spectra of at least two Lorentzians. The fast component of the relaxation spectra exhibits a relaxation time of at most 1 order of magnitude longer than that of neat CB, even though the viscosity of the PMMA matrix is several orders (at least 10 orders) of magnitude higher than that of CB liquid. On the other hand, the slow component shows relaxation times expected of CB in a highly viscous medium.

One possible interpretation of these facts, as mentioned above, is that the CB exists in two types of environments. One type of environment is a characteristic of the neat CB and the other a characteristic of a high molecular weight polymer. In another possible interpretation, we can think of the CB molecules as undergoing two types of motion: (1) the CB molecule could be rotating rapidly but with a restricted angular displacement, e.g., rotating in a conelike volume element and (2) the walls of the cone (the polymer segments) could relax, allowing the CB molecule to undergo cooperative motion with the polymer segment, resulting in a slowly relaxing component. This slow motion of the CB therefore reflects the motion of the polymer chains. Thus these two points of view could be a starting point in building a theoretical interpretation of the motions of CB molecules in PMMA. Part 2 of this work will deal with the theoretical interpretation of the data presented here.

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Rotational Relaxation of Chlorobenzene in Poly(methyl methacrylate). 2. Theoretical Interpretation

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ABSTRACT: The depolarized Fabry–Perot spectrum of chlorobenzene (CB) in poly(methyl methacrylate) (PMMA), which exhibits fast (picosecond time scale) and slow, broad-distribution (nanosecond to millisecond) relaxation times, is interpreted in terms of two theories, the "diffusion in two environments" (DITE) theory and the restricted rotational diffusion (RRD) theory. The DITE theory along with the free-volume theory was used to estimate the critical void volume per CB molecule, which allows fast relaxation, as 203 Å^3. The RRD theory was used to calculate the cone angle of rotation as well as the rotational diffusion coefficient over a range of temperature and CB concentrations.

Introduction

In part 1 of this work (see preceding paper), we reported experimental results on the dependence of the rotational relaxation of chlorobenzene (henceforth designated as CB) in poly(methyl methacrylate) (henceforth designated as PMMA) on temperature and CB concentration. We found that the Fabry–Perot spectra of CB–PMMA samples having CB concentrations equal to and greater than 20 g of CB/100 mL of the CB–PMMA mixture could best be fit to two Lorentzians, as in Figure 1, indicating that there exist at least two relaxation times which are widely separated in time scale. The wide Lorentzian, representing the fast component, is in the picosecond time scale and appears to be independent of the free spectral range (FSR), thus indicating it to have a single relaxation time or a very narrow relaxation time distribution. The half-width at half-height (hwhh) of the narrow Lorentzian, however, appears to change with the FSR, suggesting that it consists of a wide distribution of relaxation times having components detectable in the autocorrelation time scale, i.e., microseconds or longer.

In this work we propose that the results presented in part 1 can be interpreted in terms of two well-known theories: the "diffusion in two environments" (DITE) theory[1] and the "restricted rotational diffusion" (RRD) theory.[2] These theories have been used to explain the dielectric behavior of molecules trapped in matrices.[1,2] In these systems it has been observed that the dipolar auto-

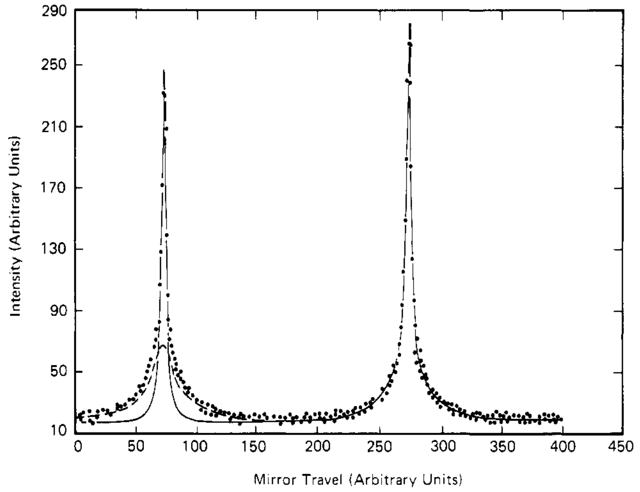

Figure 1. Fabry-Perot spectrum of PMMA containing 40 g of CB/100 mL at 60 °C.

correlation function contains an unrelaxable component (within the time scale of the experiment, e.g., >μs), a phenomenon very similar to the results presented in part 1.

