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Detailed Correspondences between Dielectric and Mechanical Relaxations in Poly(vinylethylene)

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ABSTRACT: Dielectric and dynamic mechanical measurements were carried out on poly(vinylethylene) in the vicinity of its glass transition temperature. By using four different spectrometers, data were obtained over a broad range of frequencies and temperatures. The shape of the segmental relaxation function, though weakly temperature dependent, was the same for the two experimental probes when compared at the same temperature. Similarly, the shift factors, describing the temperature dependence of the segmental relaxation time, were equivalent as measured dielectrically or mechanically. Such equivalence is consistent with a correlation between time and temperature dependencies of the segmental relaxation; moreover, it demonstrates that the correlation is maintained even when different dynamical variables (e.g., dipole moment versus modulus) are used to probe the local segmental motion. In contrast to the shape of the relaxation function and the time–temperature shift factors, the correlation times measured by the two spectroscopies bear no relationship to one another.

Introduction

The local segmental motion (LSM) of bulk amorphous polymers usually can be probed by more than one kind of spectroscopy.[1] The conventional, as well as the traditional, method of studying the viscoelastic properties of polymers is by mechanical spectroscopy.[2] Such measurements can be carried out for the modulus or the compliance of various deformations (e.g., shear, bulk, tension, etc.). Other relaxation and retardation spectroscopies have also been employed, including dynamic light scattering[3] and ultrasonic attenuation,[4] which are closely related to conventional mechanical spectroscopy. A less related technique is dielectric spectroscopy, which can be used to probe LSM if the monomer unit of the polymer has a dipole moment perpendicular to the chain axis.[5] Even though the LMS relaxation characteristics of many amorphous polymers, including the relaxation and retardation times, their temperature dependencies, and the degree of nonexponentiality of the relaxation or retardation process, have been determined by various spectroscopies, comparisons between the results have seldom been unequivocal.[1]

An obvious cause for this situation is that the different measurements were rarely made on the same sample. Potential differences, however subtle, in molecular weight, tacticity, chemical structure, etc., render any comparison uncertain. In only a very few cases have different measurements been carried out on the same sample. One such study was on poly(methylphenylsiloxane) (PMPS), in which spectroscopic data obtained by dynamic light scattering and dielectric relaxation data were compared and found to be in good agreement.[6] Another case is poly(vinyl methyl ether) (PVME), which has been studied by mechanical, dielectric, nuclear magnetic resonance, and even quasielastic neutron scattering spectroscopies.[7] Similarly to PMPS, these experimental investigations yielded good agreement with regard to the relaxation time and the degree of nonexponentiality of the LSM of PVME as probed by the different spectroscopies. Williams and coworkers[8,9] reported combined studies of Kerr effect relaxation and dielectric relaxation in poly(propylene glycol) and poly(methylphenylsiloxane) and comparisons between the results obtained by these two kinds of spectroscopies.

On the other hand, contrary results have been obtained from other amorphous polymers. For example, in polystyrene, the dynamics of the local segmental motion probed by photon correlation spectroscopy (which measures the longitudinal compliance) and by dielectric relaxation (which measures the electric compliance) were found to be very different.[10,11] In these cases,[10–12] however, measurements by different spectroscopies were not made on identical samples. Although there is no compelling reason to doubt the observed differences in relaxation characteristics in these polymers, the possibility exists that the discrepancies, or at least a part of them, are caused by the use of different samples.

A second reason that one cannot draw definite conclusions from most of the available dielectric and mechanical relaxation data is the lack of overlap of the measurement frequencies for these two techniques. The usual frequency range accessed in dielectric measurements is $10 < f < 10^6$ Hz, while most mechanical measurements operate at frequencies below 10^2 Hz. Either the dielectric measurements must be performed at lower frequencies or the mechanical measurements extended to higher frequencies before valid comparisons between the results can be made.

In view of the scarcity of dielectric and mechanical relaxation data suitable for unambiguous comparisons, we have avoided the two problems mentioned above in carrying out extensive measurements on poly(vinylethylene) (PVE). The same sample was used for both measurements, and the frequency window of the dielectric study was extended to lower frequencies to overlap that of mechanical relaxation. These results are reported here and discussed in conjunction with published data on other polymers.

