Dynamics of Polymer Chains in Solution Subject to an Electric Field Probed by Quasielastic Light Scattering

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ABSTRACT: The effect of an applied electric field (E-field) on the dynamics of polystyrene (PS) in tetrahydrofuran (THF) was studied by quasielastic light scattering. The concentration of the PS/THF solution was varied from very dilute to semidilute, and the E-field was applied up to 7.14 kV/cm. In the dilute to semidilute regime, the relaxation rate of PS increases sharply with the increase of applied E-field. The dilute regime was overlooked in previous studies. However, going beyond the semidilute to concentrated regime, the applied E-field has only a diminishing effect on the dynamics of PS/THF solution. The observed electric field induced effect is found to be closely related to the polarization current of the polymer solution.

Introduction

The static and quasielastic light scattering (QELS) techniques have been widely used to characterize the molecular weight, shape, and thermodynamic properties of polymer chains in dilute solution[1,2] and also to probe mechanical properties[3] and phase behavior[4] of the polymer solution in semidilute and concentrated regimes. More complex polymer solution systems, such as block copolymers in solvent and two polymers in a small molecular solvent ternary systems,[5−10] have also been investigated by using QELS. In all these studies, the effects of chain flexibility, polymer concentration, solvent quality, composition, etc., have been considered. However, the effects due to the application of external pressure, external imposed flow, or electric field (E-field) on the dynamics and structure of polymer solution have not been extensively carried out.

Debye and Kleboth observed in 1965 a strong decrease in the absorption coefficient in binary liquid mixtures in the vicinity of the critical point as the mixture was subjected to an E-field.[11] This effect was attributed to the E-field-induced shift in the critical point. About 6 years ago, Wirtz and Fuller found that an electric field could also induce a mixing of polymer solution following a shallow quench in the two-phase region.[12] They found that the pattern of the scattering intensity changed from circular to ellipsoid as the electric field was applied. The phenomena were explained by an induced polarization and the change of the free energy of binary mixtures due to the E-field.[13]

The effect of an E-field on the dynamics of polymer chain in solution was first reported by Price et al.[14] Upon the application of an E-field, they found an increase in the polymer solution viscosity. The relaxation rate of the time correlation function, as monitored by QELS, on the application of an E-field in solution consisting of polystyrene (PS) and tetrahydrofuran (THF) or toluene also changes. The magnitudes of these changes were found to depend on the PS molar mass, polymer concentration, nature of solvent, electric field strength, and the frequency of the applied field. They explained these results by invoking the electrorheological (ER) effect.

The ER effect is associated with the phenomenon that when an electric field is applied to a suspension of dielectric particles in a nonpolar liquid, the fluid shows a dramatic viscosity increase; in the case of a large field, the fluid even solidifies. The effect is due to the alignment of the dielectric particles that attract each other via the induced dipole−dipole interactions.[15−18] The ER effect is generally observed in heterogeneous fluids consisting of a dispersion of polarizable solid particles in an insulating fluid.

Dynamic light scattering results of PS in THF, in 1,4-dioxane (DO), and in THF/DO mixed solvent at one fixed polymer concentration near the overlap concentration (C^*), subject to an external dc electric field, were recently reported in our laboratory.[19] In THF, the relaxation rate of the intensity autocorrelation function of the scattered light is found to increase with the increase of the applied E-field; however in DO, the E-field has no effect on the relaxation rate; in mixed solvents, an intermediate effect is observed, depending on the THF content. These observations are not consistent with the ER effect, because the change in the relaxation rate is not present in DO, which is a nonpolar solvent. In addition, if the ER effect is applicable, the relaxation rate is expected to decrease, not increase, due to the increase in the solution viscosity. This is contradictory to the light scattering experimental result.

Since the work reported in ref 19 deals with only one concentration near C^*, to provide additional experimental data to help elucidate the nature of the electric field induced effect, we carry out a systematic QELS study of PS in THF by varying the concentration from the dilute to concentrated regime. We have also varied the scattering angle and the field strength in this investigation. This paper reports new experimental results.

