possible explanation is that interfacial volume fractions in their samples (again, based on a 25-Å interfacial thickness) were all lower than 20% of the pure polybutadiene fractions—perhaps too low to cause a significant effect.

In conclusion, the three-phase model, which incorporates the contribution of the interface, provides an improved ability to predict gas permeability coefficients in multiphase block copolymers. In addition, similar analyses of permeation in other well-aligned but less understood block copolymer systems may be a useful technique for estimating interfacial thicknesses.

Registry No. (S)(B) (block copolymer), 106107-54-4; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; N_2, 7727-37-9; CO_2, 124-38-9; CH_4, 74-82-8.

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"Thermodynamic Slowing Down" of Mutual Diffusion in Isotopic Polymer Mixtures

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Received March 9, 1987

ABSTRACT: The mutual diffusion coefficient, $D(\Phi)$, determined at finite blend compositions, Φ, in blends of normal (hydrogenated) and deuteriated polystyrene was found to be highly dependent on composition. $D(\Phi)$ experiences a minimum, or "thermodynamic slowing down", in the vicinity of the critical composition, Φ_c. This effect increases with decreasing temperature. This result is consistent with recent small-angle neutron-scattering measurements which indicate that this system exhibits an upper critical solution temperature. The temperature dependence of the Flory interaction parameter, χ, was extracted from the data by using a mean field prediction for the compositional dependence of D. We found that $\chi = 0.22(\pm 0.06)/T - 3.2(\pm 1.2) \times 10^{-4}$.

Introduction

Evidence of nonideal mixing has been found in a number of isotopic polymer mixtures of identical structure. The small-angle neutron-scattering (SANS) measurements of Bates and Wignall[1-4] indicate that isotopic polymer mixtures of, 1,2-polybutadiene, 1,4-polybutadiene, polystyrene, and 1,2-polybutene are each characterized by a positive χ and that each exhibits an upper critical solution temperature (UCST). SANS measurements of the apparent radius of gyration of a blend of normal and deuteriated poly(dimethylsiloxane) by Lapp et al.[5] indicate that the χ parameter is positive. However, independent SANS measurements by Yang[6] and collaborators on the polystyrene system have yielded contradictory results. they found that $\chi \approx 0$ and question the existence of the UCST.

One may consider what effect a positive χ would have on interdiffusion in binary mixtures of normal and deuteriated polymers of identical structure otherwise. If $0 < \chi < \chi_s(\Phi)$, where $\chi_s(\Phi) = \{[N_D\Phi]^{-1} + N_H(1-\Phi)]^{-1}\}/2$ is the value of χ on the spinodal,[7] then the mutual diffusion coefficient, $D(\Phi)$, should experience a minimum or a "critical slowing down" in the vicinity of the critical blend composition, Φ_c, where

$$\Phi_c = N_H^{1/2}/[N_H^{1/2} + N_D^{1/2}] \quad (1)$$

In this equation, N_H and N_D are the degrees of polymerization of the normal and deuteriated polymers, respectively. As χ approaches $\chi_s(\Phi)$, or equivalently as the temperature approaches the UCST, the system experiences large fluctuations in composition. Consequently, the effect of the "thermodynamic slowing down" of mutual diffusion should be more pronounced as the experimental temperature is lowered. In systems where $\chi \approx 0$ or at temperatures sufficiently far from the critical point, these effects should not be observed.

Previously we published a short communication where experimental evidence of critical slowing down in binary mixtures of normal and deuterated polystyrene was presented.[8] The present report is concerned with the effects of temperature on thermodynamic slowing down of mutual diffusion in these systems. These measurements were performed by using elastic recoil detection (ERD). We were able to extract the segment–segment interaction parameter from measurements of $D(\Phi)$ at different temperatures. The dependence of χ on T is compared with that which Bates and Wignall obtained in the polstyrene system using SANS. The agreement is excellent.

