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Rotational Motion of a Homologous Series of Solvent Molecules in Amorphous Poly(methyl methacrylate). 1. Studies of the Solvents

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ABSTRACT: The depolarized light scattering reorientation times of a series of *n*-alkyl *p*-chlorobenzoates (PCAB's) (with *n*-alkyl varying from methyl to *n*-pentyl) have been measured in the neat liquids and in 16% (vol/vol) solutions in CCl_4 at various temperatures. Densities and viscosities of the neat liquids and viscosities of the 16% solutions were also measured. Plots of the reorientation times for each homologue versus η/T both in the neat liquid and in dilute solution are well fit by straight lines with nonzero zero-viscosity intercepts. Tests of the scaling of the reorientation times with molecular length as predicted by hydrodynamic theories for reorientation of rigid rods were performed. The reorientation times of the entire series of neat PCAB's fit well to a straight line when plotted versus $\eta L^3/T(\ln \rho + \delta)$ where ρ is the molecular axial ratio and δ is the hydrodynamic end effect correction. The homologues in 16% CCl_4 solution also exhibited reorientation times that gave good linear fits when plotted versus $\eta L^3/T(\ln \rho + \delta)$. The slopes of the plots for the neat liquids and the solutions were the same within experimental error, indicating that the static and dynamic pair correlation factors are probably not important for the systems studied. The slopes of these plots are not as large as those predicted by the Tirado and Garcia de la Torre theory for rigid rods with stick boundary conditions. The major difference between the plots for the neat liquids and the CCl_4 solutions is that the zero-viscosity intercept is larger for the neat liquids.

I. Introduction

The rotational dynamics of small molecules in liquids has been a longstanding subject of study by liquid-state physicists.[1-4] Such topics as the relation between the single molecule and collective reorientation times, the anisotropy of the reorientation times, the viscosity dependence of the single molecule times, and the role of orientational correlations and strong intermolecular forces (such as hydrogen bonding) have all been investigated. Reorientation times of molecules in liquids are commonly interpreted by using hydrodynamic models. In principle, such theories are strictly applicable only to the motion of large particles immersed in a medium composed of much smaller molecules since they treat the solvent as a continuum. However, much experimental work has shown that the reorientation times of small molecules in solutions with similarly sized solvent molecules are often linear functions of the solution viscosity—an indication that hydrodynamic theories may be applicable. Even in the presence of "strong" interactions such as hydrogen bonding between solvent and solute, it has been shown that in many cases the reorientation time remains a linear function of the solution viscosity. Thus, the hydrodynamic description of reorientation in liquids appears to be more general than one might expect from the derivations of specific relations—particularly those relating reorientation times to solution viscosity.

There is a need to test hydrodynamic models of molecular reorientation for a homologous series of small, rodlike molecules in the liquid state and in solution. In addition, the influence of polymer matrices on the reorientation of small solvent molecules has been only rarely studied, although it is of great scientific and technological importance. In this paper, we study the reorientation of a homologous series of rodlike molecules, the *n*-alkyl *p*-chlorobenzoates (with *n*-alkyl varying from methyl to pentyl) in the neat liquid as well as some studies of the same molecules in 16% vol/vol solutions in CCl_4. We test the explicit molecular length dependence of the orientational relaxation times predicted by hydrodynamic models for the series of solvents. The major experimental technique used is depolarized dynamic light scattering using a Fabry–Perot interferometer as the predetection filter.[4] To aid in the interpretation of the experiments, the viscosities and densities of the series of solvents were mea-

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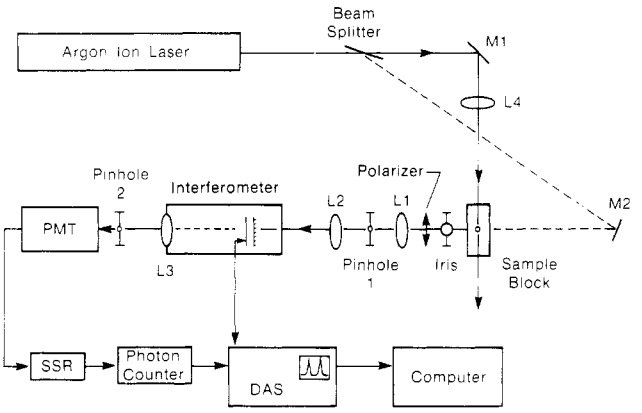

Figure 1. Schematic of the light scattering apparatus.

sured as functions of temperature. In the following paper, orientational relaxation studies of this same series of solvents in poly(methyl methacrylate) matrices are presented.

