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Solvent reorientation in polystyrene/A1248 and polystyrene/DOP systems

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Abstract. The depolarized Rayleigh spectra $I_{VH}(\omega)$ of the solvents di-2-ethylhexylphthalate (DOP) and polychlorinated biphenyl (A1248) in undiluted state and of the solutions A1248/polystyrene (PS) (c_{PS} up to 15%) and DOP/PS (c_{PS} up to 75%) were measured over the temperature range 30–140 °C using Fabry–Perot interferometry (FPI). The experimental $I_{VH}(\omega)$ of the undiluted solvents were well represented by a single Lorentzian whereas two Lorentzians were found necessary to fit the $I_{VH}(\omega)$ of the PS solutions. The variation of the intensity ratio of the two Lorentzians with temperature and the increase of the orientation time τ_0 of the solvents, upon addition of PS, show evidence of polymer-induced modification of solvent mobility. The rate of change of $\tau(c, T)/\tau_0$ with c_{PS} , which is a measure of the solvent local friction, assumes similar values for both DOP/PS and A1248/PS solutions at high temperatures.

1. Introduction

The use of depolarized Rayleigh scattering (DRS) to study the orientation of small molecules is now well established [1]. DRS provides a simple, versatile and more important, a non-destructive method to study rotational motions of pure solvents and polymer solutions, provided the solvent and/or the polymer possess optical anisotropy. The case where only the polymer is anisotropic has been studied by dynamic DRS in polystyrene (PS) solutions in carbon tetrachloride [2] and polycarbonate solutions in dioxane [3]. For these systems, the depolarized spectra consist of two components of roughly equal intensities, one with strong molecular weight dependence (Rouse–Zimm normal modes) and one roughly independent of molecular weight associated with the local segmental orientation.

The case where both the polymer and the solvent possess anisotropy has been studied utilizing the system toluene/PS [4]. The reorientation relaxation time of toluene was found to be little affected by the presence of PS up to 15% polymer concentration. This observation led to the conclusion that the local viscosity, as probed by DRS, remains similar to the solvent viscosity, even though the macroscopic viscosity increases by two orders of magnitude. The case where only the solvent possess optical anisotropy has been studied in the system chlorobenzene/poly(methyl methacrylate) (CB/PMMA) [5].

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For PMMA concentration lower than 80%, the depolarized spectra consisted of two Lorentzians. The fast component exhibited a relaxation time of about one order of magnitude longer than that of undiluted CB at the lowest measurement temperature, whereas at higher temperatures it was found to be independent of concentration. At the same time, the slower relaxing component exhibited relaxation times expected for CB in a highly viscous medium. The theories of 'diffusion in two environments' (DITE) and 'restricted rotational diffusion' (RRD) for CB [6], have been applied to describe these experimental findings and the complete RRD theory by Wang and Pecora was formulated [7]. Similar results have been obtained from the p-chlorodiphenyl methane (CPM)/PMMA mixture [8].

In the present study, in an effort to extend our knowledge and understanding of the reorientational motion of small solvent molecules in polymer solutions, we have used the solvents A1248 and di-2-ethylhexylphthalate (DOP) and the solute PS. For the A1248/PS solutions the polymer concentration (c) was in the range 0–15% and for the DOP/PS system, c_{PS} varied over the range 0–80%. Our results exhibit similarities and differences with previous studies. Furthermore, we provide evidence of polymer-induced modification on the solvent reorientational dynamics. It has recently been proposed by viscoelastic [9] and oscillatory electric birefringence (OEB) measurements [10] that the normalized solvent relaxation time τ/τ_0 , where τ_0 refers to the neat solvent, can be used as a measure of an average local friction that the solvent molecules experience in the vicinity of the polymer. We will adopt this definition for the local solvent friction and quantify our results in terms of this quantity.

2. Experimental details

The depolarized Rayleigh spectra $I_{VH}(\omega)$ were taken at a scattering angle of 90° using the apparatus described elsewhere [11]. Different free spectral ranges (FSR) were used, the lowest being 4.5 GHz and the highest 17.9 GHz with a typical finesse of 65. The data analysis consisted of fitting each peak to either a single Lorentzian (neat solvents) or a double Lorentzian (PS solutions) convoluted with the instrumental line shape. The half-width at half-height (HWHH) and the relaxation intensity of each Lorentzian was then calculated by the fitting program.

