Macromolecules 1987, 20, 1066–1069

Effects of Coupling on Polymer Chain Dynamics Probed Dielectrically: Precursor to Entanglement

K. L. Ngai and R. W. Rendell*[†]

Naval Research Laboratory, Washington, D.C. 20375-5000. *Received October 8, 1986*

ABSTRACT: The coupling model of relaxation is shown to quantitatively explain the unexpected dielectric behavior observed by Adachi and Kotaka in unentangled high molecular weight poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) solutions. With increasing concentration such that the product ϕM approaches M_e, the molecular weight between entanglements, not only does the observed loss maximum frequency f_m shift to the low-frequency side but also the loss curve simultaneously broadens on both sides of f_m. Both these behaviors are expected from the coupling model. The loss curves are quantitatively reproduced at each concentration by the model. The value of the coupling parameter n for these unentangled chains is found to increase with concentration but remain below the upper bound of $n \cong 0.41$ previously shown to characterize fully entangled linear polymers. The coupling model provides consistent explanations for both the unexpected broadening of dielectric loss of unentangled polymer solutions discussed here and the characteristic properties of fully entangled polymer systems demonstrated earlier.

Introduction

A polar group in the repeat unit of some flexible polymer chains may have a dipole component parallel to the chain contour. Stockmayer[1] called such dipolar groups in a chain molecule type A. If this is the case for a certain polymer, it will exhibit a dielectric relaxation that is identical with that of the end-to-end displacement vector **r** provided there is no reversal of directional sense of the repeat units. Hence this dielectric relaxation is directly related to low-frequency viscoelastic relaxation arising from chain dynamics. It has been shown[1] that it is adequate to use the bead–spring model of Rouse[2] and Zimm[3] to describe the long-range diffusional modes of the chain. From Zimm's treatment for a solution of the polymer chain at weight concentration c in a nonpolar solvent the contribution to dielectric relaxation from the polymer is described by the equations

$$\Delta\epsilon^* - (\Delta\epsilon)_\infty = [4\pi N_A{}^2 c/(27RTM)](\epsilon_0 + 2)^2 \sum p_k{}^2/(1 + i\omega\tau_k) \quad (1)$$

$$p_k = (Nb/k\pi)\sum_j e_j(2/N)^{1/2} \cos (jk\pi/N) \quad (2)$$

In these equations, N_A is the Avogadro number, RT the thermal energy, M the polymer molecular weight, ϵ_0 the dielectric constant of the solvent, ω the circular frequency of the applied field, Nb^2 the mean-square end-to-end distance for the entire chain, and e_j ($j = 0, 1, ..., N$) the assigned electric charges on the beads. For an unreversed sequence of type A dipoles down the entire chain, p_k vanishes for all even k modes and is inversely proportional to k for the odd modes. The first mode $k = 1$, with the longest relaxation time τ_1, is the dominant contribution to the dielectric increment given by eq 1.

The dielectric relaxation times τ_k in dilute solutions are given by the expressions[1,3]

$$\tau_k = 2M\eta_s[\eta]/(0.586RT\lambda_k{}') \quad (3)$$

for the nondraining model and

$$\tau_k = 12M[\eta]\eta_s/\pi^2RTk^2 \quad (4)$$

for the free-draining model. In these relations η_s is the solvent viscosity, $[\eta]$ is the intrinsic viscosity, and the $\lambda_k{}'$ are eigenvalues that have been tabulated for low k. The eigenvalue for the first mode, $\lambda_1{}'$, has the value of 4.04. The value of τ_1 can be identified with $1/(2\pi f_m)$, where f_m is the frequency of the observed dielectric loss maximum which is due principally to the rotational diffusion ($k = 1$) mode. For samples with sufficiently narrow chain-length distributions, Equations 1 and 2 predict a dielectric dispersion with breadth close to that for a Debye relaxation $\sim\exp(-t/\tau)$, with a molecular relaxation time τ approximately the same as τ_1. For polymers in which the $k = 1$ mode dominates, the predicted relaxation time τ_1 is nearly the same for both models. Thus, eq 3 and 4 yield eq 5 and 6, respectively. The rather strong dependence of the relaxation time τ_1 on molecular weight M means that the effect of polydispersity, if present, must be taken into account. Distribution in chain lengths gives rise to a distribution in τ_1 and broadens the dielectric dispersion.

