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Mesoscopic simulation of asymmetric-copolymer/homopolymer blends: Microphase morphological modification by homopolymer chains solubilization

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Abstract

In this work we present the results of a mesoscopic dynamic simulation study of ordered microphases modification in asymmetric-copolymer/homopolymer binary blends, where we explore the influence of the composition, packing density and solubilization of homopolymer chains into the compatible microdomains of the asymmetric copolymer. The poly(styrene)–poly(isoprene) (PS–PI) and homopoly(styrene) (HPS) molecules were built and represented by Gaussian chain models. The pure asymmetric copolymer generates spherical microdomains of poly(styrene) (PS) in the matrix of majority component, poly(isoprene) (PI), and is taken as the base for the binary blends. The mesoscopic dynamic evolution of asymmetric-PS–PI/HPS blends display a coarse-grained system sufficiently large to determine the separation of the microphase and the formation of ordered structures. The HPS chains tend to be selectively solubilized in the PS microdomains of the asymmetric copolymer, the repulsive interaction forces between homopoly(styrene) and poly(isoprene) chains assure that essentially all the HPS homopolymer exists in the PS microdomains. As the asymmetric-PS–PI/HPS composition is varied the mesoscale simulations predict ordered structures with defined morphologies of body-centred-cubic (BCC), hexagonal packed cylinders (HPC), hexagonal perforated layers (HPL) and lamellar phases (LAM). Ordered microphases appear in reverse order when the homopoly(styrene) composition is increased in the binary blend. The agreement between our mesoscopic simulation results and available experimental outcome open a new strategy to modify the microphase morphology of asymmetric copolymers.

Keywords: Morphology; Mesoscopic simulation; Homopoly(styrene)

1. Introduction

Block copolymers are fascinating materials constituted by two or more blocks of different homopolymer chains linked by covalent bonds. A remarkable property of block copolymers is their ability to self-assemble in the melt or in solution into a variety of ordered structures with characteristic dimensions between 1 and 100 nm. These ordered structures are the key to many valuable properties which make block copolymers of great nanotechnological interest [1]. Ordered structures are formed via the thermodynamic process of microphase separation due to the repulsive interaction between the components (chemical incompatibility between the homopolymer chains), and are driven by the enthalpy and entropy of demixing of the constituent components of the block

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copolymers. The enthalpy of demixing is proportional to the Flory−Huggins segmental interaction parameter χ, while entropic effects correspond to configuration, conformation and translation of different homopolymer chains. The enthalpic−entropic balance governs the structural self-organization via a process of microphase separation in these materials [2−5]; specifically in A−B diblock copolymers the immiscibility between A and B blocks induces microphase separation and self-assembly into various ordered structures. Ordered structures of diblock copolymers include spheres of A (or B) arranged on a body-centred-cubic (BCC) lattices in a matrix of B (or A), hexagonally packed cylinders (HPC) of A (or B) in a matrix of B (or A), alternating lamellar (LAM) of A and B and more complex ordered structures such as the hexagonally perforated lamellar (HPL) and ordered bicontinuous double diamond phases (OBDD) [6]. The phase behavior of ordered structures of a bulk two-component block copolymer A−B is determined by three experimentally controllable factors: (i) the overall degree of polymerization N, (ii) architectural constrains (diblock, triblock, star block etc.) and composition, and (iii) the A−B segment−segment interaction parameter. The first two factors are regulated through the polymerization stoichiometry and affect the translational and configurational entropy, while the magnitude of (largely enthalpic) χ is determined by selection of A−B monomer pairs. The main strategy employed to ordered structures control is to modify these factors in the synthetic process (variations of architecture and chain topology) and depends on polymerization techniques [7−9]. Another important way for morphology control in these materials is given by blending with homopolymer chains. Block copolymer/homopolymer blends are of major technical and scientific relevance due their interesting structural and dynamical behavior. A diblock copolymer may be blended with homopolymer chains which are identical with one of the constituent blocks or with homopolymers which are chemically different but compatibles. Symmetric-copolymer/homopolymer binary blends have been explored recently by Hashimoto et al.[10−15], they report that the microphase behavior in these systems is modified by miscibility effects and depends on the molecular weight of the homopolymer chains. Winey et al. and Court and Hashimoto [16−18], have studied the solubilization phenomenon in copolymer/homopolymer binary blends, they observed in asymmetric copolymers with lamellar and cylindrical morphologies that the microphase behavior was also affected by solubilization between polymers.

In a previous paper [19], we have explored by means of molecular dynamic simulations the morphology control and mechanical properties of a series of diblock copolymers of poly(styrene)−poly(isoprene) and of poly(styrene)−poly(methylmethacrylate). The microphase behavior of the diblock copolymers was investigated as function of the architecture, composition and segment−segment interaction. Here, we perform the study to investigate the microphase behavior control of two-component asymmetric copolymers, PS−PI, by means of polymer/polymer interfacial modification via solubilization of homopolymer compatible chains with one block of the asymmetric copolymer. Up to our knowledge, no previous DPD theoretical studies of poly(styrene)−poly(isoprene)/homopoly(styrene) binary blends have been achieved before. Current experimental studies can only provide indirect evidence of the solubilization and packing density of homopolymer chains in the corresponding diblock copolymer microdomains. In this work we use Dissipative Particle Dynamics to explore the microphase structure modification (morphology) from a mesoscopic point of view where detailed structures will allow to understand this solubilization process.