Experimental Section

The PVE was 96% 1,2-polybutadiene obtained from the Firestone Tire and Rubber Co. It had weight- and number-average molecular weights equal to 153 000 and 134 000 respec-

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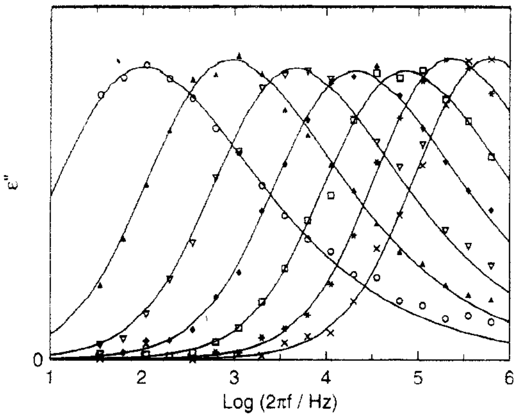

Figure 1. Dielectric loss measured in the frequency domain at seven temperatures, 280, 284, 288, 292, 296, 301, and 305 K, along with the best fits (solid curves) from eqs 1 and 2 for each temperature. The ordinate scale is in arbitrary units.

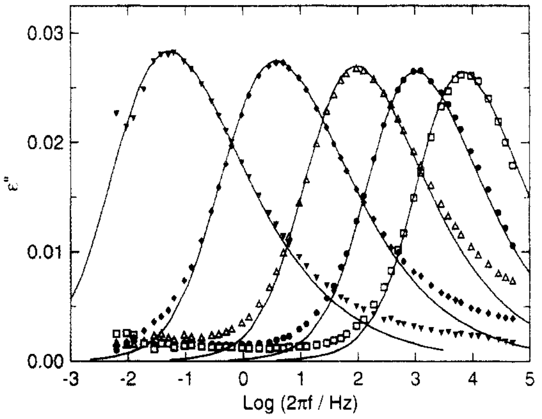

Figure 2. Dielectric loss spectra measured in the time domain at five temperatures, 268, 273, 278, 283, and 288 K, along with the best fits (solid curves) from eqs 1 and 2 for each temperature.

tively. Dynamic mechanical data were obtained with a Bohlin VOR rheometer using a parallel-plate geometry. A sample radius of 6.8 mm was used, with gaps in the range of 1–2 mm. The dynamic shear modulus was measured from 10 Hz down to as low as 1×10^{-5} Hz. In addition, mechanical measurements were also carried out in tension using an Imass Corp. Dynastat Mark II instrument.

Frequency domain dielectric spectroscopy measurements in the range from 5 to 10^5 Hz were performed using a lock-in amplifier (EG&G PAR 5208). A sample 0.2 mm thick and 12 mm in diameter was placed between the aluminum plates of a guarded capacitor; the plates were maintained at a fixed distance. A 10-pF air capacitor was used as a reference in order to minimize errors in the dielectric loss measurements. The sample cell was first evacuated and then filled with helium. A more detailed description of the experimental arrangement and the data analysis can be found elsewhere.[13] Dielectric measurements at lower frequencies were carried out by Mr. James Driscoll, using an IMASS, Inc., time domain dielectric spectrometer based on the transient current method.[14] The data were numerically Laplace transformed into the frequency domain; the obtained range of frequencies was 10^{-4}–10^4 Hz. For both dielectric techniques, the stability of the sample temperature was better than ±0.1 K.

Results

The experimental results for the frequency dependence of the dielectric loss at various temperatures for PVE are plotted semilogarithmically in Figures 1 and 2. The data shown in Figure 1 were taken with the frequency domain spectrometer, while the lower frequency data of Figure 2 are the transform of the time domain measurements. The observed dielectric dispersion corresponds to the local segmental motion (LSM) associated with the glass transition. The loss curves are fitted by the imaginary part of the complex permittivity, $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$. The latter can be determined from the Fourier transform relation:

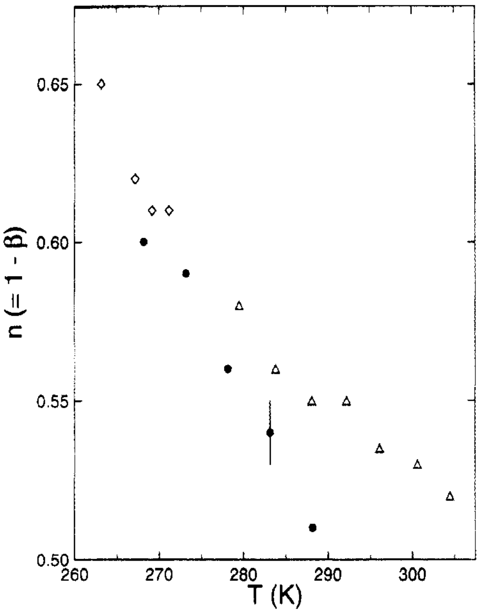

Figure 3. Temperature dependence of the stretch exponent measured dielectrically in the frequency domain (△) and in the time domain (●) and mechanically (◇).