$$\tau_1 = 1.21M[\eta]\eta_s/RT \quad \text{(free draining)} \quad (5)$$

$$\tau_1 = 0.85M[\eta]\eta_s/RT \quad \text{(nondraining)} \quad (6)$$

Dielectric relaxation due to type A dipoles have been studied experimentally by Stockmayer and co-workers,[1] and by others[4] in low molecular weight, unentangled polymer systems. The relations 1–6 give a good account of the observed relaxation times. Stockmayer[1] has suggested as early as 1967 that with an appropriate choice of polymers it should be possible to observe dielectrically the effect of entanglements on τ_1 through the transition from unencumbered to strongly entangled chains. Recently, Adachi, Okazaki, and Kotaka[5] have extended considerably the work by following the longitudinal-dipole relaxation from dilute to concentrated solution, through the semidilute region and eventually into the entanglement regime. Indeed, they have observed the effects of entanglement in *cis*-polyisoprene. These measurements will not be discussed here. In addition, they have investigated the longitudinal-dipole relaxation of linear poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) in a good solvent, chlorobenzene, in the dilute,[4] the semidilute, and the concentrated regimes.[6] From the structure of PDCPO, they have determined that it qualifies as a type A system with dipole moment parallel to the end-to-end displacement. The proportionality of the dielectric relaxation strength to the mean-square end-to-end distance $\langle r^2\rangle$ as predicted by eq 1 and 2 has been verified in dilute solution. Solutions of a linear sample PDCPO-17 with molecular weight 16 600 and $M_w/M_n = 1.26$ in chlorobenzene (ClBz) interpolating between the dilute and the concentrated regions were also studied by dielectric measurements. For bulk PDCPO the molecular weight between entanglements M_e has been

---

[†] Sachs/Freeman Associate.

estimated[6] to be 9400. The characteristic molecular weight for entanglement M_c, taken as $2M_e$, is 18 800. The molecular weight of bulk PDCPO-17 is between M_c and M_e. By the conventional criterion, the molecules of PDCPO-17 are thus considered to be unentangled in the entire range of c studied. The dependence of the frequency of the loss maximum f_m on c of this sample should reflect that of unentangled, linear PDCPO chains.

Since the interest here will be on semidilute and concentrated solutions of PDCPO-17, the dilute solution expressions 5 and 6 for τ_1 have to be replaced by free draining model expressions of the first or terminal mode of Rouse

$$\tau_1 = \zeta_0 N^2 b^2 / (6\pi^2 k_B T) \qquad (7)$$

which is appropriate for unentangled condensed systems. In eq 7 ζ_0 is the friction factor per bead, N the number of beads in a chain, and b the average distance between beads. The parallel dipole relaxation is dominated by the first Rouse mode. If all chains have the same length, the dipole correlation function $\langle \mu(t)\cdot\mu(0) \rangle / \langle \mu^2 \rangle_{eq}$ will be well approximated by a single exponential

$$\langle \mu(t)\cdot\mu(0) \rangle / \langle \mu^2 \rangle_{eq} = 8\pi^{-2} \exp(-t/\tau_1) \qquad (8a)$$

Distribution in chain lengths will introduce a distribution $g(\tau_1)$ of τ_1 in accordance with the dependence of the latter on chain length or molecular weight. The corresponding dipole correlation function is given by

$$\langle \mu(t)\cdot\mu(0) \rangle / \langle \mu^2 \rangle_{eq} = 8\pi^{-2} \int d\tau_1 \, g(\tau_1) \exp(-t/\tau_1) \qquad (8b)$$