This document is organized as follows. In Section 2 we briefly present the methodology and dynamic simulation methods employed in this work. Section 3 contains a summary of our main results and discussions of the predictions obtained for pure asymmetric copolymer and PS−PI/HPS binary blends. This section is divided in two parts, in the first part, the molecular structure of poly(styrene)−poly(isoprene) asymmetric diblock copolymer and homopoly(styrene) chains with linear architecture was mapped into a Gaussian chain model in the characteristic ratio statistical segment level. The mesoscopic parameters that display the bead−bead interaction are obtained from styrene−isoprene molecular interaction and they are advantageous to represent these systems into mesoscopic dynamics simulations. In the second part of this section, we present detailed results of the dissipative particle dynamics simulations of PS−PI pure asymmetric copolymer and asymmetric-PS−PI/HPS binary blends. It is explored the influence of the composition, packing density and solubilization of HPS chains into the compatible microdomains of the asymmetric copolymer. In Section 4 our conclusions are presented.

2. Material models and mesoscale simulation methods

2.1. Material models

The molecular structures of poly(styrene)−poly(isoprene) (PS−PI) asymmetric copolymer and homopoly(styrene) (HPS) chains were built using the Polymer Builder Module [20]. The pure asymmetric copolymer and homopolymer molecules contained 200 and 100 repetitive units, respectively, in the main chain and the linear conformation is characteristic for each polymeric system. The molecular weight for the asymmetric copolymer system is 14,707 while the homopolymer chain molar mass is 6814. The structural and conformational parameters of asymmetric-PS−PI/HPS system were calculated using the RIS Metropolis Monte Carlo (RMMC) from Accelrys Inc. and COMPASS (Condensed-phase optimized molecular potentials for atomistic simulation studies) force field [21,22]. The asymmetric-PS−PI copolymer and HPS homopolymer chains are represented by Gaussian chain models (spherical beads connected by harmonic spring) [23] where each bead represents a statistical segment of the asymmetric copolymer and homopolymer chain. All single and partial bonds in the chains are allowed to rotate during the molecular simulation except those involving bonds of the rings of poly(styrene) fragments.

The notation for the Gaussian chain models is $[\mathrm{PS}]_m$–$[\mathrm{PI}]_n$ and $[\mathrm{HPS}]_p$. The number of beads in each model was determined using the structural and conformational parameters of each system. Each model is composed of N beads, where each bead represents a large number of repetitive units (segments) of the molecular chain of which a fraction forms the PS block and the rest forms the PI block. Different segments are assumed to have equal volume; this is a necessary assumption in order to conform with the Flory–Huggins theory exposed next and for the dissipative particle dynamics model [19]. The election of the appropriate mesoscopic parameters for the representation of asymmetric copolymer and homopolymer chains is an important aspect that must be kept in mind for the subsequent mesoscopic dynamics simulations. All configurational details in the Gaussian chain models of the asymmetric-PS–PI/HPS systems are ignored; the chemistry of each block is governed by bead–bead interactions and by the molecular conformation. The bead–bead interaction between different segments is given by the magnitude of repulsion between different repetitive units.

The quantitative estimates of the bead–bead interaction for the asymmetric-PS–PI/HPS binary blends were calculated from the styrene–isoprene molecular interaction using the statistical thermodynamics model of the Flory–Huggins theory [24,25]. In this theory the miscibility is governed by Gibbs free energy of mixing,

$$\Delta G = \frac{\phi_1}{X_1}\ln\phi_1 + \frac{\phi_2}{X_2}\phi_2 + \chi\phi_1\phi_2 \tag{1}$$

where ΔG denotes the Gibbs free energy of mixing per mole, ϕ_1 and ϕ_2 are volume fractions for components 1 and 2, X_1 and X_2 are the degree of polymerization and χ is the Flory–Huggins interaction parameter defined as:

$$\chi = \frac{Z\Delta E_{12}}{RT} \tag{2}$$

where Z is the coordination number of model lattice and E_{12} is the differential energy of interaction of unlike pairs,

$$\Delta E_{12} = \frac{1}{2}(E_{12}+E_{21}) - \frac{1}{2}(E_{11}+E_{22}) \tag{3}$$

In this model, each repeating unit is defined as occupying single lattice site. The parameters ΔG, Z, ΔE_{12} and χ were evaluated by means of molecular simulations using the Flory–Huggins modified model by Fan et al. [26]. In this extension of the Flory–Huggins model, the molecules are not arranged on a planar lattice, as in the original Flory–Huggins theory, but they are arranged off-lattice (three-dimensional). The coordination number Z is explicitly calculated for each of the possible molecular pairs using Monte Carlo (MC) molecular simulations. This numerical procedure involves generating clusters in which nearest neighbours are packed around the central molecule. Average calculated Z values were employed in the temperature dependence expression of the interaction parameter. The $\Delta G(T)$ is obtained from the configurational interaction energies and coordination number as follows:

$$\Delta G(T) = \frac{[Z_{12}E_{12}(T) + Z_{21}E_{21}(T) - Z_{11}E_{11}(T) + Z_{22}E_{22}(T)]}{2} \tag{4}$$

The temperature dependence of the interaction parameters, $\chi(T)$, is calculated as a function from $\Delta G(T)$ and Z as:

$$\chi(T) = \frac{\Delta G(T)}{RT} \tag{5}$$

$$\chi(T) = \frac{(Z_{12}E_{12} + Z_{21}E_{21} - Z_{11}E_{11} + Z_{22}E_{22})}{2RT} \tag{6}$$

This methodology has been successfully employed in calculating the properties of different macromolecules [27].