Diffusion in Two Environments (DITE) Theory

A. Cage Model. In this concept we envision the existence of the CB molecule in two types of environments. In one environment, the CB molecule is in a cage (bounded by the segments of the polymer chain) whose size is sufficiently large to allow the CB molecule to undergo rotational motion with little interaction with the polymer chains. In the other environment, the rotational motion of CB is hindered by the matrix; thus motion of the CB molecule is only possible in a cooperative process involving the boundaries of the cage (polymer segments).

In conjunction with the free-volume concept put forth by Doolittle[3] and Cohen and Turnbull[4] as a model for translational diffusion phenomena in ordinary liquids and by Fugita[5] for translational diffusion of small-molecule liquids in amorphous polymers, we shall proceed to interpret rotational diffusion of CB in PMMA by using the DITE theory. To explain translational diffusion phenomena in ordinary liquids, Cohen and Turnbull[4] used the concept of the existence of a critical free volume V^* sufficiently large to allow center-of-mass displacement of the diffusing species. They related the diffusivity of liquids to the average liquid free volume per molecule, $\langle V(T, C)\rangle$, by using a relation for the probability of finding a free volume per molecule greater than or equal to a critical volume V^*

$$P(bV^*) = \exp[-bV^*/\langle V(T, C)\rangle] \tag{1}$$

In eq 1, b is a constant of order unity for low values of C and less than unity for higher values of C.

If we assume that CB in the fast environment is in equilibrium with CB in the slow environment and if eq 1 expresses the total probability of finding a CB molecule in the fast environment, then the equilibrium constant κ for the transition $\mathrm{CB_{slow}} \rightleftarrows \mathrm{CB_{fast}}$ can be expressed as

$$\kappa = \frac{P(bV^*)}{1 - P(bV^*)} = \frac{1}{\exp[bV^*/\langle V(T, C)\rangle] - 1} \tag{2}$$

Thus from eq 2 the value of the apparent critical free volume bV^* can be calculated if κ and $\langle V(T, C)\rangle$ can be experimentally measured or calculated.

For liquids composed of small molecules, Cohen and Turnbull[4] have calculated V^* from experimentally measured $\langle V(T)\rangle$. However, for small molecules in polymeric media the calculation and measurement of $\langle V(T, C)\rangle$ is much more complicated and difficult to perform unambiguously. Nonetheless, if we assume that CB is the only active molecular species which gives rise to the depolarized spectra and PMMA simply acts as a space-occupying entity, $\langle V(T, C)\rangle$ can be calculated from the free-volume fraction $f(T, C)$ (the free volume per unit volume of the sample) by dividing it by the number of CB molecules in 1 cm^3 of the sample. The number of CB molecules per cm^3 of the sample can in turn be calculated from its concentration, C, and molecular weight. The relationship between $\langle V(T, C)\rangle$ in Å^3 and the $f(T, C)$ in cm^3/cm^3, can thus be expressed as

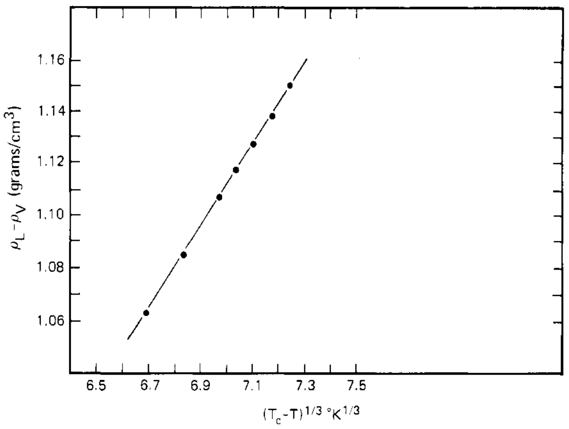

Figure 2. Density of CB as a function of temperature. (Density is computed from the thermal coefficient of volume expansion from ref 6.)

$$\langle V(T, C)\rangle = (186/C)f(T, C) \tag{3}$$

where 186 is the product of 10^{24} (Å^3/cm^3) and the CB molecular weight (112) divided by Avogadro's number (6.02×10^{23}).

