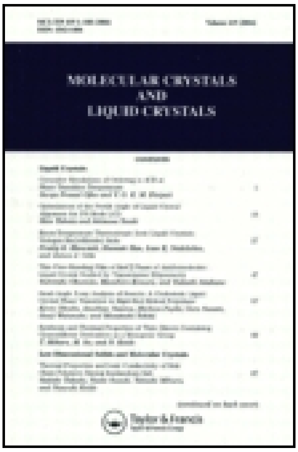


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Microscopic and Collective Dynamics in Supercooled Polymeric Liquid Crystals: Dependence on the Thermal History

L. Andreozzi [a] , E. Chiellini [b] , M. Giordano [a] & D. Leporini [a]
[a] Dipartimento di Fisica, Piazza Torricelli 2, I-56126, Pisa, Italia
[b] Dipartimento di Chimica, Chimica Industriale, Via Risorgimento 35, I-56100, Pisa, Italia

To cite this article: L. Andreozzi , E. Chiellini , M. Giordano & D. Leporini (1995): Microscopic and Collective Dynamics in Supercooled Polymeric Liquid Crystals: Dependence on the Thermal History, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 266:1, 73-83

To link to this article: http://dx.doi.org/10.1080/10587259508033633

Mol. Cryst. Liq. Cryst. 1995, Vol. 266, pp. 73–83
Reprints available directly from the publisher
Photocopying permitted by license only

MICROSCOPIC AND COLLECTIVE DYNAMICS IN SUPERCOOLED POLYMERIC LIQUID CRYSTALS : DEPENDENCE ON THE THERMAL HISTORY

L.ANDREOZZI*, E.CHIELLINI+, M.GIORDANO*, D.LEPORINI*
* Dipartimento di Fisica, Piazza Torricelli 2, I-56126 Pisa, Italia
+ Dipartimento di Chimica e Chimica Industriale, Via Risorgimento
35, I-56100 Pisa, Italia

Abstract The reorientation process of a probe molecule in a supercooled polymeric liquid crystal has been studied by non linear Electron Spin Resonance. The temperature dependence of the correlation time of the spinning motion of the probe $\tau_{||}$ and the collective viscoelastic relaxation, as given by dynamic-mechanical measurements, have been compared. In amorphous samples the Williams-Landel-Ferry law is observed, which in annealed samples is replaced by a dual Arrhenius law broken at the glass transition. A scaling law $\tau_{||} \propto \eta^{\xi}$, η being the polymer viscosity, is found in both amorphous ($\xi = 4.7\ 10^{-2} \pm 2.8\ 10^{-3}$) and partly crystalline samples ($\xi = 5.9\ 10^{-2} \pm 6.5\ \ 10^{-3}$).

INTRODUCTION

Great attention has been recentely paid to polymeric liquid crystalline materials (PLC) both from an applicative and theoretical point of view [1,2]. By properly designing the molecular architecture, it is possible to combine the polymeric character, leading to supercooled and glassy phases even at modest cooling rates, with the richness of structures and phases of anisotropic fluids. PLC assemblies exhibit peculiar features since polymer entropy is antagonistic to the liquid crystalline order[3], whilst their possible use in data storage devices has been demonstrated[1]. Information storage in the glassy phase of a nematic system was first observed by Shibaev *et al.* in 1983 [4]. More recently, Eich and Wendorff[5] described a novel form of erasable optical storage in side chain LCP's whose mesogenic unit contain the photochromic azobenzene group. In that case information is stored in the glassy state as local matrix perturbation induced by the photogenerated *cis*-forms of the azobenzene moieties. Even if a rapid progress is expected in this promising area [6,7] , relatively few microscopic studies have been reported so far [8]. Nonetheless, several topics deserve further investigations. One of the crucial parameters in storage media is the bit stability. In the PLC's case it should be identified with the maintenance of the mesogenic order in the glassy state, which is governed by the interplay between the macroscopic and the microscopic transport properties. The possible relation between the collective and the local diffusion will be addressed in the present study, which profits by our previous investigations of the local rotational brownian motion at the glass transition[9,10]. The collective, viscoelastic relaxation has been studied by dynamic-mechanical analysis whereas the microscopic orientation relaxation has been followed by linear and non-linear Electron Spin Resonance (ESR). The microscopic unit under observation is represented by a radical dissolved as a probe molecule (the so-called spin probe) in the PLC host phase. The following section outlines briefly the opportunities offered by linear and non-linear ESR spectroscopy to the study of complex fluids.

