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On the spacer and mesogenic unit QNS reorientational motion investigation in liquid crystal polyacrylate

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Abstract. — The incoherent quasi elastic cold neutron scattering data of the side chain dynamics of the backbone deuterated linear polymer polyacrylate of Benguigui et al. (J. Phys. II France 1 (1991) 451), have been successfully interpreted in the isotropic, smectic A and re-entrant nematic phases. The spacer dynamics of the twelve protons are interpreted in terms of the model according to which the protons are subjected to the transverse oscillations of the standing wave variety with only the fundamental mode of vibrations being excited. The motion of the biphenyl group, constituting the mesogenic unit, can be appropriately described in terms of the uniaxial restricted reorientational model, according to which the benzene rings are subjected, to small step stochastic angular displacements, around their para axis, within a circular segment of an apex angle \( \phi_0 \).

1. Introduction.

Currently, a large effort is being devoted to the investigation of the reorientation and internal (multiple) motions within flexible liquid crystalline molecules in various mesomorphic phases. In this respect, the measurements of the pertinent spectral densities of motion by means of deuterium magnetic resonance relaxation study (DMR), seem to be a particularly promising for gaining insight into internal dynamical processes of certain (deuterated) liquid crystals. The complications of these processes have been, for instance, well evidenced by Beckmann et al. [1] and Dong [2] in their studies of 5CB-d\(_{15}\) nematic sample. While in these works the main emphasize is set on gaining the understanding of the internal motions of an alkyl chain, there exist a large number of studies, based upon the quasielastic incoherent cold neutron scattering method (QNS), where the dynamics of the central core of the mesomorphic molecules is the central issue of the investigations. In this respect the rotational dynamics of the rigid benzylidene central part of the nematic MBBA has been successfully [3] interpreted by invoking the new model of the restricted uniaxial reorientation. Essentially, the established model of motion describes the stochastic uniaxial reorientation of the proton on the segment of a circular arc characterized by its apex angle \( \phi_0 \). Furthermore, as shown in reference [4], the model of uniaxial restricted reorientation can successfully describe the temperature dependence of the spin-lattice relaxation rates for the ring deuterons in 5CB-d\(_{15}\) sample of Beckmann et al. [1]. Consequently, from these results it is evident that also in the nematic
phase the uniaxial rotational molecular cores under suitable conditions can be, and indeed, are restricted. This reorientation can be described also as the biased rotational motion in the sense that for the molecular core in question, there exists the preferred direction — the bisector of the apex angle $\phi_0$ — along which the uniaxial stochastic restricted reorientations of the core (along its para axis) occur [3].

Recently, a particularly interesting results of a QNS investigation of the side chain dynamics of the polyacrylate polymer liquid crystal in its isotropic, smectic A, and re-entrant nematic phases have appeared [5]. The sample (comb-like liquid crystal polymer) consists of a backbone of a deuterated linear polymer to which, via a small aliphatic chains called spacers, the mesogenic units have been attached. The spacer — C$_6$H$_{12}$ chain — is known to be in an elongated configuration [5] and is linked to the biphenyl groups in the following way [5]:

$$\begin{align*}
\begin{bmatrix}
    CD_2 \\
    CD \\
    \end{bmatrix}
\end{align*}$$

where $\phi$ denotes benzene ring.

It is known that in the isotropic phase the backbone conformation is spherical, in N and Sm A phases it is oblate, while in the N$_{Re}$ phase it is prolate.

The analysis [5] of the geometry of the motion of 12 spacer protons and 8 protons of benzene rings (for the measurements of the elastic incoherent structure factor, EISF, see for instance Refs. [6, 7]) based upon three different models of the proton motion could not successfully explain the experimental data. However, two important conclusions are inferred from their study, namely: a) the contribution of spacer protons to the geometry of motion to the measured EISF is small, even in the isotropic phase, and b) the rotational motion of the mesogenic protons can not be considered as a free reorientation but is hindered instead in an undetermined way.

The biphenyl group in question is identical to the one in 5CB nematic liquid crystal and as shown by Cvikl et al. [4] it is, for this compound, subjected to the restricted uniaxial reorientation. Consequently, it is our purpose to investigate the EISF results of Benguigui et al. [5] taking this type of motion into account in conjunction with the appropriately devised model of the spacer proton motions. The task at hand is simplified by the fact that the sample is powder like, however, this unfortunately renders the conclusions to be slightly less certain.

