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P. Esnault[a]; J. P. Casquilho[a]; F. Volino[a]
[a] CENG, DRF/SPh/PCM, Grenoble Cedex, France

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On the influence of elastic modes on the N.M.R. lineshapes of polymer liquid crystals

by P. ESNAULT, J. P. CASQUILHO and F. VOLINO†
CENG, DRF/SPh/PCM, 85X, 38041 Grenoble Cedex, France

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We have studied the influence of thermally excited orientational fluctuations on the N.M.R. lineshape of a nematic monodomain. The influence is characterized by a static order parameter S_{stat} whose theoretical expression in terms of viscoelastic parameters is derived. This model is applied to the proton N.M.R. spectrum of a thermotropic main chain polymer. The values of S_{stat} are deduced from the study of the changes of the N.M.R. lineshape as a function of the angle between the static magnetic field and the nematic director. Good agreement is obtained with theoretical values calculated using estimated values of the Leslie viscosity coefficients and the Frank elastic constants. The importance of an accurate knowledge of S_{stat} for a number of problems is stressed.

In uniaxial nematic liquid crystals, the thermally induced long range orientational fluctuations of the director are described as the superposition of splay-bend ($\alpha = 1$) and twist-bend ($\alpha = 2$) elastic modes [1]. The usual ways to study these modes are quasi-elastic Rayleigh light scattering [1, 2] and nuclear spin-lattice relaxation [3]. On the other hand, the shape of the nuclear magnetic resonance (N.M.R.) spectra is also affected by these modes. In low molecular mass nematics, the vast majority of these modes is fast on the relevant time scale $\Delta\tau$ (10^{-4}–10^{-6} s) [4]. These modes contribute to the motional narrowing of the lines, but it is not possible to separate this contribution from that of the faster molecular motions. In the more viscous nematic polymers, it may be expected that an appreciable fraction of the modes are slow, producing a static broadening of the lines. A study of this broadening can therefore provide information on these modes and consequently on the viscoelastic properties of the material. This paper presents an example of such a study on a thermotropic nematic polymer.

Following Warner [4], the modes that are slow on the N.M.R. time scale $\Delta\tau$ can be characterized by a static order parameter S_{stat} given by

$$S_{stat} = 1 - \tfrac{3}{2}J, \qquad (1)$$

with

$$J = \frac{kT}{(2\pi)^3}\int_{\mathbf{q}_m}^{\mathbf{q}_{N.M.R.}}\left(\sum_{\alpha=1,2}(K_\alpha q_\perp^2 + K_3 q_z^2 + \chi_a B^2)^{-1}\right)d\mathbf{q}. \qquad (2)$$

In this equation, K_1, K_2, K_3 are the splay, twist and bend Frank elastic constants, $q_\perp$ and q_z are the components of the wavevector $\mathbf{q}$ of the modes perpendicular and parallel to the main director, and χ_a is the anisotropic diamagnetic susceptibility per unit volume of the nematic monodomain embedded in a magnetic flux density $\mathbf{B}$. The integral over the modes extends between a minimum wavevector $q_m \approx 2\pi/L$ (L is a

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† Member of CNRS.

sample dimension) which can be safely taken to zero, and a maximum wavevector $\mathbf{q}_{\text{N.M.R.}}$, which is the wavevector of those modes whose relaxation time is $\Delta\tau$. The relaxation time $\tau_\alpha(\mathbf{q})$ of the modes is given by [1, 2]

$$\tau_\alpha(\mathbf{q}) = \eta_\alpha(\Omega_q)/(K_\alpha q_\perp^2 + K_3 q_z^2 + \chi_a B^2), \tag{3}$$

where $\eta_\alpha(\Omega_q)$ is an effective viscosity which depends on the Leslie viscosity coefficients α_i and on the orientation Ω_q of $\mathbf{q}$ with respect to the mean director $\mathbf{n}_0$. Putting $\varrho_q = q_\perp/q_z$ we have [2]

$$\eta_1(\Omega_q) = \gamma_1 - \frac{\alpha_3^2\varrho_q^4 - 2\alpha_2\alpha_3\varrho_q^2 + \alpha_2^2}{\eta_b\varrho_q^4 + (\alpha_1 + \eta_b + \eta_c)\varrho_q^2 + \eta_c}, \tag{4}$$

$$\eta_2(\Omega_q) = \gamma_1 - \frac{\alpha_2^2}{\eta_a\varrho_q^2 + \eta_c}. \tag{5}$$

