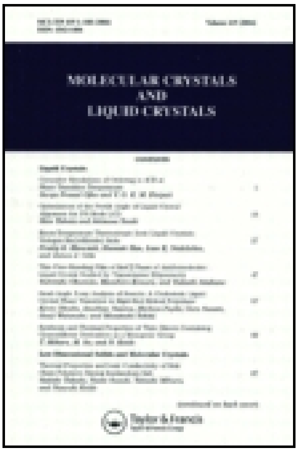

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On the Influence of the Backbone Conformations of a Side Chain Liquid Crystal Polymer on the Fast Rotational Dynamics of a Probe Molecule

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On the Influence of the Backbone Conformations of a Side Chain Liquid Crystal Polymer on the Fast Rotational Dynamics of a Probe Molecule

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Abstract Dynamical processes effective on the nanometer length scale are of interest in polymeric systems due to their importance on the structural properties of the materials. In this study, a nm scale molecular probe is dissolved in a polymeric liquid crystal and its reorientation is studied by non-linear Electron Spin Resonance spectroscopy. Different dynamic behaviours as a function of the temperature are observed. Moreover it is found that the rotational motion of the molecular probe is sensitive to the different conformations of the polymer chain, which strongly depend on the thermal history of the material.

Keywords Liquid Crystal Polymers; Polymeric Conformation; Diffusion Processes; Non Linear *ESR* spectroscopy.

INTRODUCTION

In recent years, many areas of research relating to the study of new and improved devices made from Liquid Crystal Polymers (*LCP*) have enormously developed. *LCP*s have the ability to form partially ordered melts, which show attractive physical, mechanical and rheological properties [1].

Among *LCP*s, Side Chain Liquid Crystal Polymers (*SCLCP*) are an important class of new materials with considerable application potential in a wide range of advanced technologies [1]. In particular, *SCLCP*s with photosensitive azo dye molecules as side groups turn out to be of great interest as media for optical nanorecording [2].

Being the bit stability one of the crucial parameters in storage media, these materials also provide a challenge to our fundamental comprehension of the structural and dynamic factors which promote, stabilize and maintain self-organization in polymeric systems.

The present paper reports on a study of rotational diffusion of a molecular probe with cylindrical symmetry in a *SCLCP*. The non-linear Electron Spin Resonance (*LODESR*) spectroscopy has been used to characterize fast reorientation processes having correlation times τ of about 10^{-10} *s*.

It has been found that the value of the microscopic time τ is sensitive to the conformations of the polymeric chain, which are different on the fast time-scale due to the different thermal treatments of the material. The temperature dependence of time τ follows Vogel-Fulcher (*VF*) forms which, as the temperature decreases in the mesophase region, selectively weaken, signaling the influence of the ordering constraints on the current conformation.

LODESR SPECTROSCOPY: AN OUTLINE

Great attention has been recently devoted to the study of the dynamics of probe molecules dissolved in host matrices, due to its ability to investigate phenomena pertinent to complex systems such as polymers and *LCP*s [3,4], and supercooled molecular systems [5,6]. In particular, the reorientational dynamics of paramagnetic probes, as the nitroxide spin-probes [7], has been studied by linear *ESR* and *LODESR* experiments. Linear *ESR* experiments in *X* band are sensitive to the rotational dynamics with microscopic times in the range of $10^{-12}s < \tau < 10^{-7}s$ [7-9]. On the other hand, *LODESR* experiments in X band are able to explore the $10^{-12}s < \tau < 10^{-5}s$ interval of correlation times [10-15], extending to slower dynamics the sensitivity of the *ESR* spectroscopy. The *LODESR* technique, developed in our laboratory, has been exhaustively described both from experimental and theoretical point of view [10,13,16,17]. A short outline is here provided.

In a *LODESR* experiment, a paramagnetic sample in resonance conditions is irradiated by two transverse σ polarized microwaves with angular frequencies ω_1 and ω_2. The frequencies ω_1 and ω_2 oscillate near to the Larmor frequency $\omega_0 = \gamma H_0$, γ being the gyromagnetic factor and H_0 the static magnetic field acting on the system. For *X* band experiments $\omega_0 /(2\pi) = \nu_0 \approx 10^{10}$ *Hz*. The non-linear response of the spin system to the two transverse fields manifests itself with the presence in the longitudinal magnetization M_z of harmonics oscillating at $m|\omega_2 - \omega_1|$, $m=1, 2,...$.