LINEAR AND NON-LINEAR ESR : AN OUTLINE

The Electron Spin Resonance spectroscopy has been extensively used for a long time to study the orientation dynamics of guest paramagnetic molecules dissolved in low molar mass fluids. It must be noted that the ESR signal is the weighted sum of *single particle* contributions and does not result from a *collective* response, which, instead, is detected by dynamic mechanical studies. In general, local and collective relaxation phenomena are not interelated in any obvious way. In simple fluids with low viscosity a rotating molecule is often well described by hydrodynamics. An example is given by the Debye-Stokes law $\tau \propto \eta^{-1}$ connecting the correlation time of the probe orientation τ with the shear viscosity η , *i.e.* a macroscopic quantity. In complex fluids, such as polymers and supercooled fluids, in which different length and time scales exist, local and collective relaxation may be even decoupled or related in more subtle ways [11].

The time scales investigated by linear ESR are in the range $10^{-12}\,s < \tau < 10^{-7}\,s$. This interval covers the relevant values of τ for fluids of low or intermediate viscosity, *e.g.* low molar mass liquid crystals. The lower time scales of polymeric materials are accessible to non-linear ESR which explores the range $10^{-10}\,s < \tau < 10^{-5}\,s$. This novel technique and its applications are reviewed elsewhere[9, 10]. The fact that the time windows accessible to linear and non-linear ESR overlap in the range $10^{-10}\,s < \tau < 10^{-7}\,s$ deserves attention.

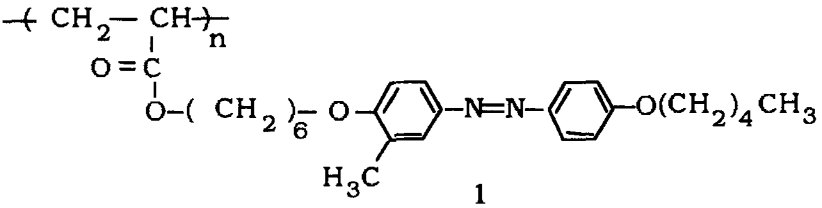
Let us define τ^{ESR} and τ^{NLESR} as the correlation times measured by linear and non linear ESR, respectively. Linear ESR measures τ^{ESR} essentially in terms of the area under the correlation function of the spin probe orientation $\phi(t)$ (*i.e.* the zero frequency value of the one-sided Fourier transform of ϕ). Non linear ESR measures τ^{NLESR} via the one-sided Fourier transform of $\phi(t)$ evaluated at the Larmor frequency $\nu_0 \approx 10\ GHz$ and should be sensitive to the early decay of $\phi(t)$ around $t \approx 10^{-10}\ s$. One may be easily convinced that, if $\phi(t) \approx exp(-t/\tau)$ then $\tau^{ESR} \approx \tau^{NLESR} \approx \tau$. Instead, if $\phi(t)$ exhibits a non-exponential form, $\tau^{ESR} > \tau^{NLESR}$ disequation is holding. Accurate measurements in the supercooled phase of polymer **1** (see below) evidenced that in the glass transition region the ratio τ^{ESR}/τ^{NLESR} becomes as high as 80 [10]. The local ordering of PLC does not explain this ratio [12], which was ascribed to the coupling between local and cooperative relaxation in polymers.

