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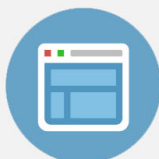
Solvent mobility in polystyrene/Aroclor solutions by depolarized Rayleigh scattering[a]

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We report evidence of modification of solvent reorientation induced by the presence of polymer in polymer/solvent systems. Depolarized Rayleigh spectroscopy (DRS) has been used to probe the rotational motion of neat Aroclor and polystyrene (PS) solutions with polymer concentration 0.05, 0.086, and 0.146 g/cm^3. The depolarized ($I_{VH}(\omega)$) spectra were recorded in the temperature range 40 to 140 °C using Fabry-Perot interferometry. Two Lorentzian lines were found to fit well the experimental $I_{VH}(\omega)$ of PS/Aroclor above 60 °C revealing two populations of solvent. The fast relaxation time τ_f is virtually insensitive to variations of PS content in contrast to a considerable slowing down effect on the slow reorientation time τ_s obtained more precisely from photon correlation and oscillatory electric birefrigence measurements at low temperatures (< 0 °C). The intensity I_s of the narrow Lorentzian component, which was found to increase rapidly below a characteristic temperature at given PS concentration, is associated with the slow orientation of the solvent in the PS environment. Surprisingly, the onset of PS induced modification occurs at rather high temperatures ($\sim T_g + 110$ K). The values of the intensity ratio I_s/I_f are rationalized in the framework of the restricted rotational diffusion model. Alternatively, the study of the single Lorentzian $I_{VH}(\omega)$ spectra of the neat solvent suggests a significant amount of orientational pair correlations and is consistent with clustering in liquid Aroclor.

INTRODUCTION

For polymer solutions, there has recently been considerable interest in the possibility of substantial alteration of solvent properties in the neighborhood of polymer chains. In particular, the observed high frequency limiting solution viscosity η'_∞ is not equal to the bulk solvent viscosity η_s for many different polymer/solvent systems.[1,2] The fact that the quantity ($\eta'_\infty - \eta_s$) can be either positive or negative is but one reason for ascribing this behavior to the solvent.[3,4] Any modification of the solvent properties by the presence of polymer chains,[5] and the concomitant dependence on polymer concentration c and temperature T, can best be examined by selective probing of the solvent itself.

The rotational motion of the solvent Aroclor 1248 (A1248), a mixture of polychlorinated biphenyls employed extensively for measurements of solution viscoelasticity and flow birefringence, in solutions containing either polystyrene (PS) or polybutadiene (PB), was recently examined by oscillatory electric birefringence (OEB).[6] For temperatures between − 17 and + 3 °C, mean solvent relaxation times $\tau(c,T)$ in the range from 1 ms to 0.1 μs were obtained; the neat solvent glass transition temperature T_g is approximately − 44 °C. A dimensionless, effective solvent friction ζ defined as $\tau(c,T)/\tau_0$, where $\tau_0 = \tau(0,T)$, the relaxation time of neat A1248, was found to depend approximately exponentially on c. The exponential coefficient, $\partial \ln \zeta /\partial c$, was essentially independent of T over this range, and equal to approxi-

mately 13 g/cm^3. This value corresponds very closely to the exponential coefficient reported[3,4] for η'_∞ for the same system and temperature range, lending considerable support to the interpretation of η'_∞ as reflecting predominantly solvent properties. In a separate study, a dimensionless, effective solvent friction ζ_D was defined as $D_0/D(c,T)$, where D was the measured solvent diffusivity.[7] In this case, $\partial \ln \zeta_D/\partial c$ was equal to 6 g/cm^3 at 28.5 °C; it is not yet clear if this difference is due to the different temperatures examined or to differences between the effect of polymer on the rotational and translational diffusivities.

Solvent molecules can undergo restricted reorientation[8] in concentrated polymer matrices, as inferred by dielectric relaxation,[9,10] depolarized Rayleigh scattering (DRS),[11] ^{2}H-NMR,[12] and Brillouin spectroscopy.[13] For example, in PS/toluene glasses ^{2}H-NMR spin echo measurements revealed both a "solid" and a "liquid" solvent fraction. One possible interpretation of the difference between ζ and ζ_D mentioned above is that at the higher temperature, the fraction of solvent relatively unhindered by PS increases. However, neither the rotational relaxation nor the diffusivity measurements revealed two populations of solvent. DRS offers a means to examine A1248 rotational dynamics at higher temperatures; although both polymer and solvent comprise anisoptropic units, they have greatly different reorientational relaxation times, so the two contributions can be cleanly resolved.

In this paper, we report DRS measurements on the same PS/A1248 system as in Ref. 6, for temperatures ranging from 40 to 140 °C, and for concentrations of 0, 0.05, 0.086,

and 0.146 g/cm^3. Two Lorentzian lines are readily resolved from the experimental $I_{VH}(\omega)$. The reorientation time and the fraction of the "mobile" A1248 are obtained from the width and the integrated intensity, respectively, of the broader spectral component. At high temperatures ($T > 100$ °C) the width of the narrower line is beyond the instrumental resolution, and is ascribed to the slower dynamics of the PS. As T decreases, the relative intensity of this peak increases, suggesting that it includes contributions from slower solvent molecules in the neighborhood of the chain. In the body of the paper, these observations are quantified, and compared with the results from OEB. In addition, some polarized ($I_{VH}(\omega)$) Rayleigh–Brillouin spectra were also recorded.

EXPERIMENTAL

The depolarized light scattering spectra $I_{VH}(\omega)$ were obtained at a scattering angle of 90° using a single-mode Ar$^+$ laser (Spectra Physics 2020) delivering 100 mW at 488 nm. The incident beam was vertically polarized relative to the scattering plane by means of a Glan polarizer with an extinction coefficient of 10^{-6}. The scattered light was collected through a Glan–Thompson polarizer with an extinction coefficient better than 10^{-7}, and frequency analyzed with a piezoelectrically driven Fabry-Perot interferometer (FPI) (Burleigh RC-110). The mirrors were 50 mm in diameter with a flatness of $\lambda/200$ and a reflectivity of about 0.98. The typical scan rate of the single pass interferometer was 0.5 sweeps/s. Three free spectral ranges (FSR) were used, 6.54, 11.09, 17.87 GHz; the typical finesse was about 65. A stabilization system (Burleigh DAS-10) was used to fix the position of the Rayleigh peak and maintain the maximum finesse. The scattered light, after passing through the FPI, was detected by a photomultiplier (EMI 9863); a narrow band interference filter was used to reject fluorescence. The depolarized spectra were accumulated in a 2048 channel multichannel analyzer (Canberra, Series 35); after repeated collection, the data were transferred to a computer for further analysis.