The *LODESR* experiments are carried out by sweeping the frequency difference between the impinging waves and by detecting the signal of the magnetization M_z parallel to H_0 , at the frequency difference $|\omega_1 - \omega_2|$. The corresponding physical process is the absorption of a photon at ω_1 (ω_2) followed by the emission of a photon at ω_2 (ω_1) [16]. The whole interpretation of the *LODESR* signal foresees the definition of two different dynamical regimes, the slow-fluctuation regime ($\tau > \omega_0^{-1}$) and the fast-fluctuation regime [10,13]. In this work, we are interested in the regime of slow fluctuations. It has been shown [10] that in this case the longitudinal magnetization relaxes to the equilibrium with a single time, the longitudinal relaxation time T_1. T_1 accounts for the energy exchanges between spin system and thermal bath embedding the spin system [18]. Its value depends both on the value of the microscopic time τ characteristic of the molecular fluctuations and on the interactions of the spin Hamiltonian [7-10,13,17,18]. In particular, for dilute solutions of nitroxides spin probes with electronic spin S=1/2 and nuclear spin I=1, the T_1 value is determined by the anisotropy of the Zeeman and hyperfine magnetic interactions and the spin-rotation interaction according to the relationship [13,15]:

$$T_1^{-1} = \left(T_1^{-1}\right)_{Z,H} + \left(T_1^{-1}\right)_{S,R} \tag{1}$$

where

$$\begin{aligned}\left(T_1\right)_{Z,H}^{-1} &= \frac{2}{5}\,\frac{\tau_\perp^{-1}}{\tau_\perp^{-2}+\omega_0^2}\left[\tfrac{1}{2}\left(F_g^{(2,0)}\right)^2+\tfrac{10}{9}\left(F_A^{(2,0)}\right)^2\right]\\ &+\frac{2}{5}\,\frac{\left(3\tau_\perp\right)^{-1}+2\left(3\tau_{//}\right)^{-1}}{\left(\left(3\tau_\perp\right)^{-1}+2\left(3\tau_{//}\right)^{-1}\right)^2+\omega_0^2}\left[\left(F_g^{(2,2)}\right)^2+\tfrac{20}{9}\left(F_A^{(2,2)}\right)^2\right]\end{aligned} \tag{2a}$$

$$\begin{aligned}\left(T_1\right)_{SR}^{-1} &= \frac{2}{27}\left[\left(\delta_{g_x}\right)^2+\left(\delta_{g_y}\right)^2\right]\times\left[\tau_\perp^{-1}+\left(\frac{I_{//}}{I_\perp}\right)^2\left(2\tau_{//}\right)^{-1}\right]\\ &+\frac{2}{27}\left(\delta_{g_z}\right)^2\times\left[\left(2\tau_{//}\right)^{-1}+\left(\frac{I_\perp}{I_{//}}\right)^2\left(2\tau_\perp\right)^{-1}\right]\end{aligned} \tag{2b}$$

In the (2a) and (2b) Equations, $\tau_{//}$ and $\tau_\perp$ account for anisotropic molecular rotations, described by spinning and tumbling correlation times, respectively. $F^{(2,m)}$, with m=0,2, are the spherical components of the tensors $\boldsymbol{g}\ \beta\ H_0$ (Zeeman) and $\boldsymbol{A}$ (hyperfine), β being the Bohr magneton. $\boldsymbol{g}$ and $\boldsymbol{A}$ are diagonal in the molecular frame when expressed in cartesian components. In (2b), $\delta g_i = g_i - g_e$ with $g_e = 2.0023$. $I_{//}$ and $I_\perp$ are the principal values of the moments of inertia of the spin probe.

By inspection, it is seen that the longitudinal relaxation of the magnetization M is driven by the component of the spectral density $J(\omega_0)$, namely by the Fourier transform of the rotational correlation function $C(t)$ calculated at ω_0 [10,13]. Therefore the *LODESR* spectroscopy is mainly sensitive to the decay at short times (of the order of $1/\omega_0$ s) of the correlation function $C(t)$ [4,11,14,15,17,19].

MATERIALS AND EXPERIMENTAL

The *SCLCP* under investigation (acronym *PMA*) was a polymethacrylate containing a (3-methyl-4'-pentyloxy)azobenzene mesogenic unit connected to the main chain at the 4-position by an hexamethylene spacer. Its repeating unit is reported in Figure 1.

