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Chain Dimensions in Poly(ethylene oxide)/Poly(methyl methacrylate) Blends

Ilan Zeroni[†] **and Timothy P. Lodge***[,†,‡]

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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The component dynamics in poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA) blends are currently of great interest,[1−7] due in part to a combination of striking observations. For example, there is a large discrepancy between direct measurements of PEO segmental dynamics and local time scales inferred from chain relaxations.[2,3,8] Also, the Lodge−McLeish self-concentration model[9] has only limited success in predicting the dynamics of this blend, in contrast to many other miscible systems, even when the self-concentration is used just as a fitting parameter.[6] While neither of these phenomena is unique to this blend, the effects are unusually large in magnitude. In an effort to understand this system in more detail, we recently obtained terminal dynamics data for both components via rheometry, using high molecular weight tracers in low molecular weight blend matrices of varying compositions and over a wide temperature range.[8] These results both confirm and extend the scope (in range of temperature and composition) of these phenomena.

Given this situation, it seems prudent to assess whether these effects could stem, in part, from unexpected equilibrium conformations. The method we used to extract component terminal dynamics—blending high molecular weight tracers in low molecular weight matrices—could be affected, for example, by significant swelling of the tracer chains.[10,11] In order to ascertain whether or not either component swells in the blend or adopts an otherwise unexpected conformation, SANS data were obtained using the National Institute of Standards and Technology Center for Neutron Research, 30 m SANS line (NG-7).[12] The blends comprised deuterated, high molecular weight tracer chains (one PEO, one PMMA) in three hydrogenated, low molecular weight matrices of varying compositions, i.e., pure PEO, pure PMMA, and 1:1 weight ratio blends. The low molecular weight matrix polymers are the same as used in the dynamics measurements described elsewhere.[8] The characteristics of the polymers used in this study are specified in Table 1. The hydrogenated PMMA was synthesized in house; details of the synthesis can be found elsewhere.[8] The hydrogenated PEO, deuterated PEO, and deuterated PMMA were purchased from Sigma-Aldrich, Polymer Source, and Polymer Laboratories, respectively. All purchased polymers were used as received. Both PEO samples are α,ω-hydroxyl-terminated. The M_n and polydispersity values of the hydrogenated polymers given in Table 1 were obtained via MALDI-TOF analysis. The MALDI recipes are given elsewhere.[8,13] Those of the deuterated polymers are taken from the certificates of analysis provided with the polymers.