The τ_1 in eq 7 can be identified with $1/2\pi f_m$ for a monodisperse sample, where f_m is the frequency of the dielectric loss maximum. From eq 7, the dependence of τ_1 on c comes from those of ζ_0 and $\langle r^2 \rangle \equiv Nb^2$. It has been shown that $\langle r^2 \rangle$ has little dependence on c in the present systems.[4,6] Thus, the c dependence of τ_1 is entirely due to that of ζ_0. On increasing c of the PDCPO-17 solutions, one expects ζ_0 to increase. Hence, according to eq 7 f_m $(=1/2\pi\tau_1)$ should shift toward low frequencies, but the shape of the normalized dielectric loss ϵ''/c when plotted vs. the logarithm of the frequency f should remain unchanged. The half-width Δ of the loss curve should be invariant with c. This is *not* observed in the dielectric measurements of the PDCPO-17 solutions.[6] Adachi and Kotaka[6] found that the loss curve broadens on both sides of the loss maximum frequency as it shifts with increasing c, and this is shown in Figure 1. They cannot find from the literature a theory that can explain this behavior quantitatively but nevertheless suggest the possibility that this effect is due to a mechanism such as cooperative motions of the chains that has not been taken into account in the bead–spring model as $M\phi$ approaches M_e and M_c (ϕ is the polymer volume fraction).

In this work we show that the mechanism in the coupling model[7-9] which takes into account the cooperative motions of chains provides a quantitative explanation for the effects observed by Adachi and Kotaka in PDCPO-17 solutions. The general nature of its mechanism suggests the applicability of the coupling model to the present system of unentangled PDCPO-17 solutions at concentrations where cooperative motions of the chains (and hence coupling between chains) are important as suggested by Adachi and Kotaka. Previously the coupling model has provided an understanding of the molecular weight and temperature dependences of the zero-shear viscosity η and self-diffusion coefficient D in entangled linear polymer systems.[7-9] We refer the reader to these references for a description of the model and its physical basis. Here we briefly summarize its essential features and predictions.

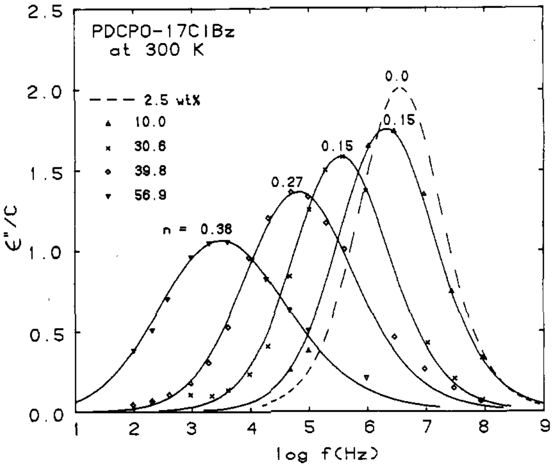

Figure 1. Data of Adachi and Kotaka for the frequency dependence of the dielectric loss ϵ'' divided by concentration c (in g cm^{-3}) for chlorobenzene solutions of unentangled PDCPO-17 at 300 K. The dashed and solid curves are from eq 15–17 based on the dominant $k = 1$ mode. The coupling parameter n_1 is found to increase with concentration but lies below the value $n_1 = 0.41$ corresponding to fully entangled chains.

Coupling Model of Polymer Chains

Consider a chain and its $k = 1$ Rouse mode. The relaxation rate is W_1 $(\equiv 1/\tau_1$, where τ_1 is given by eq 7), the Rouse relaxation rate. If the chain couples to other chains, then at some time t_c characteristic of the coupling interaction, effects of other chains on the relaxation of the chain will be felt. One effect is the slowdown of the Rouse relaxation rate W_1. The degree of slowdown depends on the nature of the coupling between chains. Several physical models[10] of calculating the slowdown of the primitive relaxation rate W_1 have all led to similar results. We find that for $t > t_c$ $(\equiv \omega_c^{-1})$ the rate is reduced by a factor that is time dependent and has the self-similar form of $(\omega_c t)^{-n_1}$ where n_1, a parameter lying between 0 and 1, is a measure of the degree of slowing down of W_1. The value of ω_c can be deduced from experimental data for several polymer systems, and it is typically in the range $\omega_c = 10^9$–10^{10} s^{-1}. In other words, the overall relaxation rate W of the $k = 1$ mode becomes time-dependent and has the specific form of

$$\begin{aligned} W(t) &= W_1 & \omega_c t &< 1 \\ &= W_1(\omega_c t)^{-n_1} & \omega_c t &> 1,\ 0 \le n_1 < 1 \qquad (9) \end{aligned}$$