II. Experimental Section

Synthesis of the Alkyl *p*-Chlorobenzoates (PCAB's). Since the *n*-alkyl *p*-chlorobenzoates with the exception of methyl *p*-chlorobenzoate are not commercially available, a series of *n*-alkyl *p*-chlorobenzoates ranging from the *n*-alkyl = methyl to *n*-pentyl were prepared by conversion of *p*-chlorobenzoic acid into the acid chloride and subsequent esterification with the appropriate *n*-alkyl alcohol. The resulting PCAB's were then purified by double vacuum distillation. The purities of the final products were assayed by gas chromatography to be at least 99.5% pure.

Methyl *p*-chlorobenzoate (C_1) is crystalline at room temperature (mp $\simeq$ 45 °C), while the others are liquids at room temperature.

Densities and Viscosities. The densities of the PCAB's were measured as functions of temperature by using specially designed and constructed micropycnometers, which gave densities to five significant figures with good precision. Viscosities were measured by using standard capillary viscometers.

Scattering Samples. Rectangular Pyrex cells with Teflon-lined plastic screw caps from Spectrocell, Inc. (RF-1010-T) were used as scattering cells. The cells were cleaned with Chromerge cleaning solution and then repeatedly rinsed with double-distilled water. The cells were finally cleaned with filtered methanol.

The PCAB's were filtered through 0.2-mm Fluoropore filters. The first four or five drops of the filtrates of the alkyl *p*-chlorobenzoates were discarded since they contained impurities washed from the surface of the filters. The PCAB's attacked the Fluoropore filters, which were the most stable among the filters available to us, so that a given filter could be used only one time for filtration.

Since the methyl *p*-chlorobenzoate (C_1) is a solid at room temperature, it had to be first melted and then filtered through the Fluoropore filters. The syringe was heated by electrical heating tape during filtration to keep the PCMB in the liquid state. The C_1 after filtration could be supercooled, since presumably dust which served as nucleation centers was removed by the filtration. Filtration was continued on each sample until the samples were shown to be "dust-free" by observation of the laser illuminated sample with a low power microscope.

Light Scattering. A schematic of the light scattering apparatus is shown in Figure 1. The light source is a Spectra-Physics 165 argon ion laser operating at 488 nm with vertical polarization. The light scattered at 90° passed through a Glan-Thompson polarizer with an extinction coefficient of about 10^{-5}. Depending on the experiment the polarizer was set to pass either the vertical or horizontal component of the scattered light. The collecting lens (1) and the pinhole (2) produce an effective point source for the interferometer. The lens (2) served to collimate the scattered light parallel to the horizontal plate. The analysis of the spectrum of the scattered light was performed by a piezoelectrically driven Fabry–Perot interferometer manufactured by Burleigh Instruments. Light emerging from the interferometer was focused into the pinhole (2) through lens (3) and gathered by an EMI 9502 photomultiplier tube cooled to −60 °C to reduce the dark count. The signal from this photomultiplier tube was then amplified and discriminated by an SSR Model 1105 amplifier–discriminator and sent to a Burleigh Instruments Data Acquisition and Stabilization (DAS) system. The main function of the DAS is to control the axial drifting or the instrumental finesse and to average and send the data to an online microcomputer, a Universe 68 manufactured by Charles River Data Systems. The free spectral range of the interferometer was measured by using the Brillouin shift of toluene as a standard. The finesse, obtained from measurements of the polarized spectra of suspensions of polystyrene latex spheres, was in the range of 50–70 for most of the depolarized experiments.

