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Computer simulation of microphase separation in ionic copolymers

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The formation of lamella microphases in symmetric neutral-ionic block copolymers has been investigated by constant volume–constant temperature (NVT) molecular-dynamics computer simulations using a generic coarse-grain model. Computations of counterion diffusion, pressure tensor, and the anisotropy of the structure factor are used to characterize the order-disorder transition (ODT). There is strong counterion condensation on the ionic blocks at temperatures well above the ODT; this creates a slight imbalance in the volume composition of the two blocks and results in a perforated lamella structure in the microphase. Below the ODT counterion diffusion is decoupled from the chain motions but is strongly anisotropic due to the microphase morphology. The high counterion diffusional mobility is discussed in terms of the relatively low value of the glass transition for the ionic blocks. [S1063-651X(99)05711-6]

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INTRODUCTION

It has long been recognized that solvent-free ionic polymers have considerable potential importance as ion conducting membranes [1]. These materials are composed of linear or branched chains with a certain fraction of charged monomers distributed either randomly or in the form of ionic blocks; oppositely charged counterions ensure overall charge neutrality. Most studies to date have concentrated on the low ion fraction ($<20\%$) so-called ionomer regime [1–4], where the appearance of small wave-vector peaks in the static structure factors, as observed for instance in small-angle x-ray scattering experiments [2], is strong evidence for the existence of intermediate range order. This order has been interpreted in terms of the existence of ionic domains formed from ion multiplets and ion clusters [1–4].

In contrast ionic polymers with high ion fractions (when dissolved in, e.g., water these would be referred to as polyelectrolytes [4]) have so far attracted much less attention although these materials do offer the possibility of achieving even higher ionic conductivity. There have been simulation studies of electrostatic shielding effects on the dimensions of isolated polyelectrolyte chains [5] and also attempts to extend predictions of Liebler's random-phase approximation (RPA) theory [6] to the case of ionic copolymers [7,8], but our understanding of these complex systems is still quite limited [4].

In this paper we report computer simulations of a symmetric diblock copolymer melt where each the linear chains are composed of one ionic and one neutral block. This composition was chosen to facilitate comparison with wholly neutral copolymers which are well understood theoretically [6,9] and have been extensively studied experimentally [9–11] and by simulations [12–17]. Continuous space molecular-dynamics simulations have been used to characterize the order-disorder transition (ODT) and to demonstrate the spontaneous formation of a well-defined lamella microphase. Counterion diffusional mobility in directions parallel to the lamella remains high at temperatures well below the ODT.

DETAILS OF THE MODEL AND SIMULATIONS

Since we are concerned with universal properties of the ionic copolymer, we use a coarse-grained generic model consisting of linear freely jointed Kramers chains of spherical bead monomers all of which are of identical size and interact via a Weeks-Chandler–Anderson (WCA) potential [the repulsive part of a Lennard-Jones (LJ) potential]:

$$\phi_{\mathrm{WCA}}(r_{ij})=4\varepsilon((\sigma/r_{ij})^{12}-(\sigma/r_{ij})^{6})+\varepsilon \quad \text{for } r_{ij}\leqslant 2^{1/6}\sigma,$$

$$\phi_{\mathrm{WCA}}(r_{ij})=0 \quad \text{for } r_{ij}>2^{1/6}\sigma. \tag{1}$$

The beads are connected using rigid bonds of length equal to the LJ repulsive parameter σ. Coulomb interactions between charges are included explicitly using an Ewald long-range correction. The total interaction potential can therefore be written as follows:

$$\phi_{\mathrm{TOTAL}}(r_{ij})=E_{\sigma}^{ij}\frac{\sigma}{r_{ij}}+\phi_{\mathrm{WCA}}(r_{ij}), \tag{2}$$

where E_{σ}^{ij} is the electrostatic potential at a charge separation of σ and

$$E_{\sigma}^{ij}=\left(\frac{q_iq_je^2}{4\pi\varepsilon_0 e_R\sigma}\right), \tag{3}$$

where the q's are charge numbers and e_R is the dielectric constant. Since the unlike charge interaction provides the only cohesive energy in the model we use $E_{\sigma}=|E_{\sigma}^{\pm}|$ as an energy scaling parameter. By choosing the ratio $(E_{\sigma}/\varepsilon)=24$ the total unlike-charge potential minimum is at exactly σ. In this case the reduced temperature can be written as $T^{*}=kT/E_{\sigma}$ or $T^{*}=kT[4\pi\varepsilon_0/e^2]\varepsilon_R\sigma$. Any particular value of T^{*} can be interpreted in terms of different

