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CONCENTRATION AND TEMPERATURE DEPENDENCE OF DIFFUSIONAL DEBORAH NUMBER DURING DODECANE TRANSPORT IN CROSSLINKED POLYSTYRENE

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Abstract – The diffusional Deborah number, De, defined as the ratio of characteristic relaxation time to characteristic diffusion time was determined as a function of concentration and temperature in the dodecane transport process in polystyrene. The characteristic relaxation time was obtained from the viscoelastic properties of dodecane/polystyrene systems measured by a dynamic mechanical analyzer. The characteristic diffusion time was obtained from the concentration and temperature dependence of the diffusion coefficient measured by NMR PGSE method. Above the room temperature the Deborah number changed significantly during isothermal transport process; however, the transport mechanism did not deviate from the Fickian transport as the order of De was still greater than 1. Around the room temperature the transport mechanisms represented by the resulting diffusional Deborah number changed significantly as the order of magnitude approached 1 with the temperature decreasing from 50℃ to the room temperature. The transport mechanism predicted from the diffusional Deborah number was verified by the diffusional exponent, n, of an exponential time-dependence of the penetrant uptake.

Key words: Diffusional Deborah Number, Characteristic Relaxation Time, Characteristic Diffusion Time, Transport Process, Viscoelastic Properties

INTRODUCTION

Characterization of the penetrant diffusion processes in polymeric systems as Fickian, Case II, Super Case II and anomalous transport [Alfrey et al., 1961], has long been of importance due to its growing applications to a variety of fields, e.g. micro-lithography, controlled drug release, and membrane separations. One of the effective ways to determine its phenomenological characteristics is the use of transport kinetics. A generalized expression for the transport kinetics is written as:

$$\frac{M_t}{M_\infty}=kt^n \tag{1}$$

where M_t is the mass of penetrant sorbed at time t, M_∞ is the mass sorbed at long times, k is a constant incorporating characteristics of macromolecule and penetrant system, and n is the diffusional exponent, which is indicative of the transport mechanism. A value of the exponent n of 0.5 implies Fickian diffusion, a value of n of 1 implies Case II diffusion, whereas for values of n of $0.5<n<1$ anomalous transport is implied for planar geometry [Ritger and Peppas, 1987].

The most theoretical approach to define the diffusional characteristics is the use of the diffusional Deborah number, De. This dimensionless group was firstly defined by Vrentas et al. [1975] as the ratio of the characteristic relaxation time of polymer chains to the characteristic diffusion time during the transport process.

$$\mathrm{De}=\frac{\lambda_m}{\tau} \tag{2}$$

Here, λ_m is defined as the mean viscoelastic relaxation time of the polymeric systems where the local solvent concentration continuously changes during transport process:

$$\lambda_m=\frac{\int_0^\infty G\lambda\, d\lambda}{\int_0^\infty G\, d\lambda} \tag{3}$$

and τ is defined as the pure diffusion time during which the solvent penetrates through the polymer sample with the diffusion coefficient, D_{12}:

$$\tau=\frac{L^2}{D_{12}} \tag{4}$$

where L is the sample thickness when the one dimensional diffusion process is assumed, D_{12} is the mutual diffusion coefficient and G the shear modulus of polymeric system. In their analysis, non-Fickian transport is postulated to be observed if the diffusional and molecular relaxational resistances are of the same order of magnitude. The Fickian behavior is reported to be shown in the temperature ranges well above the glass transition temperature or well below the glass transition temperature. In temperatures well above the glass transition temperature, the diffusional Deborah number is estimated to be much less than 1 as the pure relaxation process is much faster than the pure diffusion process, but in temperatures well below the glass transition temperature, the diffusional Deborah number is estimated to be much higher than 1 as the pure relaxation process is much slower than the pure diffusion process.

In the actual diffusion process it is difficult to determine the Deborah number and thus, to characterize the diffusion kinetics, as the relaxation and diffusion rates vary with diffusion time due to varying local concentration. The objective of this contribution

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is to represent the behavior of the concentration and temperature dependences of the Deborah number in the actual solvent (dodecane) diffusion in the polymer (polystyrene) system and to correlate the diffusion kinetics predicted from the exponent n in Eq. (1) to that obtained from the diffusional Deborah number defined by Eq. (2).