According to Fugita[5] the free-volume fraction $f(T, C)$ of a liquid–polymer mixture can be estimated from

$$f(T, C) = (1 - C)f(T, 0) + \gamma(T)C \tag{4}$$

Thus $f(T, C)$ can be readily evaluated from the free-volume fractions of the pure polymer ($f(T, 0)$) and the CB solvent ($\gamma(t)$). If we assume that the free volume of a liquid (polymer or small molecule) at absolute zero is zero (Doolittle's approximation[3]), then the free-volume fraction at any temperature is

$$f(T, 0) \text{ or } \gamma(T) = (V(T) - V_0)/V_0 \tag{5}$$

where V_0 is the volume of the polymer or CB at 0 K. Since data on $V(T)$ for many polymers and small-molecule liquids are readily available, the problem is the determination of V_0. For polymers, V_0 is impractical to determine because of the slow volume relaxation rate below T_g. However, for ordinary liquids there are approximate methods for obtaining V_0. One such method, due to Doolittle,[3] utilizes Goldhammer's rule

$$\rho_L - \rho_V = B(T_c - T)^{1/3} \tag{6}$$

where ρ_L and ρ_V are the densities of the liquid and its equilibrium vapor, respectively, and T_c is the critical temperature. The proportionality constant B can be estimated from the slope of the CB density vs. temperature plot shown in Figure 2. Using the value of B obtained from Figure 2, eq 6, and the literature[6] values of ρ_L and T_c, we calculated the V_0 of CB as 0.794 cm^3/g. The CB $\gamma(T)$ was subsequently calculated from $V(T)$ and V_0 over

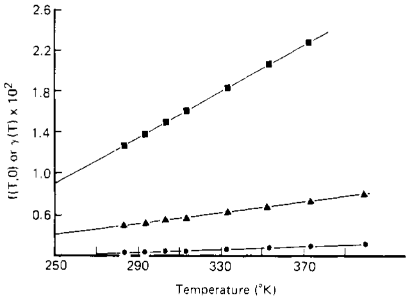

Figure 3. Plot of the free volume fraction of PMMA and CB vs. temperature: (▲) $f(T, 0)$ from eq 7; (■) $f(T, 0)$ from eq 8; (●) $\gamma(T)$ from eq 5.

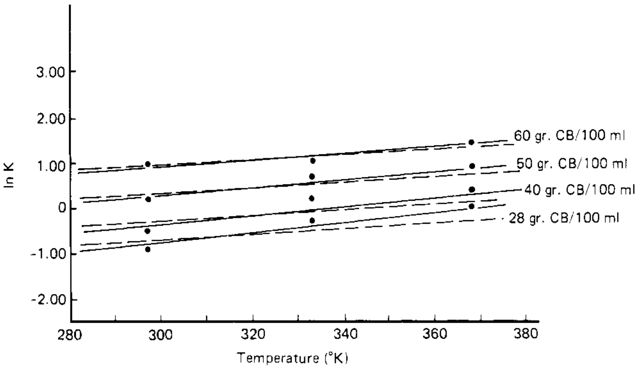

Figure 4. Plot of the equilibrium constant κ vs. the absolute temperature T: (●) obtained from the ratio of the areas of the wide (fast) and the narrow (slow) components of the Fabry–Perot spectra; (—) obtained from eq 7 and 2; (---) obtained from eq 8 and 2.

the range of temperature of interest.