III. Theoretical Background

Consider a liquid composed of optically anisotropic, cylindrically symmetric molecules of polarizability anisotropy β undergoing rotational diffusion. The optically anisotropic molecules either may be in the neat liquid or may be immersed in a solvent of optically spherical molecules. The frequency distribution of the depolarized component of the light scattered from this system may be shown to be[4]

$$I_{VH}(\omega) = A\beta^2 N g_2 \left\{ \frac{1/\tau_c}{\omega^2 + (1/\tau_c^2)} \right\} \tag{1}$$

where A is for our purposes a constant, N is the number of scattering molecules, ω is the frequency change of the scattered light from the incident frequency, τ_c is the light scattering relaxation time, and g_2 is the static pair orientational correlation function. The light scattering relaxation time τ_c is a collective rotational relaxation time which is conveniently related to the single molecule relaxation time by the Keyes–Kivelson relation[5]

$$\tau_c = (g_2/j_2)\tau_S \tag{2}$$

where τ_S is the single-molecule relaxation time and j_2 is the dynamic pair orientational correlation factor. In the absence of static and dynamic orientational pair correlations between pairs of optically anisotropic molecules, g_2 and $j_2 = 1$ and the collective and single molecule relaxation times are identical. In the case of rotational diffusion $1/\tau_S = 6\theta$, where θ is the molecular rotational diffusion coefficient. In many cases, values of g_2/j_2 may be estimated by comparing τ_c values obtained from measurements on the neat liquid with similar measurements performed on the same molecule in dilute solutions.

It has been found for a wide range of molecules that both the collective and single-molecule orientational relaxation times are linear functions of the solution viscosity with a nonzero intercept when the line is extrapolated to zero viscosity.[1-4] The slopes of these lines usually correlate well with the results of hydrodynamic theories. Hydrodynamic theories for molecules with ellipsoidal and cylindrical shapes with longest dimension L and axial ratio ρ (long axis to short axis) predict the dependences of the single molecule reorientation time on these quantities. When these predictions are combined with eq 2, we obtain for the collective reorientation times

$$\tau_c = (g_2/j_2)(4\pi\eta L^3\kappa/3kTf(\rho) + \tau_0) \tag{3}$$

where k is Boltzmann's constant, T the absolute temperature, η the solution viscosity, $f(\rho)$ a function of the axial ratio, κ an "interaction" parameter, and τ_0 the zero-viscosity intercept. The interaction parameter κ is related to the hydrodynamic boundary conditions (slip, stick, or somewhere in between slip and stick). For stick boundary conditions $\kappa = 1$ and for slip $\kappa \leq 1$ depending on the axial ratio. No calculations have been performed as yet for cylindrical molecules in the slip limit although calculations

Table I
Major Axis Lengths and Effective Axial Ratios of Alkyl *p*-Chlorobenzoates

	major axis (Å)	effective axial ratio		major axis (Å)	effective axial ratio
C_1	8.07	1.80	C_4	10.46	2.19
C_2	8.87	1.93	C_5	11.09	2.31
C_3	9.55	2.06			

have been performed for ellipsoids (as well as more exotic shapes).[6,7] The intercept τ_0 is predicted by the hydrodynamic theories to be zero, but nonzero values have been observed on a large number of systems.[1-4,8]

The function of the axial ratio $f(\rho)$ is well-known for ellipsoids[9] and will not be given here since, except perhaps for chlorobenzene, the molecules studied here are more closely approximated as cylinders. The theory for cylinders[10-18] is more difficult than that for ellipsoids because of the sharp edges of the cylinder. The theory of Broersma[11] was derived for the case where $\rho \geq 4$, much larger than the axial ratio for the PCAB's studied here and shown in Table I. The axial ratios and lengths in Table I were determined from Corey–Pauling–Koltun molecular models. Tirado and Garcia de la Torre[18] have derived expressions in the stick limit for cylinders that are presumed to be valid to axial ratios as low as two. Both the Broersma and Garcia de la Torre theories give

$$f(\rho) = 24([\ln \rho] + \delta) \quad (4)$$

where δ is known as the *end-effect correction* and is given in the Tirado and Garcia de la Torre theory by

$$\delta = -0.0662 + 0.917\rho^{-1} - 0.050\rho^{-2} \quad (5)$$

It should be pointed out that most of the hydrodynamic theories for cylinders using stick boundary conditions give results that converge at high axial ratios and the discrepancies between them occur mainly at low values of the axial ratios.

In comparing reorientation times of a homologous series of molecules such as the PCAB's in the neat liquids to the predictions of the hydrodynamic theory, it should be kept in mind that several hard to obtain factors may vary with the molecule being considered. These include the ratio g_2/j_2, κ, and τ_0. In dilution studies in solvents all of these quantities including κ and τ_0 may vary with concentration of a particular compound, although it is often found that these latter two quantities are constant if the solvents chosen interact similarly with the solute.

