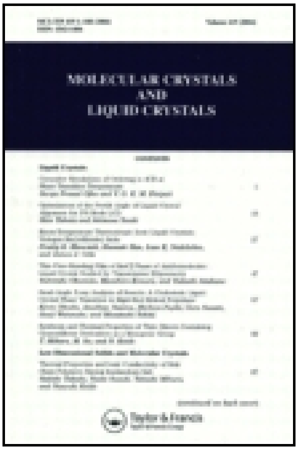

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Vibrational Spectroscopy of Polymer Liquid Crystals

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Vibrational Spectroscopy of Polymer Liquid Crystals

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In this paper we review results of the application of Raman scattering and infrared spectroscopy to the study of molecular dynamics in liquid crystalline polymers. In particular we report on the study of molecular ordering and reorientation and illustrate the results we have obtained in a newly synthesized class of side-chain liquid crystalline polymers belonging to the polyacrylate family. The physical basis and experimental methods necessary for the application of these techniques are also discussed in this paper.

Keywords: polymers, orientational order, dynamics

1. INTRODUCTION

Liquid crystalline polymers (LCP) are a fascinating state of matter in which the richness of structures and phases of anisotropic fluids is present simultaneously with the complexity of structure and dynamics of polymeric systems.[1] The anisotropic ordering of the mesogenic components of the polymeric molecule and its flexibility and conformational dynamics give rise to quite a complex interplay between orientational and conformational degrees of freedom. The times associated to molecular dynamics span several orders of magnitude, going from the picosecond range of intrachain molecular reorientations to the range of seconds of long time fluctuations of macromolecular aggregates.

The side-chain LCP's are of great interest for potential application in optoelectronics, memory devices, holography, and non-linear optics.[2] For applications in the field of optoelectronics and non-linear optics a special place is held by comb-like LCP's, in which a mesogenic side chain is attached, usually via a flexible spacer,

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to a polymeric backbone; these particular kinds of polymers are useful to realize modulators and optical switches for their non-linear optical characteristics.[3]

Among these, particularly interesting is the possibility of controlling the arrangement of the mesogenic side group using the alignment techniques typical of low molecular weight LC's, such as electric and magnetic fields, surface treatments, and at the same time maintaining such an arrangement stable because of the high viscosity of the polymer matrix which leads easily to glassy phases.

Another control possibility of the macromolecular structure and alignment is through light. Polymers containing photochromic groups, which isomerize under ultraviolet irradiation may show conformational changes in the secondary and tertiary structures.[4]

Recently liquid crystalline polymers containing photochromic groups have been synthesized.[5] Of interest here is the possibility of photoinduced isomerization of the whole macromolecule or of some fragments, due to the absorption of ultraviolet light by the photochromic group. In particular the azobenzene photochromic moiety has been used in substituted polymers such as polystyrenes and polyphosphazenes.[6]

Both from a fundamental and from an applied point of view, the understanding of the molecular dynamics is of paramount importance for these materials; vibrational spectroscopy can be quite a useful tool to study these processes on the fast time scale. In particular, fluctuation IR or Raman spectroscopies[7] have become standard techniques to study reorientational dynamics in simple molecular fluids and, with more difficulty, in liquid crystalline mesophases as well.[8] If one attempts to obtain quantitative informations, these techniques are 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 study by fluctuation Raman and infrared spectroscopy of LCP's. Up to now, most of the applications of infrared spectroscopy have been to assign vibrational bands or to monitor molecular alignment. The few articles concerning infrared spectroscopy of polymer liquid crystals study powder samples as mulls in order to determine or confirm their chemical structure; only very few papers deal with infrared dichroism in aligned mesophases.[9]

To our knowledge no Raman studies have been published on the use of fluctuation spectroscopy to obtain information on reorientational dynamics, apart from a preliminary report published by our group.[10]

In this paper we wish to explore the potential and applicability of vibrational spectroscopy to unravel some of the complexities of stochastic molecular dynamics in polymeric liquid crystalline phases. We shall focus our study on spectra, vibrational assignment, and qualitative data on molecular reorientations obtained for a specific series of side-chain LCP's, **PAn**, based on a polyacrylate backbone with the azobenzene unit in the side chain.[11]

2. FLUCTUATION RAMAN AND INFRARED SPECTROSCOPY

In fluctuation Raman and IR spectroscopy (FS) the vibrational spectral line may be considered as a carrier frequency which is modulated by several types of molecular random motions or relaxation mechanisms. The resulting line shape thus will contain contributions from rotational and translational Brownian motion and from anharmonicities. On the length scale probed by the visible light commonly used in Raman spectroscopy or by IR light, the translational contribution may be neglected.

The spectral density can be written very generally as the time Fourier transform of the appropriate time autocorrelation function (ACF) of the appropriate dynamical variable.[7] More specifically, for Raman spectroscopy such variable is the polarizability fluctuation induced by the motion: $\alpha_{ij}^{\nu} = (\partial\alpha_{ij}/\partial Q^{\nu})_0$, and for IR spectroscopy is the dipole moment fluctuation $m^{\nu} = (\partial \mathbf{M}/\partial \mathbf{Q}^{\nu})_0$. If we assume that rotational and vibrational dynamics are independent, the correlation function may be expressed as the product of the vibrational and reorientational correlation functions, and the resulting line shape will be due to the convolution of the respective Fourier transforms.

The separation of vibrational and reorientational relaxation is by no means obvious and care should be exercised in each specific case to see whether it is applicable. In general we may expect such separation to be valid if the vibrational and reorientational relaxation times are sufficiently different. The resulting line shape can then be expressed as:

$$I_i^{\nu}(\omega) = FT\langle A^{\nu}(t)A^{\nu}(0)\rangle\langle Q^{\nu}(t)Q^{\nu}(0)\rangle \tag{1}$$

where $A^{\nu} = \mathbf{m}^{\nu}$ for infrared absorption and $A^{\nu} = \beta_{ij}^{\nu}$ for Raman spectroscopy (β_{ij} being the anisotropic component of the polarizability tensor α_{ij}); $i = x, y, z$ and refers to the component of m^{ν} in the molecular frame, for the IR case. For the Raman case, $i \equiv \{i, j\}$ and refers to the appropriate components of the Raman tensor in the molecular frame.

The reorientational ACF can be obtained from Equation (1) using the so-called VV-VH experiment in Raman scattering from a simple isotropic molecular fluid. In such case in fact it is straightforward to separate the isotropic (I_{iso}) and anisotropic (I_{anis}) contributions to the scattering; in the laboratory frame we have:

$$\begin{aligned} I_{\text{iso}} &= I_{\text{VV}} - \tfrac{4}{3} I_{\text{VH}}; \\ I_{\text{anis}} &= I_{\text{VH}}; \end{aligned} \tag{2}$$

In Equation (2) VV and VH denote the two separate experimental geometries: VV is the configuration in which the Raman light is analyzed with the polarizer axis parallel to the polarization of the incident beam, whereas in the VH configuration the analyzer is perpendicular.

