

Study of the Dynamic Structure Factor in the β Relaxation Regime of Polybutadiene

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Using neutron spin echo and dielectric spectroscopy we have studied the molecular motions of 1-4 polybutadiene in the α - β relaxation regime. At the first peak of the static structure factor the relaxation times follow the temperature dependence of the viscosity, while near the second peak the Arrhenius law of the β relaxation is observed. Considering localized motions on a length scale of 1.5 Å with the barrier distribution from dielectric spectroscopy the dynamic structure factor in the β relaxation regime can be described quantitatively.

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The general relaxation map of glass forming liquids exhibits rather complex features [1]. In addition to the primary or structural α relaxation which underlies the flow processes, universally a secondary relaxation process, the β relaxation, also known as the Johari-Goldstein process [2], always appears at low temperatures merging with the α process in a temperature range 10%–20% above the glass transition temperature T_g . In the case of polymers, in particular, such relaxations occur independently of the existence of side groups and are believed to be responsible for such important mechanical properties such as ductility. Despite numerous efforts to study such motions by relaxational methods such as dielectric spectroscopy, their molecular nature is still unknown.

In principle, varying the momentum transfer $Q = 4\pi \sin\theta/\lambda$ (λ is the neutron wave length and 2θ is the scattering angle) quasielastic neutron scattering is capable of providing the space time resolution, in order to access the relaxations on a molecular level. Being a Fourier method, i.e., measuring directly the time dependent dynamic structure factor $S(Q, t)$, neutron spin echo (NSE) is particularly well suited for this task [3]. Up to now most of the NSE experiments on glass forming liquids were performed in a temperature range above the merging of α and β relaxations in a relatively narrow Q range near the first peak of the static structure factor $S(Q)$ [4,5]. These measurements have established the validity of the time-temperature superposition principle and the existence of one universal temperature scale, which are both valid for the viscosity relaxation and density fluctuations [6]. Later NSE experiments on 1-4 polybutadiene (PB) undertaken near the first minimum of $S(Q)$ revealed a decoupling of the microscopic time scale from the scale set by the viscosity relaxation [7]. Dielectric measurements brought

evidence that below the decoupling temperature the NSE relaxations appear to correspond to the β process [8].

This paper presents first systematic Q -dependent investigations of the dynamic structure factor for 1-4 PB in the α - β relaxation regime. While at the first peak of $S(Q)$ the characteristic relaxation times evaluated from the NSE spectra follow the Vogel-Fulcher temperature dependence of the α relaxation, at the second peak of $S(Q)$ these times exhibit an Arrhenius temperature dependence characteristic of the β relaxation. We present a simple model for the dynamic structure factor which naturally explains this observation. With the barrier distribution $g(E)$ for the β relaxation obtained from wide frequency range dielectric spectroscopy on the same sample a consistent fit of the NSE spectra in the β regime as a function of momentum transfer and temperature is achieved. The comparison of time scales reveals the puzzling result that the density fluctuations appear to relax about 2 orders of magnitude faster than the dipoles observed in dielectric relaxation.

The experiments were performed on a predeuterated PB synthesized by anionic polymerization. The reaction conditions used led to a statistically uniform, stereoirregular chain microstructure of ca. 52% 1,4-*trans*, 41% 1,4-*cis*, and 7% 1,2 (vinyl) units. Thus, the polymer consists of a backbone essentially without side groups ($-\text{CD}_2-\text{CD}=\text{CD}-\text{CD}_2-$) $_n$. Molecular weight and polydispersity were $M_N = 31.6 \times 10^3$ and $M_W/M_N < 1.02$ as determined by membrane osmometry and size exclusion chromatography, respectively. With differential scanning calorimetry the glass transition was determined to occur at $T_g = 178$ K.