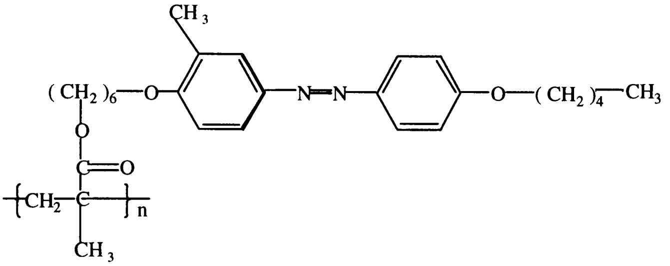

FIGURE 1 Formula of the repeating unit of *PMA*.

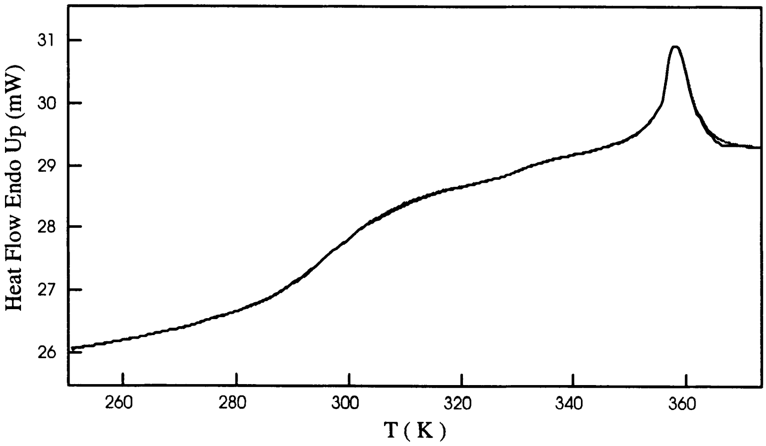

FIGURE 2 *DSC* traces for *PMA* samples.

It was synthesized following a literature general procedure [20]. It was characterized by a weight-average molecular weight of 59000 mol/g and a molar mass distribution of 3.17 .

In Figure 2, Differential Scanning Calorimetry traces of *PMA* samples are shown, recorded on heating at 20 K/min and for two different thermal treatments. The sample was previously quenched under the glass transition temperature at the rate of 200 K/min after an annealing time of 2 h at 383 K (continuous) or 358 K. The thermograms are fully coincident. This means that, from the macroscopic point of view, the samples subjected to the different thermal histories behave in a thoroughly equivalent way, as far as the glass content and the amount of the mesogenic order are concerned. Note the step at about 300 K, probably due to an increased mobility.

The isotropization T_i and glass transition T_g temperatures of *PMA*, obtained by *DSC* thermograms [21], are $T_i = 352.8 \pm 0.1$ K and $T_g = 294 \pm 1$ K, respectively. They did not show any observable change in the temperatures due to the presence of the spin probe at the work concentration. The isotropization enthalpy, calculated as the area under the isotropization peak in the *DSC* experiments, is 1.8 ± 0.1 J/g. According to this value and to *X*-ray diffrattometry, the ordered phase under T_i is nematic.

LODESR studies were performed on *PMA* samples in which *Cholestane* spin probe was dissolved. The structure of *Cholestane* (Aldrich) nitroxide spin probe [7,22] is reported in Figure 3.

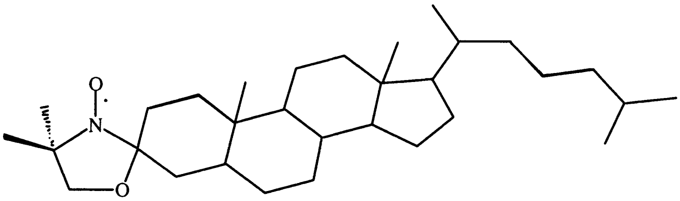

FIGURE 3 Structure of the Cholestane spin probe.

The values of its inertia moments were evaluated by developing *3D* models of the molecule [13,14], leading to the anisotropy ratio ($I_{\perp}/I_{//}$)= 12.4 .

According to the procedure detailed elsewhere [7-9], the components of the magnetic tensors of the spin probe were drawn by the powder lineshape of linear *ESR* experiments recorded at T=142.6 K. The values of the Zeeman and hyperfine tensors expressed in the molecular frame are listed in Table 1.

g_{xx}	g_{yy}	g_{zz}	A_{xx}(gauss)	A_{yy}(gauss)	A_{zz}(gauss)
2.0026	2.0092	2.0069	32.6	5.5	5.0

TABLE 1 Values of the components of the Zeeman and hyperfine (in gauss) tensors in the molecular frame for Cholestane spin probe.