Since the reorientational fluctuations contribute only to I_{anis}, we have:

$$C_{or}(t) = \langle \beta_{ij}^{\nu}(t)\beta_{ij}^{\nu}(0)\rangle = \frac{FT\{I_{\text{anis}}\}}{FT\{I_{\text{iso}}\}} \tag{3}$$

Thus FRS in principle can yield directly the reorientational ACF in the picosecond time scale. No such possibility exists in Infrared spectroscopy, since for an isotropic fluid there would be no difference in absorption of polarized light. The situation is different in liquid crystalline phases, which consist of strongly anisotropic fluids in which molecules may be aligned over macroscopic ranges. In this case it was shown[12] that the resulting IR dichroism of specific vibrational lines could yield the reorientational ACF for both spinning and tumbling as well as the order parameter $\langle P2\rangle$. In this case the ACF is obtained from the ratio of the Fourier transforms of the normalized absorption band shapes for light polarized perpendicular and parallel to the nematic axis respectively. Raman spectroscopy, although of more difficult applicability, besides the reorientational tumbling ACF can yield both the $\langle P_2\rangle$ and $\langle P_4\rangle$ order parameters.[13]

Thus in aligned anisotropic fluids such as liquid crystalline mesophases both Raman and Infrared FS may be used to obtain information on reorientational molecular fluctuations. Such a possibility has been extensively studied in the case of low molecular weight thermotropic smectics and especially nematics.[8]

In mesophases composed of polymeric molecules the system is much more complex and as we shall see it is not easy to extract the same type of information as was possible for the simpler low molecular weight LC's. In fact we have found no paper in the literature dealing with fluctuation Raman or IR spectroscopy in LCP's.

Since the time scale probed by FS is in the range of $10^{-12} \div 10^{-10}$ sec, clearly the reorientational or conformational relaxations are connected with the dynamics of molecular subunits of the monomer molecule: in the side chain, wagging or libration of the whole chain, alkyl tail conformational disorder or reorientations, relative rotations of the aromatic rings; in the main chain, fast conformational motion. Although many interesting processes in LCP's are connected with slow and very slow fluctuations, it is the fast fluctuations just mentioned which determine the local ordering and its dynamics, and this in turn affects the long time behavior. Thus the potential information obtainable by IR and Raman FS could be quite useful to understand basic behavior of LCP's.

3. EXPERIMENTAL TECHNIQUES

3.1 Synthesis of Polymers

Polyacrylate **PAn** were synthesized[18] following the synthetic procedure outlined in copulation reaction of the diazonium salt of the 4-Alkyloxyaniline **2n** with o-cresol (Figure 1). 4-Alkyloxy-2′-methyl-4′-(6-hydroxyhexyloxy) azobenzenes **4n** were prepared by etherification with 6-chloro-1-hexanol of phenols **3n** in presence of anhydrous K_2CO_3. The final reaction between hydroxylated compounds **4n** with acryloyl chloride was performed in presence of triethylamine and a small amount of free radical inhibitor. Reaction yields of all the synthetic steps were typically higher than 70%.

Polyacrylates **PAn** were synthesized by free radical polymerization of corresponding acrylates **5n** in solution with the use of 2,2′-azobis-isobutyronitrile (AIBN) as initiator (0.5% by weight) at 60°C.

Purification of the polymeric product was accomplished by two reprecipitations

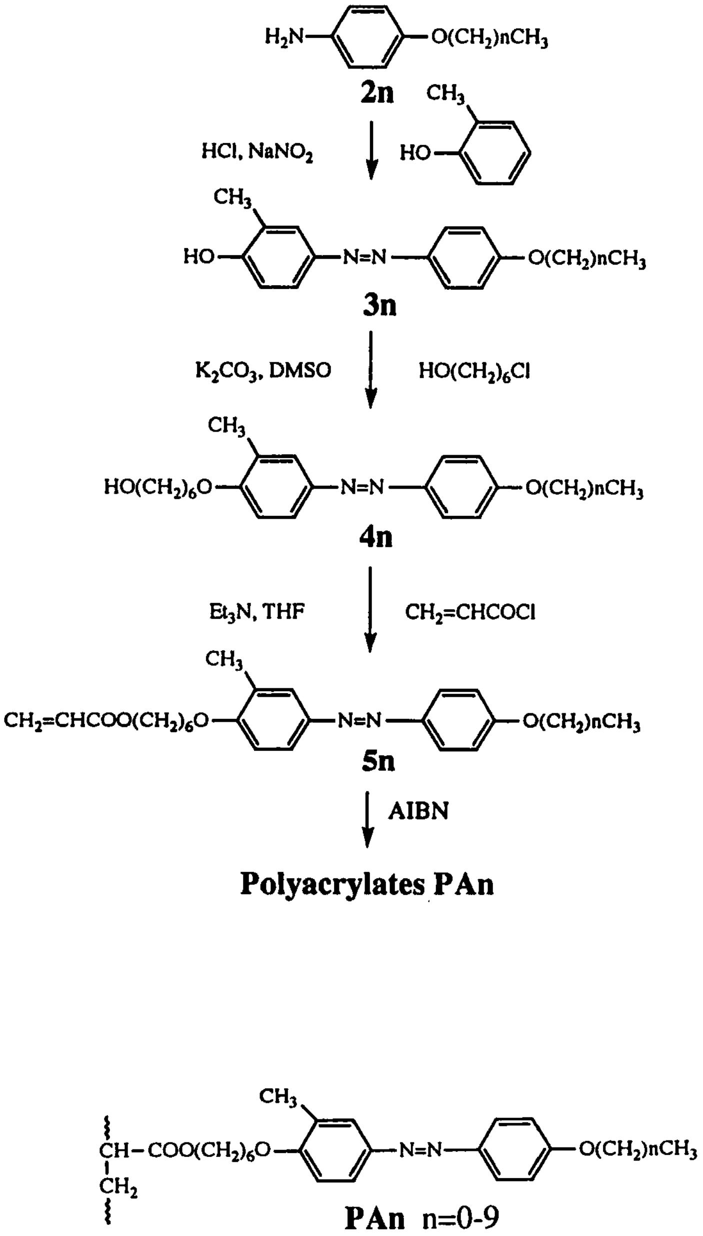

FIGURE 1 Synthetic procedure of **PAn**.

from chloroform solution into methanol and continuous extraction with methanol. Polymerization yields range between 60 and 70%.

The molecular weight characteristics of polyacrylates **PAn** were determined by size exclusion chromatography (SEC). The number average molecular weight (Mn) values were typically higher than 48,000 gmol^{-1} with first polydispersity index (Mw/Mn) comprised between 2.1 and 2.7.