NSE and broadband dielectric spectroscopy are the techniques used in this work. NSE experiments were performed by means of the IN11 spectrometer at the Institut Laue Langevin in Grenoble. As described elsewhere [3],

NSE measures directly the normalized intermediate scattering function $S(Q, t)/S(Q, 0)$, where t is time. Since incoherent scattering contributions are strongly suppressed, the signal from our deuterated PB sample is nearly entirely due to coherent scattering. The experiments were performed at the highest scattering angle available (128°), allowing us to reach a maximum Q value of 2.71 \AA^{-1} for the minimum incoming wavelength λ available (4.16 \AA). By changing the value of λ we measured $S(Q, t)/S(Q, 0)$ at 205 K for different Q values in the range $1.40 < Q < 2.71 \text{ \AA}^{-1}$, accessing the dynamics around the first and the second maxima, as well as around the minimum of the static structure factor $S(Q)$ [9]. For several Q values and, in particular, for $Q = 2.71 \text{ \AA}^{-1}$ we also measured $S(Q, t)/S(Q, 0)$ at different temperatures ranging between 170 and 300 K. The time window varies with Q from $1.8 \text{ ps} < t < 1.5 \text{ ns}$ ($Q = 2.71 \text{ \AA}^{-1}$) to $13 \text{ ps} < t < 6.3 \text{ ns}$ ($Q = 1.40 \text{ \AA}^{-1}$).

Figure 1 displays a set of characteristic NSE spectra (a) at 205 K for different Q values and (b) at $Q = 2.71 \text{ \AA}^{-1}$ for different temperatures. In a first approach the NSE data were fitted with a Kohlrausch-Williams-Watts (KWW) function, $S(Q, t)/S(Q, 0) \propto \exp[-(t/\tau_{\text{KWW}})^\beta]$, with $\beta = 0.41$ as suggested from dielectric spectroscopy (see below) for α relaxation. If an interpretation in terms of the α relaxation holds, we expect a viscositylike temperature dependence of τ_{KWW} , as reported in

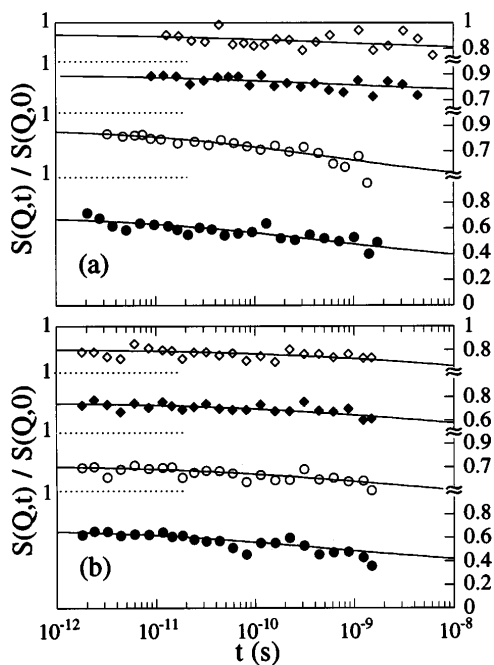


FIG. 1. Neutron spin echo spectra of PB: (a) at $T = 205 \text{ K}$ and for different Q values: \diamond , 1.40 \AA^{-1} ; \blacklozenge , 1.56 \AA^{-1} ; \circ , 1.88 \AA^{-1} ; \bullet , 2.55 \AA^{-1} . (b) At $Q = 2.71 \text{ \AA}^{-1}$ and for various temperatures: \diamond , 170 K; \blacklozenge , 180 K; \circ , 190 K; \bullet , 205 K. The ordinates corresponding to each spectrum are given on the left and right sides, respectively. Solid lines correspond to the fit by Eq. (4).

Ref. [5] for $Q = 1.48 \text{ \AA}^{-1}$. In that work, NSE data were scaled with $\tau \propto \zeta(T)/T$, where ζ is the monomeric friction coefficient obtained from viscosity measurements, and a β value of 0.45 was found. We reanalyzed those data together with the new ones at $Q = 2.71 \text{ \AA}^{-1}$ imposing $\beta = 0.41$. The obtained τ_{KWW} are shown in Fig. 2. As can be seen in this figure, the temperature behavior of τ_{KWW} is essentially different for both Q values. For $Q = 1.48 \text{ \AA}^{-1}$ the time scales can be perfectly fitted by $\tau_{\text{KWW}} \propto \zeta(T)/T$, as reported in Ref. [5], whereas for $Q = 2.71 \text{ \AA}^{-1}$ the characteristic times follow an Arrhenius-like temperature dependence: The fitting curve in Fig. 2 for $\tau_{\text{KWW}}(Q = 2.71 \text{ \AA}^{-1})$ corresponds to $\tau_{\text{KWW}} = \tau_0^{\text{NSE}} \exp(E_0/KT)$ with $\tau_0^{\text{NSE}} = 1.9 \times 10^{-18} \text{ s}$ and $E_0 = 0.40 \text{ eV}$. It follows from this analysis that around the first maximum of $S(Q)$, which is governed by interchain correlations, the dynamics are clearly related to α relaxation, whereas around the second maximum, which reflects intrachain correlations, the dynamics are connected to β relaxation.