EXPERIMENTAL

To determine the value of exponent, n, in Eq. (1), dynamic swelling experiments were performed. To determine the diffusion Deborah number, the characteristic relaxation and diffusion times were determined via the viscoelastic and diffusional properties of given systems.

1. Dynamic Swelling Experiments

A sheet of crosslinked polystyrene with crosslinking ratio, X= 0.005 mol divinylbenzene/mol styrene, was prepared. The reaction conditions were described elsewhere [Kim et al., 1993]. Dynamic swelling experiments were performed in dodecane at temperatures of 58, 70, 90, 105 and 120°C to investigate the temperature effect on the swelling behavior. The sample thickness was 1 mm and the aspect ratio (the ratio of sample length to thickness) was about 15. The samples were periodically removed from the constant temperature bath, blotted dry, and weighed until equilibrium (constant weight).

2. Viscoelastic Property Measurement

Eight dodecane/polystyrene systems containing dodecane at weight fractions of 0.0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2, were prepared to determine their viscoelastic behavior. The samples were allowed to absorb penetrant up to their corresponding equilibrium mass uptake in order to achieve uniform penetrant concentration at different temperatures. The uniformity of concentration distribution was confirmed by FT-IR spectroscopy. The glass transition temperature of each polystyrene system was determined using a special PVT apparatus (Gnomix Research, Boulder CO) measuring the specific volume under controlled cooling rates of 2°C/min [Kim et al., 1994].

Dynamic mechanical experiments were performed using a dynamic mechanical analyzer (Model 983 DMA, DuPont, Wilmington, DE) with a vertical clamp mode. Samples were cut into rectangular shapes of typical dimensions of 50×10×2.5 mm using a 16" motorized band saw (Delta, Memphis, TN) and surfaces were smoothed with a fine file. Samples had uniform faces and square edges. Each sample was coated with silicone oil to minimize dodecane release at high temperatures and then stored in a container for a week at room temperature. The oscillation amplitude was 0.4 mm. For the study of temperature dependence of complex shear moduli, $G^*(\omega)$, the experiments were performed at 1 Hz with a heating rate of 3°C/min. Liquid nitrogen was used to provide cooling in order to measure moduli below room temperature. For the study of frequency dependence of complex shear moduli, the experiments were performed by scanning the frequency at isothermal conditions. Isotherms were measured from 30°C below the glass transition temperature to 30°C above the glass transition temperature at intervals of 3°C. The frequencies chosen for this experiment were 0.03, 0.05, 0.1, 0.2, 0.5, 1, 2, and 4 Hz.

3. Self Diffusivity Measurement using PGSE-NMR Spectroscopy

Samples were prepared with dodecane at five different dodecane concentrations of 0.0, 5.0, 10.0, 15.0, and 20.0 weight % of the total mixture. A cork borer was used to punch out a stack of samples. The final samples had diameters of 6 mm and thickness ranging from 0.7 to 0.8 mm. The discs were placed in an NMR tube with a glass rod. Each tube was then sealed with Teflon tape to prevent solvent evaporation. The optimum height of the sample stack was about 8 mm.

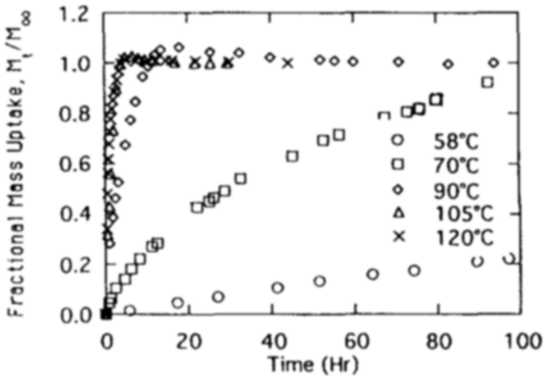

Fig. 1. Fractional dodecane mass uptake, M_t/M_∞ as a function of diffusion time at various temperatures, 120, 105, 90, 70 and 58°C.

