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Space time observation of the α -process in polymers by quasielastic neutron scattering

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Abstract. We report quasielastic neutron scattering experiments on the momentum (Q) and time (t) dependent dynamic structure factor $S(Q, t)$ on the glass-forming polymers polyisobutylene (PIB) and polybutadiene (PB). After outlining the information content of $S(Q, t)$, we exemplify the concept for the case of PB. Thereafter we present data obtained on the self- and pair correlation functions of PIB encompassing a large Q range $0.03 \leq Q \leq 3 \text{ \AA}^{-1}$. Thereby we cover the entire motional regime from translational diffusion, the Rouse modes, the α -relaxation regime up to the local relaxation processes. We investigate the limitations of the Rouse model, we present first results on the relation between the intrachain Rouse process and the α -relaxation, we show that the α -process may be understood in terms of backwards correlated sublinear diffusion and we finally obtain information on a local relaxation process in PIB which appears to connect a main chain relaxation with a methyl-group rotation.

1. Introduction

Relaxation processes in polymers have been studied for a long time employing preferentially spectroscopic techniques like dielectric or mechanical spectroscopy and NMR. By these methods relaxation maps for many polymers have been established [1]. They nearly always contain a primary α -relaxation which arrests at the glass transition temperature T_g and a secondary β -relaxation, the so called Johari–Goldstein process [2], displaying an activated behaviour through the glass-transition. In spite of these manifold investigations still detailed information about the molecular motions which are behind these processes is missing. Neutrons with their ability to provide space time analysis on atomic and mesoscopic scales have a great potential to promote deeper understanding.

The experiments presented in this short paper have been performed with neutron spin echo spectroscopy (NSE) and neutron backscattering, and were complemented in part by dielectric experiments. The paper commences with some remarks on the dynamic structure factor from combined local and diffusive relaxation processes [3, 4]. Then the approach will be exemplified on experiments performed on polybutadiene (PB). We further discuss recent investigations on PIB [5–7], where the entire spatial regime from translational diffusion, the Rouse modes, the α -relaxation to the local processes was explored.

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2. Dynamic structure factor

Neutron spin echo experiments investigate directly the intermediate dynamic structure factor $S(Q, t)$.

$$S(Q, t) = \langle \Delta\rho(Q, t)\Delta\rho(Q, 0) \rangle \quad (1)$$

where $\Delta\rho(Q, t)$ is the Fourier component of the density fluctuation to the wave vector $Q = (4\pi/\lambda)\sin\Theta$ (λ : neutron wavelength, 2Θ : scattering angle) at time t . The angled brackets denote the thermal average. For equal times equation (1) describes the usual structure factor $S(Q)$ originating from the short range order in the polymer material. The dynamic pair correlation function (equation (1)) reflects the relative motions of different atoms or molecular units with respect to each other. Recently, we have presented some considerations on the dynamic pair correlation function due to simple local jump processes and have discussed possibilities for approximations [4]. Furthermore, the dynamic structure factor due to combined local and diffusive motions was considered.

With respect to the β -process which is understood as a two site jump process the dynamic structure factor may be approximated by

$$S(Q, t) = (\langle (A_{in} + A_{fin})^2 \rangle - \langle A \rangle^2 [1 - S_c(Q)] + \langle (A_{in} - A_{fin})^2 \rangle e^{-2t/\tau(E)})_{g(E)}. \quad (2)$$

Thereby $A = (1/N) \sum_i b_i e^{iQr_i}$ is the scattering amplitude of the moving object in the initial and final state respectively, b_i is the scattering length of atom i and r_i its position vector. The inner averages stand for the orientational average while the outer describes the average with respect to the distribution $g(E)$ of jump times $\tau(E)$ or energy barriers E . $\langle A \rangle$ is the average scattering amplitude of the jumping unit in its centre of mass system and $S_c(Q)$ is the structure factor for centre of mass correlations. In the case of a pointlike jumper equation (2) reduces to

$$\frac{S(Q, t)}{S(Q)} = \left\langle \frac{S(Q) - \frac{1}{2} \left(1 - \frac{\sin Qd}{Qd}\right)}{S(Q)} + \frac{\frac{1}{2} \left(1 - \frac{\sin Qd}{Qd}\right)}{S(Q)} e^{-2t/\tau(E)} \right\rangle_{g(E)} \quad (3)$$

with d the jump distance. For statistically independent diffusive α - and local β -relaxations the combined dynamic structure factor $S^{\alpha\beta}(Q, t)$ takes the form

$$S^{\alpha\beta}(Q, t) = \varphi^\alpha(Q, t) S^\beta(Q, t) \quad (4)$$

where the α -relaxation is described by

$$\varphi^\alpha(Q, t) = \exp\{-t/\tau_{KWW}(Q) S(Q)^\beta\}. \quad (5)$$

Thereby $\tau_{KWW}(Q)$ is a Q -dependent relaxation time and β the stretching exponent.

