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Slowing Down of the Diffusion Process in Binary Polymer Mixtures of Noncritical Composition Approaching the Coexistence Curve

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ABSTRACT: The diffusion process in dPS ($M_w = 1.06 \times 10^6$ g mol^{-1})/hPS ($M_w = 2.89 \times 10^6$ g mol^{-1}) mixtures at constant temperature below the critical temperature slows down approaching the coexistence curve from the homogeneous single fluid phase region of the phase diagram. This effect can be understood in terms of the composition dependence of the thermodynamic factor $(\partial \mu_{dPS}/\partial \Phi_{dPS})_{T,P}$ in combination with the Flory–Huggins theory of polymer melts. The theoretically expected decrease of the mutual diffusion coefficient with increasing temperature along the coexistence curve approaching the critical temperature is not observed in the temperature range studied (5 K < $(T_c - T)$ < 22 K). The temperature dependence of the diffusion coefficient D is dominated by the temperature dependence of the phenomenological transport coefficient L. The apparent activation energy of the diffusion coefficient of the polymer melts studied is larger by a factor of about 10 than that of binary mixtures of low molar mass components.

Introduction

We report results of measurements of the mutual diffusion coefficient of protonated (hPS) and deuterated (dPS) polystyrene mixtures of noncritical composition. The experiments are carried out at constant temperatures below the upper critical temperature (i.e. $T < T_c$) of the system as a function of composition. They demonstrate a characteristic slowing down of the diffusion process approaching the coexistence curve from the homogeneous region of the phase diagram. Earlier work of Green and Doyle[1] concentrated on measurements of the temperature and composition dependence of the diffusion coefficient of dPS/hPS mixtures at temperatures above the critical temperature (i.e. $T > T_c$).

Experimental Section

Materials. The protonated polystyrene (hPS) had a weight average molar mass of $M_w = 2.89 \times 10^6$ g mol^{-1} and a polydispersity $M_w/M_n = 1.09$. It was obtained from Tosoh Corp. (1-11-39 Minoato-Ku, Tokyo, Japan).

The fully deuterated polystyrene (dPS) had a molar mass $M_w = 1.03 \times 10^6$ g mol^{-1} and a polydispersity $M_w/M_n = 1.07$ and was purchased from Polymer Laboratories Ltd. (Essex Road, Church Stretton, U.K.).

The phase diagram of this system has been established by Budkowski et al.[2] using materials of the same stock. The upper critical temperature has a value of $T_c = 197 \pm 3$ °C. It is about 100 K higher than the glass transition temperature T_g of PS (i.e. $T_c - T_g) \approx 100$ K.

Methods. The mutual diffusion coefficient D of a dPS/hPS mixture at a given temperature and mean composition was obtained from measurements of deuterium concentration profiles in dPS/hPS bilayers of different compositions as a function of time using the nuclear reaction analysis (NRA) technique which has been described in detail in refs 3–7. Each bilayer was used only once for the determination of a deuterium concentration profile. Figure 1 shows deuterium concentration profiles in two bilayers determined by the NRA method after different diffusion times. A small enrichment of dPS at the interface dPS, hPS/vacuum was observed in the bilayers after longer diffusion times ($t > 60$ min, see Figure 1b).[8] The solid lines in Figure 1 represent the function $\Phi_{dPS}(x) = (1/2)[\Phi^u_{dPS} + \Phi^l_{dPS} + (\Phi^u_{dPS}) \tanh((x - x_{int})/w)]$ with $w = (2/\pi)(6Dt)^{1/2}$. Φ_{dPS} is the volume fraction of dPS in the polymer mixture. The indices u and l refer to the upper and lower film of the bilayer deposited on a polished silicon substrate. w is the width of the diffusion zone. x_{int} is the coordinate of the original interface at $t = 0$. The experimentally determined value of $w_{exp}(t)$ includes a broadening caused by the finite instrumental resolution. This effect is taken into account in the data analysis (i.e. $w(t) = [w^2_{exp}(t) - w^2_{exp}(t = 0)]^{1/2}$. For

