RESEARCH ARTICLE

An environmentally friendly synergistic stabilization of emulsions using an ABC macrosurfactant and hydroxypropyl methylcellulose

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Abstract

Here, a series of non-ionic ABC based on the hydrophilic oligo- and di-(ethylene glycol) methyl ether methacrylate (OEGMA300/A and DEGMA/C), and the hydrophobic *n*-butyl methacrylate (BuMA, B) are investigated as macrosurfactants. Polymers of constant composition, and four varying molar masses (MM) were synthesized via group transfer polymerization. The higher the MM, the bigger the micelles in aqueous media, and the lower the critical micellization concentration and the stability of oil-in-water emulsions. The best-performing macrosurfactant was investigated under different conditions and it was proven that the oil phase volume fraction, and surfactant concentration strongly control the emulsion stability. The macrosurfactants show minimal dependence on the salinity of the water phase, thus offering suitability in preparation of emulsion in environments with different hardness. Emulsions stabilized by both the macrosurfactant and hydroxypropyl methylcellulose (HPMC), a naturally derived viscosity modifier, present a classical non-Newtonian behavior; the viscosity increased when increasing the MM of the HPMC. The emulsion stabilization is attributed to the synergistic steric stabilization provided by the macrosurfactant and the increased viscosity and formation of an entangled network by HPMC. This formulation leads to emulsion stability over 65% 1 year after emulsification, highlighting its potential use in commercial applications.

KEYWORDS
ABC triblock terpolymers, emulsions, polymeric macrosurfactants, viscosity modifier

1 | INTRODUCTION

Emulsions are defined as dispersions of two immiscible liquids, one of which is dispersed in the form of droplets in the second liquid, known as the continuous phase, with milk being the most stable emulsion in nature.[1]

There are two main types of emulsions, depending on the chemical nature of the dispersed and continuous phases: (i) oil-in-water (O/W) emulsions, in which the oil phase is dispersed as droplets in the continuous aqueous phase, and (ii) water-in-oil (W/O) emulsions, in which the water phase is dispersed as droplets in the continuous oil

phase.[1] Another type of emulsions, which received considerable attention owing to their increased biocompatibility, is water-in-water (W/W) emulsions, which are formed by two incompatible aqueous solutions of polymers.[2–4] Pickering emulsions, where stabilization is achieved via solid particles, have also been widely reported in the literature.[5–7] Emulsions find use in several applications, such as in food industry,[8] and enhanced oil recovery.[9] Emulsions are also used in healthcare applications as drug carriers, by solubilizing hydrophobic drugs and thus increasing their bioavailability.[10] Another use of emulsions is in the agriculture sector, with pesticide and herbicide delivery for plant treatments.[1]

Emulsions are thermodynamically unstable dispersions, with the tendency to phase separate into the two immiscible liquid phases.[8] Emulsifiers, such as small surfactant molecules, proteins, colloidal particles and polymeric macrosurfactants, are normally used to provide stability.[8,11] Emulsion stabilization is known to be achieved by several factors, such as lowering the interfacial tension, providing steric and/or electrostatic repulsion (the former is known as electrosteric), or by increasing the viscosity of the continuous phase.[12] While small surfactant molecules can reduce the interfacial tension, non-ionic polymeric macrosurfactants provide steric stabilization.[11–13]

The most well-studied polymeric macrosurfactants are diblock and triblock copolymers, with Pluronic® polymers being extensively used as dispersing and emulsifying agents.[11] Pluronic® polymers are ABA triblock copolymers consisting of ethylene glycol (EG, A block) and propylene glycol (PG, B). The architecture of the polymeric macrosurfactants plays an important role in emulsion applications with Pluronic® polymers being extensively reported in the literature for stabilizing O/W emulsions,[14,15] while their BAB counterparts featuring reverse micellisation process, may be best suited for stabilizing W/O emulsions.[11,16] The importance of block position isomerism in emulsions is highlighted by the ABA Pluronic® polymers showing de-emulsification properties on O/W emulsions, while this is not observed for the BAB analogues.[17] Methacrylate block copolymers were also investigated as emulsifiers.[18–22] While diblock copolymers based on benzyl methacrylate (BzMA) and hexa(ethylene glycol) methyl ether methacrylate (HEGMA) stabilized O/W emulsions,[20] the type of emulsions stabilized by star copolymers based on the same units was dependent on the hydrophilic content that is, star copolymers with higher hydrophilic content stabilized O/W emulsions, and star copolymers with higher hydrophobic content stabilized W/O emulsions.[18] When DMAEMA was introduced into the structure to form ionic amphiphilic macrosurfactants with ABC, ACB and BAC architecture, O/W emulsions were formed, with the ABC architecture being the most efficient emulsifier.[19] Despite their random

architecture, and thus lack of distinct blocks of different hydrophilicity, random amphiphilic copolymers based on vinyl ethers were also reported for emulsion stabilization.[23]

Hydroxypropyl methylcellulose (HPMC) is a non-ionic water-soluble polymer, which is often used as thickener[24] and emulsifier.[25,26] HPMC is a synthetic modification of the natural polymer cellulose, with hydroxypropyl and methyl substitutions on the glucose monomer,[24,27] and it is FDA approved to be used as both direct and indirect food additive, thus confirming its safe use.[24] In addition, HPMC presents reversible thermogelation upon heating, unlike other natural polymers, such as gelatin, which undergo reversible thermogelation upon cooling.[26,28] The introduction of the hydrophobic moieties on the glucose unit renders this polymer surface active by lowering the interfacial tension.[25,27]

When ionic methacrylate triblock terpolymers were previously studied as emulsifiers, it has been proven that the architecture with the hydrophobic block in the center favors emulsion stability.[19] Here, to produce an environmentally friendlier alternative, we have synthesized and present a new family of non-ionic ABC polymeric macrosurfactants, with a central hydrophobic block (B), and two outer hydrophilic blocks of different chemical nature (A and C). In this study, the B block consists of n-butyl methacrylate (BuMA), while the A and C blocks are based on poly(ethylene glycol) (PEG) methacrylate units, namely di(ethylene glycol) methyl ether methacrylate (DEGMA, C), and oligo(ethylene glycol) methyl ether methacrylate with average M_n 300 g mol^{-1} (OEGMA300, A) (Figure 1A). While we have previously investigated biocompatible copolymers based on the same combination of units as thermogelling agents in aqueous solutions,[29,30] their emulsifying properties are yet to be studied. Therefore, in the current study, we have designed and synthesized via group transfer polymerization (GTP) ABC triblock terpolymers with constant composition (A-B-C = 40-35-25 w/w%) and four different molar mass (MM) values to systematically investigate the effect of MM on the emulsifying properties (Figure 1B). Methyl oleate (MO) was used as the oil phase, as it is considered a non-hazardous compound, to produce an environmentally friendly system (Figure 1C) schematically shows the emulsification process and proposed stabilization mechanism of emulsions by the in-house synthesized macrosurfactants. To fully harness their potential, the effects of water to MO volume ratio, macrosurfactant concentration and ionic strength on the stability of the best-performing macrosurfactant have been investigated. To provide additional stabilization by increasing the viscosity of the aqueous phase in O/W emulsions, HPMC was introduced into the system, which is known to be used as thickener.[24] The effects of MM of HPMC and its concentration on the emulsion stability have been studied, and rheological measurements were
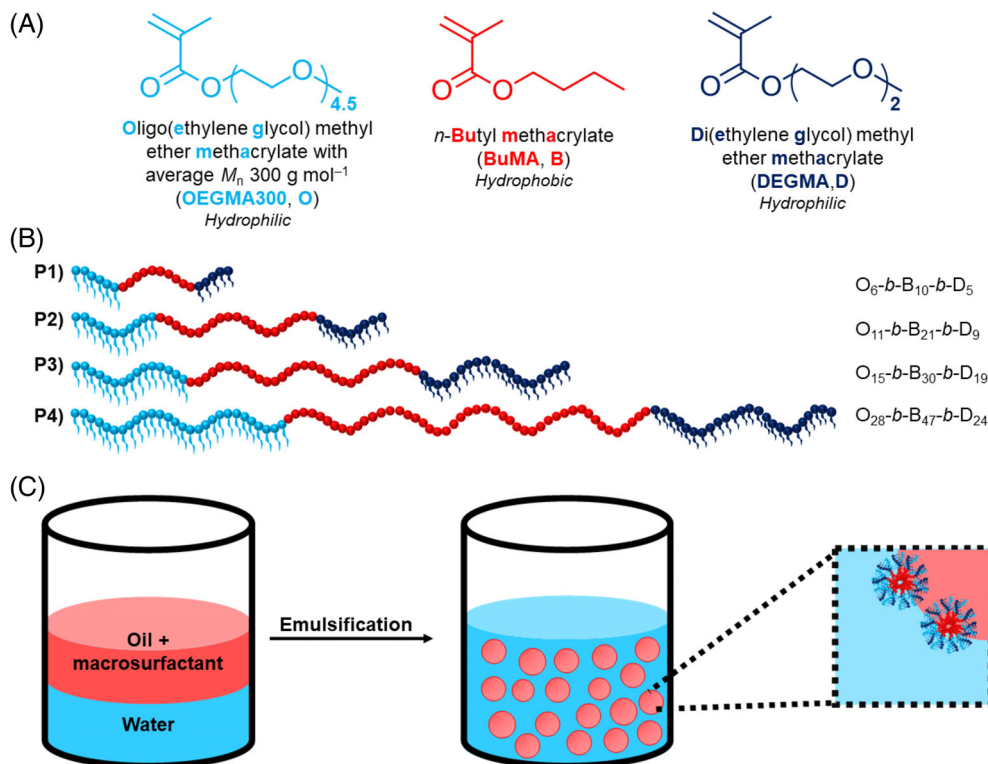
FIGURE 1 (A) Chemical structures of the monomers used for the synthesis of the ABC macrosurfactant. (B) Schematic of the experimental polymer structures of the ABC macrosurfactants synthesized in the current study. (C) Schematic showing the emulsification process and stabilization of oil in water emulsions using the in-house synthesized ABC non-ionic polymeric macrosurfactant.

performed to provide further insights on the behavior of the emulsions. The findings are discussed below.