There are at least two theories which can be used to predict $f(T, 0)$ as a function of temperature. One theory predicts a linear dependence of $f(T, 0)$ with temperature[7]

$$f(T, 0) = 7.88 \times 10^{-4}T \qquad (7)$$

The other theory predicts a $^3/_2$ power dependence on temperature[7]

$$f(T, 0) = (A/\pi^{1/2})(T/T^*)^{3/2} \qquad (8)$$

where A (which can be considered to be a packing factor) is of order unity and T^* is a characteristic temperature of the polymer. RT^* is the energy required to generate a mole of holes of volume V^*.

Figure 3 shows the $\gamma(T)$ and $f(T, 0)$ computed from eq 5, 7, and 8, assuming A to be unity and the literature-reported[7] value of 1443 K for T^*. From these values of $\gamma(T)$ and $f(T, 0)$, the values of $f(T, C)$ and $\langle V(T, C)\rangle$ were calculated with eq 4 and 3 over the temperature range of interest. Having obtained $\langle V(T, C)\rangle$, we can now proceed from eq 2 to calculate the ratio of the concentrations of CB which are relaxing fast to those which are relaxing slowly.

By fitting the calculated value of κ from eq 2 to the experimental values ($\kappa = A_W/A_N$, the intensity ratio of the wide to the narrow Lorentzian), we can calculate the critical void size associated with the fast-relaxing component of the CB molecules in the PMMA over a range of temperatures and CB concentrations. Figure 4 shows the calculated and experimental values of κ over a range of temperature and concentration for the two theories (linear as well as $^3/_2$ power dependence of the $f(T, 0)$ on temperature). At lower CB concentrations one could deduce from Figure 4 that the fit between experiment and theory is slightly better for the $^3/_2$ than the linear temperature dependence of $f(T, 0)$. At higher concentrations of CB, where $\gamma(T)$ predominates, the two models converge and both appear to fit the experimental data fairly well.

Table I
Values of bV^* Obtained from the Linear and the $^3/_2$ Power Dependence of $f(T, 0)$ on Temperature for Various CB Concentrations

CB concn, g/100 mL	bV^* linear dependence	bV^* $^3/_2$ power dependence
30	140	56
40	78.4	36.4
50	37.8	20.2
60	18.2	11.2

The only adjustable parameter in fitting the theories to the experiment is the apparent critical void size bV^*. The values of bV^* were obtained by first plotting the experimental values of κ vs. temperature for various concentrations (see Figure 4) and then making a fit of eq 2 to the data. The values of bV^* which gave the best fit of eq 2 to the data are shown in Table I. It is clear that the value of bV^* obtained depends strongly both on the solvent concentration and on the model used, i.e., the temperature dependence of $f(T, 0)$. If we set $b = 1$ at the low solvent concentrations, values of V^* for the two models used are calculated to be 140 and 56 Å^3 for the linear and $^3/_2$ power dependencies of $f(T, 0)$ on temperature, respectively. Since V_0 (the volume associated with each CB molecule at absolute zero) for CB is 147 Å^3, the total critical volumes ($V^*_T = V_0 + V^*$) associated with each CB molecule for the linear and $^3/_2$ power dependencies of $f(T, 0)$ on temperature are 287 and 203 Å^3, respectively. Thus the equivalent spheres for V^*_T have diameters of 8.20 and 7.3 Å for the linear and $^3/_2$ power dependencies of $f(T, 0)$ on temperature, respectively. These numbers are reasonable values when one considers the major axis for the chlorobenzene molecules is approximately 5.5 Å. Thus, on the basis of a comparison of the calculated diameter of V^*_T and the van der Waals diameter of the CB molecule and the log κ vs. T plot shown in Figure 4, the $^3/_2$ power dependence of $f(T, 0)$ on temperature appears to be in somewhat better accord with the experimental results than the linear dependence.

The decrease in the value of b or the apparent critical void size (bV^*) with increasing CB concentration in Table I could be rationalized as being due to the rapid increase in the mobility of the cage walls (polymer segments or other CB molecules) with increasing CB concentration. As the CB concentration increases, the PMMA segments become more mobile (plasticized) and a larger portion of the cage walls consist of the more mobile CB molecules, thus providing an environment in which CB molecules relax faster than can be accounted for solely by the increase in $f(T, C)$. This results in an increase in the experimental value of κ which is higher than could be predicted by eq 2 with a constant value of unity for b. Thus the apparent value of the critical free volume (bV^*) must be decreased by reducing b in order to maintain a good fit between the calculated value of κ and the experiment.

