Nuclear Magnetic Resonance Observation of Cyclohexane Self-Diffusion in Concentrated Polybutadiene Solutions

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ABSTRACT: The coefficient of self-diffusion of cyclohexane, in concentrated solutions of polybutadiene, was measured using a pulsed magnetic field gradient method. The polymer volume fraction was varied from 0.2 to 0.95, and the temperature range of observation was 260 K < T < 335 K. The concentration and temperature dependences of the solvent self-diffusion were analyzed according to a free volume description. These two dependences were found to be well described by using either the Fujita or WLF equations or by applying the Vrentas–Duda model. The size of the polymer jumping unit, derived from the Vrentas–Duda approach, was determined.

I. Introduction

This work deals with investigations into properties of local molecular dynamics, observed in solutions of long polymer chains. It is now well established that the terminal relaxation spectrum observed from viscoelastic measurements performed on polymeric systems reflects long-range fluctuations which occur within polymer chains.[1] These are described by introducing the mechanism of chain reptation in one tube.[2] The curvilinear diffusion coefficient D_{cv} of one long chain, along its tube, is the crucial parameter which characterizes the reptational motion. The D_{cv} coefficient is expressed from a local mobility μ_0 which is naturally divided by the number N of monomeric units in one chain; μ_0/N accounts for the displacement of a macromolecule as a whole. The local diffusion coefficient $D_0 = \mu_0 kT$ is clearly a key parameter which governs the terminal relaxation spectrum

$$D_{cv} = D_0/N \tag{1}$$

k is the Boltzmann's constant and T is the temperature of observation. The terminal time T_R is written as:

$$T_R \propto N^2/D_{cv} \tag{2}$$

Temperature or polymer concentration variations induce changes of local diffusional properties which react on long-range fluctuations. Consequently, it is of interest to attempt to characterize the local molecular dynamics in polymer systems, in different ways. It is usually considered that direct observations of segmental motions, at high polymer concentrations, can be complemented by measuring the self-diffusion coefficient of small solvent molecules. However, the local dynamics detected from solvent molecules may be insensitive to the collective character of segmental motions.

In this study, attention is focused upon the properties of polybutadiene–cyclohexane systems. Polybutadiene was chosen because the temperature dependence of the properties of the pure polymer has been extensively studied with a great accuracy by using several experimental approaches.

Thus, in the case of viscoelastic measurements, performed on pure polybutadiene systems, the shift factor a_T, which relates temperature variations to frequency shifts of the storage or the loss moduli, has been shown to vary according to the WLF equation with a temperature variable defined from the difference $T - T_g(\chi_{1,2}) - 55$. This shift factor applies over a broad range of variations of the content $\chi_{1,2}$ of monomeric units which are in a vinyl conformation; a glass transition temperature $T_g(\chi_{1,2})$ is assigned to each vinyl content.[3]

Also, the spin–lattice relaxation rate T_1^{-1} of protons or ^{13}C nuclei attached to polybutadiene chains in a melt has been shown to obey a property of homogeneity with respect to the Larmor frequency ω_0 and to a correlation time τ_c which characterizes segmental motions

$$\omega_0/T_1 = f(\omega_0\tau_c) \tag{3}$$

The temperature dependence of τ_c has been obtained by varying both the Larmor frequency and the temperature.[4] The correlation time τ_c has been shown to obey the temperature dependence given by the shift factor a_T determined from viscoelastic measurements.

More recently, the transverse magnetic relaxation time T_2^c of protons, attached to long polybutadiene chains in concentrated solutions, has been shown to be sensitive to the modulus of temporary elasticity $G_N°$ and to temperature variations according to the following equation:[5]

$$T_2^c = 0.8 \times 10^{-6}(T - T_g(\phi,\chi_{1,2}) - 50)\left(1 + \frac{4.5 \times 10^6}{G_N°\phi^{2.2}}\right) \tag{4}$$

ϕ is the polymer volume fraction and $T_g(\phi,\chi_{1,2})$ is the glass transition temperature of the polymer solution, associated with a chain microstructure defined by the vinyl content $\chi_{1,2}$.

Thus, the temperature difference $T - T_g(\phi,\chi_{1,2}) - T_r$, with T_r about equal to 50 K, is involved in viscoelastic properties as well as in nuclear spin relaxation rates.

The purpose of this work was first to establish the dependence of the self-diffusion coefficient D_s of solvent molecules upon the temperature and the polymer volume fraction ϕ. Then, starting from the well-determined free volume law observed in pure polybutadiene, it was attempted to determine the properties of the solvent molecular mobility, $\mu_s(T)$, measured in polymer solutions. The three main features which are usually taken into consideration to characterize this local dynamics parameter concern (i) the dependence of the $\mu_s(T)$ coefficient upon the free volume, (ii) the expression of the free volume as a temperature function, and (iii) the law of combination of polymer and solvent free volumes.

The pulsed field gradient NMR technique was used to measure the self-diffusion coefficient of cyclohexane. The

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analysis will be discussed according to the WLF–Fujita model and the Vrentas–Duda description.[6-8]

The experimental procedure and samples used to perform NMR measurements are described in section II. The principle of analysis of experimental results is presented in sections III and IV.

II. Experimental Section

The self-diffusion coefficient of the solvent was measured with the pulsed field gradient NMR technique as first described by Stejskal and Tanner.[9] The technique consists of labeling the protons by their Larmor precession frequencies in a spatially varying magnetic field. A magnetic field gradient was applied in the form of two pulses of magnitude G, duration δ, and separation Δ. The following NMR sequence was used: $\pi/2$–$G(\delta)$–π–$G(\delta)$–echo.

