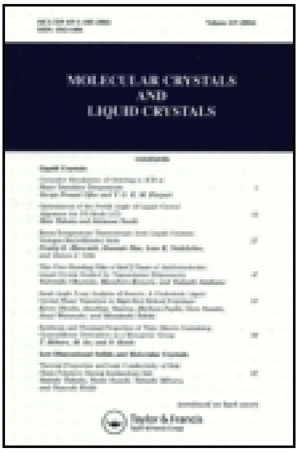

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Raman Scattering in Polymer Liquid Crystals

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RAMAN SCATTERING IN POLYMER LIQUID CRYSTALS

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Abstract In this Paper we present preliminary results of Raman scattering in oriented nematic phase of a new class of side chain liquid crystal polymers belonging to the polyacrylate family.

INTRODUCTION

For many years, Fluctuation Raman Spectroscopy (FRS) has been used to study reorientational motion of molecules is fluids[1]. When one attempts to obtain quantitative information, the technique is in practice useful only in the simplest molecular liquids. There are in fact difficulties both in the data analysis and in the theoretical modeling to connect the data to the fundamental parameters of the microscopic dynamics. Such difficulties increase with the increasing complexity of the fluid, as evidenced for instance by the scarcity of quantitative studies by FRS in liquid crystals. Some of us have however been successful in determining both the order parameters $< P_2 >$ and $< P_4 >$ and the tumbling (reorientations of the main molecular axis) diffusion coefficients in aligned nematics using FRS[2].

In this Paper we report the preliminary results of the application of FRS to the study of molecular reorientations in the much more complex polymeric liquid crystals (LCP). Raman spectroscopy has of course been used to obtain vibrational spectra and vibrational assignments in these materials[3]. To our knowledge however there is no published work on the use of FRS to obtain information on reorientational dynamics. In this work we present spectra, vibrational assignments and qualitative data on molecular reorientations obtained on a newly synthesized class of side chain LCP's belonging to the polyacrylate family[4]. Such materials feature interesting photochromic properties related to photoisomerization of the azobenzene mesogenic side chain. The data were obtained as a function of temperature in the crystal, isotropic, glassy and aligned nematic phases. In presenting and discussing our results we shall use recent data obtained for the same samples (and more particularly the $\ell = 4$ member of the family) by probe ESR and calorimetry[5].

EXPERIMENTAL

The monomer formula unit is shown in fig. 1.

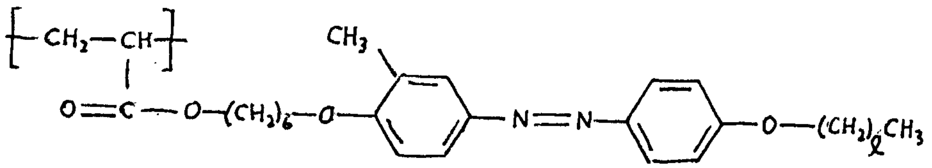

FIGURE 1. Formula unit of samples

The nematogen side chain is attached to the backbone via a flexible spacer consisting of a six carbons alkyl chain. The terminal alkyl chain may have a variable number of carbons. In our work we have studied the $\ell = 2$, 4, 5 and 9 members of this series. The first three have nematic phases with a clearing point ranging from 86 C to 120 C. The $\ell = 9$ compound has a smectic phase, and for the others there is calorimetric evidence[4,5] for a smectic-like modification of the nematic phase also. All compounds show strong thermal history effects and readily form glassy phases upon cooling. Since the Raman spectra were very similar for all members of the series, here we shall present only the result for the $\ell = 4$ sample. For details on synthesis and other characterizations we refer the reader to ref. 4.

