PHYSICAL REVIEW B VOLUME 52, NUMBER 8 15 AUGUST 1995-II

Dielectric susceptibility measurements of the primary and secondary relaxation in polybutadiene

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(Received 10 April 1995)

We present data on the dielectric relaxation in the random copolymer polybutadiene. There are two distinct peaks in the imaginary part of the dielectric susceptibility, one of which is attributable to an α relaxation and the other to a Johari-Goldstein β relaxation. The bifurcation of these two relaxations explains the previously reported decoupling of microscopic and macroscopic time scales in polybutadiene. We show that the spectral shape of the Johari-Goldstein relaxation is consistent with a log-normal response function.

Dynamical measurements of supercooled liquids demonstrate that for a wide range of substances, the relaxation time grows with decreasing temperature faster than a thermally activated process. This rapid growth has been considered symptomatic of a divergence at a finite temperature T_0. Despite considerable effort over the past several decades, the microscopic origin of the dramatic increase in the time scales remains unknown.

An entropy argument by Kauzmann[1] suggests that a phase transition, the liquid-glass transition, is responsible for the rapidly increasing relaxation times with decreasing temperature. The entropy, S, of a supercooled liquid can be calculated by standard thermodynamics as $S(T)=S(T_f)+\int_{T_f}^{T} C_p(T)/T\,dT$, where T is the temperature, T_f is the freezing temperature, and C_p is the specific heat of the liquid at constant pressure. Kauzmann showed that the entropy of the liquid, if extrapolated smoothly from higher temperature, can fall below that of the crystal at the Kauzmann temperature T_K. If the entropy continues to decrease at the same rate, the entropy will become negative at a nonzero temperature, in violation of Nernst's theorem. The conjecture that a phase transition occurs at T_0 is motivated in part by the expected change in the specific heat needed to avoid this violation of thermodynamics and by the commonly observed[2] equality, to within experimental accuracy, of T_0 and T_K.

One might expect, as in critical phenomena, universal behavior as the glass transition temperature is approached. An important task therefore, is the identification of material independent phenomena in supercooled liquids near T_0. Dynamic susceptibility probes are useful for implementing this search. All supercooled liquids exhibit a primary (or α) relaxation, which is the manifestation of structural relaxation. The average relaxation times for this relation as measured by different susceptibility probes are to a large extent independent of the probe.[3] A Johari-Goldstein (or β) relaxation,[4] is also observed in many, though not all, glass formers. This relaxation can be detected only with some probes, which vary depending on the material. At high temperatures, the two relaxation processes are not well separated from each other and appear to form a single relaxation. However, as the temperature is lowered, the frequency of the peak, ν_p, of the α relaxation becomes well separated from that due to the β process, so that a clear identification of the two distinct relaxations is possible. The β relaxation is characterized by the Arrhenius temperature dependence of its peak frequency, $\nu_p=\nu_0\exp(-E/k_BT)$, whereas ν_p for the α relaxation appears to diverge at T_0.

In this paper, we report the results of dielectric measurements on the random copolymer polybutadiene. We will show, as was first suggested by Rössler,[5] that the decoupling of the microscopic and macroscopic relaxation times, reported from neutron scattering on this material, arises from tracking the β relaxation, instead of the α relaxation, during the bifurcation of the two processes. We also will show that the β relaxation is well fit by a log-normal function, consistent with the picture of β relaxation as activated hopping over a Gaussian distribution of energy barriers.

We have studied the dielectric susceptibility, $\epsilon(\nu)=\epsilon'+\iota\epsilon''$, of *cis-trans*-vinyl polybutadiene, by measuring the impedance of a capacitor filled with the sample at fixed temperatures in the range 119–219 K, using frequency sweeps from 0.1 Hz to 1 MHz. The capacitor consisted of nine plates separated by 150-μm-thick Teflon spacers and had a dry capacitance of 1 nF. The temperature gradient across the capacitor was less than 0.1 K. The impedance was measured above 10 KHz, with an HP 4275A LCR meter, using a 1-V driving voltage and below 10 KHz with a Stanford 850 lock-in amplifier measurement of the in-phase and out-of-phase components of the response current to a driving voltage ranging from 0.8 to 5.0 V. For the calibration, the measurement was repeated at $T=81.3$ K, at which temperature polybutadiene is nondispersive throughout our frequency window. The dielectric susceptibility up to a factor of ϵ_∞, which is the high-frequency asymptotic value of $\epsilon(\nu)$, is extracted from these two measurements by dividing the low-temperature impedance by its high-temperature value.