Experimental Section

The polymers used in this study were deuteriated polystyrene (d-ps) of degree of polymerization 9.8×10^3 with a polydispersity index of 1.15 and normal (hydrogenated) polystyrene (h-ps) of degree of polymerization 8.7×10^3 with a polydispersity index of about 1.1. The d-ps and h-ps standards were purchased from the Custom Chemical and the Pressure Chemical companies, respectively.

Both mutual diffusion, D, and tracer diffusion, D^*, coefficients were determined by using ERD. In this technique, a beam of helium ions of energy 3.0 MeV is directed toward the sample at an angle 15° with respect to the sample surface. The helium ions undergo a number of collisions with target nuclei, resulting in the ejection of some of these nuclei. Of interest are the protons (H) and deuterons (D). The H and D nuclei which recoil from the surface are detected with different energies by virtue of their

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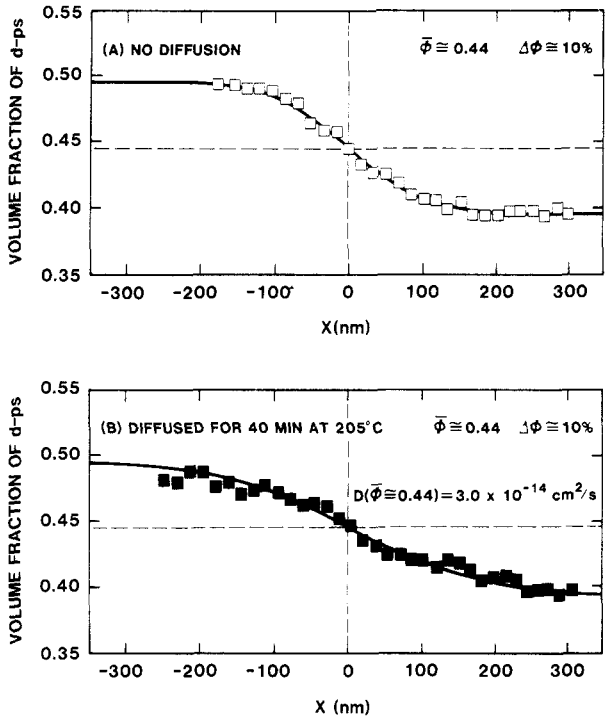

Figure 1. Volume fraction vs. depth for two films where $\Delta\Phi \approx 10\%$ and $\bar{\Phi} \approx 45\%$ (A) before interdiffusion and (B) after interdiffusion for 40 min at 205 °C.

different masses (protons take approximately one-half of the energy of the incoming beam and deuterons approximately two-thirds). Nuclei which recoil from beneath the surface are detected at energies which are lower than the corresponding surface recoil energies and are characteristic of the depth from which they recoiled. The number of nuclei which recoil from a given depth is a measure of the concentration of such nuclei at that depth. From this experiment, one gets a spectrum of particle yield (number of particles detected with an energy between $E_d - \Delta E/2$ and $E_d + \Delta E/2$ where ΔE is the energy width of a channel on the multichannel analyzer) vs. E_d. This spectrum may then be converted to one of volume fraction vs. depth. In order to determine the tracer diffusion coefficient, D^*, of d-ps, into the h-ps host a thin layer (15 nm) of d-ps was allowed to diffuse into a thick layer (1 μm) of h-ps supported by a silicon substrate. Helium ERD is used to determine the yield vs. detected energy profile of d-ps, which is then converted to volume fraction (less than 5%) of d-ps as a function of depth in PS. D_D^* is then extracted from the profile by fitting it to the solution of the diffusion equation. The tracer diffusion coefficient, D_H^*, of h-ps into a d-ps host is extracted accordingly. The details of the procedure used to extract D* and to prepare the samples are outlined elsewhere.[9,10]

The interdiffusion coefficient is expected to vary markedly with composition, and an approximate procedure is adopted. Couples were produced where on either side of the interface is a h-ps/d-ps blend, one of composition Φ_0 and the other of $\Phi_0 \pm \Delta\Phi$ ($\Delta\Phi \approx 10\%$). The initially steplike concentration profile was allowed to broaden by interdiffusion at elevated temperatures. The mutual diffusion coefficient was then extracted from the broadened profile. This procedure was adopted by Jones and collaborators[11] and Composto and collaborators,[12] who studied interdiffusion in miscible blends. During preparation of the samples, a polished silicon wafer was coated with a layer ($\sim$1 μm) of a d-ps/h-ps blend of composition Φ_0. A second layer was produced separetely by spinning a solution of composition $\Phi_0 \pm \Delta\Phi$ on a glass slide. This film, whose thickness is approximately 400 nm, was then floated onto a bath of distilled water from where it was transferred onto the surface of the coated wafer.

