Changes in Polystyrene and Poly(methyl methacrylate) Interactions with Isotopic Substitution

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Recently, Callaghan and Paul[1] presented the interaction energies for binary pairs of polymers including polystyrene (PS) and poly(methyl methacrylate) (PMMA). On the basis of the measurement of the cloud point from mixtures of PS with PMMA for different compositions of the two components, these authors were able to extract the interaction energies using equation of state arguments.[2] In this work, the authors compared their results with data that we had previously published[3] and found agreement with the temperature dependence of the interaction energy but were offset by ~20% in the absolute magnitude. This difference either was attributed to the differences in the molecular weights of the molecules or was due to the differences in the labeling. In our previous studies the PS component of the copolymer was labeled with deuterium to provide contrast for the neutral scattering studies, whereas previous authors[1,4-9] performed work on normal PS. In addition, our studies were performed on diblock copolymers, whereas previous studies were performed on homopolymer mixtures.

The data reported in the paper by Callaghan and Paul stimulated us to examine some other small single neutron scattering data obtained on diblocks where the labeling of the blocks was varied. Referring to Table I, which includes our previous work, three different labeling schemes were used where either the PS block (P(d-S-*b*-MMA)), the PMMA block (P(S-*b*-d-MMA)), or both blocks of the copolymer (P(d-S-*b*-d-MMA)) were labeled with deuterium. As in our previous studies, the Flory–Huggins segmental interaction parameter, χ, between the PS and PMMA segments was determined by analyzing the scattering of the copolymer in the disordered state by use of the correlation hole scattering formalism as discussed by Leibler.[10]

The values of χ determined from the analysis of the neutron scattering data are shown in Figure 1 as a function of the temperature. It is seen in these data that, for each different labeling of the copolymer block, χ varies linearly with $1/T$. A least-squares analysis of the data shown in Figure 1 is given in Table I. Along with these data are shown the specific characteristics of the copolymers and the results reported by Callaghan and Paul.[1]

There are several points to be made from the results shown in Table I. First, regardless of the labeling of the blocks, the enthalpic portion of χ, with the exception of that for P(S-*b*-MMA), is constant and contributes only a small amount of the total value of χ. This holds for the results of Callaghan and Paul also. The entropic portion of χ is found to vary. This variation does not appear to be systematic with the molecular weight of the copolymers or the homopolymers. However, it will be noted that, for the cases where either the PS or the PMMA block is deuterated, the entropic portion of χ is larger. When both blocks of the copolymer are labeled or normal, the entropic portion of χ is lower. Consequently, as seen with other weakly interacting systems, isotopic substitution is modifying the segmental interaction energy. These effects, most likely, will not be evident with more strongly interacting systems. What is also interesting about the results shown in Table I is that when only one of the blocks is labeled with deuterium, the effect on the interactions is most pronounced. However, when both blocks are labeled, there appears to be an offsetting effect of the labeling; i.e., χ is lower.

Table I. Flory–Huggins Interaction Parameter for PS and PMMA Diblock Copolymers

copolymer	N	f^a	$\chi_S{}^b$	$\chi_H{}^b$
P(d-S-*b*-MMA)	263	0.44	0.0284	3.902
P(S-*b*-d-MMA)	281	0.50	0.0292	3.188
P(d-S-*b*-d-MMA)	297	0.48	0.0251	3.199
P(S-*b*-MMA)[c]			0.021	3.20

[a] f is the fraction of PS monomers in the copolymer. [b] Where $\chi = \chi_S + \chi_H/T$. [c] Estimated from ref 1 where homopolymers were studied.

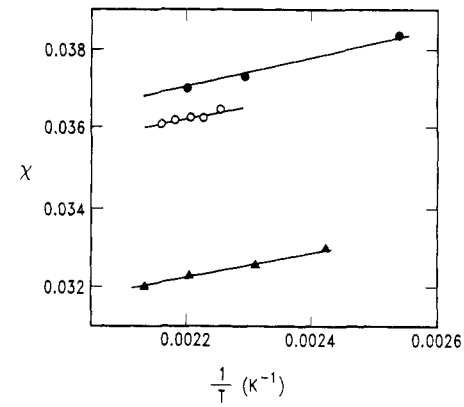

Figure 1. Flory–Huggins segmental interaction parameter, χ, as a function of $1/T$ where T is the absolute temperature for symmetric diblock copolymers of P(d-S-*b*-MMA) (●), P(S-*b*-d-MMA) (○), and P(d-S-*b*-d-MMA) (▲).

In conclusion, the results on the interaction parameter for PS and PMMA show a distinct variation with the labeling of the components with deuterium. The labeling alters only the entropic portion of χ, whereas the temperature-dependent portion of χ is the same in all cases. These variations may explain the differences in the results reported previously by us on partially labeled copolymer chains and by others on mixtures of unlabeled homopolymers.

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