There is a second feature of the non linear ESR which was exploited in the present study. One of the salient properties of polymeric phases is their strong heterogeneous character. Heterogeneities are also expected at microscopic level. Thus, the non exponential decay of $\phi(t)$ is often interpreted in terms of the distribution of local environments. On the other hand, by coupling local and cooperative relaxation one leads to *homogeneous* non-exponential decays, namely *each* spin probe relaxes with the *same* non-exponential $\phi(t)$ (a fairly popular example is represented by the coupling model by Ngai [13]). The comparison of the lineshapes of linear and non-linear ESR puts an upper limit to the lifetime of the local heterogeneities "seen" by the probe. To understand how this occurs a little more detail on ESR techniques is needed. The signal of linear ESR can be interpreted as follows. The sample is magnetized by applying a static magnetic field H_0 on the sample. The selection of a microwave field creates a "transverse" component of the magnetization $\mathcal{M}_\perp$, *i.e.* a component perpendicular to H_0 . The recovery of the equilibrium value $\mathcal{M}_\perp = 0$ is observed. The signal $\mathcal{L}^{ESR}$ is displayed as the Fourier transform of the relaxation of $\mathcal{M}_\perp$. The signal of non-linear ESR can be interpreted as follows. At $t = 0$ the "longitudinal" magnetization $\mathcal{M}_z$, *i.e.* the component parallel to H_0, is set out of equilibrium. The recovery of $\mathcal{M}_z$ to the equilibrium value is followed up to $t = t_1$ ("pre-decay" period) . At $t = t_1$ the residual magnetization is rotated at $\pi/2$ degrees with respect to H_0 and then observed up to $t = t_2 - t_1$ ("analysis" period). The signal is displayed as the Fourier transform of either the pre-decay period or the analysis period yielding the lineshapes $\mathcal{L}_d^{NLESR}$ and $\mathcal{L}_a^{NLESR}$, respectively. Information on τ^{NLESR} are drawn from the linewidth of $\mathcal{L}_d^{NLESR}$, *i.e.* the so called longitudinal relaxation time T_1. It is found that the lineshapes $\mathcal{L}^{ESR}$ and $\mathcal{L}_a^{NLESR}$ are coincident if the orientational heterogeneities have lifetimes shorter than $T_1 \approx 10^{-4}\ s$. Otherwise, $\mathcal{L}_a^{NLESR}$ differs from $\mathcal{L}^{ESR}$ and one estimates $| \mathcal{L}_a^{NLESR} - \mathcal{L}^{ESR} | / \mathcal{L}^{ESR} \approx \Delta T_1/T_1$, where ΔT_1 is the order of magnitude of the distribution of the longitudinal relaxation times due to the long-life orientational heterogeneities [14] . We have to remark that: i) the upper limit T_1 on the lifetime of the orientational heterogeneities may be set just by superimposing $\mathcal{L}_a^{NLESR}$ and $\mathcal{L}^{ESR}$, namely in a model-independent way; ii) the comparison of the intensities of $\mathcal{L}_a^{NLESR}$ and $\mathcal{L}^{ESR}$ is a sensitive tool to expose heterogeneous orientation distribution in that intensities and not linewidths are involved in the procedure.

EXPERIMENTAL

Materials

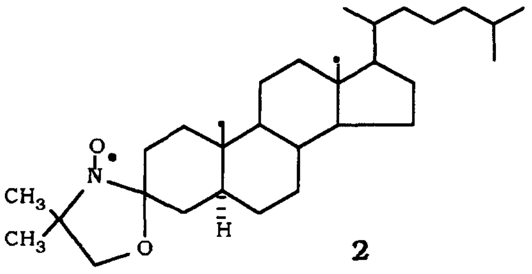
The PLC under investigation is the azobenzene-containing polyacrylate **1**, characterized by repeating units reported in the formula:



1

Polymer **1** was prepared, according to the procedure previously reported by free radical polymerization (polymerization degree : 100÷200) [6,7]. Amorphous samples of the polymer **1** were prepared by quench-cooling into water at *273 K*, whereas partly crystallized samples were subsequently annealed at *303K* for *16 h*. The transition temperatures of the polymer **1** , as measured by calorimetry, are $Tg = 293\ K$, $Tm = 353\ K$, $Ti = 365\ K$

In the ESR study the spin probe of choice is cholestane which has the following structure