The dipole correlation function

$$\langle \mu(t)\cdot\mu(0) \rangle / \langle \mu^2 \rangle_{eq} \equiv Q(t) \qquad (10)$$

will obey the rate equation

$$dQ(t)/dt = -W(t)Q(t) \qquad (11)$$

with $W(t)$ given by eq 9 if only the contribution from the dominant $k = 1$ mode is included. Solution of eq 11 yields three coupled predictions,[10] although our discussion involves only two of the three in this work. These two coupled predictions are the fractional exponential relaxation function

$$Q(t) = 8\pi^{-2} \exp[-(t/\tau_1^*)^{1-n_1}] \qquad \text{if } \omega_c\tau_1 \gg 1 \qquad (12)$$

and

$$\tau_1^* = [(1 - n)\omega_c^{\,n}\tau_1]^{1/(1-n_1)} \qquad (13)$$

Equation 12 has previously been used as an empirical description of dielectric data by Kohlrausch,[11] Williams and Watts,[12] and others. Equation 13 is unique to the coupling model and relates the effective τ_1^* in eq 12 to the primitive τ_1. They are called coupled because the same n_1 and τ_1^* appear in both equations.

For fully entangled chains in a monodisperse linear polymer system (i.e., $M > M_c$) we have previously demonstrated[7,8] how well eq 12 accounts for the shape of the terminal viscoelastic dispersion measured by stress relaxation or creep compliance for $n_1 \cong 0.41$. The coupling model predicts the time dependence and relaxation time in the presence of entanglements but does not calculate quantities such as the relaxation modulus G_N^0. With this same value of $n_1 \cong 0.41$, eq 13 predicts that the $\tau_1 \propto M^2$ dependence from the Rouse model in eq 7 is modified by entanglement effects to $\tau_1^* \propto M^{2/(1-n_1)} = M^{3.4}$ in agreement with experimental measurements of the terminal relaxation time and viscosity. In addition, the temperature dependence of the friction coefficient ζ_0 in eq 7 is predicted to be modified by eq 13, and these predictions also agree quantitatively with the data.[8] When the molecular weight M is decreased slightly below M_c, coupling between chains may still remain, although at a reduced level. The coupling parameter n_1 is reduced correspondingly. As M is decreased, the value of n_1 is expected to decrease monotonically for $M_e < M < M_c$ and then more rapidly toward zero for $M < M_e$. Of course, $n_1 = 0$ corresponds to the uncoupled systems of sufficiently short chains as described by the Rouse model.

The complex permittivity $\epsilon^*(\omega)$ as a function of frequency is given via eq 10–13 by

$$[\epsilon^*(\omega) - \epsilon_\infty']/[\epsilon_0' - \epsilon_\infty'] = 8\pi^{-2}\ \mathrm{FT}\left\{-\frac{\mathrm{d}}{\mathrm{d}t}\exp[-(t/\tau_1^*)^{1-n_1}]\right\} \quad (14)$$

for a monodisperse polymer system. In eq 14, ϵ_0' and ϵ_∞' are the limiting low- and high-frequency values of the real part of $\epsilon^*(\omega)$ and FT {...} denotes the one-sided Fourier transform $\int_0^\infty \mathrm{d}t\ e^{-i\omega t}\{...\}$.

For a polydisperse system with a distribution $g(\tau_1)$ in τ_1, the corresponding expression is

$$[\epsilon^*(\omega) - \epsilon_\infty']/[\epsilon_0' - \epsilon_\infty'] = 8\pi^{-2}\int \mathrm{d}\tau_1\ g(\tau_1)\ \mathrm{FT}\left\{-\frac{\mathrm{d}}{\mathrm{d}t}\exp[-(t/\tau_1^*)^{1-n_1}]\right\} \quad (15)$$

with

$$\tau_1^* = [(1-n_1)\omega_c^{\ n}\tau_1]^{1/(1-n_1)} \quad (16)$$

Equations 14 and 15 are valid for $\omega_c\tau_1 \gg 1$. In relation 16 an assumption is made that all chains within the distribution have the same coupling parameter n_1. This assumption is not expected to hold for a very broad distribution of chain lengths, in which case a distribution of n's is also possible.

