Decoupling of Time Scales of Motion in Polybutadiene Close to the Glass Transition

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Studying the dynamic structure factor of polybutadiene in the first valley of $S(Q)$ we observed a decoupling of microscopic and macroscopic time scales about 40 K above T_g. At higher temperatures the time scale set by the viscosity scales with the microscopic scale, while at lower T strong decoupling effects occur. We present evidence that the decoupled low-temperature relaxation is distinctly different from the high-frequency "β process." The decoupling temperature coincides with the critical temperature of the mode coupling theory.

The freezing of a liquid into the glassy state constitutes one of the major poorly understood phenomena in condensed-matter physics. Recently, important progress towards a microscopic clarification was achieved when it was discovered that mode coupling ideas may successfully be applied to the liquid-glass transition (LGT) [1-3]. When the nonlinear coupling of the density fluctuations exceeds a critical value, in their idealized schematic form, mode coupling theories (MCT) exhibit a dynamical transition from an ergodic liquidlike state to a nonergodic glassy state. Two fundamental properties of the LGT are predicted: (1) In the neighborhood of the LGT the relaxation of the density-density correlation function $S(Q,t)$ separates into two distinct relaxation steps (α, β). The α process, also called structural relaxation, rapidly slows down and is finally completely arrested at a critical temperature T_c, while the secondary β relaxation persists through the LGT. (2) The slowing down of the structural relaxation on *all* length scales can be described by a *single* universal time scale. This second, highly nontrivial prediction was confirmed by a series of neutron spin-echo experiments which all have shown that the very local relaxation measured near the first peak of the liquid structure factor scales with the macroscopic zero-shear viscosity even for "nonideal glasses" [4-7].

In this Letter we report experimental results on polybutadiene showing strong deviations from this universal scaling. While at high temperatures scaling is obeyed within experimental accuracy, starting from about 40 K above T_g the macroscopic and microscopic time scales decouple. We present evidence that this deviation from scaling does not relate to the onset of a high-frequency "β process" but rather results from a decoupling of the microscopic from the macroscopic relaxations. Incidentally, the decoupling occurs close to the critical temperature T_c determined earlier.

Mode coupling theories [1] consider density fluctua-

tions

$$\phi(Q,t) = \frac{\langle \delta\rho^*(Q,t)\delta\rho(Q,0)\rangle}{\langle \delta\rho^*(Q,0)\delta\rho(Q,0)\rangle} \tag{1}$$

as the decisive quantity in the dynamics of liquids approaching the glass transition. Thereby $\delta\rho(Q,t)$ is the time-dependent Fourier component to the wave vector $\mathbf{Q}$ of deviations from mean density. The main approximation concerns the memory function which is generally written as a polynomial in ϕ, the simplest schematic theory considering only the ϕ^2 term [2]. Then as a function of the strength of the nonlinear coupling λ spontaneous structural arrest occurs at a critical value λ_c corresponding to a critical temperature T_c. Below T_c the spectral contribution of the arrested nonergodic fraction of ϕ grows according to a $(T-T_c)^{1/2}$ law. Above T_c the strong coupling of all density modes forces the existence of a single universal time scale governing viscosity as well as short-wavelength structural relaxations. Later more elaborate versions of the theory include so-called hopping terms (linear coupling to phonons) [3]. They smear out the transition, i.e., no sharp structural arrest at $T = T_c$ is revealed. However, the spectral contribution of the structural relaxation which does not cease completely at T_c retains the $(T - T_c)^{1/2}$ singularity. Finally, the existence of hopping processes suggests $T_c > T_g$.

The experiments were performed on deuterated *cis-trans*-vinyl (47:46:7) polybutadiene (PB)

$$(-CD_2-CD=CD-CD_2-)_n ,$$
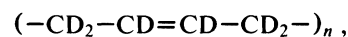
a polymer consisting only of a backbone basically without sidegroups. The randomness of the chain structure relates to the random distribution of two stable C-bond orientations (*cis* and *trans*) relative to the double bond. Two different samples of slightly different molecular weights (sample I: $M_w = 93000$, $M_w/M_n \sim 1.03$, originating from Gronski at Freiburg; and sample II: M_w

≈ 100000, $M_w/M_n \sim 1.05$, prepared at Exxon) were studied. By a specific-heat experiment the glass transition temperature was determined to be 181 K and exhibited a width of 2° [6]. Most of the data were taken on sample I, but in order to verify that the observed effects were not due to possible artifacts related to sample preparation also some measurements were performed on sample II.

