Miscibility of PS-PI diblock copolymer by Molecular Dynamic and Mesoscopic Simulations

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Abstract. Molecular dynamic and mesoscopic simulations are used to predict the morphologies of PS-b-PI diblock copolymer. Flory-Huggins interaction parameter is an intermediate parameter used to connect between both simulations. The repulsions between different beads are one of essential parameters that were calculated from the Flory-Huggins interaction parameter. The calculated repulsion is 3.79 kJ/mol. Topology parameter was calculated from polymer chain length concerning its characteristic properties. S 4 I 5 is a mesoscopic topology that was used to represent polymeric chain consisting of 50 and 44 of degree of polymerization for polyisoprene and polystyrene, respectively. The morphology at equilibrium was confirmed by free energy density and order parameters from mesoscopic simulation. The stability of obtained morphologies from the obtained pattern was confirmed. In this study, the diblock copolymers are miscible and disordered phase was obtained.

1. Introduction

Macroscopic properties of materials, especially polymer-based materials have been explored using distinct mesoscale models and a combination of molecular dynamic and mesoscopic simulations [1-3]. Block copolymer are important materials extensively used in industrial and therapeutic applications [4, 5]. Styrene has been copolymerized with other component e.g. methyl methacrylate [6, 7] and butadiene [8]. The research presented in this article is solely for block copolymers containing polystyrene (PS) and polyisoprene (PI). PS can enhance toughness of materials and improve surface properties [9] While PI is a primary component of natural rubber which is low toxicity. The morphology of the designed PS-PI diblock copolymer will be predicted.

2. Simulation methods

Molecular dynamic simulation is used to studies the bulk properties of each polymer system at 313 K. The processes were the same for both PS and PI. Initially, the polymer with different chain length was constructed. The chain length of 10, 30, 50, 70, and 90 for both of polymer were constructed. The optimum representative polymer chain length was determined. The densities of bulk polymers are 1.05

and 0.90 g·cm^{-3} for PS and PI, respectively. Each system was minimized by using the conjugate gradient method (CGM). The convergence criterion of conjugate gradient was either the root-mean-square gradient ≤ 0.1 kcal/mol/Å and energy convergence of 1.0×10^{-6} kcal/mol. The obtained configuration was refined by NPT ensemble under constant temperature and pressure for 15 ns. A time step of 1 fs was used to ensure the stability of simulation. Next, polymer chains were annealed at temperature range from 225 K to 285 K and 383 K to 433 K for PI and PS systems [10], respectively. The range of annealed temperature is the value between glass transition temperature, T_g and crystalline melting temperature, T_m of each polymer respectively. The annealed step of 10 K for 50 cycles was performed in this step. Relaxation simulation using four cycles of NPT-NVT ensemble were performed for 85 ns. Finally, 15 ns NVT ensemble was used for analysis.

In the present work, the diblock copolymer consisting of 50 and 44 of degree of polymerization for PI and PS was study. Bulk model of PI and PS and mixed systems were built in amorphous structure. NPT ensemble was performed for mixed system for equilibration. The solubility parameter of three systems were calculated to calculate the interaction parameter for mesoscopic simulation.

The mesoscopic simulation applied here is based on the dynamic mean-field density functional theory [11]. The phase separation dynamic was investigated at mesoscopic level. The simulation was performed at 313 K. The grid dimensions were $32 \times 32 \times 32$ nm^3 with the grid spacing of 1.0 nm and the bond length of bead is 1.1543 nm. A bead diffusion coefficient was set as 1.0×10^{-7}cm^{2}s^{-1}. The constant noise-scaling parameter of 75.002 was used for the numerical speed and stability with the compressibility parameter of 10.0. The total simulation time is 10 ms or the number of step is 200,000 steps.

3. Results and discussion

To determine the minimum chain of polymers which are used to represent the mesoscale system, the solubility parameter of each polymer was calculated by analysing molecular dynamic simulation trajectory. The degree of polymerization of 10, 30, 50, 70, and 90 for both of polymers were used for consideration and the results were shown in Figure 1.
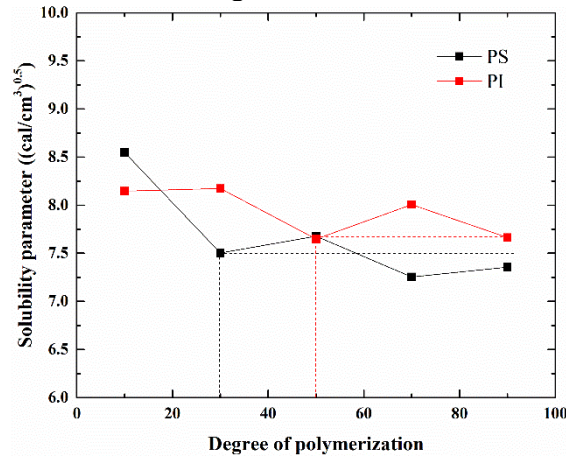
Figure 1. The solubility parameter versus degree of polymerization of each polymer

