

Coarse-Grained Molecular Simulation of Polymers Supported by the Use of the SAFT- γ Mie Equation of State

Maziar Fayaz-Torshizi and Erich A. Müller*

A framework to self-consistently combine a classical equation of state (EoS) and a molecular force field to model polymers and polymer mixtures is presented. The statistical associating fluid theory (SAFT- γ Mie) model is used to correlate the thermophysical properties of oligomers and generate robust and transferrable coarse-grained (CG) molecular parameters which can be used both in particle based molecular simulations and in equations of state (EoS) calculations. Examples are provided for polyethylene, polypropylene, polyisobutylene atactic polystyrene, 1,4-cis-butadiene, polyisoprene, their blends and mixtures with low molecular weight solvents. Different types of liquid–liquid phase behavior are quantitatively captured both by the EoS and by direct molecular dynamics simulations. The use of CG models following this top-down approach extends the time and length scales accessible to molecular simulation while retaining quantitative accuracy as compared to experimental results.

thermodynamic properties of polymer melts. In the most general case, the molecular simulation of simple fluids is performed by representing each and every atom as an individual entity, interacting with all other $N - 1$ atoms in the system, according to a prescribed force field. The exceptionally large size of an individual polymer molecule is at odds with such a detailed atomistic description. Not only is there an issue with respect to the capacity of current computers to describe the large system sizes required, there is also a disparity in the characteristic times accessible through computation and those seen in experiments. A way to bridge this gap is to systematically remove the detail (coarse grain) the molecular models. The art lies in performing this scaling without sacrificing the accuracy of the representations.

1. Introduction

Mixtures of polymer blends and solvents are known to exhibit a variety of complex phases.^[1,2] While predicting properties of mixtures of reactants, polymers and byproducts at different compositions is of paramount importance in computer aided design,^[3] be it in process design^[4] (polymerization vessels and separation units) or product design and enhancement^[5,6] (paint, coating, adhesives, etc). Many important challenges are associated with the modeling of these asymmetric mixtures. Thermodynamic models,^[5] such as equations of state (EoS) and activity models are commonly used to estimate macroscopic phase behavior of polymers (density, solubility, phase separation).

In complementary fashion, molecular simulations have been at the forefront of materials modeling of polymers,^[7–9] especially with regards to the determination of structural, dynamic, and

A second major challenge in molecular simulation of polymers is knowing a priori the regions of (im)miscibility that can be of interest to study in greater detail. Composition, molecular weight, temperature, pressure, and polydispersity can significantly affect the phase diagram of polymer mixtures. The most common phases of binary liquids as characterized by Konynenburg and Scott^[10] are presented in **Figure 1**. Different polymer mixtures exhibit these liquid–liquid phase splits with temperature (or pressure), at different global compositions. Molecular simulation of such diverse phase behavior remains a challenge particularly in the regions close to the critical solution points, where observation of such phases requires very large systems.

This work aims to address the aforementioned challenges, by presenting a method for developing coarse-grained (CG) force field parameters of polymers and solvents that can accurately predict solution phase behavior of polymers. The force field parametrization exploits the strength of a recently developed molecular based EoS, the statistical associating fluid theory (SAFT- γ Mie),^[11–13] where the fitted parameters of the EoS are intermolecular interaction parameters. A unique aspect of the model formulation is that the parameters that characterize the equation of state can be used directly in molecular simulations to not only reproduce the same thermodynamic results as the EoS, but also calculate structural, dynamic and interfacial properties. These latter properties are inaccessible to the EoS, and include polymer conformations, such as end-to-end distances and radii of gyration, dynamic properties such as glass transition temperatures, and interfacial properties like mesophase separation in block copolymers. Such properties can be easily studied using

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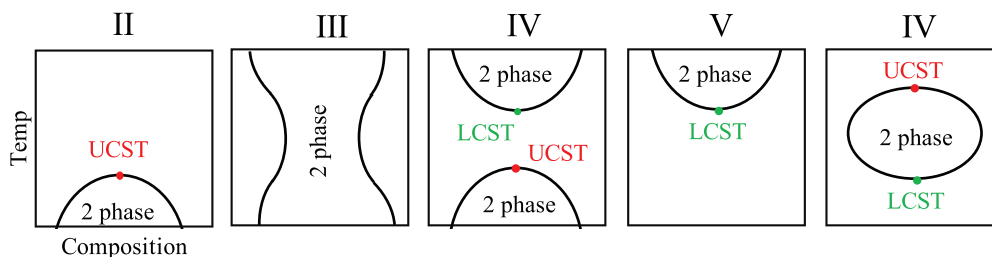


Figure 1. Phases of binary liquids as characterized by van Konynenburg and Scott,^[10] all the phase envelopes correspond to coexistence curves. The ordinate may be temperature or pressure. Lower and upper critical solution temperature are abbreviated as LCST and UCST respectively.

simulations, and therefore by coupling the force-field to an underlying EoS, a method is presented to comprehensively study polymers and their mixtures.

Although it has been shown extensively that within the SAFT framework, the EoS and results of molecular simulations are commensurate to each other,^[14–19] the extent to which this also applies to very long chains, such as polymers, has not been systematically studied. Henceforth, this manuscript details some of the procedures we have developed specifically for this family of complex fluids.

1.1. Thermodynamic Modeling of Polymer Mixtures

Many thermodynamic models are available for describing the thermodynamics of polymer mixtures based on analytical expressions with some degree of empirical fitting. Equations of state,^[20–23] activity models,^[23–26] and lattice based models^[27–39] have all been successfully employed to study pure polymer fluids and mixtures.

A particularly well suited approach is the SAFT model, which was developed from the onset with chain fluids (like polymers) in mind.^[40–42] Several versions of the SAFT theory exist, which differ in the underlying model for the monomer term. The SAFT model of Huang and Radosz,^[43] perturbed chain SAFT (PC-SAFT)^[44] and simplified PC-SAFT (sPC-SAFT)^[45] are the most popular EoS to model polymers. The advantage of the SAFT methodology comes from the fact that molecules can be modeled as linear chains of any size. Without prejudice to other versions of SAFT, the PC-SAFT model has arguably been more widely employed to characterize polymers blends and solutions with gases and low molecular weight solvents.^[45–48] For a comprehensive review of polymer modeling with PC-SAFT, the reader could refer to reviews of Guerrier et al.,^[49] and Kontogeorgis and Folas.^[23]

The latest version of the theory corresponds to the SAFT- γ Mie version.^[11] Here the constituent monomer is an isotropic bead which is described by the Mie potential, an extended version of the more common Lennard–Jones model. The equation allows the building of chain fluids from different types of monomers, effectively describing heteronuclear polymers in a natural way. Furthermore, it is built as a group contribution model and the properties of the individual chemical moieties may be back traced by fitting to thermophysical data of simple molecules. SAFT- γ

Mie EoS has been used to successfully model amines, n-alkane, alcohols, esters molecules with up to 30 carbons each molecule. Tables of fitted self and cross interaction parameters for many united-atom functional groups, such as CH₃, CH₂ and aromatic aCH, exist.^[50] Papaioannou et al.^[11] predicted densities of low density polyethylene (LDPE) in n-pentane, as a function of temperature and pressure. It was also shown that the united atom group contribution methodology could qualitatively predict the upper critical solution temperature (UCST) phase behavior of polyethylene in n-pentane, based solely on parameters fitted to n-alkanes up to n-dodecane. A more general application of the SAFT- γ Mie model includes an empirical shape factor which can be conceptually thought as capturing the effect of fused spheres. We will consider here only the results associated to a unitary shape factor, that is, sets of tangentially bonded spheres to retain compatibility with the underlying molecular model.

An advantage of this flavor of SAFT, over others is that the EoS parameters can be used directly in molecular simulations. A consequence of the EoS parameter fitting is the lumping of several atomic groups into single “beads” of the SAFT model, for example, n-dodecene is typically modeled as a homonuclear chain of four tangent beads. Effectively this process accounts for a CG of the atomistic detail of the molecule and is the essence of the top down SAFT CG force-field. Lobanova et al. used this approach to model ternary mixtures of n-alkanes (up to C₁₅), water and CO₂ with both the EoS and molecular simulations to clearly demonstrate the validity of the intermolecular interactions used as dispersion terms in the EoS.^[18] Rahman et al.^[17] followed the same philosophy and estimated CG parameters for n-alkanes where each bead represents a triad of carbons and the corresponding hydrogens. Pure component vapor liquid equilibria (VLE) were predicted for n-alkanes up to C₆₀. The alkane model was then used to calculate single phase density of low density polyethylene, which was comparable to experimental data with an average absolute deviation (AAD) of 0.8 percent. The approach has been extended to model crude oils, asphaltenes, polynuclear aromatic hydrocarbons, and other complex fluids. Polymers and polymer mixtures are a natural extension of the approach.

1.2. Molecular Simulation of Polymers

Abundant literature exists on atomistic or united atom representation simulations of homopolymer melts.^[51–59] Structural

properties such as radii of gyration and end to end distances, dynamic properties such as self-diffusion of polymers or the end-to-end relaxation times, Rouse and entanglement regimes, polydispersity, cross-linked networks, and elastic properties have all been extensively studied.

A restricting issue with atomistic simulations is that they are limited to the smallest of systems, as computational expense increases at an order of N^2 where N is the number of particles. It becomes much more challenging to simulate longer polymers and/or phase equilibria of polymers in solutions using all atom representations as the relaxation times are very long, rendering modeling at this scale futile, even with current and foreseeable computational resources.

Particle based CG is a viable alternative to atomistic simulations for large systems. There are two main philosophies of CG, namely structural CG (bottom-up) or thermodynamic CG (top-down), both of which group atoms together to form super-atoms.^[13,60] By reducing the degrees of freedom of the system, significantly less computational expense is required to calculate properties. The most common type of structure matching is achieved using the iterative Boltzmann inversion (IBI) technique, which develops the CG potential by minimizing the difference of the CG structure with the underlying atomistic one iteratively. A CG simulation is run, and the radial distribution function of the particles, as well as the angular and bonded distribution functions measured. These are compared to the underlying atomistic simulation of the same system, and the potential parameters are updated to minimize the difference between the two scales. Simulations are repeated until the difference between the local structures are minimized. There is an overwhelming amount of literature using this technique, with common polymers being modeled with accurate representation of their local structures.^[61–69] The implementation of IBI can be done as part of a bigger optimization technique taking into account structural properties at different state points.^[70] Also, the shape of the CG particles can be very versatile, as it has been shown that this technique could be applied to ellipsoidal, non-spherical (anisotropic) CG monomers too.^[71]

Accurate representation of the local structures intuitively makes IBI a robust methodology to study polymeric systems at larger scales. However, a major problem with this technique is it is not guaranteed that potential parameters are state independent.^[66,67] The interaction potentials could be dependent on density, pressure, temperature, composition, and molecular weight of the components studied.^[72,73] Structure based CG is very applicable when investigating properties of homopolymers melts in a narrow range of temperatures and pressures, as the parameters are independent on the degree of polymerization.^[74] However, application of this technique to study mixtures of polymers (blends or in solvents) is much more challenging.^[75] Few studies exist on CG modeling of polymers mixtures using IBI method. Sun and Faller^[75] studied miscibility of polystyrene polyisoprene blends at different chain lengths using state-dependent parameters, each fitted to different states. Another study was that of Reith et al.,^[72] where polystyrene and cyclohexane were CG, again it was not possible to capture local structures at both high and low concentrations with the same parameters. Qian et al.^[66] obtained CG parameters for mixtures of ethylbenzene

and polystyrene. The force field for ethylbenzene had to be modified at different temperatures, whereas the polystyrene model was state independent. Another challenge in modeling dilute solutions of polymers using IBI, as highlighted by Peters and Kremer^[73] is that the solute-solute radial distribution functions converge very slowly, requiring very long atomistic simulations to have enough statistics that account for this.

The majority of the studies on polymer solutions with structure matching^[66,72,73,76–78] attempt to capture the correct local structures of the monomers in solution at a particular temperature and pressure, but inevitably these force fields are not transferable to other state points. Other CG techniques exist, but have not been extensively applied to polymeric systems. Force matching techniques^[79,80] have been used to CG biomolecular systems, and can be extended to polymers. A promising alternative is the relative entropy method of Shell and coworkers.^[81–83] However, the authors' are not aware of it being used for polymer mixtures.

Thermodynamic, or top-down, approaches, aim to improve this issue by fitting potential parameters to macroscopic properties. Hydration energies, interfacial tensions, densities, and pressures can all be used to fit potential parameters. Again, like the case of bottom up approaches, top-down approaches have been used to model homopolymer melts of common polymers, capturing the correct densities and conformations (radius of gyration). An outstanding example of this type of approach is the MARTINI force field where a set of CG beads is parametrized against water/octanol partition coefficients. While designed for modeling surfactant systems, the MARTINI force field has been applied to the study of polystyrene, polyethylene oxide, pluronics, and polyolefins^[84–87] with transferable potentials that match the correct conformations in solvents. In all these studies conformations of polymers and densities are comparable to those of the bottom-up approaches. However, in most of these studies, liquid–liquid equilibria of polymers and solvents are only studied in narrow temperature and pressure ranges.

To our best knowledge, upper critical and lower critical phase behavior of polymers mixtures are very rarely modeled using the approaches mentioned above. The vast majority of studies of lower critical and upper critical phase behavior have been phenomenological studies, using model systems instead of real molecules. Sheng et al.^[88] accurately modeled the VLE of pure component chains formed of Lennard–Jones spherical monomers using Gibbs ensemble Monte Carlo (GEMC) simulations. It was shown that this methodology is robust in calculating phase diagrams. The use of this methodology was extended to simulations of polymer mixtures. The first GEMC simulations which modeled both LCST and UCST behavior in polymer-solvent mixtures without any adjustment parameters were carried out by Gromov et al.^[89] in 1998. In this study, mixtures of Lennard–Jones chains and spheres represented polymers and solvents respectively. LCST miscibility was observed at high pressures, whilst increasing the molecular weight led to UCST phase behavior. The key result of this work was that LJ models could be used to model phase behavior of polymer mixtures. However, real systems were not simulated in the aforementioned work. A further level of CG is achieved by considering the dissipative particle dynamics (DPD) approximation. Here particles

representing an undetermined number of atoms interact via a very soft potential. Wijmans et al.^[90] used DPD potentials with GEMC to model phase separation in polymer-solvent mixtures. It was shown that with DPD, it is possible to capture UCST phase behavior of polymer solutions. DPD simulations were used to find a closed form expression for the liquid-liquid equilibrium (LLE) phase envelope as a function of the volume fraction and the chain length of the polymers. It was shown that this correlation could accurately model the UCST phase behavior of polystyrene in methylcyclohexane, provided that the parameters of the correlations were fit to experimental data. In this study, only temperature induced phase separation was studied, and the phase envelope could only be estimated for UCST type phase separation. Vliet et al. extended the previous work to apply DPD potentials to study pressure induced phase separation of polymer-solvents.^[91] However, to achieve this, the intra and interspecies repulsion parameters were modified for each state point, clearly highlighting a lack of transferability of the parameters.

For all the systems discussed above (both top-down and bottom-up techniques) it is still challenging to study phase equilibria of real polymers in solutions and blends with quantitative accuracy, especially when investigating the critical points of immiscibility. These techniques have been successful in studying homopolymer melts accurately, but it is difficult to obtain cross interaction parameters that are independent of all temperatures and pressures using these simulation techniques.^[75] Accurate cross interaction parameters are necessary if one wants to quantitatively model polymer mixture phase behavior.

There have been very few studies on polymer-solvent mixtures using potentials obtained using SAFT- γ Mie, which are different to the work presented here. Jimenez-Serratos et al. studied the phase behavior of polystyrene in alkanes.^[92] In that study, the potential parameters were not directly fitted using the EoS, and polymers were assembled piecewise: a polystyrene molecule was modeled as an alkane backbone with a side chain composed of toluene molecules. Although this study showed promising results in terms of modeling polymers with SAFT- γ Mie EoS, it was not possible to determine the extent to which the polystyrene molecular model presented in that study could be described by the EoS. Moreover, the cross interaction parameters were not fitted with the EoS as they were adjusted using simulations. Finally, the effect of intramolecular potentials was not investigated, and the polymer was modeled as a freely rotating chain. Most recently, polybutadiene/squalene mixtures have also been studied using SAFT- γ Mie.^[93]

In a different approach, Walker et al.^[94,95] used the SAFT- γ EoS to model polyvinyl alcohols copolymers, by rescaling the parameters obtained from the EoS to model fused-sphere models of polymers. Although this is useful in obtaining the correct structural properties, this rescaling of the parameters means that further simulations are required to find optimal but different force field parameters that produce the same thermodynamic properties as the EoS. It was shown that properties such as densities, heat capacities, and glass transition temperatures could be accurately predicted for the poly(vinyl butyral) copolymers, whilst retaining the correct conformations.

2. Methodology

2.1. SAFT- γ Mie Equation of State

2.1.1. Intermolecular Interactions

Since its inception all SAFT equations of state employ the following perturbation approach, which splits the total Helmholtz free energy of a system, A^{SAFT} , into four contributions^[96–98]

$$\frac{A^{\text{SAFT}}}{Nk_B T} = \frac{A^{\text{Ideal}}}{Nk_B T} + \frac{A^{\text{Mono}}}{Nk_B T} + \frac{A^{\text{Chain}}}{Nk_B T} + \frac{A^{\text{Assoc}}}{Nk_B T} \quad (1)$$

A^{Ideal} is the contribution of an ideal gas. The next term, A^{Mono} , is a free energy contribution corresponding to isolated monomers. The third contribution, A^{Chain} accounts for m monomers forming a chain and the final contribution, A^{Assoc} takes into account short-range directional forces, such as hydrogen bonding, by assuming associating “sticky” sites on the monomers. The full mathematical description of SAFT- γ Mie EoS used in this work can be found in literature.^[11] In this work, only the first three contributions are used to model polymers, as the noncontinuous functions used to model association sites cannot currently be implemented in molecular dynamics simulations.

