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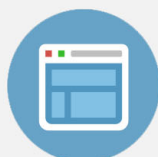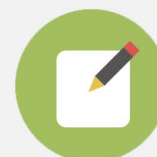
Solvent and polymer dynamics in concentrated polystyrene/toluene solutions

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Depolarized Rayleigh scattering (DRS) and dielectric spectroscopy (DS) are employed to study the solvent and polymer dynamics in the polystyrene (PS)/toluene system and for PS concentration up to 0.6 g/ml. The DRS measurements were made in the temperature range from 255 to 373 K with different interferometers making possible the separation of the "fast" solvent (in the ps time scale) from the "slow" polymer dynamics (in the ns time scale). The DS measurements were made in the temperature range from 128 to 310 K and two processes could also be observed. With DRS and DS we investigate the very different mobilities in the PS/ toluene solutions over a frequency range of ~10 decades. The prominent features of the experimental data are (i) the existence of two primary ($\alpha-$) relaxations in the macroscopically homogeneous solutions which have been analyzed using both techniques and (ii) that these relaxations reflect the polymer and solvent dynamics and display the usual Vogel–Fulcher–Tammann behavior, however, with a broad distribution of relaxation times, especially at low temperatures. The existence of two time scales in the solutions is discussed in terms of concentration heterogeneities composed of PS-rich and toluene-rich domains, large enough to exhibit two glass transitions. As a result of the strong temperature dependence for the fast solvent reorientation times the rate of change of solvent friction with polymer concentration becomes temperature dependent at low temperatures.

I. INTRODUCTION

There is a growing interest in understanding the transport properties of small molecules in polymers because of the great technological importance. The translational diffusion of penetrants in amorphous polymers has been studied both experimentally (forced Rayleigh scattering,[1] NMR[1,2]) and theoretically (molecular dynamics simulations[3,4]). The rotational dynamics of penetrants have also been studied by depolarized Rayleigh scattering (DRS),[5,6] dielectric spectroscopy (DS),[7,8] oscillatory electric birefringence (OEB),[9] and NMR.[10] These studies revealed that solvent molecules can undergo restricted reorientation in the presence of polymer chains. Theoretical models of rotational relaxation[11–14] have increased our understanding of the experimental results. Furthermore, it has been shown by means of viscoelastic[15] and OEB[9] experiments that the presence of polymer chains can have a substantial effect on the solvent dynamics. DRS[16–19] and NMR[10] studies provided further evidence for the modification of solvent properties. In all cases, this effect was rationalized in terms of the normalized solvent relaxation time $\tau(C,T)/\tau_0(T)$, where τ_0 refers to the neat solvent, which was found to display an exponential dependence on concentration at high temperatures.

The systems which have been employed mainly included the viscous solvent aroclor in polystyrene (PS), polybutadiene (PB), or polyisoprene (PI) matrices. The present study deals with the system PS/toluene which is used as an archetypal polymer solution. PS and toluene are composed of anisotropic units having very different mobilities, so that we can study both the solvent and the polymer orientational dynamics. The PS/toluene system has been examined using DRS for polymer concentrations up to 0.15 g/ml at 298 K.[20] Deuteron[21] and pulsed-gradient spin-echo NMR[22,23] have been employed to study the solvent mobility in the same system. DS[24] has also been used to identify the relaxation processes involved. Forced Rayleigh scattering was used to study the tracer diffusion in a variety of polymer solutions including the PS/toluene system.[25] Free volume theories[26] were employed to analyze the temperature dependence of the solvent self-diffusion coefficient both below and above the "solution T_g." Lastly, small-angle neutron and x-ray scattering were used to obtain the characteristic screening length (ξ_s) over the whole concentration range.[27]

While the dynamic studies provided insights regarding the different mobilities involved in the PS/toluene system, they were either made over a narrow concentration range or over a small frequency range and the detailed temperature dependence of the relaxation processes involved— both of the relaxation times and the distribution of relaxation times—is not yet known. In the present study we employ DRS and DS covering a broad frequency range (~10 decades). With these techniques we are able to probe both the solvent and polymer rotational dynamics in the macroscopically homogeneous solutions. The results show, however, that the PS/toluene solutions are microscopically heterogeneous. The heterogeneity is reflected in
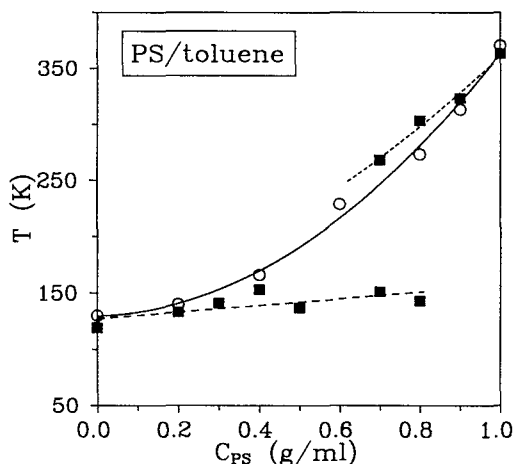
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FIG. 1. Concentration dependence of the glass transition temperature in PS/toluene solutions determined by DSC: (■) this work; (○) from Ref. 24.
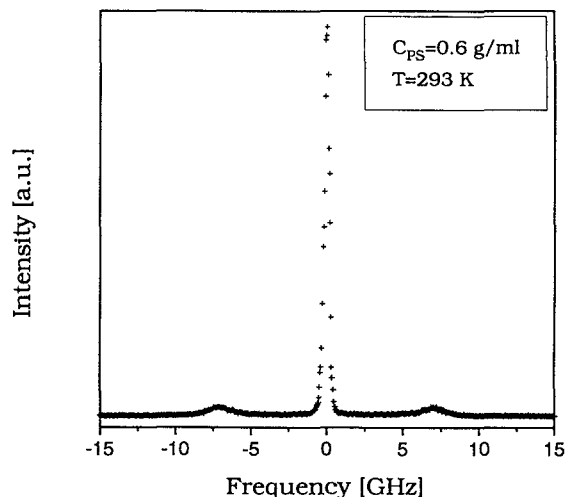

