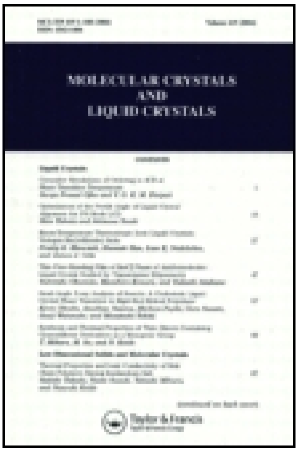

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Infrared Dichroism and Vibrational Spectroscopy of a Side Chain Polyacrylate Liquid Crystalline Polymer

J. K. Vij [a] , A. Kocot [a] , G. Kruk [a] , R. Wrzalik [a] & R. Zentel [b]

[a] Department of Microelectronics and Electrical Engineering, University of Dublin, Trinity College, Dublin, 2, Ireland

[b] Institut für Organische Chemie, Universität Mainz, 6500, Mainz, Germany

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Infrared Dichroism and Vibrational Spectroscopy of a Side Chain Polyacrylate Liquid Crystalline Polymer

J. K. VIJ,† A. KOCOT, G. KRUK and R. WRZALIK

Department of Microelectronics and Electrical Engineering, University of Dublin, Trinity College, Dublin 2, Ireland

and

R. ZENTEL

Institut für Organische Chemie, Universität Mainz, 6500 Mainz, Germany

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The infrared spectra of a polyacrylate side chain liquid crystalline polymer has been recorded and investigated as a function of temperature and the angle of polarisation of the IR incident beam. Variations in the absorbance and frequency are found to be governed by the phase transitions. The order parameter for various vibrational bands has been calculated from the infrared dichroism measurements. It is found that the liquid crystalline polymer alignment achieved by a surface treatment with polyvinyl-alcohol followed by rubbing of the windows does yield reasonable values of the order parameter. The order parameter for the alkyl chain is found to be only 15% of the maximum value; this shows a conformational disorder for the macromolecule in terms of the configuration of chains. Study of the vibrational frequency of bands with temperature shows a definite existence of the pre-transition effects especially for SmA phase. Frequencies for most of the vibrational modes are seen to change abruptly at SmA-N and N-I transitions reflecting an alteration in the intermolecular interactions at the phase transitions.

Keywords: infrared dichroism, infrared spectroscopy of a LC polymer, molecular order parameter

INTRODUCTION

Thermotropic liquid crystalline polymers with mesogenic side chains are of enormous scientific and technical interest. This is due to the possibility of being able to combine properties of the low molecular liquid crystal with those of the polymers in the same material. Infrared (IR) spectroscopy is a powerful technique for studying the orientational and the conformational changes in the molecules in mesophases.[1-7] In this paper, the orientational order in smectic and nematic mesophases has been investigated.

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†To whom correspondence should be directed.

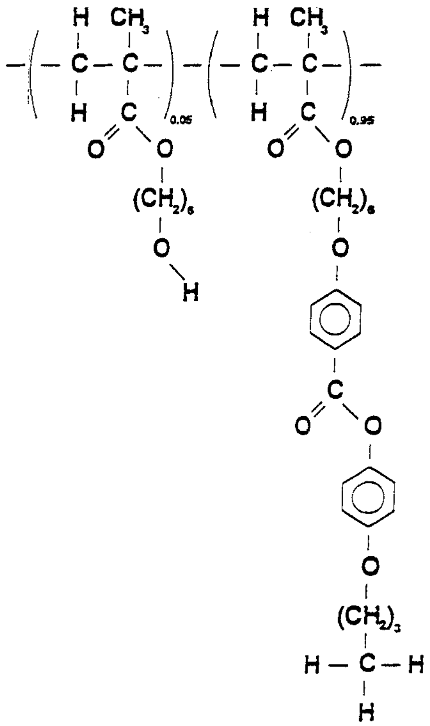

FIGURE 1 Chemical formula for the side chain L.C. polymer investigated.

EXPERIMENTAL

The liquid crystalline side chain polymer (polyacrylate) having structure shown in Figure 1 was synthesized by one of the authors.[8] The phase transition temperatures for this polymer are: G45 S_A 102 N 106 I. The phase behaviour of the sample has been determined using polarising microscopy and x-ray measurements.

The infrared spectra were recorded using a Fourier transform spectrometer Digilab FTS-60A in the frequency range 600–4000 cm^{-1} with a resolution of 0.2 cm^{-1}. The sample is aligned in the homogeneous arrangement (where the director lies in the plane of the windows) between two optically polished Si windows. This is achieved by coating windows with poly vinyl alcohol solution in water. A sandwich of Si windows was inserted in a cell whose temperature can be varied over a wide range with a temperature stability of better than ±0.1°C.