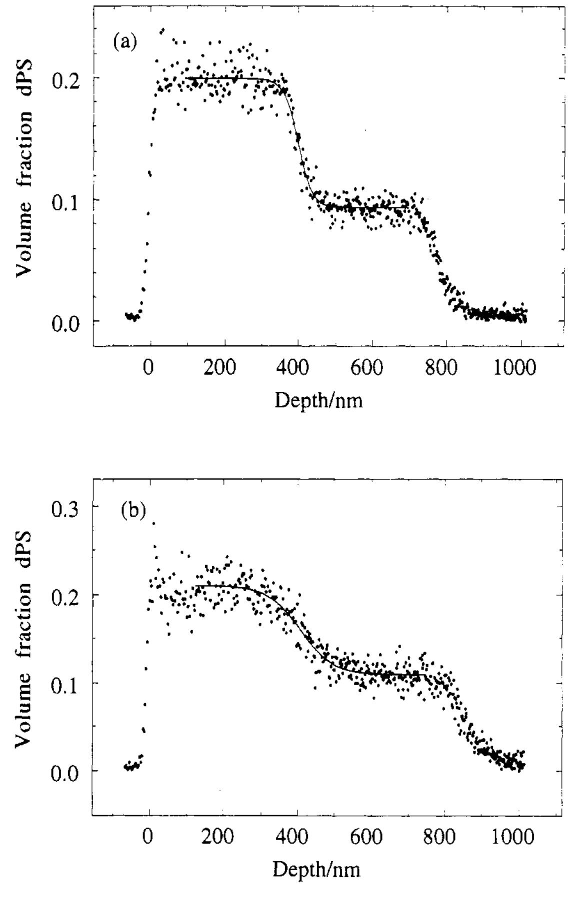

Figure 1. Concentration profiles of deuterium determined by the NRA technique in two dPS/hPS bilayers of the same mean composition ($\langle \Phi_{dPS} \rangle = 0.155$; Φ_{dPS}, volume fraction of dPS) after two different diffusion times at a temperature $T = 185$ °C: (a) $w_{exp}(t{=}0) = 38$ nm; (b) $w_{exp}(t{=}60$ min$) = 88$ nm.

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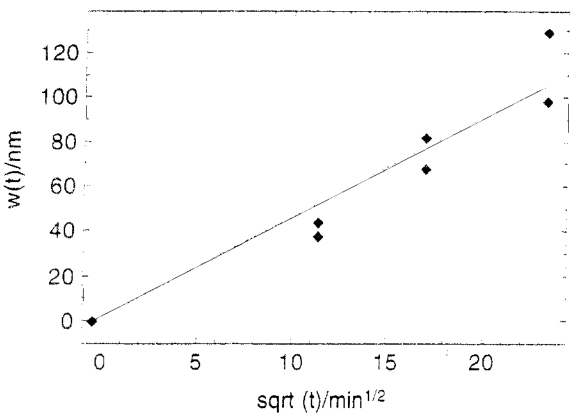

Figure 2. Plot of values of the corrected width w of the diffusion zone as function of the square root of the diffusion time (sqrt(t)). The slope of the line corresponds to a value of the diffusion coefficient of $D = 1.7 \times 10^{-15}$ cm^2 s^{-1}. The experiment is carried out at $T = 175$ °C with a bilayer with a mean composition $\Phi_{dPS} = 0.155$. The uncorrected width of the diffusion zone has the values $w_{exp}(t{=}0) = 35$ nm and $w_{exp}(t{=}545\text{ min}) = 129$ nm.

