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angular range. This can be interpreted to mean that, with annealing, the number and the total volume of the microcavities become reduced and some of the very small ones collapse and disappear altogether. Such healing of microcavities, as well as the healing of quasi-static density fluctuation depicted in Figure 7, suggests that the structural reorganization occurring in these pressure-densified samples involves not only a local segmental motion but also a cooperative motion of regions extending into tens of nanometers.

The formation of microvoids in glassy polymers subjected to deformation has been noticed by other workers.[18] Both small-angle X-ray scattering[19] and electron microscopic[20] techniques were utilized to demonstrate the microvoids which were formed as a precursor to craze formation. To explain the creation of such spherical microvoids, Steger and Nielson[19] and Argon[21] postulated the presence of certain intrinsic inhomogeneities in glassy polymers, for example, as small regions of lower segment entanglement density[20] or some kind of microporosity.[21] We are inclined to identify these weak regions, which are prone to nucleation of microvoids, with the regions of particularly low density established as a result of the density fluctuation frozen in at T_g.

Above T_g the pattern of density fluctuation present changes very rapidly in comparison to the time scale of the deformation we apply to a polymeric material. Consequently the polymer behaves mechanically as a uniform, homogeneous material. Below T_g some of the density fluctuation (i.e., the quasi-static component) persists much longer than the duration necessary for the deformation. Because of the presence of such frozen-in fluctuation, a glassy polymer, in its response to mechanical deformation, behaves as it if contains a permanent, heterogeneous flaw structure. That some component of density fluctuation indeed changes only slowly in comparison to the observation time is vividly demonstrated by the persistence of speckle patterns[22] obtainable when laser light is scattered from polymers around and below T_g. The determination of density fluctuation and proper accounting of its relaxation behavior should therefore be important not only for the understanding of the structure of glassy polymers but also for the clarification of the mechanism of craze initiation and deformation of glassy polymers.

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Registry No. Polystyrene, 9003-53-6.

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Deuterium Isotope Effect on the Compatibility between Polystyrene and Polybutadiene

Jen-Lien Lin, David Rigby, and Ryong-Joon Roe*

Department of Materials Science and Metallurgical Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012. *Received December 3, 1984*

ABSTRACT: We studied the effect of deuteration of polystyrene on the miscibility behavior of polystyrene–polybutadiene blend systems. We prepared a polystyrene having its aromatic hydrogens replaced by deuterium by starting from an ordinary polystyrene and treating it with deuterated benzene in the presence of an organometallic catalyst. We also prepared, as a control, a hydrogenated polystyrene of closely similar structure by repeating the same procedure except that this time ordinary, rather than deuterated, benzene was used. These matching pairs of hydrogenated and deuterated polystyrenes, when mixed with a polybutadiene or a styrene–butadiene random copolymer, were shown to give practically identical cloud point curves, thus indicating that the deuterium isotope effect is negligible.

Introduction

The availability of small-angle neutron scattering techniques in recent years has opened up many new avenues of research in the polymer field. In neutron scattering studies deuterated polymer molecules are often substituted for some of the usual, hydrogen-containing molecules as a means of selective labeling. Such substitution relies on the fact that the neutron scattering lengths of deuterium

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and hydrogen are very different, while the difference in other physical and chemical properties between the deuterated and hydrogenated counterparts is usually negligibly small. In some cases, however, the properties differ significantly enough to produce measurable isotope effects. For example, the difference in the melting points between polyethylene and deuterated polyethylene leads to the clustering of the latter in the crystals obtained from a mixture.[1,2] The Θ temperature of polystyrene in cyclohexane is altered when either the polymer or the solvent is deuterated.[3] In the study of polymer blends, the compatibility of polystyrene–polybutadiene[4] and polystyrene–poly(vinyl methyl ether)[5] blend systems appears to be modified when the polystyrene is substituted by its deuterated equivalents.

In this work we reexamine the question of deuterium isotope effect on the polymer blend compatibility. We have prepared pairs of hydrogenated and deuterated polystyrenes of closely similar structure and molecular weight distribution through a hydrogen (or deuterium) exchange[6,7] reaction, starting from the same batches of polystyrene samples. Compatibility of these polymers with butadiene homopolymer or styrene–butadiene random copolymer was then studied by means of cloud point measurements.