FIG. 2. Typical Rayleigh–Brillouin spectrum for the PS/toluene solution with C_{PS}=0.6 g/ml at T=293 K. The free spectral range is 20 GHz and the Landau–Placzek ratio for this sample is 2.9.

the two distinct time scales associated with the "slow" and "fast" dynamics within the polymer and solvent cooperative volumes, respectively.

II. EXPERIMENTAL SECTION

A. Samples

PS/toluene samples were prepared by thermal polymerization of pure monomer mixtures at 120 °C for 36h as described in Ref. 28. The conversion of the polymerization was about 96% at monomer fraction 0.1 and increased with increasing monomer fraction to 99% in the bulk sample. The weight average molecular weight M_w was 2.0 and 2.7×10^5 at C_{PS}=0.5 and 0.9 g/ml, respectively. The polymer volume fraction was calculated from the starting monomer volume fraction accounting for the density changes during the polymerization reaction.

The glass transition temperatures for the PS/toluene solutions measured by DSC (heating rates of 10 and 20 K/min) are shown in Fig. 1. Glass transition temperatures could be detected easily only at the ends of the concentration range. At high polymer concentrations there is a single T_g with a narrow transition range ($\Delta T_g \sim 5$ and 6 K for the C_{PS}=1.0 and 0.9 g/ml, respectively). At low polymer concentrations there is again a single T_g but with a wider transition range ($\Delta T_g \sim 20$ and 30 K for the C_{PS}=0.2 and 0.3 g/ml, respectively). At some intermediate concentrations two broad glass transitions could be resolved with the one at low T being the more pronounced. Due to the broadness of the peaks at intermediate concentrations the data points shown in Fig. 1 are subject to some uncertainty. However, the appearance of "high" and "low" T_g's at some intermediate PS/toluene concentrations and the persistence of the low T_g at higher concentrations is consistent with DSC data on other polymer solutions.[29] This effect is more pronounced here because of the very large difference in the T_g's of the bulk polymer and the neat solvent. Glass transition temperatures for the same system

have been reported earlier[24] and are included in Fig. 1 (solid line). The two data sets agree for the two extreme concentration ranges.

Light scattering investigations of concentrated polymer solutions require excellent sample quality. A measure of the sample quality is usually provided by recording the polarized Rayleigh–Brillouin (RB) spectra $I_{VV}(\omega)$. A polarized RB spectrum is shown in Fig. 2 for a PS/toluene solution with C_{PS}=0.6 g/ml at 293 K. The Landau–Placzek (LP) intensity ratio (the ratio of the central peak to the total intensity of the shifted Brillouin peaks) is 3.4 for this sample. LP ratios in the range 2.9–5 were measured for the other solutions, indicating samples of high optical quality.

B. Light scattering

The dynamics of a mixed glass comprising a broad concentration range and especially the extremely different mobilities involved require the use of Fabry–Perot interferometers (FPI) with different free spectral ranges (FSR). In the present study we have used three interferometers: (i) a planar FPI (Spectra Physics, Model 410-03) with a fixed FSR of 1017 GHz and a finesse of about 50 to record the fast dynamics associated with the solvent in the neat solvent and in the dilute solutions at high T, (ii) a tandem-FPI with an FSR of 220 GHz and a finesse in excess of 80 was used for most of the depolarized spectra, whereas an FSR of 20 GHz was used for recording the polarized Rayleigh–Brillouin spectra (Fig. 2), (iii) a confocal-FPI (Burleigh, Model CF100) with an FSR of 750 MHz and a finesse of about 60. The light source was a single mode Ar$^+$ laser (Spectra Physics, Model 165) operating at λ=514.5 nm and the incident power on the sample was $\sim$100 mW. All spectra were taken at a scattering angle of 90°. The incident beam was polarized vertically with a Glan polarizer (extinction coefficient $> 10^{-6}$) and in the scattered beam a Glan–Thompson polarizer (Halle, extinction coef-
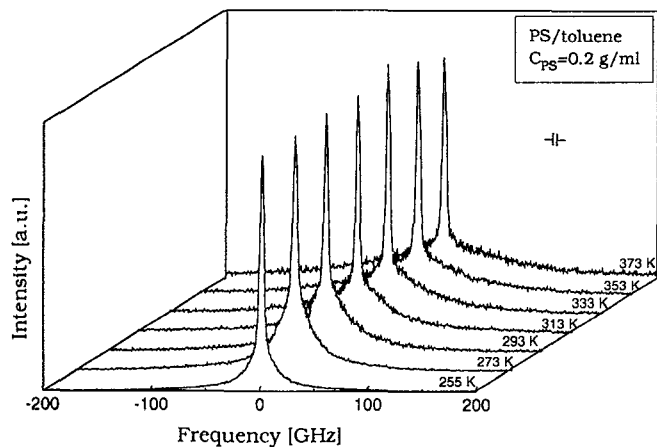
FIG. 3. Depolarized Rayleigh spectra of a PS/toluene solution with C_{PS} =0.2 g/ml as a function of temperature. The spectra are taken by means of the tandem-FPI (FSR=220 GHz). The symbol -‖- indicates the instrumental full width.