2. Theoretical outline.

Having in mind the observation of Benguigui et al. [5], according to which the contribution of the spacer protons geometry of motion to the measured values of EISF is small and viewing the drawing in (1), we postulate the model of spacer motion described below. In view that the spacer in an elongated chain, we envisage that due to the thermal motions the spacer is subjected to transversal vibrations of the standing wave form in such a way that only the fundamental mode is excited. The nodes are, consequently, at the sites of both oxygen atoms. If $s(x, t)$ denotes the instantaneous (transversal) displacement of a proton (all spacer protons are taken to vibrate in a fixed plane) at the site $x$ as measured from its equilibrium — elongated — position (the $x$-axis origin is chosen at the left oxygen atom linked to the spacer, see (1)), then one has

$$\text{EISF} = \langle e^{iQ \cdot s(x, 0)} \rangle \langle e^{-iQ \cdot s(x, \infty)} \rangle = \left| \frac{1}{2S(x)} \int_{-S(x)}^{S(x)} e^{iQ \cdot s} ds \right|^2$$

(2)
where $Q$ is the neutron scattering vector transfer and $s(x)$ is the transversal displacement of the proton at the site $x$ of the chain which is taken to be described by $s(x) = s_0 \sin \left(\frac{n \pi x}{\ell}\right)$. It can be easily shown that this expression reduces to

$$\text{EISF} = j_0^2 \left[ Qs_0 \sin \left(\frac{n \pi x}{\ell}\right) \cdot \cos \Theta \right]$$

(3)

where $j_0$ is spherical Bessel function of order 0, $s_0$ is the standing wave amplitude, $\Theta$ is the angle between $Q$ and $s(x, t)$, $n = 1$ (fundamental mode) and $\ell$ is the O-O elongated chain distance, respectively. Averaging over all orientations of vector $s$ with respect to the vector $Q$, one obtains

$$A_{Ox}(Q : x) = \langle \text{EISF} \rangle_{sp} \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{2(2k-1)(2k)!} \left[ Qs_0 \sin \left(\frac{\pi x}{\ell}\right) \right]^{2k-2}$$

(4)

the one proton (at $x$) of the spacer (subjected to the standing wave geometry of motion) contribution to the total EISF for a powder sample.

The restricted reorientation motion contribution of the biphenyl group to the EISF is given by equation (9) of Cvikl et al. [8] (or an equivalent expression given in Ref. [3]), the powder average of which reads,

$$A_{OB}(Q : r) = \langle \text{EISF} \rangle_{B} = 8 \pi \sum_{\ell=0}^{\infty} J_\ell(Qr) Y_\ell(\Theta, \varphi) Y_\ell^*(\Theta, \varphi) \cdot \frac{1 - \cos (m\phi_0)}{(m\phi_0)^2}$$

(5)

where $r = (r, \Theta, \varphi)$ is the proton position vector as measured from the center of mass of benzene rings, with the polar axis taken to lie along the para axis. $Y_\ell$ is spherical harmonics of order $\ell$ and the parameter $\phi_0$ is the allowed angular span for the restricted reorientation of rings (see Fig. 1 of Ref. [3]).

The final expression of the EISF for the two models in question (for a powder sample of a re-entrant side-chain backbone deuterated liquid crystal polyacrylate) reads,

$$\langle \text{EISF} \rangle = \frac{1}{20} \left[ \sum_{i=1}^{12} A_{Ox}(Q, x_i) + \sum_{i=1}^{8} A_{OB}(Q, r_i) \right]$$

(6)

3. Results and discussion.

In figure 1 are shown the results of the two-parameter fits ($s_0$ and $\phi_0$), as provided by the equation (6), to the experimental EISF values [9] obtained on an unoriented backbone deuterated liquid crystal polyacrylate for the low temperature $R_s$ nematic, re-entrant nematic, Sm A, and isotropic phases. It is evident, that the data are well described by suitably chosen values of parameters as indicated in figure 1. The structural parameters of the spacer and the biphenyl rings were calculated on the basis of published information [10, 11]. The different values of structural parameters used in the computation are presented in table I.

It is to be emphasized that in this computation the order parameter is taken to be 1 and no motion of the spacer O-O axis as well as of the biphenyl group para axis has been envisaged. On the basis of these assumptions the parameters obtained in the fittings seem to suggest, that the uniaxial reorientational motion of the biphenyl group is strongly hindered, the restriction being temperature dependent. Even in the isotropic phase the stochastic reorientation of the benzene rings is occurring within an angular segment of only $\phi_0 = 2.7$ rd. Evidently, it is unlikely that the rings would be subject to any kind of 360° degrees rotational motion thus corroborating a conclusion already observed in [5]. As far as the transversal displacements of
The values of the neutron elastic incoherent structure factor calculated for the case of the transverse standing wave type displacement of 12 spacer protons and the uniaxial, within an angular interval of $\phi_0$, restricted stochastic small angular step reorientation of 8 benzene rings protons of the molecular biphenyl group, are compared to the experimental data of Benguigui et al. [5]. These data were obtained on an unoriented sample of a side-chain backbone deuterated polyacrylate liquid crystal at $T = 40$ °C (low temperature re-entrant nematic), $T = 80$ °C (reentrant nematic), $T = 86$ °C (smectic A) and $T = 115$ °C (isotropic) phases. The values of parameters obtained in the fitting are: $T = 40$ °C, $s_0 = 0$ Å, $\phi_0 = 0.2$ rd; $T = 80$ °C, $s_0 = 0.2$ Å, $\phi_0 = 1.2$ rd; $T = 86$ °C, $s_0 = 0.7$ Å and $\phi_0 = 1.7$ rd, $T = 155$ °C, $s_0 = 1.1$ Å and $\phi_0 = 2.7$ rd.

