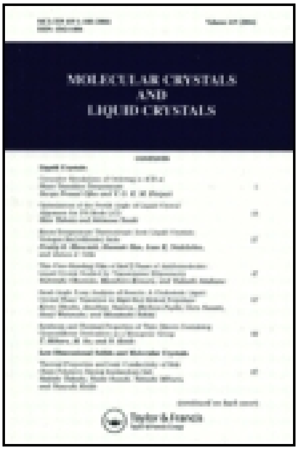

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Raman Scattering from Liquid Crystals

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Raman Scattering from Liquid Crystals

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The use of Raman scattering technique as a tool for studying local order in complex liquid crystal systems is illustrated by three examples, namely the locally anisotropic liquid L-phase, lipid membranes, and PDLC's.

Keywords: Raman scattering; Orientational order parameter; L-phase; Lipid membranes; Polymer Dispersed Liquid Crystals

INTRODUCTION

Since the pioneering work of Jen *et al.*[1], Raman scattering has been mostly used to study orientational order in nematics or smectic A phases[2]. The general idea is that, for a uniaxial liquid crystal made up by cylindrical molecules, the relevant spherical harmonics involved in the expansion of the orientational distribution function simply reduce to the even Legendre polynomials and the coefficients of the expansion are the so-called "orientational order parameters" $\overline{P}_L$ (L=2, 4,...), which are zero in the isotropic phase and saturate to unity for a completely aligned medium. Because the Raman scattering tensor is of second rank, the scattered intensity, which is proportional to the mean square of its terms, gives access not only to $\overline{P}_2$ but also to $\overline{P}_4$, contrary to most of other techniques. In addition, Raman scattering can probe local order while other experiments usually provide average values. In chiral liquid crystals, for instance, where ferroelectric and antiferroelectric phases are helicoidal, the optic axis remains parallel to the helix axis, and does not reflect, accordingly, the molecular tilt which characterizes these phases. This tilt is clearly evidenced by Raman experiments[3,4], as well as its strong fluctuations observed in the SmC$_\alpha$* phase[5]. In ferroelectric liquid crystals, charged disclination lines or more complex defects arise from the competition between the homogeneous state at the surface and the wound state in the bulk. Raman scattering has been shown to be very sensitive to these defects[3]. The purpose of this article is to demonstrate in which respect the Raman technique can be helpful in understanding the local structure of other liquid crystal systems less conventional than nematics or smectics.

PRECURSOR SMECTIC ORDER IN L-PHASE

A chiral liquid crystal series, called "nCTBB9", with chemical formula:

$$H(CH_2)_nCOO\text{-}\phi\text{-}C{\equiv}C\text{-}\phi\text{-}COO\text{-}\phi\text{-}COO\text{-}C^*H(C_2H_5)\text{-}C_6H_{13}$$

exhibits a complex order which is revealed by a large optical rotatory power (ORP) in the reputed isotropic phase[6]. In addition, a broad and strong heat capacity peak is observed within this phase, which has long been considered as related to a transition between the isotropic state and a "L-phase"[7]. Raman intensity is related to the molecular order, and is not expected to vary with temperature, as far as the phase remains isotropic. However, a monotonous decrease by about 20% has been observed in this phase on cooling, in parallel and crossed light polarizations, as illustrated in Figure 1.

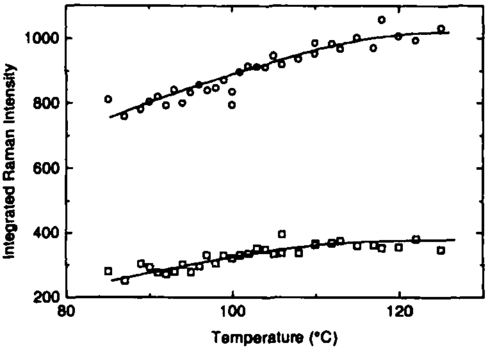

FIGURE 1 Raman integrated intensity of the C≡C bond of 14CTBB9 in the "isotropic" phase, in parallel (○) and crossed (□) light polarizations. The transition temperature to the smectic phase is 80.8°C, and the heat capacity peak is reported at 97°C[7].