B. Chlorobenzene Cluster Model. In this model we consider the CB molecules to exist as clusters or pools of various sizes in the PMMA matrix. We also assume that CB molecules in pools with sizes bigger than a critical size V^*_C will have rotational relaxation times in the neat chlorobenzene time scale and those below V^*_C will have relaxation times with an order of magnitude the same as those associated with the polymer segmental motion.

Using the same approach as that described in the cage model of part A, we can express in the same form as eq

1 the probability $P(bV^*_C)$ of finding a pool of size V^*_C or greater. The constant b is again of the order unity for low values of C and less than unity for the higher CB concentrations. As in the cage model, the problem here is again the estimation of the number-average cluster size of CB molecules $\langle V_C(T, C)\rangle$ in the PMMA matrix. Thus the total free volume of the PMMA matrix and the number of CB clusters must be known in order to calculate $\langle V_C(T, C)\rangle$.

Although it is possible to calculate the total free volume of the PMMA matrix from eq 5 and the concentration of the CB in the matrix, we have no way of calculating the number of CB clusters in the sample. Thus it is not possible to calculate the critical cluster volume V^*_C from the free-volume fraction $f(T, C)$. We need data on the $\langle V_C(T, C)\rangle$ to calculate V^*_C. Two techniques which offer some possibility of measuring $\langle V_C(T, C)\rangle$ are low-angle X-ray scattering and neutron scattering. We are currently planning to use the facilities at the Stanford Synchrotron Radiation Laboratory to perform low-angle X-ray scattering measurement on the PMMA matrix.

Restricted Rotational Diffusion (RRD) Theory

In the DITE theory discussed in the preceding section, we interpreted the two widely separated relaxation times of the spectra of the CB–PMMA samples as a consequence of the CB molecules being in "cages" whose free volumes are either below or above the critical free volume V^*. In the RRD theory we do not invoke the existence of V^* or explain the spectra of CB–PMMA samples as a consequence of differences in the size of the CB "cage" in the PMMA matrix. In the RRD theory we consider the two widely separated relaxation time scales to be a consequence of two types of motion of the CB in the PMMA matrix. The fast relaxation time is considered to arise from restricted rotational diffusion of the CB molecule (the rotation is restricted to a cone) in a cavity bounded by the PMMA segments which are considered "immobile" relative to the motion of the CB. The slow relaxation times arise from the cooperative motion between the CB molecule and the boundary of the cavity (the polymer segments). We envision that as the CB molecule rotates in the cavity, a segment of the polymer chain may move out of its way, allowing a larger angular displacement of the CB molecule. This motion results in an additional fluctuation of the scattered light with a frequency much lower than that of the faster rotation within the original cavity boundary. Since the mobility of a polymer segment depends on its length and since the rotational motion of the CB molecule will respond to motions of all the polymer segments in its neighborhood, it is expected that the slow component of CB rotational diffusion will be a broad spectrum of relaxation times.

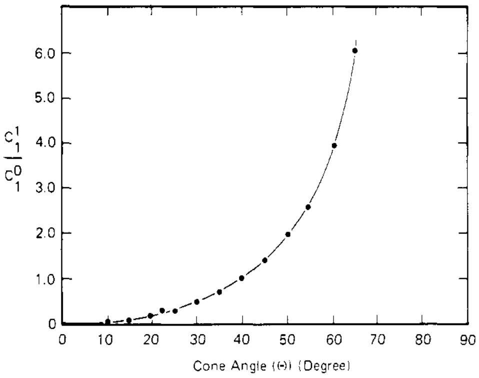

Figure 5. Plot of the scattered light intensity ratio of the fast- to the slow-relaxing components vs. the cone angle of rotation for CB in PMMA.

