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Dynamical Heterogeneity in a Miscible Polymer Blend

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ABSTRACT: Measurements of dynamic mechanical spectra in the glass transition region for miscible blends of 1,4-polyisoprene and poly(vinylethylene) are reported. In accordance with previous measurements of heat capacity and thermal expansivity, the transition zone is found to be extraordinarily broad when the blend has a high concentration of poly(vinylethylene). The application of the coupling model to the data suggests that this breadth is a manifestation of an inhomogeneous distribution of relaxation times and coupling parameters engendered by concentration fluctuations. Although not experimentally observable herein, a consequence of this dynamical heterogeneity is deviation from the principle of time–temperature superpositioning for miscible polymer mixtures in the glass transition region. The latter is consistent with solid-state ^{13}C NMR measurements reported previously.

Introduction

When the morphological heterogeneities in a polymer mixture are sufficiently small (ca. 100 Å),[1] they are unobserved by many experiments. Accordingly the demonstration of thermodynamic miscibility in ostensibly homogeneous blends usually requires more than the observation of a single glass transition. Conversely, since the chain units in a miscible blend experience the same average free volume, such mixtures invariably exhibit only one glass transition.

Mixtures of 1,4-polyisoprene (PIP) and poly(vinylethylene) (PVE) are thermodynamically miscible, as has been established by adhesion,[2,3] small-angle neutron scattering,[4,5] and proton NMR[6] experiments. Despite an absence of specific interactions, miscibility extends to very high molecular weights due to the respective similarities in the polarizability and liquid structure of the components.[4,5,7] In accord with this miscibility, PIP/PVE mixtures exhibit a single, composition-dependent glass transition. However, in blends with a high concentration of PVE (provided the microstructure of the polybutadiene is greater than 90% 1,2), the glass transition, as measured by a marked increase of either the heat capacity or thermal expansion coefficient, transpires over an anomalously broad temperature range.[4] Similarly, in these compositions the change in dynamic mechanical behavior associated with the glass transition extends over many decades of frequency.[8] It is emphasized that a broad glass transition is exhibited notwithstanding the thermodynamic miscibility of the mixture. This breadth is not associated with an incipient phase-separated morphology.

^{13}C NMR experiments have demonstrated that the molecular motions of the components in PVE/PIP blends have different temperature dependencies, with these differences magnified in blends with a high concentration of PVE that has a high 1,2-microstructure.[6] The vinyl carbons of polyisoprene develop high-frequency, isotropic motions at temperatures below that necessary for the onset of liquidlike motion of the vinyl carbons of the PVE. The differences in transition temperature observed by ^{13}C NMR for the blend components correlate with the composition dependence of the transition breadth seen in heat capacity, thermal expansivity, and dynamic mechanical measurements.

The morphological homogeneity of PVE/PIP blends ensures that the components experience the same average free volume. To the extent this quantity controls the temperature or frequency of the glass to liquid transition, a single glass transition is then a necessary consequence of miscibility. Nevertheless in the vicinity of the transition zone the molecular motions and their dependence on temperature are evidently different. The purpose of the present study was to investigate the origin of the broad glass transition and its occurrence in blends comprised predominately of PVE.

Experimental Section

The poly(vinylethylene) was 97% 1,2-polybutadiene obtained from the Firestone Tire and Rubber Co. The *cis*-1,4-polyisoprene was a high-purity grade of *Hevea brasiliensis* (SMR-L from the Ore and Chemical Corp.). Despite their high molecular weights, these polymers form a miscible mixture.[2-5] Blends are referred to herein as PVE-0 through PVE-100, where the number denotes the percentage by weight of the poly(vinylethylene).

Dynamic mechanical testing was conducted in tension with an Imass Corp. Dynastat Mark II instrument. The measurements were made over a frequency range of from 0.01 to 100 s^{-1} at various temperatures. Master curves were obtained by empirically time–temperature superpositioning the data to a reference temperature of −40 °C. For compositions in which the glass transition was sharp, measurements over 30 or 40 deg sufficed to define the transition region of the viscoelastic spectrum. For the PVE-75 sample, however, data were obtained from +35 °C down to −60 °C without completely encompassing the rubber to glass transition.