For each peak, about 800 points were fitted to either a single Lorentzian (neat A1248) or a double Lorentzian (PS/A1248 solutions). The half-width at half-height (HWHH) and the relative intensity of each Lorentzian was then calculated directly by the fitting program. The true HWHH Γ was obtained after subtraction of the instrument response function (Lorentzian) linewidth. For the broader peak, the linewidths thus determined were reproducible to within 5%. For the PS/A1248 solutions, the broader peak was independent of the FSR used, while the HWHH of the narrower peak was sensitive to the FSR, suggesting the presence of a distribution rather than a single relaxation time. Thus the HWHH of this narrow component represents only the fastest component of the distribution which can be sensed at a given FSR. On the other hand, if a distribution of relaxation times is present for this narrow peak, it should give rise to a highly nonexponential time-correlation function. This was indeed the case when the photon correlation technique was employed[21] (see Discussion). DRS spectra were recorded at temperatures from 40 to 140 °C. Typical

$I_{VH}(\omega)$ for neat A1248 are shown in Fig. 1; the instrumental linewidth is shown for comparison. These VH spectra are found to be well represented by a single Lorentzian over the T range 40 to 140 °C, without the characteristic central dip.[14] It is expected that an optically anisotropic liquid will show the central dip provided that the ratio $q^2\eta/(\rho\Gamma)$, (q being the amplitude of the scattering wave vector and ρ the density) is in the range 0.1 to 0.7 and the value of the coupling parameter R is sufficiently large. For neat A1248 this ratio was higher than 0.7 due to the high viscosity[4] η and consequently the central dip feature was absent.

Polarized Rayleigh–Brillouin spectra ($I_{VV}(\omega)$) were also recorded; the spectra could be represented by three central Lorentzians and two shifted Brillouin peaks. The unshifted peaks corresponded to the instrumental function, the "Mountain peak", and some of the intense I_{VH} contribution. Figure 2 shows $I_{VV}(\omega)$ for a solution with $c_{PS} = 0.086$ g/cm^3 at 119 °C. The HWHH of the broad Lorentzian differs by about 10% from the HWHH of $I_{VH}(\omega)$ for neat A1248. The Landau–Placzek intensity ratio ($I_R/2I_B$), often used as a criterion for good sample quality, was about 12 at low temperatures ($T < 70$ °C) and less than 3 at high temperatures ($T > 100$ °C) indicating clean samples. The reason for the higher values at low temperatures will be discussed subsequently.

The A1248 solvent (Monsanto Chemical Company, lot #KM502) was filtered through an 0.22 μm Millipore filter directly into the de-dusted scattering cell. The PS was obtained from the Pressure Chemical Company, with $M_w = 9.5 \times 10^4$ and $M_w/M_n = 1.04$. Both solvent and polymer are identical to those used in Ref. 6. Solutions were prepared gravimetrically by direct addition of solvent to polymer. Dissolution was assisted by stirring and gentle heating (< 60 °C) for a five week period prior to use.

DATA ANALYSIS AND RESULTS

The experimental $I_{VH}(\omega)$ for neat A1248, as shown for example in Fig. 1, are well described by a single Lorentzian
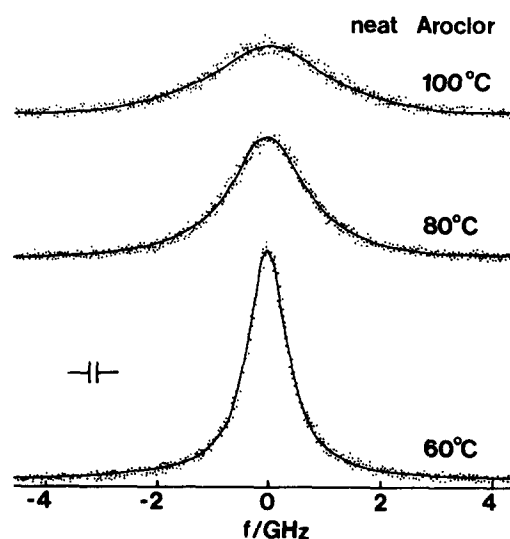

FIG. 1. Depolarized Rayleigh spectra of neat Aroclor at three different temperatures. The symbol ⊣⊢ denotes the instrumental fullwidth.
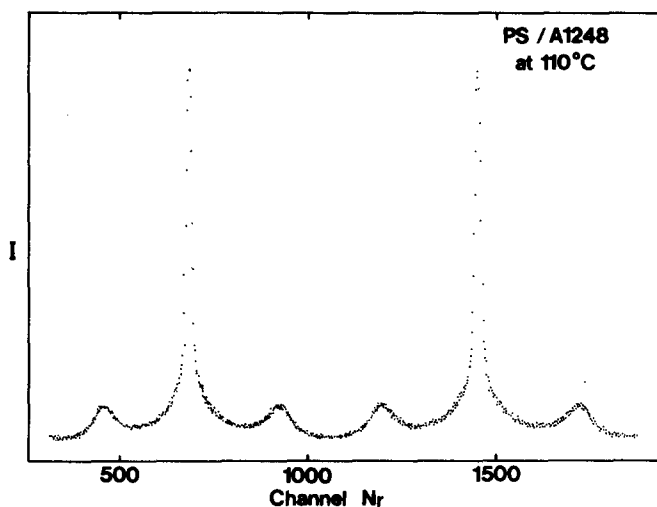
FIG. 2. Two interferometric orders of Rayleigh–Brillouin spectrum of PS/A1248 solution with $c_{PS} = 0.086$ g/cm^3 at 110 °C.

