Solvent Rotational Mobility in 1,2-Polybutadiene/Aroclor Solutions by Dielectric Relaxation and Fabry–Perot Interferometry

A. K. Rizos*

Department of Chemistry and Research Center of Crete, University of Crete, P.O. Box 1527, Heraklion, Crete, Greece

K. L. Ngai

Naval Research Laboratory, Washington, D.C. 20375-5000

Received June 2, 1994; Revised Manuscript Received August 29, 1994®

ABSTRACT: The presence of poly(1,2-butadiene) in the solvent Aroclor enhances the mean solvent rotational mobility relative to the neat solvent case even though the polymer has a higher glass transition temperature than that of the solvent. This interesting behavior found earlier by photon correlation spectroscopy is confirmed by dielectric relaxation and Fabry–Perot interferometry. The new data extend significantly the frequency and temperature ranges of observation of the modification of the Aroclor dynamics in solutions of poly(1,2-butadiene) and quantify the rate at which the addition of the polymer alters the mean solvent reorientation time as a function of temperature.

Introduction

In polymer solutions it has been firmly established both theoretically and experimentally that the relative time scales for polymer and solvent motions are intimately related to the modification of solvent dynamics upon the addition of polymers. The change of the dynamics of the solvent in polymer solutions[1–6] due to the presence of polymer chains has been demonstrated by a number of experimental investigations[7–14] using several techniques. Recently, we have presented photon correlation spectroscopic data[14] of 1,2-polybutadiene dissolved in Aroclor (A1248), a polychlorinated biphenyl extensively used in polymer solution dynamics studies. The poly(1,2-butadiene) (1,2-PB) used had a molecular weight of 4300 and a glass transition temperature (T_g) of −25 °C, which is 19 °C higher than that of Aroclor (A1248). These data showed a striking anomaly: *the reorientational relaxation time of A1248 was reduced by the addition of 1,2-PB notwithstanding the fact that the polymer has a higher T_g*. We describe this observation as anomalous because normally addition of other polymers with a higher (lower) T_g than the solvent has the effect of slowing down (speeding up) the reorientational dynamics of Aroclor. This normal behavior was violated in a 1,2-PB/A1248 solution with polymer concentration $c = 0.25$ g/cm^3 as shown in Figures 2 and 3 of ref 14.[15] The mean solvent reorientational time in polymer solution, τ_s, is shorter than that in neat solvent, $\tau_s°$. An explanation of this anomalous effect was also given in ref 14. Since this work has been published the anomalous shift has now been determined at several other concentrations. From these additional photon correlation spectroscopic (PCS) data we find that the dependence of $\log(\tau_s(c,T)/\tau_s°(T))$ on c is approximately linear as in other polymer solutions,[1–13] and thus

$$\tau_s(c,T)/\tau_s°(T) \simeq \exp(Ac) \qquad (1)$$

A is negative for our 1,2-PB in A1248, which is counter to what one might have expected based on the T_g's of the neat materials. The PCS data obtained at two temperatures are shown as the points indicated by the two open squares in Figure 1, where the label of the y-axis, $\partial \ln[\tau_s(c,T)/\tau_s°(T)]/\partial c$, can be identified with A. A possible source of this unexpected reversal of the sign of A has been offered in ref 14 from the coupling model of relaxation. In the coupling model the observed relaxation times, τ_p and $\tau_s°$, of the neat polymer and solvent, respectively, are each determined not only by the local friction but also by the dynamical constraints from neighboring molecules. When the polymer is added to the solvent, the dynamical constraints experienced by the Aroclor molecules are modified by the presence of the polymer. It was suggested[14] that a comparison between the "noncooperative" relaxation times of the neat polymer, τ_{po}, and of the neat solvent, τ_{so}, will offer an indication of whether the dynamical constraints in the solvent will be strengthened or mitigated with addition of the polymer. It was suggested that if τ_{po} were shorter than τ_{so}, then there is the possibility that the dynamical constraints in the solvent will be mitigated with addition of polymer, even though τ_p is longer than $\tau_s°$ or, in other words, the polymer has a higher T_g. Such a relation of $\tau_{po} \ll \tau_{so}$ was found to be satisfied by our 1,2-PB sample used in the experiment,[14] which indicates that it may be contributing to the observed anomaly. This possibility is consistent with the work by Amelar et al.[11] in which they found $A \simeq 0$ in 1,2-PB/A1248. These authors used a higher molecular weight 1,2-PB that has a higher T_g than ours. As a consequence, the condition $\tau_{po} \ll \tau_{so}$ is no longer satisfied, and the reversal in sign of A disappears. Our work on 1,2-PB/A1248 has stimulated more work in the same system[16] and in poly(methylphenylsiloxane)/1,1-bis(p-methoxyphenyl)cyclohexane,[17] henceforth referred to as PMPS/BMC. In these two works using dynamic mechanical spectroscopy, the neat polymers chosen have higher T_g's than those of the neat solvents, but again an anomalous negative A is observed as we observed before. Density measurements were also made for the neat solvent and the polymer solution. It was found that in PMPS/BMC the density increases with addition of PMPS. This behavior rules out a simple free volume explanation of the negative sign of A in this system because the excess volume is negative for a 10% solution of PMPS in BMC and indicates the presence of a mechanism such as that from

