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Melt Phase Behavior of Poly(oxyethylene)−Poly(oxypropylene) Diblock Copolymers

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ABSTRACT: The order−disorder transition of a series of symmetric poly(oxyethylene)−poly(oxypropylene) diblock copolymers was determined via small-angle X-ray scattering (SAXS) and used to determine the Flory−Huggins interaction parameter, χ. The χ parameter was determined using both mean field theory and fluctuation theory, and our results are compared to previously reported values. In addition, we determined the structure of a number of asymmetric diblocks via SAXS and compare the results with the phase diagram predicted by self-consistent mean field theory, allowing for conformational asymmetry.

Introduction

Block copolymers containing oxyethylene [E: OCH_2CH_2] and oxypropylene [P: $OCH_2CH(CH_3)$] are of substantial commercial interest. In particular, $E_mP_nE_m$ triblocks (commercial names Pluronic and Synperonic copolymers) are synthesized in large quantities via anionic methods and used extensively in the detergent, pharmaceutical, and personal care product industries among others.[1,2] To quantitatively understand the phase behavior of such materials, knowledge of the Flory−Huggins interaction parameter, χ, is required.[3] A range of values of χ have previously been reported in the literature.[4−7] In an effort to determine the temperature dependence of the χ parameter for mixtures of E and P segments, we have synthesized four symmetrical E/P diblock copolymers and determined their order−disorder transition temperatures (T_{ODT}) via time-resolved small-angle X-ray scattering during heating and cooling. In addition, we report ordered melt structures for some asymmetric diblocks.

Experimental Section

Synthesis and Characterization. Ten copolymers were prepared by sequential anionic polymerization, of ethylene oxide followed by propylene oxide (denoted E_mP_n where m and n are average block lengths in repeat units) or, for three samples, in the reverse order (denoted P_nE_m). The methods used followed closely that described previously for copolymer $P_{94}E_{316}$,[8] vacuum line and ampule techniques being used to eliminate moisture. The copolymers were characterized by gel permeation chromatography (GPC) to confirm narrow chain length distributions, i.e., M_w/M_n in the range 1.02−1.07. ^{13}C NMR spectroscopy gave absolute values of molar mass (M_n) and overall composition (mol % E units), hence the molecular formulas listed in Table 1.

SAXS/WAXS. Simultaneous small-angle X-ray scattering/wide-angle X-ray scattering experiments were conducted on beamline 8.2 at the Synchrotron Radiation Source, Daresbury Laboratory, UK, details of which have been provided elsewhere.[9] Samples were loaded into TA Instruments aluminum DSC pans, modified for transmission of X-rays by the insertion of mica windows.[10] The pans were heated and cooled in a Linkam DSC of single-pan design. The wavenumber scale ($q = 4\pi \sin \theta/\lambda$, where $\lambda = 1.54$ Å and 2θ is the scattering angle) was calibrated using a specimen of wet collagen (rat tail tendon).

Table 1. Structural Characteristics of Poly(oxyethylene)−Poly(oxypropylene) Diblocks Studied[a]

sample	r_V	ϕ_E	T_m/°C	phase	T_{ODT}/°C	$(\chi r_V)_{ODT}$
$P_{94}E_{316}$	455	0.694	64	hexagonal	175	13.7
$P_{43}E_{312}$	376	0.831	70	disordered		23.2
$P_{60}E_{348}$	437	0.797	70	hexagonal	118	19.7
$E_{149}P_{47}$	219	0.682	74	hexagonal	114	13.2
$E_{165}P_{46}$	233	0.708	66	disordered		13.8
$E_{172}P_{43}$	236	0.730	64	disordered		14.9
$E_{91}P_{64}$	186	0.490	60	lamellar	80	10.8
$E_{128}P_{82}$	249	0.513	62	lamellar	128	10.5
$E_{135}P_{84}$	259	0.521	62	lamellar	130	10.8
$E_{144}P_{105}$	299	0.481	62	lamellar	150	10.8

[a] The melting temperature, T_m, ordered melt structure, order−disorder transition temperature, T_{ODT}, and $(\chi r_V)_{ODT}$ determined using mean field theory were all obtained from SAXS experiments.