Experiment

The PS sample used in this study was purchased from Toya Soda and has an average molecular weight $M_w = 2.88 \times 10^6$ with the polydispersity index $M_w/M_n = 1.09$. Polymer solutions were prepared by dissolving a fixed amount PS in tetrahydrofuran (THF, Aldrich). Dust in the solution was removed by filtering through a 0.1 μm Millipore filter into a light scattering cell. The overlap concentration of the PS in THF is estimated as $C^* = (1.80 \pm 0.2) \times 10^{-3}$g/mL.[19] Solutions used in this study

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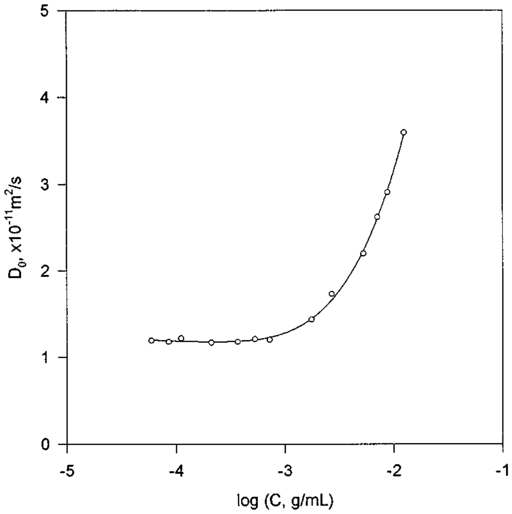

Figure 1. Polymer concentration dependence of the diffusion coefficient D_0 for PS in THF without the application of an E-field.

with concentration less than C^* will be referred to as dilute and that above C^* as semidilute.

A dc (direct current) electric field was applied to solution by two circular steel parallel plate electrodes emerged in solution. The type of electrodes and the electrode configuration are similar to those used in previous studies.[14,19] QELS measurements were carried out by using an ALV-5000 correlator with an argon laser radiation at the wavelength λ = 488 nm served as the excitation light. The temperature of the polymer solution was controlled at 25 ± 0.1 °C.

The normalized intensity−intensity time correlation function $G(q,t)$ was measured. $G(q,t)$ is related to the normalized field−field correlation function $g(q,t)$ via the Sigert relation as

$$\alpha g(q,t) = [G(q,t) - 1]^{1/2} = \int_0^\infty A(\tau) \exp(-t/\tau) \, \mathrm{d} \ln \tau \quad (1)$$

where α is the contrast factor and $A(\tau)$ gives the distribution of the relaxation times. The constrained regulation method (CONTIN) developed by Provencher[20] were used to obtain $A(\tau)$.

Results and Discussion

To obtain the background information, we first carried out dynamic light scattering from solutions with no E-field applied. We vary the concentration from very dilute ($C/C^* \cong 1/30$) to semidilute ($C/C^* \cong 6.9$) and vary the scattering angle from 30° to 150°. When the concentration is very low, the time dependence of $g(q,t)$ is nearly single exponential with the relaxation rate constant Γ proportional to q^2, the proportionality constant, D_0, being the translational diffusion coefficient of PS in THF. At higher concentration, $g(q,t)$ deviates from the single exponential. We determine the relaxation rate Γ by $1/\langle\tau\rangle$, where $\langle\tau\rangle$ is the average relaxation time, calculated by integrating the area of the time correlation. The concentration dependence of the translational diffusion coefficient ($\Gamma/q^2 = D_0$) is given in Figure 1. D_0 is nearly constant in dilute regime, but it increases rapidly with the increase of PS concentration in semidilute regime. The result is in good agreement with that in the literature.[21]

We next investigate the effect as an externally electric field is applied on polymer solutions with various concentrations. As shown in Figure 2, the PS/THF solution with C = 0.0027 g/mL, the relaxation rate increases with increasing electric field strength. This concentration is close to C^* (≈1.80×10^{-3} g/mL).