In these expressions, the twist viscosity γ_1 and the Miesowicz viscosities η_a, η_b, η_c are linear functions of α_i (the convention of [1] is adopted). The viscosities associated with pure splay ($\varrho_q = \infty$ in equation (4)), pure twist ($\varrho_q = \infty$ in equation (5)), and pure bend ($\varrho_q = 0$ in equation (4) or (5)), are

$$\eta_{\text{splay}} = \gamma_1 - \alpha_3^2/\eta_b, \tag{6}$$

$$\eta_{\text{twist}} = \gamma_1, \tag{7}$$

$$\eta_{\text{bend}} = \gamma_1 - \alpha_2^2/\eta_c. \tag{8}$$

The integral of equation (2) can be calculated exactly using stretched momenta $\mathbf{q}'_\alpha$ defined by [5]

$$q'_{\perp\alpha} = q_\perp, \tag{9}$$

$$q'_{z\alpha} = (K_3/K_\alpha)^{1/2} q_z. \tag{10}$$

The change $\mathbf{q} \to \mathbf{q}'_\alpha$ in equation (2) allows separation between radial and angular variables. Neglecting, for simplicity, the magnetic term which turns out to be extremely small in practice (see later), the final result can be written as

$$S_{\text{stat}} = 1 - \frac{3kT}{2\pi^2}\frac{\eta^{1/2}}{(\Delta\tau)^{1/2}K^{3/2}}. \tag{11}$$

Here η and K are an average viscosity and an average elastic constant defined by

$$2\eta^{1/2} = (\lambda_1 + \lambda_2)\gamma_1^{1/2} \tag{11a}$$

and

$$\frac{\lambda_1 + \lambda_2}{K^{3/2}} = \frac{1}{K_3^{1/2}}\left(\frac{\lambda_1}{K_1} + \frac{\lambda_2}{K_2}\right) \tag{11b}$$

in which λ_1 and λ_2 are dimensionless quantities which depend on ratios of viscosities and ratios of elastic constants given by

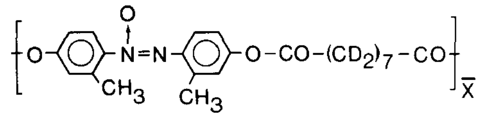
$$\lambda_1 = \frac{1}{\gamma_1^{1/2}} \times \int_0^1 \left[\gamma_1 - \frac{(K_3/K_1)^2\alpha_3^2(1-u^2)^2 - 2(K_3/K_1)\alpha_2\alpha_3u^2(1-u^2) + \alpha_2^2u^4}{(K_3/K_1)\eta_b(1-u^2)^2 + (K_3/K_1)(\alpha_1 + \eta_b + \eta_c)u^2(1-u^2) + \eta_c u^4}\right]^{1/2} du \tag{12}$$

and

$$\lambda_2 = \frac{1}{\gamma_1^{1/2}} \int_0^1 \left[\gamma_1 - \frac{\alpha_2^2 u^2}{(K_3/K_2)\eta_a(1-u^2) + \eta_c u^2} \right]^{1/2} du. \tag{13}$$

These quantities are easily evaluated numerically for any set of values of the viscoelastic parameters.

The particular polymer liquid crystal studied is a main chain thermotropic polyester of the type $(RF)_{\bar{x}}$ where R is a mesogenic unit, F a flexible spacer and $\bar{x}$ the average degree of polymerization. The technique used is proton N.M.R. (P.M.R.). A fairly well-resolved spectrum, more suitable for lineshape analysis than that of the fully protonated sample, is obtained when the spacer is deuteriated. The chemical formula of the polymer used, labelled AZA9d14 [6] is



, $\bar{x} \approx 11$.

The pure nematic phase extends between 360 and about 410 K. The value of S_{stat} can be obtained from analysis of the P.M.R. lineshapes of a nematic monodomain taken at different angles α between the main director and the static magnetic field of the spectrometer. The monodomain is obtained by cooling the sample at the required temperature in the field of the spectrometer, after annealing for approximately 20 min in the isotropic phase about 20°C above the clearing temperature. The polymer is viscous enough at all temperatures in the nematic phase so that it is possible keep the monodomain at any angle α for about 1 s (which is the minimum time necessary to record one spectrum), without any measurable change of the alignment. Figure 1 shows typical 90 MHz P.M.R. spectra (Bruker CXP 90 pulsed spectrometer) for several angles α. The observation that the shapes are not simply scaled in frequency ν by $P_2(\cos\alpha)$, where $P_2(\cos\alpha)$ is the second Legendre polynomial, is an indication of the existence of a static distribution [7]. The corresponding value of S_{stat} can be estimated in the following manner. Let $F_s(u, \varphi)$ be the static distribution of local