Results

In Figure 1 is displayed the frequency dependence of the storage modulus for five compositions. Beyond the expected shifting of the curves to lower frequency as the concentration of the lower T_g component is reduced, it is seen that the shape of the transition zone also varies with concentration. In particular, the transition of PVE-75 to the glassy state transpires much less abruptly than for the other compositions. This characteristic is more apparent in the loss moduli spectra of Figure 2. In comparison to most pure polymers, PVE has a relatively broad transition, and, as expected for miscible mixtures, the transitions in the PVE-25 and PVE-50 are somewhat broadened. The most striking feature in Figure 2, however, is the remarkably broad peak in the loss modulus for PVE-75, the extent of which encompasses both transitions of the pure polymers. In light of the irrefutable evidence for miscibility in these blends,[2-6] it is emphasized that this cannot be attributed to phase separation.

The dynamic mechanical behavior seen in Figures 1 and 2 is consistent with calorimetry and thermal expansivity results, wherein PIP blends containing a high concentra-

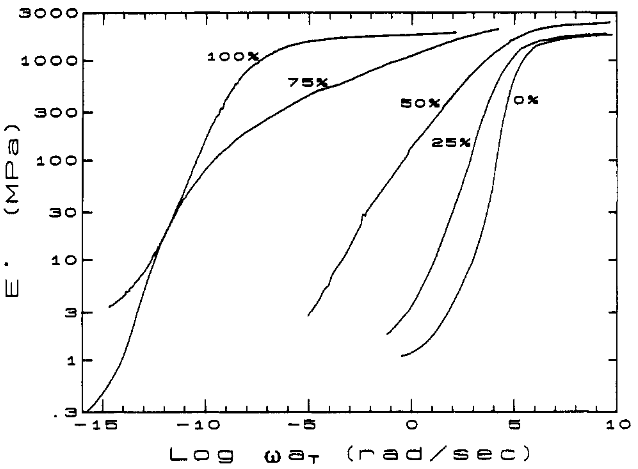

Figure 1. Frequency dependence of the storage modulus for PIP blended with the indicated amount of PVE. These results are master curves obtained by time-temperature superpositioning to a reference temperature of -40 °C.

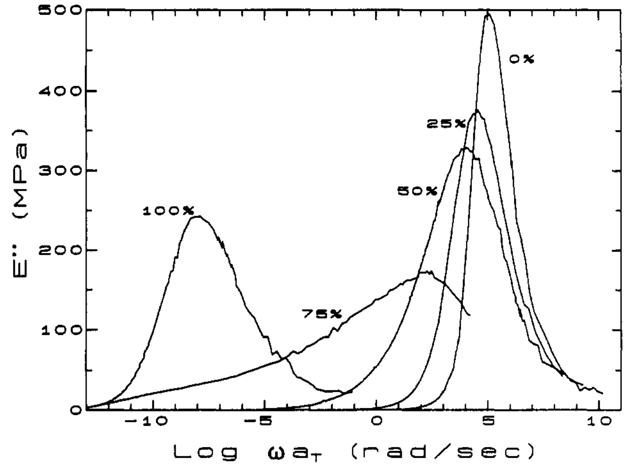

Figure 2. Loss modulus spectra at a reference temperature of -40 °C for blends of PIP with the indicated concentration of PVE. The 75% PVE composition peak was extraordinarily broad, whereby the peak was not completely defined despite data having been obtained over a 95-deg range of temperatures.

tion of PVE exhibit atypically broad glass transitions.[4,5,8] It is also congruous with observations of differing temperature dependencies for the molecular motions of the mixed polymers.[6] The issues in need of clarification are the origin of the anomalous transition breadth and the reason for its occurrence only in compositions high in PVE content.

The application of a model to the results in Figure 2 may offer insight into the phenomenon. Conformance of the experimental results to theory would provide direct information, at least commensurate with the model's physical basis. On the other hand, any inability to account for the experimental results would suggest that assumptions embodied by the model are undermined in the blends, a happenstance that can also be instructive.