FIG. 3. Depolarized Rayleigh spectra of PS/A1248 with PS concentration 0.146 g/cm^3 at two temperatures. The solid lines denote the contributions of the narrow and broad Lorentzian components of the spectrum and the symbol ⊣⊢ indicates the instrumental fullwidth.

peak (plus a baseline B) at all temperatures. For all but the 40 °C data, the spectra obtained from PS/A1248 solutions were fitted to two Lorentzian peaks, i.e.,

$$I_{VH}(\omega)$$
$$= (1/\pi)\{I_f\Gamma_f/[\Gamma_f^2 + \omega^2] + I_s\Gamma_s/[\Gamma_s^2 + \omega^2]\} + B,$$
(1)

where I_f and I_s refer to the integrated intensities of the broader ("faster") and narrower ("slower") peaks, respectively, and Γ_f and Γ_s represent the corresponding HWHH. The intensity[15] ($I_f + I_s$) is proportional to the effective optical anisotropy and number density of the scatterers, while the width Γ (after subtraction of the instrumental linewidth) is related to the collective reorientation time by $\tau = (2\pi\Gamma)^{-1}$.

As both solute and solvent are composed of anisotropic units, the depolarized Rayleigh spectrum of the solution will naturally involve two approximately weighted contributions. In the absence of polymer–solvent interactions, and for vastly different orientational dynamics, the narrower spectral component may be associated with the relatively slow reorientational dynamics of the PS chains; at the FSRs employed, the observed HWHH is the instrumental contribution. As a confirmation of this assignment, $I_{VH}(\omega)$ for a 10% solution of the same PS in the isotropic solvent CCl$_4$ at 40 °C also has an instrumental HWHH. For this solution, the viscosity is approximately two orders of magnitude lower than for the corresponding A1248 solution, and thus the PS motions much more rapid.

The two overlapping peaks in $I_{VH}(\omega)$ for a PS/A1248 solution, $c = 0.146$ g/cm^3, at two temperatures are displayed in Fig. 3. The solid lines indicate the contributions of the two components, following Eq. (1). An important feature in Fig. 3 is the increase in the ratio $K = I_f/I_s$ with increasing temperature. This suggests a possible contribution to I_s due to slowly moving A1248 molecules in the vicinity of the PS chains, which increases with decreasing temperature.
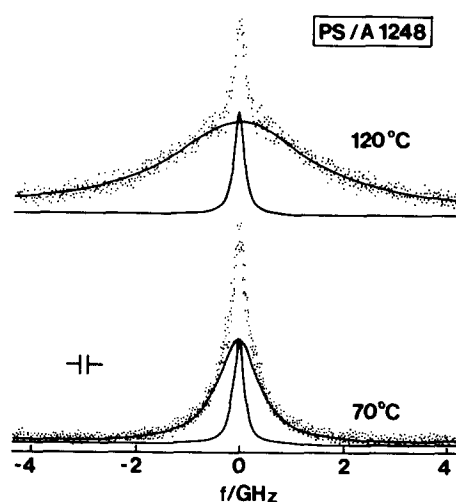
For this concentration, the solution is still well above its glass transition (≈ -41 °C).

In a previous DRS study, chlorobenzene[11] and p-chlorodiphenyl methane[16] exhibited two well-separated rotation rates when immersed in high concentration poly(methylmethacrylate) solutions ($c_{PMMA} > 40\%$). Since this polymer is a weak depolarized scatterer, the narrower Lorentzian in these systems was attributed to the slow rotational motion of the small probes. DRS measurements at such high polymer concentrations are usually feasible only if the polymer is polymerized in the solvent to minimize strain-induced light scattering. Moreover, high polymer concentrations probably contribute to different apparent reorientation rates for the broader Lorentzian when recorded with different FSRs. In contrast, with the relatively small polymer concentrations employed here, Γ_f was found to be independent of the FSR (between 6 and 18 GHz).

For the narrower peak, Γ_s is indistinguishable from the instrumental width even at the lowest FSR and highest temperature employed, except in the temperature interval from 60 to 80 °C, where I_s began to increase notably and Γ_s exceeded the instrumental HWHH. By 40 °C, the double Lorentzian fit became ambiguous, and a single peak fit was used. The single reorientation time thus obtained exhibited a larger concentration dependence than that for Γ_f at the higher temperatures. These observations will be discussed at greater length in the next section.

Figure 4 displays $I_{VH}(\omega)$ at 100 °C for solutions with $c_{PS} = 0.086$ and 0.146 g/cm^3. It can be seen that a reduction in c is accompanied by an increase in K, qualitatively similar to the effect of increasing T at fixed c. Above about 100 °C, I_s is essentially proportional to c, again supporting its interpretation as reflecting the polymer contribution. However, the increase in I_s and concomitant decrease in I_f below 100 °C suggests that I_s contains a contribution from slowly rotating A1248 molecules. In order to estimate the anisotropic scattering power of the A1248 relative to the PS which has an
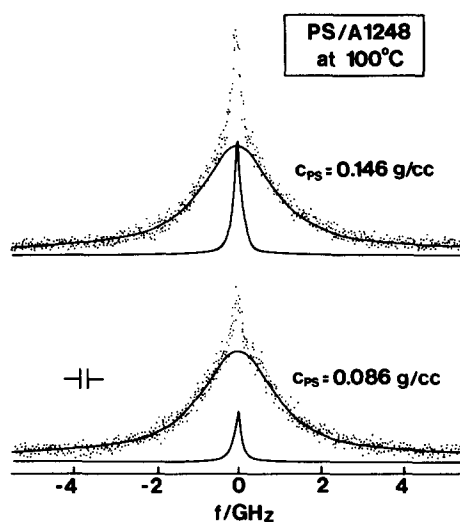
FIG. 4. Depolarized Rayleigh spectra of PS/A1248 at 100 °C for two PS concentrations $c_{PS} = 0.086$ and 0.146 g/cm³. The solid lines indicate the contribution of the narrow and broad Lorentzian components of the spectrum and ⊣⊢ denotes the instrumental width.

average optical anisotropy per monomer $\langle \gamma^2 \rangle / x = 38$ Å⁶ (x being the degree of polymerization)[17] it is necessary to estimate γ_{eff}^2 (due to the inclusion of static pair correlations[15]) of neat A1248. Using the values $n = 1.63$ for the refractive

index, $\rho = 1.45$ g/cm³ for the density, and comparing the integrated intensities for neat A1248 and a 10% PS/CCl₄ solution at 20 °C, we find $\gamma_{eff}^2 \approx 108$ Å⁶. This suggests that a monomer in an isolated PS chain is about three times less effective an anisotropic scatterer as an A1248 molecule in the neat solvent, which, together with the vastly different orientational dynamics of solute and solvent, may account for the relative ease with which the solvent contribution to the narrow peak is detected. Finally, all the reorientational relaxation times and intensity ratios are listed in Table I.