The polybutadiene was purchased from Aldrich Chemicals. The melt is composed of chains of randomly ordered 1,4- and 1,2-butadiene monomers with an average composition ratio of 80:20, respectively, a molecular weight of 6000, and a polydispersity of 1.2.

In Fig. 1(a), the dissipative part of the dielectric susceptibility of polybutadiene is presented for several tem-

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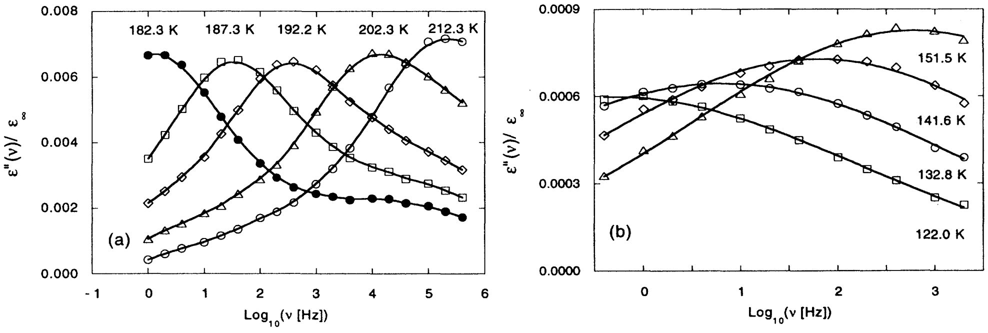

FIG. 1. The imaginary part of the dielectric susceptibility of polybutadiene, $\epsilon''(\nu)$, is shown in (a) and (b) as a function of frequency at various temperatures. The lines through the data in (b) are log-normal fits. The value of ϵ_∞ is approximately 2.

peratures. The peak frequency of $\epsilon''(\nu)$ shifts to lower frequencies with decreasing temperature; this reflects the growing relaxation time or equivalently the slowing relaxation rate. Another much smaller peak is visible in Fig. 1(b) around 10 KHz in the spectrum taken at 182.3 K. This feature is tracked more closely in Fig. 1(b) at temperatures for which the larger relaxation is below our frequency window.

We use the peak frequency as a measure of the average relaxation rate and plot this versus $1000/T$ in Fig. 2 for both relaxation spectra (●). The double branch structure displayed in Fig. 2 is typical of supercooled liquids with both an α and β relaxation. The lower-frequency branch, which corresponds to the larger relaxation of Fig. 1, is readily identified as the α relaxation, because of its non-Arrhenius temperature dependence. The fit to the α branch is a Vogel-Fulcher form, $\nu_p = \nu_o e^{-A/(T-T_0)}$.[6] The Arrhenius behavior of the high-frequency branch indicates that it is a Johari-Goldstein β relaxation and corresponds to the smaller peak in Fig. 1.

