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Cage effects on the librational motion in ionomeric homopolymers and block copolymers

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ABSTRACT

The reorientation of a spin probe strongly localized close to the ionic clusters of two different ionomers (one homopolymer and one block copolymer) is investigated by pulsed high-field electron spin resonance (ESR). The study profited from the excellent orientation resolution of the high-field ESR and detects the saturation recovery to measure the spin–lattice relaxation time T_1. Above the glass transition temperature, T_1 exhibits a new regime which exhibits the same features in both polymer phases under study. It is ascribed to the fast librations of the spin probe in the opening cage where it is hosted.

§ 1. INTRODUCTION

Molecular reorientation in disordered systems such as polymers or glasses occurs on different time scales as observed by several techniques (Richert and Blumen 1994, Spiess and Schmidt-Rohr 1994, Plazek and Ngai 1996). On approaching the glass transition, the large-scale motion becomes more and more impeded by the increasing structural constraints (Angell *et al.* 2000). Molecules, or subunits of macromolecules, are surrounded and trapped by rigid pockets, which are usually referred to as cages (Doliwa and Heuer 1998, Kasper *et al.* 1998).

Molecular motion in the presence of cages exhibits different time scales. The fast regime corresponds to the rattling of the trapped particle, the intermediate regime to the escape process of this particle and the slowest regime to the cage relaxation with its collective character. In the last few years, several studies of the cage dynamics by magnetic resonance spectroscopies have been reported (Schmidt-Rohr and Spiess 1994, Saalmueller *et al.* 1996, Xu *et al.* 1996, Vorobiev *et al.* 2000, Leporini *et al.* 2002). In particular, two-dimensional field-step electron–electron double resonance (ELDOR) was used to investigate the reorientation of trapped spin probes and spin labels in glassy polymers. The data analysis yielded libration angles in the cages of 2–10° (Saalmueller *et al.* 1996). The orientation relaxation of aligned, optically active spin probes in glassy polymeric hosts were also investigated (Vorobiev *et al.* 2000). The probe molecules were found in stochastic fast angular motion in the anisotropic cage of the matrix with an average angular displacement which has been estimated as 5–15°.

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The present study aims to characterize the libration dynamics of trapped spin probes in ionomers by resorting to the remarkable orientation resolution of high-field pulsed ESR operating at 95 GHz (Schweiger and Jeschke 2001, Leporini *et al.* 2002). It is a preliminary report on the extensive study of the cage dynamics in polymers in the time window $10\,\mathrm{ps}-100\,\mu\mathrm{s}$ to be published elsewhere (D. Leporini, V. Schädler, U. Wiesner, H.W. Spiess and G. Jeschke 2003, unpublished data).

§2. Background

The main broadening mechanism of the ESR line shape is the coupling between the reorientation of the spin probe and the relaxation of the electron magnetization via the anisotropy of the Zeeman and the hyperfine magnetic interactions. When the molecule rotates, the coupling gives rise to fluctuating magnetic fields acting on the spin system. The resulting phase shifts and transitions relax the magnetization and broaden the resonance. The high resolution of the molecular orientations related to each B value by using soft (selective) pulses is a unique feature of the high-field ESR (Schweiger and Jeschke 2001). In particular, it allows one to characterize the reorientation properties of the spin probes with their X, Y and Z molecular axes, that is the principal axes of the g and the hyperfine tensors, being aligned with the static magnetic field (Leporini *et al.* 2002). In the present paper we are interested in the very fast libration dynamics of the spin probe. To this aim, we employed a saturation recovery experiment to measure the spin–lattice relaxation time T_1 which is sensitive to the fast dynamics occurring with rates close to the electron Larmor frequency $\nu_0 = 94\,\mathrm{GHz}$. We characterize the libration of the three molecular axes of the spin probe by carrying out the saturation recovery experiment at suitable B field values to measure $T_{1\,x}$, $T_{1\,y}$ and $T_{1\,z}$.

§3. Experimental details

End-capped poly(isoprene) (PI-S10) homopolymer ($T_g = 281\,\mathrm{K}$) and poly(styrene)–poly(isoprene) (PS–PI-S24) diblock copolymers ($T_g(\mathrm{PI}) = 265\,\mathrm{K}$; $T_g(\mathrm{PS}) = 355\,\mathrm{K}$) were prepared by anionic polymerization and subsequent introduction of the ionic end groups as described elsewhere (Schädler *et al.* 1996, 1997). The ionic parts of the ionomers segregate and form nanoscale clusters. Their dynamics are severely limited by the poly(isoprene) chains in the homopolymer and becomes even more constrained in the diblock copolymer because of the anchoring of the same chains to the glassy poly(styrene) regions.

The spin probe 4-carboxy-2,2,6,6-tetramethyl-1-piperidinyloxy (4-carboxy-TEMPO) (Aldrich) was converted to its potassium salt (K-TEMPO) by titration with 0.1 mM methanolic KOH. This ensured the effective confinement of the spin probe close to the ionomeric clusters (Pannier *et al.* 2000). The spin probe concentration results in two spin probes per each ionic cluster on average. The radicals have one unpaired electron spin $S = \frac{1}{2}$ subject to hyperfine interaction with the nitrogen nucleus with spin $I = 1$.