DISCUSSION

Reorientational relaxation

The T dependence of the reorientation time τ_0 for A1248 and the faster reorientation time τ_f for PS/A1248 solutions is depicted in Fig. 5. Note that the values at 40 °C (solid symbols) were obtained from the fit of a single Lorentzian, while at the higher temperatures the values reflect the broader of the two Lorentzians. The line segments indicate values of the slower reorientation time τ_s obtained from the linewidth of the narrower peak for temperatures where the width exceeded the instrumental contribution, using two different FSRs. The dashed line at lower T corresponds to τ obtained by OEB in a PS/A1248 solution with $c_{PS} = 0.146$ g/cm³, and extrapolated to higher T. The extrapolation assumes that the dimensionless friction $\zeta \equiv \tau(c,T)/\tau_0(T)$ remains independent of T, as it was in the T interval (-17 to $+3$ °C) examined by OEB.[6] From this extrapolation it is

TABLE I. Orientational relaxation times and relative intensities of depolarized Rayleigh spectra of PS/Aroclor.

PS conc. %(g/cm³)	T (°C)	τ_f (ns)	τ_s (ns)	K
0				
	40	1.67		
	60	0.50		
	70	0.32		
	80	0.22		
	100	0.13		
	120	0.09		
	140	0.07		
5				
	40		1.9	
	60	0.47	2.2	14
	70	0.32	⋯	32
	80	0.23	⋯	37
	100	0.15	⋯	39ᵃ
8.6				
	40		2.3	
	60	0.53	1.4	2.3
	70	0.29	1.1	3.1
	80	0.25	⋯	10
	100	0.15	⋯	21
	120	0.10	⋯	21
	140	0.07	⋯	21
14.6				
	40		2.9	
	60	0.57	1.7–2.1	1.2
	70	0.38	2.4	2.4
	80	0.25	2.0–2.4	4.3
	100	0.16	⋯	8.8
	120	0.1	⋯	13
	140	0.1	⋯	11

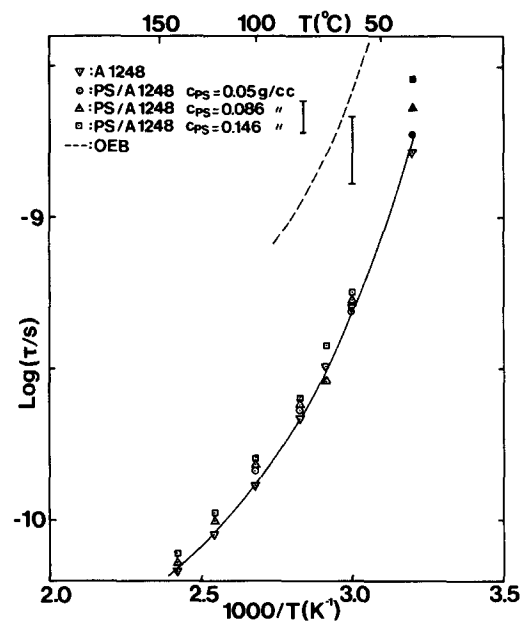ᵃ Calculated value, ⋯: the width of the narrow Lorentzian cannot be resolved.

FIG. 5. Temperature dependence of the reorientational relaxation times of Aroclor in the undiluted state and PS/A1248 solutions with different PS concentrations: ▽ single orientation time of neat solvent obtained by single Lorentzian fit of the experimental $I_{VH}(\omega)$. All empty symbols denote fast times obtained from the width of the broad Lorentzian component of $I_{VH}(\omega)$. The line segments denote time scales for the slow reorientational process (narrow Lorentzian line) whereas to draw the dashed line referred to PS/A1248 with $c_{PS} = 0.146$ g/cm³ we have assumed the same composition dependence observed by OEB at lower temperatures. The solid line denotes the fit of Eq. (4) to the experimental times in neat Aroclor.

evident that τ from OEB is in better agreement with τ_s than with τ_f obtained by DRS. This observation will be rationalized in the next section.

The strongly non-Arrhenius T dependence of the orientational time τ_0 for neat A1248 in Fig. 5 is similar to that of the shear viscosity η; this is in accordance with the Stokes–Einstein–Debye (SED) picture ($\tau_0 \sim \eta/T$) and is witnessed in other glass forming liquids.[18,19] In solution, τ_f exhibits a very similar T dependence to that in neat A1248; the c dependence of τ_f above 60 °C is quite weak, and certainly much smaller than that of the macroscopic solution viscosity. Thus, τ_f characterizes the reorientational motion of solvent substantially unaffected by the presence of PS. The insensitivity of τ_f to c has been exhibited in other concentrated polymer solutions.[11,16,20] In contrast, τ_0 in neat solvent and the slower orientation time τ_s in PS/A1248 with $c_{PS} = 0.146$ g/cm³ determined by OEB[6] at lower T differ by a factor of seven. Albeit within large error bars, τ_s measured by DRS between 60 and 80 °C differ by a similar amount. This slower motion is ascribed to the solvent, because as discussed previously, the reorientational dynamics of the PS are much slower. At 40 °C, where $I_{VH}(\omega)$ is well represented as a single Lorentzian due to the decrease in I_f and Γ_f of the broad Lorentzian, the single τ begins to shift from τ_f to τ_s as c increases.

In Ref. 6, the effect of PS on the rotation of A1248 was examined in terms of ζ and its c dependence, $\partial \ln \zeta / \partial c$; the latter quantity was approximately 13 g/cm³ over the range from -17 to $+3$ °C. The corresponding quantity can be calculated from τ_f, τ_s, and τ determined from the broad, narrow, and single Lorentzians obtained via DRS. The values thus obtained are plotted in Fig. 6, along with the results of Ref. 6. In addition, values determined from pulsed-field-gradient NMR[7] on the same system are included; in this case, ζ is taken as $D(0,T)/D(c,T)$, where D is the translational diffusivity of the solvent. If the various dynamic properties of the solvent are similarly affected by the addition of polymer, ζ should be the same from all three experiments (i.e., DRS, OEB, and NMR). As pointed out in Refs. 6 and

7, the results for OEB and NMR appear to differ, suggesting that reorientational and translation motions of the solvent are affected to different degrees by the polymer. This is not unreasonable; however, until these two measurements are performed at the same temperatures (work currently in progress) this issue is unsettled. On the other hand, both OEB and DRS reflect the correlation function[15]

$$C_{VH}(t) = \langle \delta a_{yz}(t)\delta a_{yz}(0) \rangle, \tag{2}$$

where $\delta a_{yz} = \Sigma_j a_{yz}(j,t)\exp\{i\mathbf{q}\cdot\mathbf{r}_j(t)\}$ denotes the spatial Fourier component of the polarizability density, with $a_{yz}(j,t)$ being the yz component of the laboratory frame polarizability tensor of the jth molecule, located at $r_j(t)$. For cylindrically symmetric molecules, $C_{VH}(t)$ should be an exponential decay with a collective relaxation time reflecting reorientation about the long molecular axis. Thus in principle OEB and DRS should exhibit the same effect of PS on the A1248 rotation, when employed at the same T.