3. The case of polybutadiene

On the example of 1–4 PB we now validate the concept outlined in the previous section. Figure 1 displays the essence of the results on this polymer [4]. In the upper part figure 1 shows the static structure factor of PB at different temperatures [8]. While the first peak shifts strongly with temperature, qualifying it as due to interchain correlations, the second peak hardly changes with temperature. Here covalently connected intrachain correlations dominate. Figure 1(b) presents spin echo data taken at Q_{max} , the Q value of the first structure factor peak. They are scaled to the temperature dependence set by the viscosity relaxation. Applying this scaling all data collapse to a common master curve signifying that the interchain correlations between adjacent chains decay with the same temperature law as the macroscopic flow. Trying the

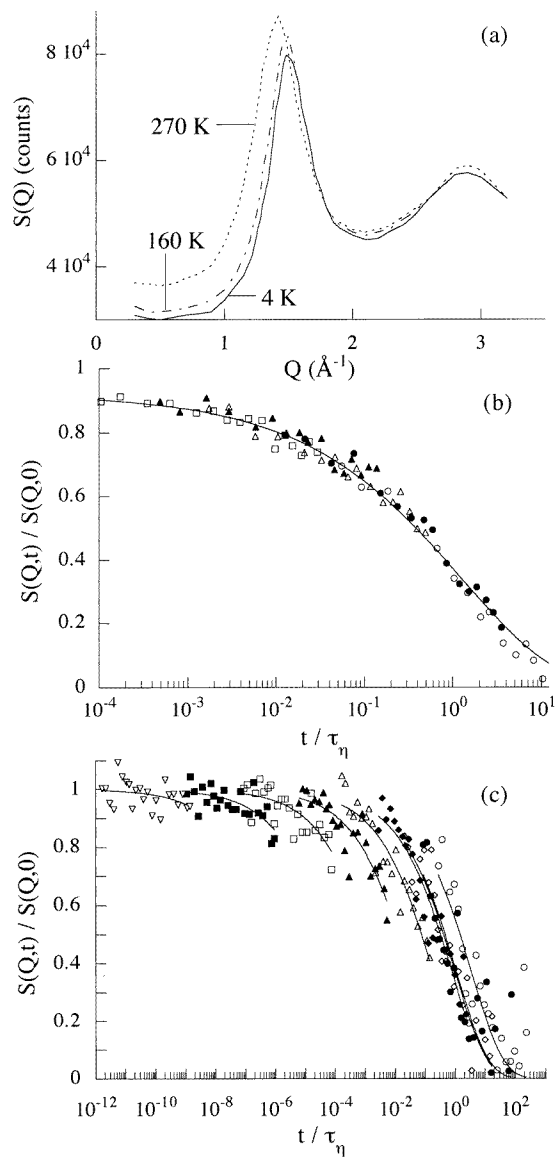


Figure 1. (a) Static structure factor obtained by D1B (ILL) for deuterated PB at different temperatures (extracted from [6]). (b) Scaling representation of the NSE data at 1.48 \AA^{-1} (\circ 280 K; \bullet 260 K; \triangle 240 K; \blacktriangle 230 K; \square 220 K); (c) the same kind of representation for 2.71 \AA^{-1} (\circ 300 K; \bullet 280 K; \diamond 260 K; \blacklozenge 240 K; \triangle 220 K; \blacktriangle 205 K; \square 190 K; \blacksquare 180 K; ∇ 170 K). Solid lines correspond to KWW functions (see text).

same scaling with data taken at the second, the intrachain peak, we obtain a strikingly different result (figure 1(c)). Here the spectra do not assemble to a master curve but keep their identity. Obviously at the first two peaks of $S(Q)$ we observe different dynamics. While at the first peak the spectra shift with the viscosity shift factor, at the second peak an inspection of the temperature dependence reveals an Arrhenius-like behaviour with the same activation energy as that of the dielectric β -relaxation.

