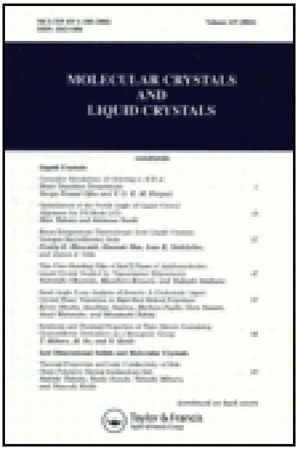

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Debye-Stokes-Einstein Fractional Law in a Polymeric Liquid Crystal: A Non-Linear ESR Study by Using Spin Probes with Different Symmetries

L. Andreozzi [a], F. Cianflone [a], G. Galli [b], M. Giordano [a] & D. Leporini [a]

[a] Dipartimento di Fisica, Piazza Torricelli 2, I-56126, Pisa, Italia

[b] Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126, Pisa, Italia

To cite this article: L. Andreozzi, F. Cianflone, G. Galli, M. Giordano & D. Leporini (1996): Debye-Stokes-Einstein Fractional Law in a Polymeric Liquid Crystal: A Non-Linear ESR Study by Using Spin Probes with Different Symmetries, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 290:1, 1-10

To link to this article: http://dx.doi.org/10.1080/10587259608031886

Mol. Cryst. Liq. Cryst., 1996, Vol. 290, pp. 1–10
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DEBYE-STOKES-EINSTEIN FRACTIONAL LAW IN A POLYMERIC LIQUID CRYSTAL: A NON-LINEAR ESR STUDY BY USING SPIN PROBES WITH DIFFERENT SYMMETRIES.

L. ANDREOZZI*[1], F. CIANFLONE*, G. GALLI$, M. GIORDANO*, D. LEPORINI*
*Dipartimento di Fisica, Piazza Torricelli 2, I-56126 Pisa, Italia
$Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126 Pisa, Italia
1 Corresponding author. E-mail: andreozz@ipifidpt.difi.unipi.it

Abstract The reorientation of spin probes with very different aspect ratios, dissolved in a polymeric liquid crystal, is studied by non-linear Electron Spin Resonance. A scaling law between the rotational correlation time τ and the macroscopic viscosity, as measured via the dynamic shift factor a_T, is found. A discussion on the current interpretations of the scaling, which takes the form $\tau \propto a_T^{\xi}$ with $0 \leq \xi \leq 1$, is given.

INTRODUCTION

Polymeric liquid crystals (PLC) combine the large versatility of synthetic polymers with the functionality of conventional low-molar-mass liquid crystals[1,2]. In the last few years, the experimental evidence that their optical properties may be varied locally in a reversible way attracted the attention to PLC, and especially to side-chain PLC with azo dye molecules as side groups (SCPLC)[2]. In this class of materials, the azo groups undergo photoinduced trans-cis-trans isomerization cycles leading to a local realignment of the optical axis, accompanied by a modulation of the index of refraction at the illuminated spots. The long-term stability of the spot is a key feature to assess SCPLCs as materials of interest for optical storage purposes[2]. The lifetime of the spot is limited by diffusion and specifically by rotational diffusion.

Magnetic resonance spectroscopies provide useful information on the microscopic and mesoscopic motions in polymeric systems. Zeuner *et al.* characterized both local and collective motions of the dipolar coupled protons of a main-chain polymeric liquid crystal by studying the dispersion of their spin lattice relaxation[3]. Local motions involve restricted rotations and internal isomerization. Collective motions were assigned to nematic order director fluctuations.

The present paper reports on a study of rotational diffusion of two probes with nearly spherical and cylindrical symmetries in a SCPLC. To this aim, the non-linear Electron Spin Resonance (LODESR) spectroscopy has been used to characterize fast reorientation processes having correlation times τ about 10^{-10} s. It is found that the temperature dependence of the microscopic time scale τ and the macroscopic transport process, characterized by the dynamic shift factor a_T of the SCPLC elastic modulus, scales according to $\tau \propto a_T^{\xi}$ with $0 \le \xi \le 1$, in agreement with our previous studies[4,5].