2.2. Mesoscale method: dissipative particle dynamics

DPD is nowadays a well-established methodology, for more thorough account on DPD see e.g. Refs. [29–34], we just give a short summary of the dissipative particle dynamics method. The DPD method, introduced by Hoogerbrugge and Koelman [28,29], is a mesoscale simulation technique that combines some of the detailed description of Molecular Dynamic (MD) but allows the simulation of hydrodynamic behavior in much larger and more complex systems constituted by particles. Español and Warren [30–32] identified the link between the DPD algorithm and an underlying stochastic differential equation for particle motion, thereby establishing DPD as a valid method for the simulation of the dynamics of mesoscopic particles. Groot et al. [33–35] have recently related the DPD method with the solutions of the Flory–Huggins theory thus allowing one to study large molecular weight systems under efficient operation conditions. Furthermore, they have demonstrated that this approach is consistent with the mean field theory. In a DPD simulation, a particle having mass $\mathbf{m}_i$ represents a small segment of polymer chains moving together in a coherent manner. These DPD particles are subject to soft potentials and governed by predefined collision rules. Like MD, the DPD particles obey Newton's equation of motion. In the asymmetric-PS–PI/HPS binary blend there are three different species of DPD particles: styrene particles (St), isoprene particles (I) and homopolymer particles (HS). Each particle is subject to soft interactions with its neighbours via three forces: conservatives ($\mathbf{F}_{ij}^{\mathrm{C}}$), dissipative ($\mathbf{F}_{ij}^{\mathrm{D}}$) and random forces ($\mathbf{F}_{ij}^{\mathrm{R}}$), and are given by

$$\mathbf{F}_{ij}^{\mathrm{C}} = \left[a_{ij}(1-r_{ij})\widehat{\mathbf{r}}_{ij}\right]\frac{\text{if}\left|\mathbf{r}_i\right| < 1}{0 \quad \text{if}\left|\mathbf{r}_{ij}\right| \geq 1} \tag{7}$$

$$\mathbf{F}_{ij}^{\mathrm{D}} = \left[-\gamma\omega^{\mathrm{D}}(r_{ij})\left(\mathbf{v}_{ij}\cdot\widehat{\mathbf{r}}_{ij}\right)\widehat{\mathbf{r}}_{ij}\right]\frac{\text{if}\left|\mathbf{r}_{ij}\right| < 1}{0 \quad \text{if}\left|\mathbf{r}_{ij}\right| > 1} \tag{8}$$

$$\mathbf{F}_{ij}^{\mathrm{R}} = \left[\sigma\omega^{\mathrm{R}}(r_{ij})\xi_{ij}\widehat{\mathbf{r}}_{ij}\right]\frac{\text{if}\left|\mathbf{r}_{ij}\right| \leq 1}{0 \quad \text{if}\left|\mathbf{r}_{ij}\right| > 1} \tag{9}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$, $\widehat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$, γ is the dissipation strength, σ is the noise strength, ω^{D} and ω^{R} are r-dependent weight functions, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, a_{ij} is a maximum repulsion strength between particles i and j and ξ_{ij} is a Gaussian noise term with the following properties: $\xi_{ij} = \xi_{ji}$, $\langle \xi_{ij}(t) \rangle = 0$, $\langle \xi_{ij}(t)\xi_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t')$.

The parameter a_{ij}, henceforth referred to as bead–bead repulsion parameters or simply as DPD interaction parameter depend on the underlying atomistic interactions and is related to the parameter χ of Section 2.1 through:

$$a_{ij} \approx \alpha_{ij} + 3.21\chi_{ij} \quad \text{for } \rho = 3 \tag{10}$$

in this way we connect the molecular character of the styrene–isoprene molecular system with the DPD system. The dissipative and random forces have two effects, they act as a thermostat (an alternative DPD thermostat has been proposed by Lowe [36]), and they allow transport properties such as the viscosity to be tuned without altering the equilibrium thermodynamics. All the forces are pairwise additive, central, and satisfy Newton's Third Law thus conserving linear and angular momentum. The forces depend only on relative positions and velocities, making the model Galilean-invariant. All forces between particles i and j vanish beyond some cut-off radius (r_c). All mesoscopic simulations were carried out in a cubic simulation box of size ($10r_c$, $10r_c$, $10r_c$) containing a total of 150 Gaussian chains and a density $\rho = 3$. The simulations were made at temperature $k_BT = 1$, this allows a reasonable and efficient relaxation for each asymmetric-PS–PI/HPS binary blend. A total of 10^5 time steps with step size $\Delta t = 0.05$ in DPD reduced units are performed for equilibration. In the simulation of asymmetric-PS–PI/HPS binary blends the mesoscopic dynamic behavior of the system is followed by integration of the equations of motion using a modified version of the Verlet algorithm [37–40]. The relative magnitudes of the three forces evolve to a steady state that corresponds to the Gibbs canonical ensemble, NVT. Integration of the equations of motion for the PS–PI/HPS system generates a trajectory through the system's phase from which thermodynamic observables may be constructed from suitable average. From this information the microscopic mechanism of mass transfer in asymmetric-PS–PI/HPS binary blends process can be observed.

3. Simulation results and discussion

3.1. PS–PI and HPS structures and Gaussian chain model

Table 1 summarizes the computed structural and conformational properties of the poly(isoprene) (PI) and poly(styrene) (PS) chains. In order to apply the Gaussian chain model to realistic block copolymers, a number of structural and conformational parameters such as polymer molecular weight, persistence length, characteristic ratio, mean squared end-to-end distance, statistical Kuhn segment length, among others parameters can be used [41]. In previous papers [19,42] we show that the (C_n) characteristic ratio give reliable results to represent the PS–PI diblock copolymer system, so we employ this statistical segment level for mapping the molecular structure of PS–PI asymmetric copolymer and HPS homopolymer chains into Gaussian chain models. The C_n statistical segment level provides a narrow number of beads in the Gaussian chain models representation. From a practical numerical point of view, it is desirable to use few beads in the asymmetric-PS–PI/HPS systems description. With the structural and conformational parameters of Table 1, the PS–PI asymmetric copolymer and homopoly(styrene) (HPS) chains are represented by the Gaussian chain models constituted by spherical beads as sketched schematically in Fig. 1. The PS–PI copolymer of asymmetric composition is represented by a model constituted by 20 beads, $[\mathrm{PS}]_3$–$[\mathrm{PI}]_{17}$, see Fig. 1(a), whereas the homopoly(styrene) (HPS) chains by a model of 10 beads, $[\mathrm{HPS}]_{10}$, see Fig. 1(b) The number of beads in each model was determined using the molar mass of diblock copolymer, molar mass of a repeat unit, degree of polymerization and characteristic ratio of each system, for more details see Ref. [42]. In this way the Gaussian chain models developed for the asymmetric-PS–PI and HPS systems describe the molecular structure at the characteristic ratio statistical segment level.