2

The rod-like shape of the radical **2** makes it suitable to probe anisotropic environments. The concentration of the spin probe C referred to the monomeric unit was $C = 10^{-2}$. The magnetic parameters of the probe **2** were optimized by careful simulation of the linear ESR lineshape , according to the procedure detailed elsewhere [15]. The best fit set for the components of the Zeeman and hyperfine tensors in the magnetic frame are $g_x = 2.0090$,

$g_y = 2.0075$, $g_z = 2.0030$, $A_x = 6$ *Gauss*, $A_y = 4.9$ *Gauss*, $A_z = 33.9$ *Gauss*, respectively. Experimental evidence shows that the spin probe molecules, even in a partially cristallized sample, remain confined in the amorphous phase [9]. It has been checked that the presence of the spin probe does not lead to any observable change in the DSC thermograms of the polymer **1**.

Experimental Techniques

Dynamic mechanical measurements were performed by a dynamic-mechanical analyzer Perkin Elmer DMA7 equipped with a control system TAC7/DX. A DEC station 325c is on-line committed to the data management. In the investigated frequency range *0.01÷50 Hz* the three-point bending geometry is used. The sample was prepared as a rectangular *18x5x1 mm* sheet, according to the procedure described elsewhere [16]. Frequency scans were carried out after having equilibrated the sample for *30 min* at the temperature of interest.

The linear ESR measurement were carried out on a Bruker ER 200D SRL spectrometer equipped with an X-band microwave bridge. The non-linear ESR spectrometer is described elsewhere [10].

RESULTS AND DISCUSSION

The spin probe **2** exhibits a nearly cylindrical shape and, consequently, the reorientation involves two types of motion : spinning around the symmetry axis and tumbling of the symmetry axis itself. Due to the relatively large molecular mass of the radical (*MW = 472*) it seems proper to assume that the reorientation process has a diffusional character described in terms of two diffusion constants $D_{||}$ and $D_{\perp}$ accounting for the spinning and the tumbling motion of the spin probe, respectively. The predecay display $\mathcal{L}_d^{NLESR}$ of NLESR technique is particularly sensitive to the spinning motion [10]. The correlation time for this motion will be denoted by $\tau_{||} = 1/6D_{||}$ and has been measured from the linewidth $1/T_1$, according to

$$T_1^{-1} = 2\frac{D_{||}}{\omega_0^2}\left\{\frac{1}{5}[(g_x - g_y)\mu_B B]^2 + \frac{4}{9}(A_x - A_y)^2\right\} \qquad (1)$$

Equation (1) assumes $(\omega_0 \tau_{||})^2 >> 1$ (typically $\omega_0 \tau_{||} > 10$) and neglects the contributions to T_1 due to the tumbling motion. The inclusion of the related corrections has proven to be not necessary being $\tau_{\perp}$ not smaller than $10\ \tau_{||}$.

Amorphous samples were analyzed directly after a quench-cooling treatment at *273 K*, whereas partly crystallized samples were furthermore annealed at *303K* for *16 h*. Measurements were carried out after having equilibrated the sample for *30 min* at the temperature of choice. In Fig.1 the temperature dependence of $\tau_{\parallel}$ in both the amorphous and the annealed samples is shown. The frequency scans to record the predecay display $\mathcal{L}_d^{NLESR}$ were carried out by setting the static magnetic field so as to detect the signal with the maximum amplitude (see Fig 2). In the amorphous case the temperature dependence of the spinning motion was fitted by the Williams-Landel-Ferry curve (WLF)

$$\tau_{\parallel} = \tau_0 \, exp(\frac{B}{T - T_\infty}) \qquad (2)$$

where τ_C is a constant, B is a pseudo activation energy and T_∞ is a critical temperature when the spinning motion ideally should be frozen in. The best fit parameters are listed in Table I. In the annealed sample the temperature dependence of the spinning motion exhibits a different trend characterized by a dual Arrhenius activation of the form

$$\tau_{\parallel} = \tau_1 \, exp(\frac{\Delta E}{kT}) \qquad (3)$$

where τ_1 is a constant, ΔE is the activation energy and k is the Boltzmann constant.