Qualitatively the experimental results follow the expectation from our considerations on the dynamic structure factor. As a consequence of the $1/S(Q)$ renormalization following equation (3) the contributions of the secondary process are strongly suppressed at Q_{max} . Therefore at the position of the first structure factor peak the dynamic structure factor is selective for the diffusive α -relaxation. At higher Q values first the quasielastic contribution becomes stronger ($(1 - (\sin Qd)/Qd)$ increases!) and secondly the effect of renormalization becomes weaker. Here $S(Q, t)/S(Q)$ becomes increasingly sensitive to local jump processes.

The PB spectra were quantitatively evaluated in terms of the structure factor presented in equations (2)–(5). Assuming pointlike uncorrelated jumpers (equation (3)) a jump distance of $d = 1.5 \text{ \AA}$ for the local process was obtained. We note that for the time scale a so far unexplained upwards shift by two orders of magnitude of the neutron compared to the dielectric results was found. Applying equation (2) and considering rotations of the stiff *cis*- and *trans*-groups as responsible for the local process a large angle rotation needs to be assumed (figure 2). The evaluation confirmed the convolution approach of the α - and β -processes and stimulated its application also for the evaluation of dielectric spectra, where normally the loss spectra due to different relaxation processes are added [1]. A number of apparent discrepancies in particular concerning the temperature dependence of the α -relaxation as seen by dielectric spectroscopy and by mechanical relaxation could be removed thereby [4].

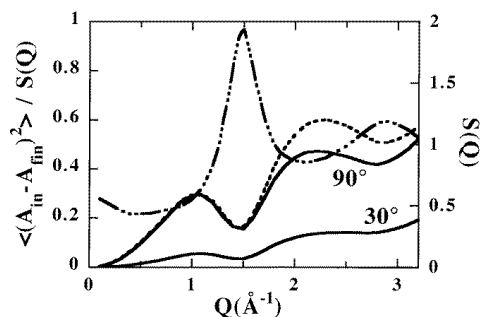


Figure 2. Inelastic contributions to the dynamic structure factor for 30° and 90° rotations of *cis*-groups in PB. The two dashed lines show the static structure factor and the inelastic contribution found from a fit of the NSE data to equation (3).

4. Results on polyisobutylene

In molecular glassformers like glycerol the α -process as it is observed by neutron scattering is a local phenomenon restricted to length scales of the size of the molecule [9]. For larger distances a cross-over to diffusion takes place, where, e.g., stretching of the relaxation function is no longer observed. Polymers on the other hand are connected objects, where the length scale of the monomer does not limit the regime of intrachain processes. It is, thus, interesting to study how the different motional mechanisms, the intrachain Rouse relaxation at length scales above a few monomer sizes, the motions at intermediate scales, the α -process and the local relaxations relate to each other.

For this purpose we have studied the relaxation dynamics of PIB (69 monomers; $M_w = 3800$; $M_w/M_n = 1.02$) in the Q regime $0.03 \text{ \AA}^{-1} \leq Q \leq 3 \text{ \AA}^{-1}$ covering all motional processes from the translational diffusion to the local relaxation processes: (i) in order to see the single chain dynamics the single chain structure factor was investigated on a deuterated sample containing 10% labelled protonated chains; (ii) the self-correlation function was investigated on a fully protonated chain and (iii) the pair correlation function was measured on a fully deuterated material.

4.1. Intrachain dynamic structure factor

Figure 3(a) summarizes the results for the average Q -dependent relaxation time $\langle \tau \rangle = \int_0^\infty \varphi(t) dt$ obtained from fitting a KWW function to the single chain dynamic structure factor as well as to the spectra related to the collective motion at two temperatures 390 and 470 K. The experimental results at both temperatures display a near power law behaviour over a large range in Q which appears to be modulated by a weak oscillation in the Q regime where $S(Q)$ displays its peak structures. We note that the characteristic times follow the temperature shift factor given by Ferry [10] on the basis of viscoelastic data. Both the data sets from the single chain structure factor monitoring the intrachain relaxation and the relaxation times from the pair correlation function, which at least at the structure factor peak is sensitive to interchain motion connect smoothly. In figure 3(b) the observed stretching parameters are displayed. Starting from low Q , we first observe $\beta \cong 1$ indicating translational diffusion; then for the intrachain structure factor with increasing Q ($Q \leq 0.15 \text{ \AA}^{-1}$) β falls to a value between 0.6 and 0.7 characteristic for Rouse relaxation before it increases again in the direction towards one (around $Q \cong 0.5 \text{ \AA}^{-1}$) indicating a tendency towards a single Debye process. Compared to the relatively high β values for the intrachain relaxations the collective dynamics is characterized by considerably more important stretching $0.3 \leq \beta \leq 0.6$ without any smooth cross over to the behaviour of the single chain dynamics.