Table I. — The distinct proton coordinates entering equation (4), of the C$_6$H$_{12}$ elongated chain (the spacer) were calculated on the basis of the information of reference [10]. The origin of the x-axis is chosen to be at the site of the oxygen atom close to the polyacrylate deuterated backbone to which the spacer is linked. The distance O–C$_6$H$_{12}$–O (where both oxygen atoms represent nodes of the transverse displacement of the spacer protons taken to be described in terms of the fundamental mode of the standing wave type oscillations in a fixed plane) is equal to $l = 9.2$ Å. The distinct proton coordinates entering the equation (5) of the biphenyl benzene rings were calculated according to the data given in reference [11]. The distances $r_i$, are measured from the center of mass of the two benzene rings and $\Theta_i$ is the polar angle which vector $r_i$ spans with the para axis of the biphenyl group.

<table>
<thead>
<tr>
<th>$x_i$ [Å]</th>
<th>1.6</th>
<th>2.6</th>
<th>3.5</th>
<th>5.1</th>
<th>6.1</th>
<th>7.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_i$ [Å]</td>
<td>3.9</td>
<td>34</td>
<td>69.5</td>
<td>2.3</td>
<td>2.3</td>
<td>3.9</td>
</tr>
<tr>
<td>$\Theta_i$ [°]</td>
<td>110.5</td>
<td>146</td>
<td>110.5</td>
<td>146</td>
<td>110.5</td>
<td>146</td>
</tr>
</tbody>
</table>
the spacer are concerned, they are almost nil at the low temperature re-entrant nematic phase and increase with increasing temperature. Whether this proposed simple explanation indeed adequately accounts for the spacer and biphenyl groups dynamics in a complicated systems, such as a liquid-crystal poyacrilate, remains to be seen when more data become available.

However, on the basis of the results presented in reference [5], one can be fairly certain that for this system the motions of the type like: a) a uniaxial circular motion along the long axis; b) a diffusive motion on a sphere of a given radius; and c) a diffusion motion inside a hard sphere of a given radius, are all to be excluded as for the spacer as well as for the rings. Peculiar to our interpretation presented above, is the fact, that owing to the sample being unoriented the measurements can be perhaps also described in terms of the restricted reorientational model only (see Fig. 2). Namely, if one chooses $s_0 = 0.0 \text{ Å}$, it follows $\langle \text{EISF} \rangle_{sp} = 1$ and equation (6) becomes a one parameter ($\phi_0$) family. As it turns out the values of $\phi_0$ obtained in the fitting are for each phase larger than before (i.e. for instance for the isotropic phase if $s_0 = 0$ then $\phi_0 \approx 3.0 \text{ rd}$) however, the circular uniaxial motion is, under

![Diagram](image)

Fig. 2. — The calculated values of the neutron elastic incoherent structure factor for an unoriented sample of backbone deuterated polyacrylate liquid crystal. Top diagram: variation of EISF as a function of the neutron scattering vector transfer, see equation (4), for the case of only the transverse displacements of the 12 spacer — C$_6$H$_{12}$ — protons as described by the standing wave type fundamental mode of vibrations. The values of amplitude of the transverse displacements $s_0$ are on the diagram increasing according to: $s_0 = 0 \text{ Å}$ (horizontal line), $s_0 = 0.7 \text{ Å}$, $s_0 = 1.1 \text{ Å}$ and $s_0 = 1.2 \text{ Å}$. Bottom diagram: variation of EISF as a function of the neutron scattering vector transfer, $Q$, calculated from equation (6) of the text for the case where $s_0 = 0 \text{ Å}$ (no motion of the spacer protons). The values of the parameter $\phi_0$ determine the angular span available for the stochastic small angular step restricted rotational reorientations of the benzene rings along theirs para axis. These values are as follows: $\phi_0 = 1.1 \text{ rd}$, $\phi_0 = 2.2 \text{ rd}$, $\phi_0 = 3.3 \text{ rd}$ and the limiting case of $\phi_0 = 2 \pi \text{ rd}$ is represented by the line having the steepest descend.
condition above, still definitely prohibited, and this conclusion is being valid in all phases. Evidently, one needs selectively deuterated (and oriented) samples in order to investigate still elusive motion in particular of 12 spacer protons of the liquid crystal polyacrylate sample in its mesomorphic phases, in conjunction with a broader range for the values of parameter $Q$. This last requirement is desired in order that the minimum in $\langle EISF \rangle_B$, which occurs around $Q = 1.4 \, \text{Å}^{-1}$, would also be detected.

References

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