Coupling Model Analysis of Data

The imaginary part of the Fourier transform in eq 14 has a peak with maximum loss at frequency f_m which is roughly equal to $1/(2\pi\tau_1^*)$. The peak broadens on both sides of f_m with increasing n. The additional integration in eq 15 for polydisperse samples further broadens the peak. Consider now the PDCPO-17 solutions in light of the coupling model. In dilute solutions the coupling of chains is negligible, i.e., $n_1 = 0$, and the departure from the Rouse–Zimm theory eq 1 and 2 is due only to polydispersity. The frequency dependence on the dielectric loss ϵ'' for a 2.5 wt % PDCPO-17 solution at 300 K is shown by the dashed curve in Figure 1, and it is found to be slightly broader than a Debye peak.[6] The distribution function $g(\tau_1)$ due to polydispersity can be determined directly from this curve by numerical analysis. After $g(\tau_1)$ has been determined from the PDCPO-17 dilute solution ϵ'' data, its functional form can be used in eq 15 at any concentration c. The dielectric loss peak for a 2.5 wt % solution at 300 K is quite symmetrical about its loss maximum frequency at about $10^{6.5}$ Hz. This feature suggests the choice of a Gaussian distribution

$$g(\tau_1)\ \mathrm{d}\tau_1 \equiv \frac{A}{\Gamma^{1/2}}e^{-\Gamma(\ln\tau_1 - \ln\tau_m)^2}\ \mathrm{d}\ln\tau_1 \quad (17)$$

where Γ^{-1} is the width of the distribution and τ_m the relaxation time at the peak of the distribution. It is reasonable to assume that chains are uncoupled in the 2.5 wt % solution, so that the coupling parameter n_1 is zero and τ_1^* equals τ_1 in eq 16. The ϵ'' data of the 2.5 wt % solution can be fit well by eq 15–17 for $n_1 = 0$ with the choices of $\Gamma = 0.45$ and $\tau_m = 1/2\pi f_m$.

With increasing concentration, the coupling between chains will become more important and the value of the coupling parameter n_1 should increase. As $M\phi$ increases toward M_c, the value of n_1 should increase toward $n \cong 0.41$ which characterizes the fully entangled linear monodisperse polymer systems. This is indeed what we observe when we apply eq 15–17 to the PDCPO-17 solution data of increasing weight percent. For convenience, the integration variable in eq 15 can be changed from τ_1 to τ_1^* by using eq 16. When this is done, the ω_c dependence in $[\ln\tau_1 - \ln\tau_m] = (1-n)[\ln\tau_1^* - \ln\tau_m^*]$ of eq 17 is seen to cancel out. The value of Γ is held fixed at $\Gamma = 0.45$ as determined from the dilute 2.5 wt % solution. The evaluation of eq 15 is then straightforward, and the value of n_1 that best fits the shape of the loss curve can be determined at each concentration. The position of the loss peak τ_m^* is shifted to the experimental value in each case. As shown in Figure 1, the calculated dielectric loss curves can reproduce the shapes of the peaks at the four other concentrations rather well. Note that n_1 starts from 0 at 2.5 wt %, increases to 0.15 in the range 10–30 wt %, to 0.27 at 39.8 wt %, and reaches the value of 0.38 at 56.9 wt %. For the 56.9 wt % solution, the $M\phi$ product is approximately equal to $M\phi \cong M_e = M_c/2$ and thus is still not fully entangled by the conventional criterion. The value of n_1 thus remains below the upper bound of $n_1 \cong 0.41$ previously shown to characterize the shape of the loss curves for fully entangled linear polymers and also predict the correct molecular weight and temperature dependences.[7-10] In other words the relevance of the coupling model for the fully entangled regime and the size of the coupling parameter determined there gives credence for the magnitudes of n_1 deduced by the coupling model also for the PDCPO-17 solutions that are not fully entangled.