Results and Discussion

Representative SAXS data illustrating morphology transitions in these EP diblocks are shown in Figure 1. This shows a heat/cool ramp for $P_{60}E_{348}$ from 30 to 180 °C and back to 30 °C. At low temperature, crystallization of the poly(oxyethylene) block leads to a lamellar structure, with Bragg reflections in the positional ratio 1:2:3. On heating to 70 °C, an abrupt melting transition occurs, characterized by a substantial increase in the q value of the first-order reflection (and hence reduction in domain spacing) and a decrease in peak width (increase in correlation length). For $P_{60}E_{348}$, the SAXS data indicate a hexagonal-packed cylinder ordered melt phase, characterized by reflections in the positional ratio $1:\sqrt{3}:\sqrt{4}$.[3] This persists on heating to 118 °C, at which temperature the intensity and width of the first-order reflection increase discontinuously, and higher-order reflections are lost. This is characteristic of the order−disorder transition. The sequence of transitions observed on heating is reversed on cooling, as illustrated in Figure 1, although with a ramp-rate-dependent thermal lag. Similar data were collected for the other nine EP copolymers, and the melting temperatures, ordered

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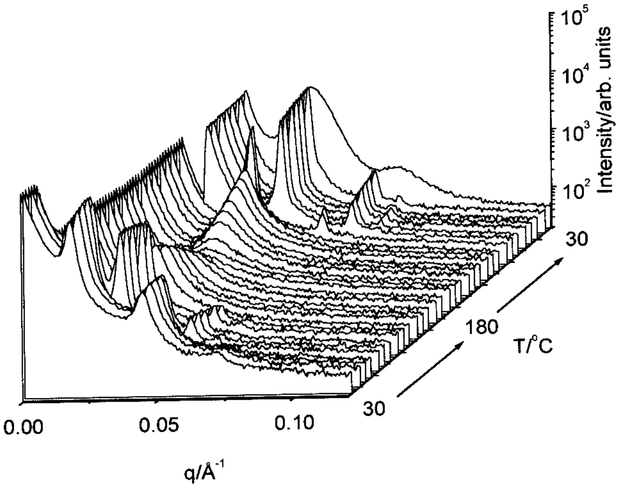

Figure 1. Stacked sequence of SAXS intensity profiles (log(intensity) vs q)) during a heat−cool cycle for $P_{60}E_{348}$. The sample was heated from 30 to 180 °C at 10 °C/min and then cooled directly at the same rate back to 30 °C.

structures, and ODTs thus obtained are listed in Table 1. It should be noted that the SAXS patterns for the melts of the four nearly symmetric diblocks only contained a single Bragg reflection, the second-order reflection being systematically absent for a symmetric diblock and higher-order reflections being suppressed due to the weak segregation of the ordered melt. Nevertheless, the assignment of a lamellar phase is consistent with the composition of the diblocks.

The results obtained are listed in Table 1. Ordered melt structures and order−disorder transition temperatures were found for seven of the copolymers. Melting temperatures were recorded for all: these served to define the low-temperature limit for observation of melt structures. Also listed is overall chain length (r_V in segments of volume equal to that of an oxyethylene unit) and volume fraction of oxyethylene (ϕ_E), both quantities being calculated using the specific volumes quoted previously.[11]