Table 1. Temperature dependent transport kinetics determined from experimental data fitted to Eq. (1)

Penetrant transport temperature (°C)	Diffusional exponent, n, analyzed from the experimental data		
	n	Lower 95% statistical confidence	Upper 95% statistical confidence
58	0.81	0.79	0.83
70	0.69	0.67	0.71
90	0.65	0.57	0.72
105	0.62	0.43	0.82
120	0.58	0.48	0.67

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

RESULTS AND DISCUSSION

1. Temperature Dependence of Dynamic Swelling Experiments

Fig. 1 shows the experimental results of fractional dodecane uptake, M_t/M_∞, as a function of time. As expected, the transport rate increased with increasing swelling temperature. The values of the exponent, n, which characterize the diffusion kinetics were determined from the slope of the plot of log M_t/M_∞ vs. log t. As shown in Table 1, the values of exponent, n, increased from 0.58 to 0.81, as the temperatures decreased from 120°C to 58°C. This indicates that the diffusion mechanism changed from Fickian to Case II, as temperature decreased to room temperature passing through the glass transition temperature. The polymeric systems remain in rubbery state at temperatures of 120°C and 105°C, as

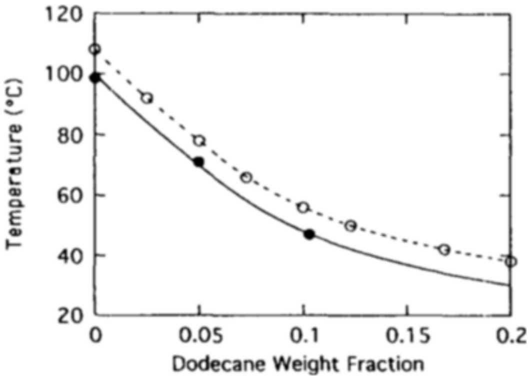

Fig. 2. Glass transition temperature of dodecane/polystyrene systems as a function of dodecane weight fraction. Open circles denote the temperature at the maximum loss peak from DMA measurement, whereas filled circles indicate glass transition temperature from PVT measurements.

the glass transition temperature of the undiluted polystyrene is 100℃. At these two temperatures the diffusion mechanism is very similar to the Fickian, because the rate of macromolecular relaxation is negligible compared to that of pure diffusion. But the state of polystyrene changes from glassy to rubbery at 90, 70, and 58℃ due to the dodecane dilution effect during the transport process. At these temperatures, the diffusion process is significantly affected by the macromolecular relaxation contribution, illustrating the characteristics of the non-Fickian behavior.

2. Concentration and Temperature Dependence of Viscoelastic Properties

Fig. 2 shows the concentration dependence of glass transition temperature for the dodecane/polystyrene systems. The glass transition temperature of dodecane containing polystyrene decreased with increasing dodecane concentration due to the plasticization effect. For each concentration, the glass transition temperature determined from the PVT measurement was about 8℃ lower than the corresponding maximum loss peak of complex shear modulus.

Fig. 3 shows the viscoelastic isotherms for the dodecane-free polystyrene sample. Based on the glass transition temperatures of given systems, the isotherms were collected from T_g-30 to T_g+30℃ for each concentration. Above T_g, the isotherms were well superposed, but below T_g the superposition was somewhat arbitrary because the magnitude of G′ or G″ did not change significantly. Because of the equivalent effect of time and temperature, the data taken at different temperatures could be superimposed on the data taken at a specified reference temperature, merely by shifting individual curves consecutively along the log ω axis about the reference temperature (glass transition temperature). The time-temperature superposition to produce master curves of complex shear moduli for the samples including different compositions resulted in the associated log a_T shift factors as shown in Fig. 4. Physically, the parameter, a_T, indicates the ratio of monomeric friction coefficient in the current temperature, T, to that in the reference temperature, T_0 [Ferry, 1980]. The time-temperature superposition requires that the same log a_T shift be applied to both the G′ and G″ isotherms.

Continuous viscoelastic spectra can be approximated to any desired accuracy by discrete spectra. The correlations in terms of discrete viscoelastic spectra are given below [Ferry 1980]:

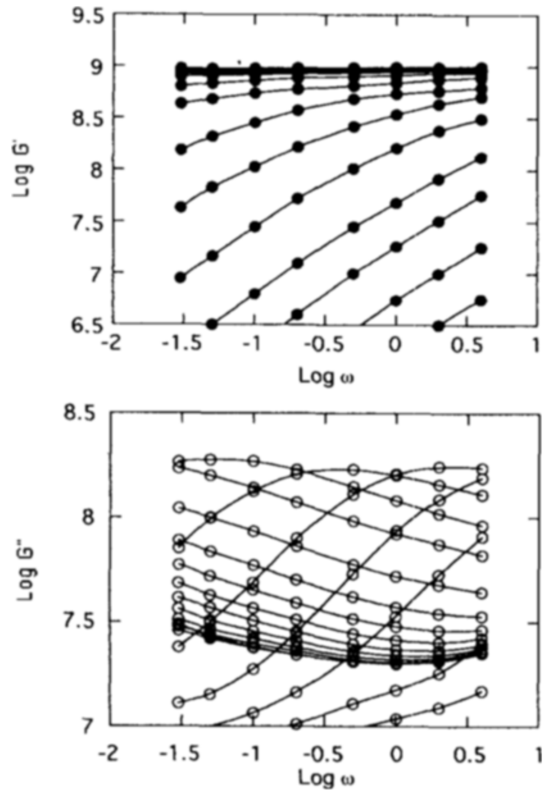

Fig. 3. Isotherms of shear storage (a) and loss (b) moduli for undiluted polystyrene from T_g-30°C to T_g+30°C in intervals of 3°C.

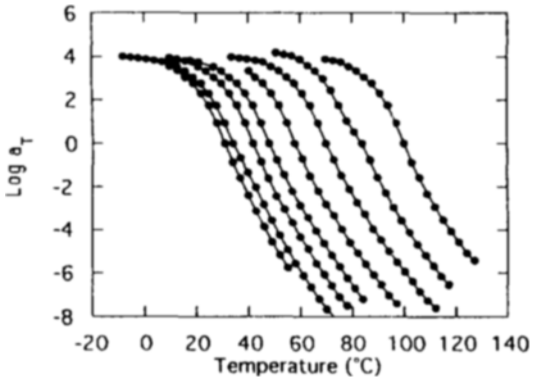

Fig. 4. Temperature dependent shift factors, log a_T, for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from right to left) determined with respect to the reference temperature of the glass transition temperature of each system.

$$G'(\omega)=\sum_i H_i \frac{\lambda_i\omega^2}{1+(\lambda_i\omega)^2} \qquad (5)$$

$$G''(\omega)=\sum_i H_i \frac{\omega^2}{1+(\lambda_i\omega)^2} \qquad (6)$$

where λ_i and H_i are discrete relaxation time and corresponding spectrum element, respectively. The correlation between H_i and λ_i was obtained by minimizing the difference between the experimentally determined dynamic moduli G′(ω) and G″(ω) and the estimated properties as in Eqs. (5) and (6) [Bird et al., 1987].

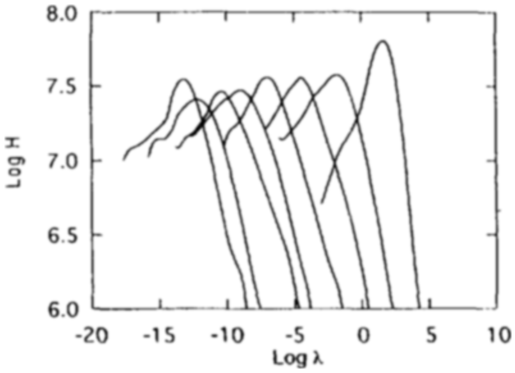

Fig. 5. Discrete relaxation spectra of dodecane/polystyrene systems at 100°C for varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from right to left).

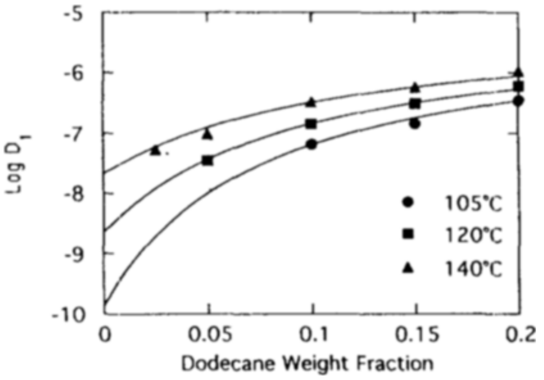

Fig. 6. Dodecane self-diffusion coefficient as a function of dodecane weight fraction in polystyrene samples at temperatures of 105, 120, and 140°C. The solid curves indicate the Vrentas-Duda model description.