Table 1. Values of the Mutual Diffusion Coefficient D of the System dPS/hPS Measured at Different Temperatures T below the Critical Temperature $T_c = 197 \pm 3$ °C[2] and at Different Mean Compositions $\langle\Phi_{dPS}\rangle$ in the Homogeneous Single Phase Region of the Phase Diagram ($\Phi_{dPS} < \Phi_{dPS,c}$; Φ_{dPS}, Volume Fraction of dPS; Subscript c, Critical Composition; $\Phi_{dPS,c} = 0.58$; See Ref 2[a]

T/°C	$\langle\Phi_{dPS}\rangle$	D/cm^2 s^{-1}	T/°C	$\langle\Phi_{dPS}\rangle$	D/cm^2 s^{-1}
192	0.062	1.4×10^{-14}	185	0.155	5.9×10^{-15}
192	0.235	5.6×10^{-15}	185	0.232	4.5×10^{-15}
192	0.323	3.0×10^{-15}	175	0.062	2.0×10^{-15}
185	0.062	9.8×10^{-15}	175	0.155	1.7×10^{-15}

[a] The uncertainty of the values of the diffusion coefficient is estimated to be $\delta D/D = \pm 0.15$ and that of the temperature $\delta T = \pm 1$ K. Each data point is the mean value of three series of measurements with five bilayers each. For details see the Experimental Section, Methods.

practical reasons the function $\Phi_{dPS}(\chi)$ is used as an approximant to the complementary error function which is the exact solution of the diffusion problem. The difference between the approximant and the exact solution is insignificant relative to the scatter of the data points. D was determined from the slope of $w(t)$ versus $t^{1/2}$ plot (see Figure 2).

The estimated uncertainty of the measured diffusion coefficient is $\delta D/D = \pm 0.15$. It is mainly caused by frozen-in concentration fluctuations of the polymers forming the bilayers. They developed during the spin casting process with solutions of dPS and hPS in toluene to generate the films at room temperature and produced "noisy" concentration profiles. Attempts to prepare bilayers without frozen-in concentration fluctuations by annealing the dPS-rich and the hPS-rich layer before forming a bilayer failed. It was not possible to separate the dPS-rich layer from its support (glass plate or quartz plate) after annealing the sample for several hours at an elevated temperature ($T \approx 180$ °C).

Results and Discussion

The experiments are carried out at three temperatures below the critical temperature (i.e. 5 K < ($T_c - T$) < 22 K. The mean compositions $\langle\Phi_{dPS}\rangle$ of the dPS/hPS mixtures are smaller than the critical composition ($\Phi_{dPS,c} = 0.580$).

The results of the measurements are compiled in Table 1 and are shown in Figure 3. The data indicate that the diffusion processes in the bilayers at constant temperatures slow down approaching the coexistence curve. The differential coefficient $(\partial D/\partial\Phi_{dPS})_T$ has negative values for $\Phi_{dPS} < \Phi_{dPS,c}$. It becomes less negative with increasing values of Φ_{dPS}. The change of $(\partial D/\partial\Phi_{dPS})_T$ with Φ_{dPS} decreases with increasing values of $(T_c - T)$.

