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Morphologies of poly(cyclohexadiene) diblock copolymers: Effect of conformational asymmetry

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ABSTRACT

Concerted experimental and theoretical investigations have been carried out to understand the microphase separation in diblock copolymer melts containing poly (1,3-cyclohexadiene), PCHD, as one of the constituents. In particular, we have studied diblock copolymer melts containing polystyrene (PS), polybutadiene (PB), and polyisoprene (PI) as the second block. We have systematically varied the ratio of 1,2-/1,4-microstructures of poly (1,3-cyclohexadiene) to tune the conformational asymmetry between the two blocks and characterized the effects of these changes on the morphologies using transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). Our experimental investigations reveal that the melts of PCHD-b-PB, PCHD-b-PS and PCHD-b-PI containing nearly equal fractions of each component and high percentage of 1,4-microstructures in the PCHD block form cylindrical rather than lamellar morphologies as expected in *symmetric* diblock copolymers. In contrast, the morphologies of PCHD-b-PB, PCHD-b-PS and PCHD-b-PI containing PCHD block with higher 1,2-microstructure are found to be disordered at 110 °C. The change in the morphological behavior is in good agreement with our numerical calculations using the random phase approximation and self-consistent field theory for conformationally asymmetric diblock copolymer melts. Also, the effects of composition fluctuations are studied by extending the Brazovskii–Leibler–Fredrickson–Helfand (J. Chem. Phys. 87, 697 (1987)) theory to conformationally asymmetric diblock copolymer melts. These results allow the understanding of the underlying self-assembly process that highlights the importance of the conformational asymmetry in tuning the morphologies in block copolymers.

1. Introduction

Microphase separation in diblock copolymers has been one of the most studied problems in soft-condensed matter physics [1–22]. It has been demonstrated [1,5] that a delicate balance of the diblock copolymer chain conformational entropy and repulsive interaction energy between the two monomeric units leads to different thermodynamically stable ordered morphologies [1–18]. Experimentally [1,13], the conformational entropy as well as the interaction energy can be tuned by the volume fraction of each block in a diblock copolymer and/or by changing the chemical nature of the monomers constituting the block copolymer. Furthermore, temperature is also a factor for the interaction energy. For an A–B diblock copolymer, its morphologies can be theoretically described (within the saddle-point approximation/mean-field theory) with three independent parameters, namely: f_A or f_B (the

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volume fraction of block A and B, respectively), $\chi_{AB}N$ parameter (characterizing repulsive interactions between the monomeric units of the type A and B for a diblock containing a total of N Kuhn segments), and the parameter characterizing conformational asymmetry [9–15,19–22], defined as $\varepsilon = b_A/b_B$, where b_A and b_B are the Kuhn segment lengths of the two blocks, respectively. Fluctuation corrections [16–18] to the mean-field theory leads to the introduction of N as another parameter so that the mean-field results are found to be strictly valid in the limit of $N \rightarrow \infty$.

The morphology diagram for a conformationally symmetric (i.e., $\varepsilon = 1$) diblock copolymer was constructed by Leibler [2] using the random phase approximation (RPA) in the weak segregation limit (so that the interfaces stay diffuse). Morphology diagrams in the strong segregation limit corresponding to sharp interfaces were constructed by Semenov [3] and Ohta–Kawasaki [4]. Later on, Matsen and Schick [6–8] used the self-consistent field theory (SCFT) to construct the phase diagram for the whole range of segregation strengths. Subsequently, these studies were extended to the conformationally asymmetric diblock copolymers by a number of researchers [9–15,19–22]. A noticeable effect of introducing conformational asymmetry in the calculations is to shift the order–order transition boundaries significantly. In particular, for symmetric volume fractions (i.e., for $f_A = 0.5$) and large enough conformational asymmetry, transition from disordered to spherical to cylindrical morphology is predicted [9–12] rather than the transition from disordered to lamellar morphology. On the experimental side, there have been a number of experimental studies investigating morphologies of block copolymers with high conformational asymmetry [13–15,19–22].

Here we report a study of the morphologies of poly (1,3-cyclohexadiene) (PCHD) diblock copolymers. The motivation behind the use of PCHD as one of the components of the diblock copolymers arises from the fact that PCHD incorporates an unsaturated 6-membered ring into the polymer chain, which may subsequently derivatized (saturated, fluorinated, sulfonated, etc.) [23,24]. Furthermore, the PCHD block in the diblock copolymers can be converted to polyphenylene, leading to a semi-conductive polymer, which is of significant importance in polymer electronics [25].