In recognition of the many modes of motions available to a long-chain molecule, the assumption of a distribution of relaxation times is a common starting point in the description of the viscoleastic behavior of polymers.[9,10] However appropriate this approach may be for rubbery and terminal zone behavior, with respect to the glass transition region, the origin of such a distribution is not obvious. Glassy motion involves segments smaller than the smallest Rouse mode. It might be presumed that a distribution of relaxations could arise as a consequence of the free volume being distributed among variously sized vacancies.[11] In fact, however, the rearranging segment volume appropriate for the glass transition is substantially larger than the largest vacancies.[12-15] Consequently only the average free volume, not its distribution, governs the glass transition.[9,16] Beyond physical arguments for rejecting relaxation time distributions in the modeling of glass transition data, it has also been shown that volume recovery experiments carried out in the vicinity of T_g are inconsistent with any assumed distribution of relaxation times.[17,18]

An alternative approach toward description of segmental relaxation and glass transition behavior is the coupling model, which has been successfully utilized for a variety of neat polymeric materials.[19,20] The essence of the model is that conformational relaxation of a single chain in bulk polymers is unobserved because this primitive relaxation is retarded by interchain interactions and correlations among the elements comprising the system. In polymeric materials these environmental interactions arise primarily from the uncrossability and the excluded volume of the polymer segments. This slowing down of the primitive motion results in a time-dependent relaxation rate. At the times appropriate for mechanical measurements (longer than some characteristic time ω_c^{-1}), the relaxation modulus is given by[20]

$$E(t) = E(0)\exp(-[t/\tau^*]^{1-n}) \tag{1}$$

where the quantity n captures the strength of the coupling between the primitive relaxation and the environment of other chains. Originally the model was derived from the assumption that the primitive relaxation was a first-order reaction. More realistic models for chain dynamics entail conformational changes that propagate along the chain by a damped diffusional process.[21] It can be shown, nevertheless, that the form of eq 1 is recovered for $t \gg \omega_c^{-1}$.[22] The effective relaxation time τ^* is related to the primitive relaxation time τ_0 according to[20]

$$\tau^* = ([1-n]\omega_c^{\,n}\tau_0)^{1/(1-n)} \tag{2}$$

For relaxation from the glassy state, the values of both τ_0 and n (and hence τ^*) depend on chemical structure. Given the complexity of undiluted polymers, these model parameters cannot be calculated directly but must be deduced from experiment. The coupling model has been applied to experimental measurements on various polymers in the glass transition zone, including polycarbonate,[12] polystyrene,[23-25] poly(vinyl acetate),[18,25-27] and others.[27-30]

From the relation between the loss and relaxation moduli[9]

$$E(\omega) = \omega\int_0^\infty E(t)\cos(\omega t)\,dt \tag{3}$$

eq 1 can be fitted to the data of Figure 2 by variation of τ^* and n. There are no a priori restrictions on the values of these parameters, other than n being a positive number not exceeding unity. For neat polymers ω_c was found to equal 10^{10} s^{-1}.[20] The dependence of the relaxation rate on chemical structure, however, means that the couplings of the respective components are not necessarily equal in a blend. Consequently for the mixtures we take

$$E(t) = E_{\mathrm{PIP}}(0)\exp[-(t/\tau^*_{\mathrm{PIP}})^{1-n_{\mathrm{PIP}}}] + E_{\mathrm{PVE}}(0)\exp[-(t/\tau^*_{\mathrm{PVE}})^{1-n_{\mathrm{PVE}}}] \tag{4}$$

where the prefactors, $E(0)$, scale with concentration. The different time scale of their local motions means that the

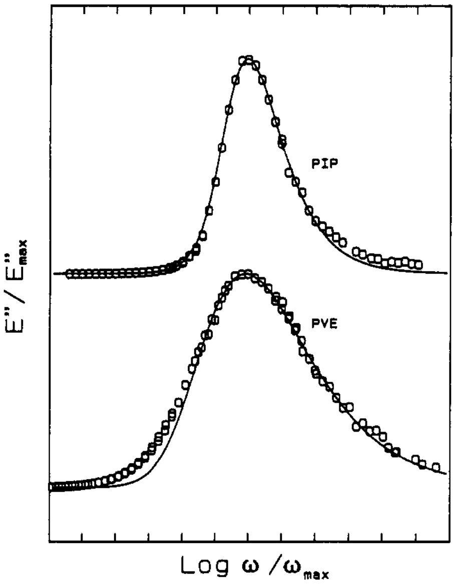

Figure 3. Loss modulus peak associated with the glass transition measured for the pure polymers (O), along with the best-fit curve calculated by eq 1.

relaxation times need not be equal, notwithstanding the equivalence of the average free volume for the blend components. In fact the differing strength of their respective couplings confers a divergence in the τ^*, as seen from eq 2.