Table 1
Structural and conformational parameters of poly(styrene) and poly(isoprene) chains

Structural and conformational parameters[a]	Poly(styrene) block (PS)	Poly(isoprene) block (PI)
Molar mass	10,417	6814
Molar mass per repeat unit	104.17	68.139
No. of rotatable bonds in system	299	399
Mean squared end-to-end distance $\langle r^2 \rangle$	4917.8 ± 437 Å^2	7198.1 ± 528 Å^2
Characteristic ratio $\langle C_n \rangle$	10.49 ± 0.49	9.03 ± 0.37
Mean squared radius of gyration $\langle S^2 \rangle$	825.85 ± 6.24 Å^2	1243.6 ± 10.1 Å^2
Ratio $\langle r^2 \rangle / \langle S^2 \rangle$	6.23	6.099
Persistence length, projection on first bond $\langle a1 \rangle$	4.72 ± 0.66 Å	10.35 ± 0.82 Å
Persistence length, mean projection on all bonds $\langle a2 \rangle$	9.36 ± 0.16 Å	7.37 ± 0.13 Å

[a] The conformational parameters of polystyrene and polyisoprene chains were obtained by averaging a large number of generated configurations, typically 750,000, the COMPASS force field was used in the RIS Metropolis Monte Carlo simulation.

We have evaluated the bead–bead interaction in these mesoscale models from styrene–isoprene molecular interaction of polymer/polymer binary mixtures by use of a combination of the Flory–Huggins theory and Monte Carlo simulations. As was mention before (Section 2.1) the Monte Carlo method, which includes constraints arising from excluded volume, provides an efficient algorithm for sampling relative orientations of the two molecules. The fundamental parameters that include the heat of mixing associated with styrene–isoprene interactions and the number of possible interaction partners, i.e., coordination number, Z_{12}, interaction energies, ΔE_{12}, were obtained by averaging a large number of generated configurations, typically 500,000.

Then, the temperature dependence of the interaction parameter, $\chi(T)$, was obtained by Eq. (6). Fig. 2 shows this temperature dependence and the values in the range 200–500 K.

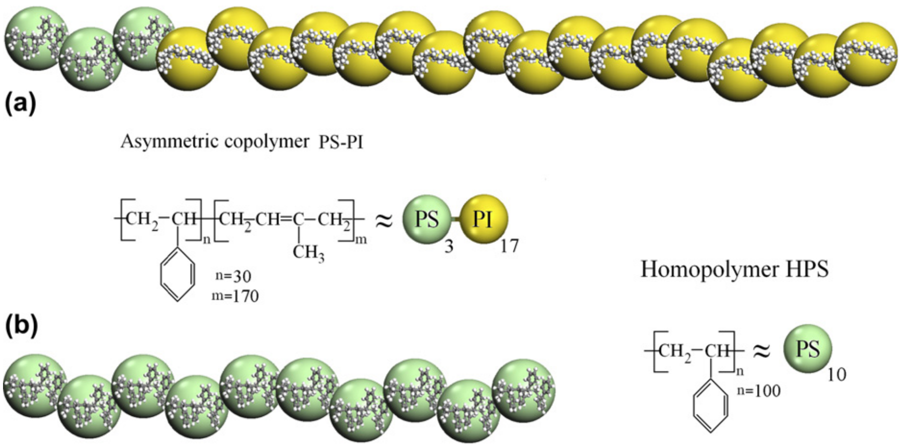

Fig. 1. Schematic representations of the Gaussian chain models of asymmetric copolymer and homopolymer chains. (a) Poly(styrene)–poly(isoprene) model of asymmetric composition. (b) Homopoly(styrene) chain model.

These values are comparable with those obtained from experimental data (solubility parameters) [43–45] using the Flory–Huggins relation [4,46], more details of these solubility parameters and experimental data are given in Soto-Figueroa et al. [19]. It is important to keep in mind that a reliable and realistic value of $\chi(T)$ is necessary as it is used as an input in Eq. (10). The styrene and isoprene fragments are incompatible in different degrees and the microphase separation occurs with temperature lowering. A small incompatibility between different styrene–isoprene fragments is amplified in giant molecules as the polymers; this fact has been exploited in the subsequent simulations.

3.2. Mesoscopic evolution of asymmetric-PS–PI/HPS blends

The PS–PI diblock copolymer of symmetric or asymmetric composition in its main block chain may be blended with homopolymers chains which are identical with block copolymers constituent blocks or with homopolymers which are chemically different from that of the constituent homopolymers. The binary blends of PS–PI asymmetric copolymer and homopoly(styrene) chains are fully described by several molecular parameters such as the initial morphology of the pure asymmetric copolymer, the weight percent of poly(styrene) in the asymmetric-PS–PI copolymer, the homopolymer molecular weight, the copolymer molecular weight, the homopoly(styrene) composition in the asymmetric-PS–PI/HPS binary blend, and interaction parameter [47,48]. All these parameters govern the microphase behavior of a binary blend of diblock copolymers and homopolymer chains, these molecular parameters are considered in the mesoscopic dynamic simulations subsequent of asymmetric-PS–PI/HPS binary system.