If the spins change their position during the time separation Δ, this results in an attenuation of the echo in addition to nuclear magnetic relaxation. The echo amplitude measured at a time 2τ is compared with the initial amplitude $A(0)$

$$\frac{A(2\tau)}{A(0)} = \exp\left(-\frac{2\tau}{T_2} - \gamma_p^2 K(G)\, D_s\right) \tag{5}$$

where γ_p, the NMR gyromagnetic constant of the studied nucleus (here proton), is the ratio of the Larmor pulsation ω_0 to the steady magnetic field $\mathbf{H}_0$; τ is the time interval between the $\pi/2$ and π pulses, and $K(G)$ is a function determined by the pulsed gradient sequence.

The translational self-diffusion coefficient can be determined from the echo attenuation induced by varying the field gradient amplitude and by keeping constant the time interval τ:

$$\frac{A(2\tau)}{A(2\tau,G=0)} = \frac{A(G)}{A(G=0)} = \exp(-\gamma_p^2 K(G)\, D_s) \tag{6}$$

$K(G)$ is given by the relation:

$$K(G) = \delta^2 G^2(\Delta - \delta/3) - \delta G G_0\left(t_1^2 + t_2^2 + \delta(t_1 + t_2) + \frac{2\delta^2}{3} - 2\tau^2\right) \tag{7}$$

G_0 is the constant gradient of the main magnetic field $\mathbf{H}_0$, t_1 and t_2 are respectively the delay between the $\pi/2$ pulse and the first gradient pulse and the delay between the second gradient pulse and the echo: $t_2 = 2\tau - (t_1 + \Delta + \delta)$.

All measurements were performed using a Bruker CXP spectrometer with a measuring frequency of 36 MHz. A home-built apparatus was used to obtain the magnetic gradient pulses. A pair of anti Helmholtz coils provides the linear gradient field. The gradient intensity G is determined by the current intensity I in the coils and by a constant G_n depending on the coil geometry: $G = G_n I$. Gradient calibration was obtained at low intensity by measuring the width of the spin echo produced by a cylindrical sample and the apparatus working in steady gradient mode. At high intensity, the field gradient was calibrated by using distilled water as a test sample and by measuring its diffusion coefficient with a short gradient pulse delay δ. Replacing G and G_0 by the expressions $G_n I$ and $G_n I_0$ in eq 8, G_n and I_0 were calibrated by fitting the linear representation of the echo amplitude: $(1/I)\ \ln[A(G)/A(G=0)]$ versus I ($I > 0$).

$$\frac{1}{I}\ln\left[\frac{A(G)}{A(G=0)}\right] = -\gamma_p^2 D_s\left[G_n^2\delta^2(\Delta - \delta/3)I - \delta G_n^2 I_0\left(t_1^2 + t_2^2 + \delta(t_1 + t_2) + \frac{2\delta^2}{3} - 2\tau^2\right)\right] \tag{8}$$

I_0 was obtained from the calculated ordinate at the origin divided by the slope of the straight line; this ratio is independent of G_n. The constant G_n was determined from the slope and the known value of the coefficient diffusion of this test sample: $D_s = 2.266 \times 10^{-5}$ cm^2 s^{-1} at 298 K.[10] As a result of these calibration procedures the value of G_n was 14.01 ± 0.04 G/cm/A and that of G_0 was 0.20 ± 0.05 G/cm. To measure cyclohexane self-diffusion in polybutadiene, δ was kept constant (δ = 6 ms) and G was varied within the range 0–80 G/cm. The delay Δ was chosen as long as possible to attenuate the polymer contribution to the spin-echo amplitude. A residual echo due to protonated chains was observed with an amplitude value between 1% and 5% depending on both the concentration and the temperature. To characterize the polymer diffusion properties, polybutadiene–deuterated cyclohexane solutions were prepared. In these solutions no diffusing species, except polymer chains, were detected. The chain self-diffusion coefficient was measured at 335 K. For a solvent volume fraction $v_1 = 0.29$, its value was found to be equal to 1.5×10^{-8} cm^2 s^{-1}, i.e., more than 2 decades smaller than the diffusion coefficient of the protonated solvent in equivalent conditions of concentration and temperature. Consequently, the residual amplitude observed in fully hydrogenated solutions can be described by a constant value N_p over the whole range of gradient intensities used to measure the solvent diffusion.[11] This approximation leads to an error less than 0.1% for the contribution of the solvent to the echo amplitude. Finally, D_s was determined by using the equation

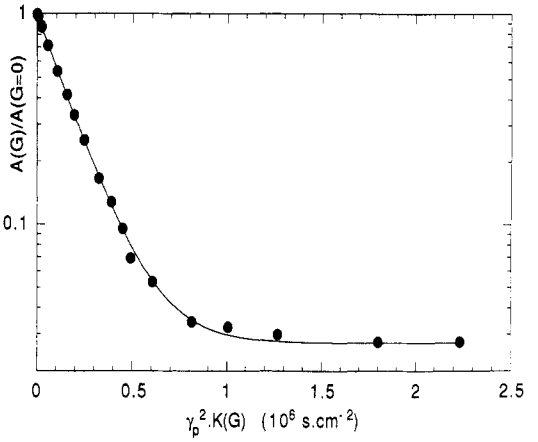

Figure 1. Spin-echo amplitude attenuation. The gradient was increasing from 0 to 25 G cm^{-1}, $\tau = \Delta = 37.5$ ms and $\delta = 6$ ms. The solvent volume fraction (v_1) and the temperature were 0.375 and 335 K, respectively. Experimental data were fitted with eq 9. The polymer contribution (N_p) was found to be equal to 2.75% of the echo amplitude at $G = 0$ and D_s equal to $(5.94 \pm 0.07) \times 10^{-5}$ cm^2/s.

$$A(2\tau,G) = N_p + A_0 \exp(-\gamma_p^2 D_s K(G)) \tag{9}$$

In all experiments, $N_p + A_0$ and $A(2\pi,G = 0)$ were found equal to each other with an accuracy better than 1% and D_s was obtained with an error fit smaller than 2%. Including error bars due to the gradient calibrations and the temperature stability (±0.5 K), the absolute values of the cyclohexane diffusion coefficients are given with an error equal to 5% (Figure 1).