In order to arrive at a quantitative comparison with dielectric β relaxation results, we have studied the dielectric response of the same sample in the frequency range 10^{-2} to 10^9 Hz in a wide temperature range. Here we will focus on the results concerning dielectric β relaxation, but we want to point out two of the results concerning the dielectric α relaxation which are important for this work: (i) Its relaxation function in the time domain can be described by assuming a KWW function and is compatible with a temperature independent $\beta = 0.41$ [10]. This result was used above. (ii) It merges with the β relaxation at a merging temperature T_M of about 220 K [10], coinciding with the decoupling temperature mentioned above.

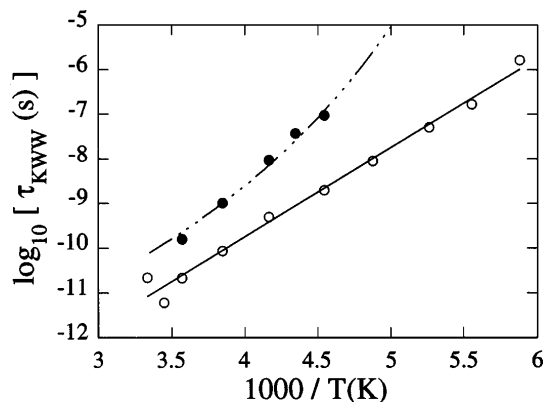


FIG. 2. Temperature dependence of the characteristic times τ_{KWW} obtained from the fits of $S(Q, t)$ by stretched exponentials with $\beta = 0.41$ at $Q = 1.48 \text{ \AA}^{-1}$ (\bullet) and $Q = 2.71 \text{ \AA}^{-1}$ (\circ). Dash-dotted line corresponds to the Vogel-Fulcher-like temperature dependence of the viscosity for $Q = 1.48 \text{ \AA}^{-1}$ and the solid line to the Arrhenius-like temperature dependence of the dielectric β relaxation for $Q = 2.71 \text{ \AA}^{-1}$.

For the dielectric β relaxation below T_g , Fig. 3 shows the temperature dependence of its characteristic time τ_{\max} . As observed by Johari and Goldstein [2], τ_{\max} varies Arrhenius-like with temperature, $\tau_{\max} = \tau_0^D \exp(E_0/KT)$, with $\tau_0^D = 3.5 \times 10^{-17}$ s and $E_0 = 0.41$ eV. In this temperature range, the measured dielectric response can be well described by assuming a superposition of Debye processes with a Gaussian distribution of energy barriers $g(E)$:

$$\Phi_{\beta}^*(\omega) \propto \int_0^{\infty} g(E) \frac{1}{1 + i\omega\tau_0^D \exp(E/KT)} dE, \quad (1a)$$

$$g(E) = \frac{1}{\sqrt{\pi}\sigma} \exp\left[-\left(\frac{E - E_0}{\sigma}\right)^2\right]. \quad (1b)$$

Here σ is the width and E_0 is the average of the distribution of activation energies. The width σ decreases linearly with temperature [$\sigma(\text{eV}) = 0.145 - 2.55 \times 10^{-4}T(\text{K})$], as shown in Fig. 3. The narrowing of the relaxation function with increasing temperature is another well established feature of the β relaxation [11]. We note that the activation energy found by dielectric spectroscopy perfectly agrees with the NSE result at high Q , providing strong evidence that the density fluctuations at short length scales indeed result from the β relaxation.