The results in Fig. 6 suggest strongly that A1248 molecules in PS solution undergo reorientational motions over at least two different time scales: (a) a fast rotation, largely unaffected by PS, seen by DRS at 80 °C and above, but not seen in OEB at lower T, presumably due to small amplitude, and (b) a slow rotation due to the proximity of PS chains. It is the latter process which dominates the OEB response at low T, but which is evident in the DRS measurements below 80 °C. Somewhat surprisingly, perhaps, this indicates that the effect is visible even 120 °C above the solution glass transition. At 40 °C, limited resolution and low intensity probably result in an observed single relaxation process in DRS which is a mixture of the two. This interpretation is supported by consideration of the relative intensities, I_f and I_s, discussed in a subsequent section, and by DRS measurements at lower T using photon correlation spectroscopy (PCS) in place of Fabry–Perot interferometry (FPI).

Before attempting a more quantitative comparison of τ obtained by DRS and OEB, it is important to examine whether the two techniques yield comparable values when employed at the same T. We have extended[21] the present FPI–DRS results (Fig. 5) to much lower T (< -12 °C) using PCS to measure $C_{VH}(t)$ defined by Eq. (2) over the time range from 1 μs to 1 s. In all cases $C_{VH}(t)$ is well represented by the Kohlrausch–Williams–Watts (KWW) form:

$$C_{VH}(t) = b \exp[-(t/\tau^*)^\beta], \tag{3}$$

where b, τ^*, and β ($0 \leqslant \beta \leqslant 1$) are fitting parameters.[17] A single relaxation process is detected between -12 and -25 °C for both A1248 and PS/A1248 solutions and the fraction of the total depolarized scattering intensity associated with $C_{VH}(t)$ is practically one. The fractional exponent β was found to be virtually independent of T, but dependent on c in a systematic fashion; for neat A1248, $\beta = 0.63$, while for PS/A1248 with $c = 0.146$ g/cm³, $\beta = 0.43$. The higher value is consistent with values found for o-terphenyl[18] and α-phenyl cresol[19] in the supercooled liquid state, and seems to be characteristic of molecular glass formers. The lower value indicates a broader distribution of relaxation times in the solution. Somewhat surprisingly, this value is close to that found for $C_{VH}(t)$ measured in neat PS near T_g.[22] This obser-
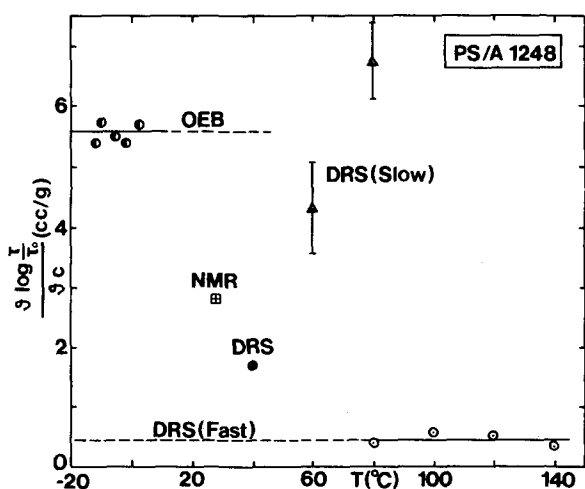

FIG. 6. The change $\partial \ln \zeta / \partial c$ of the solvent relaxation time with PS concentration against temperature for the different orientational processes (see caption of Fig. 5) probed by OEB and FPI.

vation is certainly consistent with the picture of a strongly modified solvent at these lower T. The τ^* values for neat A1248 and the PS/A1248 solution with $c = 0.146$ g/cm^3 are plotted as a function of T in Fig. 7, along with the values of τ obtained by OEB. The two experiments clearly yield very similar values of the reorientational time, even though there is some arbitrariness in the exact value of τ obtained by OEB.[6] It is useful to recall that the latter technique probes the orientational motion of the solvent A1248 which possesses significantly higher dipole moments than PS segments. Furthermore, the c dependence of τ at low T is similar between the two experiments. In contrast, at higher T the values of the faster time τ obtained by FPI, and also included in Fig. 7, are almost independent of c.

The τ_0 values (neat A1248) as obtained by OEB and PCS at low T and by FPI at high T, conform to the Vogel–Hesse–Fulcher–Tammann (VHFT) expression:[23]

$$\ln \tau_0 = \ln \tau_0^* + B / (T - T_0). \qquad (4)$$

A least-squares fit of Eq. (4) to the data in Fig. 7 yields the values $\tau_0^* = 1.8 \pm 0.2$ ps, $T_0 = 221 \pm 2$ K and $B = 645 \pm 40$ K. If the OEB data are excluded from the fit, the results are only slightly modified: $\tau_0^* = 1.3 \pm 0.1$ ps, $T_0 = 219 \pm 2$ K, and $B = 702 \pm 40$ K. These parameters may be compared to those obtained by fitting the equivalent of Eq. (4) to the T dependence of η^4: $\eta_0 = 6.6 \times 10^{-5}$ P, $T_0 = 219.8 \pm 2$ K, and $B_\eta = 824 \pm 40$ K. The viscosity data are also plotted in Fig. 7. As can be seen in Fig. 7, the T dependence of η is a little stronger than that for τ, which is reflected in the value of B_η being about 20% larger than B. For o-terphenyl,[18] for example, the agreement between B_η
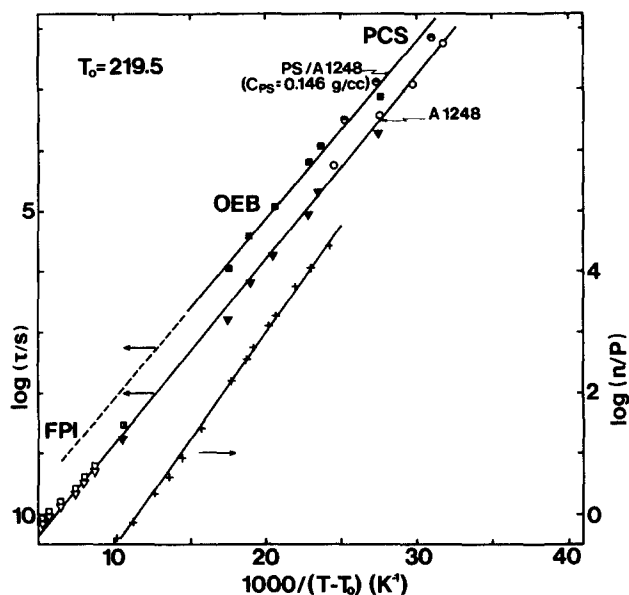
and B was much closer. In A1248 this result may imply cluster formation at low T; this point will be addressed in the last section.