It should also be emphasized that the PCAB's are asymmetric molecules and are only approximately cylinders. Thus, deviations of results from the theory for cylinders could also result from this fact.

IV. Results and Discussion

Densities and Viscosities. The densities and viscosities of the PCAB homologues and, for comparison, those of neat chlorobenzene (CB) are shown in Table II. As stated previously, the PCMB (C_1) was found to crystallize at 45 °C in the neat form so that, for this compound, no densities or viscosities were obtained below 60 °C. The effect of increasing the chain length is to lower the density.

Figure 2 shows a plot of the specific volume (v) versus the absolute temperature for the PCAB's and CB. The slopes of these plots, the specific volume, and the derived coefficients of thermal expansion are summarized in Table III. It should be noted that the coefficient of thermal expansion of CB is significantly less than those of the PCAB's. The coefficients of thermal expansion of the PCAB's appear to have an "odd–even" alternation according to the number of carbons in the alkyl chain, even though their specific volumes increase monotonically with the length of the alkyl chain. A similar odd–even effect on various physical properties has been much discussed in liquid crystal forming molecules that contain alkyl chain tails.[19-21] The odd–even effects in the liquid crystal forming systems are often attributed to an alteration of the anisotropic attractive intermolecular forces among the molecules. It is possible that a similar phenomenon is occurring in the PCAB's, although the PCAB's are not known to exhibit liquid crystal phases.

The viscosities as functions of reciprocal temperature for the PCAB's and CB are shown in Figure 3. Again, the

Table II
Densities and Viscosities of the *n*-Alkyl *p*-Chlorobenzoates

(A) Densities (g/cm³)

T (°C)	CB	C_1	C_2	C_3	C_4	C_5
20	1.1063	...	1.1393	1.1031	1.0761	1.0552
40	1.0845	...	1.1159	1.0756	1.0516	1.0316
60	1.0631	1.1359	1.0925	1.0481	1.0272	1.0080
80	1.0415	1.1076	1.0692	1.0206	1.0027	0.9844

(B) Viscosities (cP)

T (°C)	CB[a]	C_1	C_2	C_3	C_4	C_5
20	0.799	...	3.27	4.02	4.52	5.83
40	0.631	...	1.98	2.42	2.68	3.22
60	0.468	1.35	1.38	1.56	1.78	2.05
80	0.431	1.00	1.00	1.14	1.26	1.42

[a] From: *Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Ed.; CRC: Boca Raton, FL, 1981.

Table III

(A) Specific Volumes and the Coefficients of Thermal Expansion for CB and PCAB's at 60 °C

liquid	specific vol (V) (cm³/g)	$10^4\Delta V/\Delta T$ (cm³/g K)[a]	$10^4(1/V)\Delta V/\Delta T$ (K^{-1})
CB	0.9405	9.35	9.94
C_1	0.8805	11.50	13.06
C_2	0.9155	9.50	10.37
C_3	0.9545	12.15	12.73
C_4	0.9740	11.35	11.65
C_5	0.9920	11.35	11.44

(B) Slopes of the Plot of ln η versus 1/T for Neat CB and the Neat PCAB's

liquid	slope (K^{-1})	liquid	slope (K^{-1})
CB	1.10	C_4	2.20
C_2	2.03	C_5	2.43
C_3	2.19		

[a] From the slopes of the straight line fits in Figure 3.

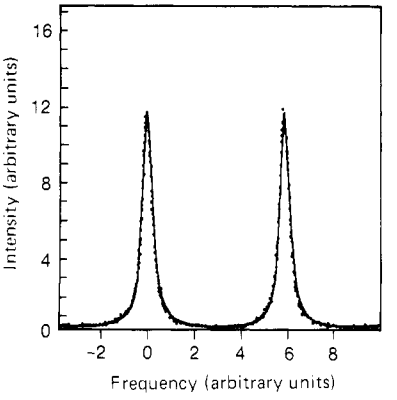

Figure 2. Fabry–Perot spectrum of depolarized scattered light from neat ethyl *p*-chlorobenzoate (C_2) at 60 °C. The continuous line represents a single Lorentzian fit to the data points.