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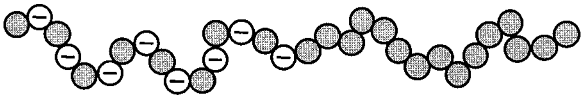

FIG. 1. Schematic of the ionic copolymer chain.

combinations of real temperature, dielectric constant, and the size of the interacting ions; for instance at $T^*=0.1$, $T\sim 400$ K if $\varepsilon_R=10$ and $\sigma=0.4$ nm. We define density as $\rho^*=N\sigma^3/V^2$, pressure as $P^*=P\sigma^3/E_\sigma$, and time as $t^*=t(E_\sigma/(m\sigma^2))^{1/2}$, where m is the mass of the bead. We use molecular dynamics in the NVT ensemble employing a Berendsen thermostat. The optimized time step Δt^* was found to be 0.044.

Our copolymer, shown schematically in Fig. 1, consists of neutral block of 15 beads, and the ionic block of 16 beads; in the latter every second bead carries an elementary charge. Eight oppositely charged beads, i.e., counterions, are included to maintain electroneutrality. Samples were confined to a cubic box with a reduced monomer density, $\rho^*=0.5$. The sample size N was either 20 or 160 copolymer chains. It was necessary to restrict the chain lengths due to the very slow structural relaxation times in these systems [18]. The chains are, however, sufficiently long to see a clear distinction between the chain motions and counterion motions.

RESULTS AND DISCUSSION

In Fig. 2 we show the temperature dependence of four properties which clearly indicate the onset of microphase separation in the ionic copolymer. These results were obtained by cooling an $N=20$ sample initially prepared as an isotropic disordered melt and equilibrated for 10^5 steps at $T^*=0.096$ which is more than twice the temperature of the ODT. The cooling to $T^*=0.024$ was accomplished incrementally in 14 stages; at each stage the system was equilibrated for 5×10^4 time steps followed by a sampling period of 5×10^4 steps.

At temperatures between 0.096 and ~ 0.04 the melt samples were homogeneous and the appearance of a strong nearest-neighbor peak in the unlike charge radial distribution functions was clear evidence for the existence of counterion condensation on the ionic blocks. Visualization of sample structures revealed that below $T^*\sim 0.04$ the structure became anisotropic and a lamella morphology could be distinguished (see Fig. 3) as would be predicted for a near symmetric block copolymer. In periodic systems the sample spontaneously adopts a layer structure which is commensurate with the periodic boundaries of the simulation cell. The negative and positive ion partial structure factors are indistinguishable for the ordered microphase and in our simulations the peaks in these structure factors show that the lamella periodicity for the $N=20$ system is $L/2$ (11.6σ) and the symmetry of the system is broken in the 100 direction while for the $N=160$ sample the periodicity is $L/\sqrt{2}(16.4\sigma)$, the broken symmetry being perpendicular to a 110 direction of the cubic cell. Due to condensed counterions the volume composition of ionic blocks is 0.62 and not 0.5 and this slight imbalance may be the cause of the perforations in the neutral layers seen in Fig. 3. Although there is experimental evidence for this kind of ''nonclassical'' structure in neutral copolymers [19], we cannot be sure at this stage whether it is truly stable or whether it is a consequence of the boundary restrictions.