FIG. 5. Dielectric loss vs frequency for a PS/toluene solution with C_{PS} =0.2 g/ml at different temperatures: (●) 128; (■) 131.6; (□) 136; (○) 140; and (△) 144 K.

ficient > 10^{-7}) was used to select the VH component. Details of the experimental setup can be found elsewhere.[30] Typical depolarized spectra taken with the tandem-FPI are shown in Fig. 3 for the PS/toluene solution with C_{PS}=0.2 g/ml in the temperature range: 255–373 K. The spectra in Fig. 3 reveal distinct features which are discussed in detail below. In Fig. 4 the concentration dependence of the $I_{VH}(\omega)$ spectra is shown at 293 K. The spectral changes in going from the neat solvent to the most concentrated solution employed here (C_{PS}=0.6 g/ml) are dramatic.

C. Dielectric spectroscopy

The dielectric measurements were made in the frequency range 10^{-1} to 10^5 Hz with a frequency response analyzer (Solartron Schlumberger 1254). The solutions were kept between two gold-plated stainless-steel plates of 20 mm diameter with a separation of ~50 μm being maintained by fused silica spacers. The sample temperature was
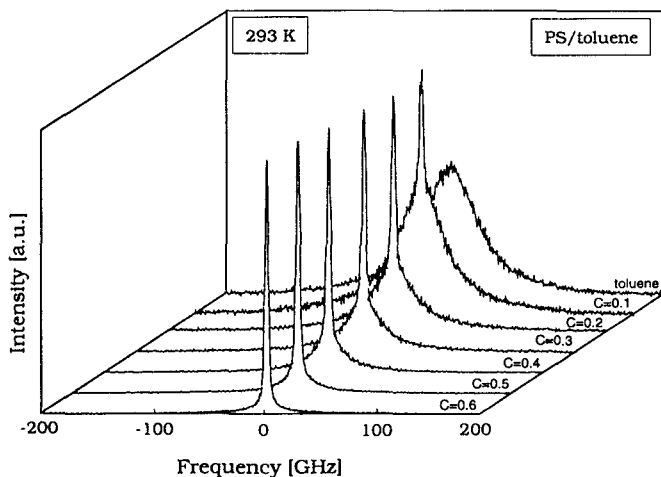

FIG. 4. Depolarized Rayleigh spectra of toluene and of six PS/toluene solutions at 293 K, taken with the tandem-FPI.
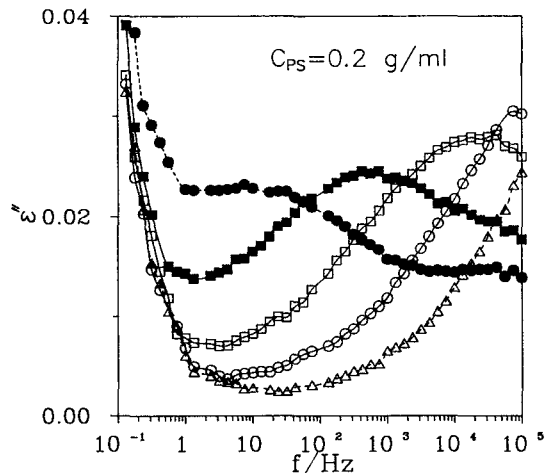
adjusted by a jet of temperature-controlled nitrogen gas in the temperature range: 128–310 K with a stability better than ±0.1 K. Details of the experimental setup are given in Ref. 31. Typical dielectric loss curves for the PS/toluene solution with C_{PS}=0.2 g/ml are shown in Fig. 5 at some temperatures.

III. DATA ANALYSIS

In the theory of DRS,[32] a measure of the anisotropic scattering power of a substance is given by the effective optical anisotropy since $I_{VH} \sim \rho \gamma_{eff}^2$, where ρ is the number density of the solute and γ_{eff}^2 is the effective optical anisotropy. The value of γ_{eff}^2 for toluene is 23 Å^6 compared to 38 Å^6 per monomer unit of PS.[33] Therefore the optical anisotropy in the PS/toluene solutions is influenced more by the polymer than the solvent. Nevertheless, the very different reorientational dynamics of the solute (on the ns time scale) and the solvent (on the ps time scale) preserve the selectivity of DRS.

The neat solvent $I_{VH}(\omega)$ (Fig. 4) have been fitted with a single Lorentzian plus a baseline (B).[17] The effect of adding PS to toluene is shown in Figs. 3 and 4. Clearly, one Lorentzian cannot describe the experimental spectra and a fit to a double Lorentzian plus a baseline is made instead

$$I_{VH}(\omega)\,|_{\text{tandem}} = \frac{1}{\pi} I_f \frac{\Gamma_f}{\Gamma_f^2 + \omega^2} + \frac{1}{\pi} I_s \frac{\Gamma_s}{\Gamma_s^2 + \omega^2} + B. \quad (1)$$