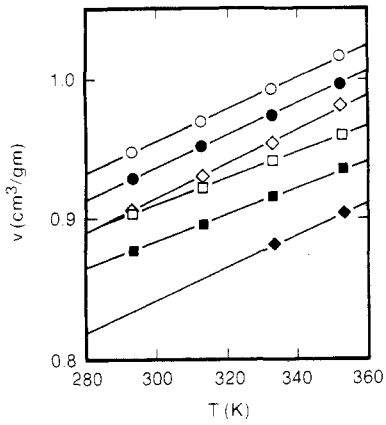

Figure 3. Specific volumes of the neat *n*-alkyl *p*-chlorobenzoates and chlorobenzene as functions of the absolute temperature. (Key: ○, C_5; ●, C_4; ◇, C_3; □, CB; ■, C_2; ♦, C_1.).

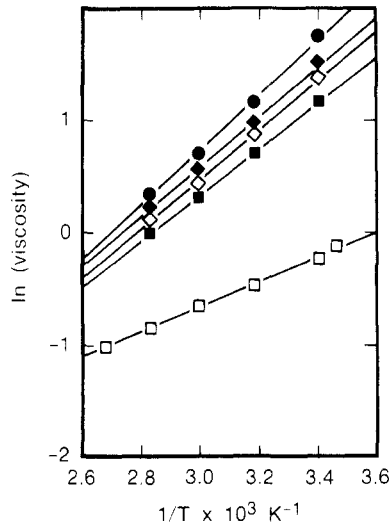

Figure 4. The natural logarithms of the viscosities versus the reciprocal absolute temperatures for the neat *n*-alkyl *p*-chlorobenzoates and chlorobenzene. (Key: ●, C_5; ♦, C_4; ◇, C_3; ■, C_2, □, CB.)

viscosity increases montonically with the alkyl chain length, and CB has a much lower viscosity than the PCAB's even though its specific volume is lower than for C_3, C_4, and C_5. Furthermore, the slopes of these plots show that the CB activation energy for flow is less than one-half that of the PCAB's. From the slopes of the viscosity versus $1/T$ plots, there is also a hint of the oscillating value of the activation energy with the alkyl chain length as shown in Table III. The viscosity for C_1 at temperatures below 60 °C was not obtained, and at 60 and 80 °C, the viscosity of C_1 was equal to that of C_2.

Depolarized Light Scattering. *All depolarized light* scattering spectra of the neat PCAB's and of the PCAB's in 16% vol/vol solutions in CCl_4 fit well to one Lorentzian plus a base line. The nonlinear least-squares fitting was performed by using the subroutine package "VAPRO" obtained from the CIT PROGRAM LIBRARY at Stanford University. The half-width at half-height (hwhh) of each fit Lorentzian was then corrected by subtracting the corresponding HWHH of the instrumental function. Figure 4 shows a typical spectrum with a single Lorentzian fit. The light scattering relaxation times were obtained from the reciprocals of the corrected HWHH's and are listed in Table IV. The light scattering reorientation times range from about 50 to 350 ps in the temperature range studied.

Figure 5 shows plots of the light scattering relaxation times of the neat PCAB's and CB versus η/T. Good

Table IV
Reorientation Times of Alkyl *p*-Chlorobenzoates in Pure Liquids and 16% Solutions[a]

Neat Liquid Reorientation Times

T (°C)	C_1	C_2	C_3	C_4	C_5
20	1.25	1.41	2.00	2.46	3.40
40	0.72	0.83	1.11	1.36	1.74
60	0.51	0.55	0.74	0.93	1.25
80	0.47	0.51	0.63	0.80	1.02

16% vol/vol PCAB/CCl_4 Reorientation Times and Viscosities

	C_2		C_3		C_4		C_5	
T (°C)	τ_c	η	τ_c	η	τ_c	η	τ_c	η
20	0.39	1.10	0.50	1.11	0.55	1.17	0.66	1.19
40	0.28	0.87	0.34	0.87	0.37	0.90	0.45	0.91
60	0.20	0.67	0.26	0.67	0.31	0.31	0.34	0.73

[a] Standard errors in the reorientation times are about ±5%. Units: $\tau_c = 10^{-10}$ sec/rad; η = cP.