Experimental Section

Two anionically polymerized polystyrenes, obtained from Pressure Chemical Co., were used as the starting material for the exchange reaction. These two polystyrenes, having nominal molecular weights of 2000 and 100 000 are given the designation 2KPS and 100KPS, respectively. The aromatic hydrogens of polystyrene can be exchanged to deuteriums by reacting the polystyrene with excess deuterated benzene in the presence of an organometallic catalyst.[6,7] The procedure we used is briefly as follows: to the solution of 2 g of polystyrene dissolved in 20 g of C_6D_6 we added 0.18 mL of the catalyst, ethylaluminum dichloride and a small amount of HCl gas as a cocatalyst. After 4 h of gentle agitation under nitrogen in a shaker, the catalyst was destroyed with water, and the polymer was isolated and dried. The deuterated samples are designated 2KPSD and 100KPSD, respectively, depending on the starting material. Their extents of deuteration were determined by NMR and were found to be 93.3% and 93.8% of aromatic hydrogens, respectively. Next, the same reaction was repeated under exactly the same conditions but this time with ordinary benzene instead of deuterated benzene. The polystyrenes thus obtained, in which the aromatic hydrogens were replaced by other hydrogen atoms from the benzene, are designated 2KPSH and 100KPSH. These two hydrogen-containing polystyrenes were prepared as a "control", that is, for the purpose of comparison with the behavior of the deuterated polystyrenes. The above-mentioned hydrogen-exchange reaction is evidently accompanied by side reactions, chain scission, and cross-linking (or chain grafting). After the reaction, the molecular weight of polystyrenes of initially fairly long chains was seen to decrease slightly, while that of initially short chains was seen to increase slightly.[6] By the above procedure of preparing the controls, we can be fairly sure of having matching pairs of hydrogenated and deuterated polystyrenes of closely similar structure and molecular weight distribution.

The molecular weight distributions of all six polystyrene samples were determined with GPC, and the average molecular weights calculated from the chromatograms are listed in Table I. All the samples were run on the same day one after the other, so that any error in the calibration would have affected all of them similarly.

For the miscibility studies, the 2000 molecular weight polystyrenes were mixed with a polybutadiene, obtained from Goodyear Chemical Co., having M_n(VPO) = 2350 and M_w/M_n (GPC) = 1.13. The 100 000 molecular weight polystyrenes were mixed with styrene–butadiene random copolymer containing 68.4 wt % styrene. Its GPC characterization data are also listed in Table I. This copolymer was prepared by radical polymerization at 60 °C in a mixed solvent containing benzene and ethylbenzene in the ratio 1:4. The conversion was confined to about 10% (18 h) in order to limit the compositional heterogeneity in the random copolymer molecules.

Table I
Characterization of Polymer Samples

sample	remarks	$10^{-3}M_n$	$10^{-3}M_w$	$10^{-3}M_z$
2KPS	Pressure Chemical Co., untreated	1.75	1.96	2.16
2KPSD	deuterated, 93.3% D	1.95	2.10	2.26
2KPSH	hydrogen exchanged	1.94	2.08	2.23
100KPS	Pressure Chemical Co., untreated	95.4	101.7	107.9
100KPSD	deuterated, 93.8% D	79.2	91.2	101.0
100KPSH	hydrogen exchanged	72.7	91.4	103.8
PBD	Goodyear Chemical Co. (CDS-B3)	2.35	2.66	
S/B random copolymer	68.4% styrene	4.56	8.58	17.5

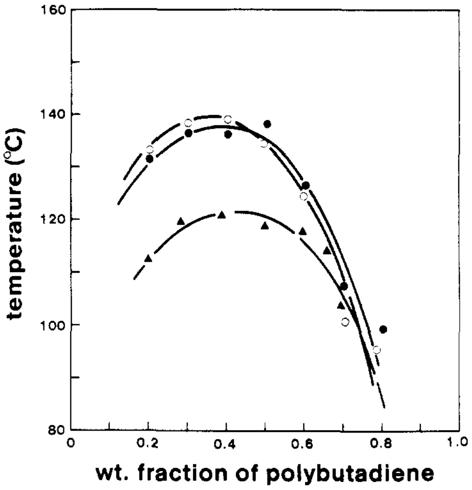

Figure 1. Cloud points obtained with mixturs containing polybutadiene (M_n = 2350) as the first component and one of the polystyrenes of approximately 2000 molecular weight as the second component. Triangles: 2KPS, ordinary polystyrene obtained from Pressure Chemical Co. Open circles: 2KPSD, deuterated polystyrene prepared by treating 2KPS polystyrene with deuterated benzene. Closed circles: 2KPSH, hydrogenated polystyrene prepared as a control by treating 2KPS polystyrene with ordinary benzene.

The cloud points of the mixtures were determined by light scattering as described in our earlier publication.[8]

Results and Discussion

The cloud points determined with the series of mixtures containing the polybutadiene as the first component and one of the 2K polystyrenes as the second component are given in Figure 1. The two polystyrenes 2KPSD and 2KPSH, which went through the exchange reaction, show about the same cloud point curves, which are clearly different from the cloud point curve obtained with the original, untreated polystyrene. Figure 2 shows the cloud points determined with the series of mixtures containing the styrene–butadiene random copolymer and one of the 100K polystyrenes. Here again, the two treated polystyrenes 100KPSD and 100KPSH give almost identical cloud point curves, whereas the cloud points obtained with