3.2 Sample Preparation and Alignment Procedures

Both Raman and IR spectra were taken on aligned samples as a function of temperature. Due to the very high viscosity of LCP's and the correspondingly long macroscopic reorientational times, the sample preparation procedures are time consuming. Another complication arose from thermal cycling memory effects; therefore our procedures had to be carefully standardized. Unless otherwise stated, the results reported here were obtained on virgin samples.

For RS, the material in powder form was placed in a cell formed by two glass plates which had been treated with polyimide and on which an ITO semitransparent electrode had been evaporated (we wish to thank TECDIS s.p.a. for giving us such plates). A 50 μ teflon spacer separated the glass plates. This assembly was then loaded onto the variable temperature cell, to which an external voltage could be applied to yield electric fields at the sample of up to 10^5 V/cm. The sample was then heated to T_c + 20°C, where T_c is the clearing temperature.

It was kept there for 60 minutes under an a.c. electric field of 20 KV/cm and a frequency of 10 KHz. Then it was cooled into the nematic phase under such field at an average rate of about 0.2 degrees per minute. Using such procedure we were able to produce reasonably well aligned samples in the planar configuration. For the IR spectra the same procedures were used, with the only difference that the sample was contained between treated plates of conducting silicon, and the thickness was approximately 10 to 15 μ.

3.3 Raman and Infrared Spectroscopy

Raman spectra were taken with a standard computer controlled Raman spectrometer in a back scattering geometry with cylindrical focusing. Excitation light power was kept as low as possible in order to minimize damage to the sample or photoinduced effects. A good compromise was a power of about 40 mW. We have used several excitation wavelengths, namely 514.5 nm, 488 nm, and the range 600–640 nm (dye laser). The results were very similar.

A troublesome problem in studying our materials by Raman spectroscopy is the presence of a strong background, which constituted at least 50% of the total signal. Such background increased with time, indicating a slow deterioration of the sample. It also increased quickly with sample damage by the laser.

The high background, the necessity of keeping excitation power low, made it difficult to obtain reliable, high quality spectra. The difficulty became almost prohibitive when the analysis procedures of FS were used, since in this case a good signal-to-noise ratio is necessary. Thus the polarized Raman spectra we report were taken with 10 sec/channel and 30 sec/channel integration times for the I_{VV} and I_{VH} spectra, for a total of about 5 hours for a single Raman line.

The raw spectra were then computer treated using homemade software, in particular background was subtracted using a spline polynomial routine and spectral smoothing was done via Fourier filtering. The results of such treatment on a typical spectrum are show in Figure 2.

Most infrared spectra were taken using a standard grating spectrometer, which was interfaced to a PC that recorded the data. Data analysis was then performed using the same routines as for Raman spectroscopy.

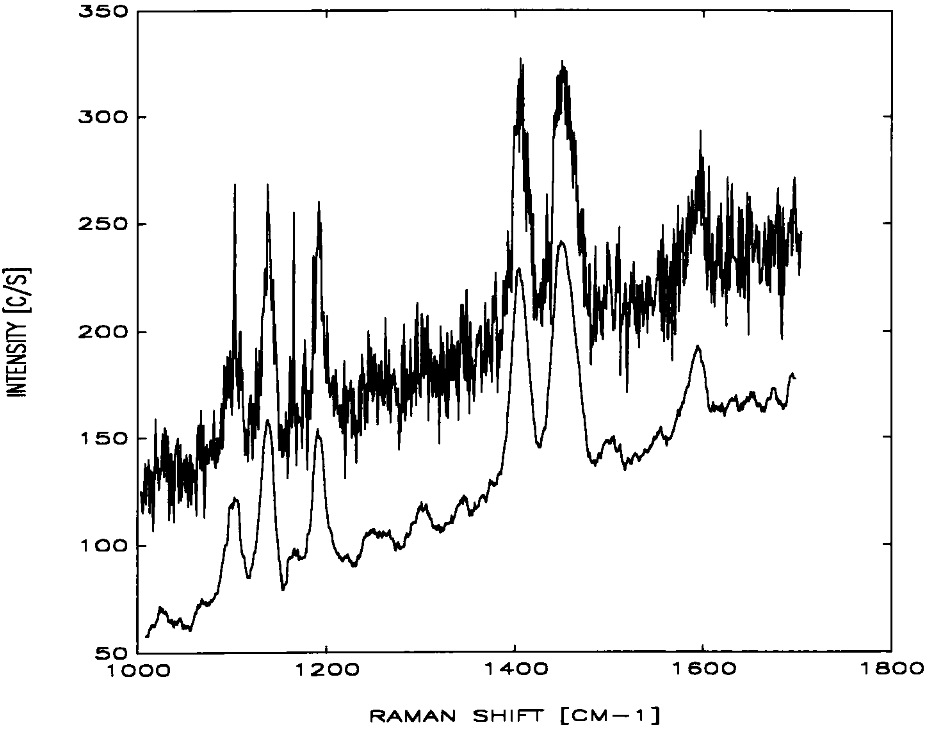

FIGURE 2 Typical Raman spectrum with Fourier filtering treatment.

4. RESULTS

4.1 IR Absorption

In Figure 3 we show a typical absorption spectrum obtained for the crystalline, nematic and isotropic phases of **PA4** for parallel polarization.

Most of the spectral features seem to be fairly insensitive to the phase of the material. We proceeded to the assignment of the vibrational modes. The spectra are similar to those of low molecular weight liquid crystals with molecular structure similar to that of the nematogenic side chain of the LCP, such as hexyloxyazoxybenzene (**HAB**), or even the simpler azoxydianisol (**PAA**). Thus we can use most of the assignments for such systems[14] as a guide. Some extra bands appear in our LCP but their assignment is fairly straightforward; in particular the band at 1738 cm^{-1} belongs to the C═O stretching vibration of the carbonyl group at the beginning of the side chain, and the broad band at 1163 cm^{-1} is most likely connected to the C—O—C stretching vibration. In Figure 4 we show the polarized spectra taken in the aligned nematic phase 60°C.