3. Results and discussion

3.1 Rotational relaxation of neat solvents

DRS spectra were recorded at temperatures from 30 to 160 °C. Typical $I_{VH}(\omega)$ for neat A1248 and DOP are shown in figure 1. One immediately notices the large difference in the integrated intensities for the two solvents. The total integrated depolarized intensity is given by

$$I_{VH} = Af(n)\rho^*\gamma^2 \quad (1)$$

where A is a constant, $f(n)$ is the product of the local field correction and the geometrical factor $1/n^2$, with n being the refractive index of the medium, ρ^* is the number density and γ^2 is the effective (due to the inclusion of static pair correlations) optical anisotropy of the scatterers. Using equation (1) and $\rho = 1.45 \text{ g c}^{-3}$, $n = 1.63$ for A1248 and $\rho =$

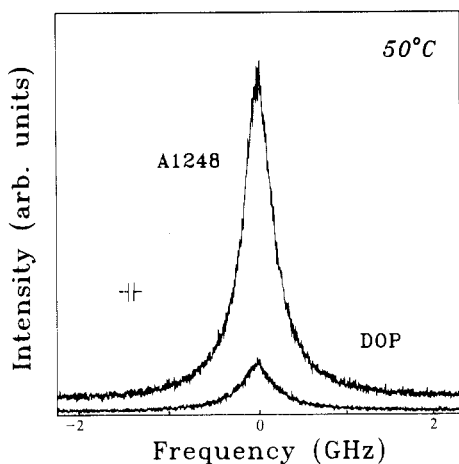


Figure 1. Depolarized Rayleigh spectra of neat A1248 (upper) and neat DOP (lower) at 50 °C. The symbol \pm denotes the instrumental full width.

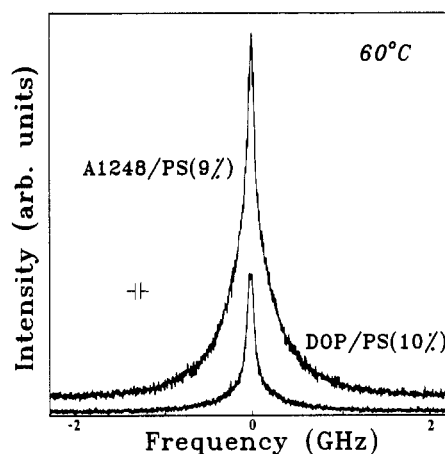


Figure 2. Depolarized Rayleigh spectra of A1248/PS (upper) and DOP/PS (lower) solutions with similar PS concentrations ($c_{PS} = 9\%$ and 10% respectively) at 60 °C obtained in consecutive runs.

0.981 g c^{-3} , $n = 1.485$ for DOP at 20 °C we obtain the γ^2 values of 108 and 32 \AA^6 for A1248 and DOP, respectively. Evidently, A1248 possesses an effective optical anisotropy more than three times higher than DOP. In this context, it is worth mentioning that the average optical anisotropy per PS monomer is $\langle \gamma^2 \rangle / x = 38 \text{ \AA}^6$ (where x is the degree of polymerization) [12]. Thus a monomer in an isolated PS chain has three times less anisotropic scattering power than a A1248 molecule and 20% higher than a DOP molecule in the neat solvent. All neat solvent $I_{VH}(\omega)$ spectra were found to be well represented by a single Lorentzian without the characteristic central dip [13, 14].