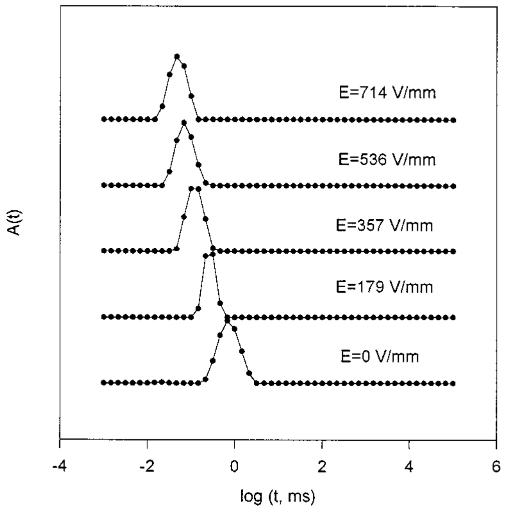

Figure 2. Relaxation time distribution obtained at the scattering angle of 30° from the CONTIN fit for PS/THF solution with polymer concentration C = 0.0027 g/mL under different E-fields.

We also fit the autocorrelation function $g(q,t)$ to a single stretched exponential function, $e^{-(t/\tau)^\beta}$. At this concentration, when no E-field is applied, the parameter β is less than 1 due to the viscoelastic effect.[23] However, in the presence of E-field, the single stretched exponential decay mode cannot adequately fit the experimental data. A systemic error between fitted curve and experimental data exists in the short delay, as shown in Figure 3. The forced fit to the single stretched exponential gives β = 1.16, indicating that the shape of the autocorrelation function is narrower than that described by a single exponential. Similar results are also found for correlation functions obtained at higher field strengths.

The q dependence of the relaxation rate obtained at different E-fields was studied by Wang and Huang in ref 19. When no E-field is applied, Γ is proportional to q^2. As the E-field is low, a $q = 0$ intercept develops. For scattering angles $\theta \leq 90°$, one finds that Γ linearly varies with q^2 according to

$$\Gamma = \Gamma_0 + q^2 D_E \quad (2)$$

where the slope D_E and the $q = 0$ intercept Γ_0 depend on the E-field, as shown in Figures 4 and 5. At low E, the slope D_E approximately varies with E^2 as

$$D_E = D_0 + kE^2 \quad (3)$$

where D_0 is the translational diffusion coefficient of PS in THF in the absence of the E-field. The constant k measures the strength of the E-field dependence. The intercept Γ_0 first linearly increases from zero as the E-field is increased, but the rate of increase slows down in the high E-field region. An imperial equation for Γ similar to eq 2 has been given in ref 19. However, due to much lower field strength used, the saturation behavior of Γ_0 with respect to the high E-field was not observed in ref 19. At the low field regime, the linear dependence of Γ_0 versus E^2 is consistent with the present result.

