

Neutron-Spin-Echo Investigation on the Dynamics of Polybutadiene near the Glass Transition

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We present neutron-spin-echo data on the structural relaxation of glass-forming polybutadiene near the glass transition. Microscopic dynamics on the scale of an interchain distance and the monomeric friction coefficient derived from macroscopic viscosity relaxation obey the time-temperature superposition principle following a common scale. The dynamic structure factor exhibits strong similarities with recent mode-coupling predictions.

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In general, polymers are good glass formers: As a consequence of structural irregularities like randomly oriented or positioned sidegroups, many polymers do not crystallize even under slow cooling but freeze into the glassy state.¹ As observed for other glass formers, this freezing process is accompanied by discontinuities in the derivatives of the thermodynamic potentials like compressibility or specific heat. In particular, singularities in the transport properties are observed: e.g., approaching the glass transition the shear viscosity diverges according to a Vogel-Fulcher law. Dynamic mechanical relaxation experiments reveal the freezing of the so-called structural or α relaxation while secondary relaxation processes are not sensitive to the freezing process. Dynamic light-scattering experiments observe long-range fluctuations in the density correlation functions.^{2,3} These relaxation functions can generally be described by a stretched exponential or a Kohlrausch law. Finally, a time-temperature superposition law is valid: If the time variable is rescaled by a temperature-dependent relaxation time $\tau(T)$, the relaxation function becomes a universal function of $t/\tau(T)$.

In this Letter we report a first microscopic study on the structural relaxation of a polymer looking on the pair correlation function in the neighborhood of the interchain peak in the structure factor $S(Q)$. We found (i) that the dynamic structure factor $S(Q, t)$ follows a Kohlrausch law. Thereby, obeying the time-temperature superposition principle, this *microscopic* relaxation function scales with the monomeric friction coefficient derived from *macroscopic* viscosity measurements; (ii) that the spectral contribution of this structural relaxation, which at the glass transition becomes nonergodic, is qualitatively proportional to the static structure factor $S(Q)$; and finally (iii) that the nonergodic fraction exhibits a strong temperature dependence below the thermodynamic glass transition.

In our experiments we studied deuterated *cis-trans*-vinyl (47:46:7) polybutadiene ($-\text{CD}_2-\text{CD}=\text{CD}-\text{CD}_2-$) $_n$. This polymer consists only of a backbone basically without sidegroups. The randomness in the chain structure is related to the random distribution of the two

stable C-bond orientations (*cis* and *trans*) relative to the double bond. The molecular weight was $M_w = 93\,000$ with $M_w/M_n = 1.03$. By a specific-heat experiment, the glass transition temperature was determined to 181 K exhibiting a width of 2°.

Figure 1 presents the outcome of a neutron-diffraction experiment at two different temperatures which was performed at the diffractometer D1B at the Institut Laue-Langevin in Grenoble.⁴ Two features are noteworthy: (i) The Q dependence of the intensity exhibits the typical behavior of an amorphous material showing two correlation peaks. (ii) While the peak at $Q = 2.9 \text{ \AA}^{-1}$ is nearly temperature independent, with increasing temperature the intensity maximum around $Q = 1.5 \text{ \AA}^{-1}$ shifts markedly and continuously⁴ towards lower values of Q . Thus, the low- Q maximum reflects mainly interchain correlations which are affected by the glass transition, while the second peak relates to a large extent to intrachain correlations which, as a consequence of the stability of the chemical bonds, do not change with temperature.

Around the position of this interchain correlation peak we have studied the dynamics of the system approaching the glass transition. The experiments were carried out

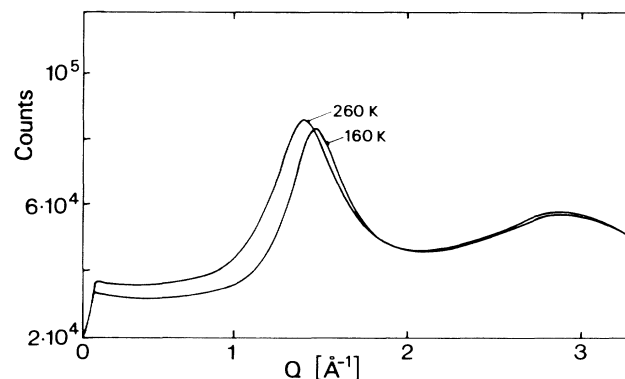


FIG. 1. The elastic intensity $I(Q)$ resembling the static structure factor $S(Q)$ obtained for deuterated polybutadiene at two different temperatures.