The spectra were recorded both for parallel and perpendicular polarisation of the incident beam. The polarisation angle is measured with reference to the direction of alignment.

RESULTS AND DISCUSSION

Figures 2 and 3 display absorbance in arbitrary units for 2 representative sections of the wavenumber range, where the polarisation angle between the incident beam

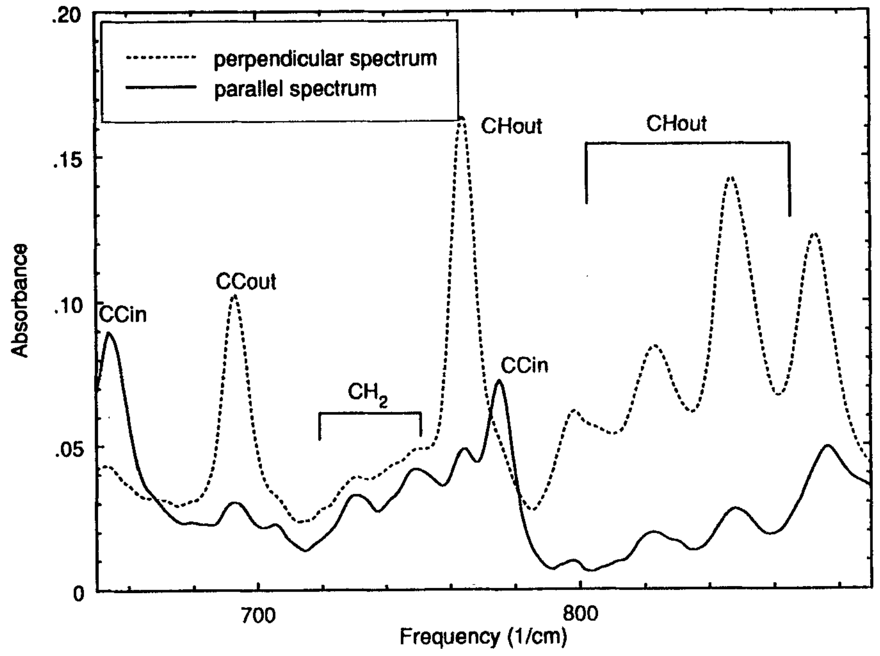

FIGURE 2 Plot of absorbance vs $\bar{\nu}$ for two polarisation angles, full-line $\alpha = 0°$, dash-line $\alpha = 90°$. The figure shows CH aromatic and CC aromatic bending vibrations as marked CC_{in}, CC_{out}-benzene ring in- and out-of-plane vibrations, CH_{in}, CH_{out}-CH aromatic in- and out-of-plane vibrations, CH_2—CH_2 rocking vibrations.

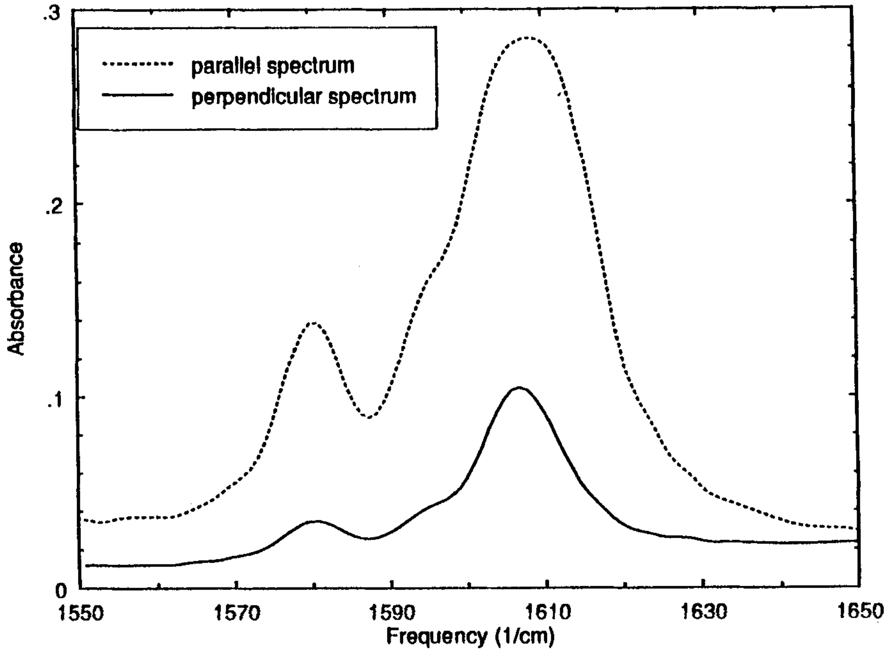

FIGURE 3 Plot of absorbance (relative units) vs $\bar{\nu}$ for two polarisation angles, dash line $\alpha = 0$, full line $\alpha = 90°$. Plot shows the behaviour C—C aromatic stretch vibrations.