In order to become more quantitative we construct in the following a simple dynamic structure factor to be compared with the data. We restrict ourselves to the temperature range below the merging temperature T_M , where the α relaxation is far away from the NSE dynamical window and thus the β relaxation is measured. The coherent intermediate scattering function corresponding to the β process can be built starting from the description used in the dielectric study: It will be given by a superposition of elemental processes with a Gaussian distribution of energy barriers [Eq. (1)].

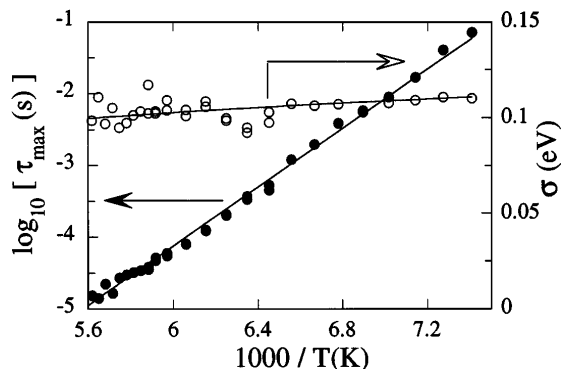


FIG. 3. Temperature dependence of the characteristic time τ_{\max} (●) and the width of the distribution of barrier heights σ (○) of the β relaxation from dielectric spectroscopy. Solid lines correspond to fits by the Arrhenius and linear laws, respectively, given in the text.

The β relaxation is assumed to be a spatially localized process [11]. The simplest picture of the elemental motion involved in this relaxation is a jump of an atom between two equivalent sites separated by a distance d with a characteristic time $\tau = \tau_0^{\text{NSE}} \exp(E/KT)$, i.e., a hopping process. The jump distance d could also depend on the barrier height E . For such hopping processes, the incoherent intermediate scattering function is given by [12]

$$\begin{aligned} S_{\text{inc}}^{\text{hop}}(Q, t) &= 1 - \frac{1}{2} \left[1 - \frac{\sin(Qd)}{Qd} \right] \\ &\quad + \frac{1}{2} \left[1 - \frac{\sin(Qd)}{Qd} \right] \exp\left(-\frac{2t}{\tau}\right) \\ &= 1 - A^{\text{hop}}(Q, d) + f^{\text{hop}}(Q, d, \tau, t). \end{aligned} \quad (2)$$

Coherent and incoherent scattering differ with respect to the presence of interference terms in the coherent scattering. Let us consider the jump motion of a pair of atoms. If such atomic jumps are uncorrelated, dynamic constructive interferences are absent, and it follows naturally that the coherent quasielastic part assumes the form of the incoherent part. Note that the interference terms from the average atom distribution remain giving rise to $S(Q)$. If the motions are correlated, it can be shown that the interference effects are small as long as the jump distances are smaller than the distance between the atom pairs. Under this assumption the coherent inelastic part can be approximated by the incoherent inelastic part and the normalized coherent scattering function can be written as

$$\frac{S_{\text{coh}}^{\text{hop}}(Q, t)}{S(Q)} = 1 - \frac{A^{\text{hop}}(Q, d)}{S(Q)} + \frac{f^{\text{hop}}(Q, d, \tau, t)}{S(Q)}. \quad (3)$$

Once the coherent scattering function for the elemental motion has been obtained it is straightforward to construct the corresponding one for the β process, which is given by the superposition of the coherent scattering functions for the elemental processes weighted by the Gaussian distribution function of the activation energies $g(E)$ given by Eq. (1b):

$$\begin{aligned} \frac{S_{\text{coh}}^{\beta, \text{hop}}(Q, t)}{S(Q)} &= 1 - \frac{1}{S(Q)} \int_0^{\infty} g(E) A^{\text{hop}}(Q, d) dE \\ &\quad + \frac{1}{S(Q)} \int_0^{\infty} g(E) f^{\text{hop}}(Q, d, \tau, t) dE. \end{aligned} \quad (4)$$

The free parameters in this model are d and τ_0^{NSE} . For d we choose the dependence on the activation energy given by the soft potential model, i.e., $d \propto E^{1/4}$ [13], giving a slight variation of d in the energy range where $g(E)$ presents significant values. We also allowed a Q and temperature dependent amplitude factor which accounts for fast processes such as phonons. The best fit