The ESR experiments were carried out on a Bruker E680 spectrometer working at 94 GHz (W band) with the Bruker Teraflex probe head. The length of a $\pi/2$ pulse is about 180 ns. The pump pulse of the saturation recovery experiment was $40\,\mu\mathrm{s}$ long. The recovery of the magnetization was detected by a two-pulse spin-echo sequence. It was fitted by an exponential law with the time constant T_1. Variable-temperature measurements with liquid-nitrogen cooling were performed using an Oxford CF935 cryostat and ITC502 temperature control unit.

Figure 1 shows the spin–lattice relaxation time of K-TEMPO dissolved in PI-S10 and PS–PI-S24. The data are scaled by using the reduced temperature T/T_g(PI). For PS–PI-S24 this scaling is expected since the ionic clusters are confined in the PI layers of the lamellar block copolymer. A temperature dependence which is consistent with a square law is observed up to T_g. This dependence has been already reported and ascribed to a second-order Raman process due to intramolecular vibrations of the spin probe (Eaton *et al.* 2001). The spin–lattice relaxation is anisotropic. It exhibits clear uniaxial features with a ratio $T_{1z}/T_{1x,y}$ of about 2.5 in agreement with previous studies on nitroxide-doped single crystals (Eaton *et al.* 2001).

Figure 1 shows that the low-temperature regime extends above the glass transition for T_{1x} and T_{1y} but T_{1z} deviates owing to a larger decrease.

At temperatures higher than the glass transition temperature T_g the cage surrounding the spin probe softens and large-scale cooperative motions unfreeze. The increased free volume is expected to enhance the amplitude and, possibly, to change the rate of the small-angle librations of K-TEMPO in the cage in close analogy with the behaviour of the local relaxation of polymeric and low-molar-mass glasses (Vogel and Rössler 2001). This opens up a further spin–lattice relaxation path. We wish to estimate the contribution to $1/T_1$. At W-band frequencies the Zeeman interaction is the most important because of the large modulation of its anisotropy during the reorientation process. The related expression is

$$\frac{1}{T_1^{lib}} = \left(g^{(2,0)}\right)^2 J_{1,0}(\omega_0) + 2 * \left(g^{(2,2)}\right)^2 J_{1,2}(\omega_0), \tag{1}$$

where $g^{(2,0)}$ and $g^{(2,2)}$ are suitable tensor spherical components and $J_{m,n}(\omega_0)$ is the Fourier transform of the correlation function of the Wigner rotation matrix $D_{l,m}^2(t)$ at the electron Larmor angular frequency ω_0. To evaluate the latter, we assume that
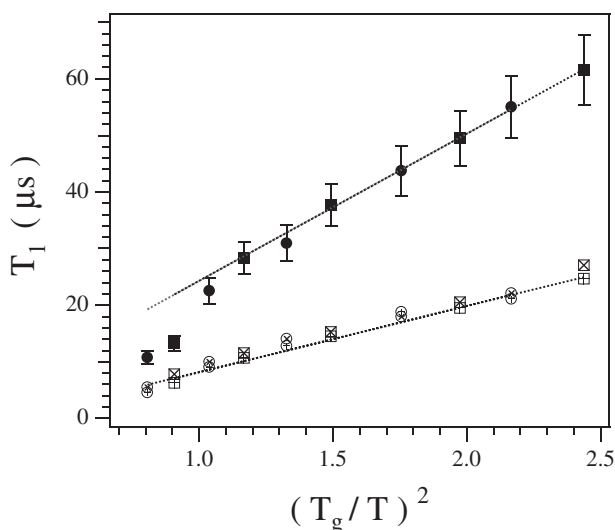

Figure 1. The temperature dependence of the spin–lattice relaxation times T_{1x} ($\boxtimes$, $\otimes$), T_{1y} ($\boxplus$, $\oplus$) and T_{1z} ($\blacksquare$, $\bullet$) of K-TEMPO in PI-S10 ($\boxtimes$, $\boxplus$, $\blacksquare$) and PS–PI-S24 ($\otimes$, $\oplus$, $\bullet$); ($\cdots$), the best-fit results according to a squared-temperature dependence. Note the change in regime above T_g for T_{1z} but not for T_{1x} and T_{1y}.

the molecule rotates around an axis with diffusion coefficient $D_\parallel^{lib}$ and that in turn the latter is wobbling with diffusion coefficient $D_\perp^{lib}$ in a cone of maximum polar angle θ_0 (Szabo 1984). Owing to the weak dependence on $D_\parallel^{lib}$ and to limit the number of adjustable parameters, the above model henceforth will be considered in the limit $D_\parallel^{lib} = 0$.