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = 1 - i\omega \int_0^\infty \phi_d(t)\, e^{-i\omega t}\, dt \qquad (1)$$

where $\phi_d(t)$ is the dipole moment correlation function. Best fits of the data are accomplished by the three-parameter Havriliak–Negami[15] function. However, we prefer to use the two-parameter Kohlrausch–Williams–Watts function,[16,17]

$$\phi_d(t) = \exp[-(t/\tau_d^*)^{\beta_d}] \qquad (2)$$

which adequately fits the data and is more readily amenable to physical interpretetation by many theoretical models, including the coupling model of relaxation.[18] It has recently been shown that for several cases the frequency relaxation function obtained by means of eqs 1 and 2 is equivalent to the Havriliak–Negami description.[19] However, the determination of n obtained by fitting the frequency dependence of the dielectric loss to the Havriliak–Negami form, then transforming this analytical representation of the data into the time domain, emphasizes the high- and low-frequency tails of the dispersion to a greater extent than fitting directly in the frequency domain to the transform of eq 2. For this reason the latter method sometimes yields slightly smaller values for the coupling parameter.[20]

From the fits of the imaginary part of the complex permittivity calculated from eqs 1 and 2 to isothermal data, we obtain the KWW stretch exponent, β_d, and the dielectric relaxation time, τ_d^*, at different temperatures. These results are plotted as a function of temperature in Figures 3 and 4. The two sets of dielectric relaxation data, taken with two different spectrometers, agree quite well. It can be seen in Figure 3 that the stretch exponent, β, decreases appreciably with falling temperature. This is similar to the results for PVAc obtained by Mashimo and co-workers.[21,22] This strong temperature dependence of the nonexponentiality parameter is to be contrasted with the nearly temperature independence of β seen in other amorphous polymers, including poly(propylene glycol),[8,23]

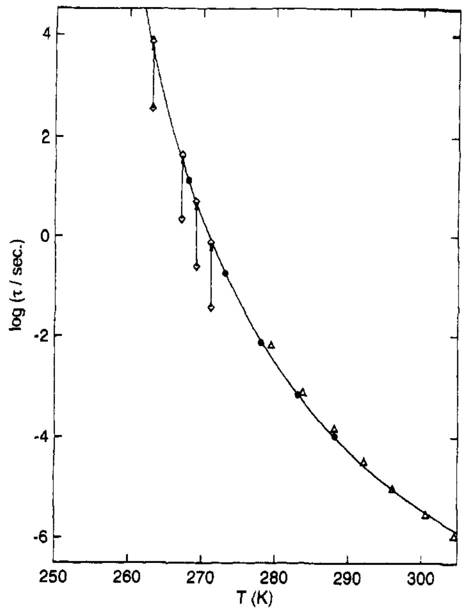

Figure 4. Temperature dependence of the segmental relaxation times measured dielectrically (△, ●) and mechanically (◇). The solid curve represents the best Vogel–Fulcher fit of eq 3 to the dielectric data. The vertical arrows indicate the shifts of the original mechanical relaxation time data by a factor of $10^{1.3}$.

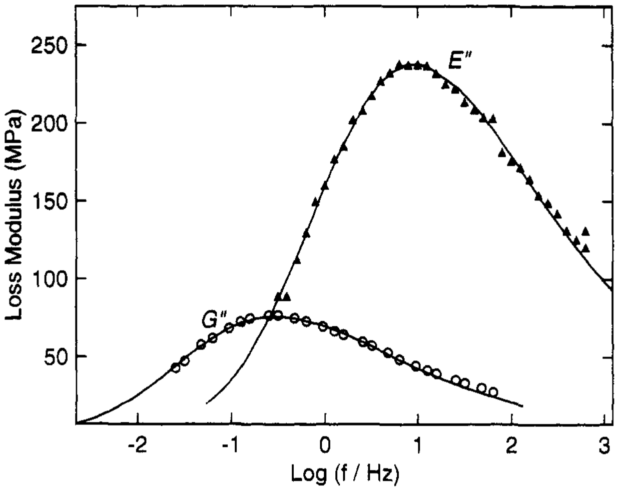

Figure 5. Dynamic mechanical loss modulus measured in shear (G'') at −6 °C and in tension (E'') at −3 °C, along with the respective best fits of eqs 4 and 5. The purpose of this figure is to show the stretch exponent is the same for G'' and E''.