The samples were prepared using a calibrated polybutadiene (polydispersity index $I_p = 1.08$) with 8% vinyl concentration and a molecular weight $M_n = 70\,000$. The polybutadiene was kindly supplied by the Manufactures Michelin. The density of polybutadiene is $d_p = 0.898$ g/cm^3 and the density of cyclohexane is $d_s = 0.776$ g/cm^3 at 293 K. The glass transitions of the samples were investigated by DSC, and T_g's were determined for solutions with a polymer fraction larger than 60%. At low polymer concentration, the solvent crystallization prevents the T_g measurement.

Depending on the model used to analyze experimental results, the solvent concentration was defined either as the volume fraction v_1 of the diffusant (Fujita–Doolittle and WLF cases) or as the solvent weight fraction ω_1 (Vrentas–Duda case).

Temperature variations were carried out over a range of solvent volume fractions going from 5% to 47.5% within a temperature interval ranging from 258 to 344 K. For the highest solvent fractions ($v_1 > 0.5$), a nonnegligible evaporation effect was detected. The isothermal concentration dependence of the self-diffusion coefficient was determined at three temperatures (T = 278, 298, and 335 K) on a more extended range of concentration: $0.05 < v_1 < 1$. At 335 K the actual concentrations were calculated from the absolute amplitudes of the magnetizations $A(0)$ and $A(2\tau,G = 0)$.

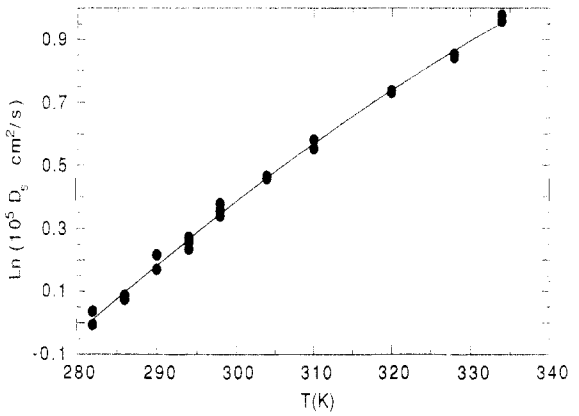

Figure 2. Pure cyclohexane self-diffusion coefficient versus temperature. Data were fitted with eq 10 and T_0 = 298 K. The continuous curve was determined by the values $D_s(T_0) = 1.41 \times 10^{-5}$ cm^2/s, $f_s(T_0) = 0.218$, and $\alpha_s = 9.4 \times 10^{-4}$ K^{-1}.

III. WLF Analysis

The temperature dependence of the solvent diffusion was analyzed according to the WLF equation relative to the self-diffusion coefficient:

$$\mathrm{Ln}[D_s(T,v_1)] = \mathrm{Ln}[D_s(T_0,v_1)] + \frac{B_d}{f_0(v_1)} - \frac{B_d}{f_0(v_1) + \alpha(v_1)(T - T_0)} \quad (10)$$

Let $f_0(v_1)$ denote the solution free volume fraction at the reference temperature T_0 and $\alpha(v_1)$ the fractional free volume expansion factor; a property of linearity was applied to both f_0 and α:

$$f_0(v_1) = (1 - v_1)f_p(T_0) + v_1 f_s(T_0) \quad (11)$$

$$\alpha(v_1) = (1 - v_1)\alpha_p + v_1\alpha_s \quad (11')$$

The p and s indices refer to the polymer and solvent, respectively.

The Fujita–Doolittle equation was used to analyze the concentration dependence at fixed temperature:

$$\mathrm{Ln}[D_s(v_1,T)] = \mathrm{Ln}[D_s(0,T)] + \frac{B_d\beta(T)v_1}{f_p^2 + f_p\beta(T)v_1} \quad (12)$$

v_1 is the solvent volume fraction, $D_s(0,T)$ is the solvent trace diffusion value, and $\beta(T)$ is defined by the difference between $f_s(T)$ and $f_p(T)$. In the following analysis $f_s(T)$ was kept independent of v_1.[12]

III.1. Neat Solvent. Temperature Dependence. The temperature dependence of cyclohexane diffusion was analyzed, considering the WLF equation with a reference temperature T_0 equal to 298 K (Figure 2). A three-parameter fit was used. The solvent free volume parameters $f_s(T_0)/B_d$ and α_s/B_d were found to be equal to 0.22 ± 0.05 and (9.3 ± 4.1) × 10^{-4} K^{-1}. These values agree with the linear temperature dependence proposed by Fujita for cyclohexane free volume parameters: $f_s = 0.217$ at 293 K and $\alpha_s = 7.9 \times 10^{-4}$ K^{-1}.[12] The uncertainty about the value of α_s/B_d determined in this work is due to the weak variation of the diffusion coefficient going from 10^{-5} cm^2 s^{-1} at 282 K to 2.65 × 10^{-5} cm^2 s^{-1} at 334 K. In the next sections, B_d was set equal to 1 and values of f and α were determined from numerical fits.