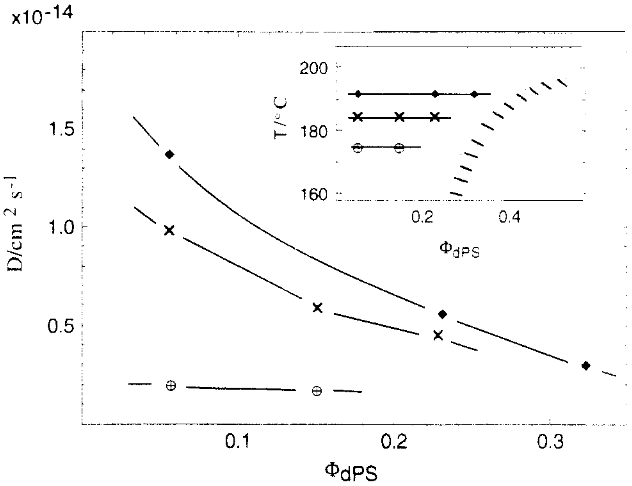

Figure 3. Mutual diffusion coefficient D of dPS ($M_w = 1.06 \times 10^6$ g mol^{-1})hPS ($M_w = 2.89 \times 10^6$ g mol^{-1}) mixtures as a function of composition in the homogeneous region of the phase diagram ($\Phi_{dPS} < \Phi_{dPS,c}$, Φ_{dPS}, volume fraction of dPS). The experiments are carried out at three constant temperatures below the critical temperature T_c ($T_c = 197 \pm 3$ °C see ref 2): (◆) $T_1 = 192 \pm 1$ °C; (×) $T_2 = 185 \pm 1$ °C; (⊗) $T_3 = 175 \pm 1$ °C. Each data point is the mean value of three series of measurements with five bilayers each. The uncertainty of the values of D is $\delta D/D = \pm 0.15$. The composition difference of dPS between the films forming a bilayer has a value of about $\Delta\Phi_{dPS} \approx 0.1$. The lines connecting the values of D measured at the same temperature are an aid for the eye only. The insert shows part of the liquid/liquid coexistence curve based on experimental data taken from ref 2. The temperatures and the mean compositions of the bilayers at which the diffusion coefficients are determined are marked in the insert.

From a thermodynamic point of view the composition dependence of D at temperatures above as well as below the critical temperature can be understood qualitatively by assuming that it is mainly determined by the temperature and composition dependence of the thermodynamic coefficient $(\partial\mu_i/\partial p_i)_{T,P}$ (μ_i, chemical potential of component i; p$_i$, order parameter of component i). It follows from the linear laws of the thermodynamics of irreversible processes in continuous systems that D is proportional to the product of a phenomenological transport coefficient (Onsager coefficient) Λ and the thermodynamic factor $(\partial\mu_i/\partial p_i)_{T,P}$. The appropriate order parameter of polymer mixtures is the volume fraction Φ_i of the component i which has the same value as the mass fraction of this component in the system under study, neglecting the small difference between the densities of dPS and hPS ($(\rho_{dPS} - \rho_{hPS}) = 5 \times 10^{-2}$ g cm^{-3}). The relationship between D and $(\partial\mu_{dPS}/\partial\Phi_{dPS})_{T,P}$ in the barycentric frame of reference is given by eq 1,[9] where Λ is a phenomenological transport coefficient ($\Lambda > 0$) and ρ is the density. At constant pressure Λ is a function of temperature and mean composition.

$$D = \Lambda[(1 - \Phi_{dPS})\rho]^{-1}(\partial\mu_{dPS}/\partial\Phi_{dPS})_{T,P} \tag{1}$$

The Flory–Huggins model of polymer mixtures in its simplest form (i.e., $N_{dPS} = N_{hPS} = N$; N, number of monomers in a single polymer chain of PS) is used to describe qualitatively the temperature and composition dependence of μ_{dPS} (see eq 2: R, universal gas constant; μ°_{dPS}, standard value of the chemical potential of dPS).[10]

$$(\mu_{dPS} - \mu^\circ_{dPS})/RT = (1/N)[\ln\{\Phi_{dPS}/(1 - \Phi_{dPS})\} + (2T_c/T)(1 - 2\Phi_{dPS})] \tag{2}$$

In eq 2 it is assumed that the Flory–Huggins parameter χ is only a function of temperature which can be expressed

