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Rotational Motion of a Homologous Series of Solvent Molecules in Amorphous Poly(methyl methacrylate). 2. Studies of the Mixtures

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ABSTRACT: The reorientation dynamics of a homologous series of *n*-alkyl *p*-chlorobenzoate solvent molecules mixed with poly(methyl methacrylate) were studied by depolarized Fabry–Perot interferometry. The *n*-alkyl groups varied from methyl to *n*-pentyl. The solvent concentrations ranged from 60 to 30 wt % and the temperatures from 20 to 80 °C. The glass transition temperatures of the mixtures were measured by differential scanning calorimetry. The light scattering spectra at the higher solvent concentrations and higher temperatures usually exhibited two distinct relaxation regions: a fast one with relaxation times of the order of several hundred picoseconds and a slow region with relaxation times in the nonosecond and slower region. The fast relaxation time and the ratio of the intensity associated with the fast relaxation to that associated with the slow relaxation are interpreted in terms of the diffusion in two types of environment theory, the restricted rotational diffusion theory, and scaling laws relating orientational relaxation times to viscosity and molecular length.

Introduction

As described in the preceding paper[1] (hereafter referred to as 1), the reorientation time of a molecule in a liquid is often a linear function of the viscosity of the liquid. This applies to the reorientation of molecules surrounded by molecules of the same or smaller size. For instance, these linear relations usually hold for neat liquids composed of small molecules and for larger molecules (including macromolecules) immersed in solvents of small molecules. It is generally not expected to hold for the reorientation time of molecules surrounded by molecules that are substantially larger than itself, although, if the size discrepancy is not too large, it applies to a surprisingly large degree.[2] An interesting case, related to the latter, which is of considerable scientific and technological importance, occurs when a large percentage of polymer molecules is added to a solvent of small molecules and one observes the reorientation of the small molecules as a function of the percentage of polymer added and the temperature.

We have previously performed measurements of the orientational relaxation times of chlorobenzene (CB) and chlorodiphenyl methane (CPM) into which large relative amounts (up to 80%) of poly(methyl methacrylate) (PMMA) have been introduced.[3,4] The systems are generally very viscous having the appearance of glasses, yet there is still part of the reorientation process occurring on the picosecond time scale. It might be expected that the reorientation times are no longer functions of the macroscopic viscosity of the composite system. In fact, it was shown in these works that the orientation of the small molecule (the solvent) relaxes by a complex multiexponential process that can be separated into two relaxation time regions. One, as mentioned above, is in the picosecond region, and the other is a broad region with relaxation times ranging from about a nanosecond to time scales slower than those easily studied by photon correlation techniques, reminiscent of the relaxation times associated with large-scale polymer segmental motion.[5-7] The faster relaxation times were close to those of the neat solvents and were insensitive to the macroscopic viscosity of the polymer/solvent mixture. For instance, the fast rotational

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relaxation times (τ_f) for an 80/20 percent PMMA/CB mixture at 24 °C was found to be 30 ps, close to the observed τ_f for neat CB of 8 ps. The τ_f for CPM, a molecule with length about 1.5 times that of CB, was about an order of magnitude higher than that of CB under similar conditions.

The rotational dynamics of CB and CPM in the PMMA matrix were interpreted in terms of their molecules being trapped in cavities bounded by a network of interpenetrating polymer chains.[3,4] To obtain semiquantitative relationships between some of the properties of those cavities, we utilized two models, the diffusion in two environments model (DITE) and the restricted rotational diffusion model (RRD).[8] In the DITE model, the solvent molecules are considered to reside in one of two types of environment: (1) a "slow" environment in which the reorientation of the solvent molecules is hindered by the polymer chains so that no appreciable reorientation may take place on the fast time scale (solvent reorientation in this environment proceeds on the slow time scale of the polymer segments) and (2) a "fast" environment in which due to either clustering of the solvent molecules or fluctuations in the "free volume" available to a solvent molecule, reorientation takes place on a picosecond time scale. In this fast environment, either the cluster size or the free volume per solvent molecule must exceed a critical value. Note that in the DITE theory, the ratio of the areas of the fast and slow Lorentzians appearing in the DLS spectra is a measure of the relative number of solvent molecules in the fast environment to that in the slow environment.[3] This theory does not make quantitative predictions for the values of the fast relaxation times, although, in the case of solvent clustering, it is expected that the fast reorientation time would be close to that of the pure solvent at the same temperature.

In the RRD theory the average environment of a solvent molecule is considered to consist of a cavity in which fast reorientation can proceed only through a restricted angle, called the "cone angle", followed by a slow relaxation of the cavity walls (composed mainly of polymer chains). Because of the confinement of the initial reorientation to a limited angular region, the apparent DLS relaxation time obtained would be faster than that expected for a molecule with the same rotational diffusion coefficient in the absence of confinement. Values of the cone angle may be obtained from the ratio of the areas of the fast to slow Lorentzians, and, from these, "corrected DLS relaxation times" may be calculated.[3,8] The slow relaxation is interpreted as correlated motion of the solvent molecules with the walls of the cavity (mainly the polymer chains).

The RRD and DITE theories are not mutually exclusive. Both are clearly oversimplified pictures of the actual structure and dynamics in these systems. There must, as envisaged in the DITE theory, be a range of environments of solvent molecules, some of which allow solvent molecules to rotate much as they would in the neat solvent, some of which allow solvent molecules to reorient through very small angles before their reorientation becomes coupled to the polymer segment motion, and some "intermediate" environments which resemble that pictured in the RRD theory. An extension of the RRD theory in which an average over an explicit distribution of cone angles is made would be most interesting. In spite of the limitations of these models, they, however, provide a useful framework for interpreting the data.

