Physics of polymers at the high field EPR italian facility: heterogeneities and fast dynamics

V. Bercu [1,2], M. Martinelli[1], C. A. Massa[1], L. A. Pardi[1], D. Leporini *[2,3]

[1] IPCF-CNR, via G.Moruzzi 1, I-56124 Pisa, Italy

[2] Dipartimento di Fisica "Enrico Fermi", Universita' di Pisa, Largo B. Pontecorvo 3, I-56127 Pisa, Italy

[3] SOFT-INFM-CNR, Largo B. Pontecorvo 3, I-56127 Pisa, Italy

Short Title: heterogenities and fast dynamics

Corresponding Author :

Prof. Dino Leporini
Dipartimento di Fisica "Enrico Fermi"
Universita' di Pisa
Largo Pontecorvo n.3
I-56127 Pisa ITALY

FAX: ++39 050 2214 333
Tel : ++39 050 2214 937 (voice)
++39 050 2214 000
E-mail: dino.leporini at df.unipi.it

ABSTRACT

The reorientation of the paramagnetic molecule TEMPO dissolved in glassy polystyrene (PS) is studied by Electron Paramagnetic Resonance spectroscopy (EPR) in a wide range of Larmor frequencies (9-285 Ghz). High-frequency EPR (HF-EPR) reveals that TEMPO rotates by small angular steps with a distribution of correlation times and is able to detect the onset of fast motion of PS. Differently, X-band EPR shows that TEMPO undergoes large-angle reorientation with virtually no distribution of correlation times and largely misses the fast dynamics of PS. A unified view is proposed.

Introduction

The study of glassy solid dynamics is a very active one [1]. Here, one is interested in the temperature range which is, on the one hand, well below the glass transition temperature T_g to neglect aging effect and consider the glassy system as one with constant structure and, on the other hand, high enough to neglect tunneling effects governing the low temperature anomalies of glasses. In previous papers the reorientation of one small paramagnetic molecule (spin probe) in glassy polystyrene (PS) was studied by high-field electron paramagnetic resonance spectroscopy (HF-EPR) [2-4]. Two different regimes separated by a crossover region were evidenced [2,3]. Below 180 K the rotational times are nearly temperature independent with no apparent distribution. In the temperature range of 180-220 K a large increase of the rotational mobility is observed with the widening of the distribution of correlation times which exhibits two components: (i) a deltalike, temperature-independent component representing the fraction of spin probes *w* which persist in the low-temperature dynamics; (ii) a strongly temperature-dependent component, to be described by a power distribution, representing the fraction of spin probes 1-*w* undergoing activated motion over an exponential distribution of barrier heights *g*(*E)*. Above 180 K a steep decrease of *w* is evidenced. The shape and the width of *g*(*E)* do not differ from the reported ones for PS within the errors [4]. The large increase of the rotational mobility of the spin probe at 180 K was ascribed to the onset of the fast dynamics detected by neutron scattering at $T_f = 175 \pm 25$ K [5, 6]. In the present paper we report on a study of the same guest/host system by conventional X-band EPR.

EPR Simulations

The EPR signal is detected in paramagnetic systems. Since most polymers are diamagnetic, 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 **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

broadens the resonance [7]. One important parameter to describe the rotational dynamics of the spin probe is the correlation time τ_l, i.e., the area below the correlation function of the spherical harmonic $Y_{l,0}$. Because of the roughness of the energy landscape and the highly branched character of the free-volume distribution, one expects that the small spin probes undergo jump dynamics in glasses [8-11]. For l =2 a simple rotational jump model yields $\tau_2 = \tau / [\ 1 - \sin(5\theta/2)/5\ \sin(\theta/2)]$, where θ and τ are the size of the angular jump and the mean residence trapping time before a jump takes place, respectively [8,9]. In the limit $\theta << 1$, τ_2 reduces to $\tau_2 = 1/6D = \tau/\theta^2$, where D is the rotational diffusion coefficient, i.e., the isotropic diffusion model is recovered. An efficient numerical method to calculate the EPR line shape is detailed elsewhere [8].