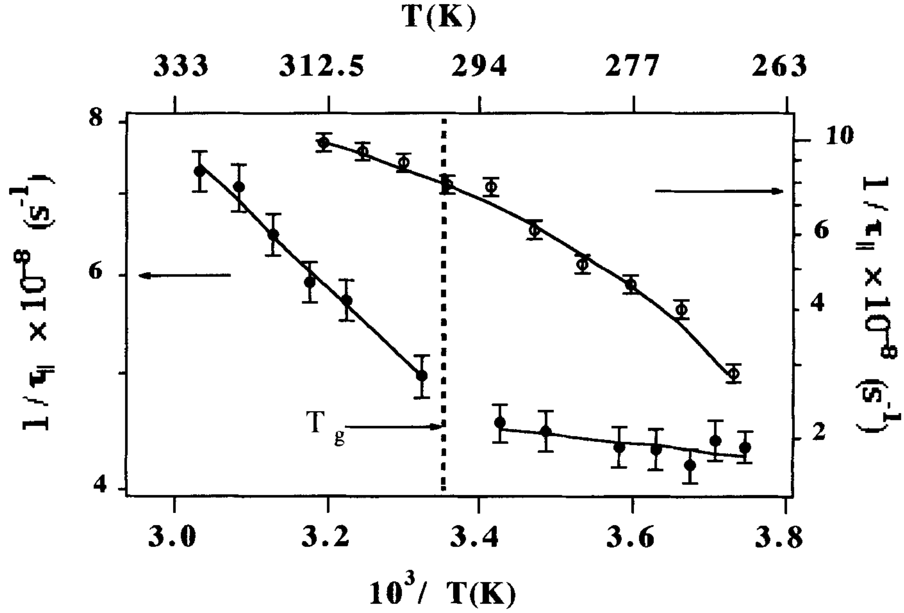


FIGURE 1 Temperature dependence of the spinning correlation time of the spin probe in the amorphous (hollow circles) and the partly crystalline (full circles) polymer. The superimposed curves are best fit curves, according to Equation 2 (amorphous) and Equation 3 (partly crystalline).

Remarkably, the change in the activation energy occurs in a fairly abrupt way at a temperature very close to the calorimetric glass transition T_g of the completely amorphous phase. It must be noted that calorimetry is able to evidence even minor influences of the annealing on the glass transition.

The relaxation processes, corresponding to both local and cooperative motions of polymers, usually extend over several decades on the time scale. In the transition zone from rubberlike to glasslike behaviour the different time scales usually exhibit a unique temperature dependence according to

$$\tau(T) = \tau_0\, a_T \tag{4}$$

where τ_0 is a constant and a_T is the so called shift factor. This peculiar behaviour is a manifestation of the time/temperature superposition principle and is usually referred to as thermorheological simplicity. It implies that data related to different dynamical processes may be collapsed on a single "universal" master curve. The resulting scaling hypothesis underlies a number of theoretical pictures of the glass transition [11,13]. The ESR spectroscopy investigates the reorientation process of a guest radical in the polymeric matrix. In light of the above remarks it is interesting to compare the reorientational local dynamics of the probe with the collective, viscoelastic properties of the polymer **1**. To this purpose, we have measured the storage modulus G' in a wide temperature range at six different frequency values in the range from 0.6 to $40\ Hz$. Both the data for the completely amorphous sample and the annealed one were shifted to recover the master curve and then the temperature dependence of the shift factor a_T [18]. The temperature dependences of the shift factor a_T and the spinning correlation time of the probe $\tau_{||}$ of both the amorphous and the annealed sample were found to be well correlated. Qualitatively, both a_T and $\tau_{||}$ are found to follow the WLF law (Equation (2)) in the amorphous sample, and a dual Arrhenius plot with a break at the glass transition in the

TABLE I WLF and Arrhenius parameters of the shift factor a_T of the polymer and the spinning correlation time $\tau_{||}$ of the probe

	a_T	$\tau_{\parallel}$
$B\ (K)$	1270 ± 20	60 ± 3
$T_\infty\ (K)$	243 ± 3	238 ± 5
$\Delta E_1\ (KJ\ mol^{-1})$	23 ± 1	1.3 ± 0.1
$\Delta E_2\ (KJ\ mol^{-1})$	190 ± 5	11.3 ± 0.2

annealed sample (Figure 1). Table I summarizes the relevant parameters to compare the ESR and the dynamic-mechanical measurements.