The orientational relaxation times obtained from the fitting program as $\tau_0 = (2\pi\Gamma)^{-1}$ are similar for both solvents. Furthermore, the τ_0 values of neat A1248 were previously [15] obtained from an extended temperature range using oscillatory electric birefringence (OEB) and photon correlation spectroscopy (PCS) at low temperatures, and Fabry–Perot interferometry (FPI) at high temperatures and found to conform to the Vogel–Fulcher–Tammann (VFT) equation:

$$\ln \tau_0 = \ln \tau_0^* + B/(T - T_0) \quad (2)$$

where $\tau_0^* = 1.8 \pm 0.2 \text{ ps}$, $T_0 = 221 \pm 2 \text{ K}$ and $B = 645 \pm 50 \text{ K}$. The stronger temperature dependence of A1248 viscosity was only one reason to invoke the picture of solvent clustering. This notion is supported by the significant amount of static orientational correlations present in A1248, from the relatively high Landau–Placzek (LP) intensity ratio at low temperatures ($\sim 40 \text{ }^\circ\text{C}$) and more definitely by the breakdown of the Stokes–Debye–Einstein equation:

$$\tau_0 = (g_2/j_2)((V_h/k_B)(\eta/T) + \tau_\infty) \quad (3)$$

where $g_2 V_h$ is the effective hydrodynamic volume of the reorienting molecule, g_2 and j_2 are the static and dynamic pair orientation correlation parameters respectively and τ_∞ is the non-zero intercept in the limit $\eta/T \rightarrow 0$. At high temperatures the effective

hydrodynamic volume for A1248 is $\sim 207 \text{ \AA}^3$ but it decreases rapidly as one approaches the glass transition temperature ([15], figure 10).

Concerning the other solvent (DOP) the situation looks more simple. The effective hydrodynamic volume at high temperatures is $\sim 170 \text{ \AA}^3$ comparable to that of neat A1248, and consistent with the similar, orientational dynamics of the two solvents at high- T . Furthermore, the LP ratio is ~ 2 at $20 \text{ }^\circ\text{C}$ and 0.2 at $140 \text{ }^\circ\text{C}$ indicating that DOP is a cluster-free solvent over the temperature range studied.

3.2. Rotational relaxation of A1248 and DOP in the presence of PS

The effect of addition of PS to A1248 and DOP can be seen in figure 2. Clearly one Lorentzian line cannot describe the experimental spectra and a fit to a double Lorentzian plus a baseline is made instead:

$$I_{\text{VH}}(\omega) = \frac{1}{\pi} I_1 \left(\frac{\Gamma_1}{\Gamma_1^2 + \omega^2} \right) + \frac{1}{\pi} I_2 \left(\frac{\Gamma_2}{\Gamma_2^2 + \omega^2} \right) + B \quad (4)$$

where I_1 and I_2 are the integrated intensities of the broader and narrower peaks respectively and Γ_1, Γ_2 are the corresponding HWHH. At high temperatures ($T > 100 \text{ }^\circ\text{C}$), the narrower peak has instrumental HWHH and is due to the slow reorientational dynamics of the PS chains. As T decreases, the relative intensity of this peak increases with the inclusion of intensity from slower rotating solvent molecules lying in the proximity of the polymer. The upturn of the relative intensity of the narrower peak with decreasing temperature and the simultaneous downturn of the relative intensity of the broader peak seems to signal the onset of PS-induced modification to the solvent [15].

The analysis of the experimental $I_{\text{VH}}(\omega)$ into two spectral components is unambiguous as long as the intensity ratio $K = I_1/I_2$ is higher than about 0.5 and $\Gamma_1/\Gamma_{\text{instr}} > 3$. For the DOP/PS system this limit is reached when the PS composition is higher than 50% [14]. For DOP/PS ($c_{\text{PS}} = 75\%$) it was not possible to resolve a broad peak at all temperatures. On the other hand, the contribution of a central spike (due to polymer motion) can reliably be extracted from the experimental $I_{\text{VH}}(\omega)$ values for K up to 30 . Such a high- K ratio could be measured [14] from the $I_{\text{VH}}(\omega)$ of a dilute DOP/PS solution with c_{PS} as low as 1% , in agreement with the calculated (equation (1)) value of K .