Because the xx term of the Raman tensor is much smaller than the zz term (where z is along the main molecular axis), this result is consistent with a progressive ordering of the molecules, which preferentially align, on cooling, perpendicular to the surfaces of the liquid crystal cell. A similar intensity decrease is observed on applying an electric field across the cell, which reinforces this assumption according to the positive dielectric anisotropy of the molecules. In addition, precursor smectic order has been recently detected by X-ray diffraction experiments[8] in the liquid phase, with smectic correlation lengths increasing up to 20 nm on cooling. Taking into account the strong chirality of these liquid crystals, as demonstrated by ORP[6], and the stability of the smectic phases at lower temperature, a competition between chiral and smectic order parameters is expected in the liquid phase of these compounds, and the L-phase is very likely locally anisotropic rather than isotropic. Raman results thus suggest that smectic order is enhanced close to the surfaces, and prove inelastic light scattering to be a useful technique to detect precursor orientational order.

ALIPHATIC CHAIN ORDERING IN LIPID MEMBRANES

Good experimental models for the cell biomembranes are lipid/water mesophases, in which lipid molecules assemble into bilayers separated by water. These lamellar systems usually exhibit a sequence of phases from L_α, where the conformation of the aliphatic chains is liquid-like, to $L_{\beta'}$ in which the chains are frozen to a nearly all-trans conformation. An intermediate phase referred to as $P_{\beta'}$ may appear at full hydration. In this phase, the chains are also frozen, but, in addition, the layers are rippled. $L_{\beta'}$ as well as $P_{\beta'}$ phases are characterized by a hexatic two-dimensional bond order within the layers[9]. Because the conformational order of the aliphatic chains seems to be strongly involved in the successive phase transitions, a specific study of these chains is helpful. In this respect, Raman scattering can probe local order of selected parts of molecules by focusing on the spectral range(s) of the relevant normal modes. The differences between Raman spectra of completely isotropic and partially ordered aliphatic chains has been already pointed out, with a special attention to lipid bilayers[10]. They result from density of states which are better peaked, in the reciprocal space, for ordered than for isotropic conformations. This is illustrated in Figure 2 for DMPC (dimyristoyl phosphatidylcholine), where it can be seen that the spectrum in the CC stretching/CCC bending region is better resolved in $L_{\beta'}$ and $P_{\beta'}$ than in the liquid L_α phase. Similar effects are also observed in the CH frequency region (2800 to 3000 cm^{-1}, not reported here).

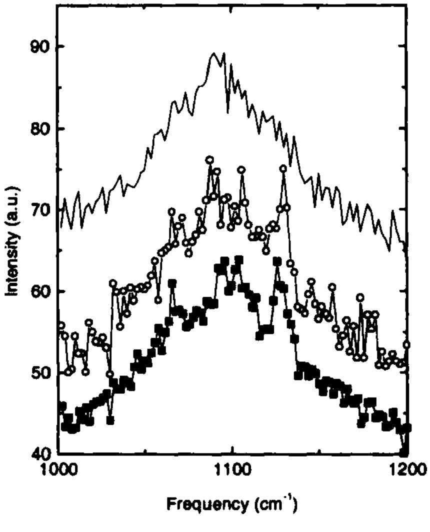

FIGURE 2 Raman spectra of DMPC in the CC stretching/CCC bending frequency region of the aliphatic chain, showing a better resolution in the $L_{\beta'}$ (bottom) and $P_{\beta'}$ (middle) than in the liquid L_α (top) phase.