The experiments were carried out at the neutron spin-echo (NSE) spectrometer IN11 at the Institute Laue-Langevin in Grenoble. As described elsewhere [8], NSE measures directly the normalized intermediate scattering function $S(Q,t)/S(Q,0)$. From our deuterated sample the measured signal results from coherent scattering, the incoherent contribution being negligibly small. The experiments were performed at a neutron wavelength of $\lambda = 4.73$ Å with 21% monochromatization, covering a time window 3.5 ps $\leq t \leq 1.4$ ns. The data were taken at a momentum transfer $Q = 1.88$ Å^{-1} in the first minimum of the static structure factor of PB [9].

Figure 1 presents a series of NSE spectra taken between 180 and 250 K. The observed relaxation function exhibits a pronounced stretched exponential decay ($\exp[-(t/\tau)^{\beta}]$) with Kohlrausch exponent on the order of 0.4. It is clear that the relaxation does not arrest at the critical temperature which was determined earlier as $T_c = 216 \pm 1$ K [10], but relaxation persists down to the glass transition temperature T_g. We note that above T_c the spectral weight of the structural relaxation stays constant—it is determined by an extrapolation of the relaxation function towards $t = 0$ (see Ref. [10])—while below T_c this weight increases, agreeing, thereby, with the earlier found $(T - T_c)^{1/2}$ law [10]. Figure 2 investigates the scaling properties of the observed relaxation process. For this purpose the dynamic structure factor $S(Q,t)/S(Q,0)$ is plotted versus $t/\tau_{\eta}(T)$. The viscosity time scale $\tau_{\eta}(T) \approx \zeta(T)/T$ is derived from the viscos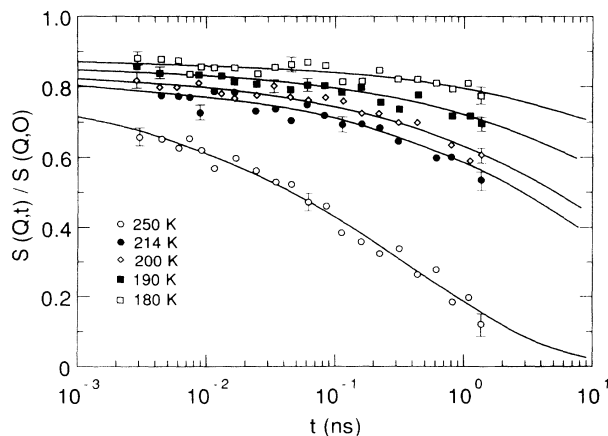ity of polymer melts via the Rouse model [11] which connects η with the monomeric friction coefficient ζ, thereby defining the microscopic scales. For PB $\zeta(T)$ has been described in terms of a Vogel-Fulcher law $\zeta = \zeta_0 \exp[1/a(T - T_0)]$ with $\zeta_0 = 1.26 \times 10^{-11}$ dyn sec/cm, $T_0 = 128$ K, and $a = 7.12 \times 10^{-4}$ K^{-1} [12]. In contrast to the earlier findings below $T \sim 220$ K the rescaled spectra do not follow a single master curve, while above 220 K with experimental accuracy they obey the scaling rule. In other words, below 220 K the microscopic relaxation does not slow down as much as the viscosity—a single universal time scale for all length scales is no longer valid.

In the scaling regime ($T > 220$ K) the functional form of the spectra was approximated by a Kohlrausch law. In a joint fit of all spectra the Kohlrausch exponent β was determined to $\beta = 0.37 \pm 0.018$, and the spectral weight f of the α process was found to be $f = 0.77 \pm 0.015$. Keeping this β value constant, each single spectrum was fitted to reveal individual spectral weights and relaxation times $\tau(T)$ for each temperature. The amplitudes f agree well with those presented earlier [10]; the relaxation rates τ^{-1} are reported in Fig. 3 in the form of an Arrhenius representation. The solid line marks the viscosity time scale. The strong deviations from scaling are evident—e.g., at 190 K the microscopic rate differs by more than 2 orders of magnitude from $\tau_{\eta}(T)$. One might object that fixing β to the value determined at high temperatures constitutes an arbitrary procedure. However, keeping the amplitude fixed to the earlier determined $(T - T_c)^{1/2}$ form [10] and fitting β and τ also results in β values very close to $\beta = 0.37$. For an independent fit of all three parameters the data are not accurate enough. We further note that a change of the stretching parameter β would only affect the numerical values of τ^{-1} but would not change the qualitative behavior.