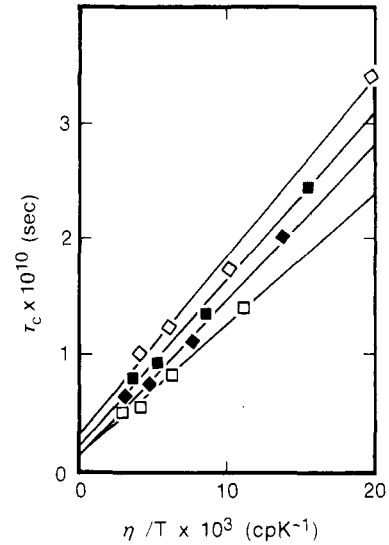

Figure 5. Light scattering relaxation times versus the viscosities divided by the absolute temperatures for the neat *n*-alkyl *p*-chlorobenzoates. (Key: ◇, C_5; ■, C_4; ♦, C_3; □, C_2.)

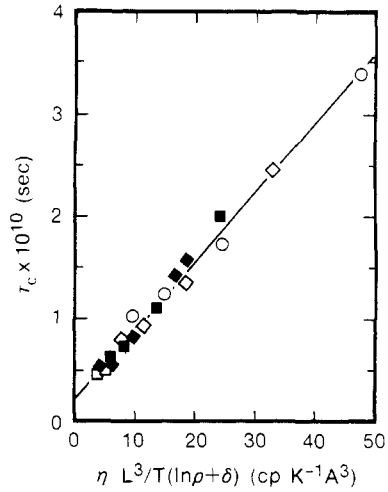

Figure 6. Light scattering relaxation times for the neat *n*-alkyl *p*-chlorobenzoates versus the viscosities times the cubes of the molecular lengths divided by absolute temperatures times (ln axial ratios plus end-effect corrections). (Key: ○, C_5; ◇, C_4, ■, C_3; ♦, C_2; □, C_1.)

straight line fits are obtained in each case. Figure 6 shows plots of the relaxation times versus $\eta L^3/T(\ln \rho + \delta)$ with δ given by eq 5 and the ρ's from Table I. Note that the fit to the straight line for all of the data is quite good. If

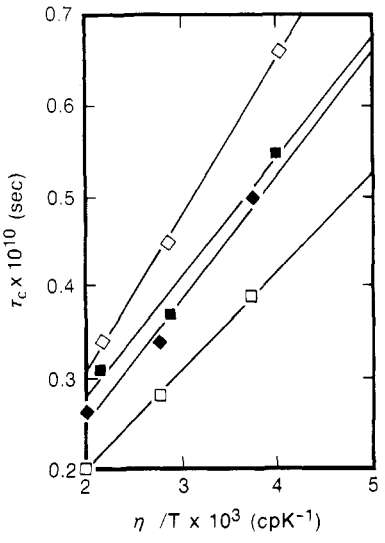

Figure 7. Light scattering relaxation times versus the solution viscosities divided by the absolute temperatures for the 16% (vol/vol) solutions of the *n*-alkyl *p*-chlorobenzoates in CCl_4. (Key: ◊, C_5; ■, C_4; ♦, C_3; □, C_2.)

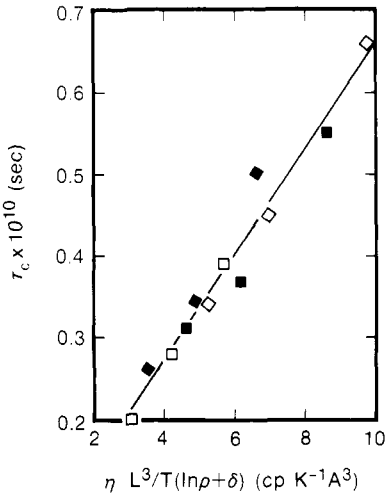

Figure 8. Light scattering relaxation times for the 16% (vol/vol) *n*-alkyl *p*-chlorobenzoate solutions versus the same quantities as in Figure 6. (Key: ◊, C_5; ■, C_4; ♦, C_3; □, C_2.)

we interpret the coefficients according to eq 3, we could conclude that $(g_2/j_2)\kappa$ probably does not vary very much over the series of PCAB's. The slope is 0.066×10^{-10} sK cp^{-1} Å^{-3} and the intercept is 0.22×10^{-10} s.