In this particular version of SAFT- γ Mie EoS, molecules are represented as chains of tangentially bonded spherical monomers (pearl necklace model), that interact with a Mie potential^[99] between two segments, i and j , at a distance r

$$u_{ij}^{\text{Mie}}(r) = C \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{\lambda_{r,ij}} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] \quad (2)$$

where ϵ_{ij} is the depth of the potential well, σ_{ij} is the characteristic length parameter which roughly relates to the distance between two segments, and $\lambda_{r,ij}$ is the repulsive exponent, controlling the softness and the range of the interaction between two segments. C is a prefactor:

$$C = \left(\frac{\lambda_{r,ij}}{\lambda_{r,ij} - 6} \right) \left(\frac{\lambda_{r,ij}}{6} \right)^{6/(\lambda_{r,ij}-6)} \quad (3)$$

In a more general formulation, the attractive exponent of the potential, here fixed at 6, can also be considered an adjustable parameter. Ramrattan et al.^[100] showed the conformality of the Mie fluids and how the pair of exponents (repulsive and attractive) are formally related.

Uniquely, input parameters of the EoS are also the parameters of the intermolecular potential, that is, $A^{\text{SAFT}} = f(\mathbf{m}, \boldsymbol{\epsilon}, \boldsymbol{\sigma}, \boldsymbol{\lambda}_r)$, where $\mathbf{m}$ is a matrix describing the number of segments of each component i in each chain, and the other bold symbols being the matrix of parameters between species i and j . Hence, the EoS is a useful parameter estimation tool to extract “top-down” interaction parameters from experimental macroscopic bulk properties of fluids. The EoS can be used to find effective parameters, $\alpha = [\mathbf{m}, \boldsymbol{\epsilon}, \boldsymbol{\sigma}, \boldsymbol{\lambda}_r]$, that minimize the error between experimental data and the calculations of the EoS. For polymers, experimental

Table 1. Polymers studied in this work. Mapping refers to the number of monomers in one CG SAFT segment.

Polymer	Symbol	Monomer	Molecules Used for Parameter Estimation	Mapping
Polyethylene	PE		n-hexane, n-decane, n-tetradecane, n-octadecane	4:1
Polypropylene	PP		2,4-dimethylhexane, 2,4-dimethylheptane, 2,4-dimethyloctane, 2,4-dimethylnonane	2:1 (1:1) ^{a)}
Polyisobutylene	PIB		2,2,4,4-tetramethylhexane, 2,2,4,4-tetramethylheptane	1:1
Atactic polystyrene	PS		sec-butylbenzene, 2-phenylpentane, 2,4-diphenylhexane	1/2:1 (1:1) ^{a)}
1,4-cis-polybutadiene	PBD		Hex-3-ene, hep-3-ene, Oct-4-ene Dec-5-ene	1:1
Polyisoprene	PI		3-methyl-3-hexene, 3-methyl-3-heptene, 4-methyl-4-octene, 2,6-dimethyl-2,6-decene	1:1

^{a)} Parameters were also fitted and are provided for a mapping ratio of 1:1.

data for small oligomers could be used where data is readily available, invoking the transferability of said parameters. In this study, saturated liquid densities and vapor pressures were chosen as target experimental data in parameter estimation. This is in accordance with previous studies,^[14,17–19,50] where it has been shown that using these two properties provides an adequate adjustment of Helmholtz free energy landscape. The objective function for the minimization is thus

$$\min_{\alpha} F_{\text{obj}}(\alpha) = \min_{\alpha} \left[w_p \sum_{i=1}^{N_p} \left(\frac{P_v^{\text{SAFT}}(T_i, \alpha) - P_v^{\text{Exp}}(T_i)}{P_v^{\text{Exp}}(T_i)} \right)^2 + w_{\rho} \sum_{i=1}^{N_{\rho}} \left(\frac{\rho_l^{\text{SAFT}}(T_i, \alpha) - \rho_l^{\text{Exp}}(T_i)}{\rho_l^{\text{Exp}}(T_i)} \right)^2 \right] \quad (4)$$

where N_p and N_{ρ} are the number of data used for pressure and saturated liquid density respectively. w_p and w_{ρ} are weights given to each type of experimental data, set to be equal to each other in this work. The Python implementation of the gSAFT package^[101] was used to find optimal parameters, where multiple (200) initial guesses sampled from a Sobol' sequence^[102] were used to find optimal solutions, with the LMFIT non-linear least squares library used to find the optimal parameters.^[103]

For multicomponent mixtures, cross interactions between different species are calculated using Lorentz–Berthelot combining rules, using only the pure component potential parameters.^[104]

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (5)$$

$$\lambda_{r,ij} = 3 + \sqrt{(\lambda_{r,ii} - 3)(\lambda_{r,jj} - 3)} \quad (6)$$

For ϵ_{ij} , the cross interaction parameter is allowed to deviate from the geometric mean of the energies of the pure components, with a state-independent adjustable binary interaction parameter, k_{ij}

$$\epsilon_{ij} = (1 - k_{ij}) \frac{(\sigma_{ii}^3 \sigma_{jj}^3)^{1/2}}{\sigma_{ij}^3} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (7)$$

2.1.2. Polymers Studied

In this study, Mie interaction parameters of six polymers were estimated using experimental data for short oligomers. Details of each polymer, its corresponding monomer unit, the molecules used to fit the pure component interaction parameters and the CG mapping are presented in **Table 1**. CG mapping is defined as the number of real monomer units per one CG segment. Mapping ratios were chosen to maximize the number of monomers per bead, whilst ensuring the CG models were able to represent real fluids. All the molecules mentioned in Table 1 and used in the parameter estimation procedure are composed of the following chemical moieties:

- Monomer units of the polymer to be CG,
- Two terminal CH_3 groups, and CH_2 groups modeled explicitly (see framework section below)

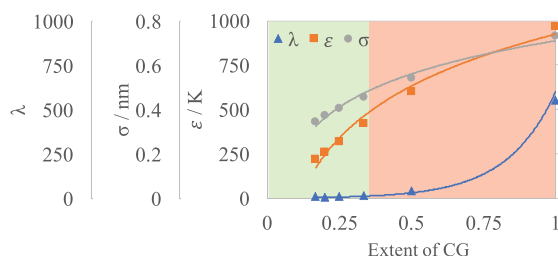


Figure 2. Mie interaction parameters estimated using VLE data versus extent of CG for n-decane. Here an extent of CG of 1:2 or 0.5 corresponds to two CG segments representing a molecule. Green and red regions mark feasible and impractical parameters for molecular simulations respectively. Lines are a guide to the eye.

To employ the SAFT models to describe small molecules, there is no inherent constraint on the level of CG employed, that is, a model bead can be used to represent an arbitrary number of atoms of the target molecule. Hence this choice is sometimes left for the user to specify.^[105]

In SAFT models, a higher mapping ratio corresponds to higher interaction energies and larger spheres. This can be seen in **Figure 2**, where the Mie interactions parameters are plotted against the extent of CG for n-decane. These parameters were estimated using saturation liquid density and vapor pressure. In this case all fitted parameters can reproduce the VLE curve, and a value of one corresponds to one molecule of decane being represented by one CG sphere. Ostensibly having a higher aggressiveness in the CG benefits the molecular simulations, since larger systems can be studied with the same computational effort. However, as can be seen from **Figure 2**, increasing the degree of CG can also lead to extremely high values for ϵ and λ_r . In this instance, a single sphere representation of n-decane would need an $\epsilon \approx 970$ K. For high values of ϵ (or λ), the accessible vapor-liquid region, that is the temperature range between the triple point and the critical point reduces significantly and can even disappear altogether.^[100,106,107] These large values of ϵ and λ_r are essentially an artifact of the equation of state not being able to account for the presence of a (more stable) solid phase. Following this argument, in the example given, a one bead model of n-decane would be unsuitable for modeling decane.

Based on this heuristic approach, a constraint was set to limit the number of carbons per bead to around four to six carbons, whilst ensuring an integer number of monomers are mapped to one CG bead. For most molecular models, this range of number of carbons per CG bead results in the lowest error. Overall, the molecular weights of each bead ranges from 50–100 g mol⁻¹.

All polymers (including those with branched alkanes) are represented as linear molecules, except for polystyrene, where a branched model is chosen, following previous studies.^[67,92] The difference between the polymers can be seen in **Figure 3**.

2.1.3. Intramolecular Interactions

Within the SAFT- γ EoS framework, no reference is made to the intramolecular potentials, as these have no bearing on the equilibrium thermodynamics. However in simulations, it is useful to include intramolecular potentials, as the size of the CG segments

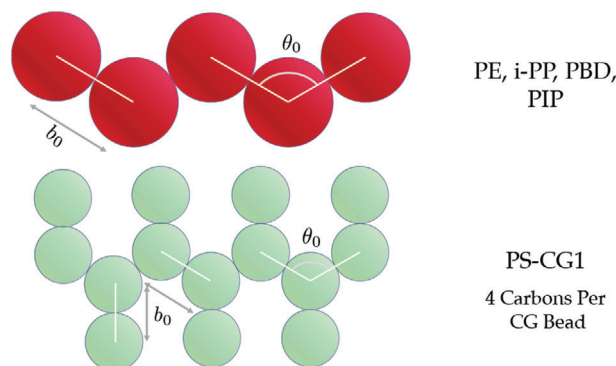


Figure 3. CG representation of the polymers used in this study. Apart from PS which is modeled as a branched polymer, all other polymers were modeled as linear chains. The parameters for θ and b_0 are given in Table 5.

are smaller than the Kuhn length of the polymers. This allows the model to have appropriate rigidity and local structure.

The intramolecular potential is given by

$$U_{\text{Bonded}} = \sum_{\text{bonds}} \frac{1}{2} k_b (b_i - b_{i,0})^2 + \sum_{\text{angles}} \frac{1}{2} k_\theta (\theta_i - \theta_{i,0})^2 \quad (8)$$

In the above equation, the bonding constraint between two adjacent beads is taken into effect by the bonds term, where b_0 is the equilibrium bond length and k_b is a harmonic bond constant. The angle θ formed between three bonded particles is constrained using the second term, with θ_0 being the equilibrium angle and k_θ being the bond constant.

Given the constraints of the theory, b_0 is set equal to σ_{ij} , and k_b , k_θ , and θ_0 are fitted to match probability distributions, $P(x)$, from atomistic simulations, fitted by weighted Gaussian distributions^[17,108]

$$P(x) = \frac{w(x)}{\sqrt{2\pi s^2}} e^{-(x-\mu)^2/2s^2} \quad (9)$$

Here x is the intramolecular variable for which the probability distribution is calculated. In this work it is either the distance ($x = b$) between two neighboring CG segments or the angle ($x = \theta$) between three neighboring CG segments. The mean distance or angle between the segments is given as μ ($\mu = b_0$ or θ_0) and s is the standard deviation of the Gaussian distribution. A weighting function $w(x)$ is used to account for the asymmetry of the distributions. $w(r) = b^2$ and $w(\theta) = \sin(\theta)$ were used as the weight functions for bond stretching and angular bending respectively. The harmonic potentials are thus given as

$$u_{\text{Bond}} = \frac{1}{2} k_b (b - b_0)^2 \approx k_B T \ln P(b) \quad (10)$$

$$u_{\text{Angle}} = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \approx k_B T \ln P(\theta) \quad (11)$$

Fully atomistic simulations were run using the OPLS-AA (all atom) force field^[109] at $T = 400$ K and $P = 1$ bar for oligomers containing eight monomers for all molecules presented in Table 1. Also the harmonic potentials for PS model was only fitted for the backbone of the polymer, as shown in **Figure 3**.

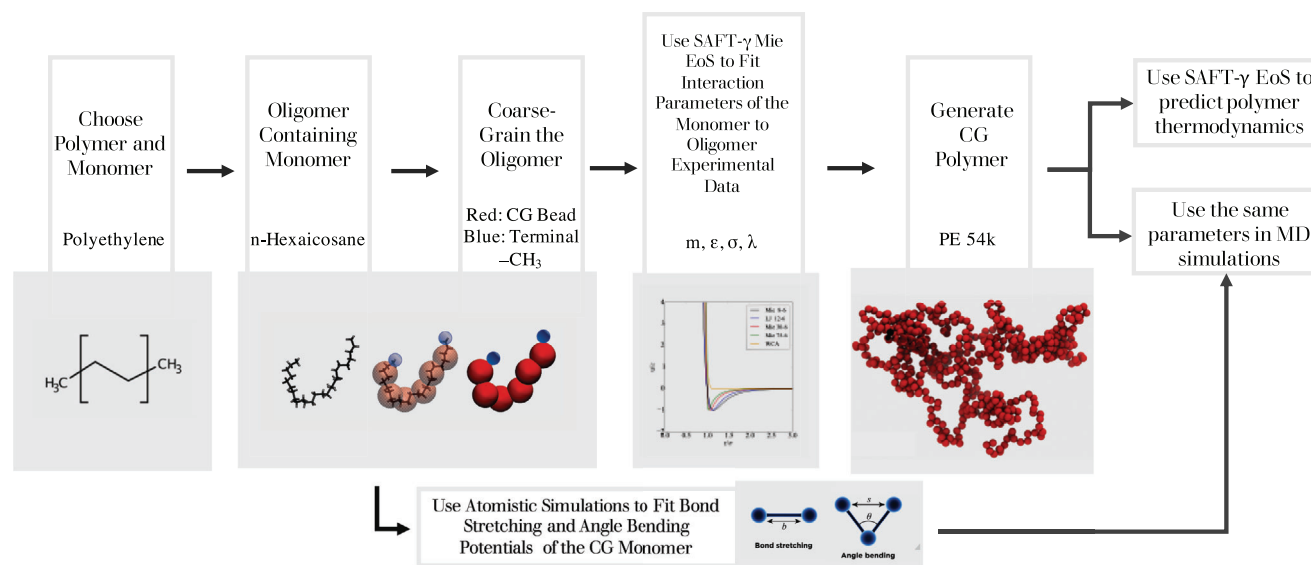


Figure 4. Overview of the proposed SAFT- γ Mie CG methodology for modeling polymers.

Table 2. Group parameters for the methyl and methylene functional groups (CH_3 and CH_2) taken from Hutacharoen et al.^[50]

Functional group	$S_k^a)$	λ_r	ϵ/k_B [K] ^{b)}	σ [Å]
CH_3	0.5726	15.05	256.8	4.077
CH_2	0.2293	19.87	473.4	4.880

^{a)} S_k is the shape factor; ^{b)} cross interaction parameter between the two species is $\epsilon_{ij} = 350.772$ K

2.1.4. SAFT- γ Force Field Framework

The overall framework employed is visually presented in **Figure 4** for the case of polyethylene (PE). Here, polyethylene is modeled as a chain of CG segments, each containing $-(\text{CH}_2)_4-$ groups. First, experimental data for n-hexacosane ($\text{C}_{26}\text{H}_{54}$) is collected, containing two CH_3 groups, and six CG monomer units. When finding parameters for the CG beads from oligomers, it is important to recognize the influence of the end groups in the parametrization. In the example provided, if one were to include the end CH_3 groups into any CG bead, it would distort the “effective” parameters. To minimize this risk, when using the EoS on oligomers, we employ the capability of the SAFT- γ Mie EoS to consider mixed (heterogeneous) chains and the inclusion of a shape factor, S_i , to consider smaller contributions, typically one or two heavy atoms and their associated hydrogens. In particular, we perform the parameter estimation of the CG bead by including, in an explicit way, the contribution of CH_2 and CH_3 groups. Experimental data of multiple oligomers (C_{10} to C_{26}) can be used simultaneously to find the best set parameters. Once optimal parameters found, polyethylene can be modeled by changing the number of CG segments in a chain.

For SAFT- γ Mie EoS, accurate CH_3 and CH_2 parameters exist that have been verified for a range of systems. The parameters are given in **Table 2** and are taken directly from Hutacharoen

et al.^[50] As mentioned before, the functional groups CH_3 and CH_2 are too small to be able to be modeled as spheres, and shape factors are used to model them. For some cases, binary interaction parameters between the monomer group and the other two groups were not fitted and Lorentz–Berthelot combining rules (with $k_{ij} = 0$) were sufficient. However, for PS, PBD, and PIP it was necessary to adjust the cross interaction parameters between the CH_3 group and the monomer to find good fits to experimental data, which can be found in greater detail in Section S1, Supporting Information.

2.2. Parameter Estimation: Non-Bonded Interaction Parameters

Molecules used to find polymer parameters and the experimental error between the calculations of the EoS and experimental data in the fitting procedure are provided in **Table 3**. All parameters were fitted using the objective function described in Equation (4) using saturated liquid densities and vapor pressures data of small molecules specified in Table 1. In order to compare the theory and literature data, overall error (for a given property x) between experimental data and theory is measured using AAD

$$\text{AAD \%} = 100 \times \frac{1}{N} \sum_i^N \frac{|x_i^{\text{SAFT}} - x_i^{\text{Exp}}|}{x_i^{\text{Exp}}} \quad (12)$$

A summary of the molecules used in fitting the interaction parameter of each polymer and the AADs in the parameter estimation procedure is provided in Table 3. For a detailed description of the parameter estimation procedure for each polymer, the reader could refer to Section S1, Supporting Information.