The recalculated moduli, G′ and G″ from the discrete relaxation spectrum were fitted well to the experimentally determined moduli for undiluted polystyrene around transition zone. Fig. 5 shows the relaxation spectra for each system at the reference temperature of 100℃. As expected, the relaxation spectrum shifted significantly to shorter times with increasing dodecane concentration.

3. Temperature and Concentration Dependence of Diffusion Coefficient

The self-diffusion coefficient was determined by plotting the logarithm of the attenuated echo height versus the duration of field gradient pulse, δ. In Fig. 6, filled circles represent the diffusion coefficients of dodecane determined from this measurement as a function of dodecane weight fraction for three different temperatures, 105, 120, and 140℃.

The temperature and concentration dependences of the diffusion coefficient are known to be well described by the free volume theory of Vrentas et al. [1980]. The self-diffusion coefficient of a penetrant, D_1, is described according to Eq. (7):

$$D_1 = D_{01}\ \exp\left[-\frac{\gamma(\omega_1\hat{V}_1{}^* + \omega_2\xi\hat{V}_2{}^*)}{\hat{V}_{FH}}\right] \tag{7}$$

Here, $\hat{V}_i{}^*$ is the specific critical hole free volume of component i, $\hat{V}_{FH}$ is the average hole free volume per gram of mixture, ω_i is the mass fraction of component, i, and γ is an overlap fraction (between 0.5 and 1) which is introduced because the same free volume is available to more than one molecule. Finally, the quantity, ξ, is defined according to Eq. (8):

$$\xi = \tilde{V}_1{}^*/\tilde{V}_2{}^* = \hat{V}_1{}^*M_1/\hat{V}_2{}^*M_j \tag{8}$$

Here $\tilde{V}_1{}^*$ is the critical volume of penetrant per mole of penetrant, $\tilde{V}_2{}^*$ is the critical volume of jumping units per mole of jumping units, M_1 is the molecular weight of the penetrant, and M_j is the molecular weight of a jumping unit.

The specific hole free volume of the mixture $\hat{V}_{FH}$ is given by Eq. (9).

$$\frac{\hat{V}_{FH}}{\gamma} = \left(\frac{K_{11}}{\gamma}\right)\omega_1(K_{21} + T - T_{g1}) + \left(\frac{K_{12}}{\gamma}\right)\omega_2(K_{22} + T - T_{g2}) \tag{9}$$

Here, K_{11} and K_{21} are free volume parameters for the penetrant, K_{12} and K_{22} are free volume parameters for the polymer and T_{gi} is the glass transition temperature of i component.

The parameters of Eqs. (7) and (9) were estimated as follows [Vrentas et al., 1980]. The critical hole free volumes, $\hat{V}_1{}^*$, $\hat{V}_2{}^*$, were estimated by group contribution theory [Krevelen, 1976] to be 1.071 cm³/g and 0.85 cm³/g, respectively. Values of K_{12}/γ and K_{22}-T_{g2} were determined to be 5.16×10^{-4} cm³/g K and −324.7 K, respectively, using the viscoelastic behavior of crosslinked polystyrene. Values of K_{11}/γ and K_{21}-T_{g1} were determined to be 0.001325 cm³/g K and −79.03 cm³/g K, respectively, using the viscosity data of dodecane. Values of D_{01} and ξ were determined to be 4.6×10^{-5} cm²/s and 0.41, respectively, using the self diffusivity data. In Fig. 6, solid curves represent the temperature and concentration dependences of the self-diffusion coefficients determined theoretically from the Vrentas-Duda free volume theory.

In the limit of zero dodecane concentration, the temperature dependence of the self-diffusion coefficient below the glass transition temperature, T_{g2}, was also expressed according to the Vrentas and Duda theory. Obviously, the temperature dependence of the dodecane free volume below T_g is the same as that above T_g, while that of the polystyrene free volume is quite different above and below T_g because of the volume frozen-in in the glassy state. In our previous analysis [Kim et al., 1994], the volume contraction parameter attributed to the glass transition was close to zero, as the effects of concentration and temperature on the free volume were negligible. Therefore, the diffusion coefficient below the glass transition temperature in this analysis, 3.16×10^{-11} cm²/s, was estimated the same as that at the glass transition temperature of the system.