ESR SPECTROSCOPIES: AN OUTLINE

The reorientational dynamics of paramagnetic molecules dissolved in host matrices has been studied by ESR experiments[6] for a long time. In the case of the nitroxide spin-probes, used in the present work, linear X band ESR experiments are sensitive to the rotational dynamics for microscopic times ranging in the interval $10^{-12}\ s < \tau < 10^{-7}\ s$. The lower and the upper limits correspond to the fast motion regime and the ultra slow motion regime respectively, in the latter region the value of the correlation time being longer than the inverse of the least anisotropy of the components of the involved magnetic tensors. In viscous liquids, such as supercooled fluids or polymers, the region of interest is the slow motion regime, where the values of the correlation times range approximately between 10^{-9} s and 10^{-7} s. On the other hand, non linear ESR X band experiments are able to explore the $10^{-11}\ s < \tau < 10^{-5}\ s$ interval of correlation times[7-12]: the short time limit is due to the current working-out of the non-linear response theory [13], and its extension is in progress, while the long time one must be ascribed to restrictions of instrumental character. Furthermore, setting up LODESR spectrometers operating at high (14 T) and low (0.03 T) magnetic fields can enlarge the application field of about three orders of magnitude on the whole.

Exhaustive descriptions, both from experimental and theoretical point of view, of the LODESR technique can be found elsewhere[13,14]. In short, LODESR spectroscopy consists of irradiating a paramagnetic sample, in resonance conditions, with two transverse resonating waves at frequencies ν_1 and ν_2, and of detecting the longitudinal ESR signal oscillating at the frequency difference $|\nu_1-\nu_2|$. The LODESR experiments can be carried out in two different ways; by sweeping the external magnetic field, field swept LODESR, or the frequency difference, frequency swept LODESR, between the impinging waves. Both these techniques are valuable tools in understanding the dynamics of complex systems with strong heterogeneous character.

In the slow motion region, it has been proved[15] that, if the tagged molecule experiences all the possible local fields during the observation time of the LODESR spectroscopy, the so called longitudinal relaxation time T_1, the system is homogeneous. As a consequence, the lineshapes of the field swept LODESR and the linear ESR turn out to be proportional[4,12,15]. This condition is observed in the present study: a single longitudinal relaxation time T_1 is therefore pertinent to all the spin packets of the paramagnetic system. Frequency swept LODESR experiments are of interest here, whose linewidths provide the T_1 value, from which quantitative microscopic dynamical information can be extracted[7,13]. In particular, the longitudinal relaxation time T_1 depends on the spectral density $J(\omega_0)$, namely on the Fourier transform of the rotational correlation function C(t) calculated at the Larmor pulsation ω_0 [7,8]. For X band spectroscopies, Larmor frequency holds $\nu_0 \approx 10\ GHz$, therefore the LODESR spectroscopy turns out to be sensitive to the decay at short times, of the order of $10^{-10}\ s$, of the correlation function C(t). In this work, we approximated the correlation decay around $10^{-10}\ s$ with a single exponential and we studied the temperature dependence of the correlation time effective at short times.

MATERIALS

The PLC under investigation is the azobenzene-containing polyacrylate, acronym PA3, whose repeating unit is:

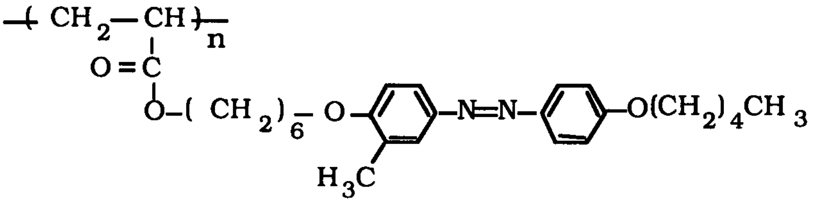

FIGURE 1 Formula of the repeating unit of PA3

and it was synthesized by free radical polymerization (degree of polymerization: 100÷200)[16]. Linear and non linear ESR studies were performed on amorphous PA3 samples in which either Cholestane or Tempo spin probes were dissolved.The structures of Cholestane (**1**) and Tempo (**2**) nitroxide spin probes[6,17] are reported in figure 2.