The *Cholestane* spin probe exhibits nearly axial symmetry. Its reorientational dynamics in *PMA* matrix is characterized by a spinning motion, around its own symmetry axis, and by a tumbling motion of the symmetry axis itself, with correlation times $\tau_{//}$ and $\tau_{\perp}$, respectively. The anisotropy ratio between them was previously determined by linear *ESR* measurements. It has been found that $\tau_{\perp}=15\tau_{//}$. Due to this relationship, in this work only the temperature dependence of $\tau_{//}$ will be shown.

The samples were prepared by mixing suitable solutions of polymer and spin probe. The molar concentration *C* of the spin probes, referred to the repeating unit of the polymer, was $C=10^{-2}$.

In this work, particular care has been devoted to the thermal treatment of the samples. They were degassed, and during this process, their temperature was progressively raised, up to the annealing temperature. Annealing procedures have been carried out at two different temperatures, 358 K and 383 K. The samples were degassed overnight. By comparing *ESR* and *LODESR* spectra, recorded for samples in tubes both sealed under nitrogen atmosphere and unsealed, no appreciable differences were detected.

The average molar masses and molar mass distribution of the polymer were determined by size exclusion chromatography with a Jasco *PU*-1580 chromatograph equipped with two Mixed-*C PL* gel columns and using both *UV* (Perkin-Elmer *LC*-75) and refractive index (Jasco 830-*RI*) detection. Standard samples of monodisperse polystyrene were used for calibration.

DSC thermograms were recorded with a *DSC7* Perkin-Elmer calorimeter, equipped with *CCA7*. Sample weights were in the range 8÷10 mg.

LODESR measurements were carried out with a home-built spectrometer, described elsewhere [16].

RESULTS AND DISCUSSION

As already stated, the *LODESR* spectroscopy is sensitive to the dynamics on the fast time-scale of the rotational correlation loss. Therefore, special care has been devoted in this work to maintain the homogeneity of the polymeric material during the measuring time. It is done in order to avoid for the most part the memory effects on the structural relaxation of the polymer and, therefore, on the relaxation on the short time-scale of the coupled molecular rotation.

To this aim, *LODESR* measurements as a function of the temperature have been carried out according to the following procedure. After annealing firstly for 2 hours at the selected temperature T_a, *LODESR* measurements are carried out on cooling for 1 hour.

After this time, the sample is re-heated and maintained at T_a for further 2 hours. The data collection re-begins by carrying out the *LODESR* measurements starting from the lower temperature of the previous step. It has been verified that, if this procedure is followed, the changes in the microscopic times are within 5 %, which corresponds to the error in the experimental data.

In Figure 4 the values of the spinning correlation times $\tau_{//}$, drawn by the *LODESR* experiments and by the Equation 1 and Equation 2, are reported for the annealing at $T_a = 383$ K.

The Figure shows a complex behaviour for the temperature dependence of the rotation of the molecular probe detected by the *LODESR* spectroscopy. Three dynamical regions can be identified.

In the high temperature region, the spinning correlation times of *Cholestane* probe in *PMA* can be nicely reproduced by assuming a Vogel-Fulcher (*VF*) form:

$$\tau = \tau_0 \; exp\left[T_b/\left(T - T_0\right)\right] \tag{3}$$

T_0 and T_b are positive constants dependent also on the spin probe [4,6,12-15].

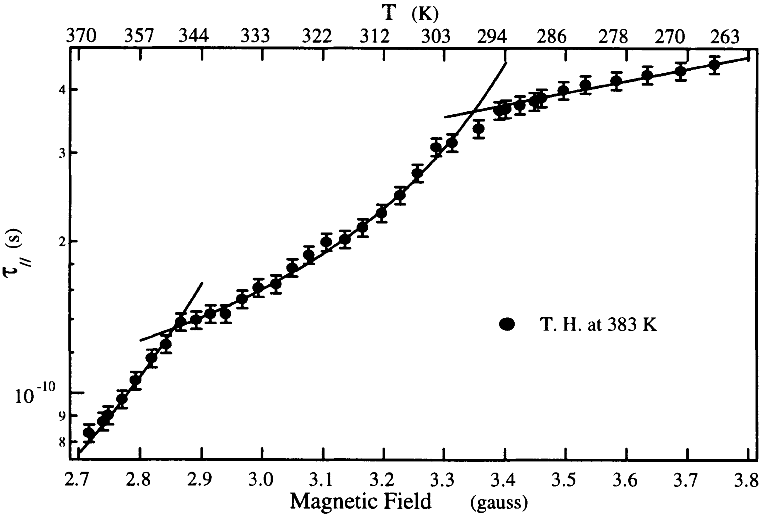

FIGURE 4 Temperature dependence of the spinning correlation times obtained by the *LODESR* spectroscopy for Cholestane dissolved in *PMA* polymer after the thermal treatment at 383 K.