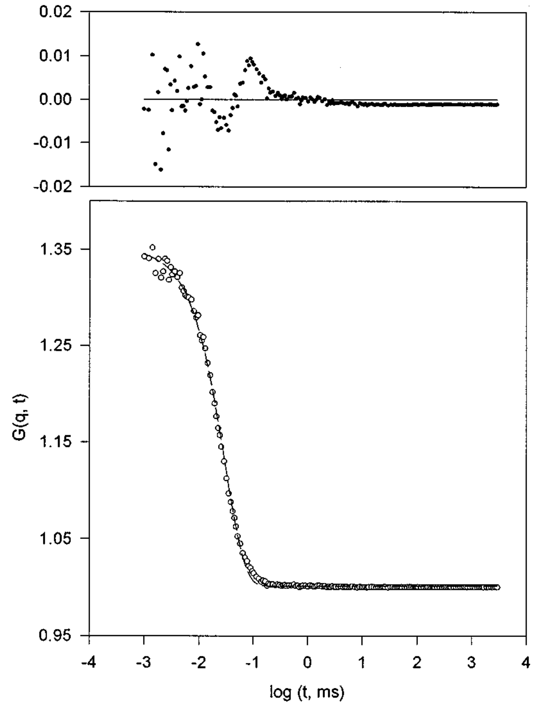

Figure 3. Autocorrelation function measured by QELS at scattering angle of 30° for the above solution of PS/THF when an E-field of 714 V/mm is applied. Dots represent the experimental data, and the solid line is the single stretched exponential fit with parameters $a = 0.592$, $\tau = 0.0510$ ms, and $\beta = 1.163$. Note the β value is greater than 1. The top is the residual distribution of the experimental data compared with the single stretched exponential fit.

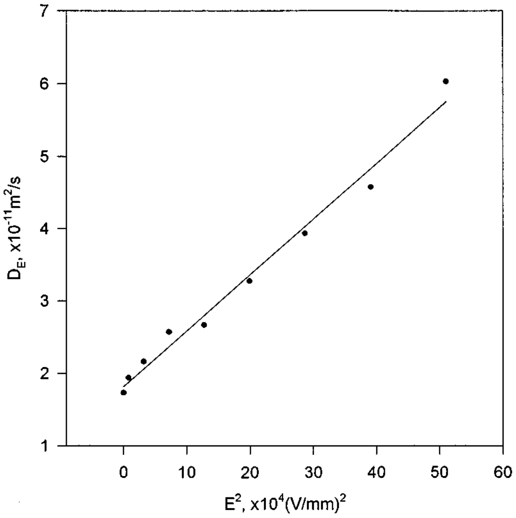

Figure 4. E-field dependence of D_E of the PS/THF solution having $C = 0.0027$ g/mL.

It should be noted that as the polymer concentration is increased to $C = 0.0124$ g/mL, which is about 7 times C^*, the effect of the E-field is greatly reduced, as shown in Figure 6. Considering the fact that in concentrated polymer solution polymer chains are overlapped and form a entangled network in solution, the electric field affects only negligible in the change of the mutual diffusion coefficient of the entangled chains.

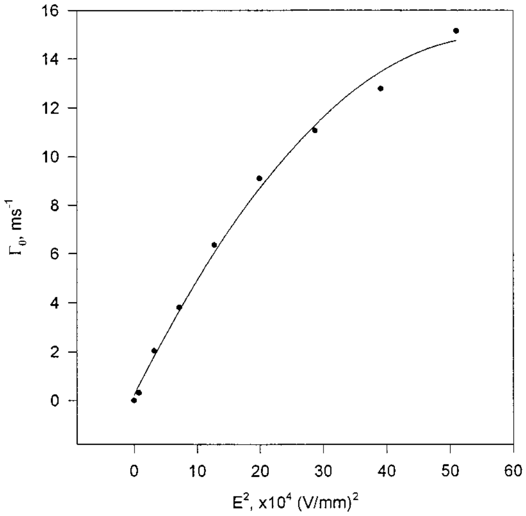

Figure 5. E-field dependence of Γ_0 of the PS/THF solution having $C = 0.0027$ g/mL.

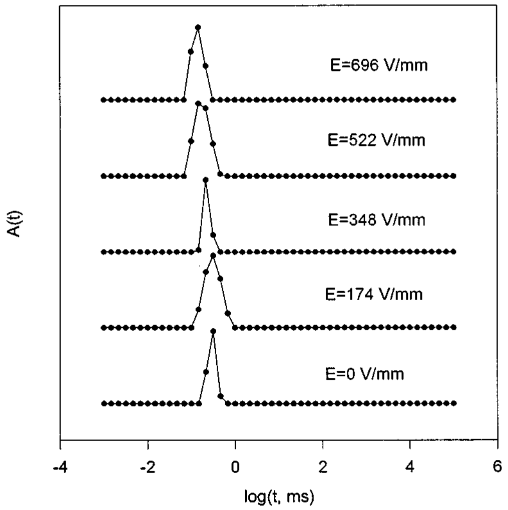

Figure 6. Relaxation time distribution for the PS/THF solution with $C = 0.0124$ g/mL at different E-fields. Note the electric field effect is greatly diminished in this solution as compared to that shown in Figure 2.