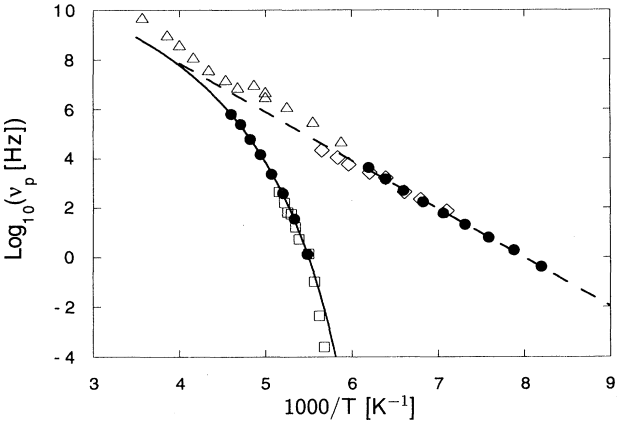

FIG. 2. A plot of the logarithm of the relaxation rate of polybutadiene vs the inverse temperature. The solid circles (●) are our measurements of the peak frequency of the imaginary part of the dielectric response. For comparison, we show relaxation rate data taken from NMR (□) (Ref. 11) and neutron-scattering (△) (Ref. 7) measurements of random coblock polybutadiene and dielectric (◇) (Ref. 9) measurements of diblock polybutadiene. The line through the lower-frequency branch is a Vogel-Fulcher fit to our dielectric data (●): $\nu_p = 2.1 \times 10^{12} \exp[-1130/(T-142)]$. The dashed line through the upper frequency branch is an Arrhenius fit to our dielectric data (●): $\nu_p = 5.3 \times 10^{15} \exp(-4528/T)$.

Recent measurements on polybutadiene suggest that as the temperature is lowered, the relaxation time as measured by neutron scattering departs from the relaxation time determined from viscosity data.[7,8] Since viscosity is not a direct measure of the relaxation time, the comparison is achieved by rescaling the viscosity data, so that it is overlaid on top of the neutron scattering data. Two significant features of this departure are that it occurs close to the previously determined critical temperature of mode coupling theory and that the temperature evolution of the relaxation time following the split is Arrhenius. From these results and given that neutron scattering probes microscopic, while viscosity probes macroscopic length scales, Richter and co-workers concluded that the microscopic and macroscopic time scales decoupled from one another.

Rössler has reinterpreted the data in terms of a bifurcation of the Johari-Goldstein β relaxation from the α relaxation. We note that dielectric susceptibility measurements of diblock polybutadiene support this possibility.[9] Diblock polybutadiene is constructed from two homopolymers, 1,4-polybutadiene and 1,2-polybutadiene, attached end to end. The dielectric measurements reveal two α and two β relaxations, which arise from the distinct relaxation properties of the constituent homopolymers. The relaxation rate of the 1,4-polybutadiene β relaxation, at a given temperature, and its temperature dependence is close to that seen by neutron scattering from the random copolymer below the "decoupling" temperature (see Fig. 2), suggesting that the neutron-scattering measurement has tracked this β relaxation. However, these measurements are on a microphase separated polymer and hence the relaxation properties may differ from those of a random copolymer, which was used in the neutron-scattering experiment. Measurements on polybutadiene using Brillouin light scattering also supports the bifurcation scenario but that technique failed to detect the α relaxation.[10] Hence, neither the Brillouin light-scattering measurements nor the dielectric measurements on block copolymer are sufficient to settle the issue of what is being measured in the neutron-scattering experiment.

Our dielectric measurements of polybutadiene, summarized in Fig. 2, show both an α and β relaxation. We have also included in Fig. 2 relaxation data for polybutadiene compiled from other sources: neutron scattering ($\triangle$) (Ref. 7) and NMR ($\square$) (Ref. 11) measurements on random polybutadiene, and dielectric measurements ($\Diamond$) (Ref. 9) on diblock polybutadiene. The similarity in temperature and slope of the β relaxation in our dielectric measurements to the microscopic relaxation observed by neutron scattering confirms that the neutron-scattering data tracks the β relaxation at lower temperatures.

The relaxation rate as measured by neutron scattering is for a given temperature a decade faster than what we measured. The difference in molecular weight and composition ratio of our sample and the one used in the neutron-scattering experiment may account for some of this discrepancy. However, Fig. 2 shows that our data is in agreement with the NMR data and the dielectric data for diblock polybutadiene, indicating that the dynamics of polybutadiene close to the glass transition are not significantly affected by differences in composition ratio and molecular weight over the broad range values, which includes the neutron-scattering sample, represented by these data sets. The discrepancy is probably due to the strong Q dependence of neutron scattering measured relaxation times. Frick, Frago, and Richter report an almost sevenfold increase in the relaxation rate when changing from $Q=1.45$ Å^{-1} to $Q=1.81$ Å^{-1} (Ref. 12) (the neutron-scattering data reproduced in Fig. 2 was taken at $Q=1.81$ Å^{-1}).