The T dependence of τ in the PS/A1248 solution can also be compared to Eq. (4). If the OEB and PCS data at low T only are used, and if T_0 is fixed at 219 K due to the relatively small T range covered, the values $\tau_0^* = 2.5$ ps and $B = 636 \pm 40$ K are obtained. Thus, the T dependence is essentially the same as in neat A1248. However, the FPI values in solution at high T clearly do not follow the same T dependence, as shown by the dashed line in Fig. 7, again indicating a bifurcation[24] in the rotational relaxation of the solvent. In this context, it is useful to examine the intensities of the two spectral components of $I_{VH}(\omega)$.

Depolarized Rayleigh scattering intensities

As discussed in reference to Figs. 3 and 4, there is an interplay[25] between the integrated intensities I_s and I_f of the narrow and broad Lorentzians, respectively; increasing T from 60 to 100 °C results in an increase in I_f and a reduction in I_s. In addition to the ratio $K = I_f/I_s$, it is possible to compare these intensities to I_0, the integrated intensity for neat A1248 under similar interferometric conditions. These various intensities, and the ratio K, are plotted in Figs. 8(a) and 8(b) as functions of T. The two main features of these data

FIG. 7. Temperature dependence of the orientational time of Aroclor in the undiluted state and PS/A1248 solution with $c_{PS} = 0.146$ g/cm^3 obtained from Fabry-Perot interferometry (FPI), oscillatory electric birefringence (OEB) and photon correlation spectroscopy (PCS) experiments. The FPI and OEB times are taken from Fig. 5 and Ref. 6, respectively. The temperature dependence of shear viscosity of A1248 is also shown for comparison. The solid lines denote fits of Eq. (4) to the viscosity data and the experimental times as descried in the text.
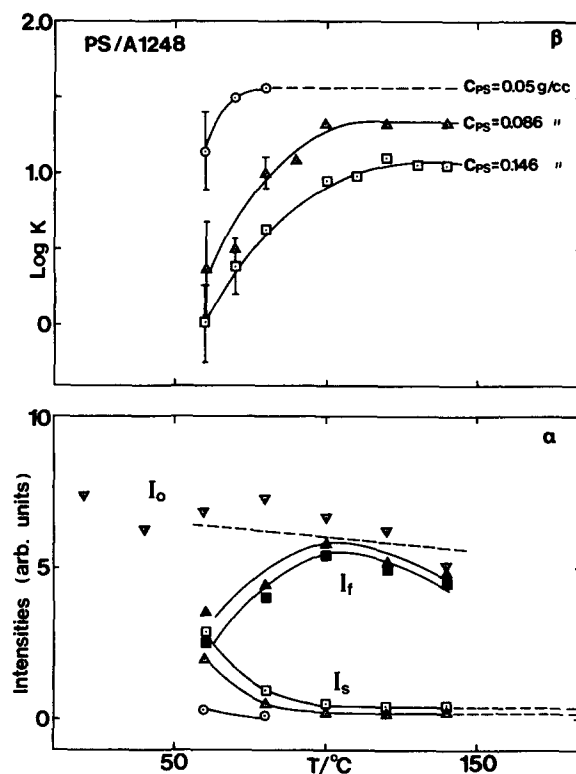
FIG. 8. (a) Depolarized Rayleigh intensities of the Aroclor in the undiluted state I_0, in PS/A1248 solutions I_f and of the slow Lorentzian component I_s due to PS and slow rotation of Aroclor hindered by PS. The dashed line denotes the computed (see in the text) intensity of the neat Aroclor from the fast I_f and slow I_s contributions. (b) The ratio I_f/I_s of the intensities associated with the narrow and broad components of the experimental spectrum. The dashed line is the computed limiting value of K at high temperatures.

are the correlation between I_s and I_f, and the rather strong T dependence of I_o, which exceeds that of the density ρ; the thermal expansion coefficient is 6×10^{-4} K^{-1} whereas the corresponding quantity for I_0 equals 23×10^{-4} K^{-1}. The latter observation supports the previously invoked picture of solvent clustering.[5,6]

The values of I_s at higher T reflect primarily the PS contribution, because $I_s \sim c_{PS}$, and because the magnitude of I_s compares well with the intensity from a PS/CCl$_4$ solution with the same c_{PS} (after correction for the local field).[16] Meanwhile, in the same T range, the intensity I_f of the broad Lorentzian is equal to I_0 (neat A1248) when corrected for dilution by the polymer. Thus, these data suggest that the solute and solvent contributions, I_s and I_f, respectively, are independent except for the effect of dilution, and that therefore the solute is "inert" in the sense of influencing the dynamics of the solvent. From Fig. 8(b), it appears that the temperature at which the high T limit of K is reached increases with c_{PS}, in agreement with both intuition and the prediction of a restricted rotational diffusion (RRD) theory.[8,26]

In the framework of the RRD model, a rodlike solvent molecule is assumed to undergo a fast, unhindered rotational diffusion, but restricted within a cone whose angle θ determines both the relaxation time τ_f and the intensity I_f. The polymer is assumed to provide an immobile, optically isotropic background. The narrow component of $I_{VH}(\omega)$ arises from the decay of residual reorientational coupling between the polymer and the rodlike solvent, i.e., relaxation of the cone walls, and is not treated explicitly in the model. In addition, the model applies to high polymer concentration and rather low T, so quantitative interpretation of the relaxation times associated with the narrow component cannot be attempted. Nevertheless, the spectral changes illustrated in Fig. 8 are consistent with the RRD model. The ratio K is larger as c_{PS} decreases, which can be interpreted as a decrease in the restriction, i.e., an increase in θ. For example, at 60 °C the RRD model gives $\theta = 44°$ for $c_{PS} = 0.146$ g/cm^3 and $\theta = 56°$ for $c_{PS} = 0.086$ g/cm^3.

