Self- and Mutual-Diffusion Coefficients in the Dodecane/Polystyrene System

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SYNOPSIS

The self-diffusion coefficient of dodecane in cross-linked polystyrene was measured using pulsed gradient spin echo nuclear magnetic resonance (PGSE–NMR) spectroscopy. The concentration and temperature dependence of the diffusion coefficient was analyzed by the Fujita and Vrentas–Duda models. Parameters describing the Fujita model were determined from fitting of diffusion data to the PVT behavior of the system. Parameters describing the Vrentas–Duda model were determined from the analysis of the viscosity of dodecane, the viscoelastic relaxation properties, and the glass transition temperature of polystyrene as well as from the diffusion coefficient of the system, measured from independent experiments. Both the Fujita and Vrentas–Duda models described well the concentration and temperature dependence of the diffusion coefficient. Mutual diffusion coefficients were determined from these results. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The diffusion coefficient is the fundamental physical property describing a diffusional process. In macromolecular systems, diffusion coefficients are typically very strong functions of temperature and concentration and cover a very broad range of values, usually from 10^{-5} to 10^{-15} cm^2/s.

Interpretation of diffusion measurements is often simplified when the experiment measures the self-diffusion of one component in a mixture that has uniform chemical concentration. Experimental determination of self-diffusion coefficients is usually carried out by (i) radiation absorption[1-3]; (ii) light-scattering techniques[4-9]; (iii) radioactive tracer methods[10-15]; and (iv) nuclear magnetic resonance spectroscopic techniques.[16-22] Among them, the last two methods are the most appropriate for measuring diffusion coefficients in polymeric solids.

Pulsed gradient spin echo nuclear magnetic resonance (PGSE-NMR) spectroscopy monitors translational motions of magnetic spins and has a number of advantages over other methods, including the following: (i) measurements are suitable for both liquids and solids; (ii) measurements require little time even for solid samples; (iii) the technique is noninvasive; and (iv) the technique affords precise measurements. The significant limitation of this method is its comparatively high lower limit of the diffusion coefficient measurement of about 10^{-10} cm^2/s.

PGSE-NMR spectroscopy has been used by several investigators to observe the solvent diffusional behavior in solvent/polymer systems. Von Meerwall and co-workers[23-27] investigated the influence of several parameters on the polymer and solvent diffusion coefficients for a variety of systems. The WLF temperature dependence and Fujita–Doolittle concentration dependence were observed for diffusion of many solvents in several cross-linked rubbers.[23,24] Penetrant diffusion rates were essentially isotropic, elongation-independent, and depended only weakly on the shape of the penetrant molecules.[25] Self-diffusion coefficients of star-branched polymers in solution depended on the molecular weight of each arm (branch) and the number of arms.[26] Self-diffusion coefficients of low molecular weight polymers in the molten state or dissolved in the identical, high

molecular weight polymers were inversely proportional to the molecular weight.[27]

Korsmeyer et al.[28] examined solute and penetrant diffusion in highly swellable polymers. The self-diffusion coefficients of water and various solutes were measured as functions of concentration using ^{1}H-NMR and ^{19}F-NMR spectroscopy. The results were analyzed using the free-volume theory.

Pickup and Blum[29] measured the self-diffusion coefficients of solvents inside swollen cross-linked polystyrene beads. Their results were compared to those in uncross-linked polystyrene samples. Self-diffusion coefficients of toluene, acetonitrile, chloroform, and dichloromethane in swollen cross-linked polystyrene beads were determined[30] by analysis of ^{13}C-NMR data for solvent exchange in and out of the beads.

In recent work in our laboratory,[31] it became necessary to analyze sorption data of dodecane through various cross-linked polystyrene in order to validate a solvent-transport model proposed by Lustig et al.[32] Dodecane was selected as the desirable solvent because it is characterized by a high boiling point (216°C), and, thus, any solvent evaporation and release from a dodecane/polystyrene sample during experimental studies would be minimal. In the present research, the temperature and concentration dependence of the dodecane diffusion coefficients in dodecane/polystyrene systems were determined using PGSE–NMR spectroscopy and were analyzed by applying two diffusion models.