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® Abstract published in *Advance ACS Abstracts*, October 1, 1994.

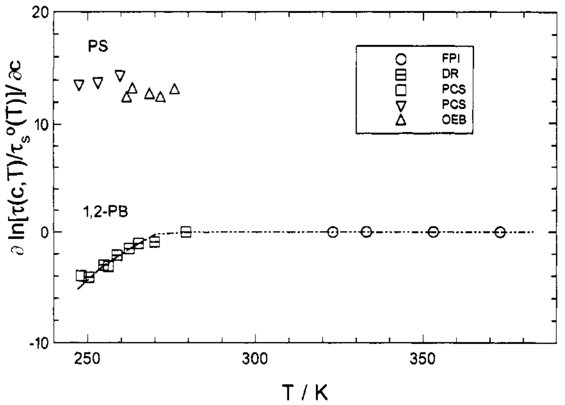

Figure 1. Plot of $A = d\ln[\tau_s(c,T)/\tau_s^\circ(T)]/dc$ versus temperature for 1,2-PB and PS solutions in Aroclor as determined by photon correlation spectroscopy (PCS), dielectric relaxation (DR), Fabry–Perot interferometry (FPI), and oscillatory electric birefringence (OEB).

the coupling model. On the other hand, in the 1,2-PB/A1248 system studied by dynamic mechanical spectroscopy,[16] density measurements reveal a positive change in volume with addition of 1,2-PB in A1248. The T_g of the 1,2-PB sample used in this investigation[16] is significantly higher than that of our sample, and as a result the condition $\tau_{po} \ll \tau_{so}$ as in the case in ref 14 is not satisfied. Nevertheless A is still negative though its absolute value is smaller than what we found in our 1,2-PB/A1248. The facts mentioned above taken together suggest the possibility that both the positive change in volume and the mitigation of dynamical constraints when 1,2-PB is dissolved in A1248 work synergistically to produce the observed anomalous effect in 1,2-PB/A1248.

The effect we have previously observed by PCS[14] is so unusual that it warrants confirmation by another measurement on the same 1,2-PB/A1248 system using different experimental techniques. The present experimental investigation using dielectric spectroscopy (DR) and Fabry–Perot interferometry (FPI) to measure the solvent dynamics is undertaken with two main objectives in mind. The first is to confirm the results of the previous PCS study.[14] The second is to use these two techniques to enhance the time window and temperature range in which the modification of the solvent dynamics can be observed (see Figure 1). In this manner we have brought the experimental data of solvent dynamics in our 1,2-PB/A1248 system into parity with those of other systems including polystyrene (PS)/A1248, polyisoprene (PI)/A1248, and 1,4-PB/A1248 as far as the wealth of information acquired is concerned.[2]

Experimental Section

The 1,2-polybutadiene (1,2-PBD) and the solvent Aroclor were the ones used for the previous study. The preparation procedure has been described in ref 14.