FIG. 1. Neutron spin-echo spectra obtained near the first valley of $S(Q)$ ($Q = 1.88$ Å^{-1}) for various temperatures. The solid lines result from fits by a stretched exponential fixing the Kohlrausch exponent $\beta = 0.37$.
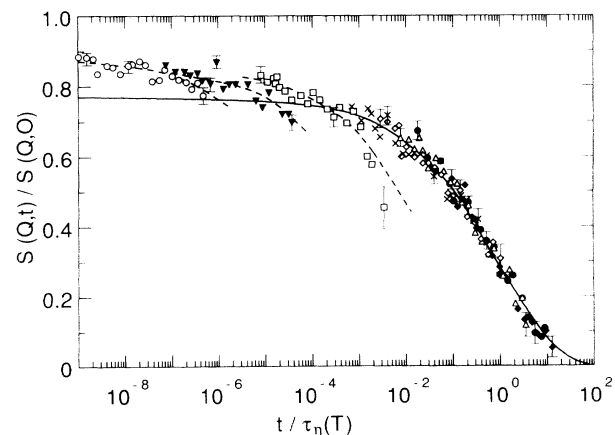

FIG. 2. Scaling representation of the spin-echo data. The scale $\tau_{\eta}(T)$ is taken from viscosity measurements. The solid line represents the master function obtained for the spectra at temperatures ≥ 220 K. The dashed lines are the result of fitting stretched exponentials to the different low-T spectra keeping $\beta = 0.37$ fixed. ◆, 280 K; ●, 260 K; △, 250 K; ◇, 240 K; ×, 230 K; □, 205 K; ▼, 190 K; ○, 180 K.
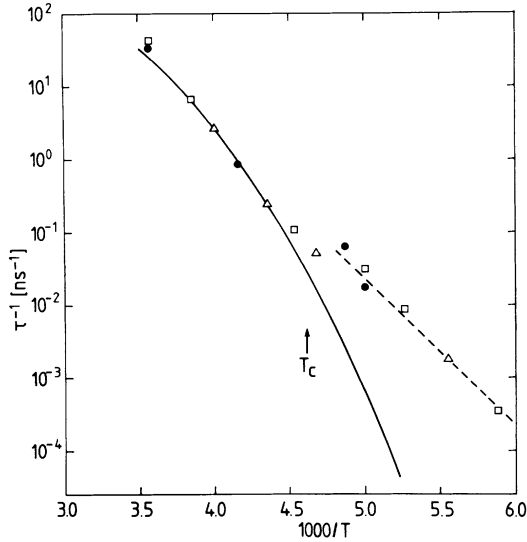
FIG. 3. Arrhenius representation of the relaxation rates obtained from fitting stretched exponentials to the spectra at different temperatures. The three symbols represent three different sets of experiments carried out in separate experimental runs. The solid line displays the viscosity time scale. The dashed line indicates the Arrhenius behavior of the low-temperature branch.

These new findings do not imply that the previously reported agreement with scaling was in error [6]. The old experiments were performed at a momentum transfer $Q = 1.45$ Å^{-1} corresponding to the maximum of the static structure factor $S(Q)$. The present experiments took place in the first minimum of $S(Q)$ where at a given temperature all relaxation times were found to be about a factor of 10 faster than at the peak. We think that this acceleration of the relaxation processes allowed the observation of the low-T relaxations within the resolution conditions of IN11. Another possibility could be that the coherent form factor of this relaxation process is such that it only contributes at high Q implying that only a particular fraction of the relaxation processes may be seen. However, we cannot exclude that the low-temperature processes are also present at lower values of Q, presently outside the range of the NSE spectrometer.

The temperature dependence of the microscopic rates as displayed in Fig. 3 looks very similar to that observed generally in dielectric relaxation [13], where the fast low-temperature branch is interpreted as the secondary relaxation or the β process. However, having already observed a fast secondary relaxation process by neutron time-of-flight (TOF) experiments, we believe that the deviation from scaling, which we report here, cannot simply be understood in terms of a local uncoupled secondary relaxation which comes into the observation window of NSE: (i) The (TOF) experiments have located this fast local relaxation process around 2 meV (≈ 0.3 ps) [14]. This relaxation phenomenon does not exhibit any tenden-

cy to shift towards lower energy if the temperature is decreased. (ii) If a slowing down of a tail of this fast relaxation would bring it into the observation window of NSE, it should come in from the left on the side of the short times. In this case the line shape should be concave rather than the convex curvature displayed in Fig. 2. Had we had a deviation from scaling at short times with a tendency to converge to the master curve, we could assume that it originates from the tail of the fast relaxation process. What we observe, however, are curves which clearly cross the master curve (see Fig. 2, $T = 205$ and 190 K). (iii) Finally, the temperature dependence of the amplitude of the observed relaxation process agrees with the earlier found $(T - T_c)^{1/2}$ law which at least in the framework of MCT identifies it as the structural relaxation.