In Figure 7, we show the concentration dependence of k, which is the parameter measuring the effect of the electric field on the mutual diffusion coefficient. One notes that k is nearly constant for the PS/THF solution in the dilute regime, but it sharply decreases to zero around C^*. This is an important result. The observation of the electric field effect at low polymer concentration is also a new result, as heretofore, it was believed that the field dependence only occurred in the concentration near C^*.[14,19] The constancy of the k value in the dilute regime attests the inapplicability of the ER model, as this model predicts the parameter k to increase with increasing polymer concentration in the low concentration regime.

The increase of Γ with increasing E suggests that particles diffuse faster in the presence of the E-field. This further suggests the presence of an excess force on the polymer chain when the E-field is applied. In ref 19, a macroscopic theory based on the Maxwell stress tensor of the polymer solution subject to an externally applied electric field was formulated. In the zeroth-order approximation, the theory predicts an increase of D_E with the electric field in a manner similar to that suggested to eq 3. However, the theory does not take into account the effect of the internal field due to the solvation effect of the polymer chain (the result in the zeroth-order approximation). The solvation effect is believed to play an important role in affecting the relaxation rate Γ under the electric field; calculations

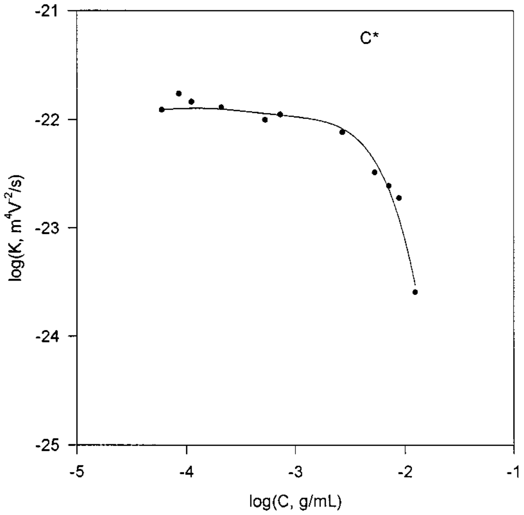

Figure 7. Concentration dependence of the *k* parameter of the PS/THF solution.

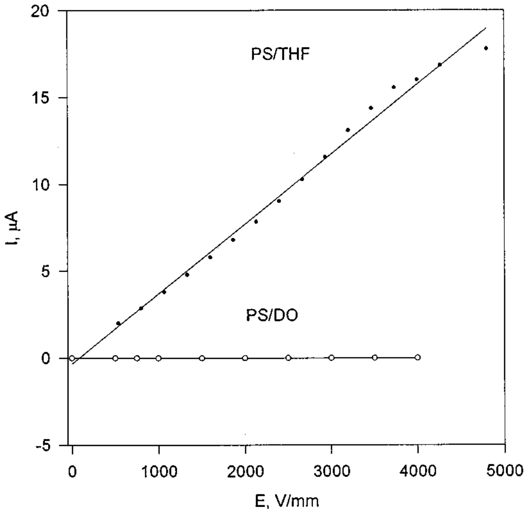

Figure 8. Relationship of the observed current and the applied E-field for dilute PS/THF and PS/dioxane solutions.

beyond the zeroth-order approximation are needed to quantitatively describe the effect of the E-field on Γ in polymer solution.

In passing, we should also mention the calculation of the effect of the E-field on the free energy on the polymer solution by Gurovich.[13] He has shown that under an E-field the change in the free energy of the polymer solution is

$$\Delta F = F_E - F_0 = -\chi E^2/\langle\Phi^2\rangle \tag{4}$$

where F is the free energy, E includes only the applied E-field, Φ is fluctuating molecular electric field, and χ is the Flory–Huggins interaction parameter between polymer and solvent. Since the thermodynamic force acting on the polymer solution at position $\vec{r}$ is equal to $-\nabla F$, the local concentration dependence would need to come from the fluctuating molecular field Φ. Since, in general, $E \ll |\Phi|$, the change in free energy due to the application of E-field as formulated by Gurovich gives only a small force only the polymer chain, and it cannot fully account for the observed E-field effect in Γ as presented here.