Figure 1A shows a plot of volume fraction vs. depth for a sample of average composition $\bar{\Phi} \approx 45\%$ of d-ps which was not allowed to interdiffuse. In this sample, $\Phi_0 \approx 50\%$ d-ps and $(\Phi_0 - \Delta\Phi) \approx 40\%$ d-ps. The line drawn through the data represents the instrumental broadening, which has a full width at half maximum

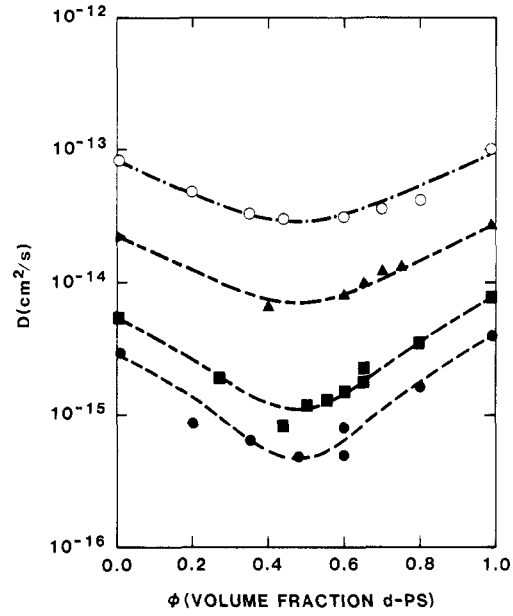

Figure 2. Plot of $D(\Phi)$ vs. Φ at 205 (○), 190 (▲), 174 (■), and 166 (●) °C.

of 100 nm (it is not the breadth of the interface). The instrumental broadening is determined in separate experiments. Shown in Figure 1B is a plot of volume fraction of d-ps vs. depth for a sample that was allowed to interdiffuse at 205 °C for 40 min. The solution to the diffusion equation for two semiinfinite slabs is[13]

$$\Phi(x) = \bar{\Phi} - (1/2)\Delta\Phi \text{ erf } [x/(4Dt)^{1/2}] \quad (2)$$

where t is the diffusion time and D is taken as the interdiffusion coefficient at the interface $\Phi_0 - \Delta\Phi/2$. This equation is a very good approximation if D does not vary rapidly with composition and if the layers are thick enough such that there is no reflection from the boundaries. The line drawn through the data is a convolution of this equation with the instrumental resolution function. The interdiffusion coefficient extracted is $D(0.45) = 3.0 \times 10^{-14}$ cm^2/s. A series of couples of different average compositions were prepared. Experiments were conducted at 166, 174, 190, and 205 °C.

Results and Discussion

Shown in Figure 2 is a plot of the interdiffusion coefficient, $D(\Phi)$, as a function of the average composition, $\bar{\Phi}$, of the blend at four different temperatures, 166 (●), 174 (■), 190 (▲), and 205 (○) °C. The stability limit of this mixture is $\chi_s(\Phi_c) \approx 2.1 \times 10^{-4}$, $N_D = 9.8 \times 10^3$, and $N_H = 8.7 \times 10^3$. It is evident that $D(\Phi)$ exhibits a minimum at the critical composition of $\Phi_c \approx 50\%$. The extent of the critical slowing down is more pronounced at lower temperatures, which is to be expected if the correlation length of the concentration fluctuations increases with decreasing T. This system clearly exhibits a UCST. At the UCST, the mixture becomes unstable and undergoes phase separation.