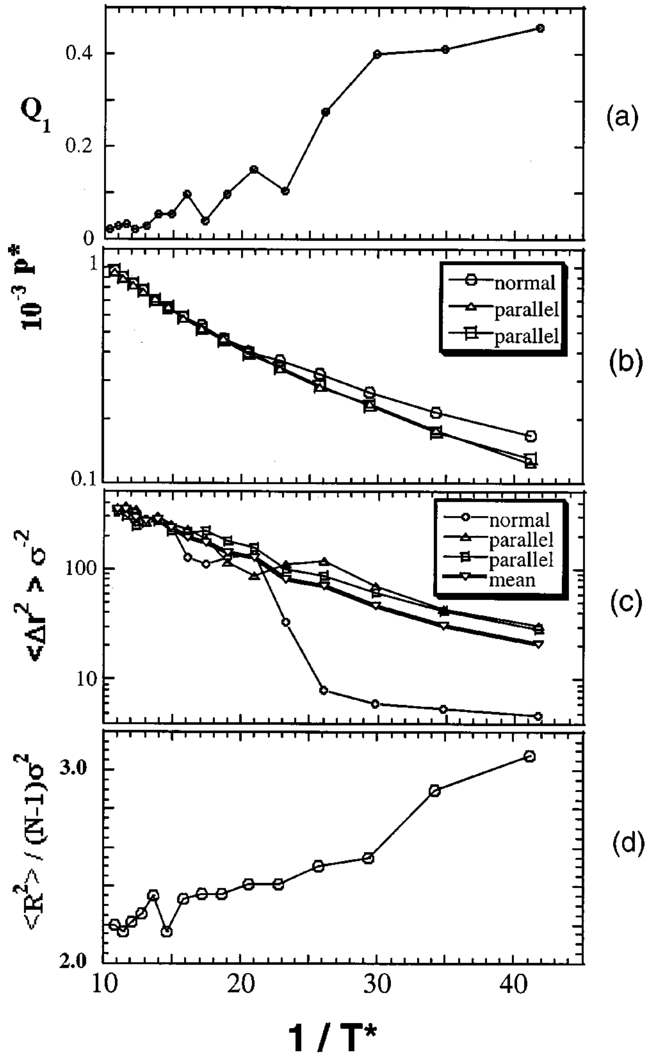

FIG. 2. Inverse temperature dependence of properties showing the onset of microphase separation on cooling the smaller ($N=20$) sample: (a) the anisotropy invariant Q_1 of the directional structure factor $S(\mathbf{k})$, evaluated for a spherical shell with $8>kL/\pi>2$, (b) pressure components normal and tangential to eventual lamella plane of the microphase, (c) mean-squared displacements for counterions normal and tangential to eventual lamella plane of the microphase after 5×10^4 time steps, (d) chain mean-squared end-to-end distance, showing chain expansion through the ODT.

The anisotropy of the structure factor [12] shows clearly the onset of structural order for wave vectors corresponding to the low-k peak in the structure factor. The principal moments of the angular distribution of $S(\mathbf{k})$ are ordered such that $\lambda_1\leqslant\lambda_2\leqslant\lambda_3$. Symmetry breakdown accompanying ODT can then be characterized by two invariants, Q_1 and Q_2. $Q_1=(\lambda_2+\lambda_3)/\lambda_1-2$ and for lamella symmetry is predicted to be significantly different from zero. It is shown in Fig. 2(a) that as the sample is cooled Q_1 gradually increases and starts to fluctuate. It then changes rapidly to a value of about 0.5, suggesting that the ODT at about $T^*=0.043$. $Q_2=(\lambda_3$

$-\lambda_2)/\lambda_1$ as expected remains close to zero. Structure factor components were calculated using

$$S_{\alpha\alpha}(\mathbf{k})=\frac{1}{N}\left\langle\left\{\left[\sum_{i=1}^{N_\alpha}(\sin\mathbf{k}_i\mathbf{r}_i)\right]^2+\left[\sum_{i=1}^{N_\alpha}(\cos\mathbf{k}_i\mathbf{r}_i)\right]^2\right\}\right\rangle_{\text{thermal average}}, \qquad (4)$$

where N is the total number of atoms, and N_α is the number of atoms of type α and the summation over label i runs through all the atoms of type α.

At high temperature in the disordered phase the diagonal components of the pressure tensor P_{xx}, P_{yy}, and P_{zz} are all equal within the statistical error [Fig. 2(a)], but at about $T^*=0.048$, the pressure in the direction of symmetry breakdown starts to increase due to the onset of lamella ordering. At $T^*=0.024$ the sample is well into the microphase-separated region and there is a significant difference in the tensor components normal and parallel to the direction of lamella ordering.