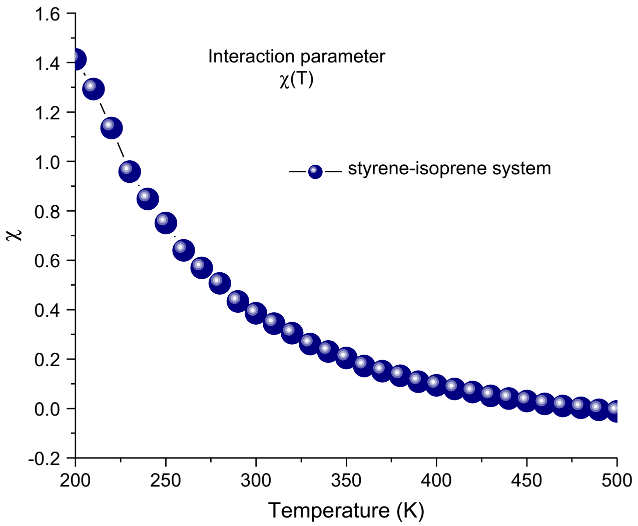

Fig. 2. Molecular interaction parameters for the styrene–isoprene system obtained by Monte Carlo molecular simulation.

The number of beads representative for each Gaussian chain model were assumed to be constant and the composition intervals analyzed for asymmetric-PS–PI/HPS binary blends range from 0.1 to 0.9 (volume fraction) of HPS with increments of 0.05. The mesoscopic dynamic simulation of pure asymmetric copolymer displays spherical morphology formed by body-centred-cubic (BCC) packing of the less dispersed component, PS, into the matrix of the majority component, PI, when the composition is 0.18 (volume fraction) of PS in PS–PI diblock chain, see Fig. 3(a). The BCC spherical morphology of pure asymmetric copolymer shows rich microdomains of a single type of homopolymer separated by interfaces; these packing are more pronounced when the composition of the diblock copolymer becomes further asymmetric, this is because the chains of a component are more extended thus allowing the formation of less planar interfaces. In this case, the conformational entropy loss of the major component is too high. Therefore, to gain conformational entropy, the chains of the majority component tend to expand along the direction parallel to interface. As a result, the polymer/polymer interface becomes convex towards the minority component. The spherical morphology obtained by simulation for the PS–PI pure asymmetric copolymer system can be compared positively with the

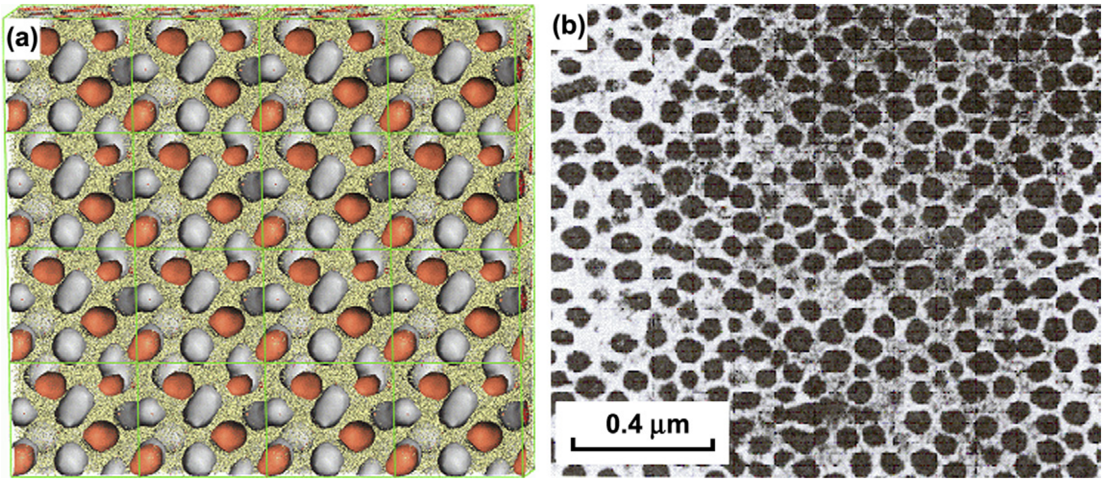

Fig. 3. Representative morphology of the PS–PI pure asymmetric copolymer. (a) Body-centred-cubic (BCC) packing obtained by dissipative particle dynamics simulation. (b) Transmission Electron Micrograph image of PS–PI diblock copolymer taken from Ref. [21].

morphologies reported by Aggarwal and Khandpur et al. [49,50], see Fig. 3(b). The picture of PS–PI pure asymmetric copolymer was constructed by assembly of 64 boxes in order to compare with the Transmission Electron Micrograph image. To our knowledge an explicit comparison between mesoscopic simulation and reported experimental data of PS–PI diblock system does not exist until now, this validates the pure asymmetric copolymer model and its mesoscopic parameters employed in this work.

The BCC body-centred-cubic morphology of the diblock copolymers pure component systems as well as in multiple component (blends) systems by MC and DPD simulations has been recently published by Windle et al. [51,52], and Groot et al. [35], in these studies they propose directly a model of beads without any a priori specification of the molecular structure. On the other hand, the models for the asymmetric-PS–PI and HPS system used in the present work were obtained from the molecular structure of the diblock copolymer and homopolymer chains and they are advantageous to represent these polymers into mesoscopic dynamics simulations, the mesoscopic parameters are acquired from the monomer–monomer interaction. Then, the use of a different monomer modifies totally the mesoscopic models and bead–bead interaction parameters and consequently the final morphology, both in the pure diblock copolymer and its blends.