Neat Aroclor

The second pertinent aspect of Fig. 8(a) is the rather strong temperature dependence of I_0 in neat A1248, which is a strong indication of nonzero static orientational pair correlations. Since dilution is an appropriate procedure to detect such correlations[27] we have studied $I_{VH}(\omega)$ for three solutions of A1248 in the optically isotropic CCl$_4$. The $I_{VH}(\omega)$ spectra retain their Lorentzian shape with increasing linewidth upon dilution. For symmetric top molecules in an inert solvent the integrated intensity I can be written as[15]

$$I = Af(n)\gamma^2\rho^2(1 + F\rho^*), \tag{5}$$

where A is a constant, $f(n)$ a function of the refractive index of the medium, ρ^* is the number density of solute and F is the static orientational pair correlation function. Equation (5) assumes an average optical anisotropy γ^2 which is independent of concentration. Using for $f(n)$ the Lorentz local field correction[28] $((n^2 + 2)/3)^2$ times the geometrical factor $1/n^2$ we have plotted in Fig. 9 $I^* = I/f(n)$ against solute
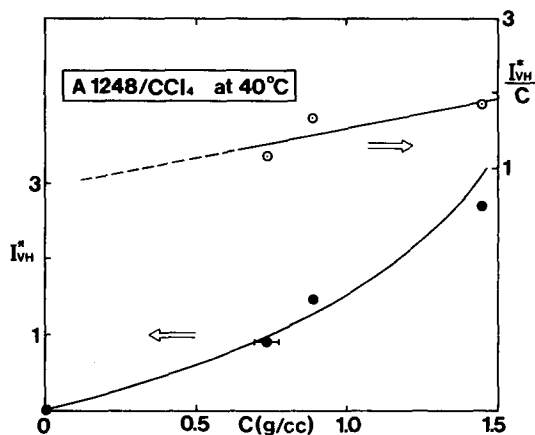

FIG. 9. The concentration dependence of the integrated intensity I^*_{VH} (corrected for the dependence on refractive index) of the Aroclor in neat state and in A1248/CCl$_4$ solutions at 40 °C.

concentration. The c dependence of I^* is apparently nonlinear as indicated by the plot I^*/c vs c also shown in Fig. 9. In the neat solvent at 40 °C $F\rho^* \approx 1$ suggesting a significant amount of static orientational correlations. The picture of clustering in A1248 invoked recently[5,6] is consistent with the intensity data of Figs. 8 and 9.

There are three additional findings that would support molecular association. First the Landau–Placzek ratio exhibits a significant increase below about 40 °C; at higher temperatures it amounts to 1.5 and 2 for Aroclor and PS/A1248 with $c_{PS} = 0.146$ g/cm^3, respectively. The observed increase in the LP value is mainly due to the increase of the polarized Rayleigh intensity, which is very sensitive to the size of aggregates. In this context, angular dependent measurements would provide an additional means to examine the nature of this clustering.[29] Second, a careful inspection of Fig. 7 would detect deviations from the fit of Eq. (4) to the experimental τ_0 values at the highest temperatures. In this temperature region, orientational interactions ($F\rho^*$) are probably weak. A third stronger evidence might be obtained from the connection between τ_0 and the macroscopic viscosity according to the modified SED equation:

$$\tau_0 = \frac{g_2}{j_2}\left(\frac{V_h}{k_B}\frac{\eta}{T} + \tau_\infty\right), \tag{6}$$

where V_h is an effective hydrodynamic volume of the reorienting molecule, $g_2 = 1 + F\rho^*$, j_2 is the dynamic correlation function,[30] and τ_∞ accounts for the nonzero intercept in the limit $\eta/T \to 0$. For uncorrelated orientation ($g_2 = 1$), V_h depends on the volume, shape of the rotating molecule and the hydrodynamic interactions with the surrounding fluid. Under stick boundary conditions, V_h is equal to the volume V_z swept out by the reorientation of the symmetry axis z. On the other hand, under slip-boundary conditions $V_h < V_z$ by a factor σ, which can be calculated from the ratio λ of the shorter (x,y) to the z axis for prolate and oblate ellipsoids.[31]

The use of the macroscopic shear viscosity in Eq. (6) rests on the assumption that the same local friction coefficient determines both reorientational relaxation and macro-

scopic friction. Such an assumption should be carefully checked. The SED equation has been shown to describe adequately the reorientation of non-interacting rigid[32] and non-rigid[27] optically anisotropic molecules. Good agreement between the experimental V_h and the hydrodynamic prediction is based upon slip rather than stick boundary conditions. In these systems, the static orientational pair correlation is found to be small ($F \sim 0$) and hence the collective reorientation time obtained from the DRS spectra effectively characterizes single particle orientation.