In this paper we report the results of experiments on the reorientation of a series of *n*-alkyl *p*-chlorobenzoates (PCAB) in PMMA where the alkyl group varies from methyl to pentyl. The main focus of this work is study of the effect of varying molecular size of the PCAB on its rotational dynamics in PMMA. As in the previous work on CB and CPM,[3,4] depolarized dynamic light scattering spectra of PMMA/PCAB mixtures over a range of composition and temperature above and below the glass transition temperatures (T_g's) were obtained. The results are interpreted in terms of scaling laws for rotational relaxation times obtained from hydrodynamic theories of rotational diffusion[2,9,10] in ordinary liquids, the DITE and RRD models, and the experimental results on the neat and dilute solution PCAB's presented in 1.

Experimental Section

The synthesis of the PCAB's was described in 1.

Commercially available methyl methacrylate (MMA) was purified (removal of inhibitor) by treatment with NaOH solution followed by several washings with double-distilled H_2O until litmus paper testing indicated the absence of NaOH. The inhibitor-free MMA was then dried by adding anhydrous Na_2SO_4 and the mixture was then vacuum distilled and stored in a refrigerator under an argon atmosphere.

Appropriate amounts of the PCAB solvent, MMA, and recrystallized AIBN initiator (0.4 wt %) were mixed in a 10-mL volumetric flask. The solution was then filtered through a 0.2-μm Fluoropore filter into the light scattering cell fitted with ground glass joints for vacuum degassing of the solution.

The filtered solutions in the scattering cells were degassed by using freeze–thaw techniques. After about three freeze–thaw cycles the samples were sealed under vacuum, and polymerization was initiated by placing the solution in a thermostatically controlled bath starting at 60 °C for one day and then raising the temperature to 115 °C. To ensure complete conversion and minimum stress in the sample, the solutions were left at 115 °C for 1.5 months. To ensure good optical quality (as measured by low values of the Landau–Placzek ratio), the samples were cooled very slowly at a rate of about 3 °C a day to room temperature. All samples except the 45% and the 60% C_5/PMMA displayed Landau–Placzek ratios in the range from 5 to 8 at 20 °C. The 45% C_5/PMMA sample exhibited a Landau–Placzek ratio of 10, while the 60% sample had such intense central line intensity that the ratio could not be measured. This fact and its readily apparent opalescence indicate that this sample is likely microscopically heterogeneous and has likely undergone a microphase separation.

The glass transition temperature (T_g) of the PCAB/PMMA and CB/PMMA mixtures were measured by using a Du Pont 1090 DSC (differential scanning calorimeter). After all the light scattering experiments had been completed on all of the samples (including the CB/PMMA samples whose light scattering behavior was previously reported[3]), the vacuum sealed scattering cells were opened and CB/PMMA and PCAB/PMMA mixtures were immediately loaded into high-pressure-sealed DSC sample cells. In this way, significant loss of the PCAB and CB solvents through evaporation was prevented. Since some of the samples were expected to have T_g's below ambient temperature, a low temperature sample cell holder was used permitting temperature scans below −100 °C. The heating rate was set at 10 °C/min, and the calorimeter was carefully set to minimize the base-line slope. The T_g's were determined from the intersections of the tangents drawn from the inflection points of the DSC thermograms.

The light scattering apparatus and data fitting procedures are described in 1.

Results and Discussion

Glass Transition Temperatures. The T_g's of all the PCAB/PMMA and CB/PMMA mixtures obtained from the DSC measurements are plotted versus the polymer concentration and are shown in Figure 1. A few notable features of Figure 1 should be pointed out. First, within the precision of the measurements, the T_g's for all the PCAB and CB solutions lie on the same curve, except for C_1 which lies consistently higher than the rest of the homologues. Second, the T_g's of PMMA with up to 30% CB or PCAB are close to ambient temperature, and mixtures

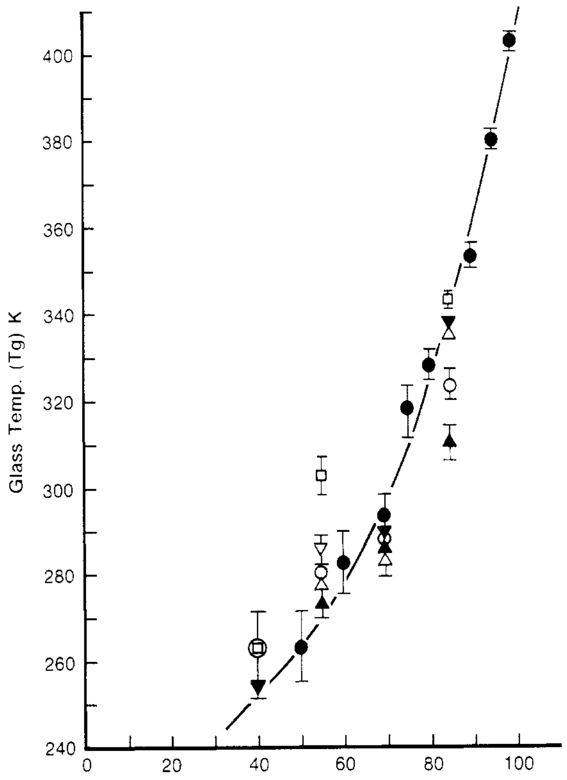

Figure 1. Glass transition temperatures versus PMMA concentrations for chlorobenzene/PMMA and *n*-alkyl *p*-chlorobenzoate/PMMA mixtures. The curve drawn through the points is meant only as a visual guide. (Key: ● CB; □, C_1; ▲, C_2; ▼, C_3; ○, C_4; △–C_5.)