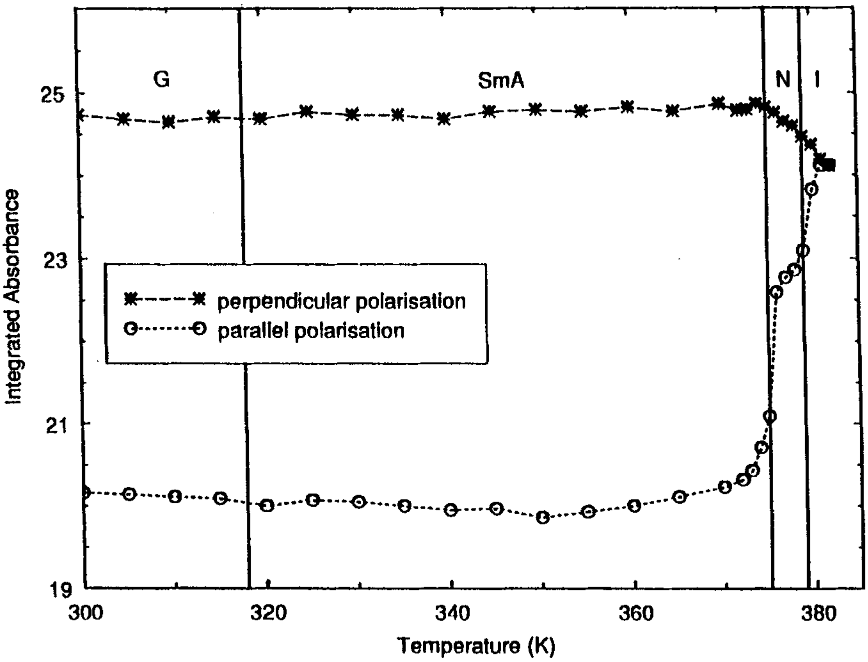

FIGURE 4 Integrated absorbance over a wavenumber band 2671–3137 cm^{-1} for two polarisation angles. 'o' pol. angle = 0° and '*' pol. angle = 90°; the band includes CH_2, CH_3 symmetric and asymmetric stretch vibrations.

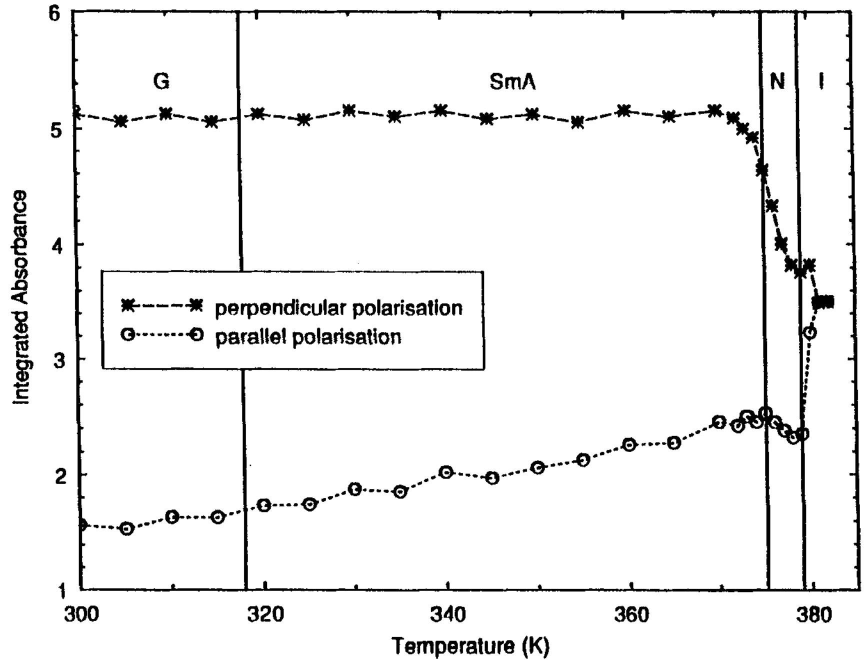

FIGURE 5 Integrated absorbance over a wavenumber band 790–860 cm^{-1} covering CH aromatic out of plane deformation, 'o' pol. angle = 0°; '*' pol. angle = 90°.

and the director is zero and 90°, respectively. The director represents the average direction of the molecular orientations. The director is therefore coincident with the average direction of the long molecular axes. This direction will therefore lie along the average direction of the transition dipole moment for those which are roughly parallel to the long molecular axis and along which maximum absorbance for such transition moments is observed when the incident beam is at zero polarization angle. Figures such as 2 and 3 are used to calculate the IR dichroism ratio. Figures 4 and 5 show area of absorbance bands as a function of temperature for the two polarisation angles of 0° and 90°. As expected integrated absorption intensities for the two polarisation angles are the same in the isotropic phase whereas these are different in SmA and N phases due to the alignment of the liquid crystalline sample. However, with the sample aligned, there is a very small difference in the integrated absorption intensities at the glass to SmA phase transition. The absorption measurements discussed above are used to determine the order parameter.