Non-bonded potential parameters for the six polymer models used in this study are given in **Table 4**. In this work, the results are only shown for the branched polystyrene and a higher CG mapping for polypropylene (2:1).

Table 3. The summary of the parameter estimations for all the polymers studied in this work.

Molecule	N_{CG}	$N_{CH_3}^+$	$N_{CH_2}^+$	AAD ρ %	AAD P_V %
Polyethylene					
n-hexane	1	2	0	0.52	0.80
n-decane	2	2	0	0.93	1.45
n-tetradecane	3	2	0	1.14	1.83
n-octadecane	4	2	0	1.51	3.54
Triacontane	7	2	0	1.23	3.23
Polypropylene					
2,4-dimethylhexane	1	2	0	2.04	3.21
2,4-dimethylheptane	1	2	1	2.96	2.76
2,4-dimethyloctane	1	2	2	2.44	5.70
2,4-dimethylnonane	1	2	3	2.92	8.70
Polyisobutylene					
2,2,4,4-tetramethylhexane	2	2	0	2.10	4.94
2,2,4,4-tetramethylheptane	2	2	1	2.54	4.71
Polybutadiene					
Hex-3-ene	1	2	0	1.90	1.20
Hept-3-ene	1	2	1	2.23	4.70
Oct-4-ene	1	2	2	2.00	8.20
Dec-5-ene	1	2	4	2.80	10.80
Polyisoprene					
3-methylhex-3-ene	1	2	0	2.40	3.50
3-methylhept-3-ene	1	2	1	1.70	4.32
4-methyloct-4-ene	1	2	2	2.30	7.30
2,6-dimethyl-2,4-decene	2	2	0	5.24	10.50
Polystyrene					
sec-butylbenzene	2	2	0	1.70	6.52
sec-butylbenzene	1	2	0	4.40	8.51
2-phenylpentane	2	2	1	3.00	5.62

Table 4. Intermolecular potential parameters of the CG polymers.

Polymer	$M_{w,CG}$ [g mol ⁻¹]	Mapping	λ_r	ϵ/k_B [K]	σ [Å]
Polyethylene (PE)	56.11	4	21.71	441.7	4.69
Isotactic polypropylene (PP)	84.16	2	24.94	571.6	5.51
1,4-cis-polybutadiene (PBD)	54.09	1	22.91	451.5	4.59
Polyisoprene (PIP)	68.12	1	23.39	514.3	4.98
Atactic polystyrene	52.08	0.5	10.67	284.6	4.16
Isotactic polypropylene (PP) ^{a)}	42.08	1	10.94	246.2	4.10
Atactic polystyrene ^{a)}	104.15	1	21.07	538.0	5.43

^{a)} Parameters were fitted and are provided, however, polymer properties are not discussed in this work.

2.3. Parameter Estimation: Bonded Interaction Parameters

Intramolecular potential parameters obtained from atomistic simulations are presented in **Table 5**. **Figure 5** shows the comparison between bonded and angular distributions from atomistic simulations and the corresponding CG simulations for PE, PP, PBD, PS. In SAFT- γ methodology, the bond distance has to be equal to the value of σ , which is shown using vertical lines for the

Table 5. Intramolecular potential parameters (Equation (9)) fitted to all atom simulations of oligomers containing eight monomer units at 400 K and 1 bar. For PE and PBD, k_θ was adjusted from 21.67 and 14.63 kJ mol⁻¹ rad⁻² respectively to match experimental radii of gyration. θ_0 and k_b are taken directly from atomistic simulations. b_0 used in this work is set to σ presented in Table 4, however, values of b_0 calculated from all atom simulations are reported ($b_{0,OPLS}$) for comparison.

Polymer	k_θ , SAFT [kJ mol ⁻¹ rad ⁻²]	θ_0 [°]	k_b [kJ mol ⁻¹ nm ⁻²]	$b_{0,OPLS}$ [nm]	$b_{0,SAFT}$ [nm]
PE	8.67	179.97	2900	0.477	0.469
PP	3.94	174.00	2356	0.490	0.551
PBD	5.63	159.30	2366	0.412	0.459
PS	12.07	118.21	2743	0.307	0.416
PIP ^{b)}	5.63	159.30	2366	0.412	0.498
PS (1:1) ^{a)}	24.21	74.77	747	0.550	0.543
PP (1:1) ^{a)}	16.08	111.11	3142	0.324	0.410

^{a)} Parameters were fitted and are provided, however, mixture properties are not provided in this work; ^{b)} For PIP, k_{bond} , k_θ , and θ_0 were modeled using the same parameters as PBD. R_G and R_E were not calculated for PIP.

bonded distances. The distribution of the bonds and angles from both CG simulations are presented using dashed lines. The angular distributions are very similar for all cases. However, for PE and PBD, k_θ was significantly lowered to match the correct radius of gyration for PE. This has the effect of shifting the distribution to smaller angles. The angular distribution of i-PP follows that of the OPLS-AA distributions for angles of 120–180°. However, below these angles there is another peak around 60°. In terms of bond lengths, it could be seen that the average bond length for SAFT- γ Mie and OPLS-AA mapping are very similar for the case of PE and PBD. For polypropylene, however, the average bond length given by SAFT- γ Mie EoS is around ten percent higher than that given by OPLS-AA mapping. For polystyrene, this difference is even greater, which is a consequence of the CG representation of the molecules within the SAFT framework. Given that the theory uses a top-down approach, where bond distances are fitted to densities and not intramolecular potentials, it may not be possible to predict the correct bond distances assuming a pearl necklace model.

2.4. Property Prediction with SAFT- γ EoS

To evaluate the quality of the predictions of properties of pure homopolymer melts via the SAFT EoS, each polymer was modeled as a chain of 500 monomers. Liquid phase densities were calculated across a wide range of temperatures and pressures using the EoS and MD simulations. At this high molecular weight, densities of polymers are no longer a function of their molecular weights, and densities are compared to those found in literature. The range of temperatures and pressures used were based on those provided by Rodgers.^[29] Polymer–solvent binary mixtures are considered, where solvents are taken to be homonuclear and presented by the SAFT CG model. Solvent parameters were either fitted using VLE data (vapor pressures and saturation liquid densities), or were taken from the Bottled-SAFT package.^[110] Three types of phase diagrams were generated for this work, namely temperature–composition (either volume or weight

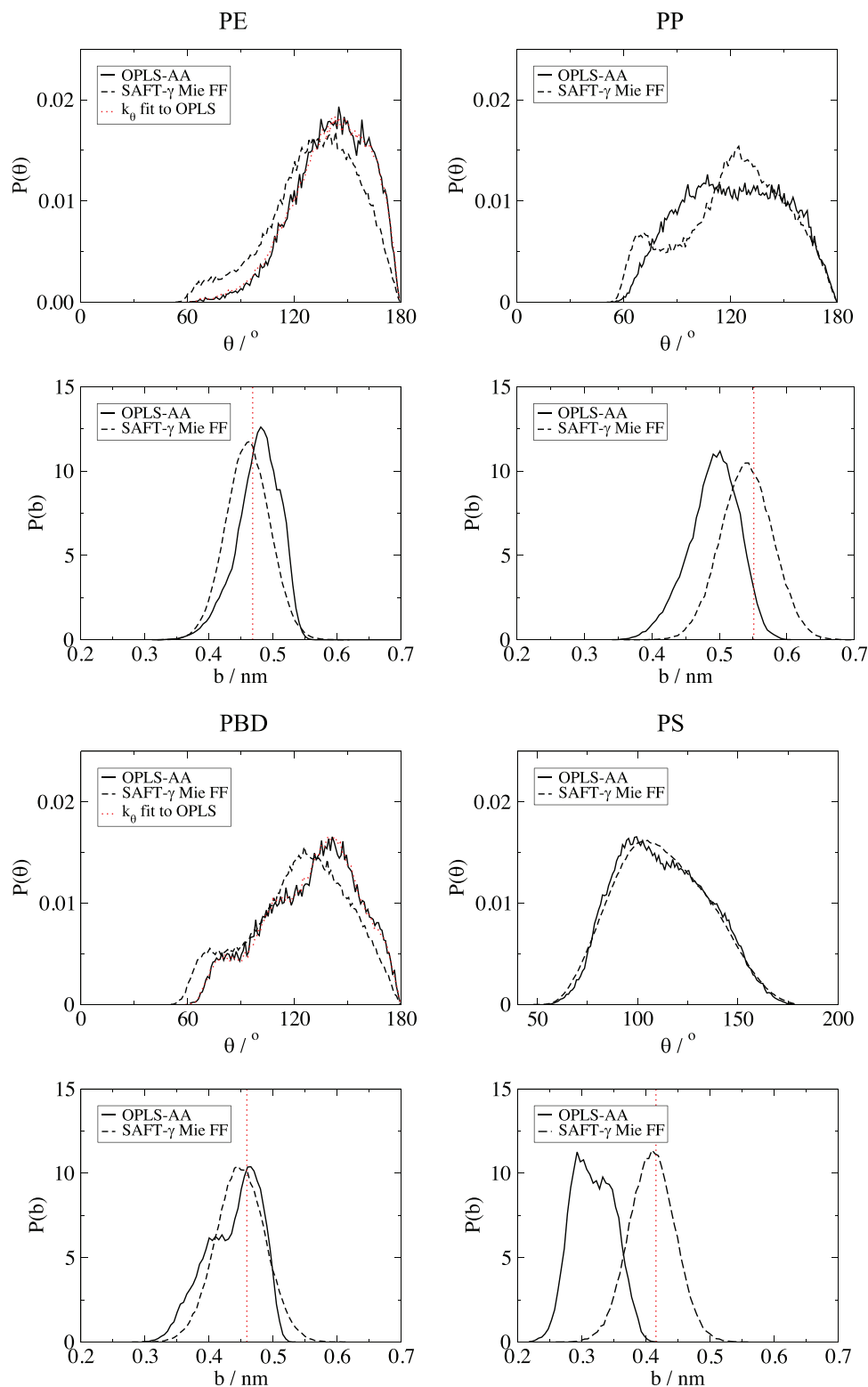


Figure 5. Angles and bonded distributions of different polymers mapped from OPLS-AA simulations at $T = 400$ K and $P = 1$ bar. Solid lines correspond to atomistic simulations, and dashed lines to SAFT- γ Mie CG FF (Table 5). For PE and PBD, k_θ is adjusted to obtain the correct radius of gyration of the homopolymer melt. The dashed vertical line corresponds to the value of σ .

fraction), pressure–composition or pressure–temperature. Unless stated, for temperature composition diagrams, the pressure at each temperature is at the vapor pressure of the solvent, corresponding to real experimental set up. Finally unless stated, the cross interaction parameters were not adjusted (i.e., $k_{ij} = 0$).

2.5. Molecular Simulations

In this study, molecular dynamics simulations were run to simulate polymers, using GROMACS/4.6.5^[111,112] and GROMACS/5.1^[113] packages. Given previous simulations studies using SAFT- γ force fields typically use time-steps (Δt) of 0.01 ps,^[92,114] the same value was used in this work. Simulations were run to ensure the robustness of the large value of the time-steps used by comparing the same simulations with identical ones using smaller time-steps. Results from larger time-step of 0.01 ps agreed with simulations using smaller time-steps of 1–2 fs, typically used in all-atoms simulations. The leapfrog algorithm was used for the numerical integration of the equation of motion. NPT ensemble simulations were used to model systems at constant pressure and temperature respectively. Nosé–Hoover thermostat,^[115,116] and Parrinello–Rahman barostat^[117,118] were used to correctly obtain the canonical or isobaric–isothermal distributions. In all simulations in this work, a cut-off of 2 nm was used without tail corrections.

Using molecular dynamics to model polymeric mixtures means that very large system sizes need to be simulated to take into account interfacial boundaries between two immiscible fluids. GEMC circumvents this problem by having two boxes composed of each of the separate phases, with no interfacial boundaries. GEMC has been used to study chains systems of up to 100 beads. In this work chains of up to 600 beads are used to model phase behavior of very large polymers in solvents. GEMC could be very slow for long chains as insertions and deletions are required to move a chain from one box to the other. This problem is exacerbated for highly dense systems. Thus direct coexistence simulations using MD was preferred given that highly parallelized packages are available. Most simulations were run up to 2 μ s as computing capacity was available. 1 μ s corresponds to 100 million time steps using $\Delta t = 0.01$ ps.

Simulations were performed using either Imperial College's HPC facilities or Thomas Cluster of UCL HPC facilities.

2.5.1. Homopolymer Melts

Once the intramolecular potential parameters were fitted using atomistic simulation, systems containing polymer melts composed of 500 CG monomer units were simulated for a range of temperatures and pressure to compare the densities to the predictions of the EoS.

Moreover, the conformation of each polymer melt was also studied by measuring radius of gyration and end to end distances of polymers in pure melt containing 300 polymers, for chains composed of up to 160 segments. NPT simulations were run at specified temperatures and pressure for 2 μ s to equilibrate the systems and a production run of 0.5 μ s was used to calculate properties. If the radius of gyration was not correctly calculated,

the value of k_θ was readjusted in the simulations in order to obtain the correct conformational properties in melt. Top-down approaches do not necessarily have to have the correct local structural properties as they are fitted to macroscopic properties, but it is important that the models have the correct R_G and R_E in melt and solution.

Radii of gyration and end to end distances were calculated using Equations (14) and (13) respectively.

$$R_{\text{End}}^2 = \langle (\mathbf{r}_N - \mathbf{r}_0)^2 \rangle \quad (13)$$

$$R_g^2 = \frac{1}{N+1} \sum_{i=0}^N \langle (\mathbf{r}_i - \mathbf{r}_{\text{com}})^2 \rangle = \frac{1}{2(N+1)^2} \sum_{i,j=0}^N \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle \quad (14)$$

2.5.2. Phase Behavior of Polymer Mixtures

For modeling mixtures, NPT simulations were run in elongated orthorhombic boxes, with the smallest side of the simulation box being at least three times the radius of gyration of a polymer molecule. To observe phase separation at a fixed pressure, NP_{zz}T simulations were run where pressure was anisotropically applied in the direction of the longest side of the simulation.

It is quite challenging to accurately measure coexistence compositions of mixtures of polymers with solvents and in blends. The interfacial region of the polymers mixtures are not planar and polymers could have different instantaneous conformations. This means that it is not usually possible to differentiate bulk and interfacial regions in simulations. In order to indicate whether phase separation has occurred in the simulation box, a novel method first proposed by Gelb and Müller^[119] was utilized to analyze local compositions in the simulation box. In this method, phase separation is inferred by studying the distribution of the local compositions of the polymer in solution. The small regions are cubes of side length of ≈ 2.0 nm. The method is visually explained in **Figure 6**. A bimodal distribution in the local composition implies an immiscibility. This method might not give exact coexistence compositions due to the interfacial effects in the simulations, however, it is used as a tool to qualitatively observe the onset of immiscibility.

3. Results: Equation of State Modeling of Polymers

3.1. PVT Prediction: From Oligomers to Long Chains

Given that the parameters were fitted to small oligomers, it is important to see the transferability of the parameters to chains of any lengths. Thus, following parameter estimation, single phase densities of pure homopolymer melts at different pressures and temperatures were calculated, with polymers being monodisperse chains of 500 CG monomer units. This was then compared with correlations of experimental data by fitted by Rodgers.^[29] In the study, Rodgers has correlated experimental PVT data of very large polymers ($M_w > 10^5$ g mol⁻³) using different equations of state, from which we have chosen the Sanchez–Lacombe correlation, where errors associated with this correlation are less than 0.05 % for pressures of up to 500 bar. Given the large molecular weights of the polymers in the experimental data, the PVT data is not affected by the molecular weight distribution of the samples.

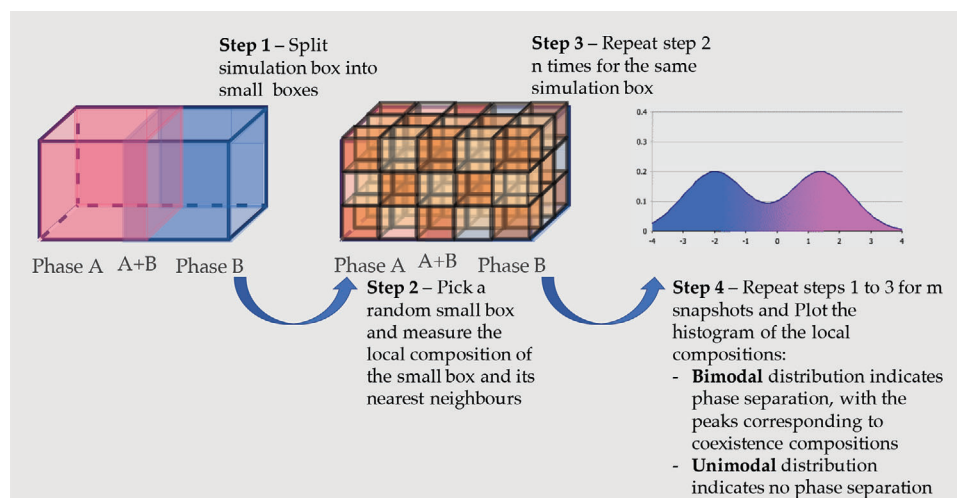


Figure 6. The method of Gelb and Müller^[119] used in this work to observe phase separation in polymer mixtures.