Although the curves in Figure 1 were all calculated with only the dominant $k = 1$ mode, there is some contribution from the higher k modes on the high-frequency side of the loss peaks. We have found that including the $k = 3$ mode only decreases the n_1 values slightly and the consistency with the fully entangled regime remains. For instance, including the $k = 3$ mode would modify eq 8 to

$$\langle\mu(t)\cdot\mu(0)\rangle = 8\pi^{-2}\int \mathrm{d}\tau_1\ g(\tau_1)\{\exp(-t/\tau_1) + (1/9)\exp(-t/\tau_3)\} \quad (18)$$

where $\tau_3 = \tau_1/9$. The $k = 3$ mode then has about 10% of the weight of the $k = 1$ mode and has a loss peak about a decade higher in log f. Therefore about 10% of the $g(\tau_1)$ which we had attributed to polydispersity is actually due to the $k = 3$ mode. The polydispersity distribution $g(\tau_1)$ is then actually somewhat narrower than we had deduced. In the presence of coupling between chains, the $k = 1$ and $k = 3$ modes will each get a coupling parameter n_1 and n_3.

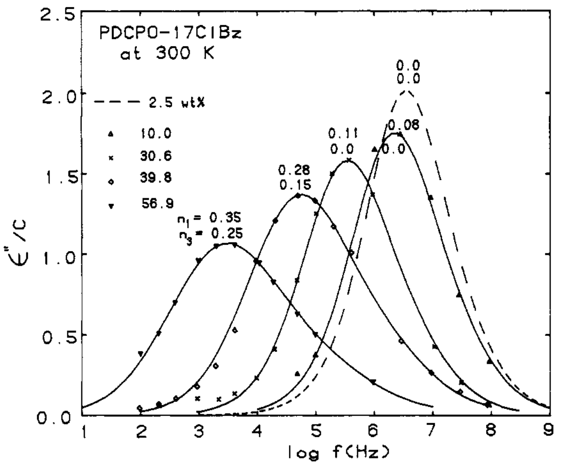

Figure 2. Data of Adachi and Kotaka (same as Figure 1). Dashed and solid curves are from the model based on both the $k = 1$ and $k = 3$ modes. The values of the coupling parameter n_1 for the $k = 1$ mode are decreased slightly compared to Figure 1.

The shorter wavelength $k = 3$ mode involves more localized motions so it will be less affected by coupling than the $k = 1$ mode. Therefore, in general, it is expected that $n_3 < n_1$. Including the $k = 3$ mode will modify eq 15 and 16 to $[\epsilon^*(\omega) - \epsilon_\infty']/[\epsilon_0' - \epsilon_\infty'] = \Delta\epsilon_1^*(\omega) + (1/9)\Delta\epsilon_3^*(\omega)$, whose $\Delta\epsilon_1^*(\omega)$ is given by eq 15. $\Delta\epsilon_3^*$ is similar to eq 15 but with n_3 and τ_3^* substituted for n_1 and τ_1^*, where $\tau_3^* = [(1 - n_3)\omega_c^{n_3}\tau_1/9]^{1/1-n_3}$. These expressions are valid for $\omega_c\tau_1 \gg 1$ and $\omega_c\tau_3 \gg 1$. Note that the relative spacing of τ_1^* and τ_3^* is completely determined by the model.

The shapes of the PDCPO-17 solution data can be examined with the $k = 3$ contribution now included. The results are shown in Figure 2. For the 2.5 wt % dilute solution where $n_1 = n_3 = 0$, the presence of the $k = 3$ mode increases the value of Γ in eq 17 from $\Gamma = 0.45$ to $\Gamma = 0.55$. For 10.0 and 30 wt %, the values of n_1 are now reduced from $n_1 = 0.15$ to $n_1 = 0.08$ and 0.11, respectively. The values of n_3 at 10.0 and 30 wt % are $n_3 = 0$. For the higher concentrations of 39.8 and 56.9 wt %, the values of n_3 are required to be nonzero. The ω_c does not cancel out when $n_3 \neq 0$ as it did in eq 15, and a value of ω_c must now be specified. We will use $\omega_c = 10^{9.2}$ s^{-1}, the value of ω_c deduced directly from experimental data of a different polymer, poly(phenylmethylsiloxane).[13] At 56.9 wt %, we find $n_1 = 0.35$ and $n_3 = 0.25$. The value of $n_1 = 0.35$ best fits the main loss peak when $\Gamma = 0.55$, and $n_3 = 0.25$ provides the best fit of the curve on the high-frequency side. We see that $n_3 < n_1$ as physically expected from the coupling model. The individual $k = 1$ and $k = 3$ contributions to the 56.9 wt % data are shown in Figure 3. A smaller value of n_3 would shift the $k = 3$ peak out to an unacceptably high frequency. Figure 2 represents a more refined analysis of the data than Figure 1, but the results are very similar. Including the $k = 3$ mode reduces the values of n_1 slightly, but the conclusions are unchanged.