polyisoprene,[24] and PVME.[7,25] This aspect of the dielectric data of PVE will be addressed elsewhere. The temperature dependence of the dielectric relaxation time can be fitted to the Vogel–Fulcher equation,[2]

$$\tau_d^* = 4.58 \times 10^{-12} \exp[823.2/(T - 239.4)] \qquad (3)$$

The dynamic mechanical spectra of PVE in the LSM region were obtained at various temperatures for the same sample of PVE used for the dielectric investigation. The loss modulus data are plotted linearly against the logarithm of frequency in Figure 5. The mechanical loss peaks have the characteristic asymmetry seen in the dielectric loss peaks and can be well fitted to the loss modulus,

$$E''(\omega) = \omega \int_0^\infty \phi_m(t) \cos(\omega t)\, dt \qquad (4)$$

calculated using the KWW correlation function

$$\phi_m(t) = \exp[-(t/\tau_m^*)^{\beta_m}] \qquad (5)$$

The mechanical stretch exponent, β_m, and relaxation time, τ_m^*, so determined are plotted together with the corresponding dielectric results in Figures 3 and 4. It can be seen that the stretch exponents for dielectric and mechanical relaxations are equal within experimental errors, and both exhibit a similar variation with temperature. The dielectric relaxation times are significantly longer than the mechanical relaxation times at any given temperature, but interestingly their shift factors, defined by

$$a_{T_d} = \tau_d^*(T)/\tau_d^*(T_0) \qquad (6)$$

and

$$a_{T_m} = \tau_m^*(T)/\tau_m^*(T_0) \qquad (7)$$

where T_0 is a reference temperature, are the same. This fact is illustrated in Figure 4. When all mechanical relaxation times are vertically shifted upward by a constant factor of $10^{1.3}$, they fall on the Vogel–Fulcher curve, eq 3, which is the least-squares best fit of the dielectric relaxation time versus temperature data.

Discussion

When the results of previous and present comparisons of dielectric and mechanical relaxations for several amorphous polymers are considered, the situation is confusing; no obvious pattern is evident. The important quantities to compare are the stretch exponents, β_d and β_m, together with their possible temperature dependencies, the correlation times, τ_d and τ_m, and their shift factors, a_d and a_m.

First we summarize the diverse results found previously: (i) In PVME there is perfect agreement for all quantities obtained from different spectroscopies including dielectric and mechanical.[7] (ii) In PMPS there is good agreement between dielectric and dynamic light scattering (DLS) for all quantities,[6] but the correlation time determined by DLS is slightly longer (but within a decade) than the mechanical retardation time obtained from the recoverable shear compliance, $J_r(t)$.[26] The stretch exponents are nearly the same, with that of J_r slightly smaller. The time window of the J_r measurements does not overlap that of DLS and hence a comparison of the shift factors cannot be made. (iii) In poly(methyl acrylate) (PMA), the DLS is faster by a factor of 4 than the dielectric time and by a factor of 35 than the shear mechanical relaxation time obtained from the frequency of the G'' maximum as $1/2\pi f_{max}$. The stretch exponent and shift factors are the same for DLS, dielectric, and mechanical relaxations.[18] Similar results are found in poly(ethyl acrylate) (PEA) which is closely related in chemical structure to PMA.[18] (iv) In polystyrene (PS) the DLS time is a factor of 10 longer than the dielectric and mechanical times.[10,11] The shift factors are nearly the same. (v) In atactic polypropylene (PP)[27] the stretch exponent and shift factor are the same for DLS and J_r. (vi) In poly(vinyl acetate) (PVAc) the stretch exponent of DLS is significantly smaller than that of dielectric relaxation.[18] The DLS shift factor has a stronger temperature dependence than the dielectric shift factor. (vii) In poly(propylene glycol) (PPG) the DLS stretch exponent is smaller than the dielectric stretch exponent.[18] The DLS shift factor has a much stronger temperature dependence than the dielectric shift factor.

Excluding cases vi and vii from the discussion for the moment, we find our current results for PVE to be the same as previous results of other amorphous polymers (cases i–v), wherein the dielectric correlation times and the various mechanical correlation times at the same temperature bear no fixed relationship to each other. This is perhaps unsurprising, since these are different probes of the local segmental motion and hence involve different dynamical variables and their correlation functions.[28,29] An interesting point remains however that the stretch exponent and the shift factor are the same for all these various probes of the local segmental motion. This observation suggests a correlation between the shift factor and the stretch exponent. In other words, when different dynamical variables (e.g., dipole moment, longitudinal modulus and compliance, shear modulus and compliance, etc.) are used to probe the local segmental motion, as long as the stretch exponents are the same, the shift factor will be the same (although the relaxation times per se may differ). These empirical facts are consistent with the coupling model of relaxation, in which the stretch exponent determines the temperature dependence of the relaxation or retardation time τ^*.[18,29]

Cases vi and vii are actually consistent with this correlation as well. For these two polymer, the stretch exponent varies significantly from one probe to another, and the corresponding temperature dependence of the shift factor changes accordingly. As has been shown previously,[18] the correlation between the stretch exponent and the shift factor on varying the probe can be explained by the coupling model on a quantitative basis.

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