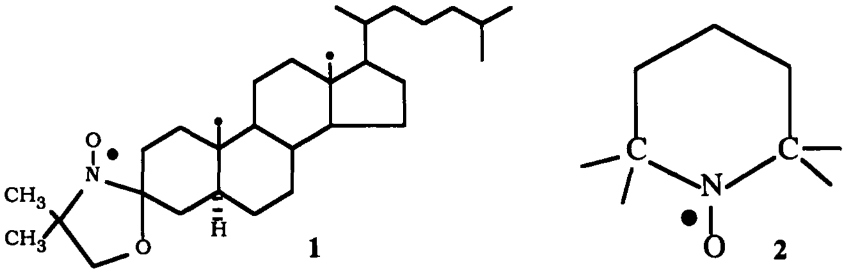

FIGURE 2 Structures of the Cholestane (**1**) and Tempo (**2**) spin probes

The samples were prepared by mixing suitable solutions of polymer and spin probe. After accurate degasing, the tubes were sealed under nitrogen atmosphere. The molar concentration C of the spin probes, referred to the polymer repeating unit, was $C=10^{-2}$. The isotropization, melting and glass transition temperatures of PA3, as obtained by Differential Scanning Calorimetry[10,16], are *368 K*, *353 K*, *293 K* respectively. DSC traces did not show any observable change in these temperatures due to the presence of the spin probes. Amorphous samples of PA3 were obtained by a convenient quenching procedure based on the calorimetric studies reported[10,11] elsewhere.

TABLE 1 Components of the Zeeman and hyperfine (in Gauss) tensors of the spin probes in the magnetic reference frame.

Probe	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}
1	2.0090	2.0075	2.0030	6	4.9	33.9
2	2.0094	2.0055	2.0019	7	6.5	33.9

The values of the components of the magnetic tensors of the spin probes were obtained by simulation of the linear ESR lineshape according to the procedure detailed elsewhere[18]. The values of the Zeeman and hyperfine tensors in the magnetic reference frame of the two spin probes are listed in table 1.

RESULTS AND DISCUSSION

The Cholestane spin probe exhibits nearly axial symmetry. The reorientational dynamics is therefore characterized by a spinning motion around the symmetry axis and a tumbling motion of the symmetry axis itself, having correlation times $\tau_{\parallel}$ and $\tau_{\perp}$, respectively. Linear ESR measurements have shown that the degree of anisotropy in the temperature interval of interest is $\tau_{\perp} = 10\ \tau_{\parallel}$. The spin probe Tempo is nearly a spherical molecule and it is assumed that $\tau_{\parallel} = \tau_{\perp} = \tau$.