EXPERIMENTAL

Sample Preparation

Sheets of cross-linked polystyrene with nominal cross-linking ratio $X = 0.005$ mol divinylbenzene/mol styrene, were prepared by bulk polymerization. Styrene monomer (Aldrich Chemical Co., Milwaukee, WI) was vacuum-distilled at 38°C/15 mmHg and was mixed with desired amounts of the cross-linking agent, divinylbenzene (Aldrich Chemical Co.) at cross-linking ratios, X, of 0.005 mol DVB/mol styrene. The mixtures were reacted at 125°C for 48 h and the reaction was completed in a vacuum oven at 125°C for 12 h to remove the unreacted monomer and undesirable impurities. Six dodecane/polystyrene systems containing 0.000, 0.025, 0.050, 0.100, 0.150, and 0.200 weight fraction of dodecane were prepared by allowing varying amounts of dodecane to diffuse into the polymer sheets. The samples were allowed to absorb up to the equilibrium

mass uptake at varying temperatures. The uniformity of concentration distribution was confirmed by FTIR spectroscopy.[33]

Self-Diffusion Coefficient Measurements by PGSE–NMR Spectroscopy

A cork borer was used to punch out a stack of prepared cross-linked polystyrene samples of the same cross-linking ratio and the same dodecane content. The final samples had diameters of 6 mm and thickness ranging from 0.7 to 0.8 mm. The discs containing a fixed amount of dodecane were placed in a flat-bottom NMR tube using a glass rod. Six NMR tubes containing from 0 to 20 wt % dodecane were then sealed with Teflon tape to prevent dodecane evaporation. The optimum height of the sample stack was about 8 mm.

The PGSE–NMR technique was used by applying a large gradient of magnetic field, G, twice for duration δ after the 90 pulse and after the 180 pulse.[20] A steady field gradient, G_0, of much smaller magnitude was also employed to narrow the echo sufficiently to facilitate measurement of the base line and to increase time and phase stability of the echo. The pulsed field gradient was used to reduce the considerable heat dissipation in the coils produced by the steady magnetic field gradient and to broaden the spin echo to measure its height more accurately.

In our experiments, measurements were performed at temperatures of 105, 120, and 140°C, using a Spin-Lock CPS-2 pulse NMR spectrometer operating at 33 MHz for protons. PGSE experiments were conducted at fixed G_0 and G and at varying δ. The time separation between gradient pulses, τ, was less than 25 ms. The steady and pulsed field gradients, G_0 and G, were 0.85 G/cm and 121.8 or 304.5 G/cm, depending on the concentration of the system and the duration of the gradient pulse. The duration of field gradient pulse, δ, varied from 0.5 to 13 ms.

RESULTS AND DISCUSSION

Analysis of Self-Diffusion Coefficient

The attenuation of the spin echo height is a function of magnetic field gradients. The height of the gradient is expressed as an exponential function of the height of the spin echo:

$$\frac{A(2\tau, G, G_0)}{A(2\tau, G = 0, G_0)} = \exp(-\gamma^2 D_s X) \qquad (1)$$

where

$$X = \delta^2 G^2(\tau - \delta/3) - \delta G G_0[(t_1^2 + t_2^2)$$

$$+ \delta(t_1 + t_2) + 2\delta^2/3 - 2\tau^2] \quad (2)$$

Here, $A(2\tau, G, G_0)$ is the height of the spin echo at time, 2τ, when both the constant field gradient of magnitude, G_0, and the pulsed field gradient of magnitude, G, are applied, whereas $A(2\tau, G = 0, G_0)$ is the height of the spin echo at time, 2τ, when only a constant field gradient of magnitude, G_0, is applied. The term δ is the duration of the magnetic field gradient pulse; γ, the gyromagnetic ratio; τ, the time separation between field gradient pulses; and t_1, the time delay between the radio frequency and the field gradient pulses, $t_2 = \tau - \delta - t_1$.

