Sensitivity of High-Field Electron Paramagnetic Resonance to the reorientation of molecular guests in glassy polymers

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The reorientation of one paramagnetic molecule in glassy polystyrene is studied by High-Field Electron Paramagnetic Resonance spectroscopy at four different Larmor frequencies between 9.5 and 285 GHz. On increasing the Larmor frequency, the lineshape exhibits larger sensitivity to the rotational motion of the radical. **Unfreezing the rotational dynamics by increasing the reorientation rate leads to considerable line *shifts*, whereas broadening effects are not dominant. The finding evidences that the paramagnetic molecule undergoes small-angle reorientation in the glassy matrix.**
Keywords: Glassy polymers; High-field Electron Paramagnetic Resonance; Rotational dynamics

1 Introduction

During the last few years continuous-wave and pulsed high-field Electron Paramagnetic Resonance spectroscopy (HF-EPR) techniques were developed involving large polarizing magnetic fields, e.g. $B_0 \cong 3T$ corresponding to Larmor frequencies about $95GHz$ (W band), [1] or even larger frequencies [2, 3]. HF-EPR is widely used in studies on soft-matter including biology [4] and polymer science [5, 6, 7]. One major feature is the remarkable orientation resolution due to the increased magnitude of the anisotropic Zeeman interaction leading to a wider distribution of resonance frequencies. **It became clearer in the last decade that HF-EPR provides more insight**

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into the molecular dynamics than the conventional X-band EPR. A recent topical book [8] and some reviews [4, 9] provide updated coverage of the field.

In the present paper we present a detailed temperature study of the reorientation of a small probe molecule in glassy polystyrene (PS) by HF-EPR at four different Larmor frequencies ($9.5, 95, 190$ and $285\ GHz$). The study proves that, on increasing the Larmor frequency, the lineshape exhibits large sensitivity to the rotational *dynamics* of the radical. **The sensitivity leads to considerable line *shifts*, whereas broadening effects are not dominant. It will be shown that the paramagnetic molecule undergoes small-angle reorientation in the glassy matrix.**

2 EPR background

The EPR signal is detected in paramagnetic systems. Since most polymers are diamagnetic, paramagnetic probe molecules (spin probes) are usually dissolved in them. The main broadening mechanism of the EPR line shape of the spin probe is determined by the coupling between the reorientation of the latter and the relaxation of the electron magnetization $\mathbf{M}$ 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, in turn, broaden and *shift* the different lines contributing to the pattern of the EPR lineshape [8]. From this respect an elementary tool to appreciate the sensitivity of the lineshape to the rotational dynamics is the distance between the outermost peaks of the lineshape ΔB (see [6] for further details). **If the spin probe is frozen, the anisotropies of the Zeeman and hyperfine tensors are not averaged and ΔB is at the maximum value $\Delta B = \Delta B_{\infty}$. When the reorientation rate of the spin probe is still very long but finite, the anisotropies of the magnetic tensors start to be averaged. In this onset regime, if the rotational jumps are *small* , ΔB decreases ($\Delta B < \Delta B_{\infty}$) with limited or negligible broadening effects. Differently, if the rotational jumps are *large*, ΔB is almost unchanged whereas linewidths are more affected. These features are qualitatively known [3]. However, to the best of our knowledge, quantitative studies concerning the above shifts for HF-EPR are missing. Recently, the issue was touched by the present authors [6] and novel results are presented here.**

3 Experimental details

PS was obtained from Aldrich and used as received. The weight-average molecular weight is M_w=230 kg mol^{-1}, polydispersity $M_w/M_n = 1.64$ and T_g=367 K. The free radical used as spin probe was 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) from Aldrich. The spin probe was less then 0.08% in weight. X-band EPR measurements were performed using a Varian (Palo Alto, CA) E112 spectrometer equipped with a Varian E257 temperature con-

trol unit and a homemade data acquisition system. High field high frequency EPR experiments were carried out on the ultrawide-band EPR spectrometer which is detailed elsewhere [10]. The used frequencies of the spectrometer are $95GHz$, $190GHz$ and $285GHz$. All spectra were recorded and stored in a computer for off-line analysis. Further details are given elsewhere [6].