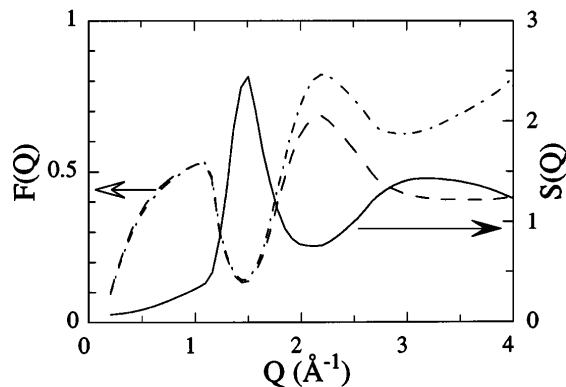


FIG. 4. Amplitude $F(Q)$ of the relative quasielastic contribution of the β process to the coherent scattering function obtained from the hopping model (dashed line) and from the rotational diffusion model (dash-dotted line) as functions of Q . The static structure factor $S(Q)$ at 160 K [9] is shown for comparison (solid line).

was obtained for $d(\text{\AA}) = 1.9E(\text{eV})^{1/4}$ implying a most probable jump distance of 1.5 \AA and $\tau_0^{\text{NSE}} = \tau_0^D/250$. Figure 1 shows the results of this fit for some of the Q values investigated at 205 K and for several temperatures at the highest Q . As can be seen in this figure, the scattering function proposed describes very well the experimental data, reproducing not only the temperature dependence but also the Q dependence of $S(Q, t)$.

Figure 4 displays the relative quasielastic contribution of the β process $F(Q)$ to the normalized dynamic structure factor as calculated on the basis of the parameter obtained through the fitting procedure described above. As can be seen the Q dependence immediately explains the qualitatively different behavior of $S(Q, t)$ at the two first maxima of $S(Q)$: The relative quasielastic contribution corresponding to the β process is very small in the neighborhood of the first peak, so there at higher temperatures we are mainly observing the contribution of the α relaxation. On the other hand, $F(Q)$ is quite high around the minimum and the second peak of $S(Q)$, explaining the Arrhenius behavior of the characteristic times of Fig. 2 at $Q = 2.71 \text{ \AA}^{-1}$ and the decoupling observed at $Q = 1.88 \text{ \AA}^{-1}$ [7].

In order to test the sensitivity of our model fitting towards the details of the microscopic mechanism of motion, we also fitted the data with a corresponding model assuming rotational diffusion of the moving atom on a sphere of radius r . As compared to single jumps this model constitutes the extreme of very high local mobility. Again imposing the distribution function of jump rates as obtained from dielectric spectroscopy, we also are able to achieve a good fit of the experimental data resulting in a rotational radius of $r = 0.75 \text{ \AA}$ and a basic time $\tau_0^{\text{NSE}} = \tau_0^D/54$. While $r = 0.75 \text{ \AA}$ corresponds well to a jump distance of $d = 1.5 \text{ \AA}$ in the hopping model, the somewhat larger prefactor originates from the generally

larger mobility imposed by the rotational diffusion model. For illustration the predicted relative quasielastic scattering for this model is also included in Fig. 4.

At the present stage the neutron scattering experiments cannot distinguish the details of the different jump models. For a small amplitude motion an extension of the experiment to significantly higher Q values would be required—a task which is presently technically not feasible. But the experiments are able to elucidate the extent of molecular motion of the β process (1.5 \AA). We note that the second peak of $S(Q)$ relates to intramolecular correlations, in particular, to the form factor of rigid $-\text{CD}=\text{CD}-$ units. If such a unit moves as a whole in the β process, one would expect strong visibility at the second peak of $S(Q)$. Thus also from this aspect the β relaxation appears to a large extent to be related to intrachain motions. Finally, the experiments also reveal the very astonishing result that the density fluctuations, which are directly seen by neutrons, obviously decay about 2 orders of magnitude faster than the dipole orientations observed by dielectric spectroscopy.

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