Test of Expected Correlation of Polymer Segmental Chain Dynamics with Temperature-Dependent Time-Scale Shifts in Concentrated Solutions

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ABSTRACT: The effects of diluent on intermolecular interactions in polymers are discussed. The coupling model expects that addition of diluent to polymer will decrease *both* the coupling parameter n and the steepness of the local segmental relaxation time shift factor $a(T)$ in a plot of log $a(T)$ against normalized temperature $(T - T_g)/T_g$, where T_g is the glass transition temperature defined as the temperature at which the relaxation time reaches 100 s. Dielectric data of Adachi and Ishida in the system poly(vinyl chloride)-tetrahydrofuran are used to verify these expectations.

1. Introduction

Recently, Plazek and Ngai[1] found in amorphous polymers a strong correlation between the dispersion of the local segmental motion (as measured by $n \equiv 1 - \beta$ where β is the stretch exponent of the Kohlrausch-Williams-Watts (KWW) relaxation function to be defined below) and the dependence of the time-scale shift factor $a(T)$ on normalized temperature difference $(T - T_g)/T_g$, where T_g is the glass temperature (defined as the temperature at which the relaxation time reaches 100 s). This correlation is expected from the predictions and interpretations of the coupling model.[2-4] Relative to a conformational transition in a single chain, intermolecular coupling of these same transitions in neighboring chains slows down the individual chain (primitive or uncoupled) relaxation rate W_0 to the self-similar time dependence $W_0(\omega_c t)^{-n}$, $0 \leq n < 1$, of the cooperative local segmental relaxation of chains in a densely packed polymer system. Intrachain cooperativity of conformational transition has been incorporated in the sense that W_0 is identified with one of the two relaxation rates of the Hall-Helfand function.[4] For $\omega_c t > 1$, in the time regime of usual relaxation measurements, the rate reduction becomes more severe for increasing values of the coupling parameter n, reflecting stronger intermolecular interactions. The consequences are (i) a stretched exponential (KWW) function

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

for the normalized relaxation function and (ii) the second relation

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

where $\tau_0 = W_0{}^{-1}$. Consider two polymers and their primitive relaxation times τ_0 and τ'_0 having similar temperature dependences

$$\tau_0 = \tau_\infty \exp\{D_0 T_0/(T - T_0)\} \tag{3}$$

$$\tau'_0 = \tau_\infty \exp\{D_0 T'_0/(T - T'_0)\} \tag{4}$$

with the same τ_∞ and D_0 but different T_0 and T'_0. The form given by eqs 3 and 4 is derivable from both the Adam-Gibbs cooperative rearranging regions[5] and the free-volume model[6]. If the two polymers have different molecular structures and intermolecular interactions, their coupling parameters n and n' will differ. The polymer having the larger n will have a stronger normalized temperature dependence for τ^* and a larger steepness index S defined as the slope d(log $a(T)$)/d(T_g/T) evaluated at $T = T_g$. Here $a(T)$ is the shift factor, $\tau^*(T)/\tau^*(T_g)$, as defined in ref 1. These results follow immediately after substituting the expressions 3 and 4 for τ_0 and τ'_0 into eq 2.[2]

The origin of the correlation of the steepness of τ^* with the size of n according to the coupling model is the dependence of the intermolecular coupling strength on the chemical nature of the monomer as well as its molecular structure. Thus poly(vinyl chloride) (PVC), having a highly polar monomer unit, is expected to have a larger intermolecular interaction strength than that of other vinyl polymers such as polyisobutylene (PIB), whose monomers interact via the weaker van der Waals forces. Similar arguments based on chemical structures can be given when comparing any other pairs of polymers considered in ref 1.