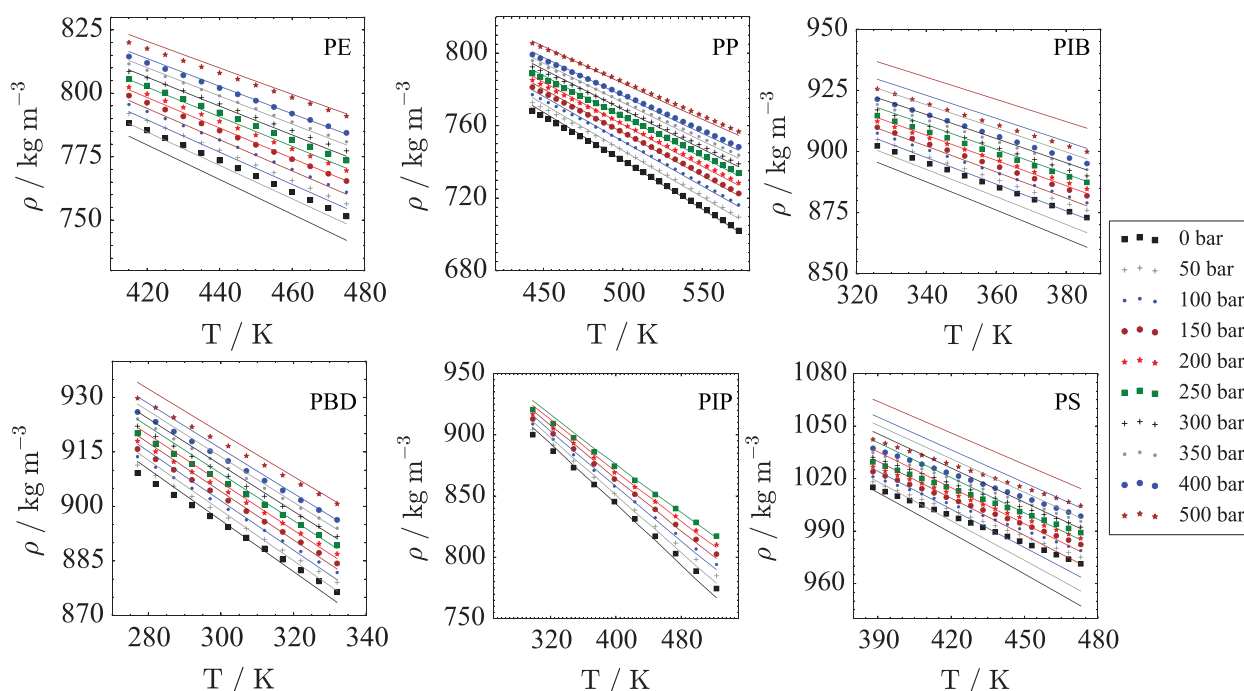


Figure 7. Prediction of homopolymer melt densities of the seven polymer studied in this work (lines), as compared with experimental data correlated by Rodgers (symbols).^[29] Larger versions of each of the subplots can be seen in Supporting Information.

The comparisons are presented in **Figure 7**. Densities were calculated for pressures ranging from atmospheric pressures to 500 bar. For polyolefins, densities agree well the results of Rodgers, with polyethylene, 1,4-cis-polybutadiene and polyisobutylene having AADs of 0.5%, 0.4%, and 0.5% respectively, and polypropylene and polyisoprene having a better agreement with AADs of 0.1%, implying that higher levels of CG (i.e., a higher mapping ratio) improve PVT calculations.

For polyethylene the agreement between the predictions of SAFT- γ Mie and LDPE is very good for higher pressures, with deviations observed at lower pressures. The overall shape of the

PVT lines are in agreement. This is also true for PBD, however for PIB, the predictions deviate at lower and higher pressures, with a steeper temperature gradient in SAFT- γ Models. However, given the prediction of these parameters, the agreement is robust.

The agreement between the predicted PVT data and those of Rodgers for polystyrene is not as robust as the previous cases. There is a 0.9% AAD over entire PT phase space, which for the case of the $P = 0$ bar, the AAD is 4.2%. The slope of the lines do not agree either. This could be due to the effect of branching which is not necessarily captured by the theory.

Table 6. Molecules used to model binary mixtures with polymers, and the self and cross interaction parameters. m_{seg} is the number of CG monomers representing each molecule.

Molecule	m_{seg}	λ_r	ϵ/k_B [K]	σ [Å]	k_i PE	k_i PP ^{a)}	k_i PIB	k_i PBD	k_i PS ^{a)}
Ethane	1	19.69	308.9	4.21	0	—	—	—	—
Carbon dioxide	2	14.14	193.2	2.85	0.050	−0.166	—	—	0.055
Ethylene	1	20.23	284.5	4.15	0	−0.102	—	—	—
Propane	1	23.17	395.8	4.81	0	—	—	—	—
n-pentane	2	14.75	307.9	4.26	0	−0.061	0	—	—
Cyclopentane	2	13.37	309.8	4.00	—	—	0	—	—
Isopentane	2	13.81	289.1	4.23	—	—	0	—	—
n-hexane	2	18.01	371.1	4.52	0	—	0	−0.045	0.011
Cyclohexane	2	13.30	338.7	4.24	—	—	0	—	0.016
2,2-Dimethylbutane	2	14.17	311.5	4.47	—	—	0	—	—
2,3-Dimethylbutane	2	14.83	328.1	4.46	—	—	0	—	—
n-heptane	2	21.27	427.0	4.77	0	—	0	—	0.007
Methylcyclohexane	2	14.68	372.3	4.50	—	—	—	—	0.016
n-octane	3	14.30	314.7	4.22	0	—	0	—	0.015
1,1,2-Trimethylpentane	2	18.59	405.9	4.92	—	—	—	−0.005	—
n-nonane	3	18.31	374.3	4.38	0	—	—	—	—
n-decane	3	21.18	417.4	4.54	0	—	—	—	—
n-dodecane	1	23.32	472.2	4.91	0	—	—	—	—
Benzene	2	13.43	346.7	3.98	—	—	0	—	—
Acetone ^{b)}	2	17.43	286.0	3.60	—	—	—	—	−0.007

^{a)} Cross interaction parameters, k_{ij} for the 1:1 mapping for PS and PP are given in Section S2, Supporting Information; ^{b)} Acetone is not modeled with only dispersions, and it is modeled as an associating molecule with parameters previously published in ref. [120].

It is feasible that if one were to fit the EoS directly to the experimental PVT data, a reduction of the error may be achieved, either by employing further adjustable parameters (e.g., the shape factor) and/or by finding other parameterizations unconstrained by the CG model. The errors quoted are not indicative of the SAFT- γ model, but of the implementations discussed herein.

3.2. Mixtures and Cross Interaction Parameters

Although cross interaction parameters had to be fitted for some of the mixtures in this work, the shape of the phase envelopes (whether lower or upper critical T/P were observed) is purely due to the free energy landscape of the polymer solvent mixture. No attempt was made to force a mixture to have any particular phase envelope by having temperature or pressure dependent cross interaction parameters, or by fitting the polymer models to mixture properties.

A summary of all the solvents used in this work and their interactions with each polymer, if fitted, is given in **Table 6**. For mixtures containing polyethylene or polyisobutylene, no adjustable cross interaction parameter was needed except for polymer blends with CO_2 . However adjustable cross interaction parameters were needed to model all mixtures of PBD, i-PP and PS. For PS and PBD the value of the k_{ij} was found to be relatively small (<5%), however, for i-PP, given the large CG mapping, much larger cross interaction parameters were required to accurately capture the phase behavior of polymer mixtures.

3.2.1. PE, PIB, and PP: Type II and V Phase Behavior

The results of different PE mixtures in n-alkanes are presented in **Figure 8**. All the phase behaviors of polyethylene in the aforementioned figure are predicted with no adjustable parameters. Pressure, temperature, and the molecular weight of the polymer are variables and both upper and lower critical phase behaviors were predicted, with quantitative agreement with experimental data.

The first case presented is the pressure induced phase separation of a small oligomer of polyethylene (C_{60} , 840 Da) in propane (**Figure 8(left)**). Here, increasing the temperature leads to a larger region of immiscibility in the P -mass diagram. Critical points and the shape of the phase envelope are in quantitative agreement. This agreement is not unexpected given that triacontane (C_{30}) was used in parameter estimation, which is only half of the length of C_{60} .

Not only mixture properties of small oligomers can be predicted with the model, mixtures of longer polymers are also predicted. In **Figure 8(middle)**, LCSTs of two medium sized oligomers (2.15 and 16.4 kDa) at a pressure of 5 MPa are presented. This was then extended to a very long PE (108 kDa) in the right plot, again showing that not only the critical points are predicted with quantitative accuracy, but also the shape of the phase envelope is in agreement with experimental data.

Finally, the UCSTs of 140 kDa PE in n-alkanes up to C12 were predicted and again agreeing with literature data without any adjustable parameters, clearly highlighting the robustness of the parameters for polyethylene (**Figure 9**).

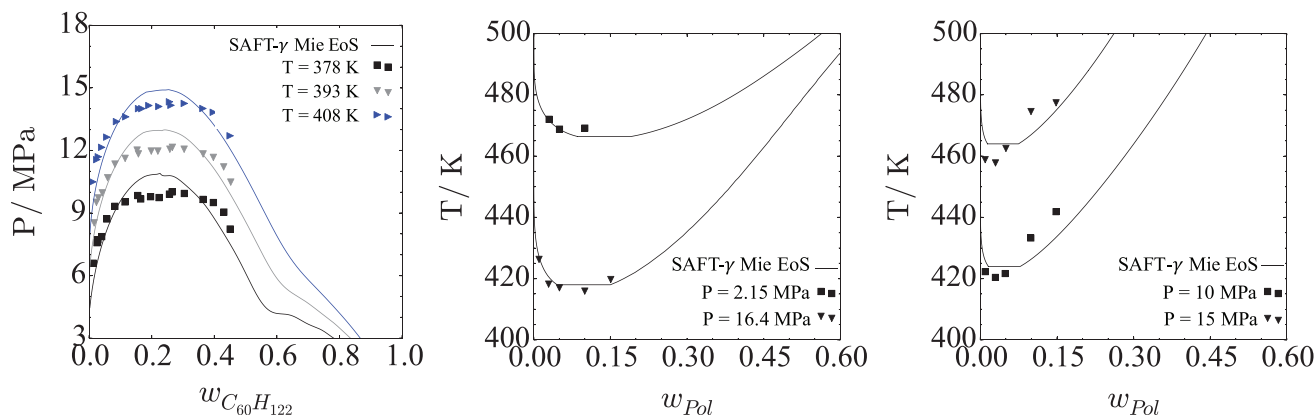


Figure 8. (Left) LLE of n-hexacontane ($C_{60}H_{122}$) and propane.^[121,122] (Middle) Effect of M_W on the LCST (Type V) of PE, n-pentane mixtures at 5 MPa.^[123] (Right) Effect of pressure on LCST (Type V) of PE, n-pentane mixtures at $M_W = 108 \text{ kg mol}^{-1}$ (1982 CG segments). Symbols are experimental data and the continuous curves correspond to the predictions of the model, with no adjustable parameters. The molecular weight of PE gets longer from left to right.

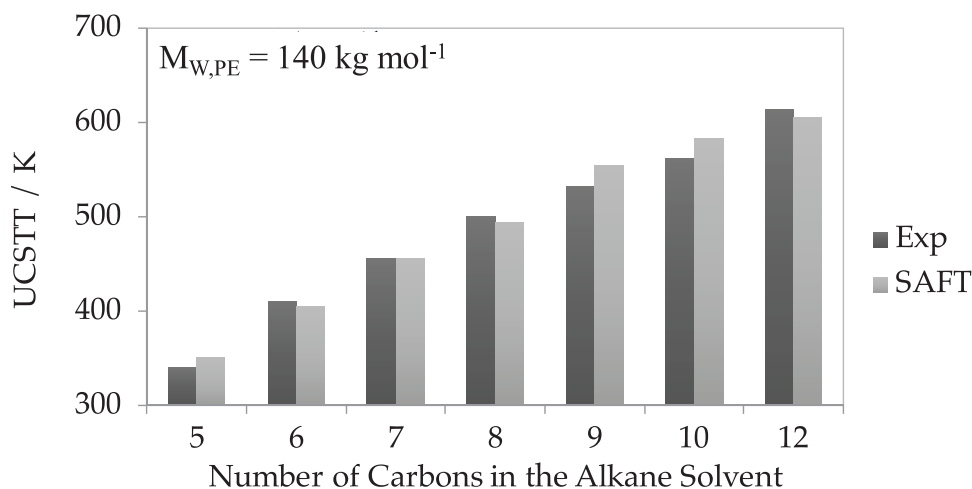


Figure 9. UCST (Type II) of 140 kDa PE in n-alkanes, compared with experimental data presented in Paricaud et al.^[124]

The phase diagram of mixtures of this PIB is then presented. In this case, LCSTs of PIB ($M_W = 112 \text{ kDa}$) were predicted for a range of solvents. Just like the case of polyethylene, the LCSTs were calculated without any binary adjustable parameters. The results can be seen in **Figure 10**. The solvents used are alkanes and benzene, with size, structure and chemistry of the solvents being variables. Remarkable agreement is observed. For all cases studied, the AAD was 2.61%. The model correctly predicts that branched isomers of alkanes have a lower LCST than the linear ones, and that cyclo-alkanes are more miscible with PIB. Miscibility also increases with increasing molecular weight of the solvent. Finally, miscibility of benzene was also correctly predicted.

Just like polyethylene and n-alkanes mixtures (Figure 8(left)), pressure induced miscibility at high pressures is also observed for systems containing polypropylene. Experimental data of polypropylene in n-pentane and propane exists for polydisperse mixtures. To assess the limits of CG, attempts were made to predict the phase envelopes of these mixtures using this model of PP with a higher degree of CG (six carbons per CG segment).

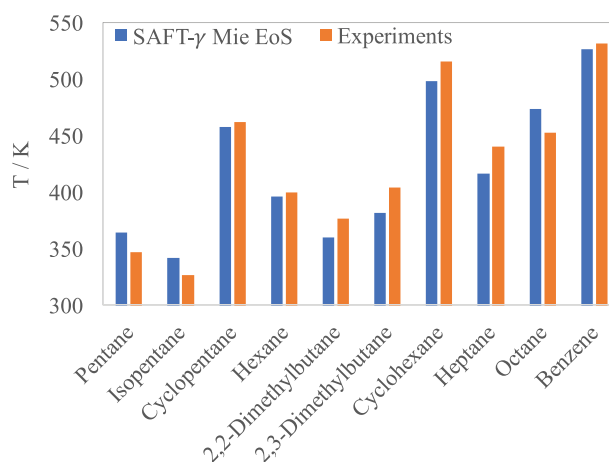


Figure 10. Prediction of LCST (Type V) of PIB in a range of solvents, with no adjustable parameters used. Experimental data were taken from Sanchez et al.^[125]

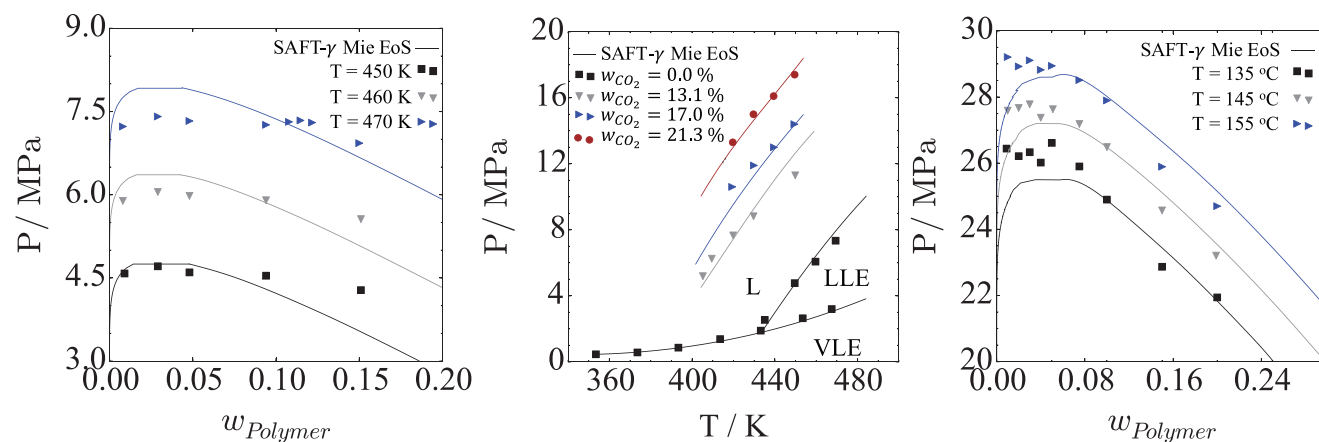


Figure 11. (Left) Pressure induced phase separation (LLE) of $M_W = 50.4$ kDa polypropylene ($M_W/M_N = 2.2$) in n-pentane. Phase diagram calculated assuming a monodisperse system. Symbols are taken from Martin et al.^[126] with a $k_{ij} = -0.061$. (Middle) PT diagram of the previous binary mixture with CO_2 added. Without CO_2 (black line), $w_{\text{polymer}} = 0.03$. (Right) Pressure induced phase separation of polydisperse PP ($M_W = 290$ kDa, $M_W/M_N = 4.46$) and propane at high pressures, symbols taken from Whaley et al.^[128]

Parameters for 1:1 mapping were also calculated and are provided in Section S2, Supporting Information. This 1:1 model for i-PP can be used to predict properties of mixtures with n-propane and n-pentane without any k_{ij} . However, a higher degree of CG is useful in molecular simulations where one can study much heavier polymers, as will be shown later. A single state-independent cross interaction parameter, given in Table 6 was required to observe the correct phase behavior. Cross interaction parameters had to be adjusted using one set of experimental data at the lowest temperatures, and isothermal pressure composition diagrams were predicted for high temperatures. It is interesting that, for PP, the values of k_{ij} listed in Table 6 are all negative, implying a favorable polymer-solvent interaction. Especially for the case of propane, a k_{ij} of -10% is an extremely favorable cross interaction parameter, implying that at higher levels of CG, the cross interaction parameters are significantly different to ideal combining rules, even for simple aliphatic chains.