First let us discuss the results on the amorphous polymer where both the viscoelastic properties and the microscopic orientation relaxation follows the WLF law (Equation 2). We note that T_∞ (DMA) $\cong$ T_∞ (NLESR) within the limits of experimental error, whereas $B($ DMA $) \cong 20\, B($NLESR$)$. In a series of papers Vrentas and Duda [19] proposed that the *translational* diffusion constants of a probe molecule and a polymer phase, D_T^m and D_T^p respectively, may be related in the limits of low solute concentrations and temperatures not much below the glass/rubber transition T_g , as

$$D_T^m \propto (D_T^p)^{\xi} \propto a_T^{-\xi} \quad ; \quad \xi = V_m / V_p \tag{5}$$

where V_m and V_p are the critical volumes of the probe and the polymer jumping units, respectively. D_T^p has the WLF form of Equation 2. The Vrentas-Duda theory provides good predictions for rigid molecules, as the probe molecule **2.** It states that both the probe and the polymer diffusion are governed by two WLF laws with the <u>same</u> critical temperature T_∞. Even if in the present work orientation rather than translation diffusion is under observation, our findings agree with the above predictions in that it is found that

$$\tau_{||} \equiv (6D_{||})^{-1} \propto a_T^{\xi} \tag{6}$$

Table I yields $\xi \approx 0.05$. In Equation (5) V_p should be the <u>cooperative</u> volume of the polymer contributing to the viscoelastic motion, whereas V_m ranges in the interval $V_p \geq V_m \geq \overline{V}_m$ where $\overline{V}_m$ is the probe steric volume. If $V_m = V_p$ ("stick" case), then $\xi = 1$ and a strong coupling between the probe molecule and the polymer jumping unit is expected. In other words, the probe molecule sticks into the polymer. In the low-coupling ("slip" case) $V_m = \overline{V}_m$ and one would compare just the steric volume of the probe with the volume of the polymer jumping unit. Let us assume that the slip case takes place. Since the monomer unit of the polymer **1** and the probe **2** have comparable volumes, it follows that the parameter $1/\xi \cong 20$ would approximately estimate the number of cooperating monomers during the viscoelastic relaxation. In fact, since $1/\xi \leq V_p/\overline{V}_m$, only the lower bound to the number of cooperating polymer units $V_p/\overline{V}_m \geq 20$ would be set. The above interpretation relies on the free-volume picture and an assumed solute/solvent low coupling which would be carefully assessed.To support this view, we note that in the investigated range of temperature $\tau_\perp/\tau_{||} \approx 10$. Similar ratios are found in allied systems [20]. The value is relatively close to the ratio $\tau_\perp/\tau_{||} \approx 5 \div 10$ which is usually found in low molar mass fluids [21], and expected on the basis of the aspect ratio of the probe

($\tau_{\perp}/\tau_{\parallel} = 4.7$)[21]. In oriented multibilayers it is found $\tau_{\perp}/\tau_{\parallel} > 100$[22]. Few reports have investigated the relation, if any, between the diffusion of macromolecules and the diffusion of large penetrants in the latter ones. Ehlich and Sillescu have studied by forced Rayleigh scattering the translation diffusion of dye molecules in several polymers and interpreted their results in terms of the Vrentas-Duda theory [23]. They found that the translational diffusion constant of the guest molecule and the polymer matrix ideally vanish at the same critical temperatures T_{∞} . In their case $0.5 \le \xi \le 0.84$.