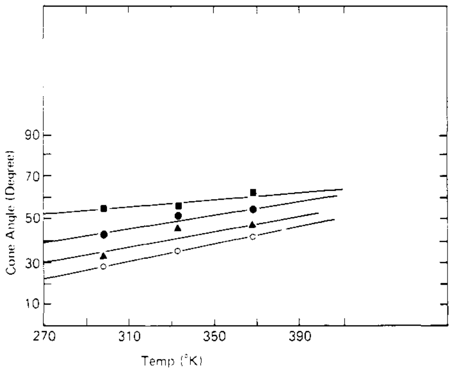

Figure 6. Plot of the cone angle of rotation of CB in PMMA as a function of temperature and CB concentration: (○) 30% CB; (▲) 40% CB; (●) 50% CB; (■) 60% CB.

The RRD theory has been suggested by Warchol and Vaughan[2] as a model for dielectric relaxation of rigid molecules trapped in glassy matrices. The experiments show an unrelaxable (within the time scale of the experiment) component of the measured dipolar autocorrelation function. Recently, Pecora and Wang used this same model to predict the depolarized light scattering spectra of molecules undergoing restricted rotational diffusion.[8] Pecora and Wang[8] have shown that as long as the angle of the cone is $\lesssim 60°$, the depolarized light scattering spectrum is given to a good approximation by

$$I_{VH}(\omega) \propto C_1^0\delta(\omega) + \frac{C_1^1}{\pi}\,\frac{\nu_1^1(\nu_1^1 + 1)D_R}{\omega^2 + [\nu_1^1(\nu_1^1 + 1)D_R]^2} \tag{9}$$

where C_1^0, C_1^1, and ν_1^1 depend on the cone angle and $\delta(\omega)$ is the Dirac delta function. Because of the intractability of modeling the case where the boundary of the cone is allowed to relax, we have assumed it to be fixed in our theoretical model. Thus, since the orientation of the cone is fixed, the term proportional to C_1^0 is an infinitely sharp spike. In a polymer system at low solvent concentration, we expect the cone itself to change orientation very slowly. Thus, we identify C_1^0 with the integrated intensity of the narrow line and C_1^1 with the integrated intensity of the wide line. Pecora and Wang[8] have shown that

$$C_1^0 = [\tfrac{1}{2}\cos\theta_0(1 + \cos\theta_0)]^2 \tag{10}$$

and

$$\begin{aligned} C_1^1 &= \tfrac{2}{5} + \tfrac{2}{5}\cos\theta_0(1 + \cos\theta_0) \\ &= \tfrac{3}{5}\cos^3\theta_0(1 + \cos\theta_0) \end{aligned} \tag{11}$$

From eq 10 and 11 the ratio of the integrated intensities of the fast to the slow relaxation process can be computed as a function of θ_0, the cone angle of rotation. A plot of this function is shown in Figure 5. Since the integrated intensities of the fast and the slow relaxation components of the Fabry–Perot spectra have been determined experimentally as a function of CB concentration and temperature (see Figure 4), it is now possible to calculate the cone angle of rotation of CB in PMMA as a function of CB concentration and temperature. Figure 6 shows that the cone angle of rotation of CB in the PMMA matrix increases with both temperature and CB concentration. It also appears that the increase in the angle of rotation of CB in PMMA follows an almost linear relationship with temperature (Figure 6).

From eq 9 we see that the relaxation time τ_R is equal to $\nu_1^1(\nu_1^1 + 1)D_R$. Pecora and Wang[8] obtained a relationship between ν_1^1 and the cone angle (Figure 7). From this