All asymmetric-PS–PI/HPS binary blends start from a random disordered state in the mesoscopic dynamics simulations, where the polymers are in a homogeneous melted state, during the temperature relaxation, we observe the microphase separation process and ordered phases generation into nanoscale domains. In this paper a transition from a homogeneous melt state of chains to a heterogeneous melt of ordered microphases-separated domains is defined to be an order-disorder transition (ODT). The description of each asymmetric-PS–PI/HPS binary blend generates a coarse-grained system sufficiently large to identify the formation of ordered structures.

As the composition asymmetric-PS–PI/HPS is varied the mesoscopic simulations generate ordered microphases with defined morphologies of body-centred-cubic (BCC), hexagonal packed cylinder (HPC), hexagonal perforated layers (HPL) and lamellar (LAM) consisting of alternating layers of different components. Table 2 summarizes the detailed characterization of microdomains for asymmetric-PS–PI/HPS binary blends.

In Fig. 4 some typical time evolution of these ordered structures' domains of simulations are shown. The left side of Fig. 4 shows three-dimensional simulations of asymmetric-PS–PI/HPS chains. Fig. 4a, corresponding to a 0.90/0.10 composition shows a BCC structure, Fig. 4c corresponding to 0.85/0.15 shows a HPC microphase, this structure is maintained up to a composition 0.80/0.20. Fig. 4e, corresponding to 0.75/0.25 shows a HPL microphase. Finally Fig. 4g shows a LAM microphase for 0.65/0.35, this microphase is maintained until the composition 0.50/0.50. From this value the microphases

Table 2
Evolution of ordered structures with defined microphases in (asymmetric-poly(styrene)–poly(isoprene)/homopoly(styrene)) binary blends

PS–PI/HPS composition (volume fraction)	Phase morphology (ordered structures)
1.0/0.0	Body-centred-cubic
0.90/.10	Body-centred-cubic
0.85/0.15	Cylinders
0.80/0.20	Cylinders
0.75/0.25	Hexagonal perforated lamellar
0.70/0.30	Hexagonal perforated lamellar
0.65/0.35	Lamellar
0.60/0.40	Lamellar
0.55/0.45	Lamellar
0.50/0.50	Lamellar
0.45/0.55	Lamellar
0.40/0.60	Lamellar
0.35/0.65	Hexagonal perforated lamellar
0.30/0.70	Cylinders
0.25/0.75	Cylinders
0.20/0.80	Body-centred-cubic
0.15/0.85	Body-centred-cubic
0.10/0.90	Body-centred-cubic