The temperature dependences of the collective τ_0 and macroscopic η shown in Fig. 7 have revealed different values for the activation parameter B [Eq. (4)], with B_η being larger. A plot of τ_0 vs η/T will therefore display significant deviations, especially at low temperatures, from the linear behavior implied by Eq. (6). These deviations are better visualized in the plot of the effective hydrodynamic volume $g_2 V_h$ versus temperature shown in Fig. 10. For the three highest temperatures $\tau_0 = (36 \pm 5)10^{-12}$ s $+ \eta/T(15 \pm 4)10^{-9}$ sK/cP from which $g_2 \tau_\infty = 36$ ps and $g_2 V_h = 207 \pm 50$ Å^3. A crude estimate of the average rotational volume about the short axes (x,y) yields $V_z \approx 360$ Å^3. Assuming the same asphericity parameter λ for Aroclor and the related biphenyl[32,33] and slip boundary conditions we find an effective volume $V_h \approx 125$ Å^3. For comparison the effective volume of the biphenyl used in Ref. 27 was found to be 104 Å^3, although it is not clear what value for the molecular volume was used in their calculations. The difference between our calculated value (125 Å^3) and the value inferred from the three highest temperatures ($g_2 V_h \approx 207$ Å^3) can be rationalized assuming either a rotational volume larger than 360 Å^3 or a g_2 value of ~ 1.7. The latter value is to be compared with the g_2 found at 40 °C (~ 2). Thus Eq. (6) seems to describe the experimental τ_0 in the high-temperature region. However, as the temperature further decreases, η increases more than τ_0 and large deviations from the linear behavior are observed below about 80 °C. At the lowest temperatures, the τ^* values obtained from the PCS measurements and the measured η would yield unrealistically small values for $g_2 V_h$ (Fig. 10).
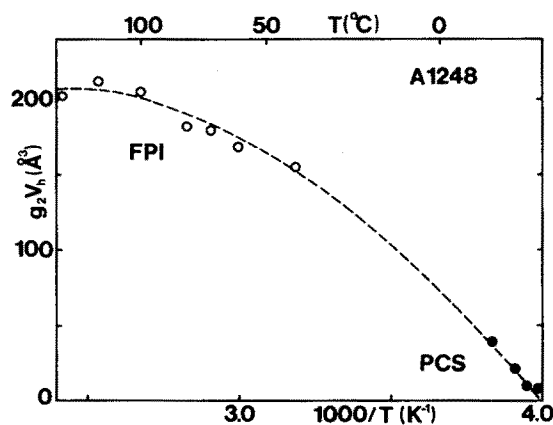

FIG. 10. Variation with temperature of the effective hydrodynamic volume $g_2 V_h$ in neat Aroclor. The values of $g_2 V_h$ are obtained from the measured orientational times τ_0 at high temperatures (FPI) and τ^* [Eq. (3), PCS] at low temperatures, according to Eq. (6). The dashed line is to guide the eye.

Similar deviations have been reported for rhodamine 6G,[34] pyridine in water[35] 2,4-pentanediol,[36] and for CPM[16] at low temperatures/high viscosities. In these cases, the orientational motion at the low temperatures does not experience the full frictional effects which are probably contained in the macroscopic shear viscosity. For Aroclor, possible clustering affects mainly η and to a lesser degree τ_0, as is evident from the intensity I_0. Recently, NMR measurements of the correlation times in two molecular glass formers[37] have also revealed a crossover in the plot τ/η versus T, in the T range where η deviates from the power law dependence characteristic of the fluid regime.

It is now interesting to compare the results of the present DRS study with the orientational times in neat biphenyl and n-heptane solutions obtained from FPI[37] and transient grating optical Kerr effect (OKE)[33] experiments. These measurements are in the η/T range $(1-5) \times 10^{-3}$ cP/K whereas the present interferometric and PCS measurements on Aroclor cover much broader range $(2-160) \times 10^{-3}$ cP/K. At $\eta/T \sim 2 \times 10^{-3}$ cP/K, FPI, and OKE experiments yield correlations times $\tau = 8-12$ ps for collective rotation around the short molecular axes characterized by a hydrodynamic volume $g_2 V_h = 70-120$ Å^3 depending on the biphenyl concentration.[38] The latter dependence observed only in the FPI experiment can arise from correlated rotations of different molecules i.e., $g_2 > 1$ in neat biphenyl. The experimental V_h is of the same magnitude as the calculated value using a reasonable approximation of the molecular shape and assuming slip-bondary conditions.[33,38] Alternatively, the reorientation time in neat Aroclor is about twice the value in liquid biphenyls such as biphenyl and diephenyl ether[39] compared at $\eta/T \sim 5 \times 10^{-3}$ cP/K. This disparity, however, can be accounted for by the revealed difference between the values of V_h in neat Aroclor and biphenyl.

In addition to the slow reorientation of the long axis, the OKE experiment[33] reveals a second fast component with correlation times 2–4 ps, probably arising from spinning around the long axis plus torsional motion of the two phenyl rings in biphenyl molecule. This fast relaxation is not seen in the $I_{VH}(\omega)$ spectrum which is well described by a single Lorentzian (Fig. 1). If we assume that the fast exponential decay in the time resolved OKE experiment is depolarized light scattering active, then the corresponding Lorentzian component in the $I_{VH}(\omega)$ has a full width 80–160 GHz which is several times broader than the free spectral range used in this experiment. Hence this spectral component will contribute to the background B [Eq. (1)] arising from the overlap of several interferometric orders of this broad line. We indeed observed a fast background B increasing with temperature. No definite assessment of its intensity without spectral resolution (using grating or broad interferometer filter) is feasible. In view of the OKE study of the reorientational dynamics in biphenyl, other origins such as collisional scattering[40] and scattering by anisotropic pairs of density fluctuations[41] are less likely.

Concluding remarks

Depolarized Rayleigh spectra $I_{VH}(\omega)$ of neat Aroclor and PS solutions with c up to 0.146 g/cm^3 were recorded

with a plane Fabry-Perot interferometer over the temperature range 40–140 °C. The experimental $I_{VH}(\omega)$ of PS/A1248 solutions were well represented by two Lorentzians. The fast reorientation time τ_f is rather insensitive to variations of polystyrene concentration c_{PS}, in contrast to the significant concentration dependence of the relaxation time τ_s obtained from OEB and PCS measurements at low temperatures in the vicinity of T_g. The intensity I_s associated with the narrow Lorentzian component increases with decreasing temperature whereas the total depolarized scattering intensity (corrected for the dilution) is very similar to that of the neat solvent. The observed increase of I_s at the expense of I_f for the broad Lorentzian is mainly due to the slow reorientation of the solvent in the macromolecular environment. This slow relaxation pathway for the fluctuations in the optical anisotropy of Aroclor fully dominates the orientation correlation function at low temperatures. It is interesting to notice that the PS induced modification occurs at relatively high temperatures ($T_g + 110$ K). In the framework of the restricted rotational diffusion,[11,24,26] the broad Lorentzian is associated with the unhindered rotational diffusion of Aroclor molecules restricted, however, within a certain cone angle.

A single Lorentzian line was found adequate to fit the $I_{VH}(\omega)$ spectra of neat Aroclor. The temperature and concentration dependences of the depolarized scattering intensity suggest a significant amount of orientational pair correlations in neat solvent. Furthermore, the finding that the solvent reorientation time τ_0 does not scale with viscosity/temperature—except at the highest temperatures—is consistent with clustering in liquid Aroclor.

ACKNOWLEDGMENTS

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