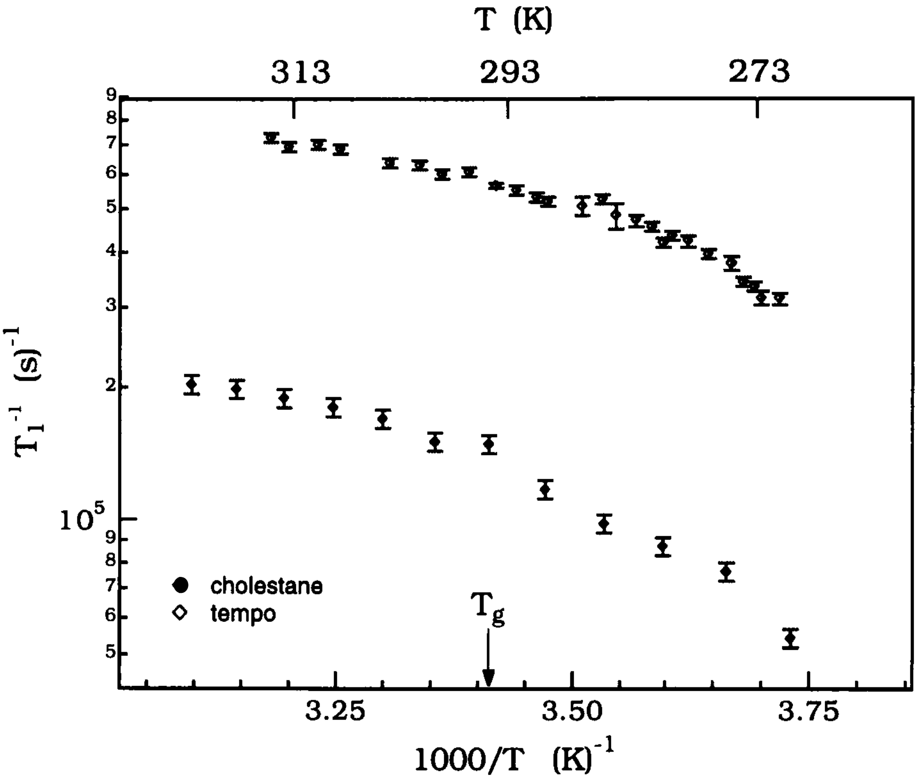

FIGURE 3 Temperature dependence of the longitudinal relaxation time T_1

The temperature dependence of the longitudinal relaxation times T_1 across the glass transition region is shown in figure 3. Owing to the reduced size, the rotational process of Tempo is faster and more effective to relax the longitudinal magnetisation. Rotational correlation times may be drawn from T_1 [8]. It is found:

$$\frac{1}{T_1} = \frac{(2\pi\gamma)^2}{2I+1}\left\{\left(\frac{2}{9}t^2+\frac{1}{10}r^2\right)\frac{\tau_\perp}{1+\omega_0^2\tau_\perp^2}+\left(\frac{2}{3}u^2+\frac{3}{10}s^2\right)\frac{\tilde{\tau}}{1+\omega_0^2\,\tilde{\tau}^2}+\sum_{i=xx,yy,zz}\frac{(g_i - g_e)^2}{9\tau_R}\right\} \quad (1)$$

ω_0 and g_e are the Larmor frequency and the free electron g-value respectively, γ is the gyromagnetic factor and $\tilde{\tau}$ is defined as $\tilde{\tau}^{-1} = (1/3)\,(2\,\tau_{\parallel}^{-1} + \tau_{\perp}^{-1})$. The other parameters are expressed in Gauss in terms of the component of the Landé and hyperfine tensors as: $r =$

$[2g_{zz} - (g_{xx} + g_{yy})]\,H$, $s = (g_{xx} - g_{yy})\,H$, $t = 2\,A_{zz} - (A_{xx} + A_{yy})$, $u = A_{xx} - A_{yy}$ where H is the static magnetic field.