The modification of the solvent by the presence of PS chains should set in when the solvent orientation time and the polymer segmental dynamics are sufficiently close. The alteration of the solvent orientational dynamics could also suggest that a continuous distribution of Lorentzians is an alternative fitting procedure to the experimental spectra at the lowest measurement temperatures (30 to $70 \text{ }^\circ\text{C}$). To check this possibility we have utilized different FSRs to measure $I_{\text{VH}}(\omega)$. Whereas the width of the broad Lorentzian component is rather insensitive to the FSRs used, the narrow peak displays a different linewidth suggesting a distribution of relaxation times at low temperatures. In fact, for the system A1248/PS a broad distribution of relaxation times is present at even lower temperatures, close to T_g , as revealed from PCS [16] and OEB [10] studies. Figure 3 shows an Arrhenius plot of the orientation time τ obtained from the broad Lorentzian component of the $I_{\text{VH}}(\omega)$ spectrum of DOP/PS solutions along with the τ_0 of the neat DOP. Solvent reorientation time increases significantly with increasing c_{PS} . On the contrary, for CB/PMMA, no measurable influence of PMMA on the orientation of CB was reported at high temperatures [5]. Similarly, for styrene/PS system [17], the orientation rate of styrene was reduced only by about 50% in the presence of 80% PS.

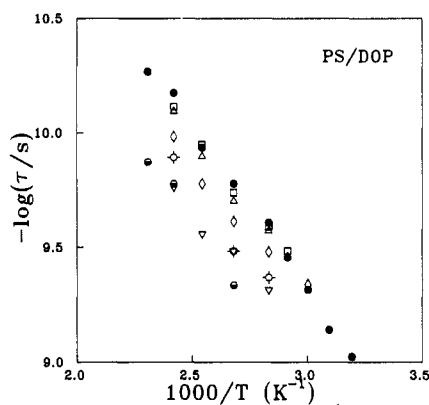


Figure 3. Temperature dependence of the reorientational time (●) of neat DOP and DOP/PS solutions with $c_{PS} = 1\%$ (□), 10% (△), 25% (◇), 37% (○), 50% (▽, ⊙).

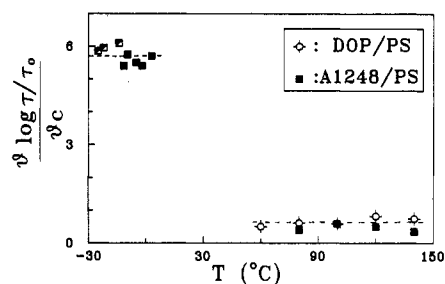


Figure 4. The rate of change of solvent friction with PS concentration, investigated by FPI at high temperatures and by (■) PCS and (□) OEB at low temperatures.

To quantify the polymer effect on the solvent reorientation we employ the ratio $\tau(c, T)\tau_0$ which increases markedly with increasing PS concentration (figure 3). For the present polymer solutions, τ/τ_0 exhibits an exponential dependence on concentration in agreement with earlier OEB studies [10]. Furthermore, the rate of change of solvent friction with polymer concentration ($\partial[\log(\tau/\tau_0)]/\partial c$) in PS solutions with A1248 and DOP, depicted in figure 4, is essentially independent of temperature at high temperatures ($T > 80^\circ\text{C}$) when examined by FPI. Both, A1248/PS and DOP/PS solutions exhibit similar behaviour at high temperatures. On the other hand, when the system A1248/PS is examined at lower temperatures, then it is the strongly modified solvent (by the slow polymer dynamics) which dominates the OEB and PCS response. Such an abrupt change of $\partial[\log(\tau/\tau_0)]/\partial c$ against temperature can be used as another way of defining the temperature range in which solvent modification starts as also manifested in the intensity ratio K in the temperature range $40\text{--}70^\circ\text{C}$ [15].

In conclusion, there are two parameters which define solvent modification: polymer concentration and solution temperature. Increasing polymer concentration, at all temperatures, has the effect of slowing down the solvent reorientational dynamics (figure 3). Decreasing the temperature, at low polymer concentrations, modifies the solvent (figure 4). The observation that in both PS solutions with low PS content, solvent modification sets in at the same temperature range ($40\text{--}70^\circ\text{C}$) should be considered more carefully and could play an important role in theoretical models of solvent induced modification. Finally, the technique of DRS has proved to be very useful in the study of the local viscosity of polymer solutions.

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