To assemble a conventional phase diagram (χr_V vs ϕ_E), the temperature dependence of χ must be determined; i.e., the coefficients A and B in $\chi = A + B/T$ should be obtained. Using order−disorder transition temperatures determined from SAXS, an expression for χ was obtained using the critical value for microphase separation computed using mean field theory.[12] These values are plotted against the reciprocal of the transition temperature in Figure 2. Strictly speaking, allowance should be made for the asymmetry introduced into the phase diagram through differences in the volume (v) and segment length (b) of E and P units, i.e., through parameter $\epsilon = (v_E b_P^2 / v_P b_E^2)$. In fact, for the E/P system, $\epsilon \approx 0.77$ and the effect will be small. In Figure 2, we have also included data points for two lamellar EP melts for which the ODT was determined previously.[13] Data points are also included from an analysis of the SANS structure factor peak from the disordered phase of a melt of $E_{33}dP_{42}E_{33}$ (d indicates perdeuterated oxypropylene) using Leibler's mean field theory, for the temperature range 46−68 °C. These data have been weighted equally with the χ values for the present series of diblocks by using the average value in the least-squares analysis. This leads to the expression

$$\chi = (-0.122 \pm 0.022) + (66.8 \pm 8.2)/T \qquad (1)$$

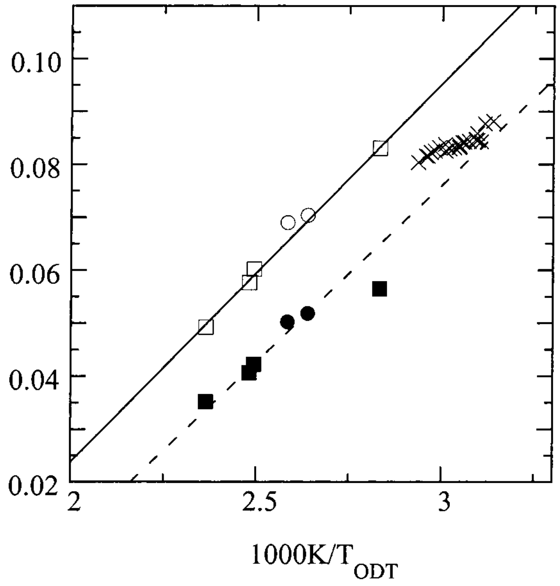

Figure 2. Temperature dependence of χ determined for a series of symmetric EP diblocks. Squares denote the present data (samples $E_{91}P_{64}$, $E_{128}P_{82}$, $E_{135}P_{84}$, and $E_{144}P_{105}$), circles represent data from ODT measurements for two diblocks characterized in previous work,[11] and crosses correspond to data from the temperature dependence of χ in the disordered state for $E_{33}dP_{42}E_{33}$.[11] The dashed line represents eq 1, obtained using mean field theory, and the full line eq 3 using fluctuation theory.

The nature of the SAXS patterns observed for the disordered phase confirms that the ODT is a transition from an ordered melt to a fluctuating melt; hence, using mean field theory will lead to an underestimate of the value of χ. An alternative is to use the expression for the critical point for symmetric diblocks obtained by Fredrickson and Helfand, allowing for composition fluctuations:[14]

$$(\chi r_V)_c = 10.5 + 41\bar{N}^{-1/3}, \quad \bar{N} = r_V b^6 \rho^2 \qquad (2)$$

Using approximate values for the segment statistical length ($b \approx 5 \times 10^{-10}$ m) and number density ($\rho \approx 1.4 \times 10^{28}$ m^{-3}), this gives (see Figure 2)

$$\chi = (-0.119 \pm 0.007) + (71.5 \pm 2.8)/T \qquad (3)$$

The expressions for χ in eqs 1 and 3 are similar to those reported for poly(oxyethylene)−poly(oxybutylene) - diblocks,[15] respectively, $\chi = -0.0535 + 48/T$ using mean field theory, and $\chi = -0.0929 + 75.6/T$ using fluctuation theory.