A summary of the assignments we propose for the main spectral feature we have observed is presented in Table I. There are strong differences in the intensities of parallel and perpendicular components of some of the bands (1601, 1503, 1255,

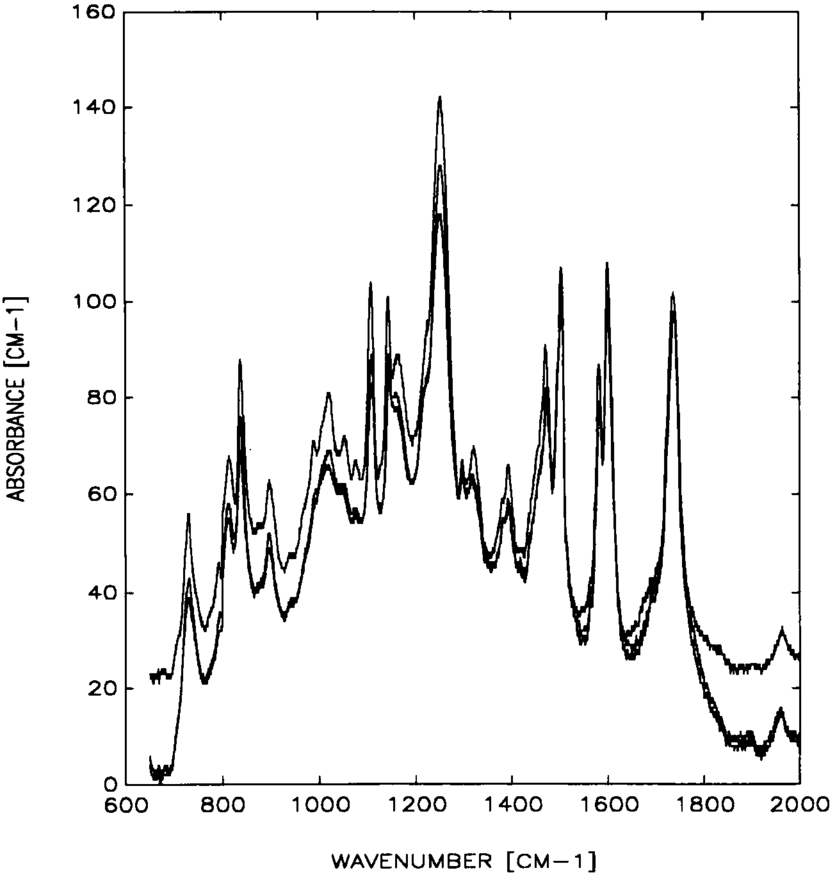

FIGURE 3 Infrared absorption spectrum in crystalline, nematic and isotropic phases.

1144, 1109 cm^{-1}); no changes for the bands at 1163, 1738 cm^{-1}, and the bands at 821, 855 cm^{-1} are transversally polarized (Figure 5).

We have studied carefully the temperature dependence of the dichroic ratio $R_d = I_{\parallel}/I_{\perp}$ for the main polarized bands of the spectrum. In Figure 6 we show the behavior of R_d for the bands at 1601, 1586, 1503 cm^{-1} (Figure 6a), at 1440, 1400 cm^{-1} (Figure 6b) and at 1144, 1109 cm^{-1} (Figure 6c). Apart from a fluctuation at about 77°C, the behavior is similar for all bands and is characterized by a maximum at 66°C, near the lower limit of the nematic phase for this compound (upon cooling).

Slightly different behavior is shown by R_d for the 1400 and 1440 cm^{-1} modes: R_d is constant at its maximum value throughout the entire nematic phase. Finally, for the 1144 and 1109 cm^{-1} modes, the maximum in R_d essentially disappears, although the fluctuations at the beginning and the end of the nematic phase persist.

The increase of R_d with decreasing temperature is typical for many longitudinally polarized bands in simple liquid crystals. In the case of LCP's it shows that at the nematic-isotropic phase transition the side chain which contains the benzene rings (responsible for the modes of Figure 6a) tend to align and such alignment increases as temperature decreases. Although the nematogenic group is attached to the main

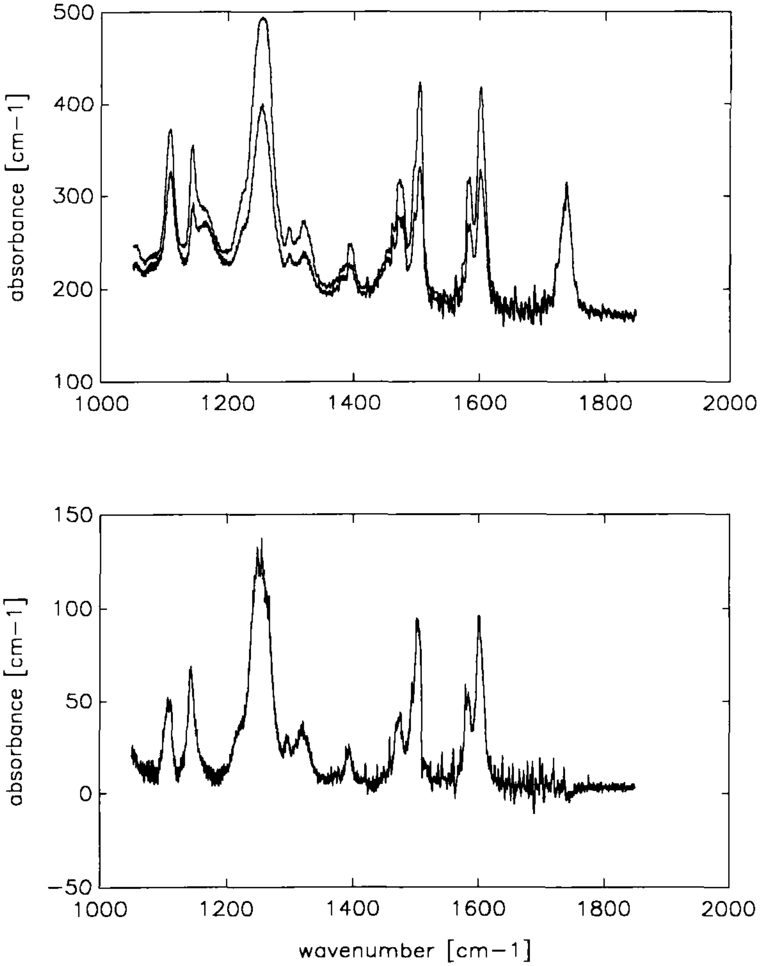

FIGURE 4 Polarized and depolarized infrared spectra (upper) and their difference (lower).

chain by a flexible spacer, its reorientational motion cannot be as free as for simple liquid crystals. In fact, such motion would look more like wagging about a pivot located somewhere in the flexible spacer.

The increased order thus may be due to a decrease in wagging amplitude and/or to a slowing down due to increased hindering. In both cases the values of $I_\parallel$ should increase for longitudinally polarized modes. The temperature dependence of the integrated band intensities $I_\parallel$ and $I_\perp$ is presented in Figure 7. Whereas $I_\parallel$ does increase with decreasing temperature, $I_\perp$ seems to be essentially unaffected.