2 │ RESULTS AND DISCUSSION

2.1 │ Chemical structure of the in-house synthesized macrosurfactants

The macrosurfactants have been in-house fabricated via GTP by sequential addition of the monomers to form triblock terpolymers, as shown in Figure 2.

The chemical structures of the in-house synthesized macrosurfactants and their precursors were determined by gel permeation chromatography (GPC) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, and the results are summarized in Table 1. The M_n values were consistently higher than the targeted MM values, a feature attributed to the deactivation of the initiator molecules, often observed when oligo(ethylene glycol) methyl ether methacrylate (OEGMA) macromonomers are used.[31,32] Most importantly, the GPC traces show monomodal distribution, with final Đ values between 1.12 and 1.17, and shift of the peak to higher MM as the polymerization progresses from the OEGMA300 homopolymer, to OEGMA300-*b*-BuMA diblock copolymer to the final OEGMA300-*b*-BuMA-*b*-DEGMA triblock terpolymer (Figures 3 and S1). This indicates the successful chain extension and formation of the desired triblock terpolymers. The compositions of the different repeated units were obtained as targeted, within the error of the technique, and the ^{1}H NMR spectra of P1, namely OEGMA300$_6$-*b*-BuMA$_{10}$-*b*-DEGMA$_5$, and its precursors are shown in Figure S2. In conclusion, four macrosurfactants have been successfully synthesized via GTP, with controlled molecular mass distributions and compositions, and varied M_n values, as desired.

2.2 │ Aqueous solution properties

While P1, P2, and P3 were water-soluble, thus enabling their characterization in aqueous solutions, P4 with M_n 19,700 g mol^{-1} was not soluble in water, thus further characterization in aqueous solvents was not feasible. It should be noted that in this polymer design, both OEGMA300 and DEGMA are considered hydrophilic, even though DEGMA homopolymer presents thermoresponse varying from 30 to 27°C as the M_n increases from 3300 to 13,900 g mol^{-1}.[33] Thus, the insolubility of P4 may be attributed to the low cloud point of the long DEGMA block when copolymerized with the hydrophobic BuMA and hydrophilic OEGMA300, leading to increased hydrophobicity of the structure.

2.2.1 │ Hydrodynamic diameter

The solutions of the water-soluble macrosurfactants at 1 w/w% in DI water were tested, which revealed their

FIGURE 2 Schematic showing the synthetic protocol followed for the fabrication of the ABC macrosurfactants via group transfer polymerization (GTP) with tetrabutylammonium bibenzoate (TBABB) as the catalyst, tetrahydrofuran (THF) as the solvent and methyl trimethylsilyl dimethylketene acetal (MTS) as the initiator.
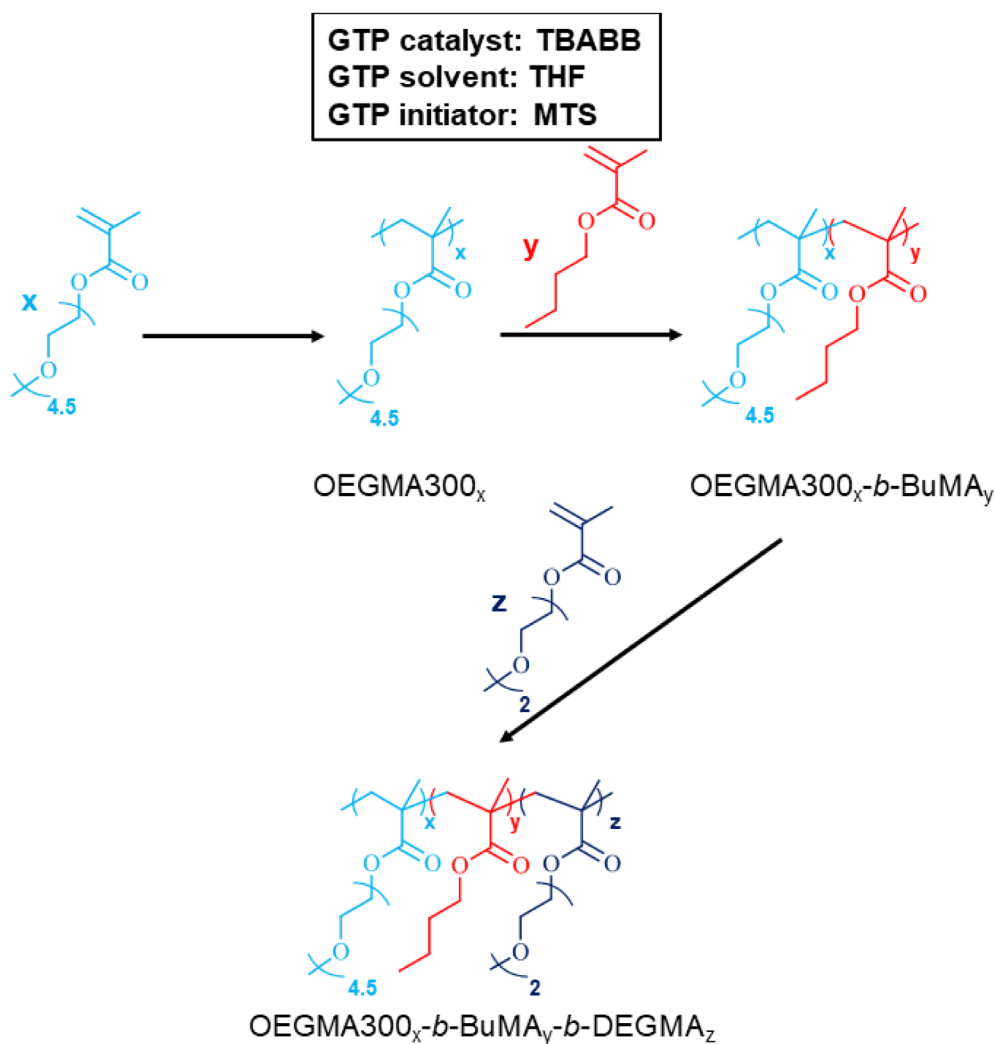
self-assembly into micelles, with hydrodynamic diameter (d_h) varying between 10 and 25 nm (Table 2 and Figure S3). As previously reported on similar systems,[29] the d_hs are slightly higher than the theoretical (calculated) values, as the theoretical calculations assume complete overlap of the hydrophobic BuMA block and neglect the contributions arising from the lengthy OEGMA300 side chains. Interestingly, monomodal distribution is observed, with polydispersity indices (PDI) varying between 0.069 and 0.134, and no unimers are detected neither by Intensity nor by Number, indicating the potency of our macrosurfactants in self-assembling into well-defined micelles. By increasing the MM of the surfactants from 4100 to 12,100 g mol^{-1}, and thus the length of the polymer chain, one would expect the size of the micelles to increase from P1 to P3. Even though P3 with M_n 12,100 g mol^{-1} self-assembles into structures bigger than P2 with M_n 7900 g mol^{-1} that is, 24.4 nm versus 15.7 nm, P1 with M_n 4100 g mol^{-1}, does not follow this trend, as it forms micelles of 21 nm size. However, one should bear in mind that the dynamic light scattering (DLS) size measurements were performed at 25 °C, a

temperature close to the cloud point (CP) of P1 (27 °C), as it will be discussed in the relevant section. To validate the hypothesis, we performed DLS on the solution of P1 at 20 °C, which revealed d_h values by Intensity and by Number at 14 and 9 nm, respectively (Figure S4). This proves that by increasing the length of the polymer chain, the size of the micelles increases, as expected, and observed before.[20,21,34]

2.2.2 | Cloud point

As both DEGMA and OEGMA300 are thermoresponsive in aqueous solutions at around 30 and 75 °C, respectively, MM-dependent,[33] we have investigated the CP of 1 w/w% aqueous solutions by turbidimetry (Table 2 and Figure S5). These experiments revealed CP values of our macrosurfactants increasing from 27 to 35 to 42 °C, as the MM increases from 4100 to 7900 to 12,100 g mol^{-1}, respectively. This trend agrees with previous observations on non-ionic surfactants,[20,22,34] including Pluronic® polymers.[35] Interestingly, P2, with M_n value determined at

TABLE 1 Targeted structural characteristics, namely polymer structures, molar masses ($MM^{theor.}$) and compositions, and experimental structural characteristics, namely number average molar mass (M_n), dispersity indices ($Đ$), compositions and final polymer structures.