$D(\Phi)$ is very sensitive to small changes in χ, particularly in regimes close to the stability limit. Hence, knowledge of $D(\Phi)$ enables one to compute χ. Mean field predictions for the compositional dependence of the mutual diffusion coefficient have been shown by Kramer and co-workers and independently by Sillescu to be given by[14]

$$D(\Phi) = \Omega(\Phi)[\chi_s(\Phi) - \chi] \quad (3)$$

where

$$\Omega(\Phi) = 2\Phi(1 - \Phi)[D_D^* N_D(1 - \Phi) + D_H^* N_H \Phi]$$

In the above equation, $\Omega(\Phi)\chi_s(\Phi)$ defines the compositional dependence of $D(\Phi)$ when the combinatorial entropy of mixing provides the thermodynamic driving force for in-

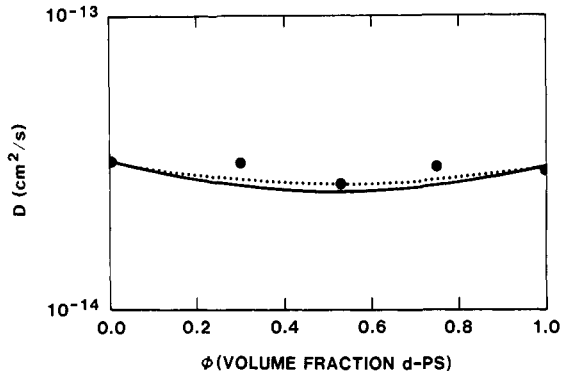

Figure 3. Compositional dependence of the interdiffusion coefficient of h-ps and d-ps of degrees of polymerization $N_H \approx N_D \approx 2.3 \times 10^3$, $\chi_s(\Phi_c) \approx 8.7 \times 10^{-4}$, and $T = 160$ °C.

Table I

T, °C	$10^4\chi$ (ERD)	$10^4\chi$ (SANS)	$10^4\chi$ (theory)
205	1.45	1.3	1.6
190	1.55	1.4	1.7
174	1.8	1.6	1.75
166	1.9	1.65	1.8

terdiffusion. $\Omega(\Phi)\chi$ is the correction to $\Omega(\Phi)\chi_s(\Phi)$ in the presence of enthalpic and noncombinatorial entropy of mixing contributions to the thermodynamic driving force. The lines drawn through the data were computed by using eq 2 in which χ is the only adjustable parameter. Its value is adjusted to give the best fit to the data in the middle of the concentration regime. The absolute error associated with the determination of χ is approximately 5×10^{-5}. Tabulated in the second column of Table I are values extracted from each set of data.

Critical slowing down effects are difficult to observe in regimes far from the stability limit as shown in Figure 3. The stability limit of this mixture is $\chi_s(\Phi_c) \approx 8.7 \times 10^{-4}$; $N_D = 2.3 \times 10^3$, and $N_H = 2.4 \times 10^3$, and the experimental temperature was 160 °C. The solid line was computed using a value of $\chi = 1.9 \times 10^{-4}$, which one would expect on the basis of the results in column 2 of Table I. However, a value of $\chi = 1.4 \times 10^{-4}$ is that which fits the data best in the middle of the concentration regime. $D(\Phi)$ is obviously not very sensitive to changes in χ in this regime. In column 3 of Table I are the results of the SANS measurements of Bates and Wignall whose mixtures had an average composition of50%. These results were obtained by using the equation

$$\chi = 0.20(\pm 0.01)T^{-1} - 2.9(\pm 0.4) \times 10^{-4} \quad (4)$$

which is at least-squares analysis of their data.[3] Like that of Bates and Wignall, our data exhibits a T^{-1} dependence (Figure 4). Our data may be fit by an equation of the form

$$\chi = 0.22(\pm 0.06)T^{-1} - 3.2(\pm 1.2) \times 10^{-4} \quad (5)$$

The agreement between both experimental results is excellent. The results presented here are further corroborated by earlier studies by Strazielle and Benoit[15] of critical phenomena in the ps–cyclohexane system. They found that the Θ-temperature was influenced markedly by whether the ps and or the cyclohexane was deuteriated. This result may only be rationalized if $\chi > 0$.