III.2. Isothermal Concentration Dependence. A more accurate determination of the solvent free volume parameters was obtained from the analysis of the concentration dependence of the solvent diffusion. This dependence was investigated within the solvent volume fraction range going from 0.05 to 1; temperatures were

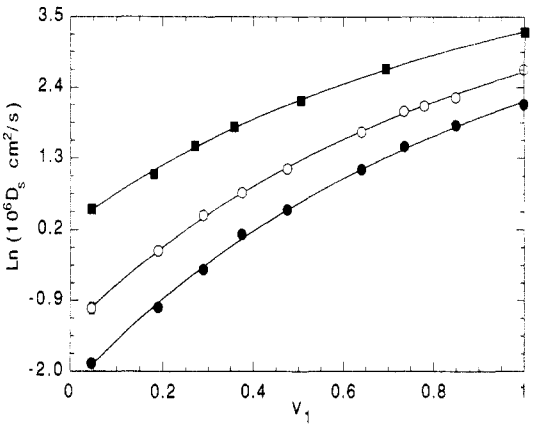

Figure 3. Concentration dependence of cyclohexane diffusion. Temperatures are 278 (●), 298 (○), and 335 K (■). Continuous curves are the best fits of the data analyzed with eq 12.

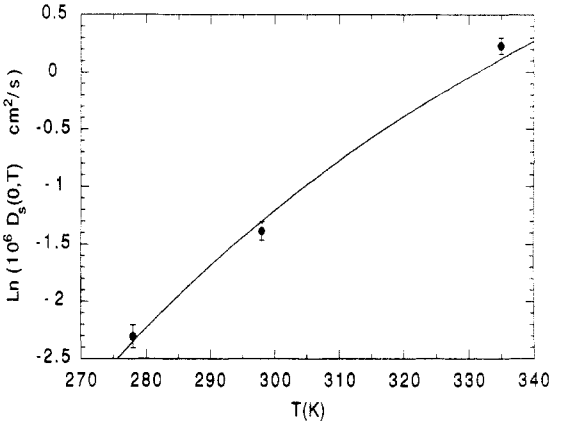

Figure 4. Temperature dependence of the trace diffusivity $D_s(0,T)$. The continuous line was calculated with polymer free parameters previously published (refs 1 and 3).

278, 298, and 335 K (Figure 3). In accordance with the Fujita–Doolittle equation, three parameters were determined: $f_p(T)$, $\beta(T)$, and $D_s(0,T)$, the trace diffusitivity. The temperature dependences of the polymer and solvent free volume fractions were found to obey the linear law:

$$f_{p,s}(T) = f_{p,s}(T_0) + \alpha_{p,s}(T - T_0) \quad (13)$$

with $f_p = 0.118 \pm 0.001$ for $T_0 = 298$ K and $\alpha_s = (7.9 \pm 0.3) \times 10^{-4}$ K^{-1}.

These results agree with f_p and α_p values previously published:[1,3] $f_p = 0.124 \pm 0.005$ at 298 K and $\alpha_p = (7.0 \pm 0.5) \times 10^{-4}$ K^{-1}. The free volume parameters of the solvent were obtained from $\beta(T)$ values; f_s at 298 K and α_s were found to be equal to 0.223 ± 0.004 and (11.8 ± 1.1) × 10^{-4} K^{-1}, respectively. Concerning the trace diffusitivity $D_s(0,T)$, two results can be considered. On the one hand, the translational friction factor ζ_0 of the polymer derived from the ratio $kT/D_s(0,T)$ is equal to (1.64 ± 0.06) × 10^{-7} dyn s cm^{-1} at 298 K; this is in good agreement with the value (1.8 × 10^{-7} dyn s cm^{-1}) derived from mechanical studies of polybutadiene.[1] On the other hand, $D_s(0,T)$ was found to obey the WLF equation describing the viscoelastic properties of the pure polymer, within the temperature range going from 278 to 335 K (Figure 4); variations of the corresponding shift factor are defined as:[1,3]

$$\mathrm{Ln}\, a(T) = \frac{2.303C_1^g(T - T_g)}{C_2^g + (T - T_g)} \quad (14)$$

with $T_g = 174 \pm 2$ K, $C_1^g = 12.5 \pm 1.3$ K^{-1}, and $C_2^g = 50 \pm 10$ K; here, $a(T)$ is equal to the ratio of $D_s(0,T)$ over

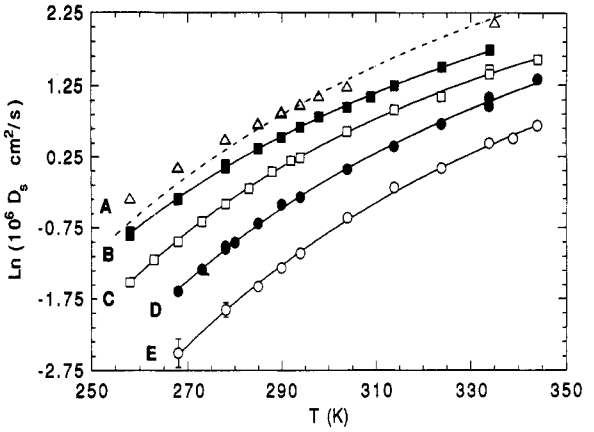

Figure 5. Solvent diffusion temperature dependence at v_1 = 0.05 (○), 0.19 (●), 0.29 (□), and 0.375 (■). Experimental data were fitted with the WLF equation and T_0 was equal to 298 K. The dashed line, relative to the solvent volume fraction v_1 = 0.475 (△), was calculated with eq 10 and the free volume parameters of the pure components determined in section III.2.