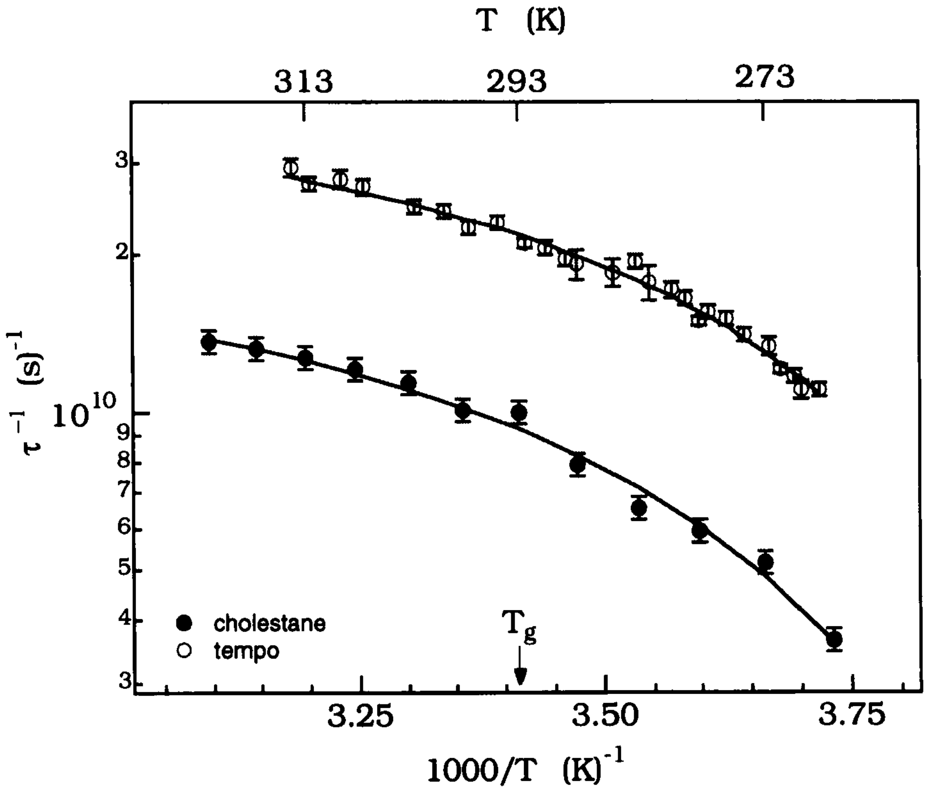

FIGURE 4 Temperature dependence of the rotational correlation times for Cholestane and Tempo spin probes in PA3. In the Cholestane case the correlation time τ refers to the spinning one $\tau_{\parallel}$.

The above expression of the longitudinal relaxation time assumes the spin relaxation to occur due to the anisotropic character of the Zeeman interaction and the hyperfine coupling between the unpaired electron spin and a nucleus having nuclear angular momentum I. In our case $I = 1$, being the electron spin coupled with the ^{14}N nucleus. The last term on the rhs of the equation accounts for the spin-rotation relaxation mechanism[19] with $\tau_R = [(\tau_{\perp})^2\tau_{\parallel}]^{1/3}$ for Cholestane and $\tau_R = \tau$ for Tempo.

The temperature dependence of the correlation times, as drawn from the above expression of T_1, is shown in figure 4. In the case of Cholestane probe $\tau_{\parallel}$ is plotted, since the contribution to T_1 coming from $\tau_{\perp}$ is small. The correction due to the spin rotation is small at the lowest temperatures investigated and larger in Tempo. Tempo rotations are faster than the spinning motion of Cholestane. The plot shows that in both cases the correlation times do not follow an Arrhenius law. Instead, good agreement with the Vogel-Fulcher (VF) form

$$\tau=\tau_0 \exp [B/(T-T_0)] \tag{2}$$

is found in both cases[4,5,9-12]. τ_0 and B are constants dependent on the spin probe, and T_0 is the Vogel temperature.

The best fit parameters are listed in table 2 and compared with the best fit parameters of the dynamic shift factor a_T of the polymer, as drawn from previous dynamic mechanical measurements[20]. a_T provides the temperature dependence of the longest relaxation times of the polymer[21]. Table 2 shows that the Vogel temperatures T_0 of the shift factor a_T and the correlation times $\tau_{\|}$ and τ are equal within the experimental errors. This suggests a scaling law of the form:

TABLE 2 VF analysis of the temperature dependence of the shift factor a_T and the correlation times $\tau_{\|}$, τ

	a_T	$\tau_{\|}$	τ
B (K)	1270±20	66±6	48±9
T_0 (K)	243±3	238±6	238±4

$$\tau, \tau_{\|} \propto a_T^{\xi}, \qquad 0<\xi<1 \tag{3}$$

To substantiate the above remark, the correlation times are plotted versus the shift factor a_T in figure 5. The log-log plots are still consistent with the scaling law (eq.3). In figure 5 a straight line with unit slope, as expected according to the Debye-Stokes-Einstein law (DSE), is also drawn. The decoupling between the rotational microscopic motion of the probes and the macroscopic transport is larger in Tempo. This is expected since Tempo is smaller in size than Cholestane. The difference in size is also evinced by the smaller values of the correlation times of Tempo with respect to the Cholestane spin probe.

The decoupling between the diffusion and the viscosity is expected if the dimension of the tagged particle becomes smaller and smaller. The intriguing aspect is that decoupling seems to occur according to fractional laws such as eq.3.

A fractional version of the Stokes-Einstein law was observed for the translational diffusion in polymers[22] and supercooled fluids[23] where it was related to recent mode coupling theories of the glass transition[24]. Further evidence about the decoupling between rotations and viscosity in supercooled *o*-terphenyl has also been reported[25] and recent ESR studies on the same material provided evidence of a fractional DSE law[26]. In spite of growing experimental evidence, the physical interpretation of the fractional laws and particularly of the exponent ξ is still lacking.