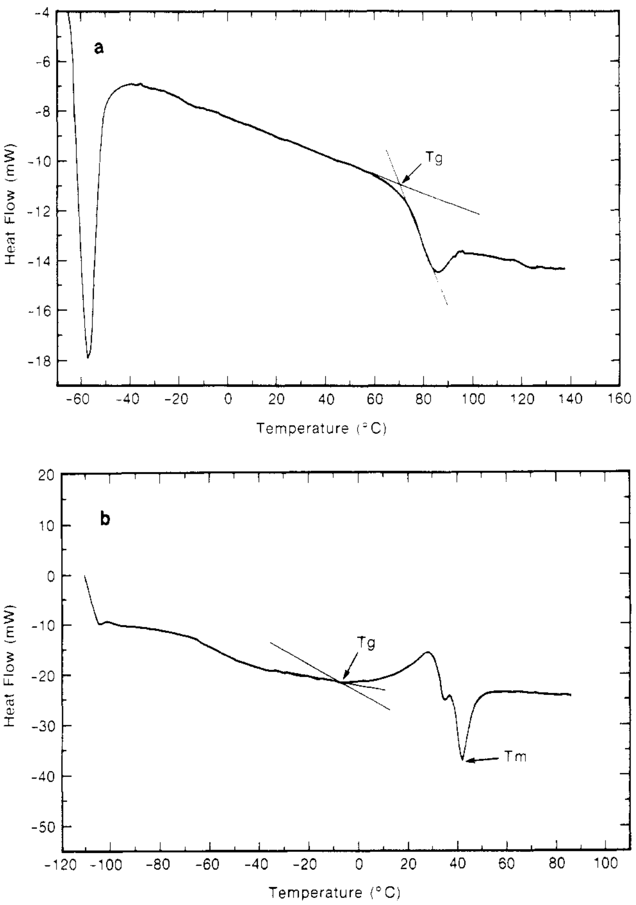

Figure 2. (a) DSC thermogram for the 15 wt % C_1/PMMA. (b) DSC thermogram for the 60 wt % C_1/PMMA mixture. Note the large uncertainty in determining T_g and the large and sharp endothermic peak indicative of a first-order phase transition (T_m).

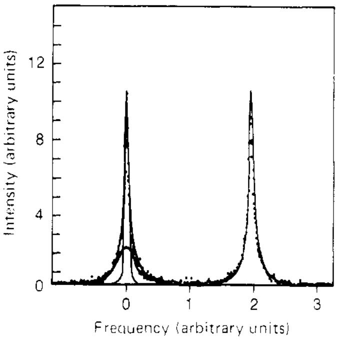

Figure 3. Spectrum of depolarized light scattered from the 60 wt % C_2/PMMA mixture at 60 °C. The solid line on the right-hand peak represents a two Lorentzian fit to the data points. On the left-hand peak both the overall fit and the two-component Lorentzians are shown.

of as low as 40% PMMA have a consistency of very soft rubber. Third, the error bars of the T_g data increase with decreasing PMMA concentration. The inflection point of the DSC thermogram that marks the T_g becomes less sharp as the concentration of PMMA falls below 60%, thereby making it very difficult to determine the T_g with precision. An extreme case of this is shown in Figure 2b for the C_1 homologue. For other homologues (e.g. C_3 and C_5), the T_g at 60% solvent is much better defined than that shown in Figure 2b, but the inflection points are still less prominent and less sharp than at lower solvent concentrations. The inflection point seen at a much lower temperature (~−70 °C) in Figure 2b was also present in the corresponding thermograms of the C_2, C_3, C_4, and C_5 homologues, in addition to the inflection point at much higher temperature (which we have assigned as the T_g). Thus, we believe that these very low-temperature inflections represent shorter range molecular motions of the polymer (e.g. side-chain motions) or solvent motions and not the longer range motions associated with T_g. We also observed in Figure 2b that the DSC thermogram for the 60% C_1/PMMA mixture showed a large and sharp endothermic peak indicative of a first-order phase transition near the melting point of neat C_1 (mp ~45 °C).

Light Scattering Spectra. A typical depolarized light scattering spectrum from a PCAB/PMMA mixture is shown in Figure 3. The spectra in general could not be represented by one Lorentzian but were well fit by a sum of two Lorentzians having widely separated line widths as in the CB and CPM cases previously studied.[3,4] The width of the fast Lorentzian corresponded to relaxation times in the hundreds of picoseconds regime while the width of the slower Lorentzian was of the same order of magnitude as the instrumental line width. The relaxation times corresponding to the slower Lorentzian were not studied because of the difficulty of deconvoluting them from the instrumental line width; however, the relative weights of the two Lorentzians in the fits were considered significant in the interpretation of the mechanism of rotation in these systems. Tables I and II show respectively the fast times τ_f and the intensity ratios of the fast to the slow component of the spectra we obtained for the PCAB/PMMA mixtures studied as functions of concentration and temperature. In the cases indicated by the blanks in Tables I and II, generally at low solvent concentrations and low temperatures, no fast Lorentzian was resolved, even when spherical Fabry–Perot mirrors with a low free spectral range (0.75 GHz) were used. As noted for the CB/PMMA mixtures, the τ_f of the PCAB in the PMMA matrices shown in Table I are