In particular, the value of the T_b parameter is affected by the probe-polymer interaction. T_0 is the Vogel temperature, where the viscosity diverges. Therefore its value is proper to the polymeric matrix. In the present case, the best fit with τ_0= (5.4 ± 0.4) 10^{-12} s, T_0= 257 ± 3 K and T_b= 300 ± 15 K is superimposed to the experimental data. The values of the fitting parameters are reported in Table 2, where the values of the parameters relevant to the annealing at T_a=358K are also shown.

It must be noted that rheological measurements on *PMA*, subjected to the same thermal histories, provided [23] in the temperature region as far as 300 K, a temperature dependence well described by *VF* law with parameters T_0= 259 ± 5 K and T_b= 1300 ± 50 K. As expected, the T_0 value from *LODESR* and rheology coincides.

T_a(K)	T.R.	τ_0(s)	T_b(K)	T_0(K)
383	HT	$(5.4\pm0.4)10^{-12}$	300±15	257±3
383	IT	$(5.9\pm0.3)10^{-11}$	78±5	256±7
358	HT	$(1.4\pm0.1)10^{-11}$	152±5	259±2
358	IT	$(7.3\pm0.3)10^{-11}$	50±3	256±4

TABLE 2 Values of the parameters τ_0 *(s)*, T_b *(K)*, T_0*(K)* of the *VF* laws of the *LODESR* experiments. Acronyms: T_a annealing temperature, *TR* temperature region, *HT* high temperature, *IT* intermediate temperature.

As the temperature is lowered, approximately in the correspondence of the clearing temperature of the *SCLCP*, a second dynamical region sets in for the correlation times. This region extends over about 51 K, ending at the glass transition temperature of *PMA*. In the Figure 4, the curve superimposed to the experimental results is obtained by a *VF* law with τ_0=(5.9 ± 0.3) 10^{-11} s, T_0= 256 ± 7 K and T_b= 78 ± 5 K.

In this dynamical region, the value of the Vogel temperature T_0 is coincident with the one obtained both by *LODESR* experiments in the high temperature region and by rheology. This means that the rotational relaxation is sensitive to the dynamics of the polymer main chain. On the other hand, the pseudoenergy of activation T_b has lowered with respect to its value in the region of high temperature. It implies a greater degree of decoupling of the dynamics of molecular probe from the one of the viscous flow of the polymeric chain [4,12]. In particular, the phenomenon starts in the correspondence of the raising of order into the polymeric matrix.

From the above results, it can be argued that the *LODESR* spectroscopy is sensitive, on the length scale of the molecular probe, to the dynamic interplay between the main chain and the nematic phase developing in the side chain of the host polymer.

In fact, as a consequence of the adopted thermal procedure, the conformation of the polymeric main chain pertaining to a non-equilibrium conformation is frequently refreshed. As the temperature is lowered, such an unrelaxed conformation of the polymeric matrix gets richer and richer of "defects" and more mobile than the equilibrium one. As a consequence, when the clearing temperature T_i is reached on cooling and the nematic order sets in, the dynamics of the main chain is easily perturbed by the presence of the orienting potential; and the new dynamical regime detected by the *LODESR* spectroscopy arises.

For temperatures less than the glass transition temperature T_g of the polymer, a further dynamical change is observed, whose temperature dependence is reproduced by an Arrhenius behaviour. The activation energy amounts to ΔE= 4.5 ± 0.3 KJ/mol. This result suggests that, below T_g, the *Cholestane* probe reorientates in a fixed environment where no structural changes take place.

To gain more insight, in the Figure 5 the dynamics of the *Cholestane* probe, dissolved in the polymeric matrix heat-treated at 358 K and 383 K, are compared.

By rapid inspection the sensitivity of the *LODESR* spectroscopy to the dynamics of the environment is apparent.

For T_a=358K, three regions still characterize the temperature dependence of the spinning correlation times; however the correlation times evidence faster motion in the sample annealed at 358 K.