$D_s(0,298\ K)$. The WLF equation was found to be insensitive to the difference between the representation of $D_s(0,T)$ or that of $D_s(0,T)/T$.

The free volume parameters determined from the isothermal analysis were used to calculate the temperature dependence of the solvent diffusion in solution, for v_1 = 0.475 (the dashed line in Figure 5). A small deviation of the experimental data from the calculated curve is perceived at low temperature.

III.3. Temperature Dependence. In this section, experimental data were analyzed by keeping the solvent concentration constant and by varying the temperature. The temperature dependence of the solvent diffusion was explored between 268 and 344 K (B–E curves in Figure 5). The WLF equation (eq 10) was considered; the free volume parameters of the solutions determined in this way were called $f_0^T(v_1,T_0)$, T_0 = 298 K, and $\alpha^T(v_1)$. Using a two-parameter fit, a reference diffusion coefficient $D_s(v_1,T_0)$ was chosen for each concentration. Values of free volume parameters describing the diffusion temperature dependence are compared to those calculated from the isothermal behavior in Figure 6. The two sets of data are in reasonable agreement with each other.

IV. Vrentas–Duda Free Volume Diffusion Model

A free volume model with the aim of predicting solvent self-diffusion and mutual diffusion properties in a polymer solution has been proposed by Vrentas and Duda.[8,13]

In that model the self-diffusion coefficient of the solvent is expressed as:

$$\mathrm{Ln}[D_s(\omega_1,T)] = \mathrm{Ln}\,D_0 - \frac{E}{RT} - \gamma\frac{\omega_1 V_1^* + \xi\omega_2 V_2^*}{V_{FH}} \quad (15)$$

with

$$\frac{V_{FH}}{\gamma} = \omega_1\frac{K_{11}}{\gamma}(K_{21} - T_{g1} + T) + \omega_2\frac{K_{12}}{\gamma}(K_{22} - T_{g2} + T) \quad (15')$$

where V_{FH} is the specific hole free volume per gram of solution and V_i^* is the specific hole free volume of component i required for one jump; ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. The D_0 constant depends on the solvent nature, and γ is an overlap factor similar to B_d used in the WLF approach; γ is introduced because a given free volume may be available to more than one molecule. E is the energy per mole that a molecule needs to overcome attractive forces which constrain it to its neighbors.

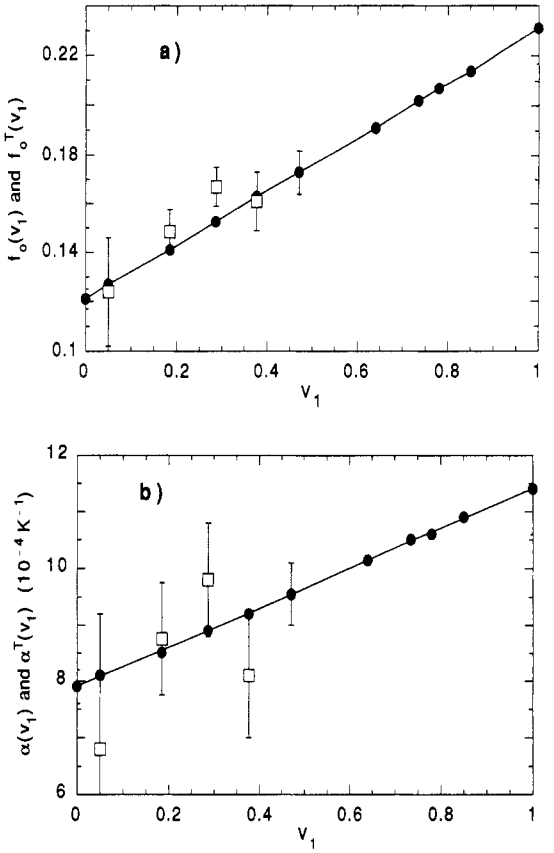

Figure 6. Solution free volume parameters obtained by analyzing diffusion data with eqs 10 and 12: (a) free volume fractions f_0 (●) and f_0^T (□) at 298 K. (b) thermal expansion factors α (●) and α_T (□).

IV.1. Numerical Values of Parameters. The two parameters γ and E are generally assumed to keep a constant value in the domain of concentrated solutions. The point concerning the absolute value of E has been discussed by Zielinski and Duda in polystyrene solutions;[13] the best prediction of solvent diffusion properties has been obtained with E equal to zero.

The specific hole free volumes V_1^* and V_2^* are identified to the specific volumes of the solvent and the polymer at 0 K. The molar volumes at this temperature were calculated following the different methods summarized and analyzed by Haward;[15] V_1^* was found to be equal to 1.008 ± 0.033 cm^3/g according to the molar volume attributed by Blitz and Sugden to each basic component of the cyclohexane molecule. The molar volume of the polymer at 0 K (V_0) can also be estimated from V_g, the molar volume at the glass transition temperature, and the equation $V_g - V_0/V_g = 0.13$.[16] By using this method and the group contribution method, V_2^* was found to be equal to 0.92 ± 0.04 cm^3/g.