Order Parameter

The orientational order in the mesophorphic phase can be described by an orientation distribution function.

The infrared absorption for a single molecule is proportional to $(\mathbf{E} \cdot \mathbf{p}_i)^2$ where $\mathbf{E}$ is the electric field of IR radiation and $\mathbf{p}_i$.

$$\mathbf{p}_i = \frac{d\mathbf{u}_i}{dq_i} \tag{1}$$

is the transition dipole moment vector with respect to the normal co-ordinate q_i of the ith mode. $\mathbf{p}_i$ corresponds to a particular vibration of a molecule.

The main advantage of IR spectroscopy lies in its possibility of studying the orientational distribution of dipoles $\mathbf{p}_i$ for those parts of the molecule where the molecular vibrations are localized. This contrasts with other techniques where the molecular orientation as a whole is investigated.

The orientational order parameter is given by

$$S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle \tag{2}$$

where θ is an angle between the optical axis (director) of the sample and the orientation position of an individual molecule (i.e., between $\vec{n}$ and $\vec{L}$, $\vec{n}$ denotes the director). In order to obtain the order parameter (S_2), the dichroism ratio R_d is calculated. R_d is defined as:

$$R_d = \frac{A_{\parallel}}{A_{\perp}} \tag{3}$$

where $A_{\parallel}$ and $A_{\perp}$ are the integrated absorbances of the bands for the linearly polarised radiation measured parallel and perpendicular to the director (optical axis), respectively.

According to Neff and Brown[9] the dichroism ratio can be expressed by

$$R_d = \frac{\cos^2 \bar{\Psi}\langle\cos^2 \theta\rangle + \frac{1}{2}\sin^2 \bar{\Psi}\langle\sin^2 \theta\rangle}{\frac{1}{2}\cos^2 \bar{\Psi}\langle\sin^2 \theta\rangle + \frac{1}{4}\sin^2 \bar{\Psi}\langle(1 + \cos^2 \theta)\rangle} \tag{4}$$

Ψ is an angle between $\mathbf{L}$ and $\mathbf{p}_i$. In this paper $\mathbf{L}$ denotes the long molecular axis of a particular molecule. $\bar{\Psi}$ is the average of all such Ψ angles.

If the transition moment $\mathbf{p}_i$ for the *i*th mode is directed along the long molecular axis, Equation (4) will be reduced to

$$R_d = \frac{1 + 2S_2}{1 - S_2} \tag{5}$$

For the bands with $\mathbf{p}_i$ normal to the long molecular axis, R_d is given by

$$R_d = \frac{2(1 - S_2)}{2 + S_2} \tag{6}$$

These results agree with those derived by Maier and Saupe[10] for $\bar{\Psi} = 0°$ and $\bar{\Psi} = 90°$, respectively. The dichroism ratio as a function of temperature has been measured for a number of vibrational bands. These are mainly the C—H out of plane ring vibrations, C—C in plane ring vibrations and CH_2, CH_3 alkyl chain vibrations.

The vibrational bands of the benzene ring, which forms a part of the mesogenic group, appear to be a good indication of an ordering in the sample. The most polarisation dependent bands are assigned to these vibrations; this follows from their high sensitivity of the IR absorbance to the polarisation of the incident beam. The C=O stretching vibrations of the ester group is found not to be so useful due to its low measured value of R_d. This behaviour for the C=O band is due to a difference in the positions of the two ester groups in the polymer structure (Figure 1); this implies that transition dipole moment of the C=O group is neither parallel nor perpendicular to the long molecular axis. The same is true for C—O stretching vibrations, these involve ether or ester oxygen and the aromatic carbon. These also lie at different positions of the macromolecule and have therefore transition dipole moments lying in different directions.