Table I
Fast Rotational Relaxation Times[a] of Alkyl *p*-Chlorobenzoates in PMMA at Various Temperatures and Concentrations

samples solv concn	20 °C	40 °C	60 °C	80 °C
(1) C_1				
30 wt %	...	...	...	...
45 wt %	...	3.2	2.5	1.1
60 wt %	4.5	2.7	1.2	0.7
(2) C_2				
30 wt %	...	...	4.9	3.2
45 wt %	...	5.4	2.0	1.1
60 wt %	4.4	2.7	1.2	0.8
(3) C_3				
30 wt %	...	...	4.9	2.7
45 wt %	...	4.8	2.5	1.2
60 wt %	4.2	2.6	1.1	1.0
(4) C_4				
30 wt %	...	...	5.6	2.8
45 wt %	...	3.5	3.0	1.5
60 wt %	4.4	2.4	1.3	0.9
(5) C_5				
30 wt %	...	...	2.2	3.3
45 wt %	...	...	2.1	1.7
60 wt %	...	2.6	1.2	1.2

[a] In 10^{-10} s/rad.

Table II
Intensity Ratios of the Fast to the Slow Component of the Spectra of Alkyl *p*-Chlorobenzoates

samples solv concn	20 °C	40 °C	60 °C	80 °C
(1) C_1				
30 wt %	...	...	...	...
45 wt %	...	0.42	0.79	1.20
60 wt %	0.51	1.30	2.16	2.72
(2) C_2				
30 wt %	...	...	0.36	0.62
45 wt %	...	1.10	1.53	2.26
60 wt %	0.56	1.47	2.20	3.42
(3) C_3				
30 wt %	...	...	0.44	0.88
45 wt %	...	0.75	1.15	1.58
60 wt %	0.60	1.14	1.43	2.84
(4) C_4				
30 wt %	...	...	0.52	0.86
45 wt %	...	0.26	0.45	0.75
60 wt %	0.50	0.74	1.02	1.31
(5) C_5				
30 wt %	...	...	0.26	0.47
45 wt %	...	0.21	0.57	1.13
60 wt %	...	1.16	0.98	1.15

not very different from those in the neat state, although the macroscopic viscosities of the PCAB/PMMA mixtures were indeed very high as evidenced by the glass temperature versus concentration plot shown in Figure 1.

The general reasons for the wide range of relaxation times displayed in the data may be explained by the DITE and RRD theories mentioned earlier. In the current article we seek a further explanation for the variation of the fast times as we vary the length of the solvent molecule.

Intensity Ratios. The free volume version of the diffusion in two environments theory (DITE) presented previously can be used to interpret the ratios of the areas under the fast to the narrow Lorentzian in the depolarized spectra of the PACB/PMMA mixtures given in Table II.[3] The density data given in Table I of 1 in conjunction with free volume theory may be used to calculate the average free volume per solvent molecule in each mixture.

The average free volume per solvent molecule, $\langle v_f \rangle$, is related to the free volume fraction, $f(T,c)$, by

$$\langle v_f \rangle = f(T,c)\mathrm{MW}/N_A \rho_{av} c \tag{1}$$

where MW is the molecular weight of the solvent, N_A Avogadro's number, ρ_{av} the density of the mixture, and c the weight fraction of solvent in the mixture. The free volume fraction is assumed to be related to the free volume fraction of the pure polymer, $\alpha(T)$, and that of the neat solvent, β(T), by

$$f(T,c) = (1 - c)\alpha(T) + c\beta(T) \tag{2}$$

The free volume fraction of the pure PMMA was calculated by using Litt's relation[11] as described previously,[3] and those for the pure solvents were estimated from the molar volumes of the pure solvents presented in 1 by using the relation

$$\beta(T) = (v(T) - v(0))/v(0) \tag{3}$$

The molar volumes at absolute zero were estimated by using the constants given by Sugden.[12]

The intensity ratio from the depolarized spectra and the average free volume per molecule may then be used to calculate the quantity bV^* where V^* is the critical free volume required by a molecule for fast orientational relaxation and b is a constant of order unity for small values of the PCAB concentration and less than unity for larger values. When the bV^* values obtained from the above calculations are plotted against L^3, reasonably good fits to straight lines that pass close to the origin are obtained for

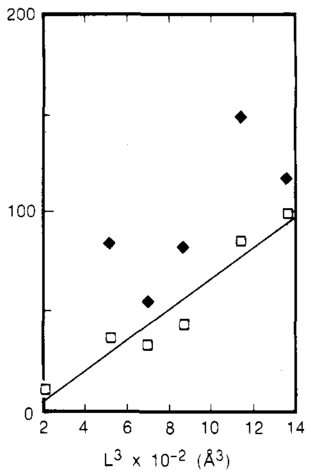

Figure 4. The bV^* versus the cubes of the molecular lengths for the CB/PMMA and PCAB/PMMA mixtures at 80 °C. The point at L^3 = 213 Å³ corresponds to CB. (Key: □, 60 wt % solvent; ◆, 45 wt % solvent.)

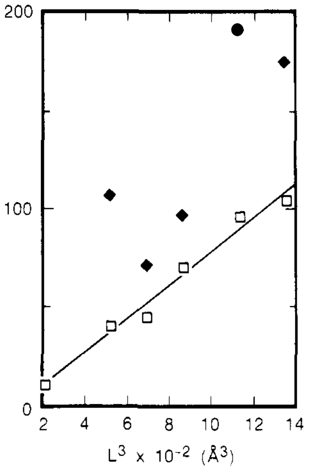

Figure 5. The bV^* versus the cubes of the molecular lengths for the CB/PMMA and PCAB/PMMA mixtures at 60 °C. (Key: □, 60 wt % PCAB; ◆, 45 wt % PCAB.)