The polymer free volume parameters K_{12}/γ and K_{22} were calculated from data reported about polybutadiene,[1,3] according to the relations proposed by Vrentas and Duda:

$$K_{22} - T_{g2} = C_2^g - T_{g2} = -124 \pm 12\ \mathrm{K}$$

and

$$\frac{K_{12}}{\gamma} = \frac{V_2^*}{2.303 C_1^g C_2^g} = (6.5 \pm 0.8) \times 10^{-4}\ \mathrm{K}^{-1}$$

where C_1^g and C_2^g are the free volume parameters of the polymer (eq 14).

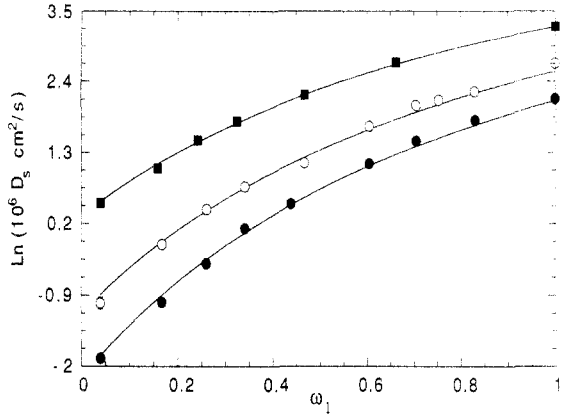

Figure 7. Concentration dependence analyzed with the Vrentas–Duda model. Temperatures are the same as in Figure 3. Values of D_0 (9.7×10^{-4} cm^2/s) and ξ (0.985) were obtained by fitting the diffusion dependence with eq 16.

The parameters D_0, ξ, K_{11}/γ, and $K_{21} - T_{g1}$ were determined by analyzing the solvent diffusion data.

IV.2. Discussion about the ξ Parameter. At a fixed temperature, D_0, ξ, and the product $K_1(T_0) = (K_{11}/\gamma)(T_0 + K_{21} - T_{g1})$ were determined by fitting the concentration dependence of the solvent diffusion with eq 15 in which E is set equal to zero and V_{FH} is expressed as $\omega_1 K_1(T_0) + \omega_2 K_2(T_0)$

$$\mathrm{Ln}[D_s(T_0,\omega_1)] = \mathrm{Ln}\, D_0 - \frac{\omega_1 V_1^* + \xi\omega_2 V_2^*}{\omega_1 K_1(T_0) + \omega_2 K_2(T_0)} \quad (16)$$

The parameter ξ is defined by the ratio $V_1^* M_1 / V_2^* M_{2j}$ where M_1 and M_{2j} are the molecular weights of the solvent and the polymer jumping unit, respectively. The numerical value of the ξ parameter can be estimated in different ways.

(i) It can be simply estimated from two given concentrations, using eq 16

$$\mathrm{Ln}[D_s(T_0,1)] - \mathrm{Ln}[D_s(T_0,0)] = \frac{\xi}{V_{FH}(\omega_1=0)} - \frac{1}{V_{FH}(\omega_1=1)}$$

with the approximation $V_1^* \approx V_2^* \approx 1$. At room temperature, the average free volume per gram V_{FH} is about 0.1 for pure polymer and about 0.25 for the solvent (see section III). From Figure 7, the estimate of ξ is 0.8.

(ii) A more accurate value of ξ was determined by analyzing the entire concentration dependence of the solvent diffusion; three temperatures were considered 278, 298, and 335 K (Figure 7). The three curves can be described by a single set of values of both parameters D_0 and ξ: $D_0 = (9.7 \pm 3.2) \times 10^{-4}$ cm^2/s and $\xi = 0.985 \pm 0.035$. The molecular weight of the polymer jumping unit corresponding to this ξ determination is 93.3, and the ratio M_{2m}/M_{2j} (M_{2m} is the monomer molecular weight) is equal to 0.58. This value is close to that (0.66) obtained for different polymers characterized by high glass transition temperatures (276 K $< T_{g2} <$ 381 K).[14]

Values of $K_1(T_0)$ were also determined in this analysis of the solvent diffusion concentration dependence. A linear dependence of $K_1(T_0)$ against T_0 was observed; it leads to $K_{11}/\gamma = (1.28 \pm 0.16) \times 10^{-3}$ K^{-1} and $K_{21} - T_{g1} = -111.5 \pm 12.5$ K.

(iii) Finally, to predict the value of the parameter ξ, a linear relation between the molar volume (V_{2j}) of the jumping unit of the polymer and its glass transition temperature (T_{g2}) has been proposed:[14]

$$V_{2j} = 0.6224 T_{g2} - 86.95 \quad (17)$$

The T_{g2} glass transition temperature of the polybutadiene sample was measured by DSC and was found to be equal to 175 ± 1 K, in good agreement with previously published values.[1,3] From eq 17 we derived the molecular weight M_{2j} (22.4) and the parameter ξ (4.1) of the cyclohexane–polybutadiene system. The value of ξ predicted in this way is far too high to account for the observed curvature of the solvent diffusion concentration dependence.