Preliminary results of the order parameter of some vibrational bands of this material were presented at the 1991 Summer Liquid Crystal conference in Lithuania.[11]

Figure 6 shows S_2 for C—H aromatic out of plane deformation vibration (765 cm^{-1}) for which $\bar{\Psi} = 90°$. The maximum value of $S_2 = 0.61$; this is somewhat lower than that compared with S_2 for low molar mass liquid crystals. It is also lower than that measured by Schätzle and Finkelmann[11] for polysiloxanes. These authors

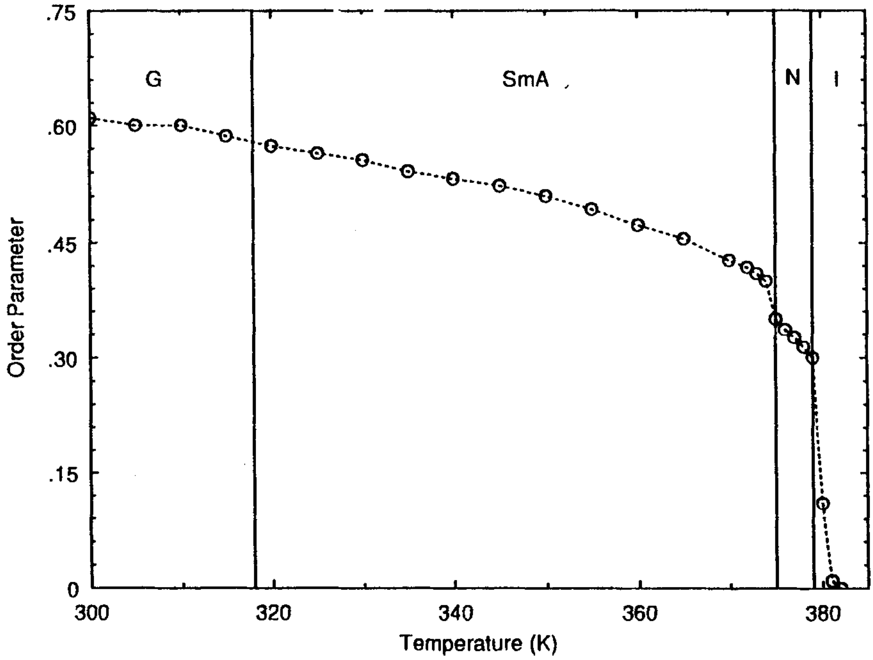

FIGURE 6 Order parameters S_2 as a function of temperature for C—H aromatic out of plane deformation vibration.

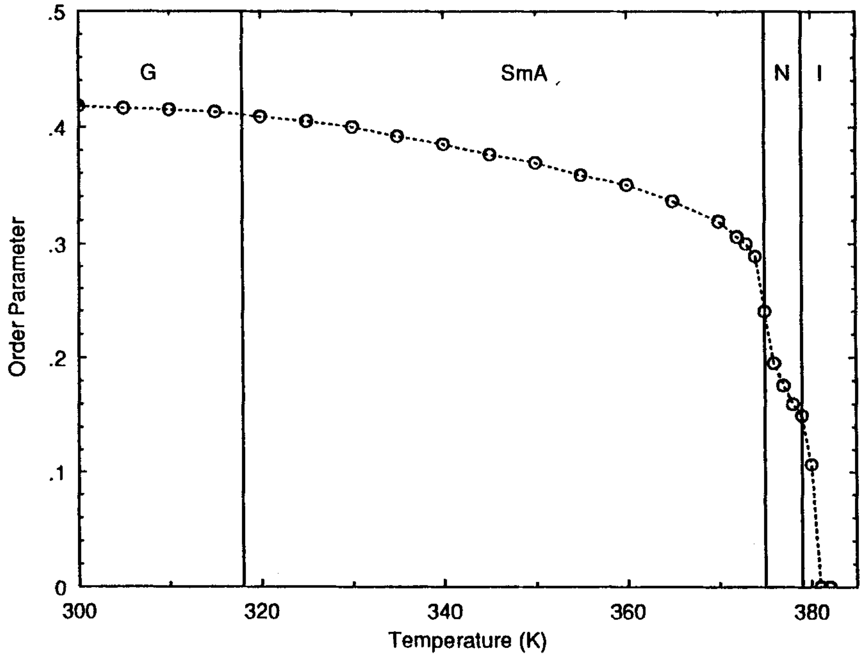

FIGURE 7 Apparent value of order parameters S_2 as a function of temperature for benzene ring C—C in plane vibrations centred at 1610 cm^{-1}.