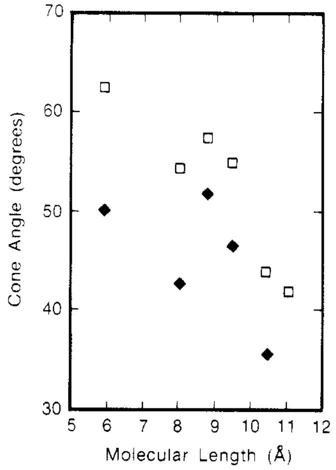

Figure 6. Cone angles versus molecular lengths for the CB/PMMA and PCAB/PMMA mixtures at 80 °C. The points at L = 6.0 Å correspond to CB. (Key: □, 60 wt % PCAB; ◆, 45 wt % PCAB.)

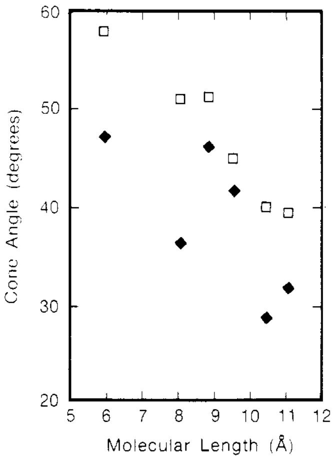

Figure 7. Cone angles versus molecular lengths for CB/PMMA and PCAB/PMMA mixtures at 60 °C. (Key: □, 60 wt % PCAB; ◆, 45 wt % PCAB.)

the 60% PCAB concentration as shown in Figures 4 and 5, so that for the 60% mixtures the bV^* appear to be proportional to the volume swept out by a solvent molecule as it rotates. The 45% PCAB data, however, vary in a nonmonotonic way with L^3.

In the clustering version of the DITE model, the average cluster size must be calculated in order to obtain the critical cluster size. Although, there are relations between the average cluster size and thermodynamic solution parameters (see, for instance, eq 8, below), the values for these parameters for the PCAB/PMMA mixtures have not as yet been measured.

Another way of interpreting the data obtained in this work is to use the RRD theory mentioned earlier.[8] As discussed above, in this theory the solvent molecules are considered to be confined to cavities formed by the polymer chains. A solvent molecule can reorient on a picosecond time scale until it reaches the walls of the cavity. In order to reorient beyond this maximum angle, the cone angle, the solvent molecule must await relaxation of the polymer segments that comprise most of the cavity walls, a very slow process compared to the initial picosecond time scale process. The cone angle for a given temperature, solvent concentration, and solvent molecular length may be calculated from the intensity ratio of the fast to slow Lorentzians in the depolarized light scattering spectra (Table II) following the calculation procedure given previously.[3] The resulting cone angles at 80 and 60 °C are presented in Figures 6 and 7. As expected at the higher concentrations, the cone angles generally decrease monotonically with molecular length of the solvent, except for C_1 which showed a lower value than expected. At the 45% PCAB concentration, however, the now familiar nonmonotonic variation of the properties of the PACB's with L^3 is evident in the derived cone angles.

The Fast Relaxation Times. In 1, we discussed the reorientation times of the PCAB's in the neat liquids and in dilute CCl_4 solutions. The reorientation times in these systems scaled with $\eta L^3/T[(\ln \rho) + \delta]$, where η is the liquid viscosity, T the absolute temperature, L the molecular length, ρ the molecular axial ratio, and δ a hydrodynamic end-effect correction defined in 1. It is of interest to test the validity of the scaling laws in the PCAB/PMMA mixtures, especially the L^3 and η dependences at constant temperature. For this case the scaling law may be written in the form

$$\tau_f = C\eta L^3 + \tau_0 \tag{4}$$

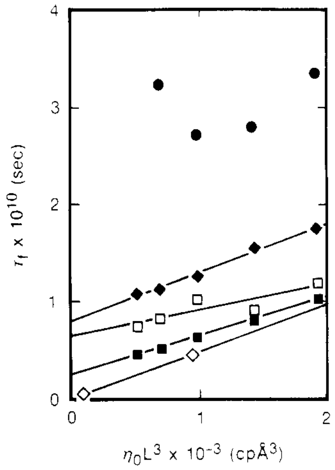

Figure 8. The fast relaxation times versus the products of the neat solvent viscosities and the cubes of the molecular lengths at 80 °C. (Key: ●, 30 wt % PCAB; ◆, 45 wt %; □, 60 wt %; ■, neat PCAB; ◇, neat chlorobenzene and chlorodiphenyl methane.)

where C is presumed to be only weakly dependent on the molecular axial ratio in the small axial ratio range of the PACB's considered here and τ_0 is a zero-viscosity intercept.