Based on eqs. (1) and (2), the dodecane self-diffusion coefficient was determined by plotting the logarithm of the attenuated echo height, $\log[A(2\tau, G, G_0)/A(2\tau, G = 0, G_0)]$, vs. the term, X, of eq. (2) as shown in Figure 1. Such plots were not always linear. This resulted from a variety of causes, such as polydispersity, restricted diffusion, and the presence of other diffusing species.[28] In this measurement, the concave shape in the final stage seemed to be caused by the effect of the polymer on the final stage of diffusion. The diffusion coefficient of dodecane determined from this measurement was plotted as a function of dodecane weight fraction at temperatures of 105, 120, and 140°C as shown in Figure 2. Some data at low temperatures are not available as PGSE–NMR could not determine very low diffusion coefficients.

According to the classical free-volume theory,[34,35] the penetrant mobility in penetrant/polymer sys-
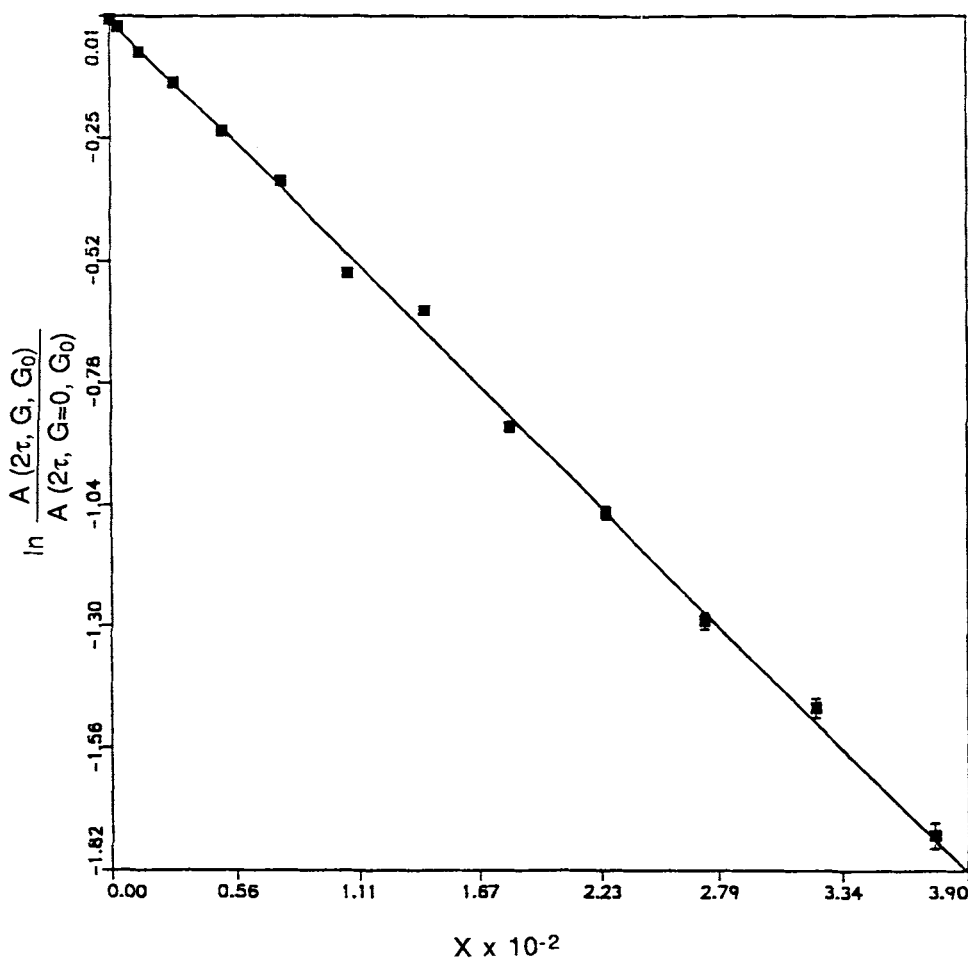