I_f and I_s are the integrated intensities of the broader (fast) and narrower (slow) Lorentzians, respectively and Γ_f and Γ_s are the corresponding half-widths at half-height (HWHH). Figure 6, shows a typical fit, using Eq. (1), to a spectrum for C_{PS}=0.2 g/ml taken with the tandem-FPI at 333 K. As both solute and solvent are composed of anisotropic units, the DRS spectrum of the solution will involve two weighted contributions. The broader component is associated with the fast reorientational motion of the solvent (ps) while the narrower component—which
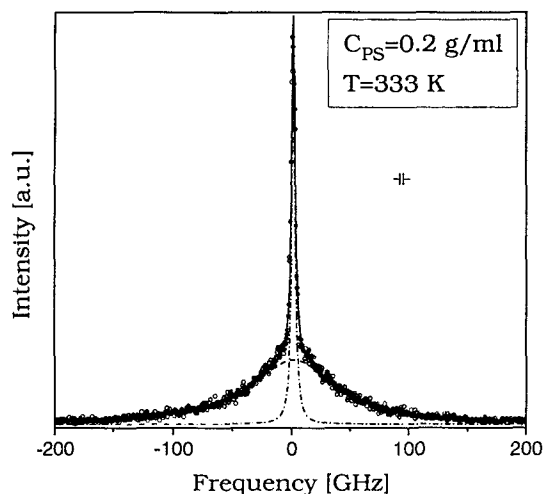
FIG. 6. Depolarized Rayleigh spectrum of a PS/toluene solution with $C_{PS}=0.2$ g/ml at 333 K, taken with the tandem-FPI (FSR=220 GHz). The solid line denotes the contributions of the narrow (dash–dot line) and broad (dashed line) Lorentzian components. The symbol -‖- indicates the instrumental full width.

has a HWHH that is indistinguishable from the instrumental width—primarily reflects the slow reorientational dynamics of the PS chains.

In order to resolve the narrow spectral component (Figs. 3, 4, and 6) we utilized a smaller FSR (20 GHz), but the dynamics associated with this component were even slower and could not be resolved. The narrow component can, however, be resolved using the confocal-FPI. A typical spectrum using the confocal-FPI is shown in Fig. 7 for a PS/toluene solution with $C_{PS}=0.4$ g/ml at 333 K. The fast process observed with the tandem-FPI is now too fast for resolution within the frequency range of this spectrometer (FSR=750 MHz) and contributes only to the baseline, leaving only the slow component well resolved.
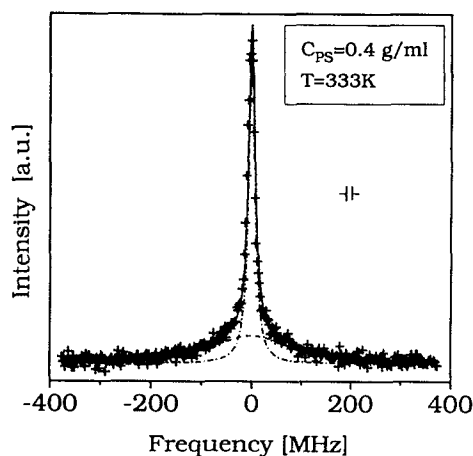

FIG. 7. Depolarized Rayleigh spectrum of a PS/toluene solution with $C_{PS}=0.4$ g/ml at $T=333$ K, taken with the confocal-FPI (FSR=750 MHz). The solid line through the experimental points is the fit using a delta function—broadened by the instrumental resolution—and a broad Lorentzian. The symbol -‖- denotes the instrumental full width.

Therefore, a single Lorentzian fit plus a delta function—broadened by the instrumental resolution—on top of a "flat" background:

$$I_{VH}(\omega)\big|_{conf}=\frac{1}{\pi}I_s\frac{\Gamma_s}{\Gamma_s^2+\omega^2}+\delta(\omega)+B' \qquad (2)$$

can describe the data taken with the confocal interferometer. All $I_{VH}(\omega)$ spectra were convoluted with the instrumental line shape. The collective reorientation times for the fast and slow components were calculated as $\tau_{f,s}=(2\pi\Gamma_{f,s})^{-1}$.

The dielectric data (Fig. 5) have been fitted to the empirical equation of Havriliak–Negami (HN)

$$\epsilon^*(\omega)=\epsilon_\infty+\frac{\epsilon_0-\epsilon_\infty}{[1+(i\omega\tau_{HN})^\alpha]^\gamma} \qquad (0<\alpha,\gamma\leqslant1) \qquad (3)$$

where $\epsilon^*(\omega)[=\epsilon'(\omega)-i\epsilon''(\omega)]$ is the frequency dependent complex dielectric permittivity, $\Delta\epsilon(=\epsilon_0-\epsilon_\infty)$ is the relaxation strength given by the difference of the low- and high-frequency values of the real part of the dielectric permittivity and τ_{HN} is the characteristic relaxation time. The parameters α and γ, respectively, describe the symmetrical and asymmetrical broadening of the distribution of relaxation times. The steep rise of $\epsilon''(f)$ shown in Fig. 5 is caused by the electrical conductivity and was fitted according to: $\epsilon''\sim(\sigma_0/\epsilon_0)\omega^{s-1}$, where σ_0 and s $(0\leqslant s\leqslant1)$ are fitting parameters and ϵ_0 is the permittivity of free space.