For isothermal diffusion in polymer/solvent systems containing a low penetrant concentration, where solvent self-diffusion coefficient, D_1 is generally much larger than polymer self-diffusion coefficient, D_2, the mutual diffusion coefficient is related to the self-diffusion coefficient according to the following expression [Duda et al., 1979]:

$$D_{12} = \frac{D_1\rho_2V_2\rho_1}{RT}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_{T,P} \tag{10}$$

Here, ρ_2 is polymer density, ρ_1 is solvent density, and V_2 is specific volume of polymer. Comparison of approximate calculations and experimental data for the toluene-polystyrene system [Duda et al., 1979] suggests that Eq. (10) is valid over a large range of concentrations.

The change of penetrant chemical potential, μ_1, in Eq. (10) may be described by the Flory-Huggins mixing theory including the

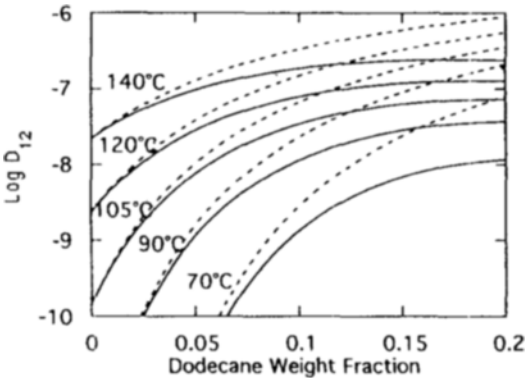

Fig. 7. Mutual (solid curves) and self-diffusion coefficient (dashed curves) as a function of dodecane weight fraction in polystyrene samples at varying temperatures from 70 to 140°C.

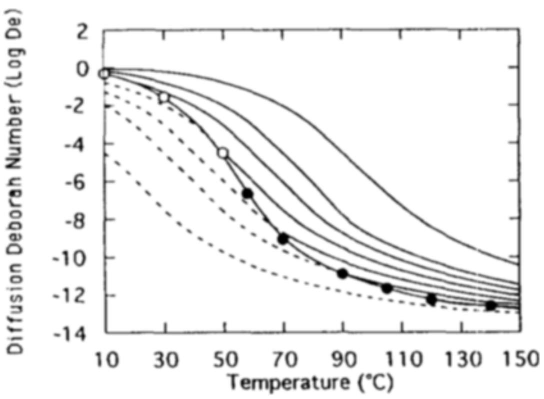

Fig. 8. Diffusional Deborah number as a function of dodecane concentration and temperature. Thicker solid curves represent diffusional Deborah number corresponding to the equilibrium dodecane concentration. Dashed curves represent imaginary diffusion Deborah number extrapolated to the supersaturated solvent concentration. Filled circles indicate the Deborah numbers determined from experimentally obtained equilibrium concentration and open circles the Deborah numbers from the equilibrium concentration extrapolated from other temperatures.

elasticity contribution of the crosslinked polymer. Fig. 7 represents the self (dashed curves) and mutual diffusion coefficient (solid curves) as a function of dodecane concentration for varying temperatures.

4. Concentration and Temperature Dependence of Diffusional Deborah Number

As mentioned before, the diffusional Deborah number is a function of concentration for an isothermal transport process because of the concentration dependence of the diffusion coefficient and viscoelastic relaxation time. The concentration and temperature dependences of the diffusional Deborah number were determined by the following procedure. First, the average relaxation time for the dodecane-free polystyrene, λ_{avg}, was obtained using Eq. (3), and the H_i ($\equiv G_i$) vs. λ_i data in Fig. 5. Then multiplication of the temperature dependent shift function, a_T, for each dodecane containing sample to the average relaxation time λ_{avg}, resulted in the calculation of the mean relaxation time, λ_m, corresponding to each concentration and temperature. The diffusion time τ was obtained according to Eq. (4) in which the sample thickness, $L=0.1$ cm, and the concentration and temperature-dependent mutual diffusion coefficients shown in Fig. 7 had been applied. By dividing λ_m by τ according to Eq. (2), we obtained the diffusional Deborah number as a function of concentration and temperature. The final behavior is shown in Fig. 8. The thicker solid curves represent the diffusional Deborah number corresponding to the equilibrium dodecane concentration within the system.