The mean field theory χ parameter (eq 2) differs substantially from that previously reported by Fairclough et al.[11] In that work, the values of χ (illustrated in Figure 2) were obtained from the temperature dependence of the small-angle peak intensity in the disordered phase, using the structure factor obtained within mean field theory by Leibler.[12] Other determinations of χ for the E/P systems relate to temperatures near room temperature. Specifically, Friday et al.[5] report a value of $\chi = 0.090$ at 30 °C based on observations of phase separation in mixtures of E and P oligomers. Fairclough et al. report $\chi = 0.089$ by extrapolation to the same temperature.[11] The present equations extrapolate to give values of 0.098 (eq 1) and 0.117 (eq 2) that are in reasonable agreement with Friday et al. In particular, the value from the mean field analysis

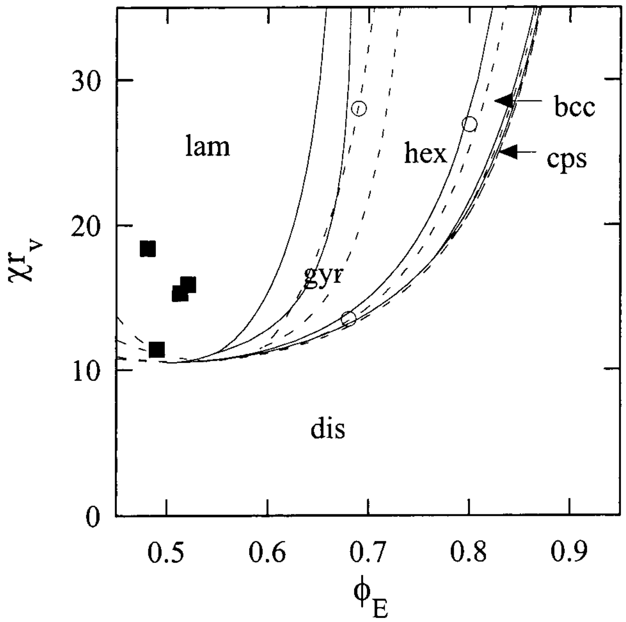

Figure 3. Comparison of phase behavior of EP diblocks with self-consistent mean field theory.[17,18] Solid line, $\epsilon = 1$; dotted line, $\epsilon = 0.65$. Equilibrium phases are as follows: lamellar (lam), gyroid (gyr), hexagonal-packed cylinders (hex), body-centered cubic spheres (bcc), close-packed spheres (cps) and disordered (dis).

(eq 1) that includes χ values obtained at lower temperatures is in better agreement. One possible reason for the discrepancy between the χ parameter obtained from the temperature dependence of the disordered state intensity and that obtained from ODT measurements for a series of diblocks is the breakdown of mean field theory at high temperatures in the disordered phase, as suggested by Maurer et al.[13]

We note here in passing that results similar to ours have been obtained for four symmetric poly(ethylene)−poly(ethylene−propylene) diblock copolymers; i.e., χ obtained from fluctuation theory was higher than that from mean field theory at a given temperature (although the slope of χ vs. T was similar), and χ obtained from fitting of the disordered state peak exhibited a different temperature dependence.[13] It was also shown in that work that all the expressions for χ for the block copolymers differed from those of blends of the corresponding homopolymers, which was ascribed to the effect of polarization and stretching of diblock molecules in the vicinity of the ODT.

The phase assignments in Table 1 reveal that the hexagonal-packed cylinder phase extends from $\phi_E = 0.682$ to $\phi_E = 0.797$. The stability region of this phase extends to lower ϕ_E than in the phase diagram of related EB diblocks, where a lamellar phase was reported for a diblock with $\phi_E = 0.711$.[15] The conformational asymmetry is smaller for the E/P system ($\epsilon = 0.77$ compared with $\epsilon = 0.65$ for the E/B system), which is consistent with the smaller shift observed. In fact, the shift of the phase boundaries in the E/B system toward the $\phi_E = 1$ side exceeds that predicted by mean field theory: see Figure 10 of ref 15. The positions of the seven ordered E/P melts on the exact self-consistent mean-field phase diagram are shown in Figure 3. The boundaries are for $\epsilon = 1.0$ (full) and 0.6 (dotted): there is no calculation for $\epsilon = 0.77$. Indications are that the asymmetry in the E/P phase diagram is also greater than catered for by theory.[16−18]

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