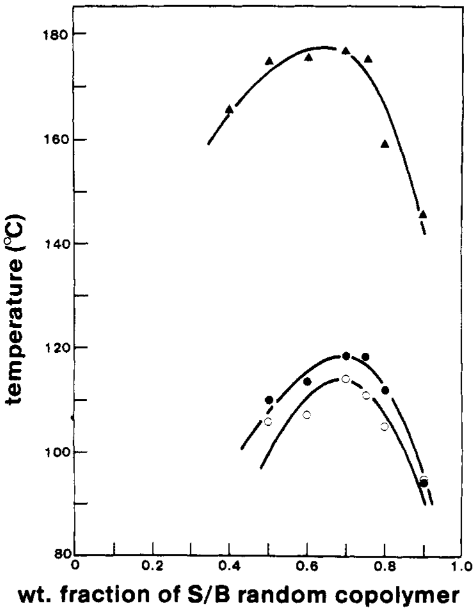

Figure 2. Cloud points obtained with mixtures containing styrene–butadiene random copolymer (M_w = 8600, styrene 68.4%) as the first component and one of the polystyrenes of approximately 100 000 molecular weight as the second component. Triangles: 100KPS, ordinary polystyrene obtained from Pressure Chemical Co. Open circles: 100KPSD, deuterated polystyrene prepared by treating 100KPS polystyrene with deuterated benzene. Closed circles: 100KPSH, a control prepared by treating 100KPS polystyrene with ordinary benzene.

the untreated polystyrene is displaced about 60 °C higher in temperature.

The matching pair of hydrogenated and deuterated polystyrenes were prepared from the same initial material by the same chemical reaction. The only difference was that for the first, ordinary benzene was used, but for the second, deuterated benzene was used. Thus the pair of polystyrenes should have very similar structure and molecular weight, irrespective of any side reactions which might have accompanied the hydrogen (or deuterium) exchange reaction. The fact that this matching pair of polystyrenes shows the same cloud point when mixed with polybutadiene or styrene–butadiene copolymer indicates that the deuterium isotope effect, if present, is negligibly small on the compatibility of the styrene–butadiene system we studied. This is to be contrasted to the previous reports by others[4,5] presenting contrary results.

Table I shows that both 2KPSD and 2KPSH have higher molecular weight than the original 2KPS, while 100KPSD and 100KPSH have lower molecular weight than the original 100KPS. This is in accord with the results obtained by Willenberg[6] and probably results from the fact that the effect of chain scission is more sensitively reflected in the average molecular weight of longer chains, whereas with short chains the chain grafting (or cross-linking) is the more important effect. As a consequence of these changes in the chain lengths, the cloud point curves have shifted upward in the case of 2K polystyrenes, but shifted downward in the case of 100K polystyrenes. The direction of change is in agreement with the direction of change in the molecular weight. But the magnitudes of change are much higher than expected from the molecular weight changes alone. To see this, we make the following simple analysis.

We have shown earlier[8] that the miscibility behavior of polymer blends, in particular of those involving styrene and butadiene constituents, can be described semiquantitatively on the basis of the Flory–Huggins free energy of mixing, which we write as

$$\Delta G_M = RT[(1/V_1)\phi_1 \ln \phi_1 + (1/V_2)\phi_2 \ln \phi_2] + \Lambda\phi_1\phi_2 \tag{1}$$

where ΔG_M is per unit volume of the mixture, V_1 and V_2 are the molar volumes, ϕ_1 and ϕ_2 are the volume fractions of the components, and Λ is the interaction energy density. On the assumption that Λ is independent of composition, the critical temperature T_C can be derived from (1) as

$$T_C = 2(\Lambda/R)V_1V_2/(V_1^{1/2} + V_2^{1/2})^2 \tag{2}$$

Taking component 1 as the polybutadiene or the styrene–butadiene random copolymer and component 2 as the polystyrene, we are interested in the variation in T_C induced when V_2 is varied. By differentiating (2) (and neglecting the small temperature dependence[8] of Λ) we obtain

$$\partial \ln T_C/\partial \ln V_2 = 1/[1 + (V_2/V_1)^{1/2}] \tag{3}$$

For polydisperse polymers, the critical temperature is determined by the weight-average as well as the z-average molecular weights[9-11] (or the molar volumes). Since the polydispersity of our samples is fairly low, we will simply use the weight averages and utilize eq 3 to calculate the expected variation in T_C induced by the changes in the molecular weight or V_2. For the 2K polystyrenes, the change in M_w is 6.6%, which should have produced 3.3% or a 13 °C increase in T_C, much smaller than the observed increase of about 17 °C. For the 100K polystyrenes, M_w has decreased after the exchange reaction by 12.6%, which should have produced a decrease in T_C of 2.9% or about 11 °C (note that V_2/V_1 is very large in this case). The observed decrease in T_C is about 60 °C. The large discrepancy between the observed and expected change in T_C suggests that the miscibility behavior of polymer blends is sensitive to the fine structure of the polymers such as the degree of branching or possibly the tacticity, in addition to the molecular weight and molecular weight distribution. Our results, on the other hand, suggest that the deuterium isotope effect is negligible at least in the styrene–butadiene system we studied.

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