Deviations from scaling with the time scale set by the viscosity have already been observed for the case of molecular tracers in polymer matrices [15] or for orientational fluctuations [16]. Furthermore, departures of the viscosity from Vogel-Fulcher to Arrhenius behavior above T_g also have been reported: e.g., for B_2O_3 [17] and ortho-terphenyl and other organic liquids [18]. For ortho-terphenyl the linear enthalpy relaxation, on the other hand, was found to follow Vogel-Fulcher behavior down to T_g [19] giving rise to speculations about a decoupling of enthalpy from viscosity relaxation. However, to the best of our knowledge a decoupling of the microscopic and macroscopic scales of the structural relaxation itself has never been reported before. The discovery of such a phenomenon constitutes the essential and novel feature of the results presented here.

As mentioned above, inclusion of a so-called hopping term into the mode coupling equation [3] removes the ideal sharp dynamical transition to nonergodicity and allows for nondiverging relaxation times also below T_c. The calculated form of the relaxation function $S(Q,t)/S(Q,0)$ exhibits features similar to the observed behavior: A fast secondary relaxation process (β relaxation) is followed by a more or less flat region—this is what remains from the structural arrest—and finally by a decay towards zero at long times. Concerning the uniqueness of time scales the MCT do not yet give a definite answer; but one may expect that a shift of dominance from the strong coupling to local relaxations, which above T_c causes the universality of scales towards possibly more cooperative motion near T_g, decouples the microscopic structural rearrangements from the large-scale relaxation responsible for the transport processes.

Another possible scenario for a decoupling mechanism has recently been given by Edwards and Vilgis [20]: They started from the observation that for polymers up to a certain length T_g depends roughly linearly on the chain length. This saturation length relates to the mean entanglement distance d_t, creating thereby, besides the molecular distances, a second length scale in the system. Now, it is supposed that long-wavelength relaxation modes with $Q \gg 1/d_t$ freeze out completely while short-wavelength

modes with $Q < 1/d_t$ may still survive. As the viscosity is dominated by the long-wavelength modes, this scenario results in a practically diverging viscosity with persisting high-Q modes. If the scenario contains some truth, the decoupling process would be unique for polymeric systems.

Finally, we draw attention to another intriguing coincidence relating to the phenomenology of Narayanaswamy [21] and Moynihan et al. [22] for enthalphy and volume relaxation. Based on the Adam-Gibbs theory [23,24], Hodge [25] recently proposed the expression $x \simeq 1 - T_0/T_g$ for the nonlinearity parameter in the above theory. For our system we obtain $x = 1 - \frac{128}{181} = 0.29$. Now assuming that the activation energy (0.39 eV) of the low-temperature Arrhenius branch in Fig. 3 relates to the volume relaxation in the glassy state, then its ratio with the Vogel-Fulcher activation energy at T_g (1.41 eV) becomes 0.28 in remarkable agreement with the Hodge prediction. This possibly fortuitous agreement may serve as further evidence for the assignment of the observed low-T Arrhenius branch as originating from structural relaxation.

In summary, studying the dynamic structure factor of PB at high Q we have observed a decoupling of macroscopic and microscopic time scales around 220 K, about 40 K above T_g. The decoupling temperature coincides with the critical temperature $T_c = 216$ K of the mode coupling theory for this system. While above 220 K microscopic relaxation and the macroscopic viscosity time scales agree, below 220 K they decouple. The microscopic low-T relaxation differs definitely from the secondary relaxation observed in neutron TOF experiments. Line shape and temperature-dependent spectral weight identify it as a structural relaxation. On the other hand, the temperature dependence of the relaxation rates show striking similarity to the "β" branch in dielectric measurements. This poses the question of whether the nearly temperature-independent fast secondary relaxation processes observed by inelastic neutron scattering in many substances relate to the T-dependent β branches seen in the dielectric experiments or whether the latter correspond to the decoupled nonideal glass behavior reported here.

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