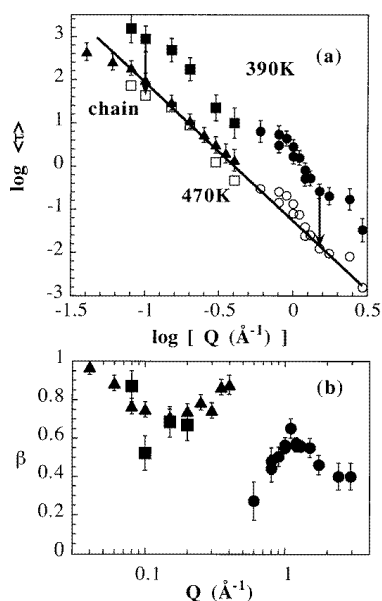


Figure 3. (a) Average relaxation times measured on differently labelled PIB samples at 390 and 470 K. Single chain structure factor at 470 K (\blacktriangle) and 390 K (\blacksquare); collective dynamics at 390 K (\bullet); data at 390 K shifted with the rheological shift factor (\square) and (\circ) [10]; (b) corresponding stretching parameters obtained from fits with stretched exponential relaxation functions.

In the low Q regime non-entangled polymer melts undergo Rouse relaxation. These segmental motions of the chain arise as a consequence of the entropic and stochastic forces acting on a segment. Besides the thermal forces from the heat bath a chain is subject to entropic forces from the conformational chain entropy which stabilize the most probable coiled state.

On the basis of this model the dynamic structure factor may be formulated as follows [11]

$$S(Q, t) = \exp[-D_r Q^2 t] \sum_{n,m} \exp \left\{ -\frac{Q^2}{6} l^2 |n - m| \right. \\ \left. - \frac{2Nl^2 Q^2}{3\pi^2} \sum_p \frac{1}{p^2} \cos \left(\frac{p\pi n}{N} \right) \cos \left(\frac{p\pi m}{N} \right) [1 - \exp(-1/\tau_p)] \right\} \quad (6)$$

where $D_r = kT/\zeta N$ is the translational diffusion coefficient, N the chain length, l the segment length and $1/\tau_p = 3\pi^2 kT p^2 / N^2 l^2 \zeta$ the relaxation rate of the Rouse mode with the mode index p . Figure 4 presents a joint fit of this model to the spectra where the monomeric friction coefficient ζ was the only fit parameter. In this fit only the low Q spectra ($Q \leq 0.15 \text{ \AA}^{-1}$) were fitted, while the theoretical curves for higher Q are predictions on the basis of the low Q measurements. From the comparison it is clear that above $Q \cong 0.15 \text{ \AA}^{-1}$ the Rouse model fails—the experimental spectra decay significantly more slowly than the Rouse model would predict.

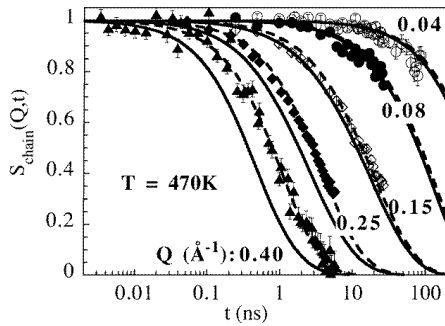


Figure 4. Selected NSE spectra on the single chain structure factor. Solid lines fitted with equation (6); dashed lines fitted under inclusion of stiffness and intrachain damping effects (see text).

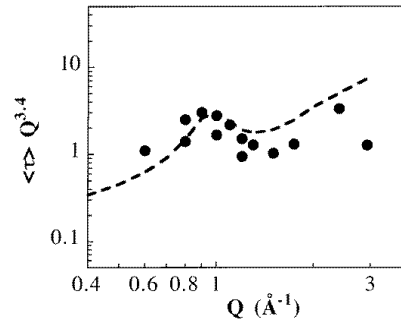


Figure 5. Q -dependent average relaxation times $\langle \tau \rangle$ from fits of the collective structure factor with stretched exponentials. Dashed line: prediction of equation (7).