No.	Targeted			Experimental			
	Polymer structure[a]	Molar mass (g mol^{-1})[b]	O-B-D (w/w%)[c]	M_n (g mol^{-1})[b]	$Đ$[b]	O-B-D (w/w%)[c]	Final polymer structure[d]
P1	O_3	1100	100-00-00	1800	1.17	100-00-00	O_6-b-B_{10}-b-D_5
	O_3-b-B_6	1975	53-47-00	2800	1.15	54-46-00	
	O_3-b-B_6-b-D_3	2600	40-35-25	3800	1.13	41-34-25	
				4100[e]	1.14		
P2	O_6	2020	100-00-00	2900	1.18	100-00-00	O_{11}-b-B_{21}-b-D_9
	O_6-b-B_{12}	3700	53-47-00	5500	1.17	51-49-00	
	O_6-b-B_{12}-b-D_6	4900	40-35-25	7000	1.19	40-38-22	
				7900[e]	1.17		
P3	O_{11}	3380	100-00-00	4900	1.09	100-00-00	O_{15}-b-B_{30}-b-D_{19}
	O_{11}-b-B_{20}	6250	53-47-00	8900	1.10	51-49-00	
	O_{11}-b-B_{20}-b-D_{11}	8300	40-35-25	11,300	1.13	36-35-29	
				12,100[e]	1.12		
P4	O_{16}	4900	100-00-00	7300	1.06	100-00-00	O_{28}-b-B_{47}-b-D_{24}
	O_{16}-b-B_{30}	9100	53-47-00	14,000	1.08	55-45-00	
	O_{16}-b-B_{30}-b-D_{16}	12,100	40-35-25	17,900	1.12	43-34-23	
				19,700[e]	1.14		

Note: O, B and D stand for oligo (ethylene glycol) methyl ether methacrylate with average M_n 300 g mol^{-1}, n-butyl methacrylate and di(ethylene glycol) methyl ether methacrylate, respectively.

[a]The theoretical MM is calculated using the following equation: $MM^{theor.}(g\,mol^{-1}) = \left(\sum_i MM_i \times DP_i\right) + 100$; 100 g mol^{-1} is the MM of the MTS part that stays on the polymer chain after the completion of dissociative GTP.

[b]The number-average molar mass (M_n) and the dispersity index ($Đ$) were determined by GPC.

[c]The compositions were determined by ^{1}H nuclear magnetic resonance (NMR) spectroscopy.

[d]The experimental polymer structure was calculated by taking into consideration the M_n values after precipitation, as resulted by GPC, and the experimental compositions, as resulted by ^{1}H NMR.

[e]The results correspond to the final polymers after precipitation.

7900 g mol^{-1}, presents a two-step thermoresponsive behavior, as revealed by the transmittance changes (Figure S5). Specifically, the transmittance drops to around 20% at 35 °C, where it remains relatively stable up to 45 °C, at which a final drop to 0% is observed. We have previously observed by small-angle neutron scattering (SANS) for a similar system, namely OEGMA300$_{15}$-b-BuMA$_{26}$-b-DEGMA$_{13}$, temperature-driven elongation of the micelles leading to gelation.[30] Therefore, the currently observed two-step thermoresponsive behavior may be related to formation of cylindrical structures at the cloud point value, which preserve the stability of the self-assembled structures in solution, followed by complete phase separation upon further heating.

2.2.3 | Critical micellization concentration

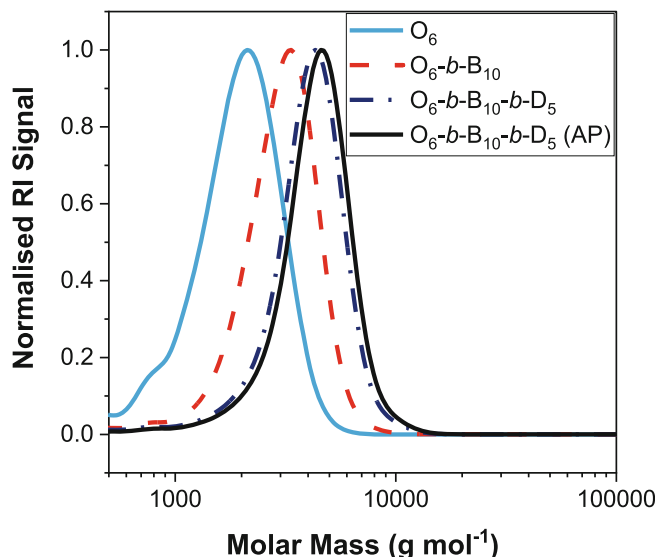The critical Micellization concentration (CMC) values of the water-soluble macrosurfactants were also investigated via DLS (Table 2 and Figure S6). It is observed that increasing the MM of the macrosurfactant from 4100 to 12,100 g mol^{-1} decreases the CMC value from 15×10^{-5} M to 2×10^{-5} M, as expected.[22,34,35] These values are within the range of previously reported CMC values for macrosurfactants (ranging from 10^{-9} to 10^{-4} M),[36–38] including Pluronic® polymers,[35] which are extensively used surfactants in industry, thus indicating the potential use of our polymers as surfactants. This feature is advantageous over conventional surfactants (CMC within 10^{-3} to 1 M),[38,39] as low concentrations of polymers will lead to micellization, with dilution possibly not interfering with the self-assembly, which is not the case for classical surfactants, due to their high CMC values.[38]

2.3 | Hydrophile–lipophile balance

Hydrophile–lipophile balance (HLB) is an important parameter that characterizes the surfactants, introduced

by Griffin in 1949, to predict whether a surfactant will produce O/W or W/O emulsions.[40,41] For example, when a surfactant is highly hydrophobic, it will preferably be dissolved in the oil phase, which will be the continuous phase, thus producing W/O emulsions.[40] Similarly, when the surfactant is highly hydrophilic, the continuous phase will be water, thus O/W emulsions will be produced. Surfactants with HLB values between 10 and 13 are predicted to form a translucent to clear dispersion, leading to O/W emulsion type, while surfactants with HLB values higher than 13 will form a clear solution, stabilizing O/W emulsions.[40] The surfactants synthesized in the current study have similar HLB values at around 12–13, as expected due to their similar composition values. Interestingly, our water-soluble surfactants dissolve in water and produce O/W emulsions, agreeing with the expected properties of their calculated HLB values.

## 2.4 | Stabilization of emulsions by the macrosurfactants

In this study, we investigated the stability of emulsions based in water and MO, a non-hazardous and environmentally friendly oil phase. However, we believe that these macrosurfactants could be used to stabilized emulsions with a different oil phase, and specifically methyl laurate, as we have previously reported the emulsifying performance of diblock copolymers based on OEGMA300 and ethyl methacrylate in methyl laurate/water emulsion systems.[22] P1–P3 were soluble in both water and MO, while P4, with M_n 19,700 g mol^{-1}, was neither water- nor MO-soluble, presumably due to its increased MM. Therefore, P4 was not used for emulsion stabilization.

2.4.1 | Effect of the MM of the macrosurfactants on the stability

The effect of the MM of the macrosurfactants on the stability of emulsions was systematically investigated by

FIGURE 3 Gel permeation chromatography (GPC) traces of Polymer 1, with experimental polymer structure oligo- and di-(ethylene glycol) methyl ether methacrylate (OEGMA)300$_6$-*b*-BuMA$_{10}$-*b*-DEGMA$_5$ before and after precipitation in dark blue dashed dotted and black solid lines, respectively. The GPC traces of its precursors are also presented: OEGMA300$_6$ in light blue, and OEGMA300$_6$-*b*-BuMA$_{10}$ in red dashed line.

TABLE 2 Experimental polymer structures, and aqueous solution properties of the ABC macrosurfactants: hydrodynamic diameters (d_hs), polydispersity indices (PDI), and cloud points, as resulted by analysis in 1 w/w% polymer solutions in deionized water, critical micelle concentration (CMC) values and hydrophile–lipophile balance values.

| | | Hydrodynamic diameter (d_h, nm) | | | | | | |
| | | | Exp. ±1[c] | | | | | |
No.	Experimental polymer structure[a]	Theor.[b]	By intensity	By number	PDI	Cloud points (CP, °C) ±1[d]	CMC values (×10^{-5} M)	HLB values
P1	O$_6$-*b*-B$_{10}$-*b*-D$_5$	5.3	21	12	0.069	27	15	13.2
P2	O$_{11}$-*b*-B$_{21}$-*b*-D$_9$	10.7	16	10	0.039	35	7	12.4
P3	O$_{15}$-*b*-B$_{30}$-*b*-D$_{19}$	17.0	24	14	0.134	42	2	13
P4	O$_{28}$-*b*-B$_{47}$-*b*-D$_{24}$	26.3	NS					13.2

Note: Not soluble (NS): the ABC triblock terpolymer with the highest MM studied is not soluble in DI water and thus further characterization of its aqueous solutions was not feasible.