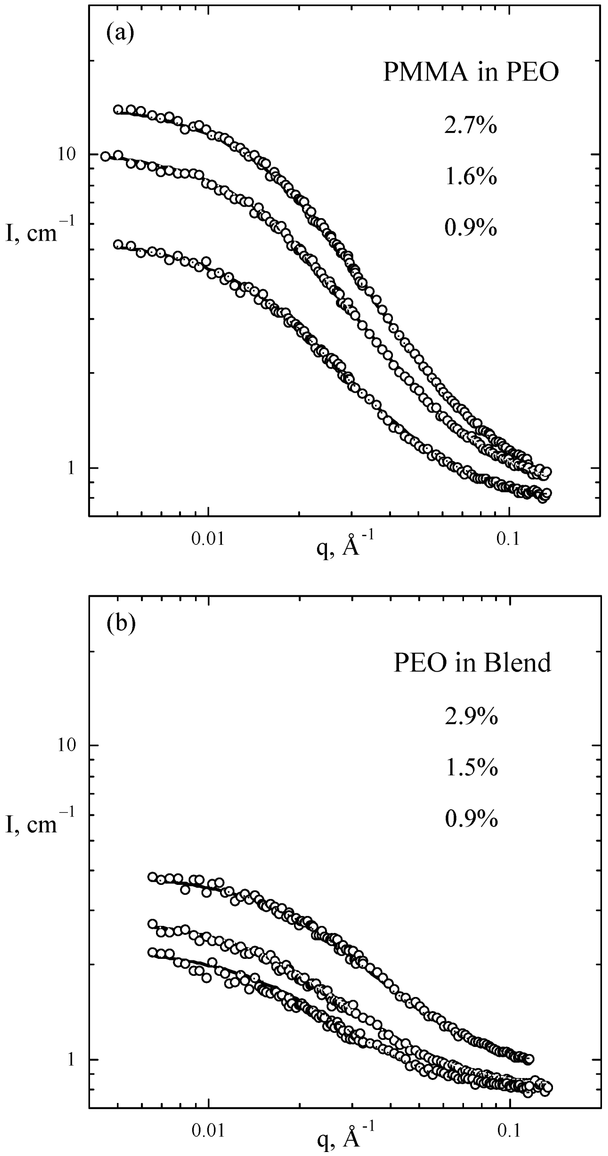

Figure 1. SANS results for (a) PMMA in PEO and (b) PEO in the blend, at the indicated tracer concentrations. Smooth curves represent fits to eq 3, as discussed in the text.

The overlap weight fraction, w^*, is estimated via

$$w^* = \frac{M_n}{\rho N_{av}} \frac{3}{4\pi R_{g0}{}^3} \qquad (1)$$

where N_{av} is Avogadro's number, M_n is the number-average molecular weight of the chain, and ρ, the matrix density, is 1130 and 1064 kg/m^3 for PMMA and PEO, respectively.[14] R_{g0} is the radius of gyration of the ideal chain, using statistical segment lengths of 6.5 and 5.6 Å for PMMA and PEO, respectively.[2] The blend density is taken as a linear interpolation of the homopolymer values. The scattering length density (a) is given by

$$a = \frac{\rho N_{av}}{m_0} \sum_i n_i b_i \qquad (2)$$

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[*] Corresponding author: e-mail lodge@chem.umn.edu.

[†] Department of Chemical Engineering and Materials Science, University of Minnesota.

[‡] Department of Chemistry, University of Minnesota.

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Table 1. Polymer Characteristics

polymer	M_n (kDa)	PDI	R_{g0} (Å)	a (m^{-2})	w^* (%)	I_{inc} (cm^{-1})[a]
h-PMMA	1.5	1.05	10	1.05×10^{14}		0.61
h-PEO	1	1.03	11	6.12×10^{13}		0.84
1:1 h-PMMA/h-PEO blend						0.89
d_8-PMMA	120	1.02	92	6.88×10^{14}	5	
d_4-PEO	49	1.06	76	6.77×10^{14}	4	

[a] I_{inc} is the measured incoherent scattering intensity.

where m_0 is the monomer molecular weight, n_i is the number of atoms of element i in each monomer, and b_i is the coherent scattering length of element i.

The tracer chain concentration was varied to enable extrapolation to infinite dilution. The tracer weight percents used were nominally 0.5%, 1%, 1.5%, and 2%. The scattering signal for the blends containing 0.5% tracer chains proved too low to be reliable, and these data are not considered further. Data were obtained at 80 °C for all samples, which is above both T_m for PEO and T_g for PMMA (ca. 53 °C for this low-M sample); data for selected samples were also obtained at 110 °C. The q range available for these measurements was 0.005−0.13 $Å^{-1}$ at a wavelength of 6 ± 0.1 Å, where q is the magnitude of the momentum transfer vector ($= (4\pi/\lambda)\sin(\theta/2)$), λ is the wavelength of the neutrons, and θ is the scattering angle in radians. This q range was obtained by combining measurements at both 3 and 11 m sample-to-detector distances. The scattering patterns were reduced and integrated using the NIST protocol; i.e., the 2-D scattering data were corrected for background scattering, sample transmission, empty cell transmission, and empty cell scattering. The data were than corrected for detector nonuniformity. Absolute intensities were then obtained, and pixels to be ignored were masked. Finally, azimuthal integration was carried out.