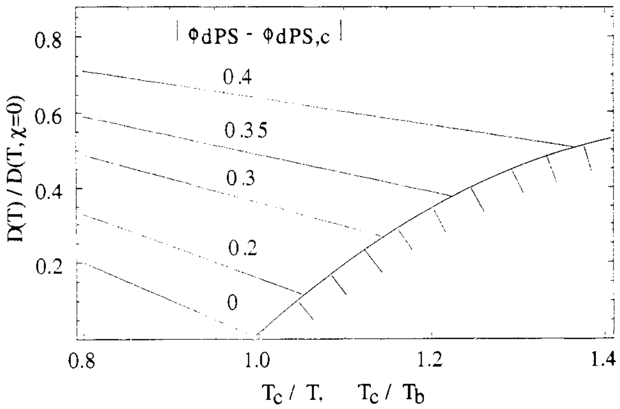

Figure 4. Graphical representation of eq 3. $D(T)/D(T,\chi=0)$ is the ratio of the mutual diffusion coefficient of a polymer mixture at temperature T divided by its hypothetical value in an "ideal polymer mixture" (i.e. $\chi = 0$) at the same temperature. Φ_{dPS} is the volume fraction of dPS. The composition dependence of the ratio (T_c/T_b) (T_b, binodal temperature) is calculated from the thermodynamic condition for the equilibrium distribution of dPS between the coexisting polymer phases (Φ'_{dPS}) and (Φ''_{dPS}) (i.e. $\mu'_{dPS}(T_b) = \mu''_{dPS}(T_b)$): $(T_c/T_b) = \ln\{\Phi'_{dPS}/(1 - \Phi'_{dPS})\}/[2(2\Phi'_{dPS} - 1)]$ with $\Phi''_{dPS} = 0.5 + \Phi'_{dPS}$.

by $\chi = \chi_c(T_c/T)$ with $\chi_c = (2/N)$. Differentiation of eq 2 with respect to Φ_{dPS} and combining the result with eq 1 leads to eq 3,with

$$D(T)/D(T,\chi=0) = 1 - (T_c/T)[1 - 4(\Phi_{dPS} - \Phi_{dPS,c})^2] \quad (3)$$

$$D(T,\chi=0) = \{\Lambda RT\}/\{N\rho[(1 - \Phi_{dPS})[1/4 - (\Phi_{dPS} - \Phi_{dPS,c})^2\}^{-1}]$$

$D(T,\chi=0)$ is the mutual diffusion coefficient of a dPS/hPS mixture in a hypothetical state in which the Flory–Huggins interaction parameter is zero ("ideal polymer mixture"). $D(T,\chi=0)$ is introduced to bring out more clearly the influence of the interaction parameter χ on diffusion and to eliminate the factor $[\Lambda(1 - \Phi_{dPS})^{-1}\rho^{-1}]$.

The limited set of data obtained in this study does not warrant the use of a more refined Flory–Huggins model[11] for the qualitative interpretation of the experimental results. The use of an expression of χ containing an enthalpic and an entropic term for the calculation of $D(T)$ using experimental data[12] obtained for the system dPS/hPS ($M_w = 1 \times 10^6$ g mol^{-1}) does not change the qualitative conclusions drawn from eq 3 (see below).

Figure 4 shows a graphical representation of eq 3 for different parameter values $|\Phi_{dPS} - \Phi_{dPS,c}|$. The calculated curves reflect qualitatively major aspects of the experimentally observed characteristic composition and temperature dependence of the mutual diffusion coefficient in mixtures of critical and noncritical composition of the system dPS/hPS at temperatures above (see Figure 2 in ref 1 and Figure 12 in ref 11) as well as below the critical temperature. Only the features relevant to mixtures of noncritical composition at temperatures below the critical temperature are mentioned in the following.

At constant temperatures corresponding to $(T_c/T) > 1$ (i.e. $T < T_c$), the value of the ratio $[D(T)/D(T,\chi=0)]$ decreases with decreasing values of $|\Phi_{dPS} - \Phi_{dPS,c}|$. The values of the differential coefficient $(\partial[D(T)/D(T,\chi=0)]/\partial\Phi_{dPS})_T$ at constant values of (T_c/T) become less negative with increasing values of $\Phi_{dPS}(\partial[D(T)/D(T,\chi=0)]/\partial\Phi_{dPS}) = 8(T_c/T)(\Phi_{dPS} - \Phi_{dPS,c})$. This is in agreement with the results of the experiments (see Figure 2).