Figure 1 Determination of the self-diffusion coefficient yielded from the slope of the straight line correlating $\log[A(2\tau, G, G_0)/A(2\tau, G = 0, G_0)]$, vs. X for the dodecane/ polystyrene system including 10 wt % of dodecane at 105°C.
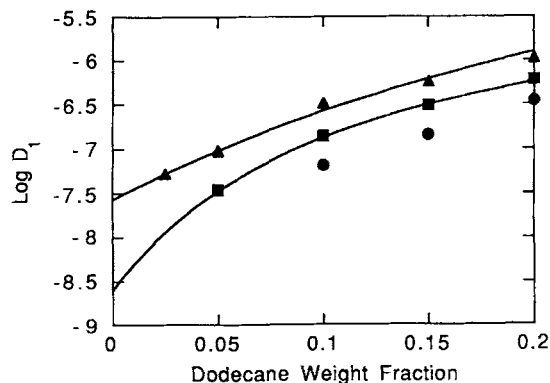
Figure 2 Dodecane self-diffusion coefficient as a function of dodecane weight fraction in polystyrene samples at temperatures of (●) 105, (■) 120, and (▲) 140°C. The solid curves indicate the Fujita model description.

tems is primarily dependent upon the average fractional free volume of the system, f:

$$D_1 = D_{10}\exp\left(-\frac{B_d}{f}\right) \qquad (3)$$

Here, B_d is an empirical constant.

For a given polymer/solvent system, the fractional free volume is a function of temperature and concentration. Fujita[36] showed that the change in fractional free volume is proportional to the diluent concentration:

$$f \cong f_2 + \beta\omega_1 \qquad (4)$$

Here, f_2 is the average fractional free volume in the pure polymer, and β, a parameter representing the contribution of dodecane to the increase of the free volume.

Substituting eq. (4) into eq. (3) and dividing by the self-diffusion coefficient at the limit of zero solvent concentration, D_0, we obtain the concentration dependence of the diffusion coefficient as described in eq. (5):

$$\ln\frac{D_1}{D_0} = -\frac{B_d}{f_2 + \beta\omega_1} + \frac{B_d}{f_2} \qquad (5)$$

The parameters, f_2, B_d, and β, in eq. (5) were determined by plotting $1/\ln(D_1/D_0)$ against $1/\omega_1$ at a given temperature. The intercept at $1/\omega_1 = 0$ represents the value of f_2/B_d and the slope of the straight line correlating $1/\ln(D_1/D_0)$ vs. $1/\omega_1$ represents the value of $f_2^2/(B_d\beta)$. When the fractional free volume of pure polymer, f_2, determined from the PVT measurements[33] was applied to the present

system, the individual parameters, B_d, β, and f_2 could be determined as seen in Figure 2. The resulting values are shown in Table I.

The temperature and concentration dependence of the diffusion coefficient was analyzed by the free-volume theory of Vrentas, Duda and their associates.[37-41] The self-diffusion coefficient of a penetrant, D_1, was expressed by the following equation:

$$D_1 = D_{01}\exp\left[-\frac{\gamma(\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*)}{\hat{V}_{FH}}\right] \qquad (6)$$

Here, $\hat{V}_i^*$ is the specific critical hole free volume of component i; $\hat{V}_{FH}$, the average hole free volume per gram of the dodecane/polystyrene system; ω_i, the mass fraction of component, i; and γ, an overlap fraction (between 0.5 and 1) that is introduced because the same free volume is available to more than one molecule. The quantity, ξ, can be determined from eq. (7):

$$\xi = \tilde{V}_1^*/\tilde{V}_2^* = \hat{V}_1^* M_1/\hat{V}_2^* M_2 \qquad (7)$$

Here, $\tilde{V}_1^*$ is the critical molar volume of dodecane; $\tilde{V}_2^*$, the critical molar volume of jumping units of polystyrene; M_1, the dodecane molecular weight; and M_2 the molecular weight of the polystyrene jumping unit.