POLYMER DISPERSED LIQUID CRYSTALS (PDLC)

PDLC's are composite materials suitable for applications such as smart windows, shutters,....They are made of liquid crystal droplets embedded into a polymer matrix, and the usual way to make them is phase separation from a blend. A new, simpler, route for their elaboration consists in the wetting of a spreaded pre-formed open porosity matrix by the liquid crystal[11]. Because the electro-optic properties of these new materials were not as good as those of more conventional PDLC's, the relationship with morphology has been looked out.

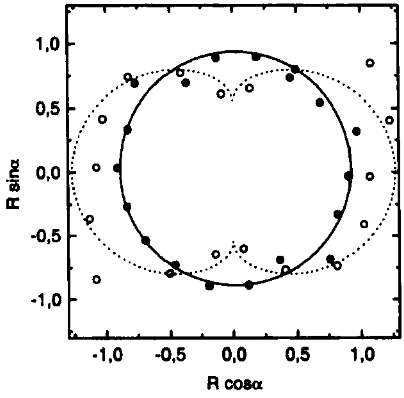

FIGURE 3 Depolarization ratio $R=I_{\perp}/I_{//}$ plotted in a polar representation as a function of the angle α of measurement of the Raman intensity with respect to the spreading direction of the polymer film. Open circles: zero field. Full circles: E=13 V.μm^{-1}. The solid and dotted lines are fits with Equation (1).

Contrary to electron microscopic observations which did not reveal any anisotropy, Raman scattering shows that the molecules are oriented closer to the normal (z axis) to the film for a direction perpendicular to the spreading (x) axis of the polymer solution. The depolarization ratio $R=I_\perp/I_{//}$ of the 1608 cm^{-1} Raman line (benzene ring breathing) has been plotted in polar representation in Figure 3, where α is the angle between the spreading direction x and the scattered light polarization. The morphology-induced anisotropy is clearly visible at zero field (open circles). On applying dc fields above about 5 $V.\mu m^{-1}$, molecules align in the direction of the field due to the positive sign of $\Delta\varepsilon$ for the liquid crystal used (E7, Merck), and the anisotropy is thus strongly reduced (full circles). This anisotropy has been quantitatively described by considering variations of the orientational order parameter $\overline{P_2}$ with respect to the spreading direction according to:

$$\overline{P_2} = C_0 + C_1 (\cos^2\alpha)^n \qquad (1),$$

where $\overline{P_2}$ is defined by reference to the normal (z axis) to the polymer film. The parameters C_0 and C_1 for n=0.05 (for which the best fit is obtained), are reported in the Table below.

	Nematic phase			Isotropic phase
E	0 $V.\mu m^{-1}$	5 $V.\mu m^{-1}$	13 $V.\mu m^{-1}$	0 $V.\mu m^{-1}$
C_0	0.502±0.037	0.652±0.011	0.629±0.014	0.603±0.022
C_1	0.148±0.037	-0.010±0.013	0.011±0.015	0.009±0.024

The parameter C_0 increases on applying the dc field, as expected for a better alignment of the molecules along the field, and the anisotropy parameter C_1 vanishes for fields larger than about 5 $V.\mu m^{-1}$.

CONCLUSION

The extension of the Raman scattering technique to the study of more complex liquid crystal systems than the usual nematic or smectic phases has been shown and illustrated by three examples : (i) In the locally anisotropic liquid L-phase, experimental Raman results are in agreement with a short range smectic order which is favoured by the surface; (ii) The freezing of the aliphatic chains in a nearly all-trans conformation in lipid bilayers is revealed, in the $L_{\beta'}$ and $P_{\beta'}$ phases, through a better resolution of the Raman spectra; (iii) The measurement of the depolarization ratio of a Raman line demonstrates an anisotropy of the orientational distribution function of the liquid crystal related with the morphology of the pre-formed polymer matrix used in a new route for the elaboration of PDLC's.

Most of the information provided by this local technique cannot be achieved using other types of experiments, and Raman scattering proves accordingly to be a very powerful tool in the study of local orientational order of liquid crystals.

Acknowledgments

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