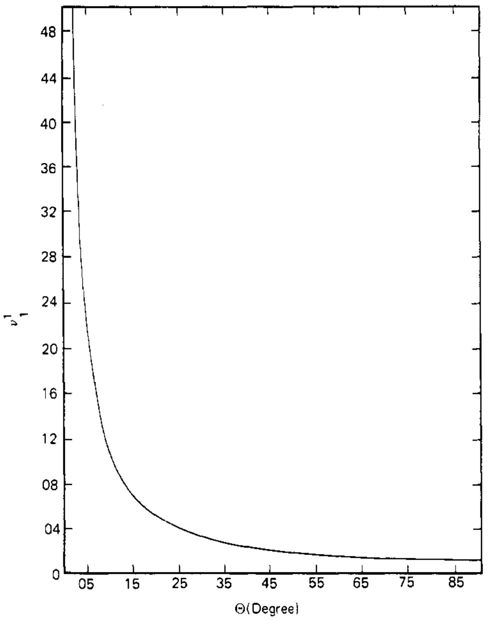

Figure 7. Plot of ν_1^1 vs. the cone angle of rotation.

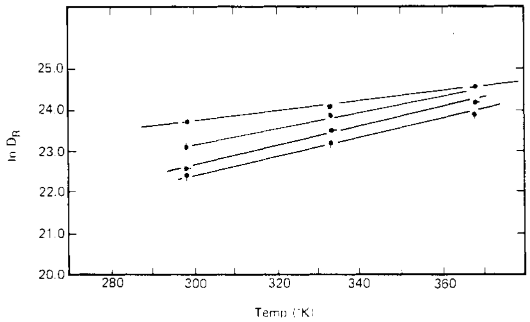

Figure 8. Plot of the rotational diffusion coefficient of CB in PMMA vs. the absolute temperature for various CB concentrations: (●) 30% CB; (●) 40% CB; (●) 50% CB; (●) 60% CB.

relationship and the experimental relaxation data it is possible to calculate the rotational diffusion constant D_R as a function of temperature and concentration. Figure 8 shows that the rotational diffusion coefficients obtained for CB in PMMA over a range of concentration show a dependence on temperature similar to that of neat chlorobenzene. Furthermore, at higher CB concentrations and higher temperatures, the D_R values for CB in PMMA approach those of neat CB. This indicates that the D_R of CB in PMMA is not controlled by the macroscopic viscosity, since the viscosities of all the PMMA–CB mixtures studied are several orders of magnitude higher than those of neat CB. The slope of ln D_R vs. the reciprocal temperature decreases significantly with increasing CB concentration. This could simply be a consequence of a change to a less hindered relaxation or lower local viscosity at the higher (60% CB) CB concentration.

Summary

We have shown that the depolarized Fabry–Perot spectra of CB in PMMA, which show two Lorentzians with widely separated relaxation times, can be interpreted by either the "diffusion in two environments" (DITE) theory or the "restricted rotation diffusion" (RRD) theory. In the DITE theory we assumed the CB molecules to reside in cages of various sizes in the PMMA matrix and that the partition between fast and slowly relaxing CB molecules is dictated by a critical cage free volume V^*. In the RRD theory we also envisioned the CB to exist in cages, but we did not invoke the existence of a cage critical free volume; rather we considered the fast-relaxation component of the Fabry–Perot spectra to arise from the restriction of the rotational diffusion of the CB molecule to a conical volume and the slow relaxation to arise from a cooperative motion between the CB molecule and the PMMA segments which form the boundary of the cage. The important parameters in both theories, however, are the molecular size of the solvent, that is, the CB molecule, and the free volume of the polymer. Thus the ultimate physical basis of both theories is the same.

Using the DITE theory in conjuction with the free-volume theory, we calculated a critical free volume V^* equal to 56 Å^3, which corresponds to a critical "cage" volume of 203 Å^3. We also found that the apparent critical free volume (bV^*) decreases with increasing CB concentration. We attributed this decrease in bV^* to the increase in the "cage" wall mobility with increasing CB concentration. We can speculate that at the higher CB concentrations there is increased coupling between the fast and slow components of the rotational relaxation spectrum. In the limit of very high CB concentration (dilute polymer solution) the slow and fast components merge into the rotational relaxation of neat CB.

Using the RRD theory, we calculated the cone angle of rotation of CB as a function of temperature and concentration. We have also calculated the rotational diffusion coefficient D_R as a function of CB concentration and temperature. The values of D_R we obtained show that it approaches the D_R for neat chlorobenzene at higher temperatures and concentrations.

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