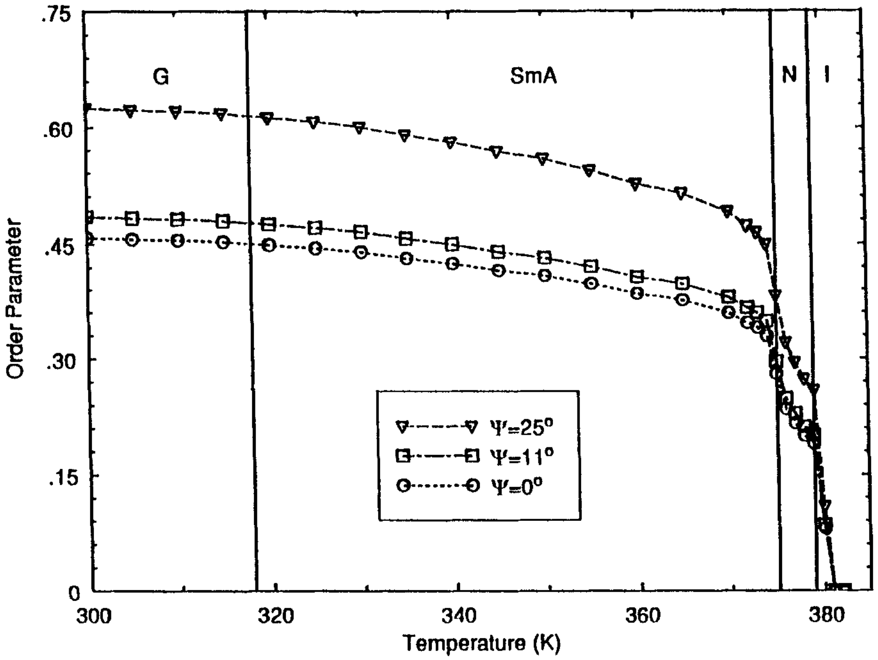

FIGURE 8 Calculated value of order parameter S_2 based on results of Figure 7 on the assumption that $\Psi = 0°$, 11° and 25°, as marked in the figure.

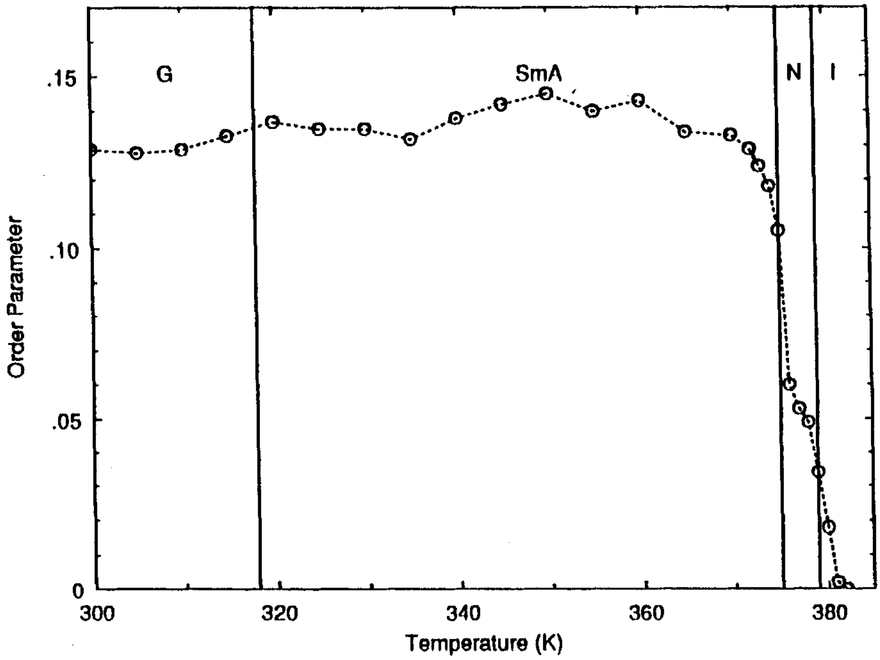

FIGURE 9 Order parameters S_2 for CH_2—CH_3 stretching vibrations of the alkyl chain as a function of temperature. The wavenumber band over which the integration is made is 2671–3137 cm^{-1}.