IV. RESULTS AND DISCUSSION

A. High frequency side—depolarized Rayleigh scattering

The reorientation relaxation times of toluene have been discussed earlier with respect to the PMMA/toluene system.[17] The temperature dependence of the reorientation times τ_0, conforms to the Vogel–Fulcher–Tammann (VFT) equation

$$\log\tau_0=\log\tau_0^*+\frac{B}{T-T_0} \qquad (4)$$

with parameters: $\tau_0^*=0.28\pm0.06$ ps, $T_0=96\pm2$ K, and $B=251\pm20$ K obtained in the T range: 125–373 K. The neat solvent reorientation times, together with the fast component of the $I_{VH}(\omega)$ spectra taken with the tandem-FPI (Figs. 3, 4, and 6), are shown in Fig. 8, in the usual Arrhenius representation. At high temperatures, the influence of the polymer matrix on the solvent dynamics is small, considering the change in the macroscopic viscosity on going from the neat solvent to the more concentrated solutions. This important observation was made earlier[20] in a DRS study of PS/toluene solutions ($C_{PS}\leqslant0.15$ g/ml). Subsequently, it has been concluded that the reorientation of small molecules, as probed by DRS, is sensitive only to the locally available free space. Our data shown in Fig. 8, demonstrate that it is the local viscosity which determines the solvent reorientation even for concentrations where the polymer is the major component.

In order to quantify the effect of the polymer on the solvent reorientational dynamics in the PS/toluene solu-
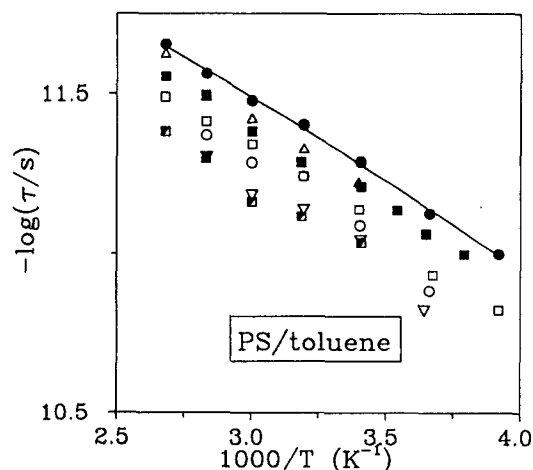
FIG. 8. Temperature dependence of the reorientational relaxation times of toluene in the undiluted state (●) and in PS/toluene solutions with different PS concentrations: (△) $C_{PS}=0.1$; (■) $C_{PS}=0.2$; (□) $C_{PS}=0.3$; (○) $C_{PS}=0.4$; (▽) $C_{PS}=0.5$; and (◩) $C_{PS}=0.6$ g/ml.

tions we use the normalized solvent relaxation time $\tau(C,T)/\tau_0(T)$, where $\tau(C,T)$ is the fast reorientation time obtained from the DRS spectra, and τ_0 refers to the neat solvent times (Fig. 9). The normalized solvent relaxation shown in Fig. 9—which represents an average local solvent friction—exhibits an exponential dependence on polymer concentration which is independent of T at the high interferometric temperatures. This observation is in good agreement with the similar concentration dependences in the systems PS/aroclor,[9,16] PS/DOP,[18] and PMMA/toluene.[17] The rate of change of the solvent friction $[\partial \log(\tau/\tau_0)/\partial C]$ is approximately constant and equal to ~ 0.5 at high T. Recently,[10] the change in the solvent dynamics upon addition of polymer was found to scale with the logarithmic difference of the time scales between the solvent and the local polymer dynamics, i.e.,
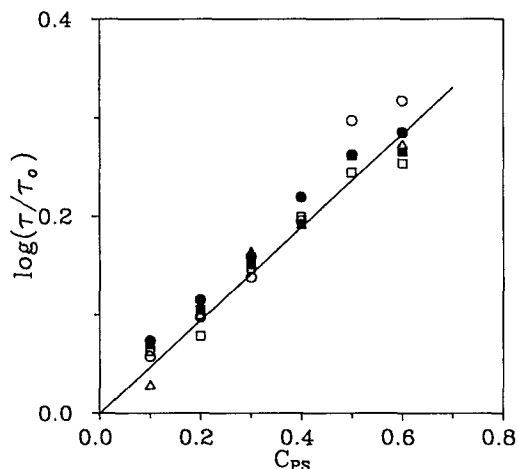
$$\frac{\partial}{\partial C} \ln \frac{\tau(C,T)}{\tau_0(T)} \sim Q \log\left(\frac{\tau_{PS}}{\tau_0}\right), \tag{5}$$

where Q is a solvent-dependent parameter. Using the neat solvent reorientation times and the segmental dynamics of PS extracted from dilute PS solutions in different solvents[10]

$$\tau_0 = 1.36 \times 10^{-12} \text{ s} + \frac{\eta}{T} 2.09 \times 10^{-9} \frac{sK}{cP} \tag{6}$$

$$\tau_{PS} = 0.5 \times 10^{-12} \frac{s}{cP} \eta \, e^{(20 \text{ kJ/mol})/RT} \tag{7}$$

we obtain a Q value of ~ 0.63 ml/g at 333 K. Using this value, we find good agreement between the two sides of Eq. (5) in the temperature range: 293–373 K. Furthermore, this value of Q for toluene agrees with an estimate made in Ref. 10 and it is smaller than the corresponding value for aroclor in its PS solutions ($Q_A \approx 1$ ml/g at 333 K obtained from DRS, Ref. 16). Since the left-hand side of Eq. (5) assumes the same value in both PS/aroclor and PS/toluene solutions we can write

$$\frac{Q_{TOL}}{Q_A} \approx \frac{\log \tau_{PS} - \log \tau_A}{\log \tau_{PS} - \log \tau_{TOL}}. \tag{8}$$

Therefore, the difference in the Q values for different solvents reflects the difference between the polymer segmental dynamics and the solvent reorientation. It is worth mentioning that in the system PS/DOP,[18] where the solvent dynamics are intermediate between the aroclor and toluene reorientational times, the Q value calculated at the same temperature ($T=333$ K) is $Q_{DOP} \approx 0.88$ ml/g. Therefore, $Q_A > Q_{DOP} > Q_{TOL}$ at high temperatures, in accordance with the size, shape (anisotropy), and T_g of the solvent molecules. At lower T, the situation becomes complicated, mainly because of the glass transition which comes into play with strong effects on the solvent and polymer dynamics (see Sec. IV B).