The actual diffusion occurs within these boundaries because the solvent concentration cannot exceed the equilibrium value. The dashed curves beyond the boundary represent the imaginary diffusional Deborah number extrapolated to the supersaturated solvent concentration. At the constant temperatures, the diffusional Deborah number decreased as diffusion continued following the vertically downward line. In the temperature range from 30 to 150℃, the relaxation rate was much higher than the diffusion rate, as all values of the diffusional Deborah number are shown to be below one. The decreasing relaxation rate exceeded the decreasing diffusion rate as the temperature decreased and the dodecane concentration increased, approaching the diffusion rate below the room temperature. Around the room temperature the values of the diffusional Deborah number were near unity. Another characteristic of the Deborah number in Fig. 8 was that the ratio of the relaxation to the diffusion rate did not change significantly as the temperature deviated the glass transition temperature even in the presence of dodecane. In our case, as the temperature deviated from the glass transition temperature to either far beyond or below the glass transition temperature, the values of the diffusional Deborah number approached the critical values of -12.5 and 0, respectively, in the logarithmic scale.

As a result, the transport mechanism characterized by Deborah number was in good agreement with that obtained from the diffusional exponent of n. In the dodecane/polystyrene system, the transport kinetics was predicted as near-Case II in room temperature, but as Fickian around and above the glass transition temperature. For the record, other similar reports supporting the present results were presented by Nicolais et al. [1979] who showed that the diffusion mechanism changed from Fickian to Case II in a n-hexane/polystyrene system, as the experimental temperatures decreased to the room temperature.

CONCLUSIONS

The diffusional Deborah number, De, is an indication of the transport kinetics, and has been determined for dodecane/polystyrene systems. The characteristic relaxation and diffusion times defining De were obtained from the fundamental viscoelastic and diffusional properties measured using dynamic mechanical analysis and PGSE-NMR spectroscopy, respectively. The diffusional Deborah number changed significantly in the isothermal transport process, as the solvent concentration changed with diffusion time. The transport kinetics indicated by the diffusional Deborah number changed from Fickian to non-Fickian as the temperature changed from above the glass transition temperature to the room temperature, and its general trend was in a good agreement with the experimental observations.

NOMENCLATURE

a_T : temperature dependent shift factor
De : diffusional Deborah number [cm^2/s]
D_a : self-diffusion coefficient for component a [cm^2/s]

D_{12} : mutual diffusion coefficient [cm^2/s]
D_{01} : concentration independent solvent self-diffusion coefficient [cm^2/s]
G : pulsed field gradients [G/cm]
G_0 : steady field gradients [G/cm]
G' : storage shear modulus [Pa]
G'' : loss shear modulus [Pa]
H_i : discrete relaxation magnitude [Pa]
K_{11} : the first free volume parameter of penetrant [cm^3/g K]
K_{21} : the second free volume parameter of penetrant [cm^3/g K]
K_{12} : the first free volume parameter of polymer [cm^3/g K]
K_{22} : the second free volume parameter of polymer [cm^3/g K]
k : sorption rate constant
L : thickness of polymer slab [cm]
M_1 : penetrant molecular weight [g/gmol]
$\bar{M}_c$: average molecular weight between crosslinks [g/crosslinking unit]
M_j : molecular weight of a jumping unit [g/unit]
M_t : solvent mass uptake at time t [g]
M_∞ : equilibrium solvent mass uptake [g]
n : sorption rate exponent
R : gas constant [atm l/gmol K]
t : laboratory time scale [sec]
T : temperature [℃]
T_0 : reference temperature [℃]
T_g : glass transition temperature [℃]
$\hat{V}_a$: specific volume of component a [cm^3/g]
$\hat{V}_a^*$: specific critical hole free volume of component a [cm^3/g]
$\hat{V}_{FH}$: average hole free volume per gram of mixture [cm^3/g]
χ_1 : polymer-solvent interaction parameter
δ : duration of field gradient pulse [ms]
γ : overlap fraction
λ_{avg} : average viscoelastic relaxation time [sec]
λ_i : discrete viscoelastic relaxation time [sec]
λ_m : characteristic viscoelastic relaxation time [sec]
μ_a : chemical potential per unit mass of a component a [atm l/g]
ρ : total mass density [g/cm^3]
ρ_a : mass density of component a [g/cm^3]
τ : characteristic diffusion time [s]
τ_p : time separation between gradient pulses [μs]
ω_a : weight fraction of component a, ρ_a/ρ

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