In this system, the representative repeating unit of PS and PI polymeric chain was found at least 30 and 50, respectively. Hence, the degree of polymerization of 44 and 50 for PS and PI were used in this study. The energy of mixing (ΔE_{mix}) can be calculated by an equation:

$$\Delta E_{mix} = \phi_I \left(\frac{E_{coh}}{V}\right)_{pure} + \phi_S \left(\frac{E_{coh}}{V}\right)_{pure} - \left(\frac{E_{coh}}{V}\right)_{mixed} \tag{1}$$

Where, ϕ is a volume fraction of each polymer, the subscripts S and I represent PS and PI, respectively. The subscripts pure and mixed demonstrate the cohesive energy density (CED) of pure components and the binary mixture, respectively. CED was obtained from the second power of solubility parameter,

which calculated from molecular dynamic simulation. After that, the Flory-Huggins parameter, χ can be calculated from ΔE_{mix} according to the equation below:

$$\chi = \left(\frac{\Delta E_{mix}}{RT}\right)V \tag{2}$$

Where, V is the molar volume, R is the molar gas constant (8.314 J/mol/K), and T is the temperature in Kelvin. χ is an intermediate parameter that is used to connect between molecular dynamic and mesoscopic simulations. It was used for a calculation of interaction energy ($v^{-1}\varepsilon$) for mesoscopic simulation as given by the equation:

$$v^{-1}\varepsilon = \chi RT \tag{3}$$

In this study, the calculated $v^{-1}\varepsilon$ was chosen to be 3.79 kJ/mol. The coarse-grained length of PS and PI is equal to 4 and 5, respectively. It was calculated from polymer chain length concerning its characteristic properties. So, S 4 I 5 is a mesoscopic topology that was used to represent polymeric chain consisting of 50 and 44 of degree of polymerization for PI (denoted as I) and PS (denoted as S), respectively. The order parameter (P) defined as the averaged volume of local density squared and overall density squared. The equation was defined as:

$$P_I = \frac{1}{v}\int_V \left[\eta_I^2(r) - \eta_I^2\right] dr \tag{4}$$

where, η_I is dimensionless density (volume fraction) for species I. The higher value of P indicates the stronger phase separation, another indicates more miscible system. The obtained morphology at equilibrium was confirmed by free energy density and order parameters as shown in Figure 2.
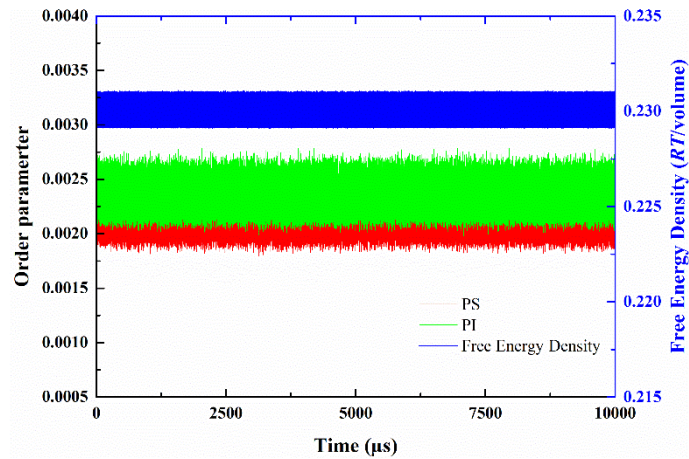
Figure 2. The evolution of the order parameters values and free energy density versus time (μs)

The variation of two parameters were found in the same tendency, their values are fluctuating around their averaged values and it indicates that the obtained morphology did not change in time evolution of 10 ms. The obtained morphology was shown in Figure 3. In this simulation, the disordered phase was obtained and the diblock copolymers are miscible in this condition [12].
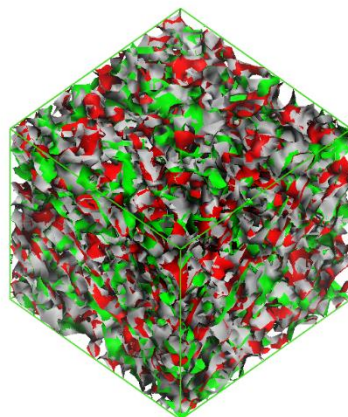
Figure 3. The obtained morphology

4. Conclusion

The combination of molecular dynamic and mesoscopic simulation was successfully used to study the phase behavior of diblock copolymer system. The mesoscopic interaction energy was chosen to be 3.79 kJ/mol which is calculated from Flory-Huggins parameter. The disorder phase was obtained in this condition indicated the miscibility of PS-PI diblock copolymer. This obtained morphology was confirm by the pattern of free energy density and order parameters.

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