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Isotope Effect in Polymer Compatibility

E. L. Atkin*[1], L. A. Kleint'jens[1], R. Koningsveld[1] and L. J. Fetters[2]

[1] DSM Research & Patents, Geleen, The Netherlands

[2] The Institute of Polymer Science, The University of Akron, Akron, OH 44325, USA

Summary

The deuterium isotope effect on liquid-liquid phase behaviour in polymer blends was investigated with Gordon's Pulse Induced Critical Scattering Method. Spinodals in mixtures of polystyrene and polybutadiene were found to be sensitive to replacement of H by D in the polybutadiene. The results indicate a difference in heat of mixing between PS/PBH and PS/PBD-6 as well as an influence on the entropy of mixing.

Introduction

In recent years quite some effort has been devoted to neutron scattering studies on macromolecular stystems in which deutereous polymers are embedded in a matrix of their hydrogenous counterpart or vice versa1). The thermodynamic nature of such systems has also received some attention. Strazielle and Benoit2) found the θ-temperature of polystyrene/cyclohexane to be influenced markedly by the presence of deuterium in either solvent and/or polymer. Kirste et al3,4) studied polymer blends and, in particular, observed the non-athermal character of polydimethylsiloxane (H/D) mixtures 4).

Experimental

In the present study we measured spinodals of mixtures of polystyrene (H) and polybutadiene (H and D) in order to establish the magnitude of a possible isotope effect. The polystyrene sample was a Polymer Laboratories product (molecular characteristics in Table I). The standard polybutadiene (PBH)(CDS-B-3) was purchased from Goodyear Tire and Rubber Co. (Akron). D_6-Butadiene was obtained from Merck, Sharp and Dohme Ltd. (Montreal) and anionically polymerized so as to yield a polymer with a chain-length distribution and a microstructure as close as possible to the PBH. Size exclusion chromatography led to the values for mass- and number-average molar masses listed in Table I.

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* Permanent address: Dept. of Chemistry Loughborough University of Technology, Loughborough, Leicestershire LE 11 3TM, UK

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Homogeneous PS/PBH and PS/PBD-6 mixtures of varying concentration were prepared in capillaries with the aid of the centrifugal homogenizer after Gordon et al[5,6]. The capillaries were inserted in Gordon's pulse-induced-critical-scattering apparatus (PICS)[7-9] which allows the intensity of light scattered by homogeneous systems to be measured as a function of temperature. Extrapolation to zero of the reciprocal intensity vs T or T^{-1} yields the spinodal temperature for the considered concentration.

Results and Discussion

Figure 1 shows the spinodals for the two systems. It is seen that they are located in different temperature ranges. Looking for possible reasons for the shift one might be inclined first to think of differences in chain-length distribution. It is known that polymer-polymer cloud-point curves in the molar mass ranges considered here are very sensitive in this respect[10-12]. Therefore, the preparation of the deuterious samples was conducted so as to imitate the chain-length distribution of the PBH as closely as possible. Table I shows the average molar masses and the M_w-value for PBD-6 corrected by a factor 54/60 to permit comparison with PBH. We believe the remaining differences not to be large enough to explain the shift of the spinodal.

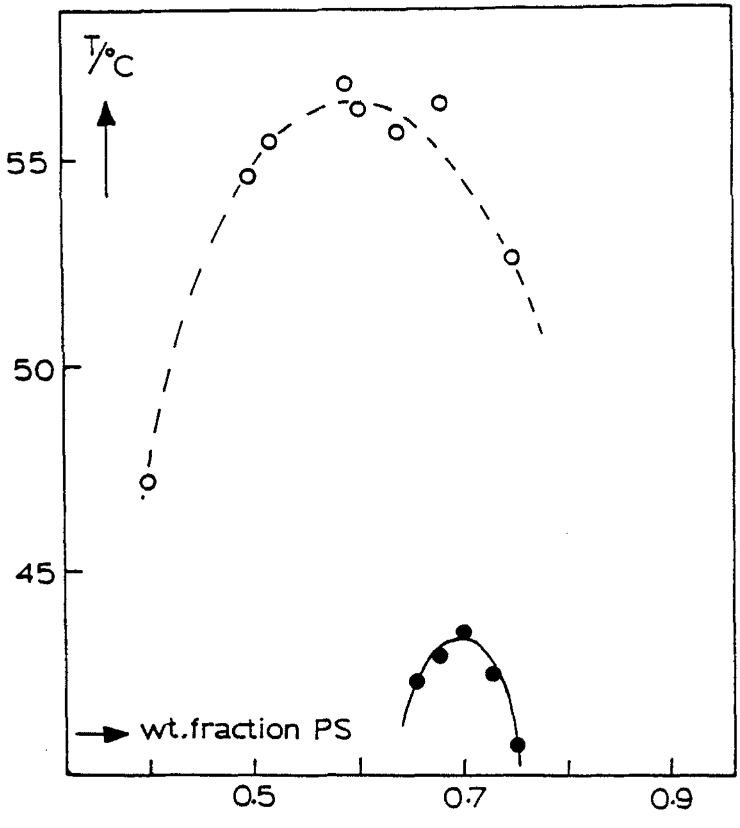

Fig. 1.
Spinodals measured by PICS[7-9] for mixtures of polystyrene with poly (D-6) butadiene) (PBD6)(--o--) and with polybutadiene (PBH) (—●—)

A second possibility is a small difference in heat of mixing between the two systems. This is quite conceivable, as has been shown by investigations on small-molecule mixtures13). However, then one would not expect the location of the maximum to shift as well, which clearly is the case. Hence, a disparity in entropy of mixing will have to be accounted for, the origin of which one might think of differences in free volume between PBH and PBD6. Except for a possible small difference in cis-trans content (Table II) the microstructures are similar and do not lead one to expect sizeable entropy differences.

A more complete analysis will be presented elsewhere.

Table I . Molar masses of the samples

	M_w (kg/mole)	M_w/M_n	M_w corrected for extra mass of D
PS	1.4_6	1.0_9	
PBH	2.6_6	1.1_3	
PBD6	3.2_6	1.1_6	2.9_3

Table II . Microstructures by C^{13} NMR

	% cis	% trans	% vinyl
PBH	41 ± 2	49 ± 2	10 ± 2
PBD	36 ± 4	54 ± 4	10 ± 2

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