Let us discuss now the effects of the annealing period on the amorphous sample. During the annealing time, crystallization takes place. It has been shown elsewhere [9,10] that the spin probe is expelled from the crystalline regions and confined in the residual part

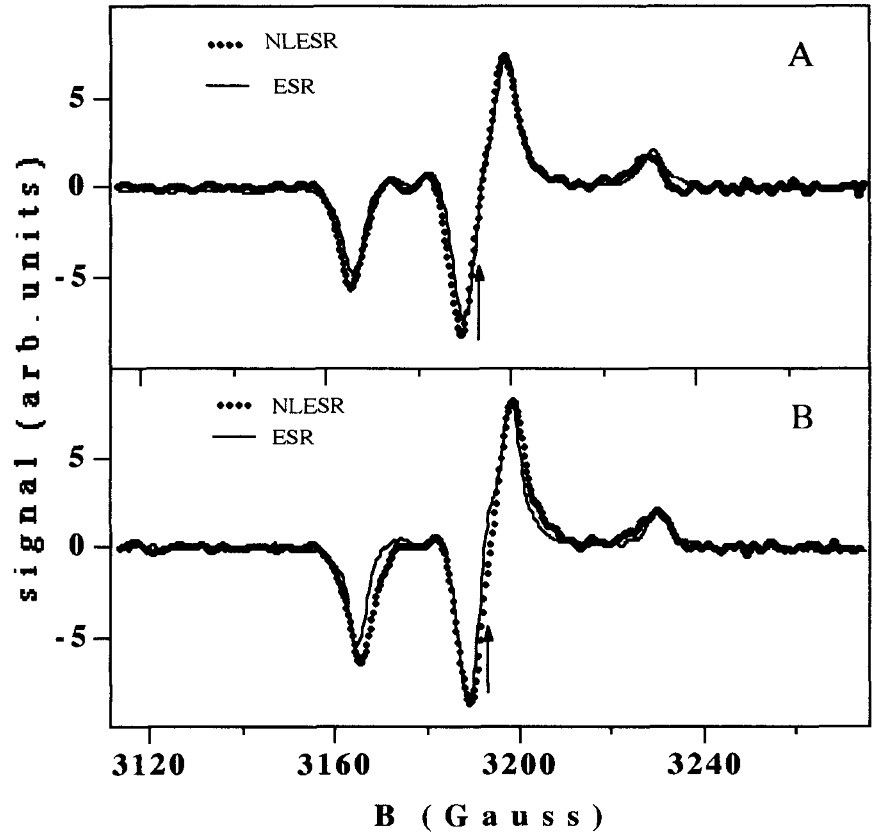


FIGURE 2 Comparison of the lineshapes $\mathcal{L}^{ESR}$ and $\mathcal{L}_a^{NLESR}$. A : amorphous polymer $T = 279.6$ K ; B : annealed polymer $T = 279.9$ K. The arrows denote the value of the static magnetic field which has been chosen to detect the predecay lineshape $\mathcal{L}_d^{NLESR}$.

of the amorphous region, which for polymer **1** is expected to be not smaller than the *70 %*. The presence of a relevant amorphous fraction in the annealed sample is also supported by the fact that the shift procedure to derive a_T is meaningful in that it is known that the time/temperature superposition principle fails in crystalline polymers [18]. The orientation diffusion of the spin probe in the new environment exhibits marked changes with respect to the case of a purely amorphous sample and the WLF trend is replaced by a dual Arrhenius law with upward convexity (see Figure 1). We ascribe the changes to the constraints of the crystalline part on the residual amorphous one. The constraints apparently reduce the degree of cooperativity below T_g , as indicated by the lower activation energy with respect to the amorphous case. A dual Arrhenius plot broken at T_g like the one reported in Fig.1 is usually observed for the translational diffusion of small penetrants (N_2 , H_2 C, Ar, Xe) in amorphous and partly crystalline polymers, where larger molecules usually diffuse according to the WLF law [23,24]. It is tempting to speculate that the downward-to-upward change of the convexity of the temperature dependence of D_T results from an increased free volume available to the penetrant. This view, if applied to rotational diffusion, supports the previous conclusion that the probe molecule rotates by disturbing a lower number of polymeric units in the residual amorphous part of the partly crystalline polymers. Notwithstanding the marked changes in the temperature dependence of both the shift factor a_T and $\tau_{||}$ occurring in the partly crystalline polymer, Equation 6 is still fullfilled with $1/\xi \cong 17$ (see Table I) . This scaling behaviour, which to our best knowledge, has been never observed up to now, is by no means not accounted for by the Vrentas and Duda approach, which deals with amorphous materials [19]. We note that the slight decrease of $1/\xi$ also points to a reduced cooperativity in the annealed polymer.