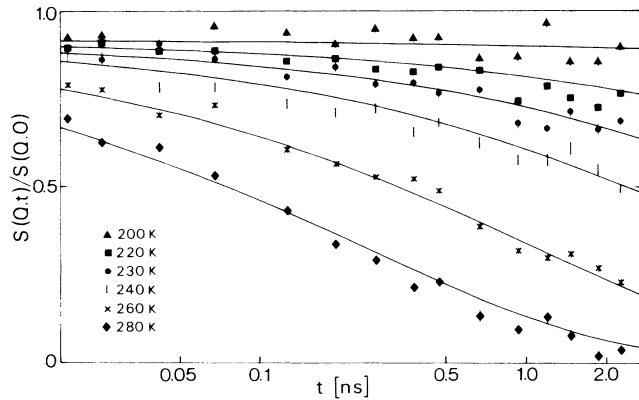


FIG. 2. Neutron-spin-echo spectra obtained near the maximum of $S(Q)$ ($Q=1.48 \text{ \AA}^{-1}$) for various temperatures. The solid lines are the result of a combined fit to a Kohlrausch law.

by employment of the spin-echo spectrometer IN11 at the Institut Laue-Langevin. In a spin-echo experiment, the change of the neutron velocity during scattering is measured directly via the Larmor precessions of the neutron spin in an external guide field H . The final neutron polarization $P(Q, H)$, thereby, is (apart from resolution corrections) directly given by the real part of the intermediate scattering function $S(Q, t)/S(Q, 0)$, the time being proportional to H .⁵ In our experiment we measured at the neutron wavelengths $\lambda = 6 \text{ \AA}$ and $\lambda = 4.55 \text{ \AA}$ covering Fourier times in the range $9 \times 10^{-3} \text{ ns} < t < 2.8 \text{ ns}$. Figure 2 presents data taken near the structure-factor maximum ($Q = 1.48 \text{ \AA}^{-1}$) for temperatures between 200 and 280 K. The observed relaxation function has a pronounced Kohlrausch behavior with a time exponent $\beta = 0.45 \pm 0.02$. Approaching T_g the relaxation is slowed down drastically and below 180 K we cannot discern any time dependence. We note further that even at 200 K $S(Q, t)/S(Q, 0)$ does not start with an amplitude of 1 but extrapolates to about 0.9. Thus, an important part of the scattering function decays outside the time window of IN11 ($t < 1 \times 10^{-11} \text{ s}$) but within the bandpass of the instrument which extends to about 10^{-13} s .

We now compare the microscopic dynamics of the interchain pair correlation function with macroscopic viscosity measurements. For this purpose we use an evaluation of viscosity data taken on polybutadiene (PB) melts in terms of the so-called Rouse model.^{6,7} For short enough chains,⁸ this model relates the viscosity to the monomeric friction coefficient ζ , which defines the microscopic time scales. For ζ , a Vogel-Fulcher behavior $\zeta = \zeta_0 \exp[1/\alpha(T - T_0)]$ with $\zeta_0 = 1.26 \times 10^{-11} \text{ dyne s/cm}$, $T_0 = 128 \text{ K}$, and $\alpha = 7.12 \times 10^{-4}$ has been found.⁷ Assuming that the microscopic time τ , relevant for the dynamics on the level of the pair correlation function, is proportional to ζ/T , we arrive at $\tau(T) = \tau_0(Q)\zeta(T)/T$. Fitting only the prefactor τ_0 which is common for all temperatures, we have rescaled the experimental Fourier times according to the time-temperature superposition

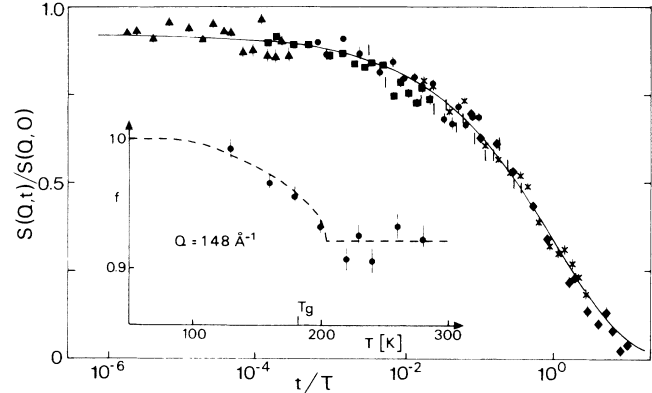


FIG. 3. Scaling representation of the spin-echo data for $Q = 1.48 \text{ \AA}^{-1}$ (\blacktriangle , 200 K; \blacksquare , 220 K; \bullet , 230 K; $|$, 240 K; \times , 260 K; \blacklozenge , 280 K). The scale $\tau(T)$ is taken from a macroscopic viscosity measurement (Ref. 7). Inset: Temperature dependence of the nonergodicity parameter $f(Q)$ near the maximum of $S(Q)$ ($Q = 1.48 \text{ \AA}^{-1}$).