The samples were contained in a cell in which temperature could be thermostatically controlled to ±0.05 C. Temperature homogeneity across the cell was estimated to be about 0.5 C; however homogeneity in the illuminated portion of the sample was much better due to the very small scattering volume. Cell walls were glass plates treated by surfactants and rubbed to achieve homogeneous alignment. Sample thickness was 80μ. At this thickness some depolarization effects due to director fluctuations were unavoidable, however signal-to-noise considerations made it difficult to reduce the thickness further. Some control measurements at a thickness of 40μ were made however, specifically at one temperature in the nematic phase to determine more precisely the reorientational relaxation time τ_r. The results on τ_r and on the degree of depolarization $\rho = I_{VH} / I_{VV}$ (see further ahead for the definitions) were within the rather large experimental error.

The virgin sample was brought to $T = T_c + 34$ C, i.e. 120 C, where T_c is the clearing temperature, and kept there for 60 minutes before being slowly cooled (at the rate of ≈ 1 C / minute) into the nematic phase. The spectra were taken at several temperatures upon cooling, down to room temperature.

Raman spectra were taken with a standard, computer controlled spectrometer in a backscattering geometry. Excitation power at the sample was kept below 50 mW with cylindrical focusing. Excitation wavelengths were 488nm; 514.5nm (argon laser) and 640nm (dye laser). Spectral bandpass was 2.5 cm^{-1}. Integration time per channel (i.e. 1 cm^{-1}) was usually 20 s, for a total run time of about 3 hours. In fig. 2 we show a typical untreated spectrum, obtained for the $\ell = 4$ member of the series at room temperature.

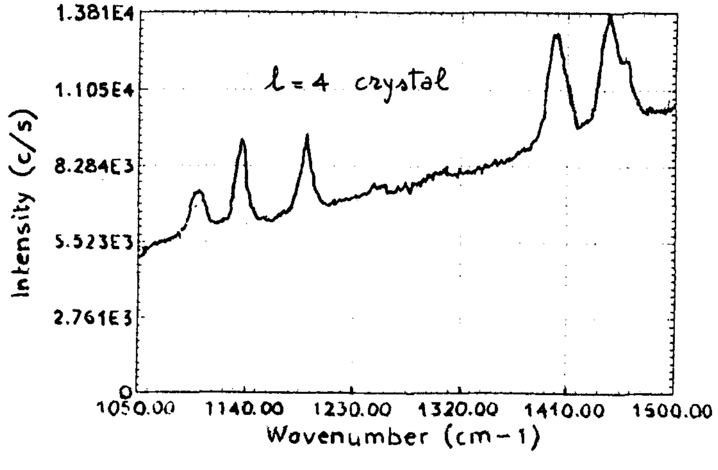

FIGURE 2. Untreated Raman spectrum of $\ell = 4$ sample at room temperature.

Note the large background signal, about twice as intense as the Raman signal. This of course considerably increased signal-to-noise problems in an already weak spectrum (these materials have a strong and rich infrared spectrum).

DATA ANALYSIS

In FRS one performs the so-called VV-VH experiment, i.e. two spectra in polarized light, one with parallel polarizer and analyzer (conventionally VV), the other with crossed polarizers (VH). From the intensities I_{VV} and I_{VH} one constructs the isotropic and anisotropic contributions to the scattered intensity:

$$I_{iso} = I_{VV} - (4/3) I_{VH}$$

$$I_{anis} = I_{VH}$$

In an aligned anisotropic fluid the factor 4 / 3 is actually a slowly varying function of the order parameters (e.g. $< P_2 >$ and $< P_4 >)^2$; however on the qualitative level of these measurements we may neglect this complication.

The actual bandshape I_{VH} is a convolution of I_{iso} with the Fourier transform of the reorientational correlation function $C_r(t)$ related to the rotational diffusion of the molecular group whose vibrational mode is being analysed. Thus FRS is a specific and local probe of reorientational diffusion: this is potentially quite useful in complex molecular systems.

In the relaxation time approximation $C_r(t)$ is a decaying exponential and its Fourier transform is a Lorentzian. From the fit of the convolution $I_{iso} \circ FT\{C_r(t)\}$ to the experimental I_{VH} we obtain the width parameter Δ (full width at half maximum); from Δ the reorientational relaxation time is obtained by:

$$\tau_r = (2\pi c \Delta)^{-1}$$

The degree of depolarization $\rho = I_{VH} / I_{VV}$ is obtained from the integral of the respective spectra $I_{VV(H)}(\omega)$, after spectral smoothing and background subtraction. A typical spectrum treated in this fascion is shown in fig. 3, and a Lorentzian fit to the band at 1139cm^{-1} is shown in fig. 4.