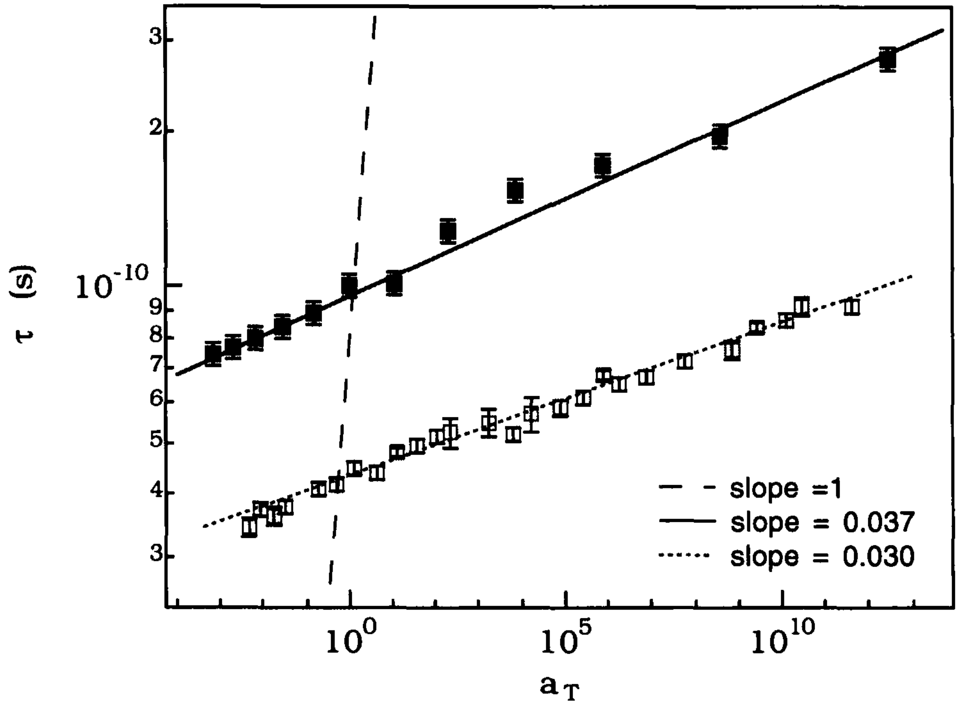

FIGURE 5 Scaling between the rotational correlation times of the Cholestane ■ and Tempo □ spin probes and the shift factor a_T. The straight lines, superimposed to the experimental data, are the best fit according to the scaling law eq.3. Cholestane: $\xi = 0.037 \pm 0.001$; Tempo: $\xi = 0.030 \pm 0.001$. The line with slope 1 is the prediction of the DSE law.

A number of theoretical attempts to account for the fractional Stokes-Einstein law are known[27,28]. However, even if quite promising, these models at the present stage of the development predict the decoupling but not the scaling form. It must be noted that elementary free volume arguments lead to eq.3 with:

$$\xi = V_g / V_h \tag{4}$$

where V_g and V_h are the volume of the guest molecule and the critical (or cooperative) volume of the host phase involved in the diffusion process, respectively[22,29]. This view, which considers the fractional law as mainly due to steric factors, is intriguing in that it provides a route to measure the cooperative volume V_h. The present investigation disagrees with the identification (eq.4) since the ratio between the volumes of the probes is about four whereas the ratio between the ξ exponents is close to one. It must be noted that eq.4 was originally derived for translational diffusion. Our results could imply that the decoupling of the translational diffusion and the rotational diffusion need different theoretical treatments in agreement with the remarks by Douglas[28]. Nonetheless, eq.4 emphasizes the role of the steric (entropic) aspects of the diffusion process and neglects the energy interactions between the tagged particle and the host medium. Moreover, steric aspects of the molecules are simply described by an effective volume even if the role of the roughness of the molecule has been pointed out some time ago by R. Zwanzig[30].

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