In contrast to assertions in the literature [12] these deviations cannot be understood as an effect of local stiffness but need to be related to intrachain friction mechanisms like dissipation through jumps over rotational barriers [13]. The dashed lines in figure 4 display a fit considering both local stiffness which is calculated on the basis of the characteristic ratio C_∞ and the chain contour length L ($1/\tau_p = (3\pi^2 kT / N^2 l^2 \zeta_p C_\infty)(p^2 + p^4 \pi^2 C_\infty^2 l_0^2 / 4L^2) p^4$) and an empirical mode damping *ansatz* ($\zeta_p \sim p^\gamma$ with $\gamma = 0.67$ where ζ_p is a mode dependent friction coefficient) allowing a very good description of the experimental results.

4.2. Collective dynamics—pair correlation

In order to connect to the collective dynamics we apply the ‘De Gennes narrowing’ prescription by Sköld [14] according to which the collective structure factor due to pair correlations may be approximated by the self-correlation in renormalizing the Q scale

$$S_{coll}(Q, t) = S_{self} \left(\frac{Q}{\sqrt{S(Q)}}, t \right) S(Q). \quad (7)$$

Motivated by the PRISM theory [15] instead of the self-correlation function, we introduce the normalized single chain structure factor discussed above. Figure 5 compares the measured

average relaxation times $\langle \tau \rangle$ for $S_{coll}(Q, t)$ with those predicted on the basis of the modified Sköld equation (7). The nearly quantitative agreement seems to indicate that like in simple liquids to a large extent the collective dynamics in the neighbourhood of the first peak in $S(Q)$ may be understood by the renormalized single chain dynamics.

While this statement seems to hold for the average relaxation times, it certainly needs to be modified for the stretching of the relaxation function. As could be seen from figure 4 the collective response is significantly more stretched than the single chain structure factor. Obviously the specific interchain interactions manifest themselves in this quantity.

4.3. Self-correlation function

We now switch to the self-correlation function. In the Gaussian approximation we have

$$S_{self}(Q, t) = \exp \left[-\frac{Q^2}{6} \langle r^2(t) \rangle \right] \quad (8)$$

where $\langle r^2(t) \rangle$ is the mean squared displacement of the atomic motion. For a stretched exponential shape equation (8) demands

$$\langle r^2(t) \rangle = 6\tilde{D}t^\beta \quad (9)$$

or a characteristic Q -dependent relaxation time

$$\tau_{KWW} = Q^{2/\beta} \tilde{D}^{-1/\beta} \quad (10)$$

see equation (5). Thus an experimental proof of the validity of equations (8)–(10) would stress the spatially homogeneous nature of the underlying motional process and qualify it as due to backwards correlated sublinear diffusion. In order not to interfere with local relaxation processes on the one hand and with Rouse relaxation on the other hand, we studied the self-correlation function in the Q regime $0.15 \text{ \AA}^{-1} \leq Q \leq 1 \text{ \AA}^{-1}$ [7]. Figure 6 displays the resulting Q -dependent characteristic times $(\tau_{KWW})^\beta$ and compares them with the Q^{-2} law which is expected according to equation (10).

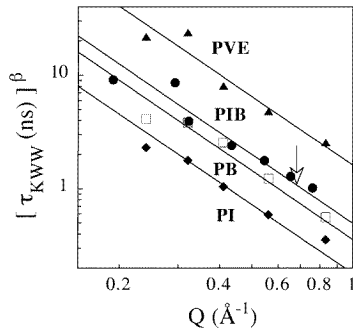


Figure 6. Kohlrausch–William–Watts times $[\tau_{KWW}(Q)]^\beta$ obtained from a fit of incoherent neutron scattering results on PVE at $T = 340 \text{ K}$ (\blacktriangle); PIB at $T = 365 \text{ K}$ (\bullet), PB at $T = 280 \text{ K}$ (\square) and PI at $T = 340 \text{ K}$ (\blacklozenge). The solid lines display Q^{-2} -law expected from equation (10). The arrow displays the value of τ_α from dielectric spectroscopy [6] for the case of PIB.