Representative results obtained at 80 °C are shown as $I(q)$ vs q in Figure 1 for PMMA in PEO (Figure 1a) and for PEO in the blend (Figure 1b). Because of the high molecular weight of the tracer chains, the Guinier function could not be used to determine the radii of gyration irrespective of the form factor. Instead, the data were fit to the Debye function to extract the radii of gyration:

$$P(x) = A\,\frac{2[\exp(-x) + x - 1]}{x^2} + B \qquad x = (qR_g)^2 \quad (3)$$

The fit parameters were obtained using the IGOR PRO software package. In eq 3, a prefactor A and a baseline correction B were included. The issue of fitting the Debye function to scattering patterns obtained from polymer coils that may be swollen, i.e., whose constituent monomers may have spatial distributions that deviate from the Gaussian distribution, has been discussed in the literature. Both theoretical and experimental results support this method.[15] The results obtained at 110 °C exhibit the same characteristics as those at 80 °C and give numerically equivalent values of R_g, within the estimated uncertainty (±4%). Figure 1 shows that both PMMA and PEO tracers yield rather low scattering intensity, and in the latter case especially the coherent intensity is only a factor of 2−4 greater than the incoherent background. Nevertheless, the extracted values of R_g were not sensitive to whether a measured baseline was subtracted or whether B in eq 3 was allowed to float.

The results for R_g as a function of concentration for both tracers in all three matrices are shown in Figure 2. The PEO values are smaller than those for PMMA, consistent with expectation based on R_{g0} (see Table 1). Within the scatter of the data, there is no clear difference between R_g for a given tracer in the three different matrices. The data are broadly consistent with a weak composition dependence, and the dashed lines correspond to linear regression extrapolations to infinite dilution. Given the scatter in the data, these fits were obtained by pooling all the PMMA data and all the PEO data. The observed intercept of 93 ± 3 Å for PMMA agrees well with the R_{g0} (92 Å), whereas for PEO the intercept (84 ± 3 Å) is apparently slightly larger than R_{g0} (76 Å). Yet, when the uncertainty is taken into account, the overall conclusion is clear. Neither PMMA nor PEO adopts conformations that vary appreciably with matrix composition, and neither polymer is either swollen or compressed significantly relative to its Gaussian conformation. Thus, the ultimate explanation for the striking dynamics of the components in this miscible blend cannot invoke anything unusual about the equilibrium average conformations.

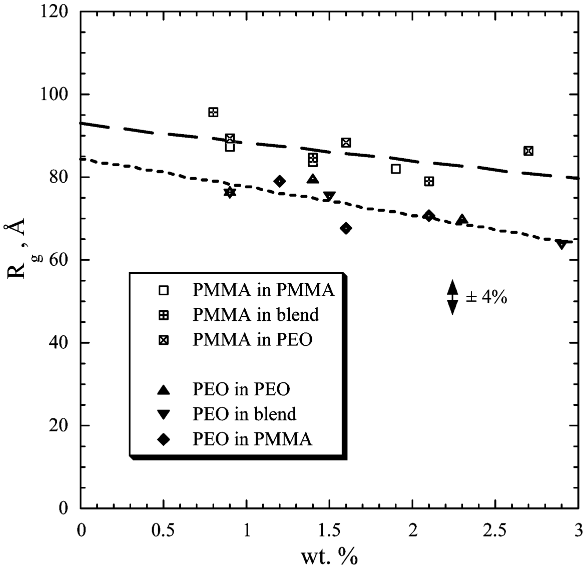

Figure 2. Measured radii of gyration as a function of tracer concentration, with extrapolations to infinite dilution shown.

Theory anticipates that large molar mass tracers in a low molar mass matrix should exhibit swelling, when the degree of polymerization of the matrix is less than the square root of the degree of polymerization of the tracer.[10,11] Evidence for this crossover has been reported for polystyrene in polystyrene.[16] Given that our PMMA and PEO tracers satisfy this criterion, one might expect to see stronger evidence of swollen conformations. However, given the relatively large values of w/w^* employed and the relatively low molar masses of the tracers, both of which act to reduce the magnitude of any swelling, plus the overall error bars, a stronger conclusion on this issue is not warranted.

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