The total spin–lattice relaxation due to both the Raman and the libration processes time is

$$\frac{1}{T_{1\,i}} = \frac{1}{T_{1\,i}^{Raman}} + \frac{1}{T_{1\,i}^{lib}}, \qquad i = x, y, z. \tag{2}$$

$T_{1\,i}^{Raman}$ is the extrapolation of the low-temperature dependence of $T_{1\,i}$ at the temperature of interest. $T_{1\,i}^{lib}$ is calculated from equation (1) by taking the ith axis as the cone axis. The model parameters are assumed to be independent of the ith axis. This leaves us with two adjustable parameters, namely the cone angle θ_0 and $D_\perp^{lib}$. The best-fit values cover a finite range. Tables 1 and 2 present selected results for PI-S10 and PS–PI-S24 respectively. If $\theta_0 < \theta_{min}$, the amplitude of the libration is too small to relax the longitudinal magnetization effectively and $T_1 \approx T_1^{Raman}$. For K-TEMPO in PI-S10, $\theta_{min} = 8.7°$. For K-TEMPO in PS–PI-S24, $\theta_{min} = 10.9°$. If $\theta_0 > 20°$, the reorientation process would lead to appreciable motional averaging of the continuous-wave ESR line shape. This effect is not observed in the experiment (Leporini *et al.* 2002). The two best-fit values per each cone angle θ_0 are related to the T_1 minimum when $\omega_0\tau \approx 1$, τ being the correlation time of the fluctuations. When $\theta_0 = \theta_{min}$, the two values coincide. At this stage we are unable to rule out one of the two solutions which are both listed in the tables.

Table 1. Best-fit of the spin–lattice relaxation times of K-TEMPO in PI-S10 at 295 K according to the confined-motion model. The experimental values are $T_{1\,x} = T_{1\,y} = 7.5 \pm 0.7\,\mu s$ and $T_{1\,z} = 13.2 \pm 1.3\,\mu s$.

θ_0 (deg)	$D_\perp^{lib}$ (G s^{-1})	$T_{1\,x}$ (μs)	$T_{1\,y}$ (μs)	$T_{1\,z}$ (μs)
8.7	3.3	6.3	6.9	13.2
14.5	1.84	6.3	6.9	13.3
14.5	50	6.3	6.9	13.3
20	1.91	6.3	6.9	13.2
20	175	6.3	6.9	13.2

Table 2. Best fit of the spin–lattice relaxation times of K-TEMPO in PS–PI-S24 at 295 K according to the confined-motion model. The experimental values are $T_{1\,x} = T_{1\,y} = 5.5 \pm 0.7\,\mu s$ and $T_{1\,z} = 10.8 \pm 1.0\,\mu s$.

θ_0 (deg)	$D_\perp^{lib}$ (G s^{-1})	$T_{1\,x}$ (μs)	$T_{1\,y}$ (μs)	$T_{1\,z}$ (μs)
10.9	5.26	5.7	6.6	10.8
14.5	3.03	5.7	6.6	10.8
14.5	29.4	5.7	6.6	10.8
20	3.05	5.7	6.6	10.8
20	111	5.7	6.6	10.8

Previous ELDOR studies of the reorientation of the spin probe 2,2,66-tetra-methyl-4-piperidone-1oxyl (TEMPONE) in glassy polymers, that is below their glass transition, proved the presence of a fast libration motion of amplitude $\alpha_1 = 4°$ and correlation time $\tau \approx 10$ ps (Saalmueller *et al.* 1996). The larger amplitudes listed in tables 1 and 2 are consistent since they refer to a temperature above T_g where the cage opens up.

Our results compare well with studies on aligned, optically active spin probes in glassy polymers, which were found to undergo fast librations in the angular range 5–15° (Vorobiev *et al.* 2000). Furthermore, a recent investigation of the reorientation of polymeric and low-molecular-weight glass formers by ^{2}H + nuclear magnetic resonance (NMR) concluded that it is characterized by an amplitude of less than 10° (Vogel and Rössler 2001).

The larger importance of the librational motion above T_g is either due to the increase in the amplitude or to the faster motion with respect to the glassy phase. The spin–lattice data do not allow us to discriminate between these possibilities. However, a coupling of the fast libration dynamics with the structural relaxation is hardly expected owing to the wide time-scale separation at T_g. On this basis we are more inclined to ascribe the shortening of T_1 above T_g to the increased amplitude of the librations as a consequence of the cage opening. The conclusion agrees with recent NMR results on organic glass formers (Vogel and Rössler 2001).

§5. Conclusions

We investigated the libration of a spin probe strongly localized close to the ionic clusters of two different ionomers (one homopolymer and one copolymer) by measuring its spin–lattice relaxation time T_1 in the glass transition region. The temperature dependence of T_1 exhibits scaling properties if the reduced temperature T/T_g is used. In the glassy regime, T_1 is dominated by intramolecular Raman processes whereas, above T_g, a new regime is observed, which is ascribed to the fast libration of the spin probe in the wider cage where it is hosted.

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