The specific hole free volume of the dodecane/polystyrene, $\hat{V}_{FH}$, is given by eq. (8):

$$\frac{\hat{V}_{FH}}{\gamma} = \left(\frac{K_{11}}{\gamma}\right)\omega_1(K_{21} + T - T_{G_1})$$

$$+ \left(\frac{K_{12}}{\gamma}\right)\omega_2(K_{22} + T - T_{G_2}) \qquad (8)$$

Here, K_{11} and K_{21} are dodecane free-volume param-

Table I Parameters of the Fujita Diffusion Model [Eq. (5)]

	Temperature (°C)	
	120	140
log D_0 (cm²/s)	−8.60	−7.57
f_2 [a]	0.0824	0.0888
B_d	0.6985	1.0311
β	0.7309	0.2199

[a] f_2 from PVT data of pure cross-linked polystyrene.[33]

eters, and K_{12} and K_{22}, polystyrene free-volume parameters. These parameters were determined for the dodecane/cross-linked polystyrene system by following the procedures previously suggested by Vrentas et al.[42,43]

The critical hole free volumes, $\hat{V}_i^*$, were replaced by the specific volumes at 0 K, $\hat{V}_i(0)$, which were estimated by group contribution theory.[44] The resulting values of $\hat{V}_1^*$ and $\hat{V}_2^*$ were 1.071 and 0.85 cm^3/g, respectively.

Values of K_{12}/γ and $K_{22} - T_{g2}$ were determined using the shift parameters of the WLF equation, $C_1 = 14.8$ and $C_2 = 48.3$, representing the viscoelastic behavior of cross-linked polystyrene.[45] The resulting values were $K_{12}/\gamma = 5.16 \times 10^{-4}$ cm^3/g K and $K_{22} - T_{g2} = -324.7$ K.

Values of K_{11}/γ and $K_{21} - T_{g1}$ were determined using the viscosity data of dodecane. The value of T_{g1} was determined based on the report of Barlow et al.[46] The resulting values of K_{11}/γ and $K_{21} - T_{g1}$ were 0.001325 and -79.03 cm^3/g K, respectively.

The values of D_{01} and ξ were determined as 4.6 $\times 10^{-5}$ cm^2/s and 0.41, respectively, using the self-diffusion coefficient data of the dodecane/polystyrene system. As the diffusion process is dominated by free-volume effects, the variation of the solvent self-diffusion coefficient with temperature and concentration can be approximated by incorporating the activation energy term, E, into an effective constant preexponential factor, D_{01}.

Figure 3 represents the temperature and concentration dependence of the dodecane self-diffusion coefficient as measured experimentally and predicted from the Vrentas–Duda's free-volume model. The experimental results were in good agreement with the theory in the rubbery region. The activation
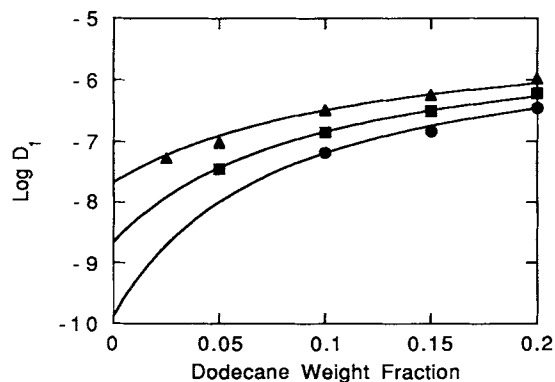

Figure 3 Dodecane self-diffusion coefficient as a function of dodecane weight fraction in polystyrene samples at temperatures of (●) 105, (■) 120, and (▲) 140°C. The solid curves indicate the Vrentas–Duda model description.
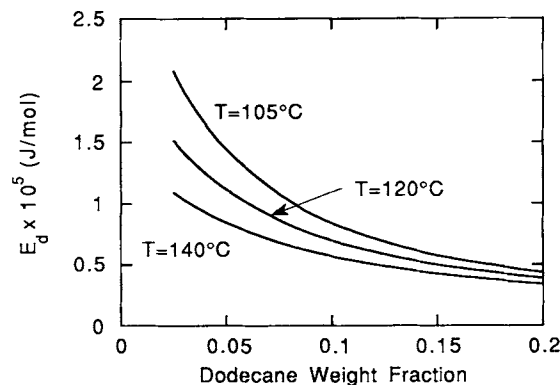