B. Low frequency side—dielectric spectroscopy

Two processes could be resolved in the dielectric relaxation experiment: (i) a slow process which is mainly determined by the polymer segmental dynamics and (ii) a fast process which is solely due to the solvent (Fig. 5). A low-temperature relaxation could also be observed but it was too fast and could not be resolved. However, since this process appears at lower temperatures than the fast solvent contribution it is likely to reflect some internal mode of toluene. In an earlier DS study[24] the three processes above were identified as α, β, and γ relaxations, respectively. Here we will not use this terminology since the so-called β relaxation does not behave like a secondary relaxation but instead has features similar to the α process (see below). Furthermore, the slow and fast DS/processes are continuations of the high frequency DRS processes. We discuss the DS results for the two relaxations in terms of the relaxation strength, the temperature and concentration dependence of the relaxation times and of the distribution of relaxation times.

FIG. 9. Reduced solvent relaxation times vs PS concentration, at five temperatures: (□) 293; (●) 313; (○) 333; (■) 353; and (△) 373 K.
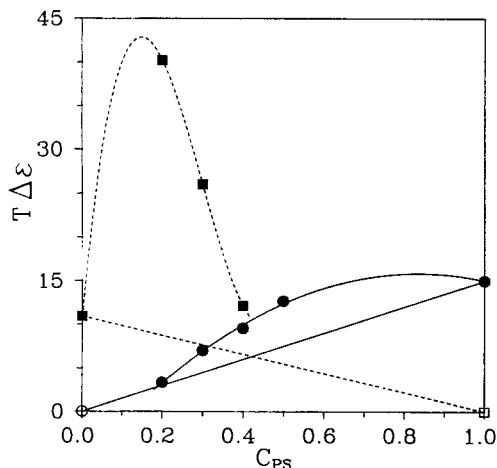
FIG. 10. Concentration dependence of the $T\Delta\epsilon$ for the slow (●) and fast (■) processes. Straight lines denote the expected behavior from dilution.
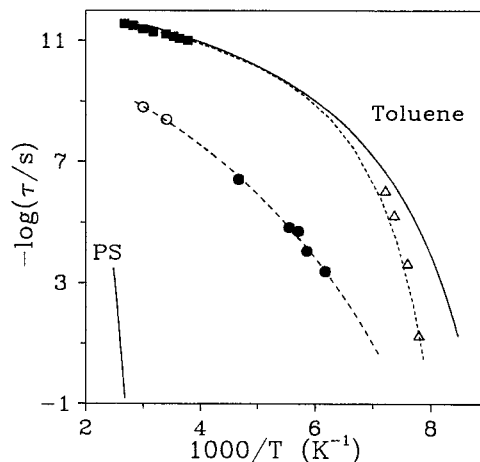

FIG. 11. Temperature dependence of the fast and slow relaxation processes in a PS/toluene solution with $C_{PS}=0.2$ g/ml. The experimental points for the fast process are (■) DRS (tandem-FPI), (△) DS. For the slow process: (○) DRS (confocal-FPI; (●) DS. The neat solvent and bulk polymer relaxations are also shown for comparison.

The dielectric relaxation strength $\Delta\epsilon$, obtained from the fit to the HN equation (3) is plotted in Fig. 10 as a function of PS concentration for the two processes. In order to account for the T dependence of $\Delta\epsilon$ we plot the product $T\Delta\epsilon$, obtained at a frequency of 1 kHz. The product $T\Delta\epsilon$ for PS was evaluated from[34] $\Delta\epsilon_{PS}=0.0376$ and the known segmental dynamics.[35] The relaxation strength is proportional to the effective dipole moment μ_{eff}, using

$$\Delta\epsilon \sim \frac{N\mu_{eff}^2}{T}; \quad \mu_{eff}^2 = g\mu_0^2, \tag{9}$$

where N is the concentration of repeating units, μ_0 their dipole moment and g is the Kirkwood reduction factor. From the monomer dipole moment[24] ($\mu_0=0.36$ D) we obtain a reduction factor $g_{PS}=0.29$ which is small compared to other bulk polymers.[36] The corresponding orientation pair correlation factor obtained from DRS[37] is $g_{PS}^{DRS}=2.6$ and given that for most bulk polymers orientation pair correlations are in the range 1–3,[37] we expect values of g, as obtained by DS, significantly different from unity ($g^{DS}<1$) since DRS measures a second order correlation function whereas DS a first order. The product $T\Delta\epsilon$ for toluene was evaluated from the effective dipole moment[34] ($\mu_{eff}=0.3$ D) and the neat solvent dynamics. The reduction factor for toluene can be evaluated from the gasphase dipole moment[38] ($\mu_0=0.37$ D) and is equal to 0.66. The corresponding value from DRS[39] is $g_{Tol}^{DRS}=1.32$. Therefore, the ratio g^{DRS}/g^{DS} differs for PS and toluene indicating different orientation angles and possibly different number of neighboring dipoles. Returning to Fig. 10, we observe that the relaxation strength for the fast process in the $C_{PS}=0.2$ g/ml solution exceeds by ~ 5 times the expected value if this process is due to toluene alone. This result implies that (i) the excess $\Delta\epsilon$ of the fast DS process—which cannot be accounted for by inclusion from the weak PS relaxation—is due to solvent association and (ii) some solvent molecules also contribute to the slow process but this contribution is negligible at $C_{PS}=0.2$ g/ml