[a]Oligo(ethylene glycol) methyl ether methacrylate with average M_n 300 g mol^{-1} (OEGMA300/O), di (ethylene glycol) methyl ether methacrylate (DEGMA/D), and *n*-butyl methacrylate (BuMA/B).

[b]The theoretical diameters were calculated using the experimental degrees of polymerization (DPs, based on the M_n values after precipitation, as determined by GPC analysis, and the experimental composition, as determined by ^{1}H nuclear magnetic resonance analysis). The following equation was used: d_h (nm) = (DP$_{BuMA}$ + 2 × DP$_{PEGMA \text{ or } DEGMA}$) × 0.254, depending on whether DP$_{PEGMA}$ > DP$_{DEGMA}$, or DP$_{PEGMA}$ < DP$_{DEGMA}$, respectively.

[c]The experimental d_hs are the mean diameters which correspond to the maximum of the peak by intensity and by number at 25 °C, as determined by DLS.

[d]The CPs were determined by UV–Vis as the temperature at which the transmittance dropped to 50%.

keeping all the other parameters, such as surfactant concentration and water to MO ratio, constant. We observed that the stability of the emulsions is strongly controlled by the MM of the macrosurfactant, with the one with the lowest MM showing its superiority at only 5 h after emulsification (Figures 4A and S7–S9). The trend that is, higher stability of emulsion by using lower MM surfactant, is apparent at 24 and 48 h. The stability of the emulsions reaches a plateau at $\varphi_{cream\ phase} \approx 0.67$, with no significant differences between the different macrosurfactants up to 28 days after emulsification. This agrees with the findings of Raduan et al. when OEGMA300-b-HexMA

macrosurfactants of similar hydrophobic content (30 w/w%) to the current study (35 w/w%) are concerned; HexMA stands for n-hexyl methacrylate.[21] This effect might be explained upon considering that by increasing the MM of the copolymer at relatively low hydrophobic content, the length of the hydrophilic block increases, thus the macrosurfactant might be preferably located more towards the aqueous phase, leading to emulsion destabilization. Optical microscopy images (Figure S10) show smaller size of emulsion droplets stabilized by P1, as compared to the other two copolymers, and especially the ones stabilized by P3, which is the macrosufactant with the highest molar mass value
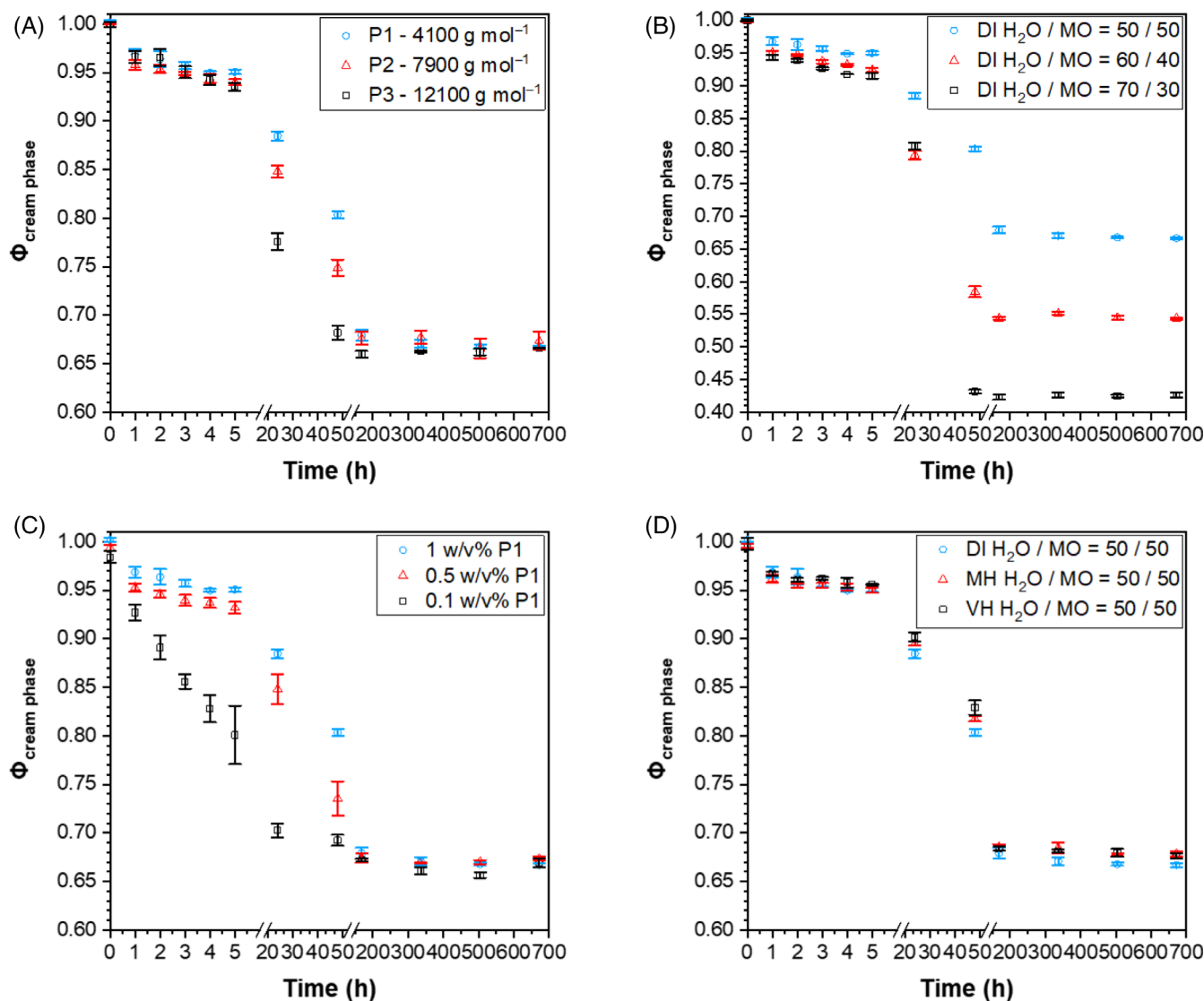
FIGURE 4 Volume fraction of the cream phase ($\varphi_{cream\ phase}$) as a function of time under different conditions. (A) Effect of the molar masses (MM) of the macrosurfactant on the stability: P1–4100 g mol^{-1} in light blue, P2–4100 g mol^{-1} in red, and P3–12100 g mol^{-1} in black. The solvent ratio was kept at DI H$_2$O/MO = 50/50, and the surfactant concentration at 1 w/v%. (B) Effect of solvent ratio, on the stability: DI H$_2$O/MO = 50/50 in blue, DI H$_2$O/MO = 60/40 in red, and DI H$_2$O/MO = 70/30 in black. The concentration of the macrosurfactant P1 was kept at 1 w/v%. (C) Effect of the concentration of the macrosurfactant P1 on the stability: 1 w/v% P1 in blue, 0.5 w/v% in red, and 0.1 w/v% in black. The solvent ratio was kept at DI H$_2$O/MO = 50/50. (D) Effect of the salt concentration on the stability: DI H$_2$O/MO = 50/50 in blue, MH H$_2$O/MO = 50/50 in red, and VH H$_2$O/MO = 50/50 in black. The macrosurfactant P1 concentration was kept constant at 1 w/v%. The experiments were performed in triplicate.

studied, which may be correlated to the stability trend. Since P1, with M_n 4100 g mol^{-1}, provided better emulsion stability, it was selected for preparing additional emulsion formulations.

2.4.2 | Effect of the volume fraction of the oil phase on the stability

It is of great interest to investigate the effect of the ratio of DI water to MO on the emulsion stability. Thus, the ratio of DI water to MO was systematically varied from 50:50, to 60:40, to 70:30, while keeping the P1 surfactant concentration constant at 1 w/w%. It should be noted that high water contents were targeted, as this would produce a cost-effective and environmentally friendlier emulsion. As evident in Figures 4B and S7, S11, and S12, the oil content plays a dominant role on the stability of the emulsions. In general, it is observed that the higher the oil phase the higher the stability of the emulsions. The enhanced stability of the emulsions with the highest volume fraction of MO ($\varphi_{MO} = 0.5$) is evident at 1 h after emulsification, and it becomes more apparent as the time progresses. In addition, the $\varphi_{cream\ phase}$ reaches a plateau, with the value increasing with the φ_{MO}. More specifically, this plateau values changes from 0.67 (at $\varphi_{MO} = 0.5$), to 0.55 (at $\varphi_{MO} = 0.4$), to 0.43 (at $\varphi_{MO} = 0.3$). This trend has been previously observed, and it is attributed to the increased packing fraction of the oil droplets, thus leading to reduced creaming.[42] As previously, the droplet size was evaluated by optical microscopy (Figure S13) and no significant differences were observed immediately after preparation.