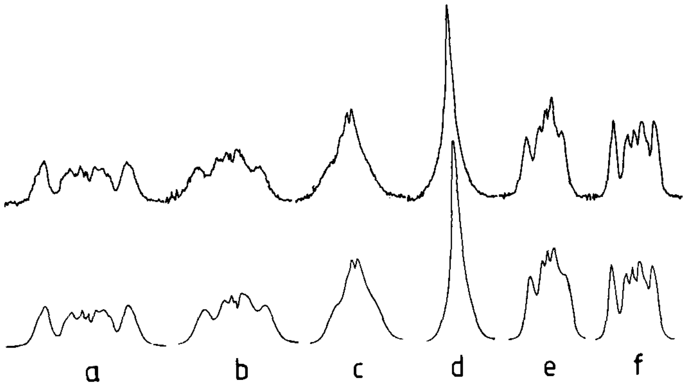


Figure 1. 90 MHz proton N.M.R. spectra of a monodomain of AZA9d14 polymer taken at 393 K for different angles α between the director and the static magetic field. (*a*) 0°; (*b*) 25·5°; (*c*) 37°; (*d*) 47°; (*e*) 76·5°; (*f*) 90°. The upper spectra are experimental. The lower spectra are calculated using a value of $S_{\text{stat}} = 0{\cdot}962$, as explained in the text.

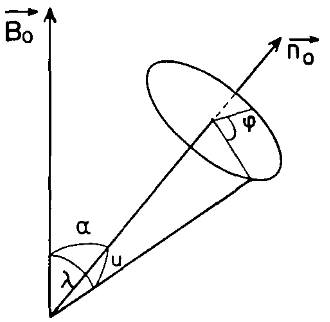


Figure 2. Definition of the various angles used in equations (14) and (15). α is the angle between the mean director $\mathbf{n}_0$ and the static field $\mathbf{B}_0$. The polar and azimuthal angles u and φ, symbolized by Ω, describe the orientation of the local director in a frame with Oz along $\mathbf{n}_0$.

directors about the main director (u and φ are the polar and azimuthal angles, symbolized by Ω). The shape $f_\alpha(\nu)$ of the line at angle α is given by [7]

$$f_\alpha(\nu) = \int \frac{1}{P_2(\cos\lambda)} f_0^{\mathrm{ref}}\left(\frac{\nu}{P_2(\cos\lambda)}\right) F_{\mathrm{s}}(\Omega)\,d\Omega, \qquad (14)$$

where $f_0^{\mathrm{ref}}(\nu)$ is the shape of the reference spectrum; that is the spectrum for $\alpha = 0$ in the absence of a static distribution. The angles λ, u, φ, α are defined in figure 2 and are related by

$$\cos\lambda = \sin u \cos\varphi \sin\alpha + \cos u \cos\alpha. \qquad (15)$$

To find the value of S_{stat}, we assume the simple functional form for F_{s} with cylindrical symmetry

$$F_{\mathrm{s}}(\Omega) = Z^{-1}\exp(A\cos^2 u), \qquad (16)$$

where Z is a normalization constant and A the single adjustable parameter of the problem, related to S_{stat} by

$$S_{\mathrm{stat}} = Z^{-1}\int P_2(\cos u)\exp(A\cos^2 u)\,d\Omega. \qquad (17)$$

On the other hand, for $\alpha = 0$, we have $\lambda = u$, and because F_{s} is a maximum at $u = 0$, the influence of the static distribution on the lineshape will be much smaller than for any other angle α. If in addition the distribution $F_{\mathrm{s}}(\Omega)$ is narrow ($S_{\mathrm{stat}} > 0{\cdot}9$), we can safely replace f_0^{ref} by f_0 in equation (14). It is then possible to calculate $f_\alpha(\nu)$ for any value of α and S_{stat}. Figure 1 shows that good fits are obtained for all angles with a single value of S_{stat}. Comparison between experimental and calculated spectra for $\alpha = 0$ shows that $f_0^{\mathrm{ref}} = f_0$ is a reasonable approximation.