Figure 4 Activation energy of dodecane self-diffusion coefficient as a function of dodecane weight fraction in polystyrene samples at temperatures of 105, 120, and 140°C.

energy can be calculated using eq. (9):

$$E_d = RT^2 \left(\frac{\partial \ln D_1}{\partial T} \right)_{P,\omega_1} \tag{9}$$

It was found that the value of E_d was a function of temperature and concentration as shown in Figure 4.

Diffusion Coefficient Below Glass Transition Temperature

In the limit of zero dodecane concentration, the temperature dependence of the self-diffusion coefficient below the glass transition temperature, T_{g2}, was expressed by the Vrentas and Duda theory.[47-49] Obviously, the temperature dependence of the dodecane free volume below T_g is the same as that above T_g, whereas that of the polystyrene free volume is quite different above and below T_g because of the volume frozen in the glassy state.

The volume contraction attributed to the glass transition was expressed by the parameter λ:

$$\lambda = \frac{\alpha_{2g} - (1 - f_2^G)\alpha_{C_2}}{\alpha_2 - (1 - f_2^G)\alpha_{C_2}} \tag{10}$$

Here, the fractional free volume of polymer at T_{g2}, f_2^G, was determined to be 0.075 from PVT measurements.[33] Using three thermal expansion coefficients corresponding to rubbery, glassy, and crystalline states, $\alpha_2 = 5.21 \times 10^{-4}$ °C^{-1}, $\alpha_{2g} = \alpha_{C2}$

$= 2.3 \times 10^{-4} \ {}^{\circ}C^{-1}$, determined from the PVT behavior of the dodecane/polystyrene system, the term λ was calculated as 0.056. As the value of parameter λ was close to zero, the effects of concentration and temperature on the free volume were negligible. Therefore, the diffusion coefficient below the glass transition temperature was assumed constant as that at the glass transition temperature of the system or $3.16 \times 10^{-11} \ cm^2/s$ as shown in Figure 5.

Determination of Mutual Diffusion Coefficient

For isothermal diffusion in dodecane/polystyrene, the mutual diffusion coefficient, D_{12}, was related[37] to the self-diffusion coefficients, D_1 and D_2. For low dodecane concentrations when D_1 is much larger than D_2, the mutual diffusion coefficient can be determined from the self-diffusion coefficient according to the following expression[37,50]:

$$D_{12} = \frac{D_1 \rho_2 \hat{V}_2 \rho_1}{RT} \left(\frac{\partial \mu_1}{\partial \rho_1} \right)_{T,P} \qquad (11)$$

Here, ρ_2 is the density of polystyrene; ρ_1, the density of dodecane; and $\hat{V}_2$, the specific volume of polystyrene. Comparison of the approximate calculations and the experimental data for the toluene–polystyrene system[51] suggested that eq. (11) can be used for predictive purposes over a wide range of concentrations.

The dodecane chemical potential, μ_1, can be expressed in terms of the Flory–Huggins mixing theory that includes the elastic contribution of the cross-
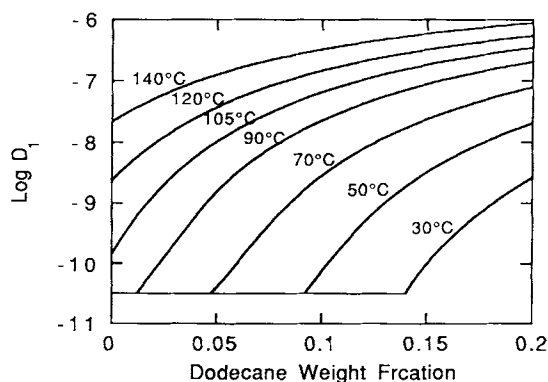