A. Dielectric Relaxation Spectroscopy (DR). The DR measurements were performed with a Hewlett-Packard HP-4284A impedance analyzer in the frequency range of 20 to 10^6 Hz, with the sample temperature controlled (±0.1 °C) by a Novocontrol Quatro system.

B. Depolarized Rayleigh Scattering (DRS). The light source was an Ar^+ laser (Spectra-Physics 2020) operating at λ = 488 nm with a power of 300 mW. The incident beam was polarized vertically (V) with respect to the scattering plane using a Glan polarizer. The horizontal (H) polarized scattered light was measured using a Glan-Thomson polarizer (Halle-Berlin). The depolarized Rayleigh scattering spectra (VH) were taken at a scattering angle of 90° using the same light source as for the PCS measurements. The scattered light was frequency analyzed with a piezoelectrically scanned Fabry–Perot interferometer (FPI) (Burleigh RC-110). A Burleigh DAS-10 stabilization system was used to fix the position of the Rayleigh peak and maintain maximum finesse. The scattered light after passing through the FPI and a narrow-band interference filter to remove fluorescence was detected with an EMI photomultiplier tube. Finally, two interferometric orders were accumulated in a 2048 multichannel analyzer (Canberra series 35).

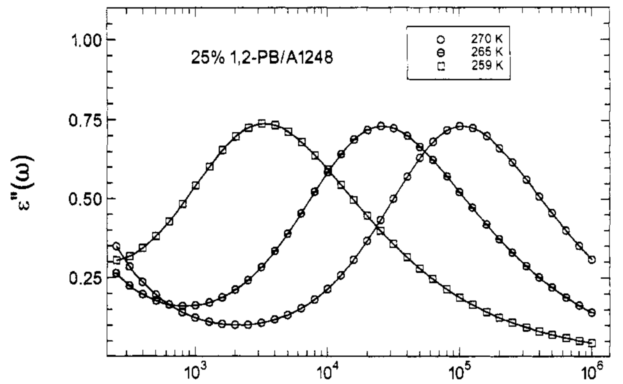

Figure 2. Dielectric loss data for the 25% 1,2-PB solution in A1248 at 259, 265, and 270 K.

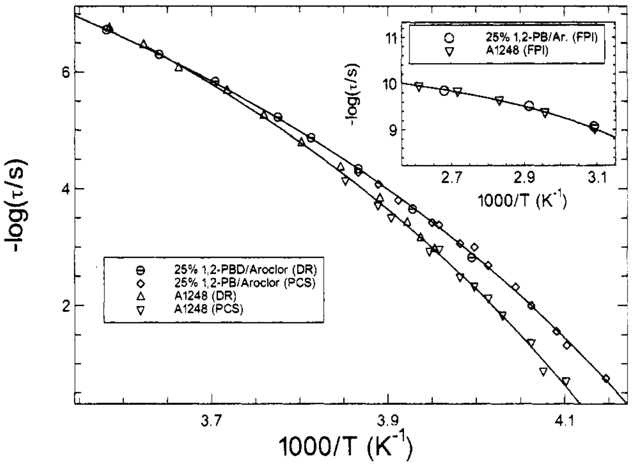

Figure 3. Temperature dependence of the modification of Aroclor dynamics in 1,2-PB/A1248 solutions. The data shown here are the reorientational relaxation time of the neat A1248 and 25% 1,2-PB solutions in A1248 obtained by dielectric relaxation (DR), photon correlation spectroscopy (PCS), and depolarized Rayleigh scattering (FPI) shown in the inset. The PCS data are reproduced from ref 14.

Results and Discussion

Figure 2 shows a plot of the dielectric loss data at three different temperatures for the $c_{1,2\text{-PB}} = 0.25$ g/cm^3 sample. It is important to mention that the dielectric strength of the solvent A1248 dominates the experimental spectrum. To compare PCS and DR data on the same samples directly, we have consistently undertaken the same data analysis in the time domain by using a previously applied standard procedure.[9] The temperature dependence of the resulting τ is then depicted in Figure 3 along with the values from the previous PCS measurements of ref 14.