law. Figure 3 presents the following result: For more than 7 orders of magnitude in the rescaled time t/τ , the spin-echo data follow a Kohlrausch law, where the temperature scale has been derived from a macroscopic measurement. Defining a monomer diffusion coefficient $D = kT/\zeta = l^2/6\tau(T)$ from the magnitude of $\tau(T)$, we obtain the very reasonable microscopic jump length of $l = 2.07 \pm 0.006 \text{ \AA}$. Thus, the dynamics at the level of the interchain pair correlation function scale directly with the monomeric friction coefficient derived from a macroscopic experiment. The freezing of all polymer relaxation modes, from the slowest mode which dominates viscosity to the fastest modes which are observed in our experiment, follows the same scale of $\tau(T)$. This result is by no means trivial and recently has become the subject of theoretical debate.⁹

Figure 3 shows much more clearly than Fig. 2 that for $t/\tau \rightarrow 0$ $S(Q, t)/S(Q, 0)$ does not extrapolate to 1 but approaches a value distinctly smaller than 1 (0.917 ± 0.008). This observation shows that at the glass transition only a fraction of the dynamic structure factor becomes nonergodic, while a substantial part does not freeze. In order to learn about the Q dependence of the nonergodic fraction, we have performed spin-echo experiments at Q values on both sides of the peak in $S(Q)$. In order to reach Q values higher than $Q = 1.5 \text{ \AA}^{-1}$, we employed shorter-wavelength neutrons ($\lambda = 4.55 \text{ \AA}$). The nonergodic fraction $f(Q)$ was obtained by extrapolation of data at two different temperatures (220 and 260 K) according to the time-temperature superposition principle. Figure 4 displays the Q dependence of $f(Q)$ and compares it with that of the static structure factor $S(Q)$. Obviously the peak in $S(Q)$ finds its counterpart in the Q dependence of $f(Q)$. In addition, Fig. 4 presents the obtained Q dependence of the relaxation rates. Commencing at higher Q 's around the maximum position of

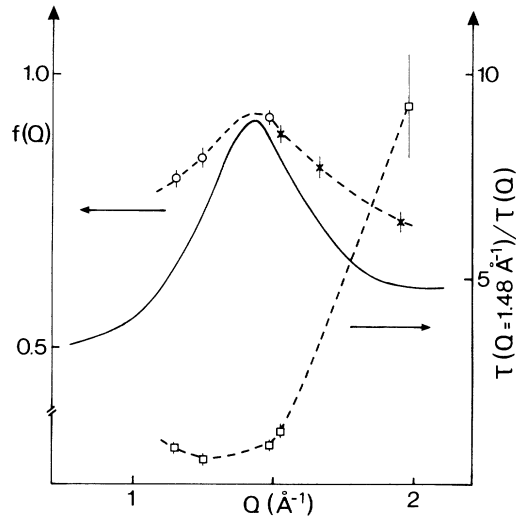


FIG. 4. Q dependence of the nonergodicity parameter $f(Q)$ (\circ , $\lambda = 6 \text{ \AA}$; \times , $\lambda = 4.55 \text{ \AA}$) and the ratio of the relaxation rates $\tau(Q = 1.48 \text{ \AA}^{-1})/\tau(Q)$. The solid line represents the static structure factor $S(Q)$ at 230 K.

$S(Q)$, the jump rates $\tau(Q)$ decrease strongly and appear to pass through a broad minimum, a result which qualitatively could be understood in terms of the so-called de Gennes narrowing¹⁰. Correlations which are preferred by a system build up the maximum in $S(Q)$ and consequently decay more slowly.

Finally, the inset in Fig. 3 presents the temperature dependence of the nonergodic fraction measured at the peak position of $S(Q)$. Above 200 K, $f(Q)$ measures the spectral contribution of the structural relaxation. Its value fluctuates around the result from the scaling representation of the data in Fig. 3 (dashed line) and basically stays constant. Below about 200 K the structural relaxation freezes and becomes nonergodic. Here $f(Q)$ measures the nonergodicity. We note that $f(Q)$ increases gradually and reaches its limiting value of 1 only far below the glass transition ($T_g = 181 \text{ K}$). Thus, fast motional processes at a time scale well above 10^{-10} s , but below 10^{-13} s become effective already well below T_g .

