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DEUTERIUM ISOTOPE EFFECT ON THE COMPATIBILITY BETWEEN
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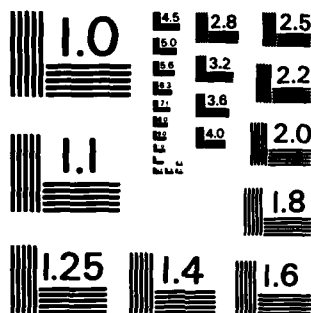
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We studied the effect of deuteration of polystyrene on the miscibility behavior of polystyrene-polybutadiene blend systems. We prepared a poly- styrene having its aromatic 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 homogeneous polystyrene of closely similar structure by repeating the same procedure except that this time ordinary, rather than deuterated,		

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benzene was used. These matching pairs of hydrogenous and deuterous 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.

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TECHNICAL REPORT NO. 12

Deuterium Isotope Effect on the Compatibility
between Polystyrene and Polybutadiene

by

J. L. Lin, D. Rigby and R. J. Roe

Prepared for Publication

in

Macromolecules

Department of Materials Science
and Metallurgical Engineering
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INTRODUCTION

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

Two anionically-polymerized polystyrenes, obtained from the Pressure Chemical Company, were used as the starting material for the exchange reaction. These two polystyrenes, having the nominal molecular weights of 2,000 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 followed: to the solution of 2g of polystyrene dissolved in 20g of C_6D_6 we added 0.18ml of the catalyst, ethylaluminium dichloride and a small amount of HCl gas as a co-catalyst. After four hours 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 hydrogenous 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 crosslinking (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 hydrogenous and deuterous 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 MW polystyrenes were mixed with a polybutadiene, obtained from Goodyear Chemical Company, having M_n by (VPO) of 2350 and M_w/M_n ratio (by GPC) of 1.13. The 100,000 MW polystyrenes were mixed with styrene/butadiene random copolymer containing 68.4 weight % 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 of 1 to 4. The conversion was confined to about 10% (18 hours) in order to limit the compositional heterogeneity in the random copolymer molecules.

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

Table I shows that both 2KPSD and 2KPSH have higher MW than the original 2KPS, while 100KPSD and 100KPSH have lower MW 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 crosslinking) 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 earlier⁸ that the miscibility behavior of polymer blends, in particular of those involving styrene and butadiene constituents, can be described semi-quantitatively on the basis of the Flory-Huggins free energy of mixing, which we write as

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

where ΔG_M is per unit volume of the mixture, V_1, V_2 are the molar volumes, ϕ_1, 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

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

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 dependence⁸ of Λ) we obtain

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

For polydisperse polymers, the critical temperature is determined by the weight-average as well as the z-average molecular weights^{9,10} (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 13° increase in T_C , much smaller than the observed increase of about 17° . 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° (note that V_2/V_1 is very large in this case). The observed decrease in T_C is about 60° . 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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Table I
Characterization of Polymer Samples

Sample	Remarks	M_n	M_w	M_z
2KPS	Pressure Chemical Co. Untreated	1.75×10^3	1.96×10^3	2.16×10^3
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

LEGEND TO FIGURES

Figure 1. Cloud points obtained with mixtures 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 Company. Open circles: 2KPSD, deuterated polystyrene prepared by treating 2KPS polystyrene with deuterated benzene. Closed circles: 2KPSH, hydrogenous polystyrene prepared as a control by treating 2KPS polystyrene with ordinary benzene.

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 Company. 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.