Thus the $E(0)$, n, and τ_0 are all freely adjustable in attempting to fit eq 4 to the measured $E''(\omega)$ via eqs 2 and 3. Loss modulus spectra were numerically calculated by using different algorithms for low[31] and high[32] values of the coupling parameter. The results of this fitting for neat PVE and PIP are displayed in Figure 3. It is observed that the behavior of the pure polymers in the glass transition region conforms to the coupling model. The obtained values of n for PIP, 0.50, and for PVE, 0.74, are in reasonable agreement with a recent determination from photon correlation spectroscopy applied to these polymers near T_g.[33] The success of the coupling model in describing these data on pure polymers and in providing a consistent determination of the relevant relaxation parameters is unsurprising in light of many prior results.[12,18,23-30]

Application of the model to the mixtures, however, proves less satisfactory (Figure 4). Although a reasonable fit can be obtained for the PVE-25, the frequency dependence of the loss modulus for blends with higher PVE concentrations is at odds with the form of eq 4 for any combination of parameter values. The justification underlying the use of eq 4 is that associated with each component is a primitive relaxation, the latter being slowed down by coupling to the surroundings. This yields two stretched exponential decays, each contributing to the observed relaxation. The central assumption is that in the mixtures all segments of a given component relax equivalently. Apropos the arguments concerning the inappropriateness of a distribution of relaxation times in describing glass transition phenomena, this assumption is valid for neat polymers. Mixtures evidently present a different situation.

The local composition within a mixture is known to fluctuate about its average value. Indeed the scattering contrast arising from such concentration fluctuations underlies the characterization of blend thermodynamics by scattering experiments.[34] Concentration fluctuations have previously been identified as a mechanism for broadening of relaxation spectra in the glass transition region.[35,36] Chain segments of a given component will experience differing local environments and hence their relaxation will not be equivalently perturbed by neighboring segments. Consequently, in mixtures each component will not be associated with a single n and τ^*. For both components these will be distributed about values appropriate for the average composition. Obviously eq 4 is then inadequate to describe the experimental $E''(\omega)$ spectra for blends.

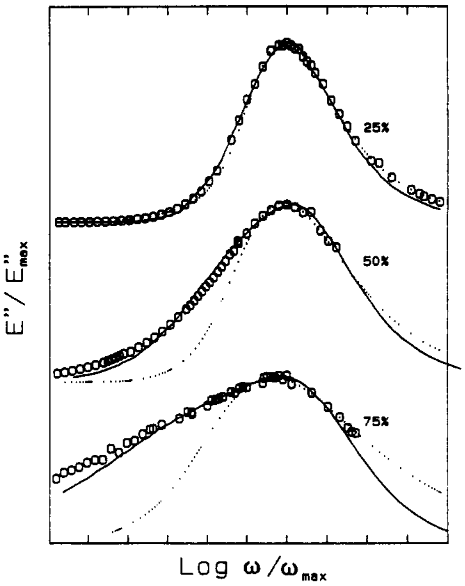

Figure 4. Peak in the loss modulus for three blend compositions as measured (O), calculated by using eq 4, which assumes uniformity in the relaxation of the respective components (•), and via eqs 5 and 6 by assuming an inhomogeneous distribution of relaxation times for both components (—). It can be seen that postulating a distribution in both n and τ^* for each component is necessary to obtain agreement between theory and experiment for PVE-50 and PVE-75.