For the neat CB and PCAB, η is simply the viscosity of the neat liquids (η_0), but for the PCAB and CB/PMMA mixtures, the viscosities of the mixtures are very high (the T_g of these mixtures are close to ambient temperatures) and the predicted value of τ_f using reasonable estimates for C (for instance those of the neat liquids) would be many orders of magnitude larger than those observed in our experiments. We thus attempted to interpret the η appearing in the scaling law as some "local viscosity" (η_l) of the solvent/polymer mixture. Unfortunately, this interpretation is not very useful without further assumptions since we have no measure of η_l except that from the τ_f we have obtained in this work. Therefore, we tested scaling laws which assume that there is a local viscosity η_l that is a fixed multiple of the pure solvent viscosities η_0 for the whole series of PCAB's in the mixtures at a given temperature and solvent composition. This ansatz would be expected to be most valid at high solvent concentrations and high temperatures in which the local environment of a solvent molecule is likely to not be very different from that in the neat liquid. Under these conditions, the environment of a given solvent molecule would be composed largely of other solvent molecules and of polymer chains that would be more mobile than they would be at lower

Table III
χ Parameters of Alkyl Acetates in PMMA[a]

solvents	χ parameter	solvents	χ parameter
methyl acetate	...	n-butyl acetate	0.500
ethyl acetate	0.475	n-pentyl acetate	0.507
n-propyl acetate	0.487		

[a] From ref 20 and 21.

solvent concentrations and temperatures.

Figure 8 shows plots of τ_f versus $\eta_0 L^3$ at 80 °C for the neat PCAB's and the 45% and 60% PCAB/PMMA mixtures. The data for the neat liquid and the 45% mixture are well fit by straight lines (coefficients of linear correlation $R = 1.00$ and 0.99, respectively) while the data for the 60% mixture show more scatter ($R = 0.87$). Assuming linear relationships, we may write

$$\tau_f^m = C\eta_1 L^3 + \tau_0^m \tag{5}$$

$$\tau_f^0 = C\eta^0 L^3 + \tau_0^0 \tag{6}$$

where τ_f^m and τ_f^0 are the fast rotational relaxation times observed in the PCAB/PMMA mixtures and the rotational relaxation times have been previously reported in 1 and have been discussed there from a slightly different point of view.

Equations 5 and 6 imply that the ratio of η_1 to η_0 is given by

$$\eta_1/\eta_0 = (\tau_f^m - \tau_0^m)/(\tau_f^0 - \tau_0^0) \tag{7}$$

The values of η_1/η_0 may be calculated from eq 7 and Figure 8, giving values of 1.3 and 0.65 for PCAB concentrations of 45% and 60%, respectively, at 80 °C. This result implies that the local viscosity for the 60% solution is in fact less than that of the neat liquid.

This odd behavior of the 60% concentrations in Figure 8 can perhaps be explained by the solvent clustering phenomena that are commonly observed in polymer/poor solvent mixtures.[13-16] The cluster size of the solvent in the polymer matrix, defined as the mean number of solvent molecules per solvent cluster, can be expressed as a function of the Flory interaction parameter χ and the solvent volume fraction ϕ_1:[16-19]

$$\mathrm{Cs} = 1/(1 - 2\chi\phi_1) \tag{8}$$

It may be seen from eq 8 that as χ approaches 0.5, the cluster size grows very rapidly with solvent concentration, leading eventually to a microphase separation.[19]

The χ values for the PCAB/PMMA mixtures have not been measured. We may, however, as a guide to the dependence of χ on the alkyl chain length, use the χ values for the alkyl acetate/PMMA mixtures.[20,21] These values are shown in Table III. From Table III, we might expect that the C_4 and C_5 PCAB have a higher probability of forming large clusters or to microphase separate than the lower homologues. What was probably a microphase separation was visually observed as an opalescence in the 60% C_5/PMMA mixture at ambient temperature, a phenomenon similar to that observed by Misra et al. for water in a copolymer of PVA/PVB.[19] In addition, as mentioned above, attempts to measure the Landau–Placzek ratio in the 60% C_5 mixture were unsuccessful because of the overwhelming intensity of the central line.

If the C_4 and C_5 do form clusters of a few tens of molecules at high temperature and high concentration, the local viscosity in these large clusters would most likely approach those of the neat solvents. Thus, one might expect the τ_f in these systems to be closer to those of the neat solvents than in a PCAB/PMMA solution with no microphase separation. Thus, the 60% plot in Figure 8 should, if this point of view is correct, probably be represented by two straight lines, one passing through C_1, C_2, and C_3 with a higher η_1/η_0 and one passing through C_4 and C_5 with lower η_1/η_0. At 45% PCAB and 80 °C, it appears that no significant amount of phase separation occurred since all the PCAB homologues can be represented with a single straight line.

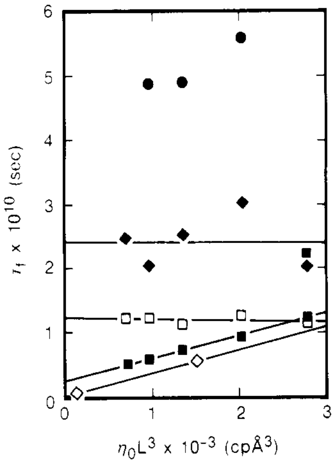

Figure 9. The fast relaxation times versus the products of the neat solvent viscosities and the cubes of the molecular lengths at 60 °C. (Key: ●, 30 wt % PCAB; ◆, 45 wt %; □, 60 wt %; ■, neat PCAB; ◇, neat CB and CPM.)

Another interesting observation that may be made from Figure 8 is that both the neat CB and CPM have considerably lower τ_f than those of the neat PCAB's for equivalent $\eta_0 L^3$ values. If a straight line is drawn between the two data points for neat CB and CPM at 80 °C, the resulting line has a slope approximating that of the neat PCAB but has an intercept close to the origin. If we assume that CB and CPM are homologues (probably not a poor assumption considering their similarities in structure), then the factor C in eq 4 must be similar for the PACB homologues and CB/CPM "homologue".