As may be seen, not only for PIB but also for polyvinylether (PVE), PB and polyisoprene (PI) the Gaussian approximation is valid within experimental uncertainty. The motional processes under consideration take place at length scales shorter than those of the Rouse relaxation (failure of the Rouse model for PIB above $Q = 0.15 \text{ \AA}^{-1}$) and time scales

comparable with the α time scale (see arrow in figure 6). Thus, the neutron results on the self-correlation function show that at these length and time scales the motional processes are homogeneous in space and time and are a consequence of sublinear diffusion. (For an extended discussion of this point see Colmenero *et al* in this proceedings.)

4.4. Observation of the α -process at the structure factor maximum

As outlined in section 2, at the structure factor maximum a study of $S(Q, t)$ is particularly sensitive to the α -relaxation. For PIB, which is one of the most investigated polymers, rheological experiments e.g. on the temperature dependent compliance reveal a different temperature dependent shift factor [10] than spectroscopic techniques like NMR [16] and ESR [17]. It is therefore interesting to compare NSE measurements of $S(Q, t)$ at Q_{max} with predicted spectroscopic and rheological temperature laws. Figure 7 displays time temperature shifted NSE spectra taken at different momentum transfers. In the upper part we display the outcome of shifting with the rheological shift factor a_F [10]. We observe a collapse of all spectra onto a single master curve which can be well described by a stretched exponential. While at Q_{max} the stretching exponent $\beta = 0.55$ agrees with the rheological area, with increasing Q the stretching increases, while the temperature dependence appears not to be affected. In the lower part of figure 7 we present a scaling approach of the NSE data at Q_{max} based on a typical spectroscopic shift factor [17]. Obviously, this scaling does not assemble the spectra from a master curve.

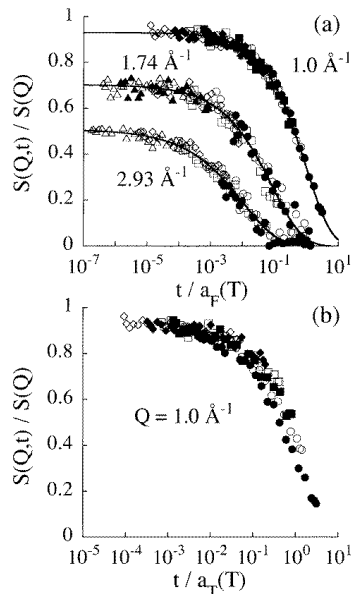


Figure 7. Scaling representation of the NSE spectra using the shift factors given by Ferry [10] (a) and Törmälä [17] (b). The reference temperature is 390 K. (a) also includes master curves obtained by shifting spectra $Q = 1.74 \text{ \AA}^{-1}$ and 2.93 \AA^{-1} with the shift factor a_F . Symbols correspond to different temperatures: 270K (Δ); 280 K (\blacktriangle); 300 K (\diamond); 320 K (\blacklozenge); 335 K (\square); 350 K (\blacksquare); 365 K (\circ) and 390 K (\bullet). Solid lines are fits to KWW functions.

In Q_{max} the pair correlation function is dominated by the relative motion of adjacent chains. The observation that both mechanical relaxation as well as the pair correlation function at Q_{max} are described by the same temperature and time dependent relaxation function strongly indicates that the temperature and time dependence of the mechanical relaxation relates to the

relative chain motion on the level of adjacent chains. On the other hand the discrepancies with the temperature law based on the spectroscopic data which in principle are also sensitive to microscopic motions show that those data, in particular NMR, are not selective for specific dynamics like the pair correlation function but subsume all local motions including segmental relaxations which apparently leads to a weaker temperature dependence.

4.5. Local motion

Other than for PB, in the case of PIB at all Q values (including those corresponding to the second structure factor peak ($Q = 2.93 \text{ \AA}^{-1}$)) shifting with the rheological shift factor $aF(t)$ leads to experimentally acceptable single master curves. Depending on Q , however, the relaxation times and the stretching parameters change (see figure 3(b)). Stretched exponential functions can be interpreted and represented by distributions of relaxation times $g(\ln \tau)$. The observation that away from Q_{max} the NSE spectra decay in a broader time range indicates the presence of extra relaxation processes not contributing to the α -process. However, while in the case of PB at high Q the secondary relaxation processes dominate the spectra—an Arrhenius temperature law characteristic for the dielectric β -process is observed—for PIB the contribution of the β -process only induces shape change and must be much weaker.