The detailed behavior of R_d is different for different vibrational modes, namely, C—C ring stretching, CH-in-plane bending, alkyl tail CH_3, CH_2 bending. Thus these modes are influenced differently by the orientational motion of the side chain. Particularly interesting is the behavior of R_d for the CH-aromatic bending modes at the upper end of the nematic range (Figure 6b): such abrupt increase cannot be due solely to the incipient orientational ordering of the side chains. Probably some

TABLE I

Raman and IR band assignment for the main spectral features

INFRARED	RAMAN	ASSIGNMENT	INFRARED	RAMAN	ASSIGNMENT
1738 m		C=0 stretching		1250 w	benz. ring – O stretch
1601 s	1590 sh	C=C stretching of benzenic rings	1226 sh		–N = N– stretch and CH aromatic bend
1586 m	1600 sh	"		1192 s	CH_3 twist
1503 s	1490 w	"	1163 m, broad		alkyl chain–O stretch
1472 m	1495 sh	"	1144 s	1139 s	CH aromatic in-plane bend
1460 m	1460 sh	δ CH_3 and δ CH_2	1109 s	1102 m	"
1445 w	1445 s	"	1050 w		C–C stretchings of alkyl chains
1400 w	1402 s	"	1022 vw		"
1380 vw		"	995 sh		"
1320 w		"	900 m		
1296 w	1300 w	"	842 m		CH aromatic out of plane
	1290 vw	"	816 w		"
1254 vs, broad	1260 vw	C–C aromatic stretch			

bonding between hydrogens of aromatic rings of nearby chains takes place as the chains align, and this would affect the $I_{\parallel}$ intensity.

Although the phase transitions do not alter the spectra very much, small but definite discontinuities occur both in intensity and peak position at the phase transitions. In Figure 8 we show some results. The most important feature of these data is that they consistently indicate a transition in the range around 60°C, besides the nematic-isotropic clearing point. At such temperature we also observe the inversion in the temperature behavior of R_d.

The existence of a transition at this temperature is confirmed by calorimetric data,[15] which feature a specific heat anomaly in this temperature range which, depending on thermal history, becomes a true peak. In this same range anomalies

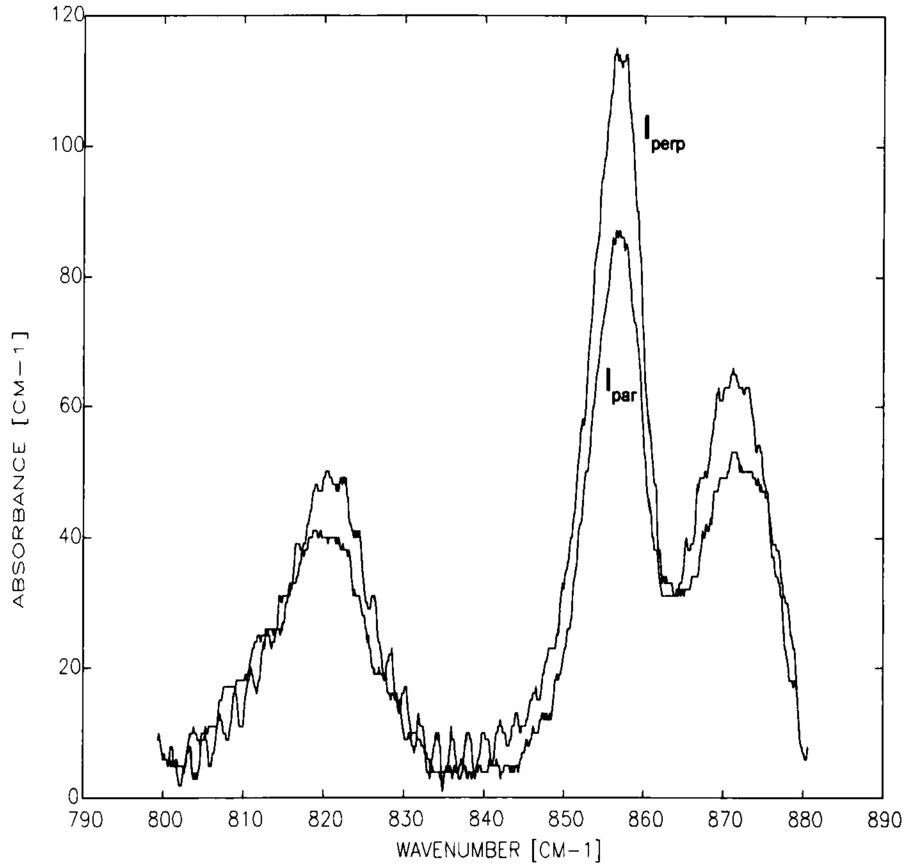

FIGURE 5 Infrared spectra of the transversally polarized bands at 821 and 855 cm^{-1}

in the temperature dependence of the relaxation time are visible in EPR spectra. In fact the structural situation seems to be quite complex: before reaching the glassy state, the sample goes through intermediate phases in a way which is dependent on thermal history and cycling. In particular the sample may feature a quasi-smectic phase, at least as far as local probes such as Raman or IR spectroscopies can tell. In fact, the dichroic ratio R_d is high and essentially independent of temperature, and such a result is also found for low molecular weight liquid crystals.[16]

Later we shall present some more evidence for this hypothesis, which we note also yields a simple explanation for the behavior of R_d (especially that shown in Figure 6b). It is still unclear why R_d decreases with decreasing temperature in the glassy phase. If however we accept the existence of a locally smectic phase at higher temperatures, then the decrease in R may be due to a disorientation of the smectic islands as the sample goes through the transition to the glassy state. This is certainly a puzzling result which warrants further investigation. A more detailed investigation of these effects is in progress and will be published elsewhere.[15]