and it increases at $C_{PS}\geqslant 0.3$ g/ml. Since both processes are cooperative in nature, we can evaluate the effective g' factor in the solvent environment as

$$\frac{T_s\Delta\epsilon_s}{T_f\Delta\epsilon_f} = \frac{g_{PS}}{g_{Tol}}\left(\frac{\mu_0^{PS}}{\mu_0^{Tol}}\right)^2 \tag{10}$$

under the assumption that $g_s \approx g_{PS}$. For the solution with $C_{PS}=0.2$ g/ml we obtain $g' \approx 3.3$ which is five times higher than the neat solvent value. The same quantity evaluated for the $C_{PS}=0.3$ g/ml solution is equal to 1.0 being 1.6 times higher than the corresponding value for the neat solvent.

The dynamics associated with the fast and slow processes as obtained from the combined DRS and DS measurements on the same samples are shown in Fig. 11 for the PS/toluene solution with $C_{PS}=0.2$ g/ml. The high frequency data points for the fast and slow processes are obtained from DRS measurements with the tandem and confocal-FPI, respectively. The low frequency points are from DS and the times shown in the figure are the τ_{max} ($=1/2\pi f_{max}$). Solid lines in Fig. 11 indicate the bulk polymer and neat solvent dynamics. There are two pertinent features in Fig. 11. First, there are two distinct time scales in the PS/toluene solutions and secondly that neither process is Arrhenius. Earlier NMR[22,23] and DS[24] studies on the solvent dynamics in PS/toluene solutions failed to identify the fast process—associated with the solvent dynamics—as being a non-Arrhenius process probably because of the smaller frequency range. In the present study we follow the solvent orientational dynamics over a frequency range of ~ 10 decades. The solvent orientational dynamics in the $C_{PS}=0.2$ g/ml solution confirm to the VFT equation (4) with parameters: $\log \tau_0 = -12.2$ (τ in seconds), $B=186$ K and $T_0=111$ K. The same parameters for the PS segmental dynamics in the same solution are $\log \tau_0 = -11.4$, $B=667$ K and $T_0=80$ K. The smaller T_0 for the slow process means that at lower frequencies the

two processes cross. However, the PS segmental dynamics are obtained from a smaller frequency range (~6 decades) and therefore the experimental uncertainty in determining the VFT parameters is higher than for the fast process.

The existence of two distinct time scales in the PS/toluene system appears to be a general feature for the dynamics of concentrated polymer solutions. Two α relaxations have also been observed in the PS/DOP[19] and PMMA/toluene[17] solutions. However, in the SCPE/DOP system[40] a single, albeit broad α-relaxation was observed. A possible explanation for this is that in the latter system both components are polar and the single α relaxation can be the result of interactions between the polymer and the solvent. The finding of two time scales in some polymer solutions has some implications with respect to glass formation. Glass formation and cooperativity are two concepts which are strongly related in theoretical approaches to the glass transition.[41,42] According to the cooperativity picture, glass formation requires a cooperative volume V_α with a characteristic length $\xi_\alpha(\sim V_\alpha^{1/3})$. The temperature dependence of ξ_α is governed by the VFT temperature T_0;[43] $\xi \sim (T - T_0)^{-2/3}$ and cooperativity is expected to break down only at high temperatures. The characteristic length ξ_α, has been estimated to be in the order of 20 Å near T_g.[44] Implicit in the two VFT dependences in the present system, is the existence of concentration heterogeneities large enough to exhibit their own glass transition. The length scale of the PS-rich and toluene-rich domains should be in the order of 20 Å near the corresponding T_g. It is worth mentioning that at low frequencies, both processes have very broad distributions arising from composition fluctuations.[45] In the usual Kohlrausch–Williams–Watts representation $[g(t) \sim \exp(-t/\tau_{\mathrm{KWW}})^\beta]$ the exponent assumes values: $\beta_s = 0.41$ and $\beta_f = 0.2$, respectively for the slow and fast DS processes. These values should be compared with the distributions in the bulk polymer and neat solvent. Near T_g, $\beta_{\mathrm{PS}} = 0.4$ as measured in the VH geometry[35] and a distribution of relaxation times is also reported for toluene at T near T_g $(\beta_{\mathrm{Tol}} \sim 0.5)$.[46] The latter, however, becomes a single relaxation at higher T.[17] We recall here that in the PS/DOP system[19] the two primary relaxations were equally broad at low T ($\beta_{\mathrm{KWW}} \approx 0.2$).