2.4.3 | Effect of the surfactant concentration on the stability

To investigate the effect of the best-performing in-house synthesized macrosurfactant, P1, on the stability of the emulsions, emulsions at constant DI water to MO ratio 50:50, but various surfactant concentrations were fabricated. The maximum surfactant concentration in the total emulsion was equal to 1 w/v%, and it was decreased to 0.5 and 0.1 w/v%, and the effect on the emulsion stability over time was monitored (Figures 3C and S7, S14, and S15). As expected, increased stability with surfactant concentration was observed, which was evident only 1 h after emulsification. Interestingly, the emulsions formed by 1 w/v% (blue symbols) and 0.5 w/v% (red symbols) shows similar pattern in stability. In more detail, the $\varphi_{cream\ phase}$ decreased slightly by 0.02 up to 5 h, and it was further decreased at 24 and 48 h, reaching a plateau at $\varphi_{cream\ phase} = 0.67$ after 1 week. On the other hand, at surfactant concentration

equal to 0.1 w/v%, the $\varphi_{cream\ phase}$ substantially decreases by 0.2 at only 5 h, a value which is 10 times higher than the change observed for the higher concentrations. Further decrease to 0.7 at only 24 h is observed, reaching a plateau in less than 1 week. The instability of the emulsions formed at 0.1 w/v % (=2.4 × 10^{-4} M) of P1 might be attributed to the surfactant concentration being only slightly higher than its CMC value of 1.5 × 10^{-4} M. The reduced stability of the emulsion with 0.1 w/v% P1 is supported by its increased droplet size (Figure S16), which may have led to quicker destabilization. The effect of surfactant concentration on the emulsion stability has been previously reported, with the effect being attributed to the enhanced coverage of the surface of the oil droplets, thus preventing creaming.[42,43]

2.4.4 | Effect of the ionic strength on the stability

To simulate the use of tap water as a potential cost-effective alternative to DI water, we have prepared water samples of different salinity, namely moderately hard (MH, NaHCO$_3$: 96 mg L^{-1}, CaSO$_4$·2H$_2$O: 60 mg L^{-1}, MgSO$_4$: 60 mg L^{-1}, and KCl: 4 mg L^{-1}) and very hard (VH, NaHCO$_3$: 384 mg L^{-1}, CaSO$_4$·2H$_2$O: 240 mg L^{-1}, MgSO$_4$: 240 mg L^{-1}, and KCl: 16 mg L^{-1}) water. The experiments were performed at constant concentration of P1 macrosurfactant equal to 1 w/v% and aqueous to MO volume ratio of 50:50. No considerable changes have been observed between emulsions with different ionic strength (Figures 4D and S7, S17, and S18), which is also supported by the microscopy images, which revealed comparable size of emulsion droplets between the samples (Figure S19). This may be due to the stabilization of the emulsions by the non-ionic macrosurfactant being sterically favored, rather than electrostatic stabilization offered by ionic macrosurfactants. This indicates the superiority of our macrosurfactants and their suitability to be used as emulsion stabilizers at high ionic strength values.

2.4.5 | Summary

Our in-house synthesized macrosurfactants successfully stabilized O/W emulsions, whose stability was dependent on the MM of the macrosurfactant, the φ_{MO}, and the surfactant concentration. Independence of the stability on the salinity of the aqueous phase shows promising properties of these non-ionic macrosurfactants. Even though emulsion stability was compromised over time, with the $\varphi_{cream\ phase}$ decreasing, as expected, complete solvent

separation that is, complete phase separation of water and MO, was not observed for at least 1 month. This shows that our macrosurfactants could be used to stabilize emulsions for different applications.

2.5 | Synergistic stabilization by P1 macrosurfactant and HPMC viscosity modifier

To design a new system with potentially enhanced emulsion stability, we have combined our best-performing emulsifier, namely P1, with HPMC, which has been previously used as emulsifier,[25,26] and viscosity modifier.[24] Two HPMC polymers with different MM values, namely $HPMC_{84kDa}$ and $HPMC_{120kDa}$, were studied, to investigate the effect of the MM of HPMC on the emulsion's stability. In addition, the concentration of the HPMC was targeted at 0.05 and 0.25 w/v%, to investigate its effect, and thus the effect of viscosity, on the stability of the emulsions. The $\varphi_{cream\ phase}$ as a function of time is shown in Figure 5A, with the system containing no HPMC shown in blue circles for comparison, the emulsions stabilized by both P1 and $HPMC_{84kDa}$ shown in red (triangles pointing upwards for 0.05 w/v% and squares for 0.25 w/v%), and the emulsions stabilized by both P1 and $HPMC_{120kDa}$ shown in black (triangles pointing left for 0.05 w/v% and rhombi for 0.25 w/v%).

The MM of the HPMC additive and its concentration show a clear effect on the stability of the emulsions (Figures 5 and S20–S23). When the concentration of the HPMC is kept at 0.05 w/v%, the stability clearly increases as the MM of the HPMC increases. While the system with no HPMC reaches equilibrium ($\varphi_{cream\ phase} = 0.67$) in only 1 week, the emulsions with 0.05 w/v% $HPMC_{84kDa}$ and $HPMC_{120kDa}$ reached similar values in 4 weeks' time, indicating that small amounts of HPMC have significant effect on the stability. To prove the synergistic effect of
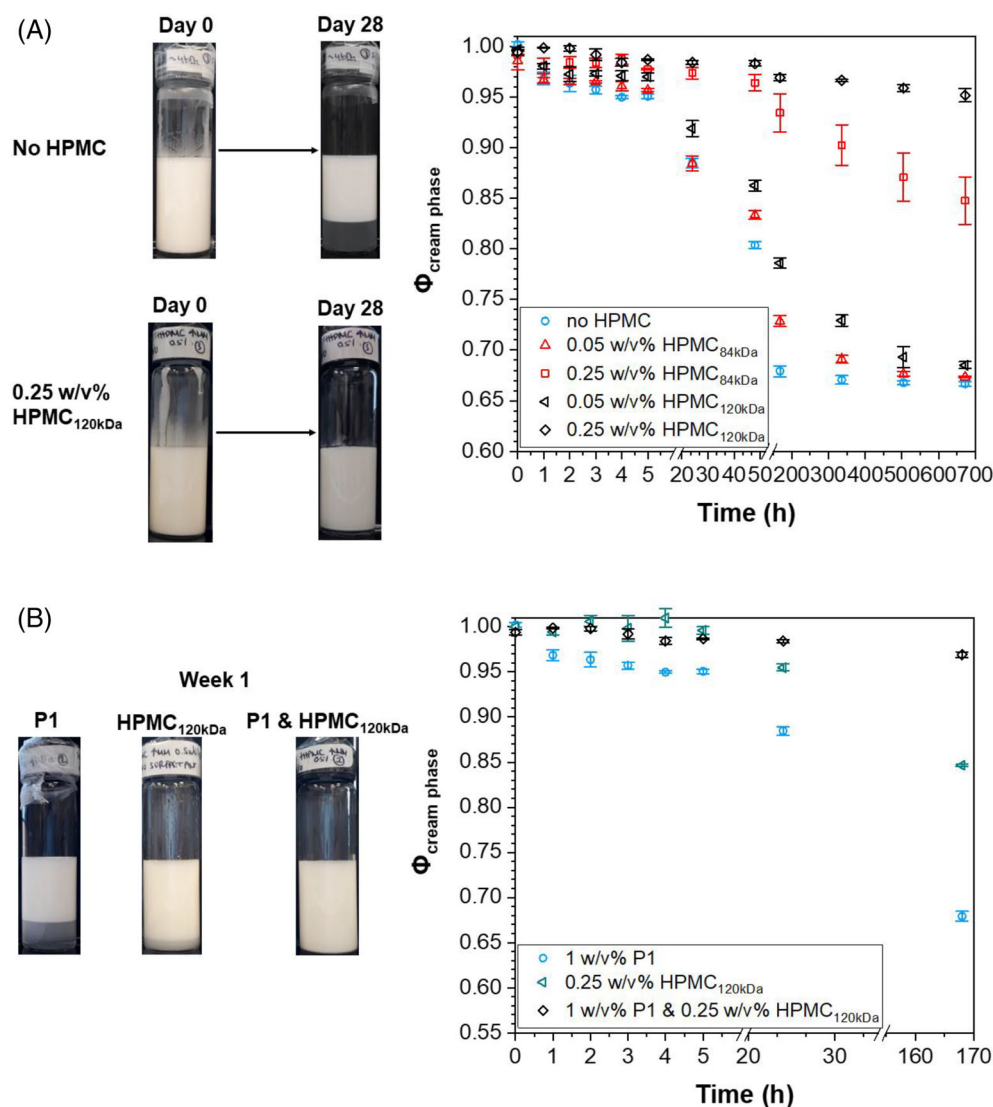
**FIGURE 5** Synergistic stabilization of emulsions by the P1 macrosurfactant and the hydroxypropyl methylcellulose (HPMC) viscosity modifier. (A) Effect of the viscosity modifier HPMC on the stability of the emulsions containing P1 as macrosurfactant: stability by P1 only (no HPMC) in blue circles, stability by both P1 and $HPMC_{84kDa}$ at 0.05 w/v% in red triangles pointing upwards and at 0.25 w/v% in red squares, and stability by both P1 and $HPMC_{120kDa}$ at 0.05 w/v% in black triangles pointing left and at 0.25 w/v% in black rhombi. The concentration of the macrosurfactant was kept at 1 w/v% and the ratio of DI H_2O/MO = 50/50. (B) Comparison of the emulsion stability up to 1 week after emulsification between 1 w/v% P1 macrosurfactant (blue circles), 0.25 w/v% $HPMC_{120kDa}$ viscosity modifier (turquoise triangles) and both 1 w/v% P1 and 0.25 w/v% $HPMC_{120kDa}$ (black rhombi).

both P1 macrosurfactant and HPMC, emulsions with only 0.05 w/v% HPMC were fabricated, with the $\varphi_{\text{cream phase}}$ reaching the value of around 0.7 in only 5 h after emulsification (Figure S20). Therefore, it is demonstrated that the combination of both P1 and HPMC produces a new system with increased emulsion stability.