The first PP mixture modeled here is the case of 50.4 kDa polypropylene-pentane mixture. Experimental data from Martin et al.^[126] for this system is for a polydisperse system ($M_W/M_N = 2.2$). However, following Gross and Sadowski, the polymer is modeled as monodisperse. For this system, it was not possible to predict the phase behavior of the binary mixture, and a k_{ij} had to be fitted to the data at the lowest temperature, and the phase separation predicted at other temperatures. The results can be seen in Figure 11(left). The shape of the phase envelope is not captured well. But the phase behavior is correctly captured only at the lower polymer weight fractions (<10 wt%). This can be seen in Figure 11(middle), where the curve of LLE and VLE are correctly predicted for a polymer ($w_{\text{polymer}} = 3\%$). Not only is it possible to observe the LCST at the correct conditions for the binary mixture, the shift in the LCST due to the addition of CO_2 is also correctly captured. For the ternary mixture, the cross interaction parameter for PP, n-pentane is already fitted to the binary mixture. Binary interaction between n-pentane and CO_2 was fitted to VLE data^[127] (found in Section S3, Supporting Information). Binary interaction between CO_2 and PP was then fitted to the ternary experimental data at the highest CO_2 concentration, once all other

Table 7. Components representing a polydisperse propylene, as modeled by Gross and Sadowski.^[46] For this three pseudo-component mixture, $M_N = 65.91$ kDa, $M_W = 290$ kDa.

Pseudo-component	M_N	Mass fraction
1	35 761	0.50843758
2	504 684	0.479290585
3	2 438 723	0.012271832

parameters were known. The model could predict ternary PT diagrams for systems of up to 10% polymer weight fraction (found in Section S3, Supporting Information).

Finally a polydisperse propylene-propane system was also modeled, again demonstrating the viability of the model to predict pressure induced phase separation. The polydisperse polymer was modeled using three pseudo components, with molecular weights taken directly from Gross and Sadowski^[46] and presented in Table 7. A state-independent k_{ij} was found to be robust to predict not only the critical pressures, but also the shape of the phase envelope.

This clearly, shows that independent of the CG mapping, provided a robust parametrization, the SAFT- γ Mie EoS is a viable method in modeling polymer melts and blends. For a lower degree of CG, for example, PE and PIB, it was possible to predict phase envelopes of mixtures with alkanes without adjustable parameters. However, with a higher degree of CG (six carbons), a state-independent k_{ij} was necessary to obtain the correct phase behavior. The cross interaction parameters are negative, implying more favorable cross species interactions.

3.2.2. Polybutadiene: Type III and IV Phase Behavior

Low molecular weight 1,4-cis-polybutadiene is known to exhibit two types of phases yet to be presented here: Type IV, where both UCST and LCST LLE regions are present in the system, as well as Type III, where the LCST and UCST regions join to form one

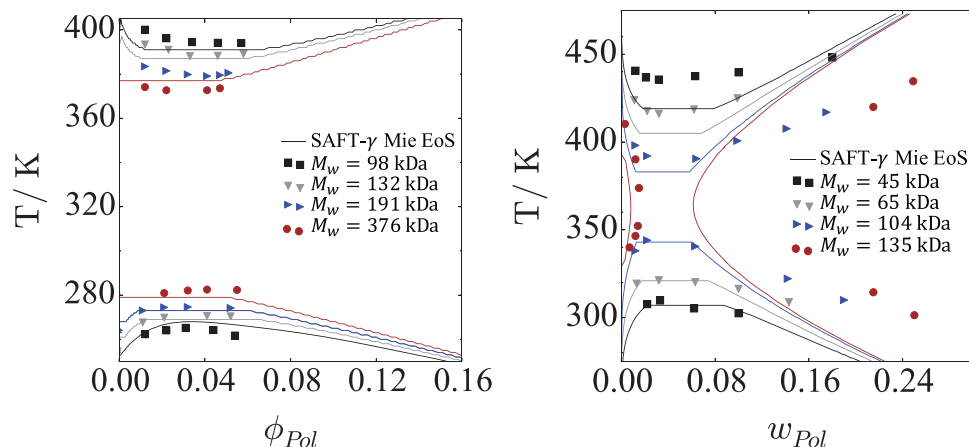


Figure 12. Temperature-polymer composition phase diagram of a binary mixture of PBD in (left) n-Hexane, and (right) 1,1,2-Trimethylpentane. symbols correspond to experimental data taken from Delmas et al.^[129]

LLE region, with two regions of miscibility at high and low polymer compositions at intermediate temperatures. With increasing molecular weights, the difference between the upper and lower critical regions becomes smaller, as the regions grow closer to each other. For PBD in n-hexane, the LCST and UCST regions are insensitive to the molecular weights of the polymer up to 400 kg mol⁻¹, whereas for branched alkanes, as previously discussed for polyisobutylene, mixtures become more immiscible at much lower molecular weights. It is this greater immiscibility that leads to the coalescence of the two regions at higher molecular weights.

Just like polypropylene, mixtures of PBD with the aforementioned solvents could not be predicted, and a cross interaction parameter had to be fitted to the experimental data of the highest polymer molecular weight. This is different to previous polymers with a mapping of four carbons to a CG segments. It could be that the presence of unsaturated bonds in the polymer could lead to different interactions with the saturated solvents.

Knowing the cross interaction parameter, polymer-solvent miscibility regions were predicted at different polymer molecular weights. The optimal k_{ij} values for PBD are presented in Table 6 and the phase envelopes can be seen in Figure 12. To observe the correct phase behavior of PBD n-hexane mixtures, a k_{ij} of -4.5% was necessary, making the cross interaction between the polymer and the solvent highly favorable to ensure that no hourglass phase diagram was observed even at very high polymer molecular weights. This is different for mixtures with the octane isomer, where a very small k_{ij} of less than -0.5% was necessary.

The shape of the phase envelope does not agree with the shape of the experimental data, however, critical points are correctly calculated for both mixtures and it is possible to obtain the hourglass shape for the octane isomer with minimal adjustment of the cross interaction parameters.

3.2.3. Polystyrene: Type III and IV Phase Behavior

To assess the viability of the PS parameters in modeling mixtures, the classic phase diagram of polystyrene-solvent mixtures first presented by Schultz and Flory in 1952^[130] was modeled by

the main PS model presented with a mapping ratio of 1/2:1, with 4 carbons in a monomer corresponding to one bead. This is also compared with a model of 1:1 mapping (with cross interactions given in Supporting Information). For both models, the phase diagram of PS-cyclohexane at different molecular weights was calculated. The results are shown in Figure 13(left). Both models can predict critical temperatures accurately. Remarkable agreement, however, is only observed for the 1:1 mapping ratio (with $k_{ij} = -0.002$), where the shape of the PS-cyclohexane diagram is perfectly captured. This is in contrast with the branched PS model, which can only predict the critical temperatures accurately. However, in this work the branched model is proposed for PS, following previous^[67,92] approaches and in order to investigate the effect of branching on the agreement between simulations and the theory. Apart from the PS-cyclohexane mixture, all other solution phase behavior presented here uses the branched model for polystyrene.

PS-cyclohexane and PS-methylcyclohexane mixtures are known to exhibit type III phase behavior, with both UCST and LCST phases observed for a given mixture. For the case of PS in cyclohexane, the effect of molecular weight on miscibility is demonstrated with the model capturing the correct critical behavior, with both LCST and UCST being calculated. In the case of PS-methylcyclohexane mixtures, the effect of pressure on the critical point of fixed M_w polystyrene is studied. In this case $M_w = 405$ kg mol⁻¹.

For polystyrene mixtures, a k_{ij} is required to calculate the correct critical regions. The value of k_{ij} is small ($<2\%$). For polystyrene in cyclohexane, molecular weight does not significantly change the critical temperatures. However, pressure improves the miscibility of polystyrene and cyclic alkanes at higher temperature, pushing the LCST higher, with the UCST region unaltered. The predictions of the model matches that of the experimental data.

Given that type IV phase behavior can be observed with PS-cyclohexane mixtures, the PS parameters were then used in modeling mixtures with a range of solvents. First, mixtures of PS and n-alkanes were modeled. High M_w polystyrene does not dissolve in alkanes. However, at low molecular weights (less than 10 kDa),

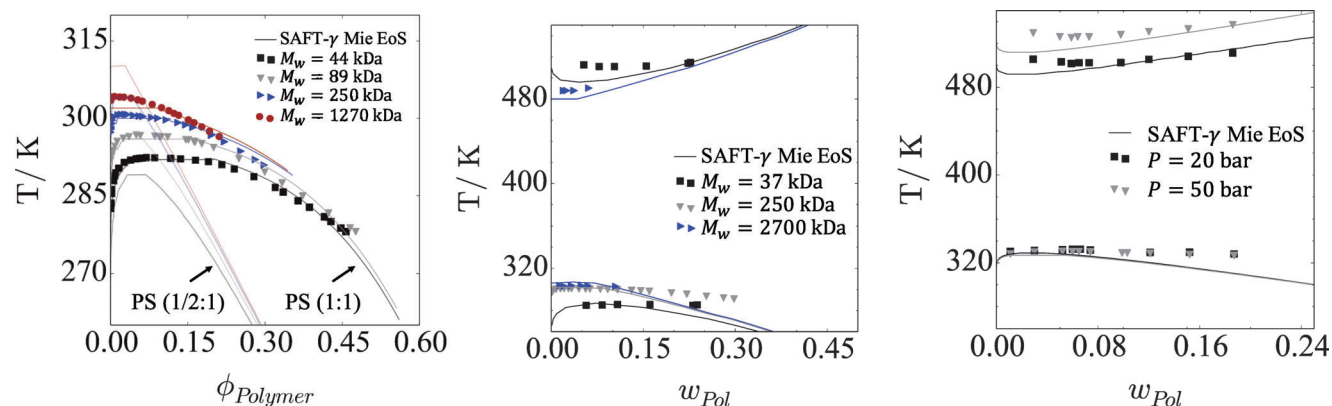


Figure 13. Phase behavior of polystyrene in (Left, Middle) cyclohexane and (Right) methylcyclohexane mixtures. Symbols are experimental data. (Left) UCST of PS-cyclohexane modeled with two polystyrene models of mapping ratios of 1/2:1 and 1:1, compared with experimental data of Shultz et al.^[130] (Middle) PS-CG1 cyclohexane LCST and UCST compared with experimental data.^[131] (Right) $M_W = 405$ kDa PS-CG1 LCST and UCST with experimental data.^[132] Symbols are experimental data.

there is a region of miscibility that can be observed experimentally. Below certain polymer molecular weights, PS-alkane mixtures exhibit both LCST and UCST behaviors. Again like the case of PBD and trimethylpentane, increasing the molecular weight leads to more immiscibility and the two regions coalesce. This is clearly demonstrated in **Figure 14**. For the case of PS in *n*-hexane, the onset of coalescing occurs around a M_W of 4.8 kDa, whereas in *n*-octane, this occurs around 10.3 kDa. Again, the SAFT- γ methodology is robust in calculating the critical temperatures, with the correct phase diagrams of low M_W PS in *n*-alkanes correctly captured.

In this work, all solvents used so far, in order to investigate polymer phase behavior, have been non-polar and non-associating. This is to ensure that when the use of Mie potentials in describing the interactions is valid. For these systems, the parameters can be used in molecular simulations to study phase behavior of polymers in solution, capturing both LCST and UCST temperatures.

However, to test the limit of the model, a mixture of PS in a polar solvent (acetone) is also modeled. Kouskoumvekaki et al.^[131] had previously studied polystyrene in cyclohexane and acetone using PC-SAFT. No set of parameters could estimate both the LLE of PS-acetone and PS-cyclohexane. The result calculated in this work is presented in Figure 14. An accurate phase diagram of the mixture was only calculated for PS-CG1, with $k_{ij} = -0.007$. The parameters for acetone were taken from elsewhere,^[120] without any fitting.

Just like the case of polypropylene, the polystyrene can also be used in modeling ternary phase diagrams of polystyrene mixtures with CO_2 . The results for ternary mixtures could be seen in Section S4, Supporting Information.

3.2.4. Polymer Blends

Three polymer blends are modeled in this work, namely PBD-PIP, PS-PBD, and PS-PIP. **Table 8** given the binary interaction parameters used to model polymer blends.

The first system studied here is that of PBD-PIP blends. Polyisoprene and polybutadiene blends exhibit LCST behavior.^[134]

Table 8. Polystyrene CG monomer interaction parameters, for the two models proposed.

Polymer 1	Polymer 2	k_{ij}
PBD	PIP	-0.00110
PS	PBD	-0.02521
PS	PIP	-0.04171

The results of EoS modeling and experimental data for a blend of 81 kDa polyisoprene with 55 kDa polybutadiene are presented in **Figure 15**. The correct LCST could be calculated using a $k_{ij} = -0.0011$. This adjustment is extremely small and the phase envelope is extremely sensitive to the blend binary interaction parameter. For example for the case of no adjustment, full phase separation was observed. It is interesting that the model predicts the correct type of phase behavior (i.e., Type V phase behavior with an LCST LLE region). This correct phase behavior is pure prediction.

Many cases of polymer blends also exhibit UCST phase behavior. Common blends in modeling such systems are PS-PBD and PS-PIP. To test if the model could predict the correct UCST type of phase behavior in the aforementioned blends, the proposed PS model was used, with the comparison between EoS and experimental data seen in Figure 15 shows the phase diagram of low M_W PS-PBD blends. The cross interaction parameter was fitted to the case with lower molecular weight PS. It can be seen that, just like the previous phase behavior of the two PS models studied in this work, both models can calculate the correct critical temperatures with varying molecular weights, however, the shape of the phase envelope does not correspond to the experimentally observed phase envelope. It is still remarkable that the parameters can correctly predict a UCST phase behavior, without fitting pure component parameters to blend data.

For the case of PS-PIP mixtures, the PS model is not compatible with modeling the blend at all. This can be seen in Figure 15. Like the PS-PBD blend The cross interaction parameter was fitted to the data with the lower molecular weight PS. Increasing the M_W of PS leads to an overestimation of the UCST.