The wide frequency window attainable with dielectric spectroscopy makes it useful for exploring the susceptibility spectrum of glass formers, which typically spans several decades at half maximum. Dixon and coworkers[13] used dielectric spectroscopy to discover a three parameter scaling form onto which the dielectric response for many glass forming liquids could be reduced. The material-dependent parameters are full width at half maximum, W, peak frequency ν_p, and the strength of the response $\Delta\epsilon=\epsilon_0-\epsilon_\infty$, where ϵ_0 and ϵ_∞ are, respectively, the low- and high-frequency asymptotic values of $\epsilon(\nu)$. A broad range of fragile glass forming materials (see Ref. 2 for a review), including a few polymeric systems,[14] have been successfully scaled this way. The recent discovery that the dielectric response of crystalline cyclo-octanol, which has orientational disorder that also scales onto the same curve, indicates that this scaling form has a wider range of applicability than had previously been suspected.[15] It has also recently been shown that the scaling form implies a limiting width at which the static susceptibility may diverge.[16]

The successful description of the low-frequency side of the α relaxation, $\nu<\nu_p$, with the scaling curve implies that $\epsilon''(\nu)$ is proportional to ν in that region. This is not the case for polybutadiene; ϵ'' varies much less rapidly in this region of frequency. The anomalous frequency dependence is probably due to the presence of two α peaks in close proximity. This conjecture is plausible, given the following observations. (i) This phenomenon is commonly seen in polymeric systems such as poly(propylene glycol) (PPG),[14] though the peaks are further separated in that polymer than in polybutadiene. (ii) Experiments with diblock polybutadiene show a merging of the 1,2-polybutadiene and 1,4-polybutadiene peak in the mixed phase.[9] The environment seen by the monomers in the mixed phase of diblock copolymer melt must be almost identical to the environment seen by the monomers in a random copolymer melt. Therefore, we might expect merging of α peaks in random polybutadiene as seen in diblock polybutadiene. (iii) If both the α and α' peak have low-frequency tails that vary linearly with frequency, then we should be able to see the linear dependence at frequencies below the peak frequency of the lower-frequency peak. An abrupt change of slope is seen at the lowest frequencies on a log-log plot. Hence, there are several different relaxation phenomenon that overlap with one another in our frequency window so that the scaling form is obscured and is thus inapplicable to polybutadiene.

Evidence for material independent behavior may be seen in dielectric response data for the β peak. For o-terphenyl and benzyl-chloride toluene, Wu and coworkers[17,18] showed that a log-normal function of frequency accounts for all the data. A physical motivation for a log-normal spectrum can be given if we postulate the existence of independent degrees of freedom that relax by activated hopping over energy barriers, and that the distribution of barrier heights for any given temperature is Gaussian. The dielectric susceptibility may then be expressed as a Debye relaxation with a distribution of relaxation times:

$$\epsilon(\nu)=\epsilon_\infty+\frac{\Delta\epsilon}{\sqrt{\pi}\sigma}\int_0^\infty dE\,\exp\{-[(E-\bar{E})/\sigma]^2\}\times\frac{1}{1-\iota(\nu/\nu_0)\exp(E/k_BT)}\,, \tag{1}$$

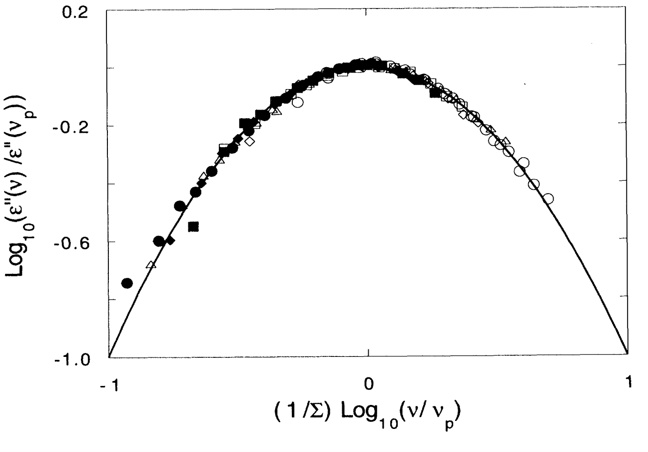

FIG. 3. A composite plot of the imaginary part of the dielectric susceptibility for the β relaxation showing $\log_{10}(\epsilon''(\nu)/\epsilon''(\nu_p))$ vs $(1/\Sigma)\log_{10}(\nu/\nu_p)$, where ν_p is the peak frequency and Σ is the width parameter in Eq. (2). Each different symbol represents the data taken at a different temperature in the range $T=122.0$–156.4 K. The line through the data is a parabola representing a log-normal fit.