There is a significant increase of copolymer square end-to-end distance as the system is cooled through the ODT and the two dissimilar blocks become separated in space, as shown in Fig. 2(d). Similar effects have been noted in simulations of nonionic copolymers [16]. There are departures from Gaussian ideality even in the initial (high-temperature) regime but this chain expansion is largely due to fact that the system is in the semidilute regime. In contrast to the case of the overall dimensions the individual blocks show remarkably little extension over the whole temperature range and in the case of the ionic blocks we attribute this to efficient electrostatic screening of charged monomer repulsions by condensed counterions. Screening of this kind have also recently been observed in simulations of isolated ionic chains [5] for Coulomb interaction strengths above the critical value for Manning condensation. In that case the collapse was interpreted in terms of dipole interactions between ion pairs [20]. In the ionic copolymer melt the electrostatic screening is even more effective and the ionic structure below the ODT is more comparable with that of a molten salt [21].

A quantity of considerable interest in these ionic systems is the counterion diffusion constant which is related to the ionic conductivity. As the system undergoes separation the counterions distribute themselves in the alternate ionic layers and consequently the counterion mobility in a direction normal to the layers decreases rapidly at the ODT as shown in Fig. 2(c). In the direction parallel to the lamella planes the diffusional mobility remains high over the whole temperature range studied.

The mean-squared displacements of the charged monomers were found to be an order of magnitude smaller than the counterions at long times and this decoupling of the diffusional motions is another important consequence of electrostatic screening. The high counterion mobility in the region of the ODT can also be related to the low value of the glass-transition temperature for the ionic blocks. In the case of homopolymers with the same composition as the ionic blocks studied here but at much the higher density of 0.93 the glass transition appears at ~0.014 [18]; for the lower density used here one expects the glass transition to be at an even lower temperature.

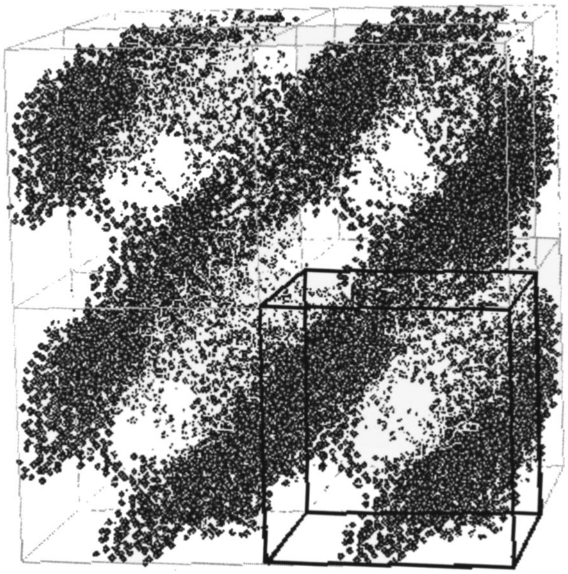

FIG. 3. Instantaneous snapshot of the microphase structure in the 160 chain system at a temperature of $T^*=0.24$; eight neighboring periodic cells are shown to emphasize the perforated lamella morphology.

The theory of neutral diblock copolymers is well established [6,22,23] both in the strong and weak segregation limits. In the latter regime Leibler's RPA theory [6] gives a free energy expansion in composition fluctuations by combining Gaussian chain entropic contribution with effective interaction energy expressed by the Flory χ parameter. This theory predicts that the ODT should occur at $\chi\cong 10.5/N$ for an neutral symmetric block copolymer, where N is the degree of polymerization. The RPA theory has been extended to the case of ionic copolymers [7,8] and theoretical discussion has been widened to include the ionomer regime where strong and even superstrong segregation regimes are predicted [3,4,22]. Using the theory of Marko and Rabin [8] we calculate an effective value of $\chi=0.6$ at the ODT as compared to 0.34 for the neutral case with our value of N. The theory, therefore, predicts that the ODT should be occurring at a much lower (reduced) temperature than in neutral copolymer. The theory, however, uses standard Debye-Huckel theory to determine the screened Coulomb interactions.