Material and Methods

PS was obtained from Aldrich and used as received. The weight-average molecular weight is M_w = 230 kg/mol, 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 control unit and a homemade data acquisition system [12].

Results

Fig.1 shows the comparison between the experimental results at 108 K and 123 K and the best fits with the isotropic rotational jump model. At such temperatures assuming either rotational diffusion ($\theta = 20^0$) or jump reorientation ($\theta = 80^0$) do not lead to marked differences in the quality of the fits. Fig.2 shows that, on increasing the temperature, jump reorientation provides better agreement with the experiment. Notice that at 183 K the residual broadening of the EPR lineshape decreases due to the averaging of the superhyperfine interaction by the rotation of the methyl groups of TEMPO which unfreezees at about 180 K. Fig.3 shows that the diffusional model largely disagrees with the experiment at 213 K. On the other hand, the jump model agrees better, especially in the plateau-like region between about 3276 G and 3296 G, whose occurrence is a distinctive feature of the jump-like motion [8]. Changing the

rate of the reorientation when τ_2 is in the range of few nanoseconds results in strong changes of the lineshape [8]. This sensitivity helps to identify the range of possible values of τ_2 at 213 K. In fact, the simulations with $\theta = 80^0$ plotted in Fig.3 show the extreme values of τ_2 , i.e. outside that range the fit worsens. Since the deviations from the fit are not remarkable one is led to the conclusion that there is no evidence of a marked distribution of correlation times at 213 K. Fig.4 shows the Arrhenius plot of τ_2. Compared to the huge increase of the rotational mobility evidenced by HF-EPR [2,3], no anomaly is clearly seen at 175 K, the onset temperature of the fast dynamics of PS [5, 6].

Discussion

It is interesting to compare the above results with the ones from HF-EPR concerning TEMPO in PS [2-4]. HF-EPR revealed that : i) TEMPO rotates by small angular steps, i.e. diffusion-like, ii) a broad distribution of correlation times is apparent, especially above 180 K, iii) TEMPO detects the onset of fast dynamics of PS. Differently, according to X-band EPR: i) TEMPO rotates by wide angular jumps, ii) the distribution of correlation times, if any, is narrow, iii) the onset of PS fast-dynamics is largely missed. The two pictures may be understood by reminding two key features of HF-EPR due to the enhanced anisotropy of the Zeeman interaction: i) the large orientation resolution (few degrees) [13], ii) the limited sensitivity to jump reorientation (e.g. see Fig.3 of ref.[3]). From this respect, HF-EPR is able to perceive the possible small-angle motion of TEMPO in the cage of its first neighbours, which appears to be better coupled to the fast dynamics of glassy PS, but is less affected by large-angle reorientations. Differently, the conventional X-band EPR largely misses the finest details of TEMPO reorientation due to the lower orientation resolution but its lineshape exhibits distinctive features which evidence jump reorientation (e.g. the presence of the extended plateau region between about 3276 G and 3296 G [8]).

A remarkable result of the present study is that the jump reorientation of TEMPO , differently from the small-angle motion observed by HF-EPR [2-4], does not exhibit a distribution of correlation times. Previous studies of spin probes in glassformers and polymers carried out by conventional EPR always observed jump reorientation [8,9]. Instead, the absence of a distribution of correlation times was reported for TEMPO in the glassformer OTP [8], but not for TEMPOL in Poly(vinyl acetate [9]. Any conclusion about the above findings for TEMPO in PS must be

conservative at the present stage. However, it must be pointed out that the absence of distribution is observed when the spin probe is loosely coupled to the host as in the present study and in OTP [8] and not when a stronger coupling is present, e.g. H-bonding [9]. This suggests that a weaker coupling facilitates averaging of the heterogeneous distribution at lower angular resolution whereas , at least for TEMPO in PS, it is evidenced by the excellent orientation resolution provided by HF-EPR [2,3].