Conceptually, the origin of the broad glass transition becomes apparent. As seen in the figures and reflected in the magnitude of its coupling parameter, pure PVE has a broader transition (more strongly coupled) than PIP, and indeed than most other polymers.[12,18,23-30] The addition of PIP to form a mixture introduces a variety of local environments by engendering concentration fluctuations. The broad relaxation spectrum of PVE thus becomes displaced over a range of central frequencies. The superpositioning of these relatively broad peaks results in a very broad loss modulus spectrum. At lower PVE concentrations, although composition fluctuations still transpire, the significantly narrower PIP peak now dominates the spectrum. The superpositioning of a fairly narrow peak about a range of frequencies effects only a modestly broadened resultant spectrum.

The coupling model can be extended to incorporate these ideas; however, the absence of detailed information concerning blend heterogeneities and their influence on relaxation presents a formidable obstacle. While some information can be extracted from scattering experiments, quantitative data regarding the concentration fluctuations is lacking, as is knowledge concerning the dependence of either n or τ_0 on local composition. Earlier workers assumed a Gaussian distribution of logarithmic relaxation times, with no influence of concentration on the shape of the relaxation function.[36] Herein the broadening of the blend spectra is ascribed to the effect of local composition on the degree of coupling of the segmental motions. The particular relaxation time distribution exhibited by the

Table I
Relaxation Parameters for Polyisoprene/Poly(vinylethylene) Mixtures[a]

blend	component	n	τ_{0i}, s	$E(0)$	a
PVE-0	PIP	0.50	4.9×10^{-8}	1820	
PVE-25	PVE	0.64	3.4×10^{-8}	1100	4.3×10^{4}
PVE-25	PIP	0.55	4.4×10^{-8}	1200	4.3×10^{4}
PVE-50	PVE	0.66	6.9×10^{-8}	1560	2.0×10^{2}
PVE-50	PIP	0.60	2.8×10^{-8}	830	1.7×10^{3}
PVE-75	PVE	0.73	2.7×10^{-7}	1670	1.1×10^{2}
PVE-75	PIP	0.63	1.1×10^{-7}	713	3.0×10^{2}
PVE-100	PVE	0.74	6.3×10^{-6}	1650	

[a] From eq 1 for the pure polymers and eqs 5 and 6 for the blends.

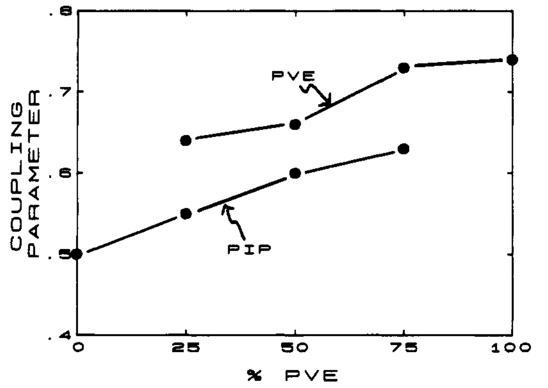

Figure 5. Value of the coupling parameter determined for the two polymers as a function of the mixture composition.

mixture is a consequence only of this change in coupling. Calculations were carried out by assuming concentration fluctuations produce a normally distributed range of values of the coupling parameters of each component. Thus, the relaxation modulus for each component is taken to be

$$E_i(t) = E_i(0)\int_0^1 \exp(-a_i(n-n_i)^2)\exp\left(-\frac{t}{\tau^*_i(n)}\right)^{1-n} \mathrm{d}n \tag{5}$$

where

$$\tau^*_i(n) = ([1-n]\omega_c^{\ n}\tau_{0i})^{1/(1-n)} \tag{6}$$

in which n_i represents the mean value of the coupling parameter for component i and a_i is a measure of the concentration fluctuations. The effective relaxation time of a segment is determined from eq 2, where ω_c is taken to equal 10^{10} s^{-1}. Equations 5 and 6 in conjunction with eq 3 allow a calculation of $E''(\omega)$ for the mixtures, and these results are displayed in Figure 4.

A summary of the best-fit values for all parameters is given in Table I. The particular values used to generate the curves in Figure 4 should not be taken too seriously, given the degree of arbitrariness embodied in, and necessary to apply, eq 5. The principal point of the exercise is demonstration of the concept that concentration fluctuations will broaden the glass transition, with the effect amplified when the major component is inherently broad.