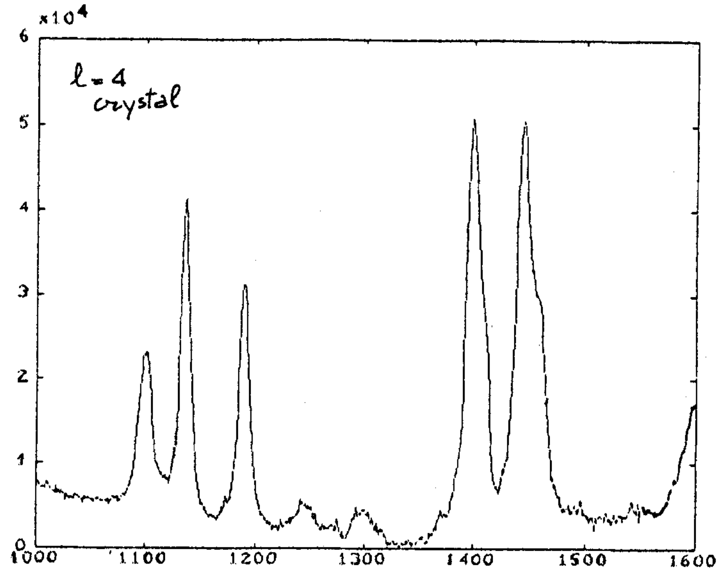

FIGURE 3. Computer treated Raman spectrum (= 4 at RT).

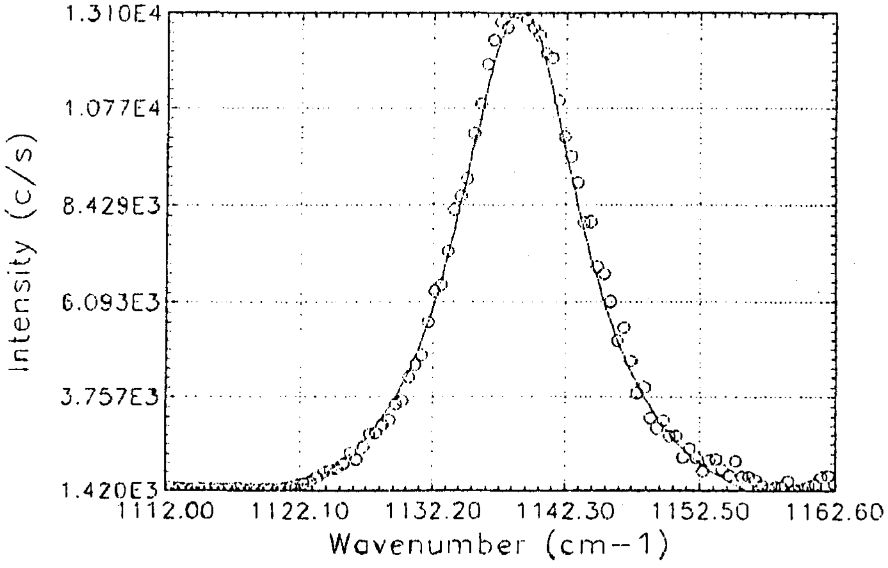

FIGURE 4. Lorentzian fit to Raman band at 1139 cm^{-1}.

For our measurements we focussed on the 1139 cm-1 line which as we shall see corresponds to the in-plane benzene ring C-H vibrations. This line should be strongly polarized and its bandshape should be indicative of reorientational fluctuations in the side chain.

Given the overall weakness of the spectra, the strong background and the alignment we were able to achieve, the data noise remained too high to yield more than qualitative values of τ_r , for which the estimated error is ± 15%. Thus before more sophisticated treatment and analysis of the data is attempted, efforts should be made to reduce the background (which persists even with excitation at 640nm), and to produce better aligned samples. Work is in progress in both these directions.