A quantitative evaluation in terms of the dynamic structure factor of equations (3) to (5) as expected yields a very small β -jump distance of only $d = 0.6\text{--}0.75 \text{ \AA}$ [5]. As in the case of PB the evaluation was based on the dielectric results for the β -process in PIB and here other than for PB a very good agreement also with respect to the absolute relaxation rates was found.

Assuming everything was settled, the outcome of a study of the self-correlation function came as a big surprise. The essence of these results is displayed in figure 8 where the elastic incoherent structure factor (EISF) for PIB is shown. The EISF ($t \rightarrow \infty$), being the Fourier transformed of the asymptotic part of the self-correlation function for a particular process active in the temperature range under consideration, bears information on the spatial extent of this motional process. The dashed lines in figure 8 correspond to jumps in a double minimum potential with $d = 2.7 \text{ \AA}$; the solid lines display the expectation for a methyl group rotation. These data show that a jump distance of $d = 0.7 \text{ \AA}$ disagrees completely with the observed EISF.

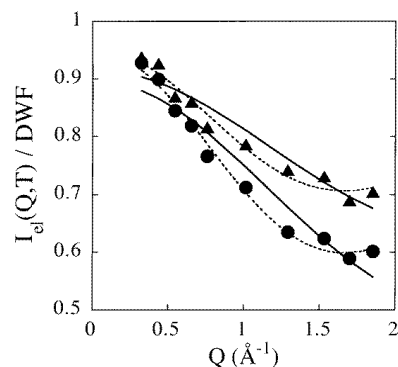


Figure 8. EISF for the local relaxation process in PIB [6]. The symbols correspond to $T = 260 \text{ K}$ (\blacktriangle) and $T = 280 \text{ K}$ (\bullet). The dashed line corresponds to a fit to a two site jump process ($d = 2.7 \text{ \AA}$); the solid lines describe the EISF for a methyl group undergoing 120° jumps.

In order to solve this puzzle one has to understand the different nature of what is seen in a coherent and incoherent experiment. While the self-correlation function measures the total displacement of a tagged particle, the pair correlation function contains transition between atomic configurations (equation (2)). If A_{in} and A_{fin} are equal, as it is the case for methyl group rotation, then this motion is not seen in the coherent scattering. With this in mind the available information may be interpreted as follows. On the one hand earlier NMR results

[17] on this process were explained in terms of methyl group rotation; on the other hand dielectrically such a methyl group motion could not have been observed. Similarly the methyl group motion is invisible in coherent scattering, while it contributes strongly to the self-motion. Thus we have to conclude that in PIB local conformational motion must be directly coupled to methyl group rotation in a way that the methyl group only moves together with the conformational change. We note that such a behaviour has been identified earlier by 2D NMR in polymethylmethacrylate (PMMA), where the side group motion was found to occur together with a backbone motion [18].

5. Summary and conclusion

We presented a simple analytical approach to the pair correlation function of a glass forming polymer and exemplified its validity on neutron spin echo results on PB. Thereafter we displayed new experimental results on PIB where we covered an exceptionally large range of two orders of magnitude in momentum transfer. In the corresponding spatial range all relaxation processes which this polymer is exhibiting were accessed. In the range $0.03 \leq Q \leq 0.15 \text{ \AA}^{-1}$ the data are well described by the Rouse dynamics which also predicts the correct diffusion coefficient. At large Q -values the Rouse picture breaks down and chain specific stiffness and intrachain friction process take over. Turning to the collective dynamics which is studied in the peak regions of $S(Q)$, we find that the observed average relaxation rates are nearly quantitatively predicted by a Sköld type 'De Gennes narrowing' *ansatz*, if we use the normalized single chain dynamic structure factor instead of the prescribed self-correlation function. From incoherent scattering we found that the self-correlation function within experimental uncertainty follows the Gaussian approximation indicating thereby homogeneous dynamics on the time and length scales of the α -process. At the structure factor maximum the temperature dependent NSE data follow the rheological shift factor and demonstrate that rheological flow and interchain motion on the scale of nearest neighbour chains exhibit the same basic temperature dependence. Finally, a combination of dielectric, NMR coherent and incoherent neutron results leads to an understanding of the β -process in PIB as a combined methyl group and main chain motion.

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