Figure 5 Concentration and temperature dependence of dodecane self-diffusion coefficient in polystyrene samples both in rubbery and glassy states, described by the hole free-volume model at varying temperatures.
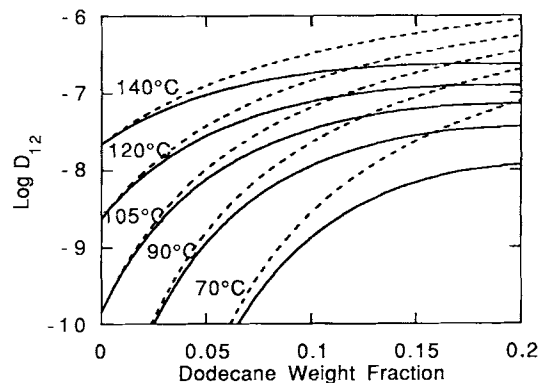

Figure 6 Mutual (solid curves) and self-diffusion coefficient (dashed curves) as a function of dodecane weight fraction in polystyrene samples at varying temperatures from 70 to 140°C.

linked polystyrene:

$$\mu_1 - \mu_{10} = RT \left[\ln(1 - v_2) + v_2 + \chi_1 v_2^2 \right.$$
$$\left. + \frac{M_1 \hat{V}_1}{\hat{V}_2 \bar{M}_c} \left(1 - 2\frac{\bar{M}_c}{M} \right) \left(\frac{1}{2} - \frac{1}{3} v_2^{2/3} \right) \right] \qquad (12)$$

Here, v_2 is the volume fraction of the polymer component; χ_1, the dodecane–polystyrene interaction parameter; M_1, the dodecane molecular weight ($=170$ g/gmol); and $\bar{M}_c$, the molecular weight between cross-links in polystyrene ($=5100$ g/gmol), as determined in a previous publication.[31] Substitution of eq. (12) into eq. (11) led to eq. (13), which was used to determine the mutual diffusion coefficient:

$$D_{12} = D_1 v_2 \left[v_2(1 - 2\chi_1 v_1) \right.$$
$$\left. + \frac{M_1 \hat{V}_1}{\bar{M}_c \hat{V}_2} v_1 \left(\frac{1}{2} - \frac{1}{3} v_2^{-2/3} \right) \right] \qquad (13)$$

Parameters χ_1, $\hat{V}_1$ (cm^3/g), and $\hat{V}_2$ (cm^3/g) were expressed as a function of temperature (expressed in °C)[31,33] by eqs. (14)–(16):

$$\chi_1 = 1.7131 - 0.00575T \qquad (14)$$

$$\hat{V}_1 = 1.3081 + 1.294 \times 10^{-3}T$$
$$+ 1.822 \times 10^{-6}T^2 \qquad (15)$$

$$\hat{V}_2 = 0.9166 + 5.8419 \times 10^{-4}T \qquad (16)$$

Figure 6 represents the calculated mutual diffusion coefficient as a function of dodecane concentration at various temperatures.

CONCLUSIONS

The self-diffusion coefficient of dodecane in cross-linked polystyrene was measured using the pulsed gradient spin echo NMR spectroscopy. Based on the free-volume models of Fujita and Vrentas–Duda, the description of the concentration and temperature dependence of the diffusion coefficient could be determined accurately from the experimentally measured diffusion data. The principal advantage of the Vrentas–Duda free-volume model is that the self-diffusion coefficient can be predicted over a wide range of temperatures and concentrations. Equation (11) was used to correlate the mutual and self-diffusions in conjunction with the thermodynamic expression for the dodecane/polystyrene system, as it has been found before[51] that this equation is valid for solvent weight fractions as high as 0.75 and in several solvent/polymer systems.

Above the glass transition temperature, the experimentally determined diffusion data were described well by free-volume models. Below the glass transition temperature, the predicted diffusion behavior based on the hole free-volume model was not supported by the experimental data, as the specific free volume below the glass transition temperature was almost the same as that of the glass transition temperature, T_{g2}. Generally, the diffusion behavior below the glass transition temperature is significantly dependent upon the molecular structure and its formation conditions.

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