This method for estimating S_{stat} is rather accurate because for α near the magic angle ($\sim 54°$), the lineshape is dominated by the static distribution. Figure 3 shows S_{stat} for several temperatures in the nematic phase of AZA9d14, together with the usual nematic order parameter S deduced from the main splitting of the $\alpha = 0$ spectra as previously described [8]. Note that S includes both static and dynamic contributions to the orientational disorder. Comparison between absolute values of S and S_{stat}

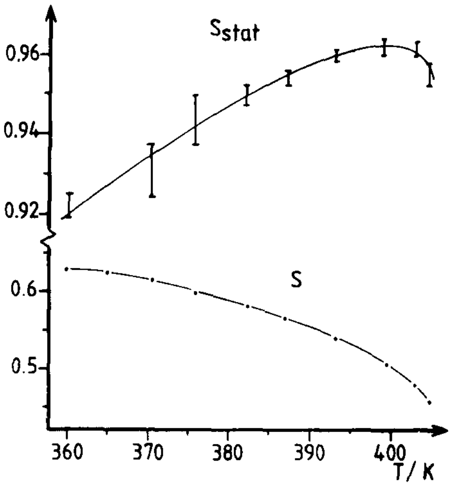


Figure 3. The static order parameter S_{stat} and the usual nematic order parameter S for polymer AZA9d14 versus temperature.

shows that the contribution of the static modes to S is rather small, supporting the usual analyses of the $\alpha = 0$ P.M.R. lineshapes in terms of extreme narrowing models [9]. Whereas the behaviour of S is classical, namely it decreases with increasing temperature, S_{stat} first increases, flattens off in the middle of the nematic phase and even decreases near the clearing point. This behaviour is qualitatively explained in terms of equation (11). This equation shows that the temperature dependence of S_{stat} is essentially governed by the ratio of $(\text{viscosity})^{1/2}$ to $(\text{elastic constant})^{3/2}$. Both quantities decrease with increasing temperature. The observed behaviour suggests that at low temperature, S_{stat} is dominated by the decrease of the viscosity, whereas at high temperature, the decrease of the elastic constant dominates.

A more quantitative test of equation (11) can be made only if all the viscosity coefficients and all the elastic constants are known. In [10], an N.M.R. method is proposed to estimate four out of the five Leslie coefficients. We have employed an improved [11] version of this method to estimate these coefficients at one temperature (383 K). The results are, in kilopoise (kP): $\alpha_1 = -11{\cdot}50$, $\alpha_2 = -15{\cdot}65$, $\gamma_1 = \eta_{\text{twist}} = 15{\cdot}70$, $\eta_c = 15{\cdot}77$. From these values, we deduce $\alpha_3 = \alpha_2 + \gamma_1 \approx -0{\cdot}05$, $\eta_b = 2\alpha_2 + \gamma_1 + \eta_c \approx 0{\cdot}17 \approx \eta_{\text{bend}}$, $\eta_{\text{splay}} \approx \gamma_1$. The viscosity η_a is unknown. However, combining the various inequalities that the viscosities must satisfy [12, 13] it can be shown that η_a is smaller or equal to $2(\eta_b + \eta_c) + \alpha_1 - \gamma_1 \approx 4{\cdot}60$ kP. On the other hand, there is no known example of nematics in which η_a is found to be smaller than η_b. Consequently, for our polymer at 393 K, we expect that η_a lies between $\sim 0{\cdot}2$ and 4·6 kP. It is possible to be more precise. Indeed, the value of η_a found for low molecular mass nematics [1, 14–17] and for a lyotropic TMV solution [18] is close to $\sim 3\eta_b$. The situation is probably similar for our polymer as suggested by shear viscosity measurements [19], so that we can reasonably assume that η_a is close to 0·5 kP. Incidently, we confirm with this sample that the viscosity coefficients can be classified into two distinct groups, namely the large and small viscosities, which differ by more than one order of magnitude [10]. The large viscosities are η_{splay}, η_{twist}, η_c, the small ones are η_{bend}, η_a, η_b. A similar result was found previously with lyotropic nematic polymers [18].