We now discuss our results in terms of recent microscopic theories of the glass transition. After their successes in the understanding of liquids, the application of mode coupling concepts led also to considerable progress towards a microscopic theory of the glass transition.¹¹⁻¹⁴ The theory considers density fluctuations as the most important low-frequency processes and describes the glass transition as an essentially dynamic phenomenon. Ergodicity breaking is understood as a result of strong nonlinear coupling between the density fluctuations. Structural arrest occurs at a "critical temperature T_c " somewhat above the thermodynamic glass

transition. From this microscopic point of view, the density fluctuations are of prime interest. They are directly revealed by the scattering function $S(Q, t)$ which we measure with neutrons and a detailed comparison becomes possible. The theory results in a two-stage relaxation behavior leading to

$$S(Q, t)/S(Q, 0) = f(Q)\phi(t) + h(Q)F(t/\tau_c). \quad (1)$$

Above T_c the first component $f(Q)\phi(t)$ relates to the structural relation while below T_c it measures the amount of structural arrest. The second part, the so-called scaling contribution, describes fast motional processes not related to transport phenomena. Concerning the structural relaxation, the following predictions are made: (1) All structural relaxations follow a common scaling law of the form $\phi(t) = \phi(t/\tau)$. Thereby the scale is universal. (2) Their spectral contribution is constant above T_c and increases according to a characteristic $(T_c - T)^{1/2}$ law below T_c . The amplitude of the increasing fraction is measured by $h(Q)$. (3) Qualitatively, the Q dependence of $f(Q)$ resembles that of $S(Q)$. However, no analytic expression is available. (4) Finally, at the maximum of $S(Q)$, the relaxation rate at a given temperature passes through a minimum. Explicitly $1/\tau(Q) \sim [h(Q)/f(Q)]^{1/b}$ is predicted. The exponent b is expected to be slightly larger than the Kohlrausch exponent β .¹⁴

Before we compare with our data, we would like to emphasize that these theoretical predictions are based on calculations for simple liquids while polymers are long-chain molecules. Nevertheless, the experimental results exhibit remarkable similarities with the theory: First of all, similar to the results of Mezei, Knaak, and Farago on an anorganic glass,¹⁵ we find two well separated time regimes of polymer relaxation, the fast processes occurring outside the observation window of the neutron-spin-echo spectrometer. Applying neutron-time-of-flight techniques on a protonated PB sample, we recently observed an anomalous intensity buildup around 1-meV energy transfer ($1.5 \times 10^{12} \text{ s}^{-1} \text{ rad}^{-1}$) which we associate with the high-frequency process.¹⁶ Following the list of theoretical predictions for the structural relaxation, our experiment shows good qualitative agreement in all four points, namely, (i) the data establish impressively the predicted validity of the t/τ -scaling law in relating macroscopic (viscosity) relaxation to microscopic motion on the scale of interchain distances, a result which has been reported recently also for an anorganic glass.¹⁵ (ii) As shown by the dashed line in the inset of Fig. 3, the temperature dependence of $f(Q)$ is compatible with the prediction (2) if $T_c \approx 250 \text{ K}$ is chosen. The data support a constant $f(Q)$ above T_c and one in agreement with a $(T_c - T)^{1/2}$ behavior below T_c . We note that in an earlier attempt to define T_c using incoherent quasielastic scattering in the ω domain, we estimated $T_c \approx 220 \text{ K}$,¹⁶ 15° higher than the present value, while the glass transi-

tion temperature for the protonated material is found at $T_g = 186$ K only 5° above the value for the deuterated material. However, in the ω domain an extrapolation of the structural relaxation to $t/\tau \rightarrow 0$ is inherently much more difficult than in the time domain. (iii) Qualitatively, the Q dependence of the spectral contribution $f(Q)$ follows that of the static structure factor $S(Q)$. According to Goetze¹³ this may be understood in the following way: We consider $S(Q)/T$ as the generalized susceptibility at the wave vector Q . If $S(Q)$ is large, the system is soft and fluctuations may arrest spontaneously. As a result, the nonergodicity $f(Q)$ is large. On the other hand, in the Q regime where $S(Q)$ is small, the system reacts stiffly and consequently fluctuations do not arrest easily. Therefore, the amplitude of the fast processes $h(Q)$ remains large. (iv) Comparing the relaxation rates at $Q = 1.5 \text{ \AA}^{-1}$ and $Q = 2 \text{ \AA}^{-1}$, we find $\tau(Q = 1.5)/\tau(Q = 2.0) = 6.8 \pm 1.2$. Taking $b = 0.5$ and inserting the measured values for $f(Q)$ and $h(Q) = 1 - f(Q)$, we obtain 8.5 ± 1.7 , in good agreement with the measured rate ratio.

Summarizing, in a glass-forming polymer we have followed the microscopic relaxation in the neighborhood of the interchain correlation peak through the glass transition. As the most remarkable results, we observed the following: (i) That the chain dynamics on the scale of a nearest-neighbor distance and the monomeric friction coefficient derived from macroscopic viscosity measurements obey the time-temperature superposition principle with the same scale $\tau(T)$; and (ii) that the measured dynamic structure factor $S(Q, t)$ reveals striking similarities with the predictions of the mode-coupling approach.

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