This result is in agreement with a molecular relaxation driven by a more rigid environment. In fact, greater density of the polymer is obtained by annealing at 358K and it is expected that the generated conformation provides to the molecular rotation a reduced volume with respect to the volume available at the same temperature after the annealing at 383 K.

For T_a=358 K, in the high and intermediate temperature regions, the temperature dependence of the spinning correlation times can be reproduced by *VF* laws, with values (also listed in Table 2) τ_0 =(1.4 ±

0.1)10^{-11} s, $T_0 = 259 \pm 2$ K, $T_b = 152 \pm 5$ K and $\tau_0 = (7.3 \pm 0.3)10^{-11}$s, $T_0 = 256 \pm 4$ K and $T_b = 50 \pm 3$ K respectively.

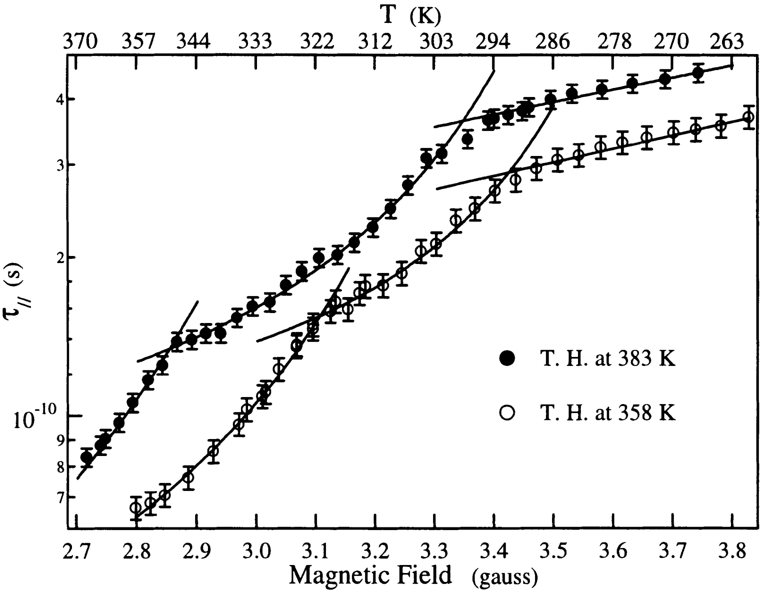

FIGURE 5 Comparison between the temperature dependence of the spinning correlation times by the *LODESR* spectroscopy in samples heat-treated at 358 K and 383 K.

The T_b values signal that the dynamics of the molecular probe undergoes at an ever-increasing level the influence of the site where it is placed. Because the T_b values are smaller, the dynamics following the annealing at 358 K turns out more local in character. In order to "follow" the dynamics of the polymeric chain [4,12] characterized by T_b =1300 K, it needs a greater cooperative level.

It is worthwhile to note that both in the high and intermediate temperature region, the ratios between T_b(383) and T_b(358) are comparable. This finding underlines the heterogeneous character of the relaxation and is according to the picture that the differences, in the relaxation in the different temperature regions, can be ascribed to the effects of the orienting potential on the conformation of the polymeric chain.

The departure from the high temperature behaviour in the sample conditioned at 358 K happens at a temperature lower than the clearing point of the *SCLCP*.

This is probably due to the fact that the current conformation of the polymeric chain pertains to a less mobile environment. Therefore, at short times of the relaxation, the effects imposed on the polymeric conformation by the constraints of the orienting potential become particularly effective at the lower temperatures.

On the other hand, it must be noted that the *DSC* thermograms, on a very longer time scale and for both the thermal histories, signaled the presence of mobility changes in the same range of temperatures.

As in the previous thermal treatment, the low temperature activated regime starts approximately at the glass transition temperature of the *PMA*. The activation energy holds ΔE= 4.9±0.5 KJ/mol. The activation energy coincides for the different thermal treatments, and so it can be concluded that the dynamics of the spinning correlation times is driven by the same dynamical process.

In conclusion, the local character of the *LODESR* spectroscopy, sensitive at short times, evidenced the possibility of detecting, at the level of the molecular scale, the effect of the different annealing procedures on the sample. This is at variance with the findings of the Differential Scanning Calorimetry and Rheology [23] which, for the same thermal histories, did not show any difference.

It has been also shown the possibility of modulating the cooperative degree in the diffusion processes by suitably choosing ranges of temperature and annealing procedures.

In conclusion, from the above findings, it seems that it is possible to identify methods and principles for the definition of the dimension and the stability of the cooperative photoinduced regions.

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