The ratio $[D(T)/D(T,\chi=0)]$ is expected to decrease (see Figure 4) along the coexistence curve with increasing temperatures approaching the critical point. This is not observed in the temperature range used in this study. The diffusion coefficients extrapolated to the liquid/liquid phase boundary (i.e. $D(\Phi'_{dPS})$) decrease with increasing values of $(T_c - T'_b)$ (Φ'_{dPS}, is the volume fraction of dPS of the mixture at the binodal temperature $T'_b(\Phi'_{dPS} < \Phi_{dPS,c})$).

In the system dPS/hPS the temperature range $(T_c - T_b)$ in which a decrease of the diffusion coefficient with increasing temperatures along the coexistence curve can be observed is expected to be small (i.e. $(T_c - T_b) < 1$ K) and experimentally difficult to reach. In binary mixtures of low molar mass components this effect is observed in a wide temperature range around the critical point (i.e. $(T_c - T_b) \leq 10$ K).[13,14] The difference in the behavior of the two types of systems is caused by the fact that the apparent activation energy E_a of the diffusion process in dPS/hPS mixtures is larger by a factor of 10 (dPS/hPS: $E_a \approx 140$ kJ mol^{-1} [12]) than that in mixtures of low molar mass components. Consequently, in the dPS/hPS system the influence of the thermodynamic factor $(\partial\mu_{dPS}/\partial\Phi_{dPS})_{T,P}$ on the diffusion coefficient shows up clearly only in experiments carried out at constant temperatures. In experiments carried out as a function of temperature the changes of the diffusion coefficient are dominated by the temperature dependence of the Onsager coefficient Λ (see Figure 2, change of $(\partial d/\partial\Phi_{dPS})_T$ at constant Φ_{dPS} with $(T_c - T)$). This is also the reason for the fact that the experimental diffusion coefficient data obtained in the homogeneous region of the phase diagram do not reflect the expected increase of the apparent activation energy E_{app} of the diffusion process approaching the temperature of phase separation.

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References and Notes

(1) Green, P. F.; Boyle, B. L. *Macromolecules* **1987**, *20*, 2471.
(2) Budkowski, A.; Steiner, U.; Klein, J.; Schatz, G. *Europhys. Lett.* **1992**, *18*, 640.
(3) Klein, J. *Science* **1990**, *250*, 640.
(4) Chaturvedi, U. K.; Steiner, U.; Zak, O.; Krausch, G.; Klein, J. *Phys. Rev. Lett.* **1989**, *63*, 616.
(5) Chaturvedi, U. K.; Steiner, U.; Zak, O.; Krausch, G.; Schatz, G.; Klein, J. *Appl. Phys. Lett.* **1990**, *56*, 1228.
(6) Steiner, U.; Krausch, G.; Schatz, G.; Klein, J. *Phys. Rev. Lett.* **1990**, *56*, 1119.
(7) Steiner, U.; Chaturvedi, U. K.; Zak, O.; Krausch, G.; Schatz, G.; Klein, J. *Makromol. Chem., Macromol. Symp.* **1991**, *45*, 283.
(8) Budkowski, A.; Steiner, U.; Klein, J. *J. Chem. Phys.* **1992**, *97*, 5229.
(9) Groot, S. R. D.; Mazur, P. *Non-Equilibrium Thermodynamics*; North-Holland Publishing Co.: Amsterdam, 1963.
(10) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1985.
(11) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(12) Schwahn, D.; Hahn, K.; Streib, J.; Springer, T. *J. Chem. Phys.* **1990**, *93*, 8383.
(13) Ikier, C.; Klein, H.; Woermann, D. *J. Chem. Phys.* **1992**, *96*, 859.
(14) Schmitz, J.; Belkoura, L.; Woermann, D. *J. Chem. Phys.* **1994**, *100*, July.