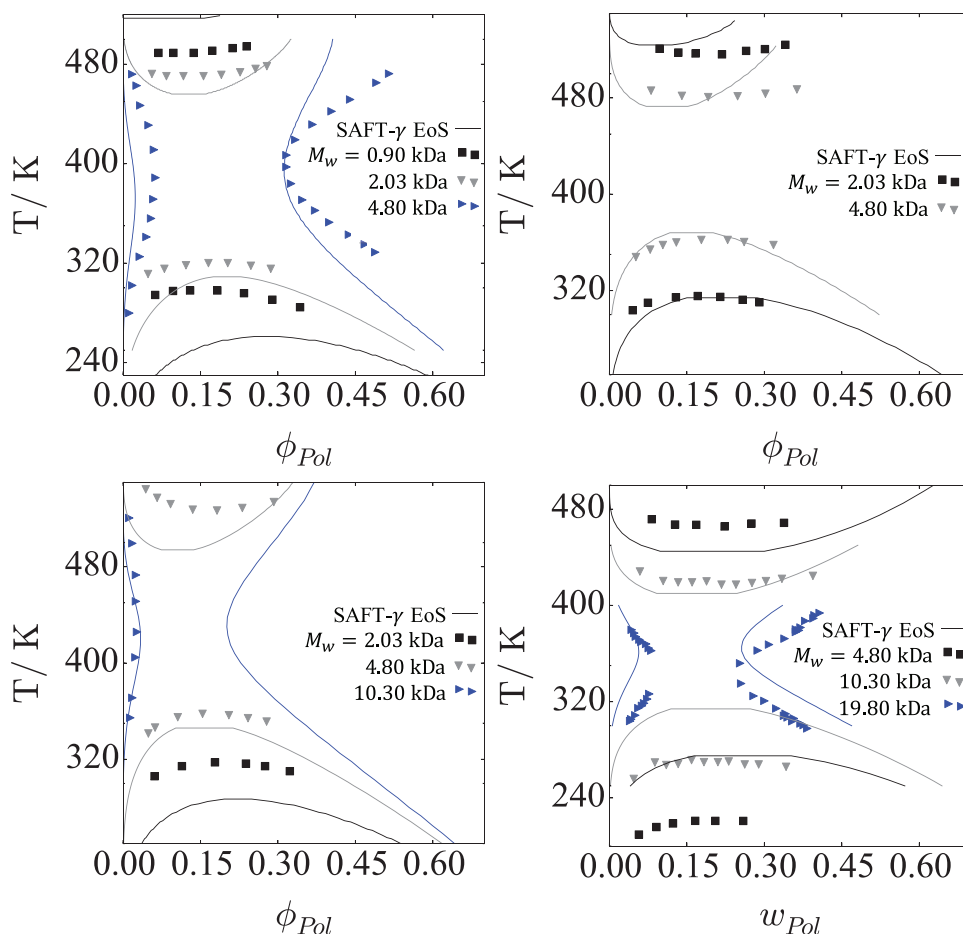


Figure 14. Binary phase behavior of polystyrene in n-alkanes and acetone. Results are only shown for the PS-CG1 model, with binary interaction parameters given in Table 6. Solvents are (top left) n-hexane, (top right) n-heptane, (bottom left) n-octane with experimental data of Cowie et al.^[133] and (bottom right) acetone, with data taken from Kouskoumvekaki et al.^[131]

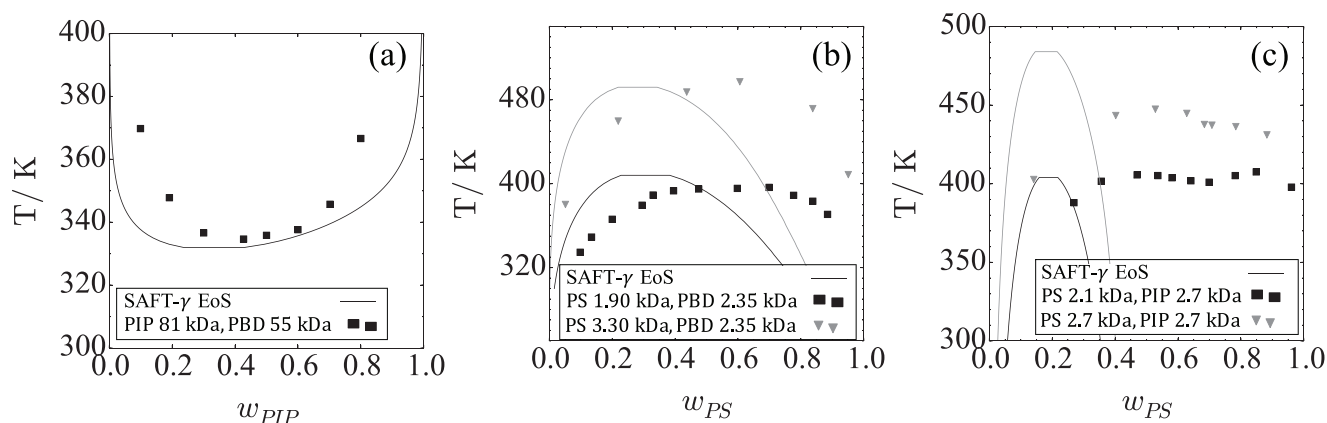


Figure 15. a) Phase behavior of polymer blend of PIP ($M_w = 81$ kDa) and PBD ($M_w = 55$ kDa). Symbols are experimental data taken from Jeon et al.^[134] b) Blends of PS (1.9 and 3.3 kDa) and PBD (2.35 kDa), symbols being experimental data taken from Voutsas et al.^[135] c) Blends of PS (2.1 and 2.7 kDa) and PIP (2.7 kDa), with symbols being experimental data of Kwei et al.^[136]

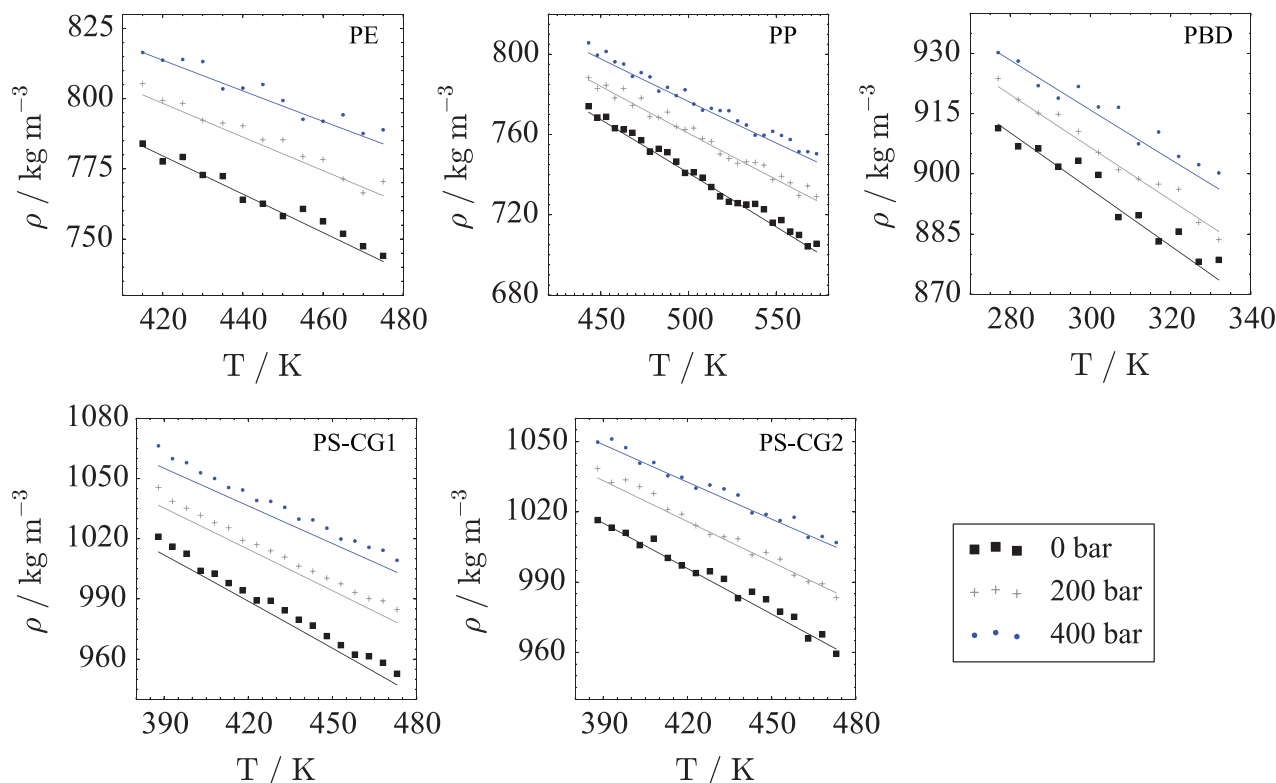


Figure 16. PVT data of 500 monomer units of different polymers in melt at different temperatures and pressures. Lines correspond to the calculations of the EoS and symbols are simulations in this work.

The reason for the discrepancy between the experimental and theory in modeling blends of polystyrene could be due to the fact that PS is modeled as a branched polymer, however, the equation of state itself does not discriminate between a branched or a linear polymer, thus affecting the shape of the phase envelope. The effect of branching is investigated in the simulation section.

4. Results: Simulation of Polymers

4.1. Simulation of Homopolymer Melts

Densities of 500 CG segment polymer melts were calculated and compared with the calculations of the EoS, using the non-bonded parameters in Table 4 and the bonded parameters in Table 5. The results are presented in Figure 16. For each polymer, except PS-CG1, the difference between simulations and the EoS was less than 0.2%, indicating a quantitative agreement between the simulations and the EoS. However for the case of PS-CG1, where polystyrene is modeled as a branched polymer, simulations slightly overpredict densities (0.6%) compared with the EoS. However, this overprediction was still less than 1%.

The next step is to therefore calculate structural properties such as R_G and R_E , as well as isothermal mechanical properties.

4.2. Conformational and Mechanical Properties

Radius of gyration and end-to-end distances of polymers melts were calculated for chains up to 160 CG beads. In order to test

that the system is well equilibrated, the end-to-end autocorrelation function, $C(t)$, for each chain length was calculated, using the following equation:

$$C(t) = \frac{\langle \mathbf{R}_E(0) \cdot \mathbf{R}_E(t) \rangle}{\langle \mathbf{R}_E^2 \rangle} \quad (15)$$

where $\mathbf{R}_E$ is the end-to-end vector of all molecules in the system and the brackets indicate an ensemble average. The time it takes for the end-to-end distances to become uncorrelated is called the relaxation time. Simulations were run longer than the relaxation time of the polymers to ensure an equilibrated system, as can be seen in Section S5, Supporting Information, where an example for PE is presented.

To showcase the quality of the SAFT- γ force field in calculating the conformational properties of homopolymer melts, here an example for PBD is shown in Figure 17. The results for the other polymers are of similar quality and detailed in Section S7, Supporting Information. Gestoso et al. have investigated properties of 1,4-cis-polybutadiene with atomistic simulations. Just like the case of polyethylene, the value of k_θ had to be adjusted in order to calculate the radius of gyration accurately. Without adjustment, the radius of gyration was overestimated by almost 40% for the highest polymer which was composed of 180 CG segments. Hadjichristidis et al.^[137] investigated end to end distances of polybutadiene, which was used to adjust k_θ . The results can be seen in Figure 17. The characteristic ratio was calculated to be 4.7, which corresponds to those calculated in literature.^[138]

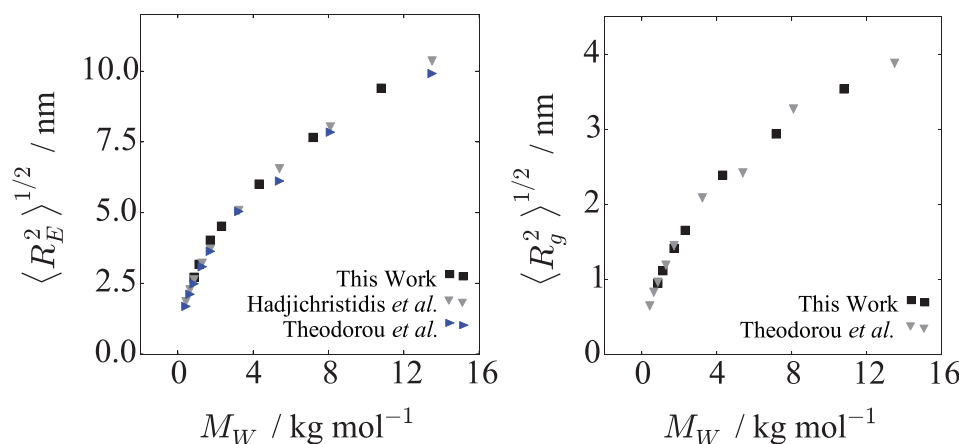


Figure 17. Radius of gyration, R_G , and end-to-end distance, R_E , of PBD as compared with simulations of Theodorou et al.^[138] and experimental data from Hadjichristidis et al.^[137]

Table 9. Structural and mechanical properties of the polymers studied in this work. $P = 1$ bar for all cases.

Polymer	N_{CG}	κ_{Lit} [10 ⁻³ MPa ⁻¹]	κ_{SAFT} [10 ⁻³ MPa ⁻¹]	T_K [K]	$C_{\infty, Lit}^{[139]}$	$C_{\infty, SAFT}^{\dagger}$	$T_{C_{\infty}}$ [K]
PE	160	1.92 ± 0.03 ^[140]	1.96 ± 0.03	400	8.2 ^[139]	8.41 ± 0.04	450
PP	150	1.62 ± 0.02 ^[141]	1.62 ± 0.03	500	6.2 ^[139]	6.42 ± 0.04	450
PBD	160	1.35 ± 0.02 ^[142]	1.42 ± 0.03	413	4.7 ^[138]	4.74 ± 0.06	413
PS	160	1.13, ^[143] 0.93, ^[65] 1.64 ^[92]	2.13 ± 0.04	500	8.5 ^[139]	8.92 ± 0.03	450

Moreover, in order to compare the results to other results in literature, characteristic ratios and isothermal compressibilities of the polymers were calculated and are summarized in Table 9. The characteristic ratio of a polymer, C_{∞} , was calculated

$$C_{\infty} = \lim_{N \rightarrow \infty} \frac{R_E^2}{(N-1)b^2} \quad (16)$$

where b is the backbone carbon–carbon bond length (assumed to be 0.154 nm), N is the degree of polymerization and R_E the end-to-end distance.

Isothermal compressibility, κ , was calculated using the following equation in an NPT ensemble simulations

$$\kappa = -\frac{1}{\langle V \rangle} \left(\frac{\partial \langle V \rangle}{\partial P} \right)_T = -\frac{1}{k_B T \langle V \rangle} (\langle V^2 \rangle - \langle V \rangle^2) \quad (17)$$

It can be seen in Table 9 that the polymer models studied in this work are generally robust in predicting mechanical and conformation properties as they are in agreement with those calculated experimentally or from all atom simulations.

4.3. Polymer–Solvent Phase Behavior

Here, a comparison is made between the calculations of EoS with simulations for binary mixtures containing the polymer. Three solvents namely n-pentane, n-hexane, and n-heptane are used. Each of the solvent molecules are modeled as two spheres tangentially bonded to each other with a distance of σ . The non-bonded

Table 10. Potential parameters of n-pentane, n-hexane, and n-heptane used in simulations, for the bonded potential $b_0 = \sigma$.

Molecule	m_{seg}	λ_r	ϵ/k_B [K]	σ [Å]	k_b [kJ mol ⁻¹ nm ⁻²]
n-pentane	2	14.75	307.9	4.258	6300
n-hexane	2	18.01	371.1	4.517	6300
n-heptane	2	21.27	427.0	4.766	6300

and bonded interaction parameters are given in Table 10. Saturation properties of all the solvents matched calculated via MD simulations agreed with experimental data and could be seen in Section S8, Supporting Information.

4.3.1. Polyethylene and Temperature Induced Phase Separation (LCST)

For mixtures of PE with solvents, LCST phase behavior has been experimentally observed at high pressures.^[123] To assess the correspondence between the calculations from the EoS and the simulations, two different M_W of polyethylene were simulated in a mixture with n-pentane. The first polyethylene–solvent mixture studied is an oligomer with a $M_W = 2.15$ kg mol⁻¹, corresponding to 39 CG beads. NPT simulations were run at a global composition of 20 wt%, with 200 molecules of polymer and 25 000 solvent molecules in the system, with a total of 58 000 CG segments (≈ 520 000 atoms) in the system. Five simulations

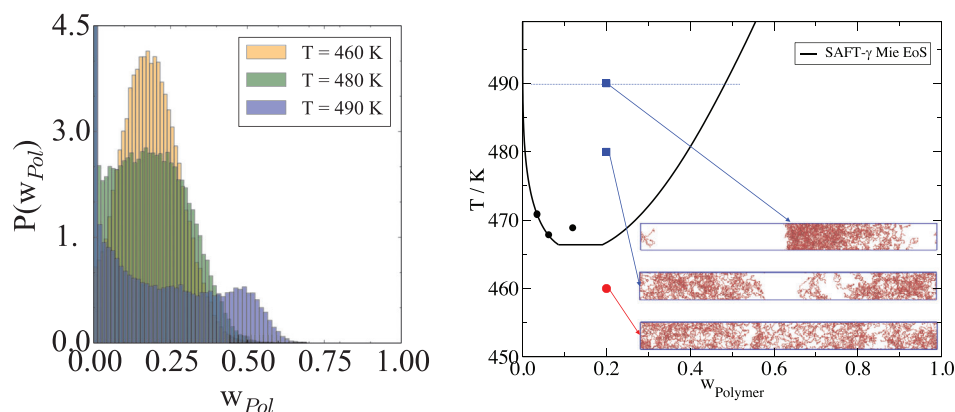


Figure 18. Phase diagram of PE-n-pentane mixtures, $M_{W, \text{polymer}} = 2150$ Da (39 CG beads), $P = 5$ MPa. (Left) Local composition distributions at different temperatures, (right) Comparing simulations with the EoS and experimental data. Curve corresponds the SAFT- γ EoS, black circles correspond to experimental results of Xiong et al.^[123] Filled blue squares are the global compositions ($w_{\text{polymer}} = 0.2$) and patterned squares are the compositions calculated from the local density method. Snapshots of the final configurations of only the polymers at different temperatures are also presented, clearly demonstrating the LCST phase behavior.

were run between 450 to 490 K at a constant pressure of $P_{zz} = 5$ MPa. The simulation box was initially set up as an orthorhombic elongated box with the dimensions $L_z = 10 L_x$, $L_x = L_y \approx 15$ nm, and the molecules were inserted. The box was equilibrated at 10 bar and 450 K, in the isobaric-isothermal (NPT) ensemble, with isotropic pressure coupling. Once the box was small enough that the reduced density $\rho \sigma^3 \approx 0.8$, NP $_{zz}$ T simulations were run at the correct temperature (460–490 K) and pressure (5 MPa). The critical temperature of n-pentane is 470 K and therefore, it was assumed that n-pentane above this temperature would be in the supercritical region.

The method previously described in Figure 6 was used to assess immiscibility by measuring local densities in small (2 nm^3) cubic subregions in the simulation box. Visual observations of the simulation box, were also used to observe the onset of temperature induced LCST phase behavior. This can clearly be seen in Figure 18(left). The onset of phase separation occurs between 460 and 480 K, as predicted by the EoS. The distribution of the local compositions at 460 K is unimodal, corresponding to a single phase mixture, and at 490 K it can be clearly seen that the distribution is bimodal, corresponding to a system composed of polymer rich and polymer lean phases. At 490 K, the polymer rich phase has a composition of 50 wt% polymer. This is compared to the calculations of the EoS in Figure 18(right). The composition of the polymer rich phase at 490 K is very similar in value for both methods, however at 480, although there is a phase separation and there is a bimodal distribution, the polymer rich phase has a composition very close to the global composition, around 25 wt% polymer, thus making it difficult to calculate the composition of the polymer rich phase precisely.