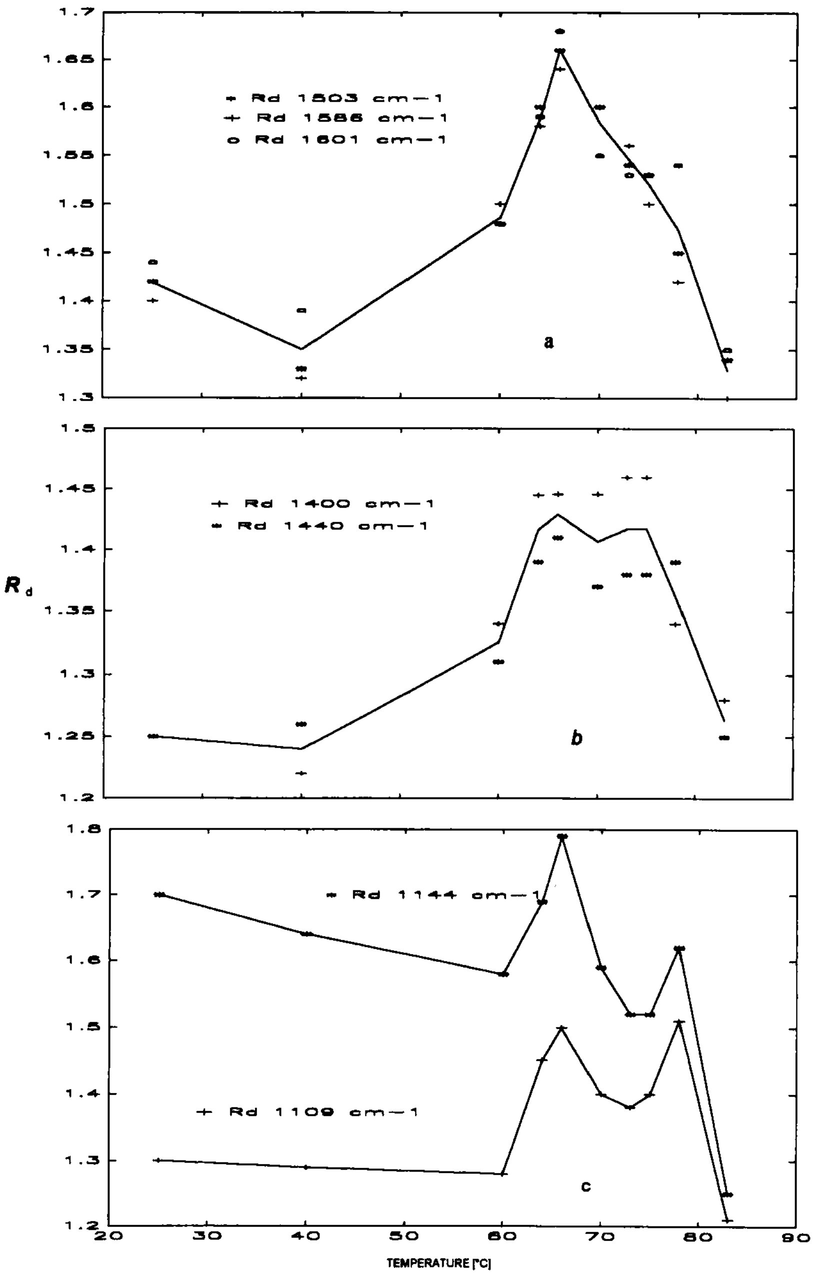

FIGURE 6 Dichroic ratio R_d of 1601, 1586, 1503 (Figure 6a), 1400, 1440 (Figure 6b), 1144, 1109 cm^{-1} (Figure 6c) infrared bands.

4.2 Raman Spectroscopy

As stated earlier, we were not able to find any applications of fluctuation Raman spectroscopy to LCP's in the literature. Thus the first part of the work reported

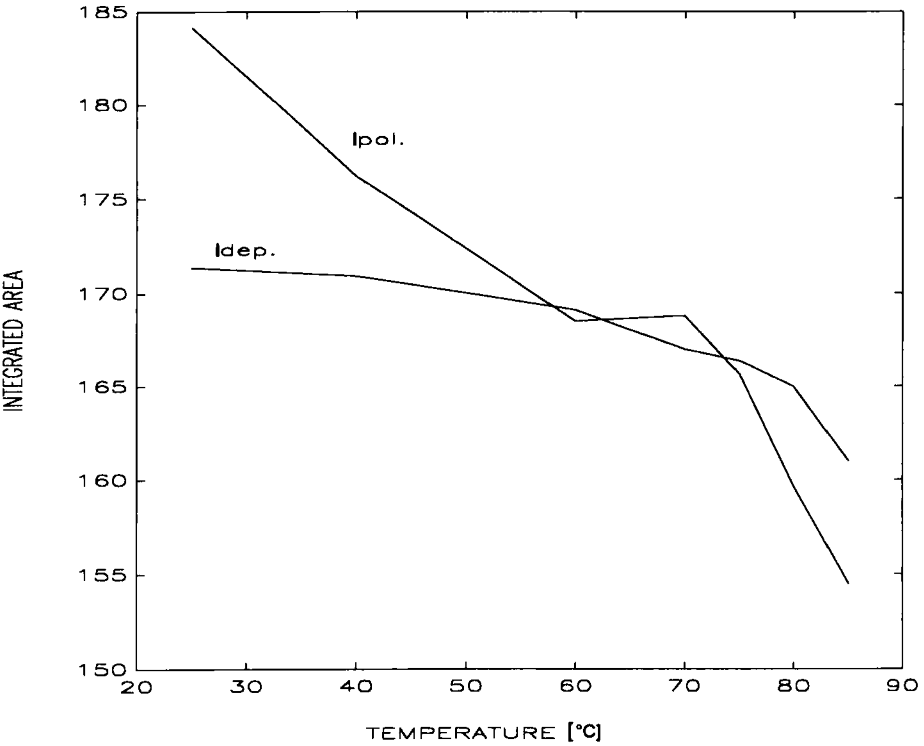

FIGURE 7 Temperature dependence of the integrated band intensity $I_{\parallel}$ and $I_{\perp}$.

here deals simply with the detection and interpretation of Raman scattering in the specific family of LCP's we have studied. Although we investigated several members of the family, from $n = 0$ to $n = 9$ (we recall that n is the number of methylene units in the alkyl tail at the end of the side chain), the spectra we found were essentially identical. Thus in the following we shall discuss only the $n = 4$ sample, **PA4**. In Figure 9, we show the Raman spectra of **PA4** in the solid, nematic and isotropic liquid phases respectively.

The spectra are essentially the same, apart from some change in the background. This is consistent with the IR result, and indicates again that most of the detectable spectral features are related to the mesogenic side chain. Such conclusion is confirmed by the Raman vibrational assignments shown in Table I. Again for such assignments we relied on the similarity of the spectra with those of chemically similar low molecular weight LC's such as **PAA**.

In Figure 10 we show the polarized and depolarized Raman spectra of **PA4** in the planar configuration at 66°C. From spectra such as these, in principle the order parameters $\langle P2\rangle$ and $\langle P4\rangle$ may be obtained by taking the spectra in three experimental geometries[17]: (I_{zz}, I_{zx}), where z is parallel to the nematic axis, and (I_{xx}, I_{xz}) in the homeotropic configuration, i.e., with the nematic axis in the y direction. Furthermore, it is necessary to find a Raman line whose corresponding tensor is strongly uniaxial. Such conditions are particularly stringent and make the deter-