At 60 °C linear relationships between the τ_f and $\eta_0 L^3$ are preserved for the neat PCAB homologues and the neat CB/CPM homologue. However, marked changes occur in the $\tau_f - \eta_0 L^3$ relationship for the PCAB/PMMA mixtures as shown in Figure 9. At 60% PCAB concentration, the τ_f appears to be independent of $\eta_0 L^3$ or in fact to have a slightly negative slope. Thus, the reorientation appears to be speeding up slightly as the viscosity length cubed product increases. At 45% τ_f appears to oscillate with $\eta_0 L^3$.

The RRD theory can also be used to rationalize some of the anomalies in the τ_f versus $\eta_0 L^3$ plots in Figures 8 and 9. If the solvent molecules in the PMMA can indeed be envisaged to be restricted on the fast time scale to reorientation through the cone angle, an apparent speeding up of the fast relaxation time would be expected upon restriction as long as the local environment (say, the local viscosity) is not very different from that of the neat solvent. From the cone angles derived from the intensity ratios in the mixtures, the factor corresponding to the speeding up of the reorientation may be derived, and a corrected reorientation time denoted by τ_f^* may be found.[3,8] The τ_f^* are ploted in Figures 10, 11, and 12 for the 80, 60, and 40 °C systems, respectively.

Note that for the 80 °C systems, the 60% PCAB/PMMA mixtures now exhibit a linear dependence on $\eta_0 L^3$ ($R = 0.99$) with a slightly larger intercept than the neat liquids and a somewhat larger slope. The ratio of the slope of the straight line fit to the 60% solution data to that for

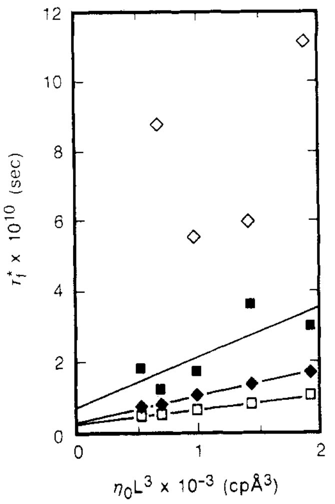

Figure 10. The fast relaxation times corrected for the cone angle effect versus the products of the neat solvent viscosities and the cubes of the molecular lengths for the PCAB/PMMA mixtures at 80 °C. (Key: ◇, 30 wt %; ■, 45 wt %; ◆ 60 wt %; □, neat PCAB.)

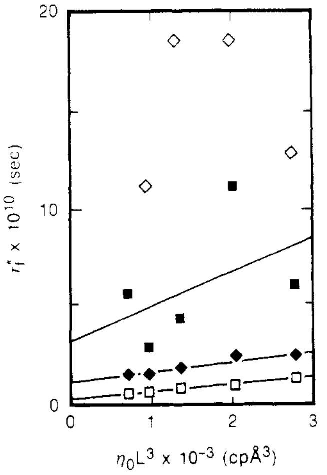

Figure 11. The fast relaxation times corrected for the cone angle effect versus the products of the neat solvent viscosities and the cubes of the molecular lengths for the PCAB/PMMA mixtures at 60 °C. The straight line drawn through the 45% data points is meant only as a visual guide. (Key: ◇, 30 wt %; ■, 45 wt %; ◆, 60 wt %; □, neat PCAB.)

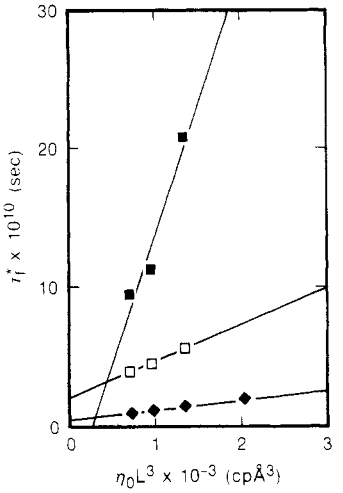

Figure 12. The fast relaxation times corrected for the cone angle effect versus the products of the neat solvent viscosities and the cubes of the molecular lengths for the PCAB/PMMA mixtures at 40 °C. The straight line drawn through the 45% data points is meant only as a visual guide. (Key: ■, 45 wt %; □, 60 wt %; ◆, neat PCAB.)

the neat liquids is 1.8. Thus, in terms of the interpretation given above, the local viscosity in the 60% mixture is 1.8 times that in the neat liquid. The 45% and 30% mixtures do not show a monotonic dependence of τ_f^* on $\eta_0 L^3$.

The 60 °C data in Figure 11 shows a marginal linear fit to the 60% solution data ($R = 0.90$) and, again, nonmonotonic behavior for the 45% and 30% mixtures. The linear fit to the data for the 60% mixtures exhibits a larger intercept than for the neat liquids and only a slightly larger slope. It appears that this mixture at this temperature is near the transition between the behavior where the local viscosity hypothesis appears to be valid (for instance, for the 60% solution at 80 °C) and the region where one observes nonmonotonic behavior in the corrected reorientation times. The ratio of the slope for the 60% mixtures to that for the neat solvents is 1.33.

The data at 40 °C in Figure 12 is consistent with the above interpretation. It is, however, not possible to draw definite conclusions since only three data points are available for the 60% and 45% mixtures.