Despite the retardation in emulsion destabilization, phase separation still occurs, with the emulsion phase reducing to around 70% after 28 days, thus compromising the shelf-life of the product. To tackle with this issue, we increased the concentration of HPMC to 0.25 w/v%. In line with the previous observations, the stability of the emulsions produced by both P1 and 0.25 w/v% HPMC was highly dependent on the MM of HPMC that is, the higher the MM of HPMC, the higher the stability of the emulsion. Interestingly, enhanced stability was observed 28 days after emulsification, with the samples containing $HPMC_{84kDa}$ maintaining stability at 85%, while the samples containing $HPMC_{120kDa}$ remained stable up to 95%. As a comparison, emulsions containing no polymeric macrosurfactant were also tested. When emulsion with only 0.25 w/v% $HPMC_{84kDa}$ was fabricated, the $\varphi_{\text{cream phase}}$ decreased to 0.89, only 24 h after emulsification (Figure S24). Assessing the progress of this emulsion 6 days after emulsification, the $\varphi_{\text{cream phase}}$ dropped to 0.70. When the emulsion formed only by 0.25 w/v% $HPMC_{120kDa}$ is concerned, the $\varphi_{\text{cream phase}}$ reduced to 0.95 after 24 h, lower than that of the emulsion formed by both P1 and $HPMC_{120kDa}$ under the same conditions ($\varphi_{\text{cream phase}} = 0.99$). The $\varphi_{\text{cream phase}}$ reduced further to 0.85 1 week after emulsification, while the $\varphi_{\text{cream phase}}$ of its corresponding emulsion containing the macrosurfactant remained at 0.97 under the same conditions (Figure 5B). These results show a synergistic stabilization of the emulsions by both the polymeric macrosurfactant P1 and the HPMC viscosity modifier. Most importantly, we have identified a new formulation containing 1 w/v% of the in-house synthesized non-ionic macrosurfactant and 0.25 w/v% $HPMC_{120kDa}$, which produces emulsions stable up to 95% for 28 days after emulsification.

The emulsions were tested via optical microscopy immediately after preparation, and the samples without viscosity modifier was compared to the ones with HPMC additive as viscosity modifier with different molar mass and concentration values. It is evident in Figure S25 that the addition of viscosity modifier contributes to decreased droplet size. In addition, the higher the molar mass of the HPMC and the higher the additive concentration, the smaller the droplet size. These observations support that the reduced droplet size contributes to enhanced stabilization of the emulsions, in line with the previous observations.

The stability of the best-performing formulation, namely the sample containing 1 w/v% P1 as macrosurfactant and
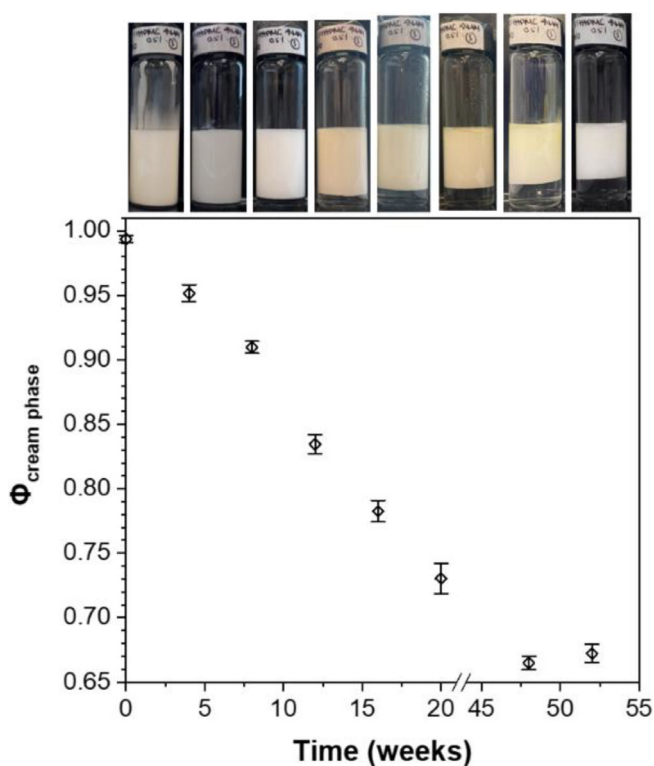
FIGURE 6 Stability of the emulsions containing 1 w/v% P1 as macrosurfactant and 0.25 w/v% of hydroxypropyl methylcellulose $(HPMC)_{120kDa}$ as viscosity modifier. The ratio of DI H_2O/MO = 50/50.

0.25 w/v% $HPMC_{120kDa}$ as viscosity modifier, was monitored over a year. As seen in Figure 6 and S26, when monitoring the stability over a period of 20 weeks (around 5 months), the stability of the emulsions decreased in a controlled manner, but the $\varphi_{\text{cream phase}}$ remained higher than 0.70. Surprisingly, the $\varphi_{\text{cream phase}}$ remained stable and higher than 0.65 a year after emulsification. Pluronic® F68 has previously been reported to stabilize emulsions, with the stability timeframe being dependent on both the oil phase and water phases, with enhanced stability up to 11 weeks when soybean oil is used.[44] This indicates that this synergistic action of our in-house synthesized macrosurfactant and HPMC as a viscosity modifier produces emulsions with increased stability over a year, indicating the potential of this system to be used in emulsion applications required increased shelf-life.

Investigating the rheological properties of the best-performing emulsions is of great importance. Thus, fresh emulsions with 1 w/v% P1 and 0.25 w/v% either $HPMC_{84kDa}$ or $HPMC_{120kDa}$ and constant rate of aqueous phase to oil phase 50:50 were subjected to flow sweep, amplitude sweep and frequency sweep measurements (Figure 7).

As can be seen in Figure 7A, higher viscosity values are obtained for the samples containing viscosity
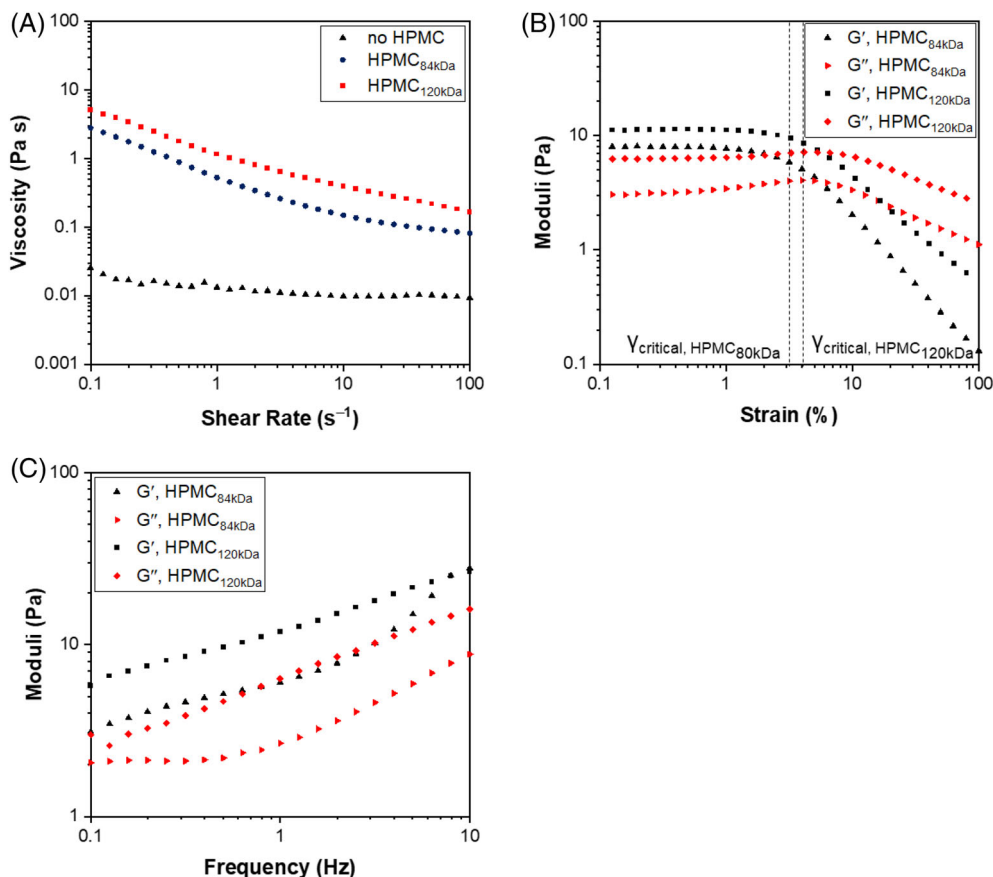
FIGURE 7 Rheological properties of emulsions with 1 w/v% P1 macrosurfactant (4100 g mol^{-1}) and ratio of aqueous to oil phase 50/50 v/v%. (A) Viscosity as a function of shear rate for emulsions containing no viscosity modifier/ no hydroxypropyl methylcellulose (HPMC) (black triangles), 0.25 w/v% HPMC$_{84kDa}$ (blue circles), and 0.25 w/v% HPMC$_{120kDa}$ (red squares). (B) Storage modulus (elastic modulus, G', in black) and loss modulus (viscous modulus, G'', in red) as a function of strain for emulsions containing 0.25 w/v% HPMC$_{84kDa}$ (triangles), and 0.25 w/v% HPMC$_{120kDa}$ (quadrilaterals). (C) Storage modulus (elastic modulus, G', in black) and loss modulus (viscous modulus, G'', in red) as a function of frequency for emulsions containing 0.25 w/v% HPMC$_{84kDa}$ (triangles), and 0.25 w/v% HPMC$_{120kDa}$ (quadrilaterals).