RESULTS AND DISCUSSION

Only in the 1000 to 1600cm^{-1} spectral range could we find reasonably strong peaks. Thus in what follows we shall limit our discussion to this range. Apart from minor features, in this range we clearly identify six peaks, of which three are more or less clearly doublets. The assignments are as follows[3]:

1102 cm^{-1} (doublet), C-C stretching of main and side chain; 1139 cm^{-1}, C-H in-plane bending of rings in side chain; 1192 cm^{-1}, C-H_3 twist in side chain; 1402 cm^{-1} (doublet), C-C stretching of side chain rings; 1445 cm^{-1} (doublet), C-H_2 bending of main and side chain; 1594 cm^{-1}, benzene ring C-C stretching.

Of these peaks, only the 1139 and 1594 cm^{-1} peaks were sufficiently polarized in the aligned nematic phase. Of these two, we chose to analyse the stronger and better shaped peak at 1139cm^{-1}. In fig. 5 we show the raw Raman spectra of the ℓ=4 sample in the solid, nematic and isotropic phases respectively.

It is clear that the spectra show very little sensitivity to the phase transitions, at least in their overall features. Actually, we found that the background signal was more sensitive, changing in shape and decreasing in intensity as temperature was increased.

The degree of depolarization of the 1139cm^{-1} peak was found to be about .45 and roughly independent of temperature in the nematic phase of the ℓ = 2 sample (sample thickness 80 μ); a subsequent measurement on the ℓ = 4 sample (thickness 80 μ) yielded ρ = 0.3, also essentially constant (although a weak increase with increasing temperature could be detected) in the nematic phase. The control measurement with the 40 μ thick sample yield ρ = 0.27; an improvement, however within the experimental error. With the ℓ = 4 sample then reasonable alignment was achieved, although still not totally satisfactory.