Finally in Fig.2 we compare the lineshapes of the linear ESR and non linear ESR in the analysis mode $\mathcal{L}^{ESR}$ and $\mathcal{L}_a^{NLESR}$, respectively. The two spectral profiles are virtually coincident when the probe is dissolved in both the amorphous and annealed polymer. In light of the above remarks we conclude that the probe explores all the orientational sites in a time shorter than $T_1 \approx 10^{-4}\ s$ which represents the upper limit on the lifetime of microscopic orientation heterogeneities at $T = 300\ K$. We stress once again that this conclusion follows simply by superposing the two curves and therefore is completely model independent.

REFERENCES

1. Side Chain Liquid Crystal Polymers , edited by C.B.MacArdle (Blackie, Glasgow, 1989).
2. A.M.Donald, A.H.Windle, Liquid Crystalline Polymers (Cambridge

University Press, 1992).

3 M.Warner, in Side Chain Liquid Crystal Polymers , edited by C.B.MacArdle (Blackie, Glasgow, 1989).

4. V. Shibaev, S.Krostromin, N.Plate', S.Ivanov, V. Yu Vetrov and I.Yakovlev Polym.Commun.24, 364 (1983)).

5. M.Eich, and J.H. Wendorff, Makromol.Chem. Rapid.,Commuin., 8, **467** (1987).

6. A.S.Angeloni, D.Caretti, M.Laus, E.Chiellini, and G.Galli, J.Polym. Sci. Polym.Chem.Ed., 29, 1865 (1991).

7. G.Galli, E.Chiellini, M.Laus, D.Caretti and A.S.Angeloni, Makromol. Chem. Rapid Commun., 12, 43 (1991).

8. U.Wiesner, N.Reynolds, C.Boeffel and H.W.Spiess Makromol. Chem. Rapid Commun., 12, 457 (1991).

9. L.Andreozzi, M.P.Fontana, F.Francia, M.Giordano, D.Leporini and M.Rateo, J. Non-Cryst. Solids in press.

10. L.Andreozzi, M.Giordano and D.Leporini, J.Phys.:Conden.Matter in press.

11. J.Jäckle, Rep.Prog.Phys., 49, 171 (1986).

12. G.R.Luckhurst private communication.

13. K.L.Ngai, A.K.Rajagopal, and S.Teitler, J.Chem.Phys., 88, 5086 (1988).

14. S.Mancini, C.Donati and D.Leporini in preparation.

15. L.Andreozzi, M.Giordano and D.Leporini, Appl.Magn.Reson. , 4, 279 (1993).

16. M.Laus, E.Chiellini, L.Andreozzi, D.Ferri and D.Leporini , this volume.

17. L.Andreozzi, C.Donati, M.Giordano and D.Leporini, Phys.Rev.E. , in press.

18. J.D.Ferry, Viscoelastic Properties of Polymers (Wiley, New York, 1980).

19. J.S.Vrentas, J.L.Duda, J.Polym.Sci.: Polym.Phys.Ed., 23, 275 (1985); *ibid.* 23, 289 (1985).

20. K.Wassmer, E.Ohmes, M.Portugall, H.Ringsdord and G.Kothe, J.Am.Chem. Soc. , 107, 1511 (1985).

21. G.R.Luckhurst and C.Zannoni, Proc.R.Soc.Lond.A, 353, 87 (1977).

22. M.A.Hemminga and P.A. de Jager in Spin Labeling Theory and Applications , edited by L.J.Berliner and J.Reuben (Plenum, New York , 1989); H.Tanaka and J.H.Freed, J.Phys.Chem., 88, 6633 (1984).

23. D.Ehlich and H.Sillescu, Macromolecules , 23, 1600 (1990).

24. V.T.Stannett, W.J.Koros, D.R.Paul, H.K.Lonsdale and R.Baker, Adv.Polym.Sci., 32, 80 (1979).