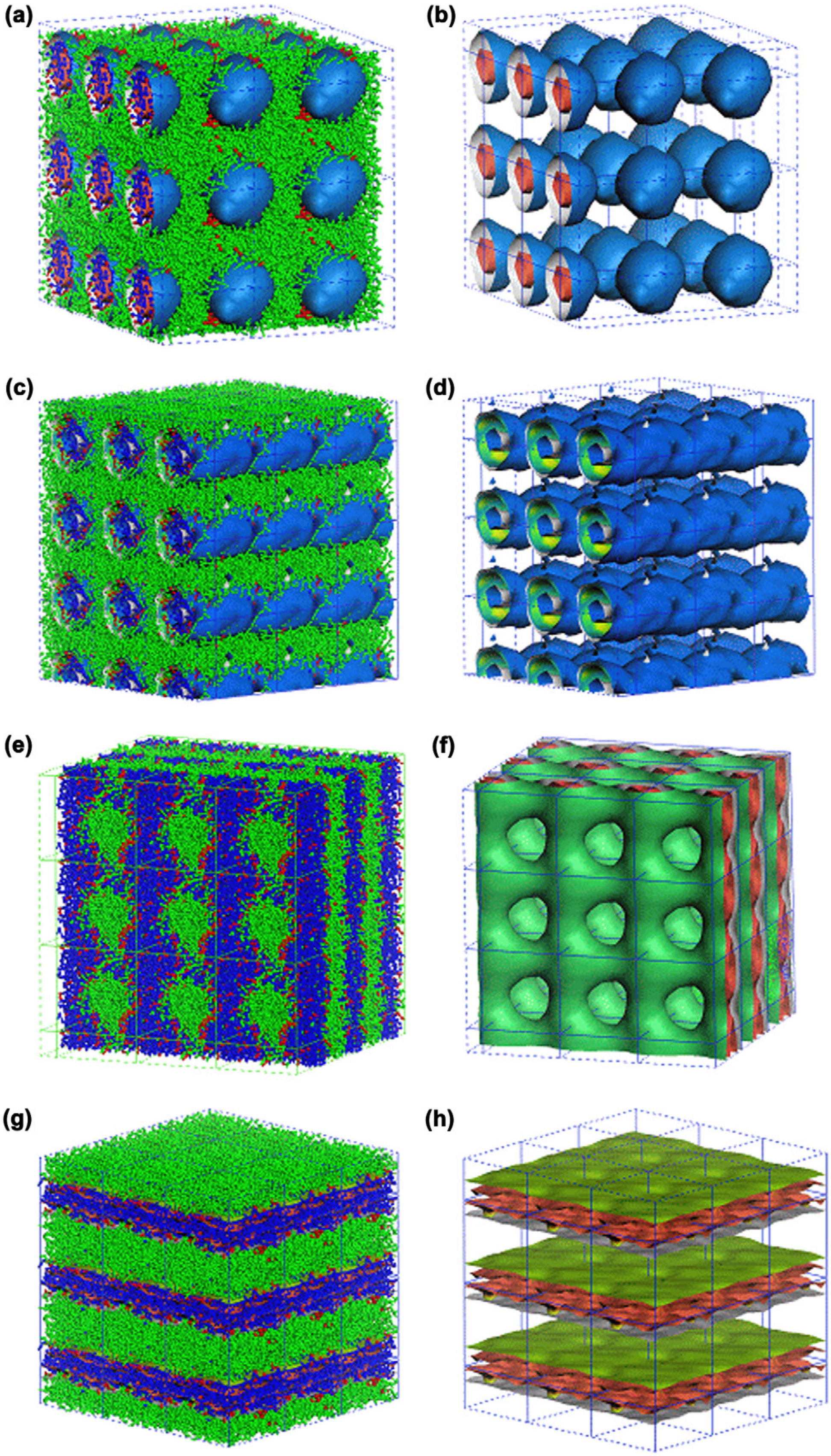

Fig. 4. Equilibrium morphologies of ordered microphases and microdomain isodensities of the PS–PI/HPS binary blends as modeled by DPD. (a, b) Body-centred-cubic (BCC). (c, d) Hexagonal packed cylinders (HPC). (e, f) Hexagonally perforated lamellar (HPL) and (g, h) lamellar (LAM). For the respective compositions see text and Table 2.

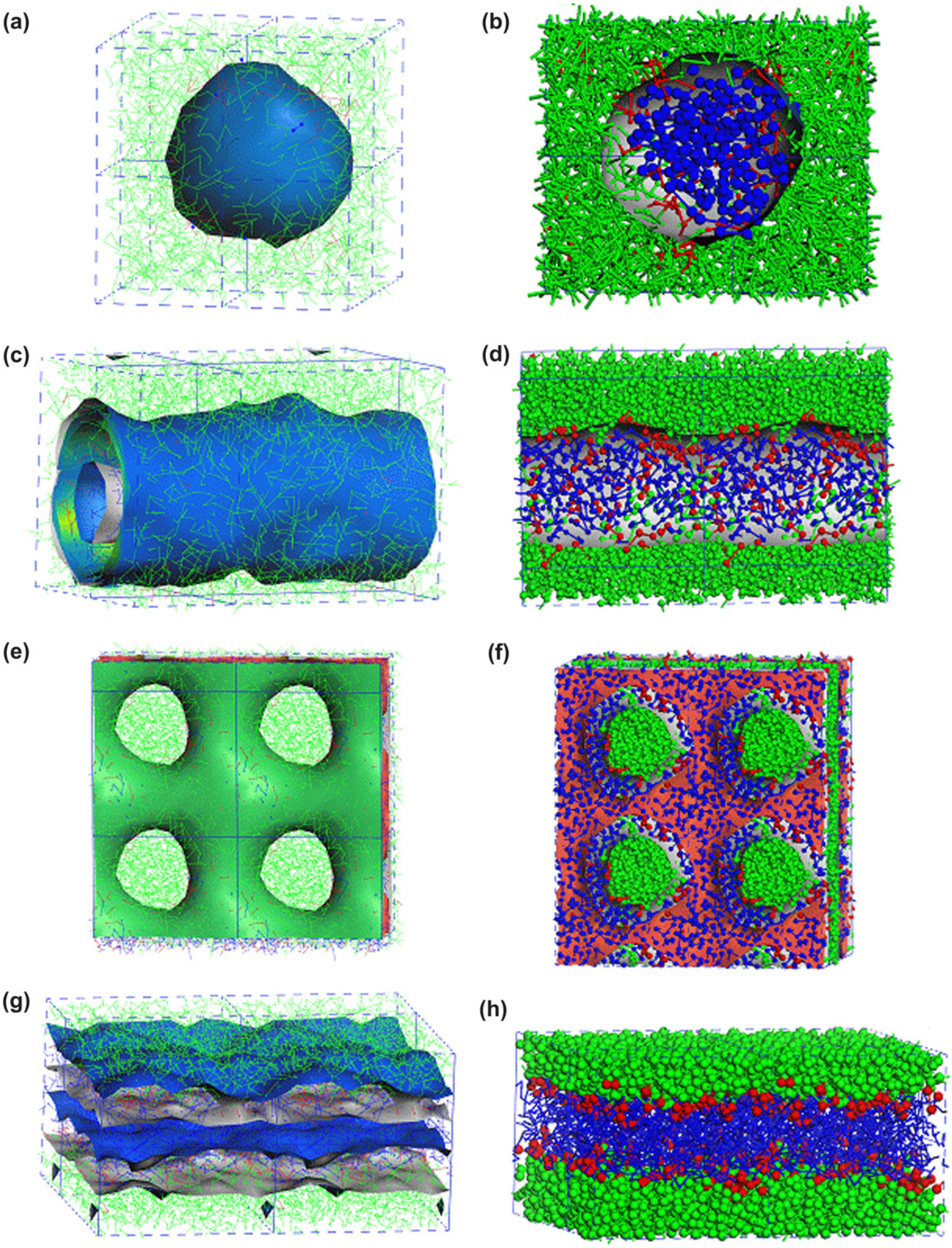

Fig. 5. Solubilization and packing density of homopoly(styrene) chains into the microdomains space of asymmetric copolymer. (a, c, e, and g) Ordered microdomains evolution, BCC to LAM. (b, d, f, and h) Ordered microdomains slice. The homopoly(styrene) chains tends to cause a swelling of the PS microdomains in all directions to the interface, causing changes in packing density of PI and PS microdomains, and therefore morphology modification.

are inverted and the morphologies evolve in the opposite sense. Fig. 4(b, d, f, and h) shows the corresponding three-dimensional simulations of asymmetric-PS–PI/HPS isodensities profiles for the same composition values as before. In all cases we observe the microphase separation in the binary blends in the analyzed composition interval, this behavior is in agreement with the reported experimental observations for these systems (the experimental results show a microphase separation with a rich variety of these structures) [10–18,53,54].