The two experiments yield clearly very similar values of the reorientational time of A1248 over a considerable temperature range. Furthermore, the DR data extend the measurements to significantly higher temperatures. Another interesting aspect of the dielectric data is the observed merging of the reorientational times of pure A1248 and A1248 in the presence of polymer at higher temperatures, which, as we shall see, is confirmed by the FPI data taken at even higher temperatures.

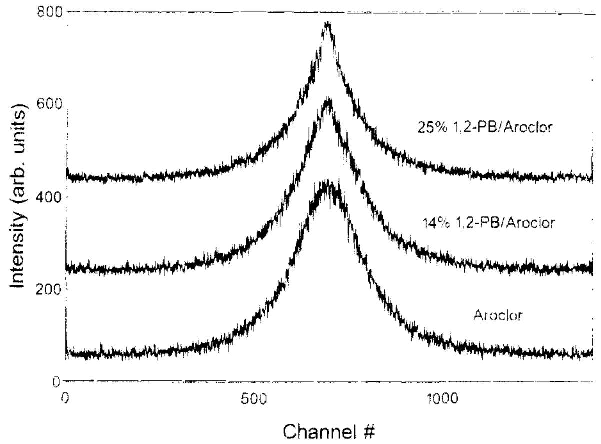

Figure 4. Depolarized Rayleigh spectra of 1,2-PB/A1248 taken at 353 K for neat Aroclor and two 1,2-PB/Aroclor solutions with 14 and 25% 1,2-PB.

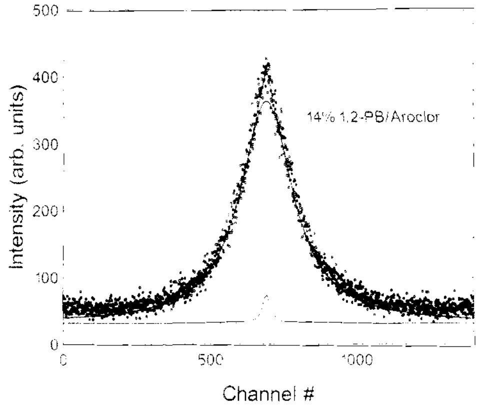

Figure 5. Least squares fit (solid curve with peak height equal to 363) of the depolarized Rayleigh spectrum (data points) for the 14% 1,2-PB/A1248 solution. The small contribution of the polymer (narrow peak of low intensity) to the total depolarized intensity is shown as the solid curve at the bottom.

Typical depolarized Rayleigh spectra (DRS) taken at 353 K for neat Aroclor and Aroclor solutions of 1,2-PB containing 14 and 25% polymer are shown in Figure 4. The depolarized spectra were fit to either one or a sum of two Lorentzian functions plus a baseline, considering the overlap of the neighboring orders:

$$I_{\mathrm{VH}}(\omega) = \frac{1}{\pi}\sum_{i=1}^{2} I_i \frac{\Gamma}{\Gamma^2 + \omega^2} + B \qquad (2)$$

where I and Γ are the integrated intensity and half-width at half-height (hwhh) and B is the background. All depolarized spectra were then convoluted with the instrumental line shape and the hwhh, and the integrated intensity of each Lorentzian was calculated from the fitting routine. The collective reorientation time was computed from $\tau_2 = (2\pi\Gamma_2)^{-1}$. A least squares fit of eq 2 to the depolarized Rayleigh spectrum of the 14% 1,2-PB/A1248 solutions is shown by the solid curve with rounded top and peak height equal to 363 in Figure 5. The integrated intensity is proportional to the effective optical anisotropy γ_{eff}^2 and is given by the expression

$$I_{\mathrm{VH}} = A f(n) \rho^* \gamma_{\mathrm{eff}}^2 \qquad (3)$$

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, and ρ^* is the number density of the solute. The 1,2-PB with an average optical anisotropy of 3.5 Å^6 makes only a small contribution to the total depolarized intensity (data points in Figure 5) and corresponds to the narrow peak of low intensity shown at the bottom of Figure 5. On the contrary, Aroclor with a large effective optical anisotropy of 108 Å^6 dominates the depolarized spectrum.