As is mentioned in ref 14, the validity of the linear correlation between V_{2j} and T_{g2} is questionable for low glass transition temperatures ($T_{g2} \leq 250$ K). In this work, eq 17 cannot be used to predict the value of the parameter ξ; indeed, this relation leads to $V_{2j} \simeq 0$ at $T_{g2} = 150$ K which is the glass transition temperature of poly(dimethylsiloxane), for example; it leads to a very high ξ value for a usual organic solvent in PDMS. The toluene diffusion coefficient was measured, at room temperature, in PDMS–toluene solutions.[17] The ξ parameter in this system was determined by considering the Vrentas–Duda equation (eq 15). The solvent free volume parameters were chosen to be equal to those published for toluene:[13,14] $K_{11}/\gamma = 1.45 \times 10^{-3}$ K^{-1}, $K_{21} - T_{g1} = -86.32$ K, and $V_1^* = 0.917$. The polymer parameters K_{12}/γ and K_{22} were determined from the WLF parameters of the polymer and the calculated value of V_2^* (0.80 cm^3/g): $K_{22} - T_{g2} = -81$ K and $K_{12}/\gamma = 8.25 \times 10^{-4}$ K^{-1}. From the diffusion data we determined D_0 and ξ: $\xi = 0.83 \pm 0.02$ and $D_0 = (4.1 \pm 0.1) \times 10^{-4}$ cm^2/s. We can observe that the values of the parameter ξ characterizing PDMS–toluene and PB–cyclohexane solutions lead to the same value of the ratio M_{2j}/M_{2m}: the jumping unit size is 1.7 times greater than the monomer unit one.

IV.3. Size of Polymer Jumping Units. Two main features must be noted about the size of one jumping unit of polymers. In Figure 8a we have reported polymer jumping unit volumes measured in this work and data previously published about other polymers.[14] The comment about the validity range of eq 17 is clearly illustrated, and a simple correlation law between V_{2j} and T_{2j} is not evidenced. However, the molecular weights M_{2j} and M_{2m} of all these polymers are simply correlated (Figure 8b). A standard value (1.5 ± 0.3) of the ratio M_{2j}/M_{2m} has been proposed in the case of polymers with high glass transition temperatures;[14] this value applies reasonably to polymers investigated in this work.

IV.4. Analysis of Data at Constant Concentration. The solvent free volume parameters K_{11}/γ and $K_{21} - T_{g1}$ were also determined by analyzing the temperature dependence of the solvent diffusion at four concentrations (Figure 9). The curves B–E were fitted with eq 12 in which $E = 0$ and D_0 was kept constant and equal to its previously determined value: $D_0 = 9.7 \times 10^{-4}$ cm^2/s. A single set of the free volume parameter values was found, in agreement with the previous determination: $K_{11}/\gamma = (1.15 \pm 0.08) \times 10^{-3}$ K^{-1} and $K_{21} - T_{g1} = -95 \pm 14$ K. The dashed line in Figure 9 (curve A) relative to the solvent weight fraction $\omega_1 = 0.44$ was calculated with eq 15 and the parameters listed in Table I. The temperature dependence of the solvent diffusion coefficient is well described by the calculated curve; the agreement with the absolute value of the diffusion coefficients is fairly good.

V. Discussion

In this work, it is shown that the concentration and temperature dependences of the solvent diffusion can be analyzed either by considering WLF–Fujita equations or by applying the Vrentas–Duda description. This result is based on the specific value of the parameter ξ. As has been pointed out by Vrentas and Duda, each of the two

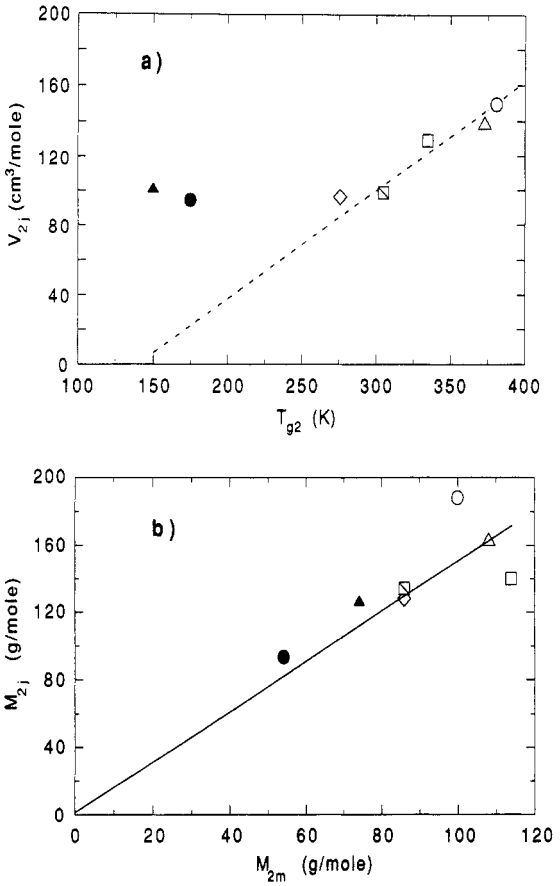

Figure 8. (a) Jumping unit volumes of polymers versus the glass transition temperature. The open symbols represent data of ref 14: (○) PMMA, (▲) PS, (⊠) PEMA, (□) PVAc, and (◇) PMA; the solid symbols are relative to this work: PDMS (▲) and PB (●). (b) Correlation between the polymer jumping unit molecular weight and the monomer one. Symbols are the same as in Figure 8a; the slope of the line is $^3/_2$ (ref 4).