The onset of phase separation in the first case of low M_w PE in n-pentane is very close to the critical point of the solvent, and consequently phase separation is only observed in a very small region of temperature. By increasing the molecular weight of the polymer, the lower critical point decreases significantly away from the critical point of the solvent.

The second case of polyethylene in n-pentane is for a polymer of molecular weight 16 400 Da, corresponding to 292 CG beads. The simulation set up was set to be identical to the previous

simulation of shorter length polyethylene. As can be seen from Figure 19(left), it is possible to observe phase separation for a much larger range of temperature in this system, as the phase separation starts at temperatures far lower than the critical point of the solvent. The comparison between the EoS, the experimental data, and the simulations is clearly shown in the aforementioned figure. There is a close correspondence between all three approaches in calculating the LCST, however, the shape of the phase envelope is slightly narrower in simulations relative to the predictions of the EoS. By simple inspection of the final simulation snapshots as shown in the figure, it is possible to see that there is a clear phase separation at $T = 430$ K as the temperature is increased from 410 K. Less mixing is also observed at higher temperatures. The local composition distributions can be seen in greater detail in Figure 19(right). It is clearly seen that there is a deviation from the global composition at temperatures higher than 410 K. Therefore, no adjustable parameters are required to model polyethylene-alkane solvent mixtures and that at least qualitatively, the EoS and the simulations are in agreement.

The significance of the study of PE is to demonstrate that this approach presented in this manuscript can be used to reliably simulate Type V (LCST) phase behavior of polymer solutions with quantitative accuracy. This is the main highlight of this CG approach. Moreover, not only is it possible to observe the same behavior in simulations as calculated by the EoS, it is also possible to observe transport and structural properties. In terms of conformational properties, it could be seen in Figure 20 that R_G and R_E of the long chain PE decreases with increasing temperature. Again this is another indication that the polymer contracts to minimize its contacts with the solvent.

4.3.2. Polypropylene: Pressure Induced Phase Separation and the Effect of k_{ij}

As shown previously (Figure 11), polypropylene and n-pentane mixtures undergo mixing with increasing pressure. In this section, mixtures of 50.4 kDa polypropylene (600 CG beads or 11 000

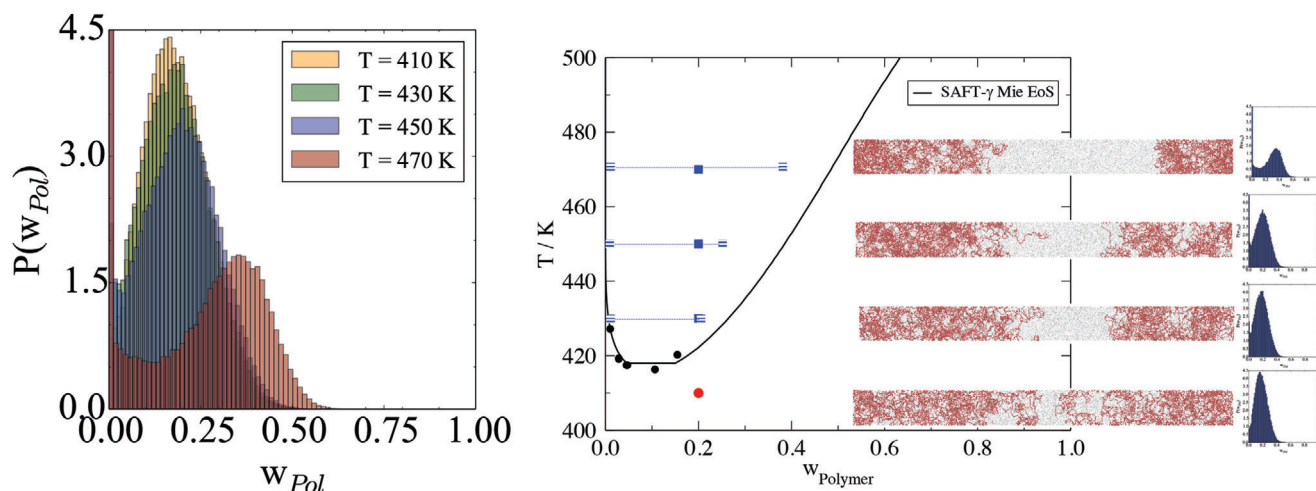


Figure 19. Phase diagram of PE-n-pentane mixtures, $M_{w, \text{Polymer}} = 16\,400$ Da (292 CG beads), $P = 5$ MPa. (Left) Local composition distributions at different temperatures, (Right) Comparing simulations with the EoS and experimental data. Curve corresponds the SAFT- γ EoS, black circles correspond to experimental results of Xiong et al.^[123] Filled blue squares are the global compositions ($w_{\text{polymer}} = 0.2$) and patterned squares are the compositions calculated from the local density method. Snapshots of the final configurations of only the polymers at different temperatures are also presented, clearly demonstrating the LCST phase behavior.

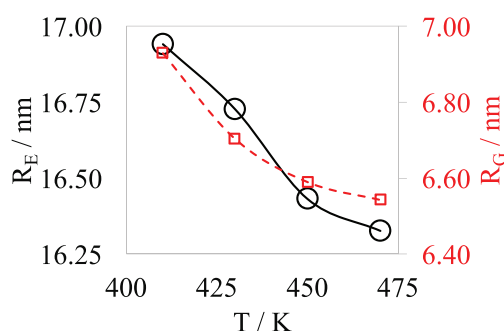


Figure 20. R_E and R_G versus Temperature of 16 400 Da PE in n-pentane.

atoms) and n-pentane were simulated at different global compositions and at different pressures. For each system, polymers were added to 40 000 solvent molecules to have global compositions of 15 to 35 wt% polymer. The box dimensions were around $35 \times 22 \times 22$ nm in order to ensure that the boxes are at least twice the size of R_G . The temperature of the system was set to 470 K and the cross interaction parameter was set to the value of $k_{ij} = -0.061$ calculated previously. The full phase diagram of regions of miscibility and immiscibility can be seen in the local composition distributions in **Figure 21**. Where a bimodal distribution was observed, it was assumed the mixture is immiscible, and where a unimodal distribution was observed miscibility was assumed. Of particular interest is the middle column with the global composition at 25 wt%. The distribution diagrams clearly demonstrate a change in miscibility of the polymer in solution at different pressures. Moreover, the row of different global compositions at 40 bar also clearly highlights a change of miscibility with increasing polymer content in the system. The column at a global composition of 15% contains only bimodal distributions, whereas that of 35% shows only unimodal distributions.

The phase map shown in **Figure 21** is superimposed onto the predictions of the EoS in **Figure 22**. The EoS and the simulations

agree in the prediction of the systems studied. This shows that the value of k_{ij} given by the EoS can be used realistically to model not only temperature and molecular weight dependent phase behavior as shown previously, but also the immiscibility due to pressure. Accurate correspondence between the theory and simulation is observed given a single adjustable parameter for all state points in the phase diagram. This transferability of the potential parameters allows the models to be predictable in other regions of the phase space.

4.3.3. Polystyrene: Type II (UCST), Type III (Hourglass), and Type IV (UCST+LCST) Phase Behaviors

Polystyrene solutions in n-hexane and n-heptane are known to exhibit Type IV phase behavior at low molecular weights. Upon increasing the molecular weights, the separate phase envelopes of LCST and UCST coalesce forming a single region of immiscibility, that is, Type III phase behavior.

In order to assess the effect of chain geometry on phase behavior, the PS-CG1 (i.e., the branched polymer) was used in mixtures with n-hexane and n-heptane. Two different M_w of PS were used; 2.03 and 4.80 kDa, corresponding to 39 and 92 CG beads per molecule respectively. As previously parametrized, $k_{ij} = 0.0113$ for PS-n-hexane mixture, and $k_{ij} = 0.007$ for PS-n-heptane mixtures. Each system was composed of 20 000 solvent molecules with a global composition of 30 or 50 polymer wt%. Like previous cases, an elongated orthorhombic simulation ($L_z \approx 8 L_x$) was used in an NPT ensemble. However, unlike previous cases, the system pressure was changed at every temperature so that the system pressure was at the vapor pressure of the solvent (approximately along the three-phase line), commensurate with the experimental set-up.

The local composition distributions of 2.03 kDa PS-n-hexane (30 wt% polymer) mixture is presented in **Figure 23**. For the first time in this work, there is a qualitative discrepancy between the

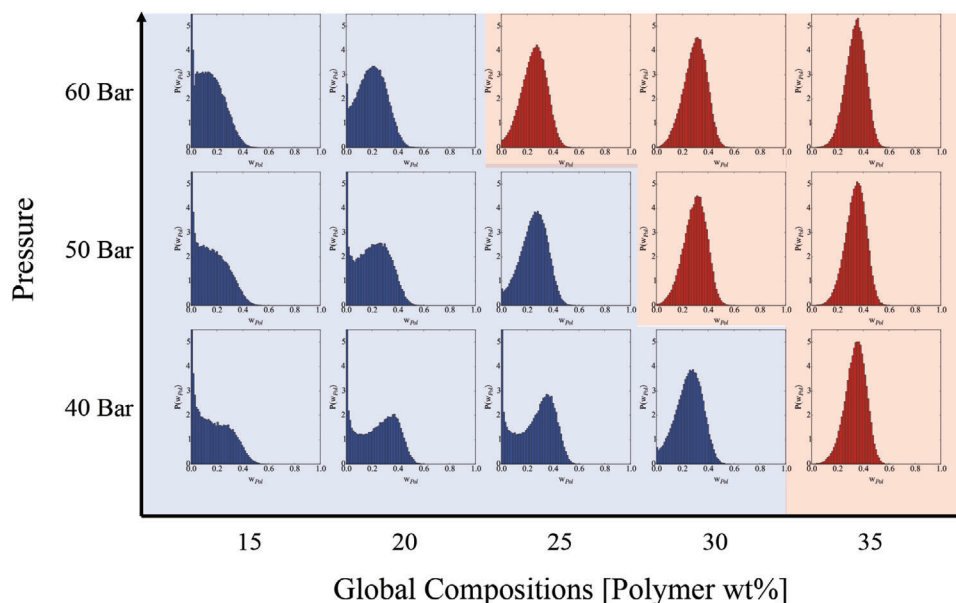


Figure 21. Local composition distributions of i-PP-n-pentane mixtures, $M_{w, \text{Polymer}} = 50.4$ kDa (600 CG beads), $T = 470$ K. Blues indicates regions where phase separation was observed (bimodal distribution) and reds are regions the mixture is miscible (unimodal distribution).

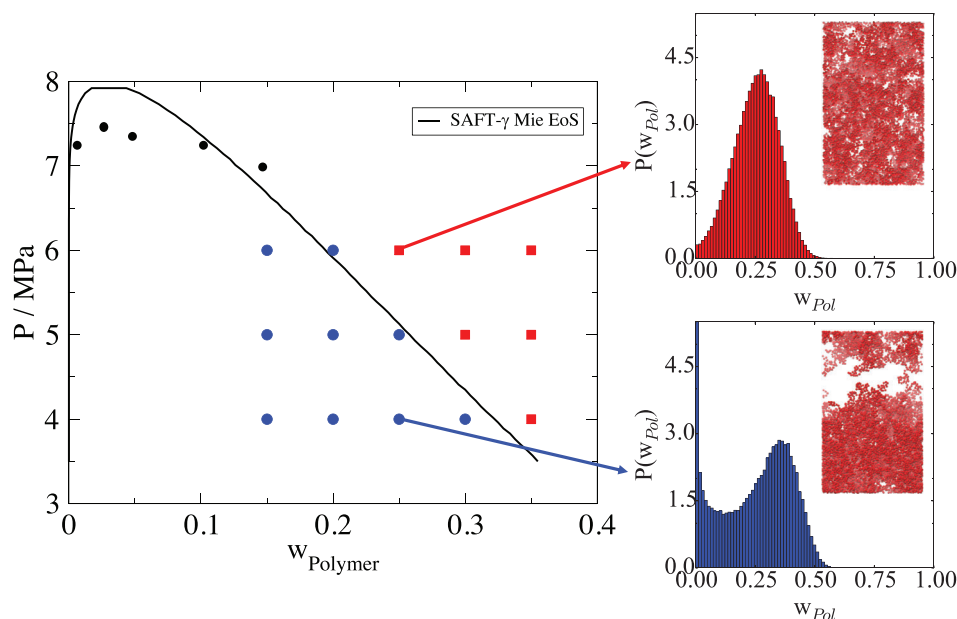


Figure 22. Phase diagram of i-PP-n-pentane mixtures, $M_{w, \text{Polymer}} = 50.4$ kDa (600 CG beads), $T = 470$ K. Line corresponds to the calculations of the SAFT- γ EoS, black circles correspond to experimental results from Martin et al.^[126] Blue circle are the global compositions (w_{polymer}) at pressures where phase separation was observed and red circles are the global compositions at pressures where phase separation was not observed. Snapshots of the final configurations of only the polymers at different temperatures are also presented, clearly demonstrating the pressure induced phase separation, with accurate correspondence between simulations and theory. $k_{ij} = -0.061$ as calculated using the EoS.

critical point calculated in the EoS and that shown in the simulations. The phase diagram of this system as obtained from simulations does not show any LCST behavior at higher temperatures. A unimodal distribution is observed for any temperatures above 300 K. However, the UCST phase envelope in simulation and theory are almost the same. For the lowest two temperatures

(250 and 285 K), it was possible to determine the composition of polymer in each LLE phases and they were found to be in quantitative agreement with the theory. One reason no LCST behavior was observed could be due to the effect of branching of the polymer. As has been previously reported in literature, increases in the degree of branching can lead to more miscibility as the size

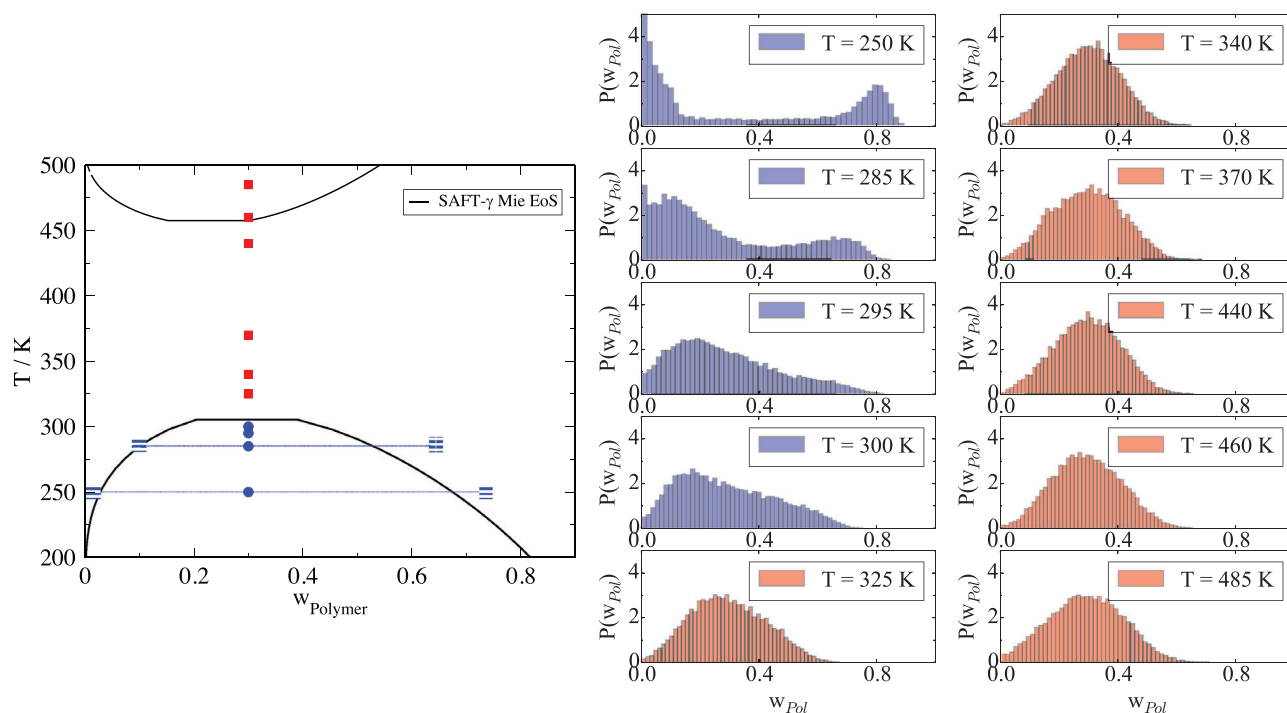


Figure 23. Phase diagram of PS-CG1-n-hexane mixtures, $M_{w, \text{Polymer}} = 2030$ Da (40 CG beads). Line corresponds to the calculations of the SAFT- γ EoS. Filled blue circles are the global compositions ($w_{\text{polymer}} = 0.3$) where phase separation was observed and patterned squares are the compositions calculated from the local density method. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures are also presented, clearly demonstrating the onset of miscibility at higher temperatures. Unlike the EoS predictions, no LCST phase behavior was observed for this system.

of the molecule (R_G) is smaller for a branched polymer relative to its linear isomer. This leads to a smaller radius of gyration. In essence the molecule size becomes more similar to that of the solvent molecules and the solvent and the polymer molecules become more alike. Consequently the components of the system become more miscible.^[144–148] The exact same behavior is observed for the same M_w polymer in n-heptane, where it is possible to observe UCST phase behavior correctly, yet no LCST phase behavior is observed.