We have compared our results for the ionic copolymer with simulations of a wholly neutral copolymer in which all the counterion beads are removed and the charged polymer beads are replaced by LJ interaction centers [24]. In the latter case the ODT is observed at a reduced temperature $kT/\varepsilon=0.10$, which is approximately 2.5 times larger than in the ionic system. The definition of temperature in the ionic model, however, does not take into account the mutual screening of unlike pair interactions. It is more useful to compare the ratio of the total cohesive potential energies per bead in the two systems at the ODT and in this case the two systems are more closely comparable; this energy divided by the appropriate value of kT is -6 for the ionic copolymers, while for the LJ system it is -5.

CONCLUSION

We have presented a generic coarse-grain model for simulation studies which can be used effectively to study microphase separation in ionic copolymers. Ion condensation screens the intensity and range of the electrostatic interactions and for the near symmetric block copolymer studied here this leads to microphase separation which has very similar characteristics to that observed in purely neutral copolymers. It also results in decoupled diffusion of counterions. The dimensions of the microphase may be distorted by boundary conditions but such effects can be reduced by using controlled pressure cooling. Such simulations are already underway and will be reported elsewhere.

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[1] A. Eisenberg and M. King, *Ion-Containing Polymers* (Academic, New York, 1977).
[2] J.-P. Gouin, F. Bosse, D. Nguyen, C. E. Williams, and A. Eisenberg, Macromolecules **26**, 7250 (1993).
[3] I. A. Nyrkova, A. R. Khokhlov, and M. Doi, Macromolecules **26**, 3601 (1993).
[4] A. N. Semenov, I. A. Nyrkova, and A. R. Khokhlov, in *Ionomers: Characterization, Theory, and Applications*, edited by S. Schlick (CRC, Boca Raton, FL, 1996).
[5] R. G. Winkler, M. Gold, and P. Reineker, Phys. Rev. Lett. **80**, 3731 (1998).
[6] L. Leibler, Macromolecules **13**, 1602 (1980).
[7] P. Gonzales-Mozuelos and M. Olvera de la Cruz, J. Chem. Phys. **100**, 507 (1994).
[8] J. F. Marko and Y. Rabin, Macromolecules **25**, 1503 (1992).
[9] F. S. Bates and G. H. Fredrickson, Annu. Rev. Phys. Chem. **41**, 525 (1990).
[10] A. K. Khandpur, S. Forster, F. S. Bates, I. W. Hamley, A. J. Ryan, W. Bras, K. Almdal, and K. Mortensen, Macromolecules **28**, 8796 (1995).
[11] G. H. Fredrickson and E. Helfand, J. Chem. Phys. **87**, 697 (1987).
[12] H. Fried and K. Binder, J. Chem. Phys. **94**, 8349 (1991).
[13] K. Binder and H. Fried, Macromolecules **26**, 6878 (1993).
[14] A. Weyersberg and T. A. Vilgis, Phys. Rev. E **48**, 377 (1993).
[15] L. A. Molina and J. J. Freire, Macromolecules **28**, 2705 (1995).
[16] G. S. Grest, M.-D. Lacasse, K. Kremer, and A. M. Gupta, J. Chem. Phys. **105**, 10 583 (1996).
[17] R. D. Groot, and T. J. Madden, J. Chem. Phys. **108**, 8349 (1998).
[18] C. Wong and J. H. R. Clarke (unpublished).
[19] M. W. Matsen and F. S. Bates, Macromolecules **29**, 1091 (1996).
[20] A. R. Khokhlov and E. Y. Kramarenko, Macromolecules **29**, 681 (1996).
[21] J. H. R. Clarke, W. Smith, and L. V. Woodcock, J. Chem. Phys. **84**, 2290 (1986).
[22] A. N. Semenov, Zh. Éksp. Teor. Fiz. **88**, 1242 (1985) [Sov. Phys. JETP **61**, 733 (1985)].
[23] E. Helfand and Z. R. Wassermann, Macromolecules **9**, 879 (1976); **11**, 960 (1978); **13**, 994 (1980).
[24] M. Banaszak and J. H. R. Clarke (unpublished).