A major question in the τ_f versus ηL^3 plots is the physical meaning of the zero-viscosity intercept. Various conjectures have appeared in the literature concerning its significance (or lack of significance), but there is as yet no satisfactory explanation.[2,22,23] This is a particularly interesting question in the PCAB systems since the major difference between the PCAB's and CB and CPM neat liquids lies in the intercepts. One is tempted to use the strength of the intermolecular attraction (cohesive energy density) differences between the PCAB homologues and the CB/CPM homologues as a likely physical phenomenon correlated with the values of the τ_0^0. We note that in 1, we found large differences in the intercept (for slightly different, but basically equivalent plots) for the neat PCAB's and those in 16% solutions in CCl_4 while the slopes were almost identical. In the 80 °C, 45% and 60% PCAB/PMMA mixtures the intercepts in Figure 10 become larger than that for the neat solvents, while for the 60%, 60 °C mixtures, the major difference from the neat solvent data is in the intercepts.

Conclusion

The reorientation of the series of solvent molecules in PMMA is very complex, and more data, particularly thermodynamic data, are necessary to produce a complete picture of the reorientational motion of these solvents in PMMA. Some tentative conclusions may, however, be drawn from the data at hand.

The C_5 sample appears to have microphase separated at the higher solvent concentrations. The evidence for this, as noted above, includes the inability to measure the Landau-Placzek ratio for the 60% C_5 sample, its readily apparent opalescence, its high values for the fast to slow intensity (which gives a higher derived cone angle than might be expected for a molecule of its length), and its ratio $\tau_f^0/\tau_f^m \simeq 1$. Furthermore, the high values for χ for the analogous *n*-pentyl acetate/PMMA mixture indicates that this system is likely to be near a phase separation point. It is also possible that the 60% C_4/PMMA mixture might be near a phase separation point at high T, although the evidence for this is far from conclusive.

The C_1 compound gives lower cone angles, higher bV^*, and higher τ_f's than might be expected from the trends in these quantities for the higher homologues, especially at low solvent concentrations and low temperatures. This behavior might be attributed to the somewhat higher T_g's (and consequent lower polymer chain mobility) of these samples. For instance, the 45% C_1/PMMA sample appears to have a T_g about 25 °C higher than the C_2 sample of the same concentration. The high melting temperature of the neat C_1 and the endothermic peak detected in the DSC thermogram of the 60% C_1/PMMA sample near this temperature (see Figure 2b) also indicate that C_1 might be prone to forming solidlike dimers or higher aggregates in the PMMA.

The RRD model combined with the local viscosity and hydrodynamic scaling theories gives a consistent explanation of the τ_f^m at high T and high solvent concentrations. At low solvent concentrations and low T the environment of a solvent molecule differs strongly from that in the neat liquid so that the scaling laws predicted by this simple theory are no longer obeyed.

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Registry No. PMMA, 9011-14-7; methyl *p*-chlorobenzoate, 1126-46-1; ethyl *p*-chlorobenzoate, 7335-27-5; propyl *p*-chlorobenzoate, 25800-30-0; butyl *p*-chlorobenzoate, 27942-64-9; pentyl *p*-chlorobenzoate, 97222-04-3.

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Structure and Dynamics of Epoxy Polymers

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ABSTRACT: Laser light scattering and small-angle X-ray scattering (SAXS) studies have been made of the curing of epoxy resins from 1,4-butanediol diglycidyl ether with *cis*-1,2-cyclohexanedicarboxylic anhydride. The epoxy resin before its gel point is soluble in methyl ethyl ketone, and the scattering techniques can be used to determine the molecular weight, the fractal dimension, and the molecular weight distribution of the branched epoxy polymer during each stage of the initial polymerization process. After gelation, SAXS remains a useful technique for studying the branched polymer structure in terms of the concept of fractal geometry for random systems.

I. Introduction

The kinetics and mechanism of copolymerization of epoxide resins with anhydrides or amines, with or without a catalyst, have been of interest because these materials often constitute an important component in reinforced composites. However, the mechanism of the curing reaction of epoxide and anhydrides has been somewhat uncertain as a number of partially conflicting reaction mechanisms have been proposed in recent years.[1] In this paper, we are interested in studying the structure and dynamics of branched epoxy polymer products during different stages of the curing process. By developing a methodology whereby we can examine the details of the branched epoxy polymer structure, we hope to be able to relate properties of some aspects of the microstructure with macroscopic properties of the epoxy resins. Thus, our approach represents only the first phase of our epoxy studies with emphasis on the determination of fundamental macromolecular parameters, such as the weight average molecular weight M_w and the molecular weight distribution MWD of branched epoxy polymers, and the nature of branched structure in terms of its fractal geometry.[2] Ultimately, the possibility of in situ determination of such properties before the gel point using the noninvasive scattering techniques will be investigated. In order to avoid complications related to intermolecular interactions, our experiments deal mainly in the dilute solution regime, ignoring at this time studies of structures and dynamics of epoxy resins in concentrated solutions of their own reaction bath. An earlier communication[3] has detailed the use of fractal geometry as an application to branched epoxy polymer characterizations.

II. Experimental Methods

1. **Materials.** 1,4-Butanediol diglycidyl ether (DGEB, M_w = 202.3) and *cis*-1,2-cyclohexanedicarboxylic anhydride (CH, M_w = 154.2) were purchased from Aldrich Chemical Co. and used without further purification since the same experimental results were obtained when both components were purified by vacuum distillation. The catalyst (CA), benzyldimethylamine (M_w = 135.2, courtesy of Gary L. Hagnauer, Polymer Research Division, Army

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