The dependence of the respective coupling parameters on composition is presented in Figure 5. A PVE-rich environment is markedly effective in coupling to the primitive relaxation. This not only gives rise to a broadened glass transition in pure PVE but also effects stronger coupling of the relaxations of both PIP and PVE in their mixtures. Figure 5 illustrates that the value of the coupling parameter is governed both by the nature of the relaxing element and by its environment.

A consequence of eq 5 is that the mixtures should no longer be time–temperature superpositionable, as can also be inferred from the different temperature dependencies for the respective molecular motions.[6] The shift factor is related to the segmental friction coefficient, ζ, according to[25]

$$a_T = [\zeta_T/\zeta_{T_0}]^{1/(1-n)} \tag{7}$$

Obviously, given the differences in n, the shift factors for the two components will be different and hence the time–temperature superposition principle should not apply to the behavior of miscible blends in the glass transition region. This breakdown of time–temperature superpositioning will be accentuated in mixtures comprised of polymers with very different coupling parameters. Even when this situation prevails, as with the present blends, the failure to superposition is not obvious in data obtained over only a few decades of frequency (viz., Figures 1 and 2). Withal blend master curves for the glass transition region can only approximate the actual frequency dependence at the given reference temperature.

A breakdown in time–temperature superpositioning has previously been observed for miscible blends of poly(ethylene oxide) and poly(methacrylate) in the terminal region of the viscoelastic spectrum.[37] Consistent with tracer diffusion measurements in polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) blends,[38] this failure suggests a difference in the friction factor for the components of the blends. It has been demonstrated, however, that such a result can arise when the extent of chain entanglement (as reflected in the ratio of the molecular weight to the entanglement molecular weight) differs significantly for the components.[39] In PIP/PVE blends in which the average numbers of entanglements per chain were within a factor of 2 of one another, the rubbery and terminal regions of the viscoelastic spectrum have been shown to behave in accordance with the time–temperature superposition principle.[40]

It is seen in Figure 2 that the frequencies of the maxima in the loss modulus are weighted toward that of the pure polyisoprene. For PVE/PIP blends wherein the PVE was comprised of only 85% 1,2-polybutadiene units, mixtures in which the anomalous broadening of the transition zone is absent, it has been reported that the composition dependence of the glass transition temperature follows thermodynamic formulations based on random arrangement of the chain units.[2] Such a result is consistent with the absence of specific interactions in regular mixtures. The present study, however, demonstrates that the particular frequency (or temperature) at which the loss modulus has its maximum magnitude is unrelated to thermodynamic considerations. The congregation of the viscoelastic spectra of the blends toward the high-frequency PVE-0 peak, apparent in FIgure 2, is a manifestation of the contribution of the sharp PIP transition to the blend behavior. The precise location of the $E''(\omega)$ maximum is largely a consequence of the more abrupt transition behavior of PIP relative to PVE; hence, the application of thermodynamically based mixing rules[41,42] to the temperature dependence of loss modulus maxima is problematical.

Summary

The anomalous breadth of the glass transition zone in blends of PIP with a high concentration of PVE reflects the disparities in the dynamics of the components. Thermodynamic miscibility presupposes morphological homogeneity down to the segmental level and a uniform average free volume throughout the mixture. Neither of these, however, necessarily occasions a convergence in the relaxation spectrum and its temperature dependence for the components of a miscible blend; hence, inhomogeneous line broadening can eventuate. When one component of the mixture has an inherently broad glass transition, moreover, the exceptional breadths in the transition zone observed for PIP/PVE mixtures can result.