The elastic constants are not known for our sample. Data concerning elastic constants of main chain thermotropic polymers are very scarce in the literature. For a similar polymer with ten methylene groups in the spacer, studies of solutions in para-azoxyanisole (PAA) [20] suggest that K_3 (and K_1) increase slightly with increasing polymer concentration, but remain of the same order of magnitude as for pure PAA. For a main chain polymer with different mesogenic units and five methylene groups in the spacer, the values: $K_1 \approx 3 \times 10^{-6}$ dyn and $K_2 \lesssim K_3 \approx 3 \times 10^{-7}$ dyn have been found [21]. All these results are self-consistent and suggest that $K_2 \lesssim K_3 < K_1$ with a factor of ~ 10 between K_1 and K_2 and ~ 1 between K_2 and K_3. In order to evaluate the quantities λ_1 and λ_2 in equations (12) and (13), we assume for the ratios K_3/K_1 and K_3/K_2 the values 0·1 and 1. With the previous viscosity coefficients, we obtain $\lambda_1 \approx 0{\cdot}39$ and $\lambda_2 \approx 0{\cdot}41$. With these results, it is possible to estimate η and K. With $T = 393\,\mathrm{K}$, $S_{\mathrm{stat}} = 0{\cdot}962$, $\Delta\tau \approx 10^{-4}\,\mathrm{s}$, we obtain $\eta \approx 2{\cdot}50\,\mathrm{kP}$ and $K \approx 1{\cdot}05 \times 10^{-6}$ dyn. Taking into account the uncertainties on the various quantities involved, we estimate the overall uncertainty on η and K to ± 50 per cent. We note that η is intermediate between large and small viscosities and that K is of the expected order of magnitude. The quantity $\eta/\Delta\tau \sim 2{\cdot}5 \times 10^7\,\mathrm{erg/cm^3}$ is the mean energy per unit volume associated with the modes whose relaxation time is $\Delta\tau$. This value is much larger than the magnetic energy $\chi_a B^2 \sim 50\,\mathrm{erg/cm^3}$ ($\chi_a \sim 10^{-7}$ [22], $B = 22\,000\,\mathrm{T}$) showing that the magnetic term can be neglected in the calculations, as stated earlier. Finally, the average P.M.R. cut-off wavelength $\lambda_{\mathrm{P.M.R.}}$ defined as

$$\lambda_{\mathrm{P.M.R.}} = 2\pi(\Delta\tau K/\eta)^{1/2} \approx 130\,\text{Å}$$

is comparable to the average polymer length ~230 Å, but still significantly larger than the size of the repeating unit (~21 Å). This result shows that for this polymer, all modes with wavelengths up to a molecular length are slow on the N.M.R. time scale, but they contribute only little to the orientational disorder, as revealed by the large values of S_{stat}. For low molecular mass nematics, the cut-off wavelength is much larger and this contribution is completely negligible [4].

This analysis implicitly assumes that the observed static broadening originates only from the slow elastic modes and not from poorly aligned microdomains or orientation-dependent homogeneous broadening. Poorly oriented microdomains would show up experimentally as extra intensity around the centre of the P.M.R. spectrum whose shape is not or little affected by rotation of the sample. This would lead to a (much) poorer agreement between simulated and experimental spectra; that is not observed. The homogeneous broadening on the other hand can also be neglected because the spin–lattice relaxation time T_1 is not shorter than $10^{-2}\,\mathrm{s}$ and is not expected to vary with α by more than a factor of two [23]. This value is much larger than $\Delta\tau \sim 10^{-4}\,\mathrm{s}$ corresponding to $(2\pi\Delta\tau)^{-1} \sim 1\,\mathrm{kHz}$, which is a minimum value able to produce a measurable broadening of the various lines of the P.M.R. spectra, in particular near the magic angle.

To summarize, we have shown that in polymer liquid crystals, the elastic modes contribute to the N.M.R. lineshapes in a way which can be quantified. This contribution appears as an additional broadening of the individual components of the spectra, and is characterized by a static order parameter S_{stat}. This parameter is a function of the viscoelastic parameters, via the α_i and K_1, and of the strength of the magnetic interactions via $\Delta\tau$. The value of S_{stat} will thus be different according to the spins that are observed, all other things being equal. In particular, we expect on general grounds that S_{stat} is smaller for deuterons than for protons. This feature is qualitatively observed with our partially deuteriated sample. The determination of S_{stat} may be considered as a method to study the elastic modes and/or to obtain information on the viscoelastic parameters of the medium via the measurement of $\eta^{1/2}/K^{3/2}$ (cf. equation (11)). Knowledge of S_{stat} is also important for the study of N.M.R. lineshapes, either to interpret the equilibrium spectra in terms of molecular structure and dynamics, or to interpret the time dependence of the spectra during the return to equilibrium of rotated monodomains [10, 11].

To conclude, we can say that the present study is a rationalization of the usual observations that the N.M.R. spectra of nematic monodomains are less well resolved for viscous samples than for less viscous ones. We have seen here that although viscosity is certainly the leading parameter, the effect is in fact governed by an interplay between viscosity and elasticity. In particular, the best resolved spectrum (S_{stat} maximum, cf. figure 3) is not necessarily obtained at the highest temperature, where the viscosity is a minimum.

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