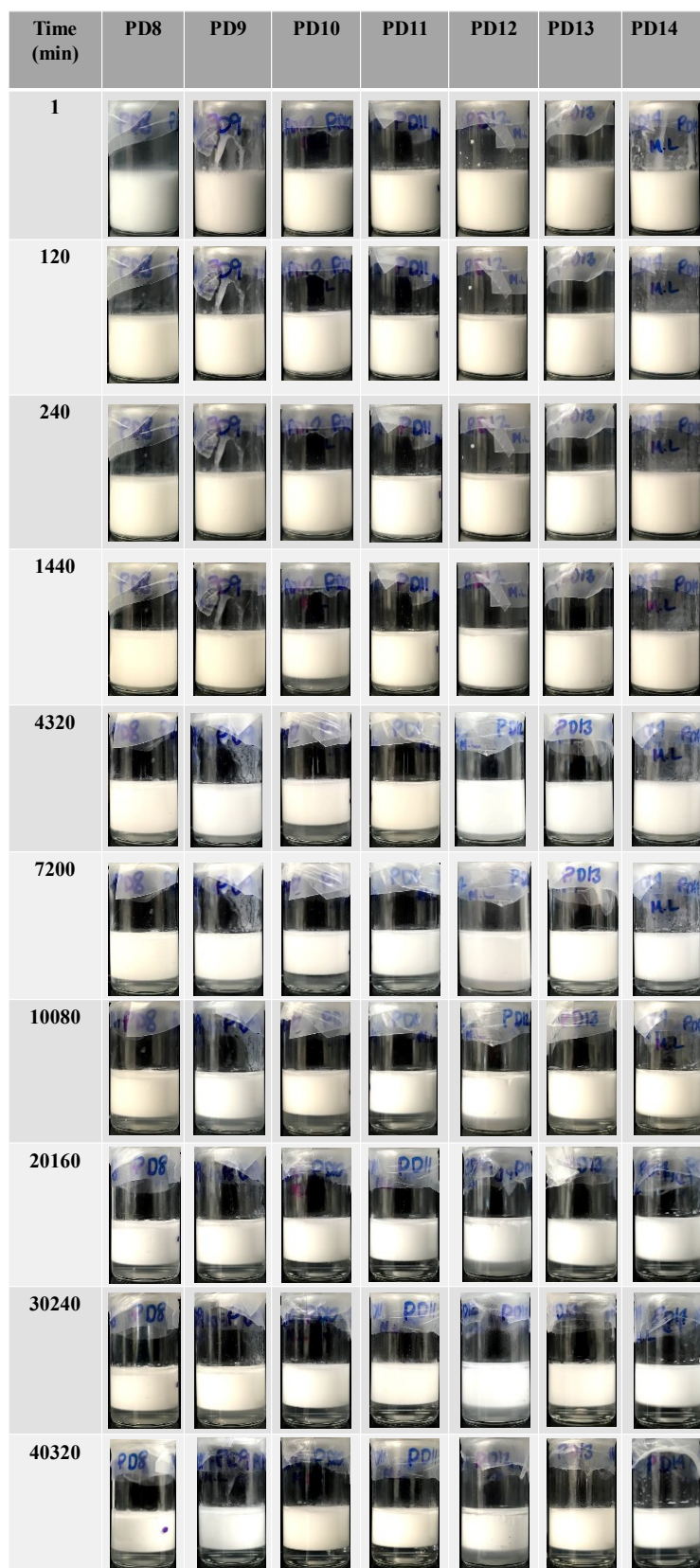


Figure 23. Images of emulsions taken at different time scales. A 1 w/w % copolymer was mixed with equal weights of methyl laurate and water.

Table 10. The fraction of the cream phase-resolved for BuMA-DMAEMA based polymers (Family B) at different times.

PD8-PD14							
ϕ cream							
time	D8	D9	D10	D11	D12	D13	D14
1	0.919	0.949	0.933	0.923	0.945	0.93	0.937
120	0.906	0.897	0.89	0.894	0.916	0.928	0.918
240	0.902	0.904	0.879	0.877	0.915	0.917	0.916
1440	0.812	0.860	0.744	0.850	0.840	0.882	0.862
4320	0.732	0.791	0.670	0.746	0.797	0.850	0.818
7200	0.684	0.743	0.669	0.692	0.731	0.782	0.780
10080	0.636	0.704	0.664	0.667	0.653	0.734	0.731
20160	0.633	0.675	0.664	0.636	0.641	0.715	0.685
30240	0.632	0.653	0.660	0.631	0.629	0.710	0.682
40320	0.625	0.641	0.659	0.618	0.598	0.702	0.637

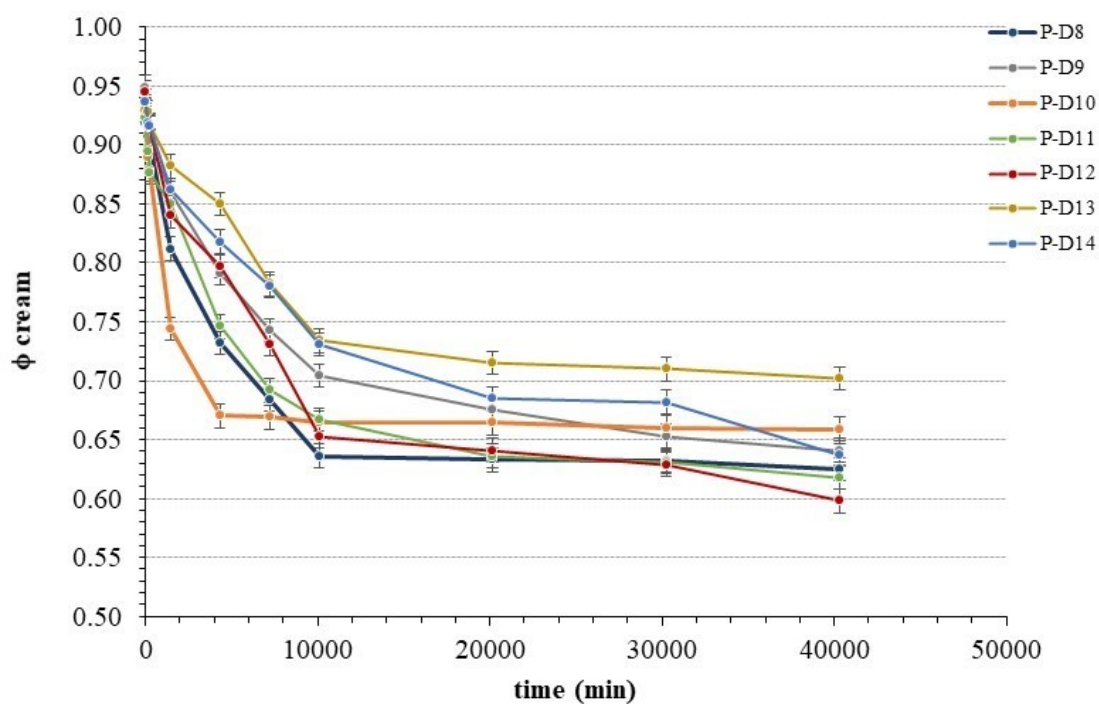


Figure 24. The graph shows the fraction of cream phase-resolved for BuMA-DMAEMA based polymer series (Family B) over time.