In Figure 7 a plot of the orientational relaxation time versus η/T for the 16% solutions is shown. Note that the slopes of these plots are the same within experimental error as those for the plots for the neat liquids in Figure 5, although the zero-viscosity intercepts are quite different.

In Figure 8, we show plots of the relaxation times versus $\eta L^3/T(\ln \rho + \delta)$ for the 16% solutions of the C_2 to C_5 homologues. A single straight line fits the points from all the PCAB's listed with slope 0.065×10^{-10} sK cp^{-1} Å^{-3} and intercept 0.011×10^{-10} s. Again the zero-viscosity intercept is quite different from that in the corresponding plot for the neat liquids (Figure 6), but the slope for the 16% solution is, within experimental error, the same as that for the neat liquids. Table V contains a summary of these results.

Comparing the slopes found for the neat liquids with those predicted from the hydrodynamic theory (eq 3), we find that $(g_2/J_2)\kappa \approx 0.53$ (see Table V). If we further assume that the major quantity varying when the solutions are diluted is g_2/j_2 and that the interaction parameter κ does not vary with dilution, we expect that for the 16% solutions $g_2/j_2 \approx 1$ and therefore for the neat liquid $g_2/j_2 \approx 1$ and $\kappa \approx 0.53$. Thus, if these estimates are correct, they imply that the viscosity-dependent part of the reorientation times of the PCAB's in the neat liquid and in dilute CCl_4 solutions is consistent with the hydrodynamic theory with substick boundary conditions. A more detailed comparison with the theory is not possible since no calculations have as yet been performed for cylinders with slip boundary conditions or with conditions between slip and stick. We might, however, compare the value of κ we estimate from the experiments with those obtained from calculations with slip boundary conditions for ellipsoids of revolution of the same axial ratios as for our models of the PCAB's. The axial ratios of these molecules vary between 2.32 and 1.78 (Table I). For ellipsoids of revolution in the slip limit, we find that κ would vary from about 0.2 to 0.3.[6] Thus, the κ we estimate is somewhat higher than this. This could mean any or some combination of the following: (1) that the boundary conditions are between slip and stick, (2) that they are slip and that for cylinders κ is higher than for ellipsoids of the same axial ratio, (3) that the 16% solutions are not dilute enough to ensure that $g_2/j_2 = 1$ (in this case the $g_2/j_2 > 1$, and the κ we obtain is in fact higher than the true κ which would be closer to the slip limit), or (4) that deviations from cylindrical shape of the PCAB's are important.

The zero-viscosity intercepts clearly do not follow eq 3. If g_2/j_2 were $\sim$1, then, if eq 2 applied, the intercepts for the neat liquids would be the same as for the 16% solutions. The value of g_2/j_2 needed to make the intercepts consistent is $\sim$20, an extraordinarily large number. Thus, it appears that dilution in the solvent has changed the nature of the zero-viscosity intercept. The physical meaning of the intercept is as yet not clear, although a wide range of suggestions have been made. These include the suggestions that it is an artifact of the data plotting procedure, an inertial contribution to the reorientation time, and that it results from a coupling between quantities analogous to molecular torques and angular velocity.[1,2,22] Whatever its meaning, it clearly varies drastically between the neat liquids and the 16% solutions.

Table V
Slopes and Intercepts of Reorientation Time Plots

(a) τ_c versus η/T Plots

	slopes × 10^7 (s K/cP)	intercepts × 10^{10} (s)
	Neat Liquids	
C_2	0.11	0.14
C_3	0.13	0.14
C_4	0.14	0.21
C_5	0.15	0.32
	16% PCAB/CCl_4	
C_2	0.11	−0.021
C_3	0.14	−0.029
C_4	0.13	0.015
C_5	0.17	−0.045

(b) τ_c versus $\eta L^3/T(\ln \rho + \delta)$

	slopes × 10^{10} (s K/(cP Å^3))	intercepts × 10^{10} (s)
neat liquids	0.066	0.22
16% solutions	0.065	0.011
prediction of eq 3 assuming $(g_2/j_2)\kappa = 1$	0.126	...

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Registry No. C_1, 1126-46-1; C_2, 7335-27-5; C_3, 25800-30-0; C_4, 27942-64-9; C_5, 97222-04-3.

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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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