modifier compared to the control emulsion stabilized only by the P1 macrosurfactant, indicating that the increased viscosity of the samples might be the mechanism of additional stabilization offered by HPMC. In addition, the higher the MM of the HPMC, the higher the viscosity of the sample. Nevertheless, the emulsions stabilized by both P1 and 0.25 w/v% HPMC behave as non-Newtonian fluids, presenting a classical shear-thinning behavior that is, decrease in viscosity by increase in shear rate. Shear-thinning behavior was previously reported on emulsion formulations, including both W/O emulsions, and[45–47] O/W emulsions,[48–50]

The linear viscoelastic area of the emulsions was determined by performing strain sweeps at fixed frequency of 1 Hz (Figure 7B). As revealed, the emulsions behave as an elastic gel-like material with the elastic (storage, G') modulus being higher than the loss (viscous, G'') modulus when subjected to strain below their critical

value. Below the critical strain, the magnitude of storage and loss moduli are independent on the strain applied, and the magnitude of G' is higher for the emulsion formed by HPMC$_{120kDa}$ compared to the one consisting of HPMC$_{84kDa}$. Above the critical strain value, which is slightly higher for the HPMC$_{120kDa}$ emulsion, the moduli decline rapidly, and a crossover is observed, above which the sample behaves as a viscous liquid ($G'' > G'$).

The frequency-dependent behavior of the emulsions was investigated at constant strain (%) at 1, a value within the linear viscoelastic area of the sample (Figure 7B). The frequency sweeps reveal an elastic behavior of the emulsions, as $G' > G''$ at all frequencies tested, a trend that has been previously shown to be dependent on the content of the internal phase,[51] and the exact chemical composition of the HPMC used.[27] In addition to this observation, the values of G' and G'' are highly dependent on the frequency, and more specifically, they increase as the applied

frequency increases. These features are characteristic of the formation of an entanglement network responsible for stabilizing the emulsion, as previously reported.[27] Increase of the moduli with the frequency might be explained upon considering that the lower the frequency, the less often the strain is applied, thus the network slightly rearranges, while increasing the frequency at which the strain is applied, the bonds forming the network remain in place, thus forming a stronger elastic gel.

3 | CONCLUSION

In this study, four non-ionic ABC macrosurfactants based on the hydrophilic OEGMA300, the hydrophobic BuMA, and the hydrophilic DEGMA, of constant composition and different MM values were successfully synthesized via GTP. While the macrosurfactant of highest MM was not water-soluble, the other ABC macrosurfactants formed micelles in water, with the size of the self-assembled structures increasing with the MM of the polymer. Most importantly, the longer the length of the polymer chain, the lower the CMC values. When investigating the stability in oil-in-water (O/W) emulsions formed by using methyl oleate as the oil phase, it was observed that the lower the MM, the higher the stability. It was demonstrated that the best-performing macrosurfactant was the one with MM at 4100 g mol^{-1} (P1), and thus it was used for further investigating its emulsifying properties under different conditions. It was observed that the water to oil phase ratio, had a great impact on the emulsion stability, while the surfactant concentration also affected the stability. It was found that the emulsions stability was not affected by the water hardness, thus indicating the suitability of our macrosurfactants in use with hard water supply. Synergestic stabilization by the ABC macrosurfactant and by HPMC, with the MM and concentration of the HPMC strongly controlling the stability that is, the higher the MM and the higher the concentration of the HPMC, the higher the stability. These trends are supported by the microscopy images, which revealed that smaller droplet sizes are related to systems with enhanced emulsion stability. Rheological measurements were performed on these emulsions, and it was observed that they behave as non-Newtonian fluids. These emulsions show characteristics of elastic gel behavior, with the emulsion stabilization being attributed to network formation. Most importantly, we developed and present a specific formulation produced by 1 w/v% P1, 50/50 water to oil, and only 0.25 w/v% HPMC$_{120kDa}$ showed emulsion stability over 95% over 1 month after emulsification. Importantly, our best-performing formulation retained stability over 65% a year after emulsification, indicating its potential use for emulsion fabrication requiring increased shelf-life.

4 | EXPERIMENTAL

4.1 | Materials

The monomers used for the synthesis of the macrosurfactants, namely BuMA (99%), DEGMA (95%), and OEGMA300 (94%) were purchased from Sigma Aldrich, UK. Sigma Aldrich, UK, was also the provider of 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, free radical inhibitor), basic aluminum oxide (Al$_2$O$_3$·KOH), calcium hydride (CaH$_2$, ≥90%, desiccant), deuterated chloroform (chloroform-*d*, 99.8 atom %D, CDCl$_3$, nuclear magnetic resonance, NMR, solvent), methyltrimethylsilyl dimethylketene acetal (MTS, 95%, GTP initiator), tetrahydrofuran (THF, inhibitor-free, HPLC grade, ≥99.9%, GTP and gel permeation chromatography, GPC, solvent), magnesium sulphate (MgSO$_4$) low MM HPMC (MM ≈ 84,000 g mol^{-1}, viscosity 2600–5600 cP, 2% in H$_2$O at 20 °C, HPMC$_{84kDa}$), and high MM HPMC (MM ≈ 120,000 g mol^{-1}, viscosity 100,000 cP, 2% in H$_2$O at 20 °C, HPMC$_{120kDa}$). Deionized (DI) water was purchased from HACH, Germany (conductivity: 1 μs cm^{-1}, SiO$_2$: 300 μg L^{-1}, Cl$^-$: 20 μg L^{-1}). Benzoic acid and tetrabutyl ammonium hydroxide (40% in water), reagents needed for the synthesis of the GTP catalyst, namely tetrabutylammonium bibenzoate (TBABB) and methyl oleate (MO, technical grade) were purchased from Acros Organics, UK. Filters were purchased from Fischer Scientific: poly(tetrafluoroethylene) (PTFE) hydrophilic syringe filters (0.45 μm pore size, 25 mm diameter) and Nylon syringe filters (0.45 μm pore size, 25 mm in diameter). Poly(methyl methacrylate) (PMMA) standard samples used for the GPC calibration (MM = 2000, 4000, 8000, 20,000, 50,000, 100,000 g mol^{-1}) were purchased from Fluka, Sigma Aldrich, UK, while VWR Chemicals was the provider of *n*-hexane. PhytoTech Labs was the provider of potassium chloride (KCl, ACS reagent). Sodium bicarbonate (NaHCO$_3$) was purchased from Tocris Bioscience, while calcium sulphate dihydrate (CaSO$_4$·2H$_2$O) was acquired from FluoroChem.

4.2 | Preparation of artificial hard water samples

Samples of MH water and VH water were prepared by dissolution of salts in DI water, purchased from HACH, following concentration values previously reported[52]: (i) MH water (NaHCO$_3$: 96 mg L^{-1}, CaSO$_4$·2H$_2$O: 60 mg L^{-1}, MgSO$_4$: 60 mg L^{-1}, and KCl: 4 mg L^{-1}) and (ii) VH water (NaHCO$_3$: 384 mg L^{-1}, CaSO$_4$·2H$_2$O: 240 mg L^{-1}, MgSO$_4$: 240 mg L^{-1}, and KCl: 16 mg L^{-1}).

4.3 | Preparation for GTP

BuMA and DEGMA were purified by passing through aluminum oxide activated basic to remove the acidic impurities and the free-radical inhibitor. DPPH was added to prevent undesired free radical polymerization, followed by the addition of CaH_2 to remove humidity. Both monomers were distilled under vacuum prior to the polymerization. On the other hand, OEGMA300 was mixed with THF (50/50 v/v%), and the mixture was passed through basic alumina and stirred over CaH_2. The glassware needed for vacuum distillations and GTP were dried in an oven at 140 °C overnight. The GTP initiator, MTS, was distilled under vacuum prior to use, while the GTP catalyst, TBABB, was synthesized via a procedure previously reported by Dicker et al.[53]

4.4 | Group transfer polymerization

The ABC macrosurfactants were synthesized via GTP, and the synthesis of Polymer 1 is given as an example. 10 mg of TBABB were added in a round-bottom flask, which was immediately sealed and purged with inert argon. THF (34 mL) was injected in the polymerization flask, followed by the addition of MTS (1.0 mL, 0.85 g, 5 mmol). OEGMA300 solution (50 vol% in THF, 9.4 mL, 4.9 g, 16 mmol) was directly filtered into the flask by using PTFE filters. After the completion of the polymerization (15 min monomer consumption for the GTP technique), two aliquots of 0.1 mL each were withdrawn for GPC and NMR analysis. The addition of BuMA (4.8 mL, 4.3 g, 30 mmol) followed, and once the diblock copolymer was formed, DEGMA (3.0 mL, 3.1 g, 16 mmol) was injected to facilitate the chain extension to the triblock copolymer. After each step, samples were withdrawn for GPC and NMR analysis.