4 Results and discussion

Fig. 1 shows the temperature dependence of the distance ΔB at 9.5 GHz, 95 GHz,190 GHz,285 GHz of the spin probe TEMPO in PS. The evidence that ΔB is still changing at temperatures as low as $50K$ proves that the reorientation motion of TEMPO is detectable even at such low temperatures. According to **the qualitative analysis of ref.[3] and** the findings of ref.[6], the changes of ΔB with the temperature signal that TEMPO in glassy PS, i.e. at $T < T_g$, proceeds by *small* angular jumps. **Note that, according to HF-EPR studies at** $250GHz$ **[3], the almost identical spin probe PDT in supercooled toluene-**d_8**, i.e. at** $T > T_g$**, was found to reorientate by** *large* **jumps. The finding is interesting and will deserve further investigation.**

Fig. 1 clearly shows that at lower frequencies ΔB changes less and proves the higher sensitivity of HF-EPR to the rotational dynamics. Noticeably, as noted above, the small-angle rotational dynamics affects the *position* of the lines contributing to the pattern of the HF-EPR lineshape more than their *width*. In fact, Fig. 2 shows the temperature dependence of the average linewidth of selected lines of the HF-EPR lineshape. It is seen that the width approaches a plateau value below $180K$ signaling less sensitivity to the TEMPO reorientation than the quantity ΔB which is a measure of the position of the lines. The interpretation of the large influence of the rotational dynamics on the *position* of the lines depends on the marked frequency-dependence of the latter [5]. Even an elementary discussion of the effect goes beyond the purpose of the present note and will be presented elsewhere.

5 Conclusions

The reorientation of one paramagnetic molecule in glassy PS is studied by HF-EPR at four different Larmor frequencies. **The findings of the present paper are twofold. First, it provides further experimental and quantitative evidence of the dynamical lineshifts of the HF-EPR lineshape in the onset regime of the small-angle rotational dynamics when the latter unfreezes. Second, it is also found that the reorientation of molecular guests in disordered glasses may proceed by diffusive steps as well and not necessarily by large angular jumps.**

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Figure captions

Figure 1: Temperature dependence of the quantity ΔB of TEMPO in PS at 9.5 GHz, 95 GHz,190 GHz,285 GHz. Dashed line: guide for the eye.

Figure 2: Average linewidth of the three (190 GHz and 285 GHz) , and two (95 GHz) high-field outermost peaks of the lineshape. Inset: width of the high-field outermost peak of the lineshape at 9.5 GHz. See ref.[6] for details.

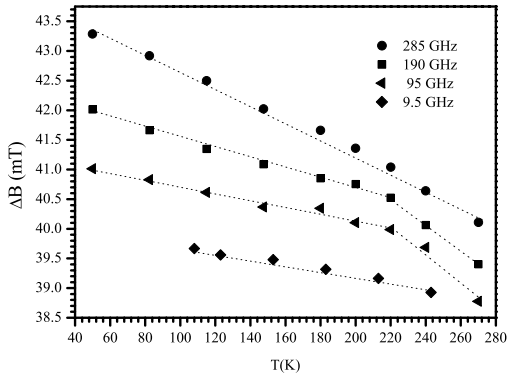
285 GHz
190 GHz
95 GHz
9.5 GHz
ΔB (mT)
T(K)
43.5
43.0
42.5
42.0
41.5
41.0
40.5
40.0
39.5
39.0
38.5
40
60
80
100
120
140
160
180
200
220
240
260
280

FIGURE 1

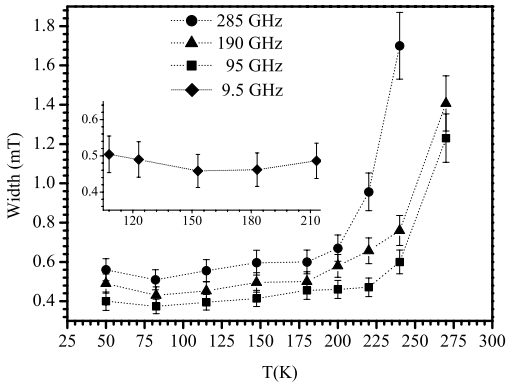

FIGURE 2