FIGURE 1

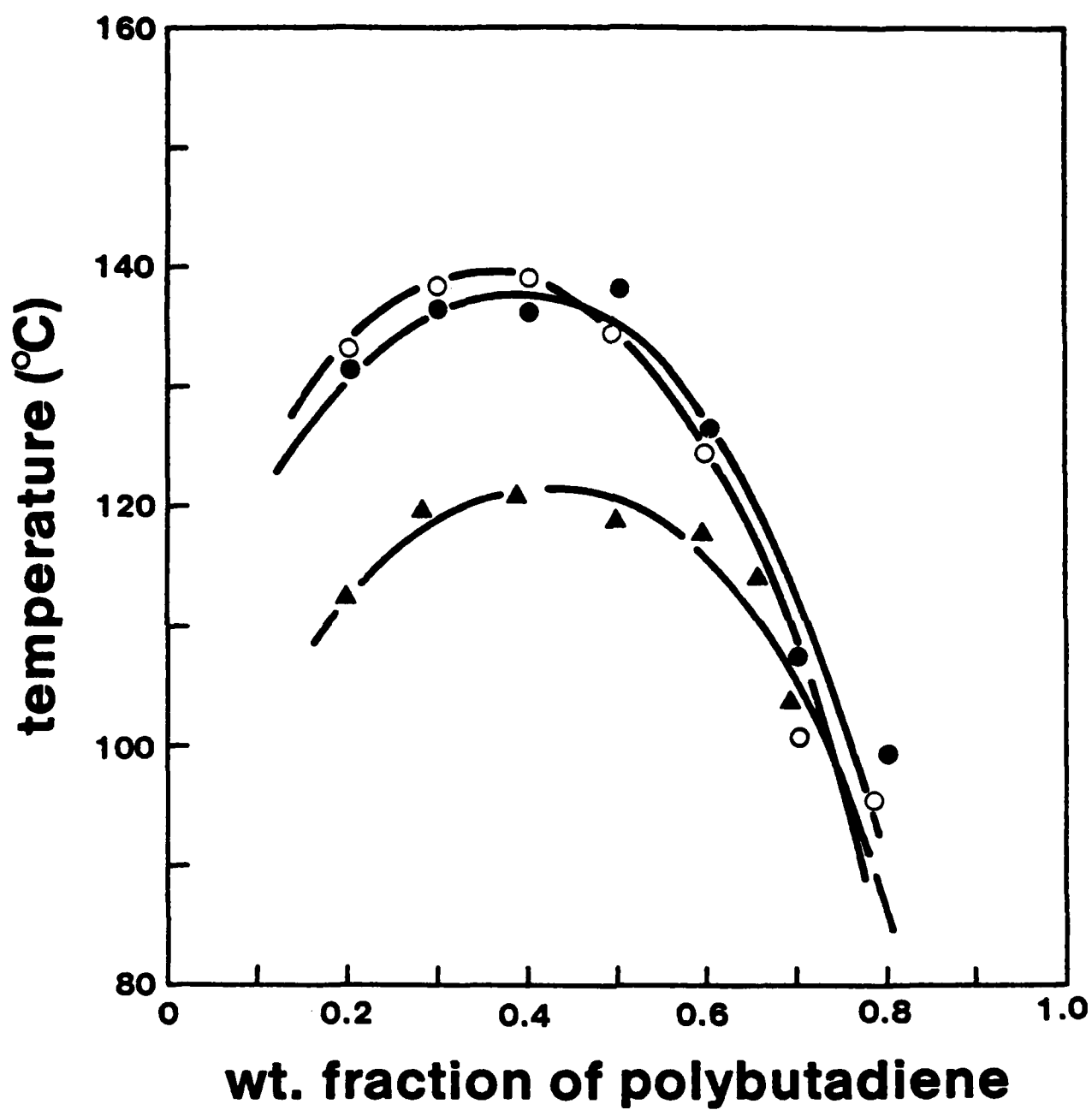
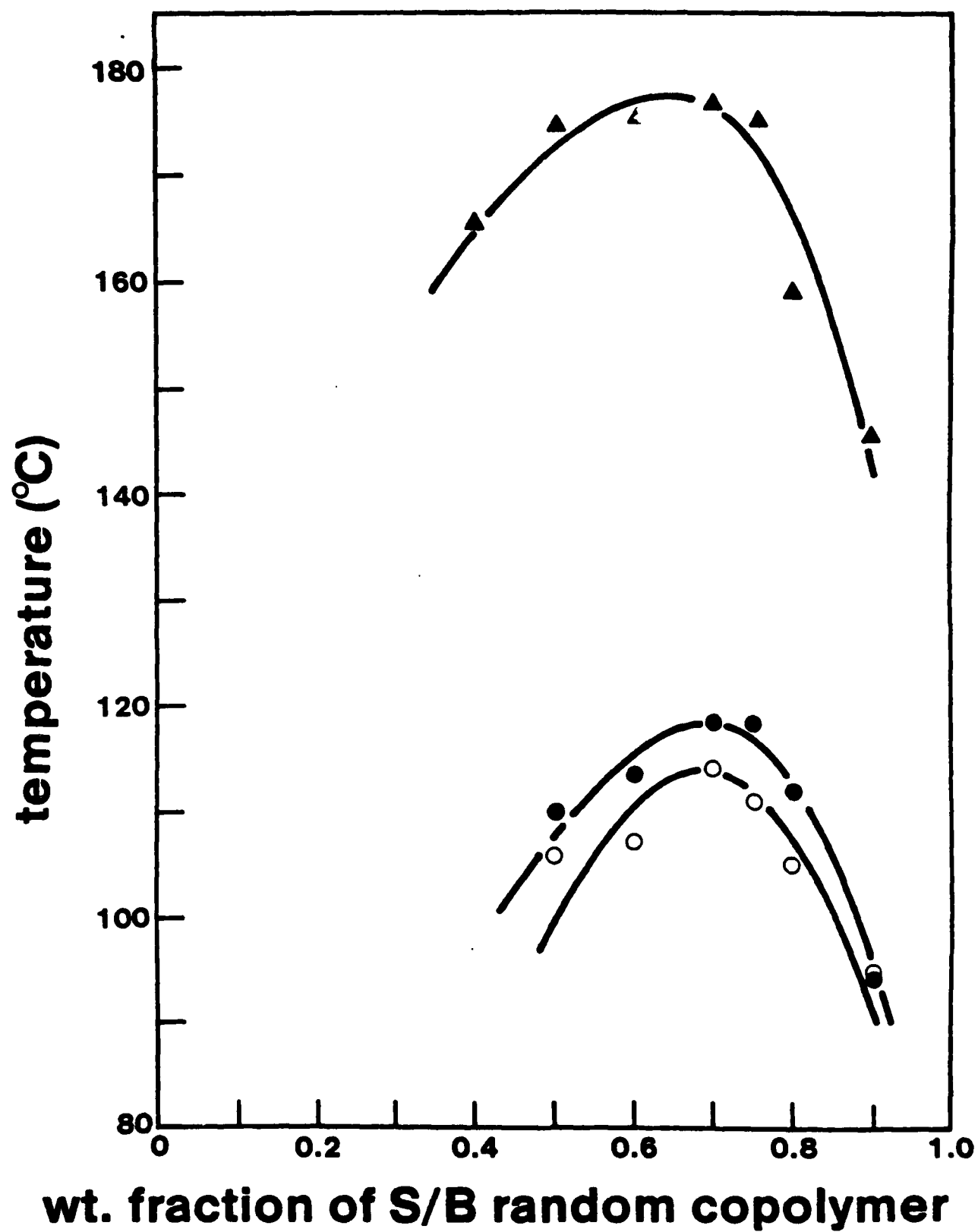


FIGURE 2



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