where k_B is the Boltzmann constant, $\bar{E}$ and σ characterize the Gaussian distribution, ν_0 is the characteristic activation rate, and E is the energy barrier height. In the limit that the Debye width ($\simeq 1.14$ decades) is much less than σ/k_BT,

$$\epsilon''(\nu) \approx \frac{\Delta\epsilon}{\sqrt{\pi}\Sigma}\exp[-[(\log_{10}\nu - \log_{10}\nu_p]/\Sigma)^2] , \quad (2)$$

where $\Sigma = \sigma/\ln(10)k_BT$ and $\nu_p = \nu_0 \exp(-\bar{E}/k_BT)$ (Ref. 19).

We measured the spectral response of the β relaxation for polybutadiene and found the dissipation peak to be a log-normal function of frequency. Data for $\epsilon''(\nu)$ are plotted in Fig. 1(b) along with log normal fits. In Fig. 3, all the data is presented in scaled form. Some deviation from log-normal behavior is found at low frequencies for $T = 156.4$ K (●), however this is attributable to the high-frequency tail of the α relaxation, which intrudes into the β-relaxation spectrum at this temperature. The fitting parameter Σ is plotted versus $1000/T$ in Fig. 4.

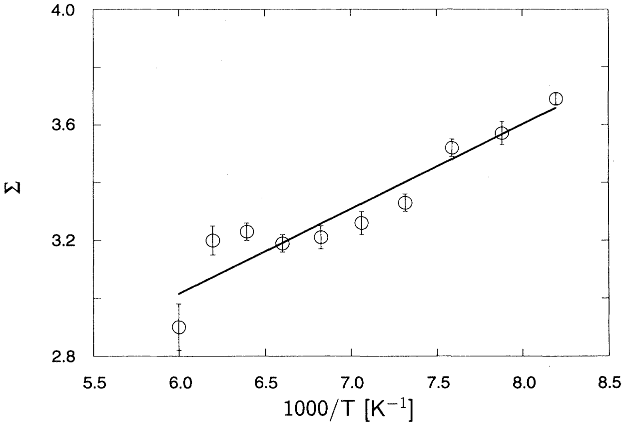

FIG. 4. The width parameter of Eq. (2) for the β relaxation, Σ, vs the inverse temperature.

It is apparent from the fitting parameters that the distribution of energy barriers is temperature dependent. From our data, we obtain $\Sigma = 1.26 + 293/T$ and $\ln(\nu) + 15.7 - 1970/T$. Hence, $\sigma/k_B = 2.90T + 675$ and the attempt frequency is $\nu_0 \simeq 10^{16}$, which is much larger than typical phonon frequencies. The large attempt frequency suggests that $\bar{E}$ is temperature dependent.[20] The microscopic origin of this temperature dependence is unknown.

In conclusion, we have found two distinct peaks in the dielectric spectrum of the random copolymer polybutadiene. The temperature evolution of the peak frequency of the larger peak is non-Arrhenius and is well fit by a Vogel-Fulcher form; we attribute this peak to an α relaxation. We were unable to determine the spectrum of this relaxation, because its features were obscured by other overlapping relaxations. We identified the smaller peak as a β- or Johari-Goldstein relaxation based on the Arrhenius temperature dependence of the peak frequency and the fact that the shape of this peak is log-normal.

The identification of the α and β relaxation in polybutadiene and the temperature evolution of these explains the anomalous behavior of the relaxation time in polybutadiene observed with neutron scattering. Neutron-scattering measurements of the relaxation time show a departure of the relaxation from relaxation times measured by viscosity. However, we have shown that this is the result of tracking the α relaxation about a bifurcation temperature of the α and β relaxation, and then tracking the β relaxation below the bifurcation temperature as was first suggested by Rössler.

We thank Narayanan Menon for the numerous suggestions and insights that helped complete this project. We also thank Robert Leheny for many fruitful discussions. This work is supported by NSF DMR 01-11733.

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