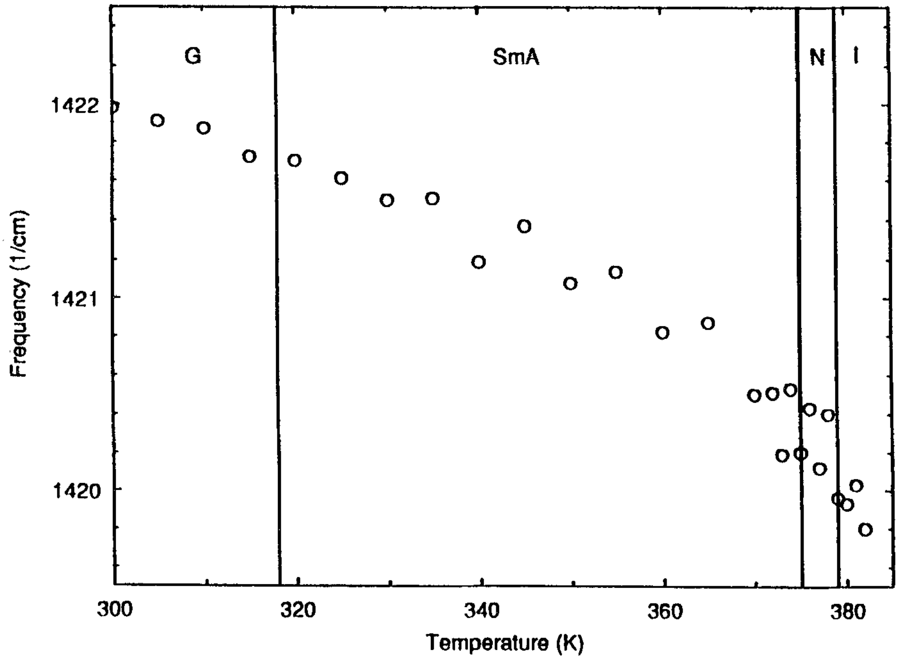

FIGURE 10 Vibration frequency in cm^{-1} vs temperature, the band is assigned to C—C aromatic-in-plane deformation vibration.

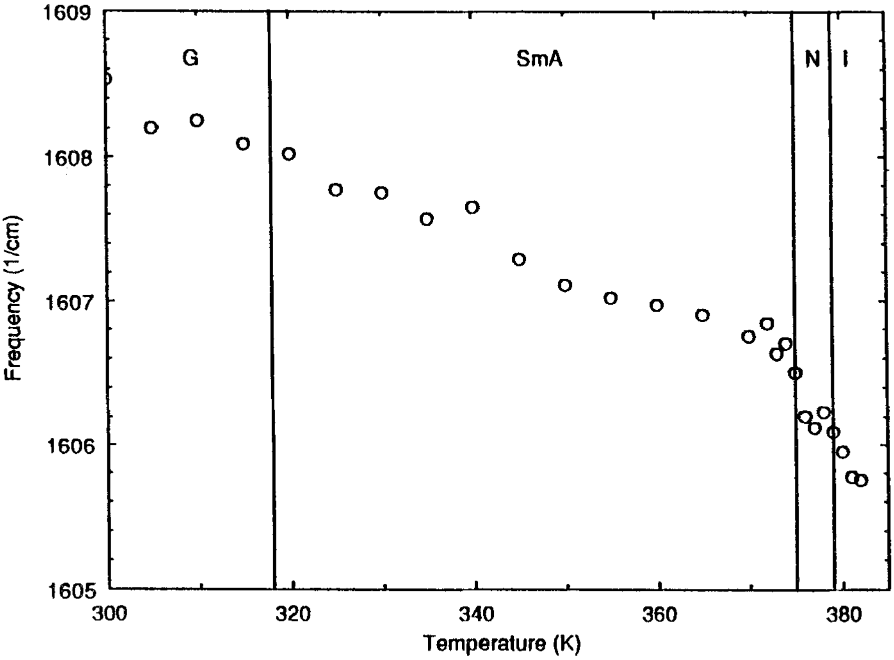

FIGURE 11 Vibration frequency in cm^{-1} vs temperature, the band is assigned to C—C aromatic stretching vibration.

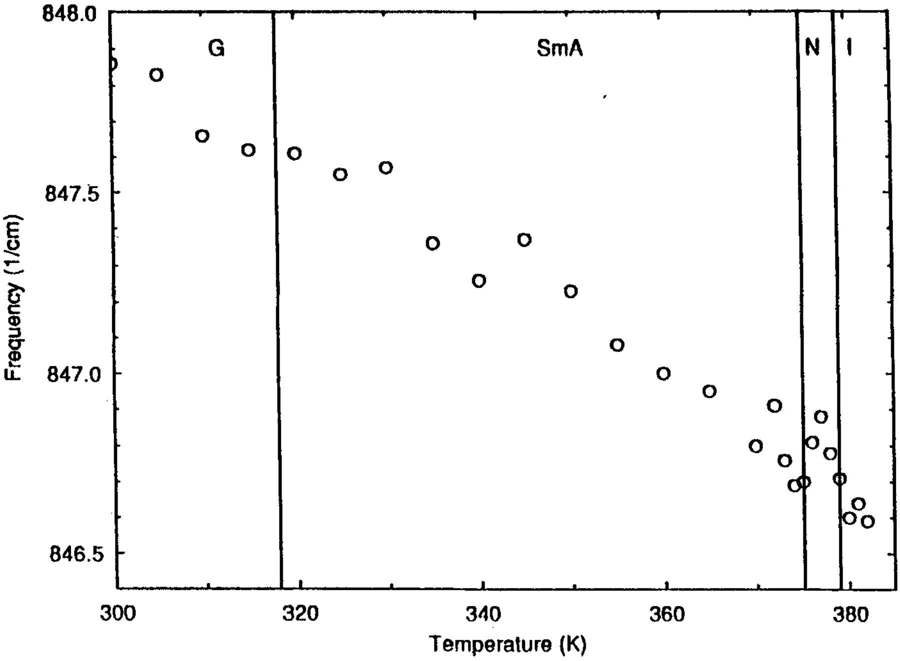

FIGURE 12 Same as Figure 11. The vibrational band is assigned to C—H aromatic out-of-plane deformation.