The segmental dynamics in the PS/toluene solutions with $C_{\mathrm{PS}} = 0.5$, 0.4, 0.3, and 0.2 g/ml are compared in Fig. 12. Evidently, there is a pronounced concentration dependence for the slow process. This can be rationalized by the use of the "fragility" factor D ($= 2.303 B/T_0$), introduced by Angell[47] to account for the "strength" of a glass. D decreases systematically from 19 to 6 in going from the $C_{\mathrm{PS}} = 0.2$ to 0.5 g/ml. Therefore, in this notation, the segmental dynamics in the $C_{\mathrm{PS}} = 0.2$ g/ml solution represent a less fragile glass as compared to the $C_{\mathrm{PS}} = 0.5$ g/ml solution. The distribution of relaxation times also displays a small but noticeable concentration dependence changing from 0.41 to 0.33 in going from the $C_{\mathrm{PS}} = 0.2$ to the $C_{\mathrm{PS}} = 0.5$ g/ml solution. In fact, the distribution of relaxation times in the PS environment in the less concentrated solution ($C_{\mathrm{PS}} = 0.2$ g/ml) is similar to that in bulk PS.[35]
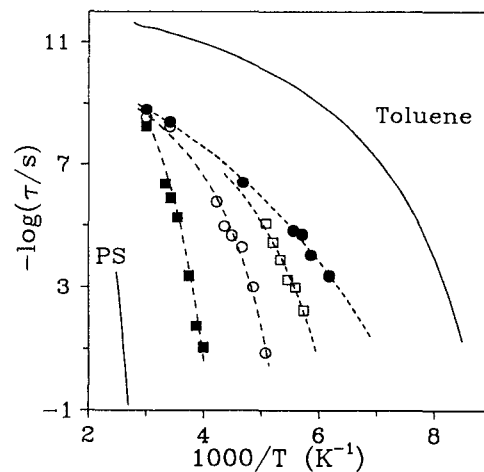

FIG. 12. Temperature dependence of the slow relaxation process in the PS/toluene solutions with C_{PS}: (●) 0.2 g/ml; (□) 0.3 g/ml; (○) 0.4 g/ml; and (■) 0.5 g/ml. The high frequency experimental points are from DRS (confocal-FPI) and the lower frequency data are from DS. Dashed lines are fits to the VFT equation and solid lines indicate the neat solvent and bulk polymer dynamics.

In Fig. 13 we plot the normalized solvent relaxation time $\tau(C,T)/\tau_0(T)$ as a function of C_{PS} for different temperatures. The emphasis here is on the low temperature side of the fast process and the relaxation times are obtained from the VFT fits to the solvent relaxation. A prominent feature of Fig. 13 is the nonlinearity of the average local solvent friction which is in sharp contrast to the situation at high T (Fig. 9). Furthermore, the departure from linearity becomes more pronounced at high polymer concentrations. The rate of change of solvent friction with polymer concentration at low T and at high C_{PS} becomes temperature dependent and this is a result of the VFT behavior of the solvent reorientational dynamics (Fig. 11). Previous studies on the reorientational dynamics of solvent molecules in the presence of polymer matrices[9,16,17] were
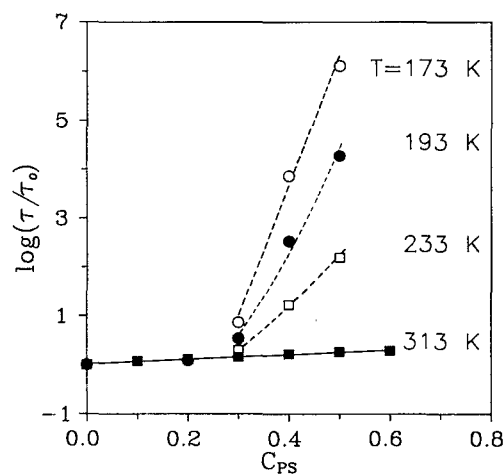

FIG. 13. Temperature dependence of the fast relaxation process in PS toluene solutions, reduced to the neat solvent relaxation times. Notice the nonlinearity at low temperatures and high polymer concentrations which is in contrast to the situation at high T (Fig. 9).

usually made at low polymer concentrations and/or high temperatures so that the pronounced effect shown in Fig. 13 did not show up.

Polymer solutions are believed to be homogeneous down to a very small length scale (screening length). Furthermore, it is assumed that a single time scale exists in the mixed glass which is given by the T_g of the mixture. However, static and dynamic experiments show otherwise. The excess low-angle scattering at polymer concentrations above the chain overlap concentration (C^*) in SANS[48] and SAXS[27] experiments provides evidence that a single length scale is insufficient for characterizing concentrated polymer solutions, and that a second length scale is required. Furthermore, the present and other dynamic experiments reveal that a single time scale is also insufficient to describe the dynamics in the PS/toluene system. Deuteron NMR experiments[21] thus separated the diluent mobility in the PS/toluene solutions into solid and liquid components. The respective average correlation times differed by ~5 decades and this difference increased with C_{PS}. In the present study we identify the two distinct time scales as reflecting the relaxations within the cooperative volumes associated with the polymer and the solvent in a macroscopically homogeneous solution. These time scales have been identified as two α processes which display the usual VFT behavior. As a consequence of that, the system is partially ergodic even below the high T_g (slow process), since solvent reorientation persists to temperatures down to the low T_g (fast process). Thus, the system becomes strictly nonergodic only at temperatures below the low T_g.

V. CONCLUSIONS

In the present work the solvent and polymer orientational dynamics have been examined on the PS/toluene system for polymer concentrations up to 0.6 g/ml using depolarized Rayleigh scattering and dielectric spectroscopy. The principal conclusions may be summarized as follows:

(i) Two distinct time scales exist in the macroscopically homogeneous PS/toluene solutions which are associated with the polymer (slow) and solvent (fast) dynamics.

(ii) Both processes display non-Arrhenius temperature dependences and conform to the VFT equation.

(iii) As a result of the VFT behavior for the solvent reorientational dynamics in the solutions the rate of change of solvent friction with polymer concentration becomes temperature dependent, at low temperatures.

(iv) The distribution of solvent reorientation times is very broad at low temperatures but exhibits a strong temperature dependence which is consistent with the picture of solvent clustering, especially at low C_{PS}.

The results presented here demonstrate that a single time scale is inadequate for describing the orientational dynamics in some concentrated polymer solutions.

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