Instead of comparing the intermolecular strengths of different polymers, we can start with one polymer such as PVC and modify the intermolecular interactions by adding a diluent. In the usual situations where the glass temperature of the diluent is lower than that of the polymer,[7-9] the time scale of structural relaxation of the diluent though possibly modified by the dissolved polymer is expected to be short compared with that of the local segmental relaxation polymer in concentrated solution. Further addition of diluent will continue to reduce the intermolecular interaction strength, the degree of rate slowing down, and hence the coupling parameter n according to the coupling model. For PVC, a diluent such as tetrahydrofuran (THF) will screen the polar interactions between the polymer molecules and thereby reduce their intermolecular interaction strength. On the basis of this picture, a couple of predictions can be made: (1) the coupling parameter n will decrease or the stretch exponent β will increase monotonically and (2) the steepness of log $a(T)$ or log τ^* in the plot versus normalized temperature $(T - T_g)/T_g$ (as defined in ref 1) will decrease with the addition of THF. These two predictions, being explicit and simultaneous, are worth checking out by experimental data. It turns out dielectric measurements of the effect of the diluent THF on the local segmental motion of PVC had been made by Adachi and Ishida.[10] Their data are discussed and analyzed to compare with the predictions made here.

2. Temperature Dependence of the Segmental Relaxation Time

Adachi and Ishida (AI)[10] made extensive low-frequency, 0.10-10^5 Hz, dielectric relaxation measurements of con-

Table I

PVC, wt %	T_g, K	n from $2\epsilon''(\max)/\Delta\epsilon$	n from fit to $\epsilon''(f)$	S^d	polymer, n	S
38	166.40	*a*	0.43	55.3	PIB, 0.45[c]	46[c]
51	194.96	0.52	0.51	78.10	PI, 0.50[c]	62[c]
84	274.54	0.65	*a*	117.7	PP, 0.65[c]	137[c]
100	348.96	0.80	0.76[b]	129.0	PVC, 0.76[c]	190.5[c]

[a] Data not available. [b] From mechanical relaxation data of Cama. [c] From Plazek and Ngai, ref 1. [d] $-T_g[\mathrm{d}\log a(T)/\mathrm{d}T]_{T_g}$.

centrated solutions of PVC in THF. Several relaxation processes were observed and the molecular motions involved identified. In this work, we are interested only in the primary or α relaxation, which has been assigned by AI to segmental motions of PVC. Strong support for this assignment came from comparing the glass transition temperature T_g from differential thermal analysis for a heating rate of 2 K/min, with the dielectric glass transition temperature T_g' defined as the temperature at which the dielectric relaxation time of the α relaxation reaches 100 s. They found that T_g agrees well with T_g' for all concentrations of PVC studied. From now on we do not distinguish T_g' from T_g and write both as T_g. Study of the concentration dependence of the high-frequency dielectric constant ϵ_∞ in the temperature region where α relaxation was observed had led them to conclude that the α process is due to the segmental motion of PVC alone and not to cooperative motion of polymer and solvent.

The frequency dependences of the dielectric constants ϵ' were measured at fixed temperatures. The temperature dependence of f_m, the frequency at the loss maximum, was well fitted by the Vogel–Fulcher–Tammann–Hesse (VFTH) equation

$$\log f_m = A - B/(T - T_0) \tag{5}$$

The parameters A, B, and T_0 were tabulated for PVC concentrations of 38, 51, 59, 84, 89, and 100% by weight. From the temperature dependence of f_m, given by eq 5, the glass transition temperature defined by $f_m(T_g) = 10^{-2}/2\pi$ Hz can be calculated. The values of T_g so determined for several concentrations are listed in Table I. With these T_g values, the dielectric relaxation shift factors $a(T)$ defined by

$$a(T) = f_m(T_g)/f_m(T) \tag{6}$$

are plotted in a logarithmic manner against the normalized temperature difference $(T - T_g)/T_g$ in Figure 1. We find that the steepness of the variation of $\log a(T)$ with T_g/T decreases with addition of diluent. We shall return to compare the steepness of the concentrated PVC solutions with those of other undiluted polymers after a discussion of the dependence of the coupling parameter n on polymer concentration.