4.5 | Polymer recovery

The ABC macrosurfactants were recovered by precipitation in *n*-hexane, which was removed by decanting. The polymers were dried in a vacuum oven for 10 days, to remove any traces of toxic solvents, namely THF and *n*-hexane.

4.6 | Confirmation of the polymer structure

4.6.1 | Gel permeation chromatography

The molar mass characteristics, such as number average MM, M_n, and dispersity index, Đ, of the final ABC macrosurfactants and their linear precursors were determined by GPC in THF at a concentration of 10 mg mL^{-1}. For this experiment, an Agilent SECcurity GPC system (Agilent technologies UK Ltd.) was used, which is equipped with a Polymer Standard Service (PSS) SDV analytical linear M column (SDA083005LIM, dimensions: 300 × 8.00 mm, particle size: 5 μm, separation range: 0.1–1000 kg mol^{-1}), an Agilent guard column (PL1110-1520, PLgel Mixed, dimensions: 50 × 7.5 mm, particle size: 5 μm), an Agilent 1250 refractive index (RI) detector, and a "1260 Iso" isocratic pump. The measurements were run at a flow rate of 1 mL min^{-1}.

4.6.2 | NMR spectroscopy

The composition of the ABC macrosurfactants and their precursors was determined by NMR analysis. The samples were dissolved in $CDCl_3$ at a concentration of 10 mg mL^{-1}, and the experiment was performed by using a JEOL 400 MHz spectrometer.

4.6.3 | Characterization in aqueous solvents

P1 (4100 g mol^{-1}), P2 (7900 g mol^{-1}), and P3 (12,100 g mol^{-1}) are water-soluble, thus their aqueous solutions were characterized as described below. P4 (19,700 g mol^{-1}) was insoluble in water, thus further characterization in aqueous solutions was not feasible.

4.7 | Dynamic light scattering

4.7.1 | Hydrodynamic diameters

The hydrodynamic diameters (d_H) of the macrosurfactants at 1 w/w% in DI water were investigated by DLS. The measurements were performed at 25 °C, using a Zetasizer Nano ZSP (Malvern Instruments Ltd.) instrument. The solutions were filtered once using Nylon filters, to remove any dust particles or big aggregates. The scattered light was collected at a backscatter angle of 173°. The results are reported as the mean values that correspond to the maximum of the peak by intensity and by number as resulted after three measurements. The theoretical diameters were calculated using the experimental degrees of polymerizations (DP), as resulted by GPC an NMR analysis. It was assumed that the macrosurfactants self-assemble into spherical core-shell micelles, with BuMA as the hydrophobic core, and both DEGMA and OEGMA300 forming the hydrophilic corona. Assuming complete overlap of BuMA blocks,

extended backbone with each unit having length of 0.254, Equation 1 was used:

$$d_H = (DP_{BuMA} + DP_{longest\ hydrophilic}) \times 0.254\ nm. \quad (1)$$

4.7.2 | Critical micelle concentration

DLS was also used to determine the CMC values of the macrosurfactants. The following concentrations (M) in DI water were tested: 0.001, 0.0005, 0.00025, 0.0001, 0.00005, 0.000025, 0.00001, 0.000001, 0.0000001. The samples were filtered five times using Nylon filters to remove any dust particles or big aggregates that would interfere with the measurement. The measurements were performed at 25 °C. The kilocounts per second were recorded 10 times for each sample, and the average kilocounts per second as a function of polymer concentration was plotted. The CMC was determined as the intercept point of the two tangent lines of this curve.

4.7.3 | Ultraviolet–visible spectroscopy

An Agilent Cary UV–Vis Compact Peltier ultraviolet–visible (UV–Vis) spectrometer was used to determine the CP values of 1 w/w% polymer solutions in DI water, defined as the temperature at which the transmittance dropped to 50%. The experiment was performed at a heating rate of 1 °C min^{-1} and data were collected every 1 °C at 550 nm.

4.7.4 | Hydrophile–lipophile balance

The hydrophile–lipophile balance (HLB) values of the macrosurfactants were calculated using the Equation (2), where WH and WL correspond to the weight fractions of the hydrophilic blocks and lipophilic/hydrophobic blocks, respectively. We assume that at room temperature, both OEGMA300 and DEGMA are hydrophilic, while BuMA is hydrophobic.

$$HLB = W_H / (W_H + W_L) \times 20. \quad (2)$$

4.7.5 | Emulsification

The emulsions were prepared by dissolving the macrosurfactant in the oil phase, namely MO, followed by addition of the aqueous phase. P1 (4100 g mol^{-1}), P2 (7900 g mol^{-1}), and P3 (12,100 g mol^{-1}) were soluble in methyl oleate, while P4 (19,700 g mol^{-1}) was neither water-soluble nor oil-soluble, thus it was not used for emulsion preparation. The volume of the emulsions was kept constant at 9 mL. The emulsification was performed by using a T10 basic Ultra-Turrax®, equipped with an S10N-10G dispersing element, purchased from IKA. The samples were emulsified for 1 min, with speed equal to 4 (14,450 rpm when tested in 4 mL water). All experiments were repeated in triplicate, and the results are the average values of the three repeats.

4.7.6 | Determination of the type of emulsions

The type of emulsions was determined by adding the emulsion droplets in MO and DI water. When the droplet is dispersed uniformly in water, but precipitates in methyl oleate, then the emulsions are O/W. On the other hand, when the emulsion droplet precipitates in water, but is dispersed uniformly in oil, the emulsions are W/O.

4.7.7 | Monitoring the emulsion stability

The stability of the emulsions was monitored by taking photographs at specific time intervals after emulsification. The photographs were recorded using a Samsung Galaxy A3 (2017).

4.7.8 | Analysis of the emulsion stability

The images were analyzed using ImageJ.[54] The volume fraction of the cream phase was calculated using Equation (3):

$$\varphi_{cream} = \varphi_{cream\ phase} / \varphi_{sample}. \quad (3)$$

4.7.9 | Stabilization of emulsions using the ABC macrosurfactants

The three soluble macrosurfactants were tested at a final concentration of 1 w/v%, and a ratio of DI water to MO 50:50. The best-performing macrosurfactant, namely P1 (4100 g mol^{-1}) was chosen for subsequent experiments:

1. The DI water to MO ratio was varied from 50:50 to 60:40 to 70:30, while keeping the concentration of the surfactant constant at 1 w/v%.
2. The concentration of the surfactant was varied from 1 to 0.5 to 0.1 w/v%, while keeping the ratio of DI water to MO constant at 50:50.

3. The salt concentration was varied from DI water to MH water to VH water, while keeping the concentration of the surfactant constant at 1 w/v%, and the ratio of DI water to MO constant at 50:50. For more information about the exact salt concentration, refer to the relevant section.

4.7.10 | Stabilization of emulsions using the best-performing ABC macrosurfactant, P1, and a viscosity modifier

The best-performing macrosurfactant, namely P1 (4100 g mol^{-1}) was dissolved in MO with a final concentration in the emulsion kept constant at 1 w/v%. The ratio of the aqueous phase to MO was kept constant at 50:50. Two different viscosity modifiers were used, namely HPMC$_{84kDa}$ and HPMC$_{120kDa}$. The viscosity modifiers were dissolved in DI water at a concentration of 0.1 w/v% and 0.5 w/v%, which they served as the aqueous phase, thus their final concentrations in the emulsion were 0.05 and 0.25 w/v%, respectively.

4.7.11 | Optical microscopy

The emulsions were imaged immediately after formulation using an Olympus microscope. A droplet of the freshly made emulsion was placed between two cover glass slips (VWR, borosilicate glass, 24 × 24 mm, thicnkess no. 1) and the sample was transferred directly to the microscope for imaging.

4.7.12 | Rheology

Rheological measurements were performed on fresh emulsions stabilized by both P1 at 1 w/v% and the viscosity modifier HPMC at 0.25 w/v%. Two different viscosity modifiers were used, HPMC$_{84kDa}$ and HPMC$_{120kDa}$. The ratio of the aqueous phase to MO was kept constant at 50:50. The experiment was performed by using a TA Discovery HR-1 hybrid rheometer (TA Instruments, UK), equipped with a 40 mm parallel steel plate (996921) and a Peltier temperature control unit, at 25 °C. The following type of measurements were performed: (i) viscosity as a function of shear rate, (ii) amplitude sweep by keeping the frequency fixed at 1 Hz, and (iii) frequency sweep by keeping the strain (γ) fixed at 1%, which is within the linear viscoelastic area of the sample, determined by (ii). The viscosity as a function of shear rate was also performed on fresh emulsion stabilized by P1 only at 1 w/v% and MO to DI water at 50:50 for comparison.

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