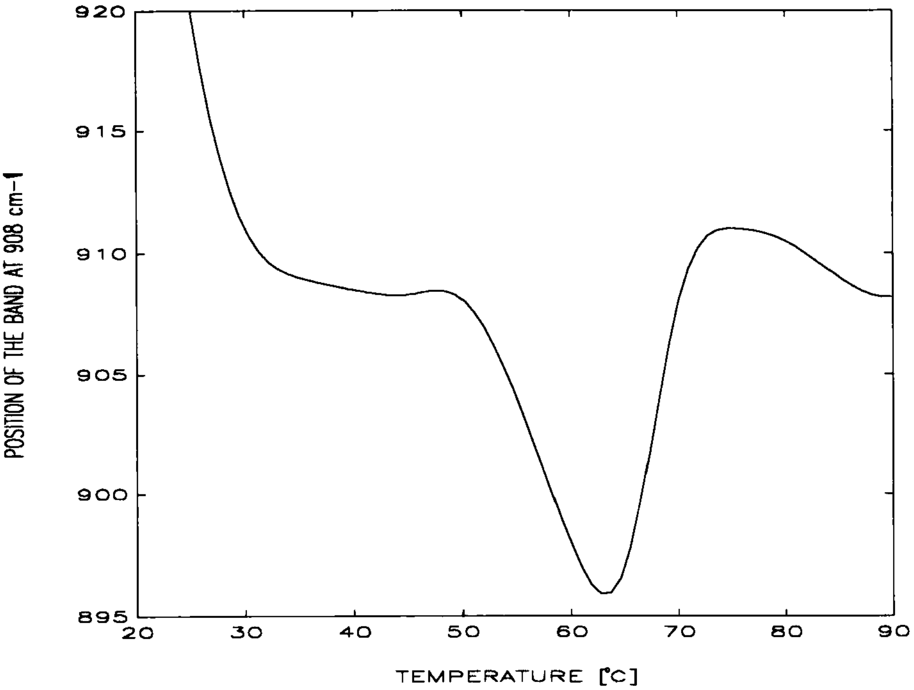

FIGURE 8 Temperature dependence of the position of 908 cm^{-1} infrared band.

mination of the order parameters quite laborious. The situation becomes even more prohibitive if we attempt to use the method of Kirov *et al.*[13] to obtain also the reorientational diffusion coefficient.

Given the preliminary nature of our work on LCP's, we took the Raman spectra only in the I_{xx}, I_{zx} planar geometry, and compared the results with those obtained for the same geometry in low molecular weight LC's. Then we extrapolated to the qualitative behavior of the order parameters. For this we chose the Raman line which could be reasonably assigned to a uniaxial tensor, namely the totally symmetric in-plane aromatic bend at 1139 cm^{-1}.

In Figure 11 we show the behavior of its degree of depolarization $\rho = I_{zx}/I_{xx}$ versus temperature. Such behavior reproduces well the data obtained for low molecular weight LC's in the same configuration. Thus the planar nematic alignment obtained by the application of the 10 KHz electric field is confirmed and the order parameter value at 66°C should be about 0.5–0.6, i.e., very similar to what was observed with IR dichroism.

Again in the spirit of obtaining only qualitative information, we tried to study the rotational diffusion in the side chain. We chose to determine the half width (FWHM) of the 1139 cm^{-1} line using the convolution method, having assumed a Lorentzian profile for the band. In such case the reorientational relaxation time connected with the fluctuations which give rise the dominant contribution to the line shape is given by:

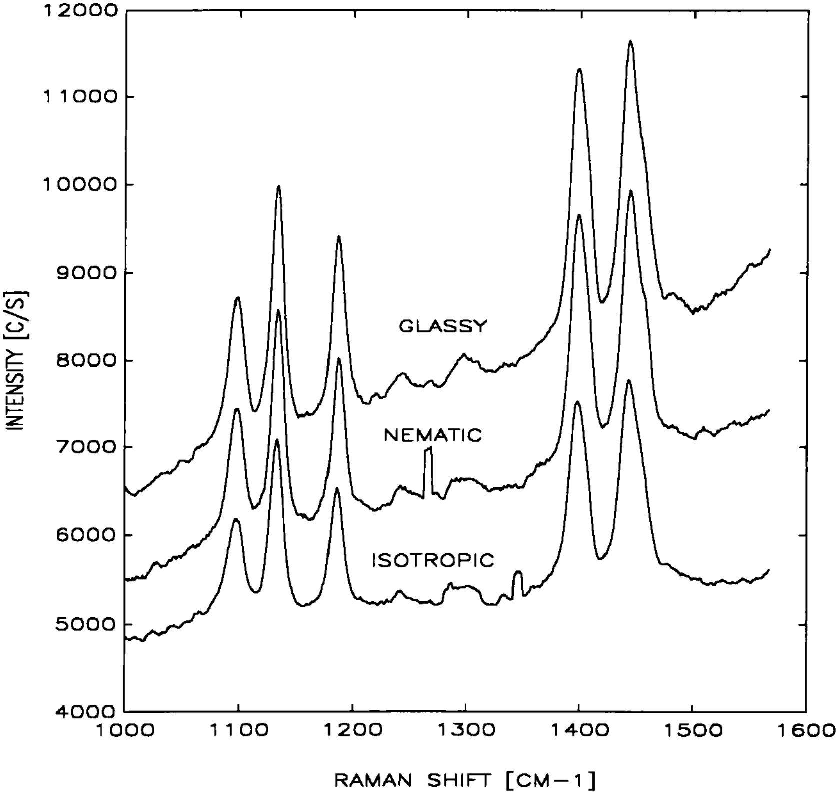

FIGURE 9 Raman spectra of **PA4** in glassy, nematic and isotropic phases.

$$\Delta_{xx} - \Delta_{zx} = \frac{\hbar}{\tau} \qquad (4)$$

The vibration is connected with the side chain benzenic rings, then τ is related to reorientations of the rings, either about the main chain axis, or about an axis perpendicular to the molecular plane. If the Raman tensor were strongly uniaxial, the spinning fluctuations would not modulate the Raman polarizability in the laboratory frame, and hence should not contribute to the line width. This would leave only "tumbling" fluctuations. However in this case the relaxation time measured (approx. 4 ps) would be too short, compared with the values obtained for low molecular weight LC's. Until more quantitative information is available, we tend to interpret τ as an average relaxation time which is indicative of internal motional degrees of freedom of the side chain.