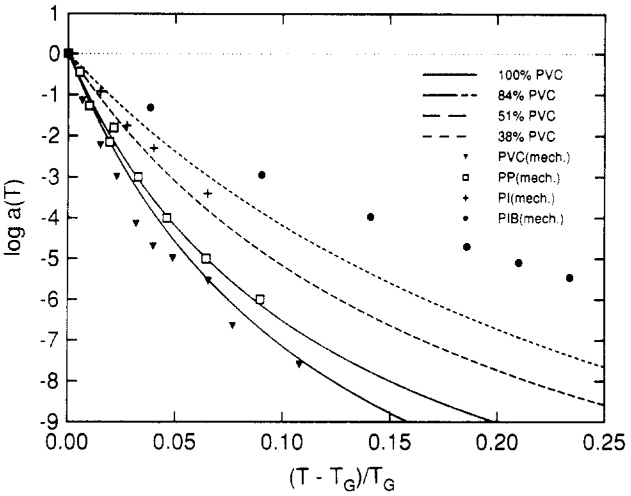

Figure 1. Plots of $\log a(T)$ of the local segmental relaxation versus the normalized temperature difference $(T - T_g)/T_g$ for four concentrated PVC–THF solutions. Also included in this plot are similar data from shear viscoelastic (mechanical) measurements of the local segmental relaxation in four undiluted polymers. For an explanation of the choice of these other polymers and the source see the text and Table I.

3. Concentration Dependence of the Coupling Parameter

Adachi and Ishida (AI) measured the frequency dependences of the dielectric constant ϵ'' of the local segmental relaxation. Their data for several concentrations were given in tables in ref 10. The low-frequency side of the loss peak has an excess contribution presumably from conductivity relaxation. The presence of the low-frequency conductivity relaxation in dielectric response hampers the normal procedure of determining the coupling parameter n by fitting the usually skew-symmetric shape of the loss peak by the Fourier transform of the KWW function (1).[2,11] Perhaps for this reason AI have resorted to an analysis of the values of $2\epsilon''(\max)/\Delta\epsilon$ for the α relaxation to determine its dispersion. For each solution, the value of $2\epsilon''(\max)/\Delta\epsilon$ was evaluated near the temperature at which the α dielectric loss peaks at 1 kHz. Here $\epsilon''(\max)$ denotes the maximum value of the dielectric loss and $\Delta\epsilon \equiv \epsilon_0 - \epsilon_\infty$ is the relaxation strength determined from a Cole–Cole plot. As is well-known, the ratio $2\epsilon''(\max)/\Delta\epsilon$ is unity if the relaxation is a Debye process with $\exp[-(t/\tau)]$ as the correlation function, i.e., dispersionless. When there is dispersion the ratio falls below unity, and it decreases monotonically with increasing dispersion. It can be seen from Table II of AI that the ratio decreases, and hence the dispersion increases, with increasing PVC concentration. There is a large volume of relaxation data including those from dielectric spectroscopy[2,11,12] that show the local segmental relaxations of amorphous polymers are well described by the KWW relaxation function. In particular it is valid for PVC.[13] Hence we can deduce the ratio $2\epsilon''(\max)/\Delta\epsilon$ for the KWW functions $\phi(t)$, eq 1, at various values of the coupling parameter from the Fourier transforms

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left[-\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}\right] \exp[-(i\omega t)]\,\mathrm{d}t \tag{7}$$

The values of the ratio for 10 values of n in the range $0 \le n \le 1.0$ are determined from our previous[2] calculations of $\epsilon^*(\omega)$ and plotted in Figure 2. From this plot, by interpolation, we determine the coupling parameters for the solutions except 38%. The dielectric loss peak of the latter has a significant contribution from conductivity relaxation as evident from the plots of ϵ' and ϵ'' versus temperature or frequency. In this case a more reliable determination of n is given by fitting the frequency dependence of the dielectric loss peak, weighing heavily on data points on the high-frequency side of the peak. The values of the coupling parameter determined by both methods whenever possible are listed in Table I. The results obtained are consistent with the concentration dependence of the "width of the distribution of relaxation times" given in Figure 13 of ref 10 deduced by AI from an analysis based on a model of a distribution of activation energies.