One additional experimental result to support the importance of the solvation effect of the polymer chain by the solvent molecules is the correlation of the electric field induced effect for Γ with the electric conductivity measurement. Shown in Figure 8 is the current vs voltage relation measured in the dilute PS/THF solution ($C = 4.9 \times 10^{-4}$ g/mL). Over the range of E-field covered, I is proportional to E for the PS/THF solution; the current follows Ohm's law. On the other hand, the electric conduction result for PS/dioxane solution (also shown in Figure 8) indicates that the conduction current is practically zero over the same voltage range.

In the metal–insulator–metal configuration, the current passing through the polymer solution is determined by the volume–conductivity property of the insulator (polymer solution in the present case) and is limited by the charge injection characteristics of the electrode–insulator interface. If the metal (electrode) has a higher Fermi level than the insulator, the electron flow from the metal into the insulator will result on contact. Such contact results in electron accumulation at the interface and subsequent transport of the accumulated charge by the electric field. The electric current measured in the external circuit will depend on the charge-transportation mechanism through the insulator. The difference between THF and dioxane is that THF is polar and dioxane is nonpolar. Since the PS chain by itself has a negligible dipole moment, it acquires a dipole moment by solvation of THF molecules. In the presence of an externally applied electric field E, there will be a force given by $(p\cdot\nabla)\Omega$ acting on the chain segment, where p is the segmental electric dipole of the solvated PS chain and Ω is the local field, related to the external field E in a complex manner. The total force is the sum of all segmental contribution. This force as also modified by the chain Brownian motion provides a mechanism to generate the polarization current as the external field is applied. It contributes the partial current measured at the external circuit, the rest being the polarization current of the THF. The interaction of the polarization current with the solvated PS modifies the PS chain dynamics. However, as the PS concentration is increased beyond the semidilute regime, solvated PS chains form a transient network, and the interaction of the collective dipole moments in the network with the polarization current does not result in a net movement of the PS chains. As a result, the PS segments are less affected by the current. Hence, the E-field has a diminishing effect on the diffusion of the PS chain in the solution as the concentration is increased beyond the semidilute and concentrated regimes. On the other hand, in the PS/dioxane system, the PS chain is solvated by molecules that have no dipole moment. As a result, there is no polarization current due to the solvated chains or solvent molecules, and no current flows through the solution. Consequently, the interaction of the solvated PS/dioxane chain with the external electric field only occurs through a higher order induced dipole effect. The induced dipole effect is probably not important at the field strength considered, and the effect of the E-field on this solution is only negligible.

Summary and Conclusion

In conclusion, we have provided a detailed QELS study of the effect of an externally applied electric field on the PS/THF solution over a wide range of the polymer concentration. The result confirms the fact that the applied E-field has an important effect on the relaxation rate of the autocorrelation function of the intensity fluctuation of the scattered light in the PS/THF solution with concentration varying from the dilute to semidilute regime. The relaxation rate is increased with the strength of the externally applied field. We have found the effect rapidly decreases as the solution concentration increases beyond the semidilute to concentrated regimes. We have shown that the observed result cannot be accounted for by the electrorheological effect, and the observed electric field induced enhancement of the relaxation rate in the PS/THF solution is closely related to the polarization current induced in the polymer solution. In the PS/dioxane solution, the polarization current is negligible, and there is no observed electric field induced enhancement in the mutual diffusion coefficient. By considering the mechanism associated with the polymer segmental dipole moment owing to solvation, we have thus provided a rational picture to account for the observed E-field induced effects in dynamic behavior of polymer solutions.

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