That such motions are associated with a relaxation time which is essentially independent of temperature in the nematic phase, is an indication that the side chains are fairly rigidly packed, as they would be in a smectic-like structure. Such locally smectic structure is very reasonable to expect for a nematic side-chain LCP. Firstly, some members of the **PAn** family we studied actually go through a true smectic phase before becoming nematic. Also, the persistence length of the main

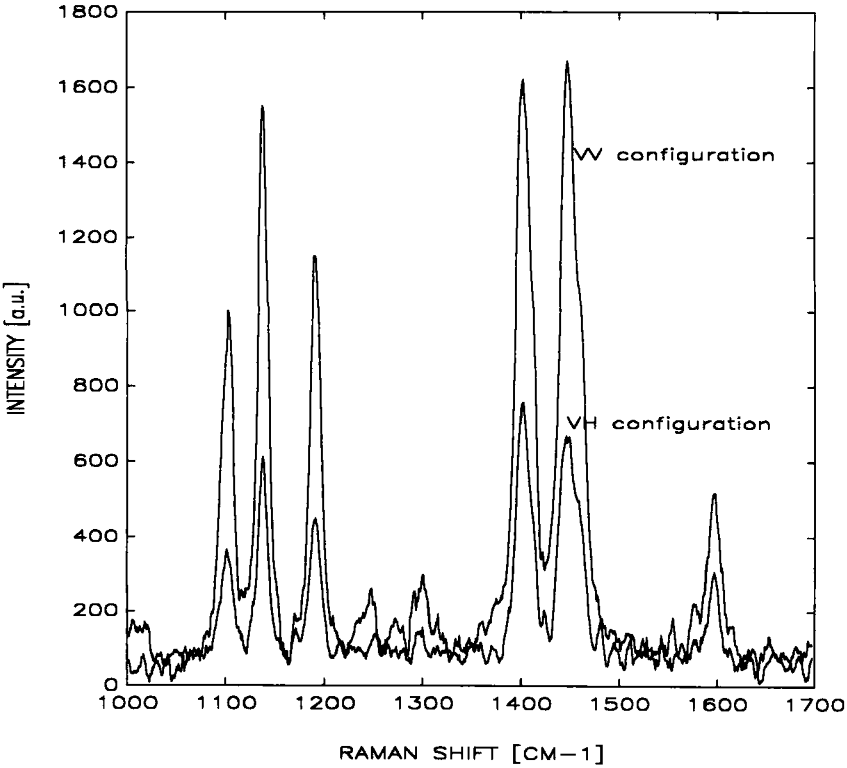

FIGURE 10 Polarized and depolarized Raman spectra in the planar configuration at 66°C.

chain extends over many side chains. The mutual play between the persistence of the main chain in a given direction and the tendency of the side chains to align thus gives rise to smectic-like islands (Figure 12) in which the side chains are more rigidly packed: in particular, the translational mobility parallel to the side chain axis should be greatly reduced. Furthermore, tumbling motion should be reduced to a sort of "dangling" libration about the pivot located somewhere in the alkyl chain flexible spacer which connects the side chain to the main polymer chain.

These considerations, which however must be supported by further, more quantitative evidence, would yield the key for the interpretation of the spectral changes observed in the 60 to 70°C range by infrared spectroscopy.

5. CONCLUSIONS

Application of Raman and Infrared spectroscopy to the study of ordering and dynamics of LCP phases has yielded some interesting new results, particularly those concerning the anomalies in the behavior of the IR dichroic ratio, and the conclusions about the existence of smectic-like islands in the nematic phase. Given the scarcity of work on vibrational spectroscopy of LCP's, it is difficult at present time to make a more general assessment of its usefulness. Certainly as far as the more

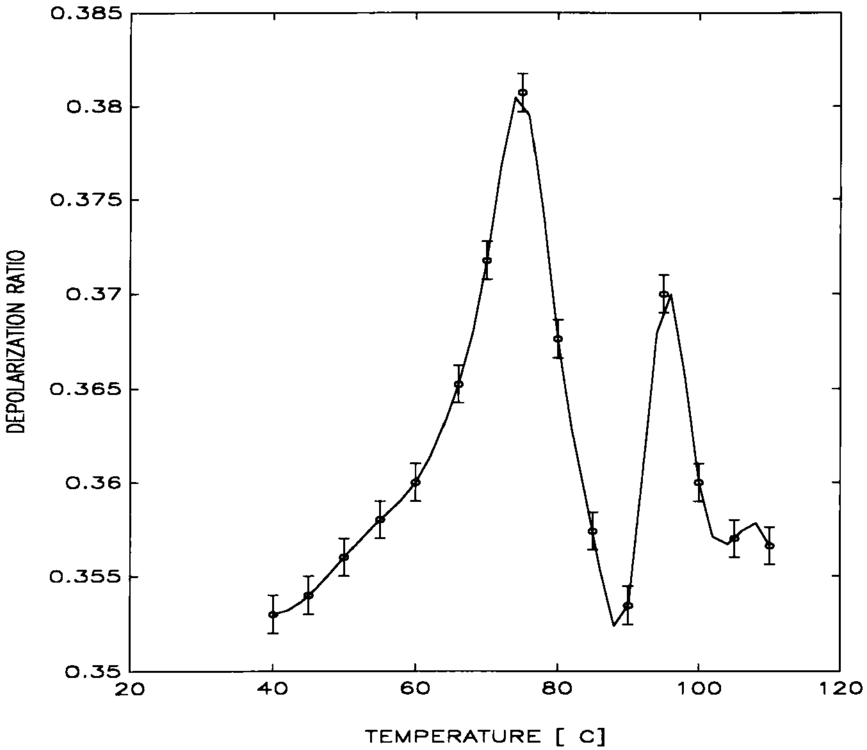

FIGURE 11 Degree of depolarization of Raman band at 1139 cm^{-1}.

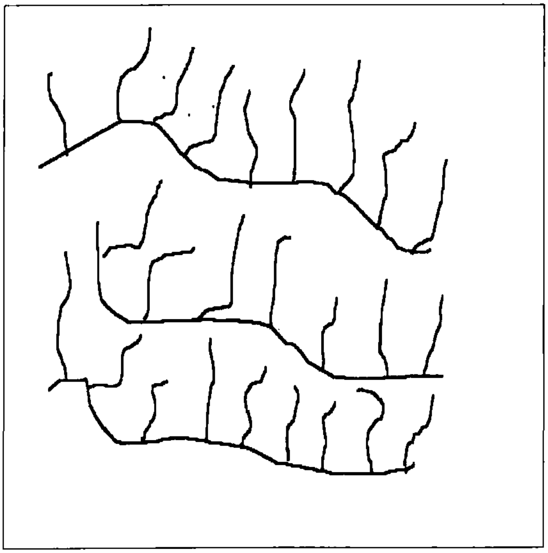

FIGURE 12 Typical geometry of smectic-like islands of our samples.

traditional applications of vibrational spectroscopy are concerned, our results and what can be found in the literature indicate the usefulness and feasibility of Raman and Infrared spectroscopies: chemical structures, symmetry, vibrational assignments. The problems however arise when more quantitative information is sought, particularly concerning diffusional dynamics. In this case perhaps infrared spectroscopy can still yield useful information with a reasonable amount of effort, whereas Raman spectroscopy poses technical problems at the experimental level which at present make the application of the technique quite time consuming and cumbersome. Since however the amount of information potentially available with Raman spectroscopy is considerable, some effort should be devoted to using coherent non-linear Raman spectroscopies, with which many of the problems (background luminescence, signal-to-noise ratio, problems with Fourier transforms) should almost vanish.

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