The origins of these effects appear to be reasonably well understood. Bates and Wignall[3,4] have shown that one may make estimates of χ based on the polarizability and segmental volume change that results from mixing a normal and deuteriated polymer of identical structure otherwise:

$$\chi \simeq 2\pi^2 I[(\alpha/V)_H - (\alpha/V)_D]^2/3k_BT \quad (6)$$

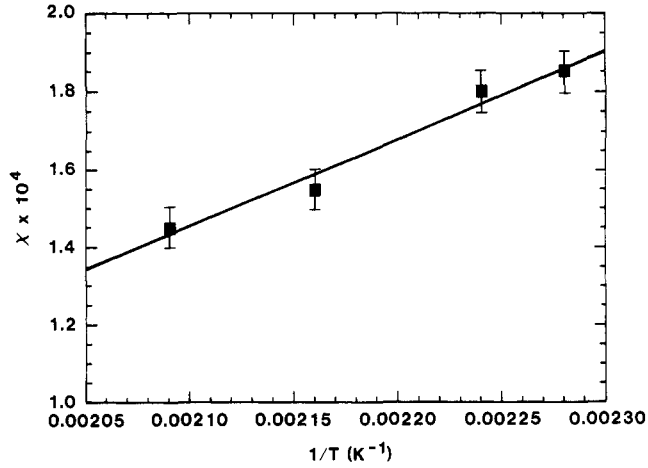

Figure 4. Dependence of χ on $1/T$.

Here k_B is the Boltzmann constant, I is the ionization potential, $(\alpha/V)_H$ is the ratio of the polarizability to the segmental volume of the normal polymer, and $(\alpha/V)_D$ is that of the deuteriated species. Estimates of the polarizability and segmental volume change for the ps–d-ps mixture were made by Bates and Wignall based on molecules such as eq benzene and toluene. The values of χ calculated from eq 6 are in qualitative agreement with experiment (Table I). Of particular importance, however, is that it correctly predicts the existence of the UCST.

Conclusion

We have clearly demonstrated the existence of thermodynamic or critical slowing down effects on mutual diffusion in binary mixtures of normal and deuteriated polystyrene. This effect increases as the experimental temperature is decreased, which strongly suggests that the system exhibits an upper critical solution temperature. The temperature dependence of the Flory interaction parameter, χ, was extracted from the data by using the mean field predictions for the compositional dependence of the mutual diffusion coefficient. It is in excellent agreement with the SANS measurements of Bates and Wignall and in agreement, at least qualitatively, with theory. It is in total disagreement with the results of Yang et al. Similar experiments in other systems are being pursued.

Acknowledgment. We thank E. J. Kramer and F. S. Bates for useful discussions and N. D. Wing for technical assistance. This work, performed at Sandia National Laboratories, was supported by the U.S. Department of Energy under Contract DE-AC04-76DP00789.

Registry No. Deuteriated polystyrene, 27732-42-9; polystyrene, 9003-53-6.

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Thermal Analysis of the Conformational Disorder in Semicrystalline Poly(vinylidene fluoride) and Poly(trifluoroethylene)

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Received May 27, 1987

ABSTRACT: Differential scanning calorimetry was used to explore the changes in heat capacity and latent heat of poly(vinylidene fluoride) and poly(trifluoroethylene) between the glass and melting transition temperatures. In contrast to more rigid polymers, poly(fluoroethylenes) show no detectable "rigid amorphous" fraction. Evidence of conformational disorder (condis crystals) in both polymers is discussed. For poly(vinylidene fluoride) a condis glass transition is proposed to exist at 360 K for the α-crystal form. A condis to condis crystal transition on cooling seems to occur at 350–360 K. A third level of conformational order that is involved in the ferroelectric properties of poly(vinylidene fluoride) can be forced by an electric field above about 380 K (poling), but it remains frozen (glassy) up to the melting temperature, i.e., there is no Curie temperature. Semicrystalline poly(trifluoroethylene) is also known to have a conformationally disordered structure. Above the rather broad glass transition it already has the heat capacity expected for the liquid, an indication that amorphous and condis glass transitions may overlap in the temperature range from 230 to almost 400 K.