Acknowledgments

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Figure Legends

Figure 1: Best-fits of the experimental EPR lineshapes of TEMPO in PS at 108 K and 123 K. The magnetic parameters of TEMPO being used in the computations are g_x= 2.00994, g_y= 2.00628, g_z= 2.00212, A_x= 5.8 G, A_y= 5.5 G, A_z= 34.7 G. At 108 K the correlation times τ_2 are 93.45 ns and 30.73 ns for the jump angles $\theta = 20^0$ and 80^0, respectively; a Gaussian convolution with widths 2.35 G ($\theta = 20^0$) and 2.0 G ($\theta = 80^0$) accounted for the residual broadening. At 123 K the correlation times τ_2 are 59.47 ns and 23.5 ns for the jump angles $\theta = 20^0$ and 80^0, respectively; a Gaussian convolution with widths 2.0 G ($\theta = 20^0$) and 1.8 G ($\theta = 80^0$) accounted for the residual broadening.

Figure 2: Best-fits of the experimental EPR lineshapes of TEMPO in PS at 153 K and 183 K. At 153 K the correlation times τ_2 are 33.98 ns and 16.72 ns for the jump angles $\theta = 20^0$ and 80^0, respectively; a Gaussian convolution with widths 1.8 G accounted for the residual broadening. At 183 K the correlation times τ_2 are 25.48 ns and 11.30 ns for the jump angles $\theta = 20^0$ and 80^0, respectively; a Gaussian convolution with widths 1.5 G ($\theta = 20^0$) and 1.1 G ($\theta = 80^0$) accounted for the residual broadening.

Figure 3: Best-fits of the experimental EPR lineshapes of TEMPO in PS at 213 K. A Gaussian convolution with widths 1.3 G ($\theta = 20^0$) and 1.1 G ($\theta = 80^0$) accounted for the residual broadening. See text for details.

Figure 4: Arrhenius plot of the best-fit values of the correlation times τ_2. The onset temperature of the fast dynamics of PS, T_f =175 ± 25 K [5, 6], is marked.

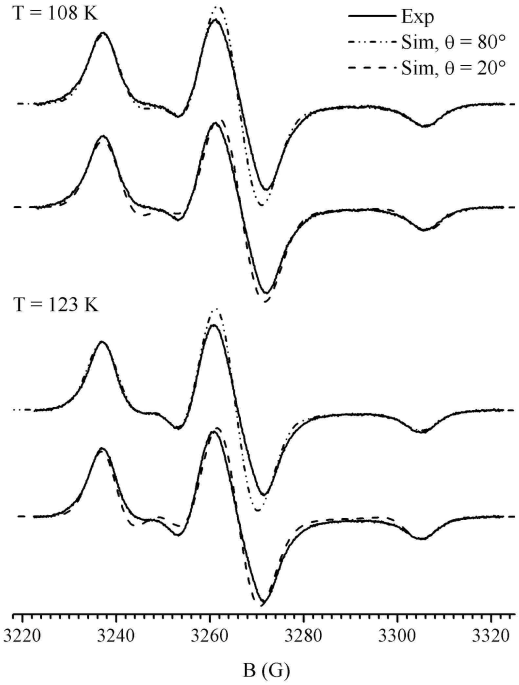

Fig.1
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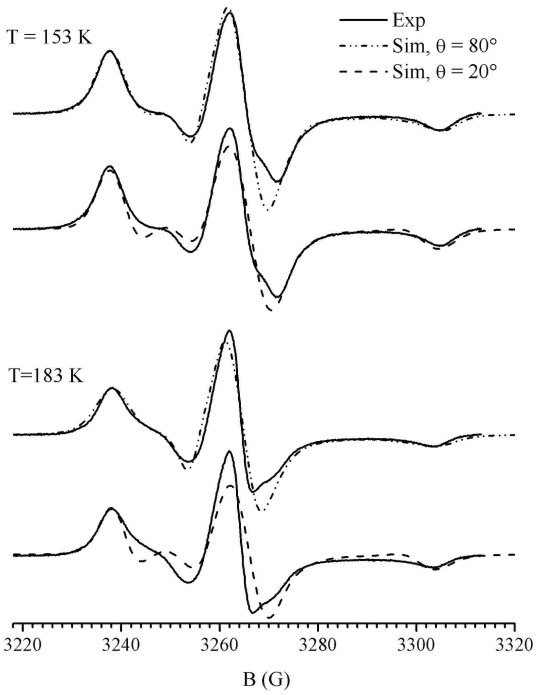