The ordered structures microphase evolution of asymmetric-copolymer/homopolymer binary blends can be understood in terms of the effects of the homopolymer chains solubilization, packing density and entropic interactions (conformational, configurational and translational) on the corresponding microdomains space of the pure asymmetric copolymer. As was noted above, the PS–PI asymmetric copolymer evolves via the process of microphase separation and generates spherical microdomains of homopoly(styrene) dispersed into the matrix of poly(isoprene), Fig. 3. When the pure asymmetric copolymer is blended with homopoly(styrene), the HPS chains tend to be selectively solubilized in the PS microdomains of the microphase-separated asymmetric copolymer and the repulsive interaction forces between homopoly(styrene) and poly(isoprene) chains assure essentially that all the HPS homopolymer chains exists in the PS microdomains. In composition of 0.05 of homopoly(styrene) in the asymmetric-PS–PI/HPS binary blend, the homopoly(styrene) chains are fully solubilized in the spherical ordered microdomains of poly(styrene) block, the PS–PI diblock copolymer of asymmetric composition maintain its ordered structure of body-centred-cubic (BCC) packing, the HPS chains are segregated towards the domain centre leading to an increase in interfacial area per block and causing a swelling of the poly(styrene) microdomains. The swelling of the PS spherical microdomains of the asymmetric-copolymer, cause a growth in the directions both parallel and perpendicular to the interface, this lead to a difference in segmental density in PS and PI microphases. In order to retain normal liquid-like densities, the PS microdomains must extend and/or PI microdomains must contract, this in turn, can lead to a change in the interface curvature of PS and PI microdomains and therefore in the microphase morphology, as shown in Fig. 5.

When the volume fraction of the homopoly(styrene) continues increasing (with increments of 0.05) in the spherical microdomains space of PS until a limit value of concentration, the spherical microdomains are collapsed with their near neighbours and the body-centred-cubic microphase disappears and a new ordered phase of hexagonal packed cylinder evolves, see Fig. 5(a) and (c), this is a sphere–cylinder transition. The BCC microdomain's fusion leads towards large convex interfaces with HPC cylindrical packing, in these ordered structures we can observe that the homopoly(styrene) chains are segregated preferentially into centres of the cylindrical microdomains with which it is compatible (in all case the low molecular weight HPS chains are selectively solubilized in the microdomains space of microphases-separated diblock copolymer with spherical morphology) see Fig. 5(b) and (d), this is valid for BCC, HPC, HPL and LAM geometries. The homopoly(styrene) chains' distribution in the domain centre depends on the enthalpic and entropic interactions between the homopolymer and the asymmetric copolymer domains. When the volume fraction of the homopoly(styrene) chains continues increasing in the asymmetric-PS–PI/HPS binary blend, the hexagonal packed cylinder microdomains reach their maximum packing density, the microdomains are joint with its near neighbours, the hexagonal packing disappears and wider cylinders are formed. With the composition increase the entropic interactions modify the polymer/polymer interface and therefore the interface tends to become less curve, hexagonally perforated lamellar ordered phases are generated, see Fig. 5(e). In the HPL microdomains the low molecular weight homopoly(styrene) chains are solubilized completely in the PS microdomains, the homopoly(styrene) chains tend to be distributed uniformly in the domain centre as shown in Fig. 5(f). When the volume fraction of both components in the asymmetric-PS–PI/HPS binary blends is the same a (LAM) lamellar morphology consisting of alternating layers of different components evolves. The composition, packing density, enthalpic and entropic interactions reach an balance what allows the formation of ordered structures with planar interfaces, as shown in Fig. 5(g).The homopoly(styrene) chains are fully solubilized in the lamellar ordered microdomains of poly(styrene) block, see Fig. 5(h). Upon increasing the homopoly(styrene) fraction (now major component in the asymmetric-PS–PI/HPS binary blends) the ordered structures with defined microdomains appears in a reversed order, see Table 2, the interface curvature effect is more pronounced when the composition of the PS–PI/HPS binary blends is more asymmetric.

4. Conclusions

We have performed mesoscopic simulations of the poly(styrene)–poly(isoprene)/homopoly(styrene) binary blends through dissipative particle dynamics, to explore the microphase morphological modification of PS–PI asymmetric copolymer via solubilization process of homopoly(styrene) chains. In our approach the diblock copolymer model and its interaction come directly from the molecular structure and the RIS Monte Carlo simulation. In this way, the mesoscopic parameters represent the real PS–PI molecular structure in contrast with simulations where these parameters are arbitrary.

The mesoscopic dynamic evolution of asymmetric-copolymer/homopolymer blends generates a coarse-grained system sufficiently large to determine the separation of microphases and the formation of ordered structures with defined morphologies; body-centred-cubic (BCC), hexagonal packed cylinder (HPC), hexagonal perforated layers (HPL) and lamellar (LAM) were obtained. The ordered structures evolution of asymmetric-PS–PI/HPS binary blends is controlled by the initial morphology of the pure asymmetric copolymer, the HPS composition in the asymmetric-PS–PI/HPS binary blend, the homopolymer molecular weight, the interaction parameter, solubilization and packing density of homopolymer chains. The homopoly(styrene) chains segregates preferentially into centres of the microdomains with which they are compatible, this is valid for BCC, HPC, HPL and LAM geometries. The homopolymer distribution depends on the enthalpic and entropic interaction between the homopolymer and the asymmetric copolymer microdomains. The excellent agreement between our mesoscopic dynamic simulation results and available experimental results open a new strategy to modify the microphase morphology of diblock copolymers of asymmetric composition. Tailoring the distribution of identical chemical blocks provides a powerful method to modify the properties in these materials, helps to improve existing polymeric materials, the design of novel materials with tailor-made properties for given applications, the optimization of production processes and finally the reduction of production cost.

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