Introduction

In a major thermal analysis effort of linear macromolecules the ATHAS data bank of heat capacities was established.[1] This data bank has served as a basis for the interpretation of thermodynamic properties. In this connection the heat capacities of all poly(fluoroethylenes) in the solid state were linked to their frequency spectra[2] and the heat capacities of the liquid states were measured and united in an empirical addition scheme, capable of predicting C_p starting from the glass transition temperature to decomposition.[3]

With the heat capacities of the limiting amorphous and crystalline states known to a precision of better than ±5%, it is now possible to discuss the properties of the semicrystalline polymers. In this paper we will present measurements on partially crystallized poly(vinylidene fluoride) (PVF2) and poly(trifluoroethylene) (P3FE). The results are linked to the possible existence of conformational disorder (condis crystallinity)[4] in these polymers. Since at low temperature the polymers show frozen disorder, there should be glass transitions of the condis states.[4]

To get some insight into the possible conformational disorder, the molecular mechanics of a single PVF2 chain was calculated before, estimating electrostatic, torsional, and van der Waals interactions of a 32 carbon atom chain section.[5] The results of this computation were that the isolated PVF2 chain does not have, as one might expect, two distinct potential energy minima close to the basic TGTḠ conformation of the α-crystal form. For poly(tetrafluoroethylene) (PTFE),[6] in contrast, two distinct trans-conformation minima exist at a ±15° rotation angle and provide the explanation for its condis crystallinity between 303 and 605 K.[7] The isolated PVF2 chain may instead assume a bond angle between 114° and 118° and torsional angles of the gauche conformations between 40° and 80° without major changes in potential energy (<1 kJ/mol).[5] Intermolecular constraints of the crystal must thus fix the observed conformations at lower temperature and conformational disorder similar to that in PTFE may well be expected at higher temperature. It will be shown below that condis crystallinity is likely to exist also in P3FE but that distinct differences exist between the poly(fluoroethylenes) that are in need of detailed study by more motion-specific analysis techniques such as dielectric or NMR methods.

Experimental Section

The poly(vinylidene fluoride) (PVF2) was obtained from Polysciences, Inc. Its molecular weight was 120 000 and by ^{1}H and ^{19}F NMR, 11% reverse addition was found. The as-received sample was a semicrystalline mixture of the α- and β-crystal modifications that converted to pure α on recrystallization (checked by X-ray diffraction).

The poly(trifluoroethylene) was an uncharacterized sample of sufficiently high molecular weight to have little influence on thermal properties.

All calorimetry was performed with a computer-interfaced Perkin-Elmer DSC 2. The analog output was converted to digital form with a Nelson Analytical, Inc., Model 860 voltage-to-frequency converter. Details of the computer software (IBM XT personal computer) were developed by Laboratory Microsystems, Inc. More detailed description of instrumentation and computation have been published earlier.[3] Sampling length of data was 0.5 s, 15–25-mg samples were enclosed in aluminum pans. Sapphire reference material was used. The temperature range of measurement was from 220 to 500 K. The calorimeter was thermostated at about 200 K with a mechanical refrigeration unit. All runs were made at a heating rate of 10 K/min in a dry nitrogen environment.

We also used the Perkin-Elmer DSC 2 for crystallization experiments with cooling rates between 5 and 80 K/min.

Du Pont thermal analyzers (types 990 and 900) were used for evaluation of glass transition temperatures and for crystallization runs on very fast cooling.

Results

Typical DSC curves of PVF2 and P3TFE are shown in Figures 1 and 2. Included in these figures are the calculated heat capacities of the solid, liquid, and semicrystalline samples. The data for the solid are computed from the approximate vibrational spectrum as outlined in detail in

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