Another motivation behind this work is the rich chemistry of the PCHD block itself. The microstructures (1,2- vs 1,4-) of a PCHD chain, as shown in Fig. 1, can be tuned readily through altering polymerization conditions [26,27]. Change in microstructure affects PCHD properties such as glass transition temperature and flexural strength [28,29]. Furthermore, the 1,2- and 1,4-microstructures of PCHD are chemically different monomers with different strengths of short-range interactions. Thus, tuning the relative amounts of these microstructures allows tuning of the interaction energies of the PCHD blocks with other block copolymer components.

Morphological behavior of PCHD contained block copolymers has been studied previously by Natori *et al.* [28,29], He *et al.* [30], and David *et al.* [31] Natori *et al.* [29] investigated symmetric diblock copolymers of polystyrene-b-polycyclohexadiene (PS-b-PCHD) and triblock copolymers (PS-PCHD-PS and PCHD-PS-PCHD). They found that the microphase separated morphologies for PS-PCHD were poorly ordered but both triblocks showed distinct lamellar structures. Their PCHD blocks had high 1,2-microstructures (~50%). Natori and coworkers [28] also studied the phase behavior of polybutadiene (PB) and PCHD triblock copolymers, where both PB and PCHD chains had high 1,2- content, and found less well ordered morphologies, noting that "microphase-separated structures seemed to have disappeared, depending on the CHD/Bd component in triblock copolymers or the molding conditions". He *et al.* [30] studied the morphology of block copolymers of PCHD and polyisoprene (PI) having high molecular weight (>100,000), rather high polydispersities (in the range 1.3–2.1), and high (50%) 1,2- content in the PCHD. When cast from cyclohexane, a sample containing 86% PI showed a phase separated morphology with a PI continuous phase.

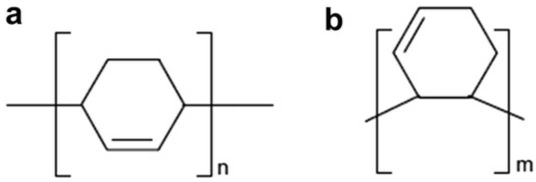

Fig. 1. Chemical structures of the PCHD chain containing 100% 1,4-microstructure and 1,2-microstructure are shown in a) and b), respectively.

David *et al.* [31] studied PS-b-PCHD diblock copolymers with high 1,4-microstructures (>90%) and f_{PCHD} lying in the range 0.30–0.38. For these samples, they reported classical [1,2] cylindrical morphology i.e., hexagonally packed cylinders (containing PCHD in the core) dispersed in a PS matrix. In addition, depending on the processing conditions (casting solvent, presence of PS homopolymers in the as-synthesized samples) a core–shell morphology has been reported [31]. In the core–shell morphology, the core consists of PS (majority component) and the shell is made up of PCHD. These core–shell cylinders are dispersed in PS matrix with long range order. However, it is not clear from these experiments [31] whether the core–shell morphology is equilibrium or a metastable state. As noted above, these diblock copolymers, prepared without the use of polar additives to limit chain transfer and termination reactions, did in some cases contain PS homopolymer [31]. We must point out that theoretically [32,33], the core–shell morphology is predicted to be an outcome of polydisperse diblock copolymer chains. However, these calculations are strictly valid in the strong segregation limit (corresponding to $\chi_{AB}N \rightarrow \infty$) and we are not aware of any field theoretical calculations predicting such morphology at finite $\chi_{AB}N$.

With this brief review of the pertinent work in the literature, we present the outline of this paper. This paper is organized as follows: details of the synthesis and morphological characterizations are presented in the next section. It is followed by the self-consistent field theory (SCFT) used to carry out a numerical study of the morphologies in conformationally asymmetric diblock copolymers. Results and discussion are presented in the following section and the paper ends with the Conclusions. Discussion of the RPA and straightforward extension of the Brazovskii–Leibler–Fredrickson–Helfand (BLFH) to conformationally asymmetric diblock melts is presented in the supplementary material.

2. Experimental

2.1. Synthesis

The PCHD diblock copolymers were synthesized using anionic polymerization and the details have been reported elsewhere [34,35]. Two different initiating systems were used to polymerize 1,3-cyclohexadiene. The first initiating system was n-BuLi/N,N,N′,N′-tetramethylenediamine (TMEDA) in a 4/5 M ratio, which produced a PCHD block containing ~50% 1,2- and ~50% 1,4-microstructure [26]. The second system used was sec-BuLi/1,4-diazabicyclo[2.2.2]octane (DABCO), which gave a PCHD block containing ~95% 1,4- and ~5% 1,2-microstructure [27].

In a typical polymerization of the present study, to synthesize PS-PCHD diblock copolymer, 6.8 g of styrene was reacted with 0.324 mmol of sec-BuLi in 140 mL of benzene in a n-BuLi washed