Increasing molecular weight of the polymer, leads to a lower miscibility at higher temperature, and the effect of branching is not as significant. The phase diagram of 4.80 kDa in n-hexane is that of Type III (hourglass shaped). In this work, two global compositions of 30 and 50 polymer wt% were simulated, with the 30% being fully within the immiscibility region at all temperatures and the 50 wt% being miscible in a temperature range of 350–450 K. As can be seen from **Figure 24**, not only is it possible to observe the hourglass phase behavior in simulations, there is quantitatively accurate agreement between the theory and simulation. For the 50% polymer composition, the local composition distributions at 370 and 430 K are unimodal, albeit slightly skewed. Conversely, local composition distributions at 30% polymer composition are nonunimodal, indicating phase separation at all temperatures. The composition of the polymer rich phase agrees well with the calculations of the theory, with the polymer rich phase having a higher polymer weight fraction at 250 K than at 470 K, with a minimum in the polymer content of the polymer rich phase at around 370 K. At 370 K, the polymer lean phase

is composed of around 10 wt% polymer, which shows the existence of another miscibility region at low polymer weight fractions around that temperature too.

As can be seen in **Figure 25**, Type IV phase behavior can be simulated for the case of 4.80 kDa PS-n-heptane mixtures. PS is more soluble in n-heptane than it is in n-hexane, meaning that even though the hourglass phase behavior is observed for mixtures of 4.80 kDa PS in n-hexane, due to greater solubility of PS in n-heptane, the two phase envelopes do not coalesce and therefore type Type IV phase behavior is observed, with two separated regions of immiscibility in the phase diagram. Simulations were carried out with the global composition being set to 30 polymer wt%. Temperature was set to a range of values with intervals of 25 K. It could be seen in **Figure 25** that even though the critical temperatures are in accordance with the predictions of the EoS, the shape of the UCST phase envelope is broader with a slight overprediction of the UCST relative to the EoS.

Contrary to the 2.03 kDa PS mixtures with n-hexane and n-heptane, it is possible to observe LCST phase behavior in simulation for the 4.80 kDa PS. In both simulation and the EoS, the LCST is around 475 K with the phase envelopes being in quantitative agreement.

4.3.4. Polymer Blends

A polymer blend of 1.90 kDa PS and 2.35 kDa PBD as previously presented in **Figure 15b** was simulated. Here, like the previous

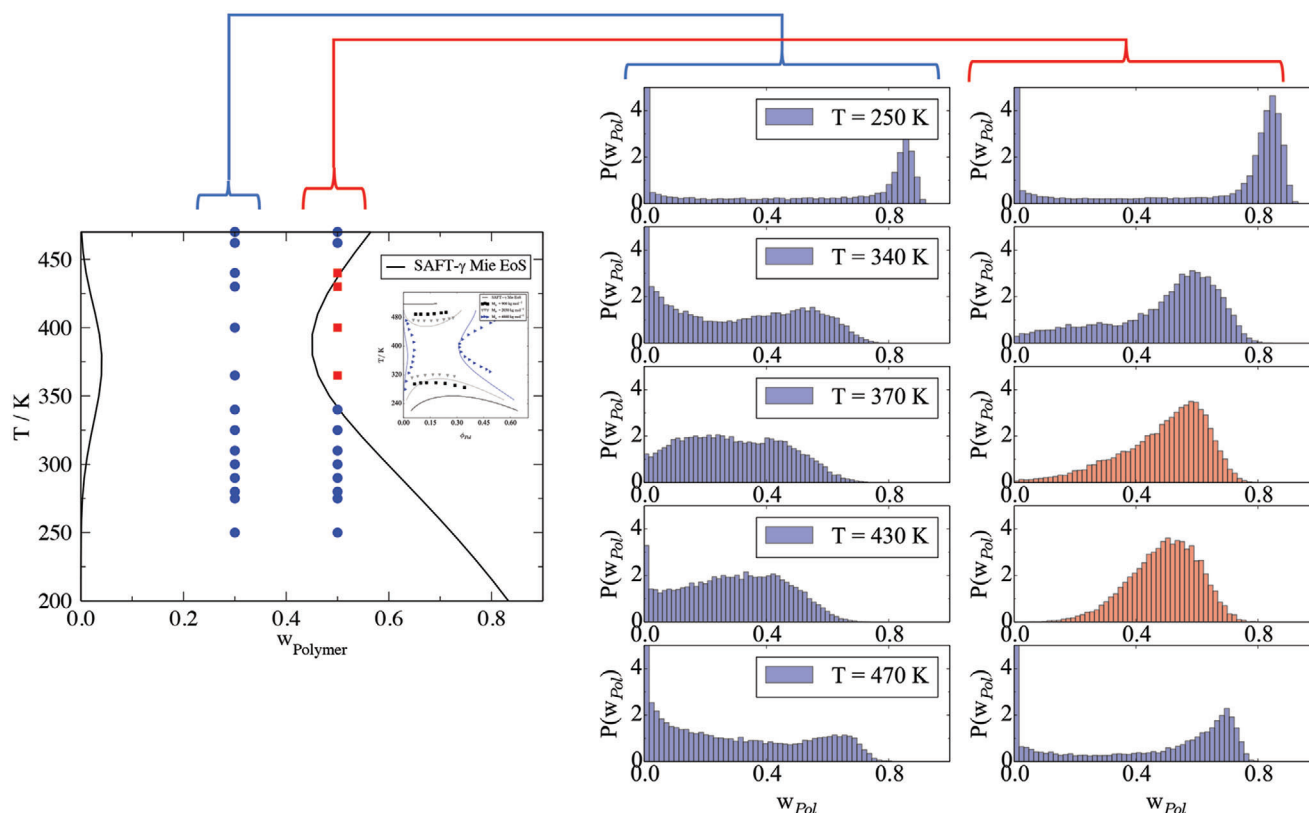


Figure 24. Phase diagram of PS-CG1-n-hexane mixtures, $M_{W, \text{Polymer}} = 4800$ Da (92 CG beads). Line corresponds to the calculations of the SAFT- γ EoS. Filled blue circles are the global compositions ($w_{\text{polymer}} = 0.3$ and $w_{\text{polymer}} = 0.5$) where phase separation is observed. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures and compositions are also presented, with each row being at the same temperature. It can clearly be seen that for $w_{\text{polymer}} = 0.3$ binodal distributions exist at all temperature, whereas at $w_{\text{polymer}} = 0.5$ unimodal distributions can be observed for $T = 370\text{--}430$ K. Clear correspondence between theory and simulations is observed.

simulations of polystyrene in this work, the polystyrene was modeled as a branched polymer. It has been shown that this model is robust in reproducing the polymer-solvent phase behavior. Simulations were run for a system containing 1300 polystyrene molecules and 840 1,4-cis-polybutadiene molecules corresponding to a global composition of 50 wt% PS. A total of number of CG segments summed up to 84 000, corresponding to nearly 800 000 atoms. Temperature was changed but the pressure, P_{zz} was fixed at 1 bar. The ratio of $L_Z:L_{X,Y}$ was set to 4:1 and each simulation was run for 500×10^6 timesteps, with $\delta t = 0.01$ ps. Like the previous cases, a cut-off of 2.0 nm was used in all simulations, with no tail corrections.

The adjustable parameter between the two polymers for this mixture is $k_{ij} = -0.025$ as given in the theory. However, when this interaction parameter was used, significant overestimation of the UCST was found. Polymer blends are much more sensitive to the cross interaction parameters as each component is composed of many monomers. So the slightest changes in the cross interaction parameter can significantly affect the miscibility of the two components. k_{ij} was changed slightly from -0.025 to -0.028 , with the phase diagram presented in Figure 26. This change in the k_{ij} is less than 1 K, and it is not a significant deviation from the predictions of the theory. As shown in the figure, it is possible to observe the UCST behavior of this PS-

PBD mixture, however the shape of the phase envelope is not commensurate with that which was calculated with the EoS. Surprisingly, there is quite a good agreement between simulations and the experimental results from Voutsas et al.^[135] This could be due to the conformational structure of the polymer, namely the branching that is not considered in the EoS but accounted for in the simulations.

As mentioned before, it is possible to simulate polystyrene models with a mapping ratio of 1:1, and blends of PS and PI have been modeled using this polystyrene model. The results can be seen in Section S9, Supporting Information. However, given the success of the current PS model proposed in this work, it was not deemed necessary to use other CG mappings for PS.

5. Discussion and Outlook

It has been shown that the SAFT- γ approach proposed can be used to model the types of phase behavior of polymer-solvent mixtures as can be seen in Figure 1 with quantitative accuracy. Apart from the case of 2.03 kDa PS in n-hexane and n-heptane, the phase behavior of the polymers are in exact agreement with the calculations of the EoS. The CG potential parameters used in the EoS can be directly used in simulations to reproduce the phase envelopes with an increase in speed of orders of magnitude

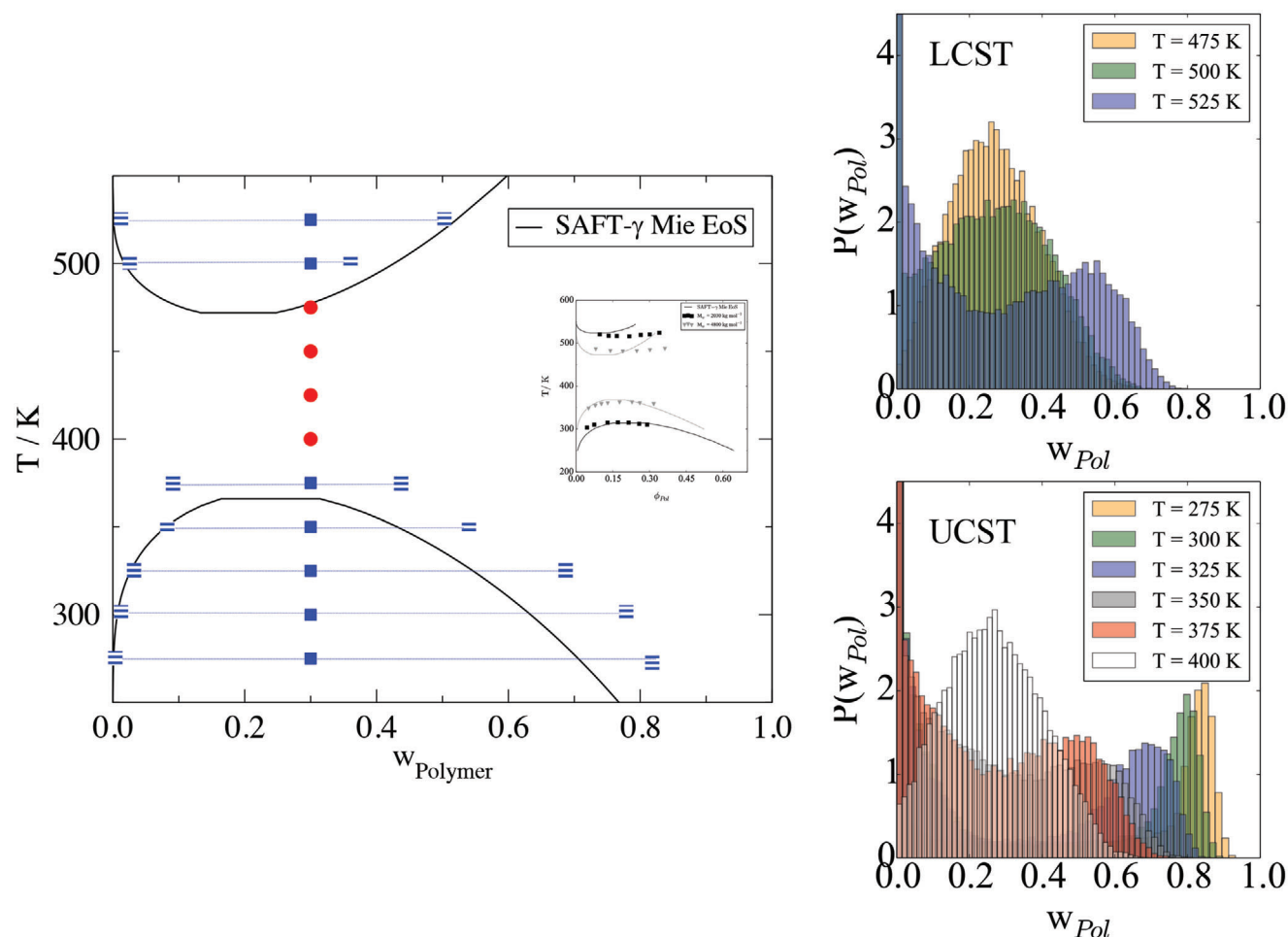


Figure 25. Phase diagram of PS-CG1-n-heptane mixtures, $M_{W, \text{Polymer}} = 4800$ Da (92 CG beads). Line corresponds to the calculations of the SAFT- γ EoS. Filled blue circles are the global compositions ($w_{\text{polymer}} = 0.3$) where phase separation was observed and patterned squares are the compositions calculated from the local density method. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures are also presented, clearly demonstrating the onset of miscibility at higher temperatures and lower temperature. It can clearly be seen that at intermediate temperatures there is a unimodal distribution corresponding to miscibility.

as compared to atomistic simulations, without any loss of fidelity. The robust parameter estimation methodology makes the potential parameters transferable to a wide range of pressures, temperatures, molecular weights of the polymer, and compositions of the mixtures, rendering this method very useful in obtaining reliable force fields for polymers.

For the cases of polyethylene and polypropylene, the LCST and pressure induced separation behavior simulated have not, to our knowledge, been simulated before. However, it is important to note that the PS-n-alkanes mixtures presented here have already been studied by Jimenez-Serratos et al.^[92] with SAFT type potentials. The parameters that were studied by Jimenez-Serratos et al. were not fitted for polystyrene specifically. In that model, the backbone of the branched polymer was modeled as a $(\text{CH}_2)_3$ group. The branches were modeled as a segment of a two segment homonuclear toluene model. Thus, there is an issue with extent of the representability of the polymer to a real polystyrene molecule. Moreover, the cross interaction parameters between the n-alkanes and the polystyrene model were manually altered

with a k_{ij} parameter, without explicitly checking the validity of the parameters with the EoS. This means that the experimentally correct phase behavior might not be observed using the previous model.

In this work, an effort has been made to ensure the representability of the force field parameters with the equation of state prior to their application in molecular simulations. It has been shown that both inter and intra-species parameters are reliable that simulations can directly reproduce the same phase behavior of the polymer as calculated by the EoS without any adjustments to the parameters. Although the EoS might not have the same shape of the phase envelopes as the experiments, the qualitative agreement between experiments, theory and simulation makes this methodology potentially useful in studying polymer solvent systems.

Attempts were made to simulate poly(styrene-co-isoprene), however given the very long chain lengths equilibration remains a challenge. Equilibration of polymer-solvent mixtures is much faster in simulations given the fast diffusion of

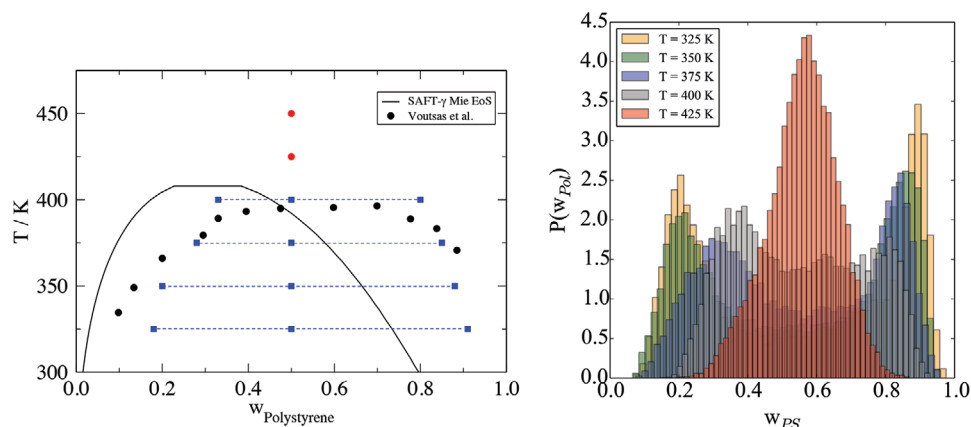


Figure 26. Phase diagram of low M_w PS (1900 Da)–PBD (2350 Da) blend, corresponding to 36 and 43 CG beads respectively. Line corresponds to the calculations of the SAFT- γ EoS. Black circles are experimental data from Voutsas et al.^[135] Filled blue squares are the global compositions ($w_{\text{polymer}} = 0.5$) where phase separation was observed and patterned squares are the compositions calculated from the local density method. Red squares are the global compositions at temperatures where phase separation was not observed. The local composition distributions at different temperatures are also presented, clearly demonstrating the onset of miscibility at $T = 425$ K. Even though intermolecular potentials were fitted using the EoS, the shape of the phase envelope matches the experimental data and is different to the EoS. The interaction parameter, k_{ij} was changed from -0.025 to -0.028 in order to observed the correct UCST.

the solvent molecules. Even for low molecular weight polymers as presented here it is possible to equilibrate systems with millions of timesteps. However, the only cases where microphase separation could be observed for chain-lengths exceeding 100 segments is by having very large k_{ij} parameters, causing spontaneous demixing. With the k_{ij} parameters developed in this work, the unlike interactions are not strongly unfavorable. This makes it difficult to observe microphase separation of block copolymers starting from either a demixed or a mixed system.

Keywords

coarse-graining, equation of state, molecular dynamics, polymers, statistical associating fluid theory

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are accessible via a link found in the supplementary material of this article.

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