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References and Notes

(1) Roland, C. M. In *Handbook of Elastomers—New Developments and Technology*; Bhowmick, A. K., Stephens, H. L., Eds.; Marcel Dekker: New York, 1988; Chapter 6.
(2) Roland, C. M. *Macromolecules* **1987**, *20*, 2557.
(3) Roland, C. M. *Rubber Chem. Technol.* **1988**, *61*, 866.
(4) Trask, C. A.; Roland, C. M. *Macromolecules* **1989**, *22*, 256.
(5) Roland, C. M.; Trask, C. A. *Rubber Chem. Technol.* **1989**, *62*, 896.
(6) Miller, J. B.; McGrath, K. J.; Roland, C. M.; Trask, C. A.; Garroway, A. N. *Macromolecules* **1990**, *23*, 4543.
(7) Trask, C. A.; Roland, C. M. *Polym. Commun.* **1988**, *29*, 322.
(8) Roland, C. M.; Lee, G. F. *Rubber Chem. Technol.* **1990**, *63*, 554.
(9) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(10) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, 1986.
(11) Bueche, F. *Physical Properties of Polymers*; Interscience: New York, 1962.
(12) Ngai, K. L.; Rendell, R. W.; Yee, A. F. *Macromolecules* **1988**, *21*, 3396.
(13) Malhotra, B. D.; Pethrick, R. A. *Eur. Polym. J.* **1983**, 457; *Polym. Commun.* **1983**, *24*, 165.
(14) Curro, J. J.; Roe, R.-J. *Polymer* **1984**, *25*, 1424.
(15) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241.
(16) Fischer, E. W.; Hellman, G. P.; Spiess, H. W.; Horth, F. J.; Ecarius, U.; Wehrle, M. *Macromol. Chem. Phys. Suppl.* **1985**, *12*, 189.
(17) Ng, D.; Aklonis, J. J. In *Relaxation in Complex Systems*; Ngai, K. L.; Wright, G. B., Eds.; Government Printing Office: Washington, DC, 1985; p 53.
(18) Rendell, R. W.; Ngai, K. L.; Fong, G. R.; Aklonis, J. J. *Macromolecules* **1987**, *20*, 1070.
(19) Ngai, K. L. *Commun. Solid State Phys.* **1979**, *9*, 127; **1980**, *9*, 141.
(20) Ngai, K. L.; Rendell, R. W.; Rajagopal, A. K.; Teitler, S. *Ann. N.Y. Acad. Sci.* **1986**, *484*, 150.
(21) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.
(22) Ngai, K. L.; Rendell, R. W., unpublished results.
(23) Plazek, D. J.; Ngai, K. L.; Rendell, R. W. *Polym. Eng. Sci.* **1984**, *24*, 1111.
(24) Ngai, K. L.; Plazek, D. J.; Deo, S. S. *Macromolecules* **1987**, *20*, 3047.
(25) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 619.
(26) Rendell, R. W.; Ngai, K. L. *J. Chem. Phys.* **1987**, *87*, 2359.
(27) Ngai, K. L.; Mashimo, S.; Fytas, G. *Macromolecules* **1988**, *21*, 3030.
(28) Ngai, K. L. In *Non-Debye Relaxation in Condensed Matter*; Ramakrishnan, T. V., Lakshmi, M. R., Eds.; World Scientific: Singapore, 1988; p 94.
(29) Ngai, K. L. *Polym. Prepr.* **1981**, *22* (2), 289.
(30) Fytas, G.; Ngai, K. L. *Macromolecules* **1988**, *21*, 804.
(31) White, C. T.; Ngai, K. L.; Rendell, R. W., unpublished results. See also ref 17.
(32) Williams, G.; Watts, D. C.; Dev, S. B.; North, A. M. *Trans. Faraday Soc.* **1977**, *67*, 1323.
(33) Kanetakis, J.; Fytas, G. *International Discussion Meeting on Relaxation in Complex Systems*; Heraklion, Greece, June 18–29, 1990.
(34) de Gennes, P.-G. *Scaling Concepts in Polymers Physics*; Cornell: Ithaca, NY, 1979.
(35) Shears, M. S.; Williams, G. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 608.
(36) Wetton, R. E.; MacKnight, W. J.; Fried, J. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 158.
(37) Colby, R. J. *Polymer* **1989**, *30*, 1275.
(38) Composto, R. J.; Kramer, E. J.; White, D. M. *Macromolecules* **1988**, *21*, 2580.
(39) Ngai, K. L.; Plazek, D. J. *Macromolecules*, in press.
(40) Roland, C. M. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 839.
(41) Couchman, P. R. *Polym. Eng. Sci.* **1987**, *27*, 618.
(42) Aubin, M.; Prud'homme, R. E. *Polym. Eng. Sci.* **1988**, *28*, 1355.