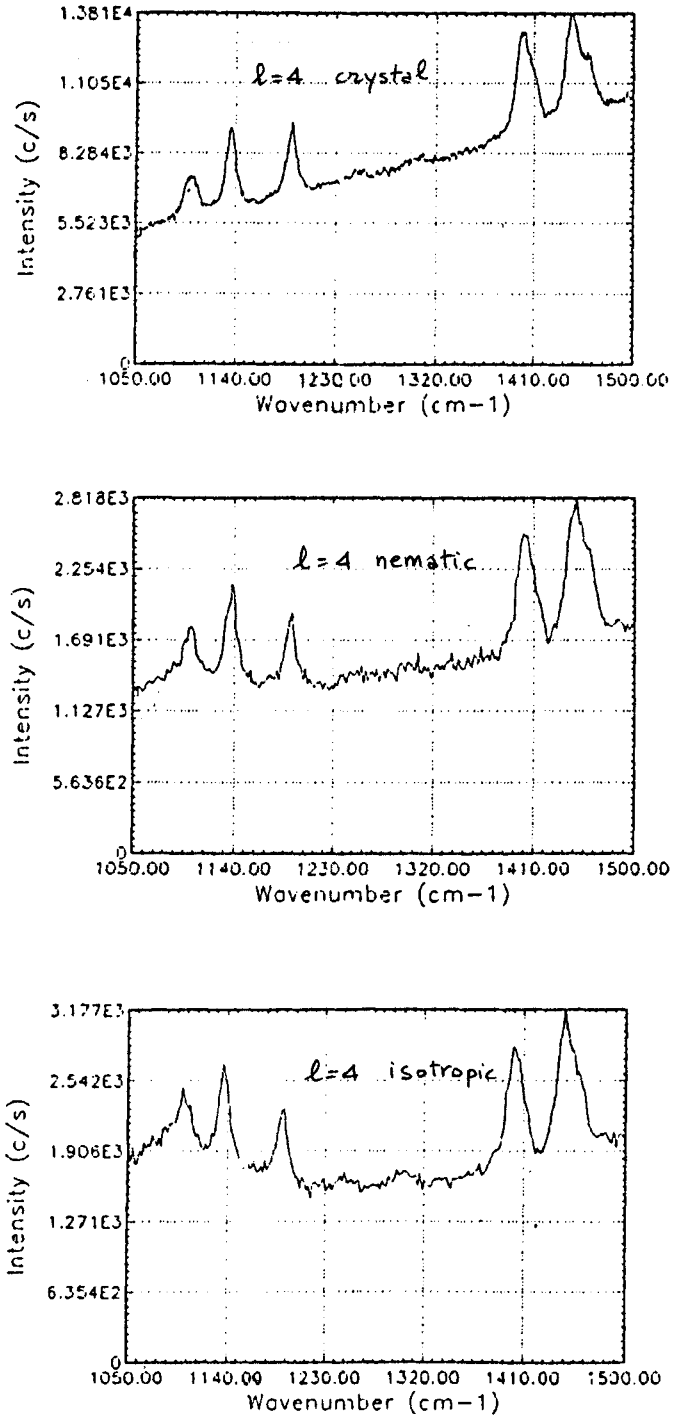

FIGURE 5. Raman spectra of the =4 sample in crystal, nematic and isotropic phases.

All the peaks of the spectrum had halfwidths of the order of 10cm^{-1}, which were roughly independent of temperature. The bandshape analysis of the 1139 cm^{-1} peak yielded a relaxation time which was also essentially independent of temperature, with a value of about 4 ps.

We shall now briefly discuss these results. Firstly, the relatively high degree of depolarization in the nematic phase may be due to unsatisfactory alignment; for a uniaxial mode, in small molecular weight nematics, $\rho \approx$ 0.15 for an order parameter $< P_2 >$ 0.7. However in the more complex situation of a LCP, the 1139cm^{-1} mode might not be totally uniaxial.Thus we estimate that in our $\ell = 4$ sample the nematic order parameter could be as high as 0.5. At this point not much more can be said, measurements on more carefully aligned samples (e.g. with applied electric field) are needed.

The samples are sufficiently aligned however to allow some qualitative considerations on the value and temperature behavior of the relaxation time τ_r. For the case of a uniaxial mode in a small molecular weight nematic, FRS should yield the so-called "tumbling" relaxation time. However the values we have obtained in LCP's are too fast, much more like the "spinning" relaxation times found in small molecular weight LC's. If we also consider that we are observing the mode of a molecular subgroup of the side chain, which is itself attached to the backbone, then the type of motion we are observing must be some kind of wagging of the benzene rings relatively to the alignment axis. If the time scale of this motion is similar to that for spinning, then the measurement would become sensitive to the benzene ring rotations as well. Thus, the relaxation time we measure may actually be some average over these two types of motion. At any rate, the side chain appears to be quite flexible, with fast internal reorientations.

The other conclusion concerns the temperature independence of τ_r. In small weight LC's the tumbling relaxation time of the single molecules decreases with increasing temperature according to an ordinary Arrhenius-like law. However the slower tumbling motion observed by fluorescence depolarization spectroscopy[6] in small weight LC's appears to be essentially independent of temperature in the nematic phase. Such motion seems to be due to reorientational fluctuations of the molecular cage which surrounds the fluorescent probe molecule, in the general framework of structural relaxation models[7]. Temperature independence of reorientational fluctuations is also observed in smectic phases of small weight LC's[8]. Thus from our data on LCP's in their nematic phase we tentatively conclude that the side chains although locally very flexible, are constrained in a smectic-like local structure. Such structure may be due to the fact that it is difficult for the polymer backbones to cross, especially when the side chains are nematically ordered. Thus the side chains find themselves in a locally smectic region, characterized by a range which should be connected to the polymer persistence length.

From this point of view there is supporting evidence from EPR data[5], which show, among other things, that in the monotropic nematic phase there may be smectic-like regions which become crystal nucleating centers at room temperature, depending on the thermal history of the sample.

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