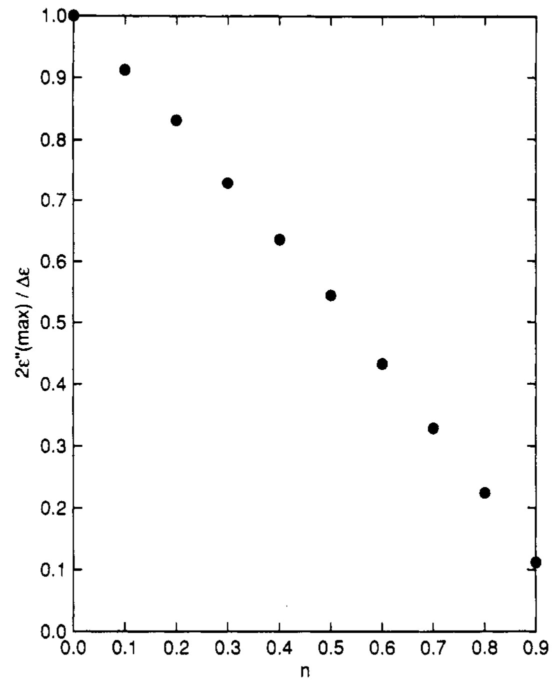

Figure 2. Plot of the ratio $2\epsilon''(\max)/\Delta\epsilon$ calculated from the KWW relaxation function $\exp[-(t/\tau^*)^{1-n}]$ against the coupling parameter n.

By inspection of Table I, it is clear that the coupling parameter decreases monotonically from the bulk PVC value around 0.75 with the addition of the diluent THF, as predicted by the coupling model.

4. Discussion and Conclusions

Extending the work of Plazek and Ngai[1] to concentrated solutions we make two predictions (see Introduction) on the trends of the temperature dependence of the shift factor $a(T)$ and the coupling parameter n with diluent concentration. The results of the last two sections by and large have confirmed these two predictions. An immediate consequence of these confirmations is that the correlation between the steepness of $a(T)$ in a normalized temperature plot with the coupling parameter n found by Plazek et al.[1] continues to hold for polymer solutions (see Figure 1) at least for PVC in THF. We have calculated the steepness index S, defined by $S = -T_g[\mathrm{d} \log a(T)/\mathrm{d}T]_{T_g}$, for several solutions. Their values (Table I) correlate well with the coupling parameters. Among many undiluted polymers studied, PVC has the largest coupling parameter.[1] This can be rationalized by the strong intermolecular interactions in PVC because of the polar nature of the interactions. As diluent is added, the strength of the intermolecular interactions is reduced by solvent screening. The reduction of the coupling parameter as well as the steepness index S are consequences of this reduction. It would be interesting to compare the shift factor of a PVC–THF solution with that of a different undiluted polymer that has approximately the same coupling parameter as that of the PVC–THF solution. For example, 84% PVC–THF solution has $n = 0.65$, which is almost the same as the coupling parameter for undiluted atatic polypropylene (PP).[1] Similarly, 51% PVC–THF solution has $n = 0.51$, which is comparable to that of undiluted polyisoprene (PI) or natural rubber,[1] and 38% PVC–THF has $n = 0.43$, which is comparable to that of undiluted polyisobutylene (PIB).[1] The shift factors of these three polymers have been obtained from shear viscoelastic measurement in ref 1. They are taken over and replotted in Figure 1. The close proximity in location of the shift factor of a particular PVC–THF solution when compared with that of the corresponding undiluted polymer with about the same n is noteworthy. These results strengthen our belief that intermolecular interaction and cooperativity determine the coupling parameter, and hence the KWW exponent $\beta = 1 - n$, as well as the signature of the shift factor in the Laughlin-Uhlmann-Angell plot[14-16] of $\log a(T)$ versus T_g/T or versus $(T - T_g)/T_g$.[1] The work presented here offers a new look into local segmental relaxation of concentrated polymer solutions. The correlations obtained will be of interest for any theory or model of glass transition in diluted as well as undiluted amorphous polymers. In the future, it would be of interest to relate this correlation for local segmental relaxation for concentrated solutions to the characteristics of prominent secondary relaxations such as the phenylene ring motions in polycarbonate when the polymer is plasticized by diluents.[17]

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