The values of the reorientational times from the FPI data as extracted from the broad component of the $I_{\mathrm{VH}}(\omega)$ show no alteration in the solvent dynamics in the presence of the polymer and verify the results from the dielectric data taken at the highest temperature accessible by this technique. The data points from FPI shown in the inset of Figure 3 reiterate the point that there is no solvent modification by the 1,2-PB in the high-frequency and high-temperature region. This behavior is similar to that exhibited by Aroclor solutions of polyisoprene and 1,4-PB.[1-13]

Conclusion

In this work we have presented additional photon correlation spectroscopic data and new dielectric relaxation and Fabry–Perot interferometric studies of the reorientational dynamics in solutions of 1,2-PB in A1248. The entire data set enables us to quantify the rate, A, at which the addition of polymer alters the mean solvent reorientation time. The DR data confirm that A is negative for our 1,2-PB/Aroclor solutions and verify the anomalous acceleration of the solvent rotational mobility previously reported by a photon correlation spectroscopic study. As expected, the FPI data show no modification of the solvent dynamics at higher temperatures as was observed before in other polymer/solvent systems. We suggest that it would valuable to measure, like Gisser and Ediger[13] did, the relative dynamics, i.e., the quantity $\tau_{\mathrm{poly}}/\tau_{\mathrm{s}}^{\circ}$, for a dilute Aroclor solution of our 1,2-PB to see (1) whether it has the same sign as A and (2) what is the value of the scaling factor, Q, required to bring A and $\tau_{\mathrm{poly}}/\tau_{\mathrm{s}}^{\circ}$ into quantitative agreement with each other.

References and Notes

(1) Schrag, J. L.; Stokich, T. M.; Strand, D. A.; Merchak, P. A.; Landry, C. J. T.; Radtke, D. R.; Man, V. F.; Lodge, T. P.; Morris, R. L.; Hermann, K. C.; Amelar, S.; Eastman, C. E.; Smeltzly, M. A. *J. Non-Cryst. Solids* **1991**, *131-133*, 537.
(2) Lodge, T. P. *J. Phys. Chem.* **1993**, *97*, 1480.
(3) Johnson, R. M. Ph.D. Thesis, University of Wisconsin, 1970.
(4) Merchak, P. A. Ph.D. Thesis, University of Wisconsin, 1987.
(5) Stokich, T. M. Ph.D. Thesis, University of Wisconsin, 1989.
(6) Strand, D. A. Ph.D. Thesis, University of Wisconsin, 1989.
(7) Morris, R. L.; Amelar, S.; Lodge, T. P. *J. Chem. Phys.* **1988**, *89*, 6523.
(8) von Meerwall, E. D.; Amelar, S.; Smeltzly, M. A.; Lodge, T. P. *Macromolecules* **1989**, *22*, 295.
(9) Fytas, G.; Rizos, A.; Floudas, G.; Lodge, T. P. *J. Chem. Phys.* **1990**, *93*, 5096.
(10) Rizos, A.; Fytas, G.; Lodge, T. P.; Ngai, K. L. *J. Chem. Phys.* **1991**, *95*, 2980.
(11) Amelar, S.; Krahn, J. R.; Hermann, K. C.; Morris, R. L.; Lodge, T. P. *Spectrochim. Acta Rev.* **1991**, *14*, 379.
(12) Glowinkowski, S.; Gisser, D. J.; Ediger, M. D. *Macromolecules* **1990**, *23*, 3520.
(13) Gisser, D. J.; Ediger, M. D. *Macromolecules* **1992**, *25*, 1284.
(14) Rizos, A. K.; Ngai, K. L. *Phys. Rev. B* **1992**, *46*, 8126.
(15) There is an error in the labeling of Figure 2 of ref 13. It should be $\log_{10}(t/s)$ instead of $\ln(t/s)$.
(16) Santangelo, P. G.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 3859.
(17) Roland, C. M.; Santangelo, P. G.; Ngai, K. L.; Meier, G. *Macromolecules* **1993**, *26*, 6164.