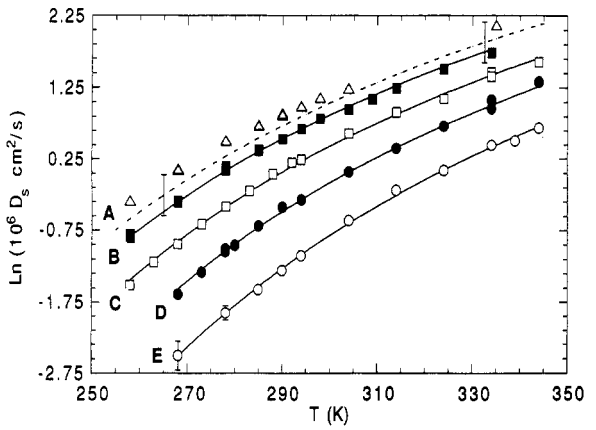

Figure 9. Temperature dependence of the solvent diffusion at $\omega_1 = 0.04$ (○), 0.17 (●), 0.26 (□), and 0.34 (■). Data were analyzed with eq 15 in which E is set equal to zero. The dashed line ($\omega_1 = 0.44$) was calculated according to eq 15 with the parameters listed in Table I; the accuracy on D_0 determination is illustrated by error bars on the dashed curve.

models can be used if the solvent and the polymer jumping units have equal sizes ($M_1 \approx M_{2j}$).[12] The Vrentas–Duda equation and the Fujita one are identified to each other when the condition $\xi V_2^*/V_2^\circ = V_1^*/V_1^\circ$ is fulfilled (V_2° and V_1° are the specific volumes of the pure components).[18] This is the case for the cyclohexane–polybutadiene system characterized by $M_1 = 84$ and $M_{2j} = 93$ on the one hand and by $\xi V_2^*/V_2^\circ = 0.81$ and $V_1^*/V_1^\circ = 0.78$ on the other hand. Free volume parameters of the pure components determined from the Fujita–WLF analysis were found to

Table I. Parameters of the Cyclohexane–Polybutadiene (8% Vinyl) System

Vrentas–Duda model	WLF–Fujita model[a]
$D_0 = (9.7 \pm 3.2) \times 10^{-4}$ cm²/s	$D_s(T_0) = (1.41 \pm 0.01) \times 10^{-5}$ cm²/s
$V_1^* = 1.008 \pm 0.033$ cm³/g	$D_s(0,T_0) = (2.45 \pm 0.05) \times 10^{-7}$ cm²/s
$K_{11}/\gamma = (1.15 \pm 0.08) \times 10^{-3}$ K⁻¹	$\alpha_s = (11.8 \pm 1.1) \times 10^{-4}$ K⁻¹
$K_{21}-T_{g1} = -95 \pm 14$ K	$f_s(T_0) = 0.223 \pm 0.004$
$T_{g1} = 155 \pm 3$ K	
$\xi = 0.985 \pm 0.035$	
$V_2^* = 0.92 \pm 0.03$ cm³/g	
$K_{12}/\gamma = (6.50 \pm 0.85) \times 10^{-4}$ K⁻¹	$\alpha_p = (7.9 \pm 0.3) \times 10^{-4}$ K⁻¹
$K_{22}-T_{g2} = -124 \pm 12$ K	$f_p(T_0) = 0.118 \pm 0.001$
$T_{g2} = 174 \pm 2$ K	

[a] Reference temperature $T_0 = 298$ K.

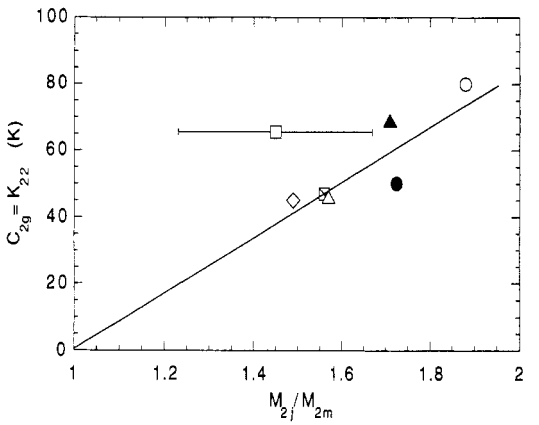

Figure 10. C_2^g representation as a function of the ratio M_{2j}/M_{2m} (same symbols as in Figure 8).

be in good agreement with the literature data. The Vrentas–Duda equation was used to determine the solvent parameters D_0, K_{11}/γ, and $K_{21} - T_{g1}$ and to identify the polymer jumping unit. The values of free volume parameters obtained in this work for cyclohexane are close to those previously published by Zielinski and Duda for other organic solvents.[14]

As is shown in Figure 8b a standard value (1.5 ± 0.3) of the ratio M_{2j}/M_{2m} can be defined. The free volume parameter K_{22} (equal to C_2^g) can also be given a standard mean vlaue: 59 ± 14 K, for all these polymers. However, a phenomenological correlation between M_{2j}/M_{2m} and C_2^g may be evidenced by taking the dispersion of data around the mean values into consideration (Figure 10). The linear relation $K_{22} \approx 85(^*M_{2j}/M_{2m} - 1)$ describes this correlation except PEMA (poly(ethyl methacrylate)) for which the ratio M_{2j}/M_{2m} is less accurately determined (from data in Figure 2 of ref 14, its estimate is 1.45 ± 0.22). This linear correlation between the free volume parameter C_2^g and the ratio of the polymer jumping unit size to the monomeric unit one cannot be considered as a well-established result. A more extensive set of accurate data is necessary to distinguish between a dispersion effect around the mean values and a real monotonous variation.

The last point, to be discussed here, concerns the thermal dependence of the polymer transverse relaxation time T_2^c. In eq 4, a reference temperature equal to $T_g(\phi,\chi_{1,2}) + T_r$ was evidenced; T_r was found to be independent of the polymer volume fraction and equal to 50 K for the cyclohexane–polybutadiene system.[5] This value must be compared with the free volume parameters K_{12} (60 ± 17 K) and K_{22} (50 ± 10 K). In ref 5, the transverse relaxation process of protons attached to entangled polymer chains was supposed to be sensitive to the free volume available to segments to rotate in space.

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