Fig.2
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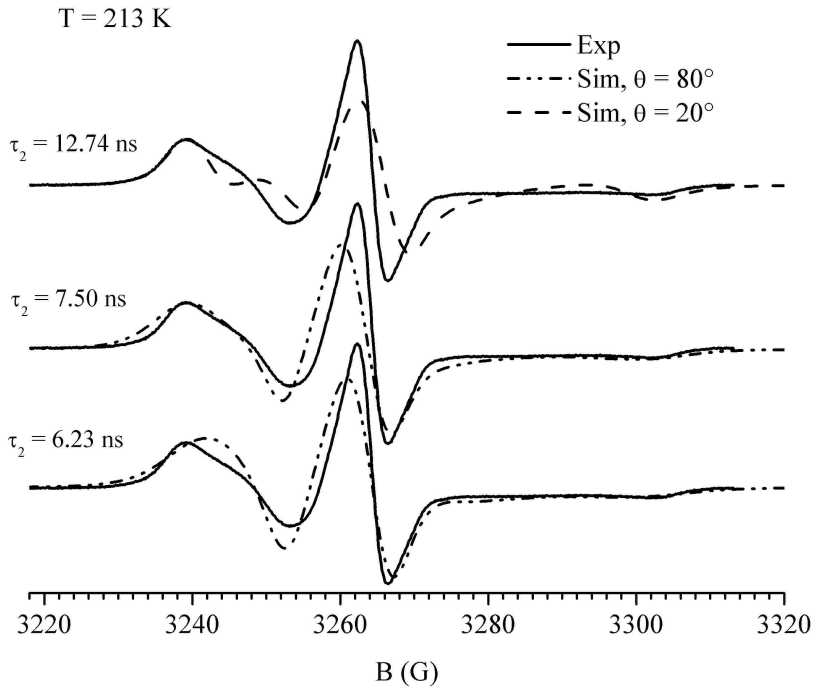

Fig.3

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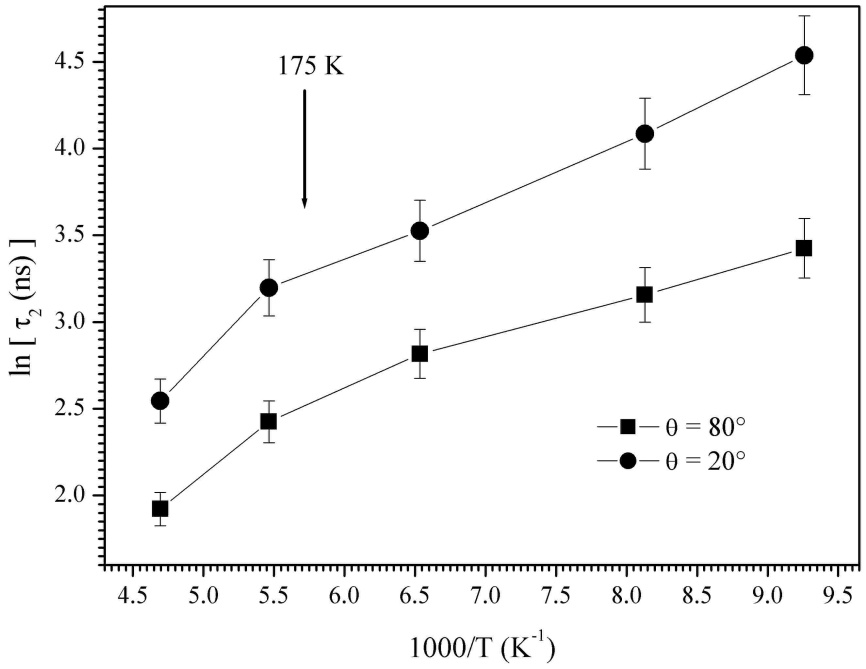

Fig.4

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