The coupling model thus provides a physical mechanism to account for the broadening of the $\epsilon''(f)$ curves for unentangled chains with increasing concentration. The values of the coupling parameter all remain below the upper bound of $n_1 \lesssim 0.41$. As mentioned previously, the coupled relations 12 and 13 have been quantitatively tested for fully entangled monodisperse polymers. The value of $n_1 \cong 0.41$ obtained by fitting eq 12 to the terminal dispersion was previously shown to predict the correct molecular weight and temperature dependence of τ_1^* from eq 13.

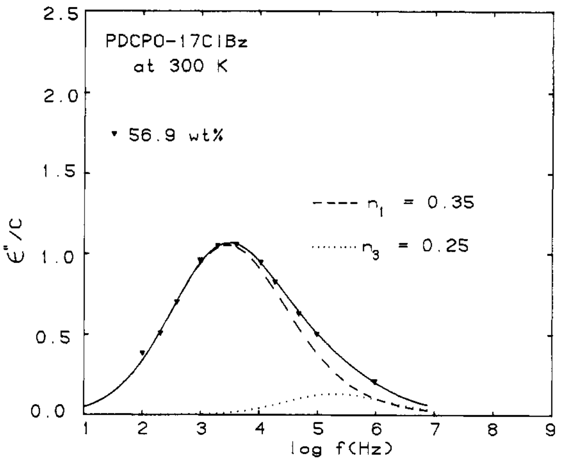

Figure 3. Separate contributions from the $k = 1$ and $k = 3$ modes at 56.9 wt % corresponding to Figure 2.

In principle, the coupling model can also be used to predict the concentration dependence of τ_1^*. In Figures 1 and 2, the positions of the loss peaks were adjusted to correspond to the data. However, we should be able to predict the relative shift in the loss peak with c from eq 13. The value of $n_1 = n_1(c)$ increases with c as was shown in Figure 1 and 2. This will predict a shift in τ_1^* to longer times with increasing c by eq 13. However, there will be an additional shift in τ_1^* due to the c dependence of τ_1. As mentioned previously, this dependence comes from the friction coefficient $\zeta_0 = \zeta_0(c)$. In principle, the $\zeta_0(c)$ dependence on c could be taken from any viable theory such as those based on free volume considerations. However, the $\zeta_0(c)$ dependence for PDCPO solutions is not presently available so that we are not able to test eq 13 for the $\tau_1^*(c)$ dependence on c.

Acknowledgment. This work was supported in part by ONR Contract N00014-85-R-RC24001.

Registry No. PDCPO (SRU), 26023-26-7; PDCPO (homopolymer), 25511-62-0.

References and Notes

(1) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539 and references therein.
(2) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(3) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(4) Adachi, K.; Kotaka, T. *Macromolecules* **1983**, *16*, 1936 and references therein.
(5) Adachi, K.; Okazaki, H.; Kotaka, T. *Macromolecules* **1985**, *18*, 1687.
(6) Adachi, K.; Kotaka, T. *Polym. J. (Tokyo)* **1986**, *18*, 315.
(7) Ngai, K. L.; Rendell, R. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 46.
(8) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2159; **1986**, *24*, 619 and references therein.
(9) McKenna, G. B.; Ngai, K. L.; Plazek, D. J. *Polymer* **1985**, *26*, 165.
(10) For a review see: Ngai, K. L.; Rendell, R. W.; Rajagopal, A. K.; Teitler, S. In Proceedings of Conference on Dynamic Aspects of Structural Change in Liquids and Glasses, New York, Dec. 1-3, 1985; *Ann. N.Y. Acad. Sci.* **1987**, 180.
(11) Kohlrausch, R. *Pogg. Ann. Phys.* **1847**, *12*, 393.
(12) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *66*, 80.
(13) Ngai, K. L.; Fytas, G. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1683.