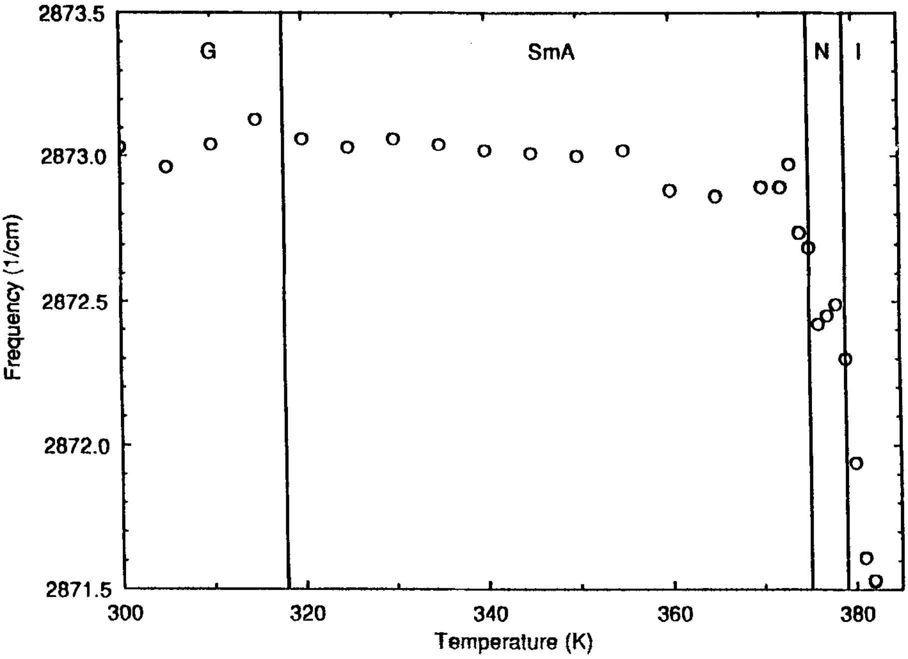

FIGURE 13 Vibrational frequency in cm^{-1} vs temperature. The band is assigned to CH_3 symmetric stretching vibrations.

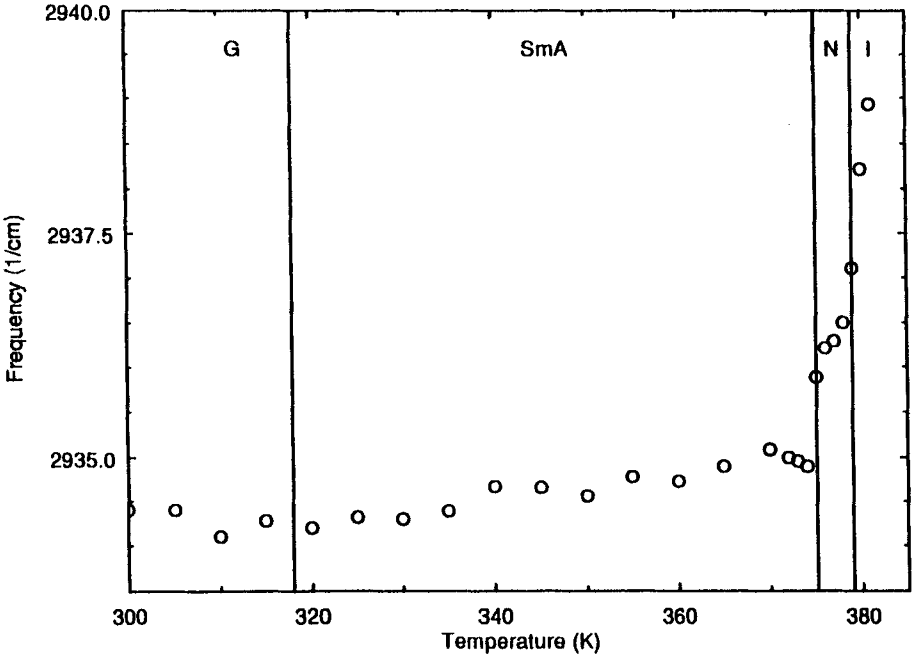

FIGURE 14 Same as Figure 13, this band is assigned to CH_2 asymmetric stretching vibration. Note an increase in the frequency at SmA to N phase transition.

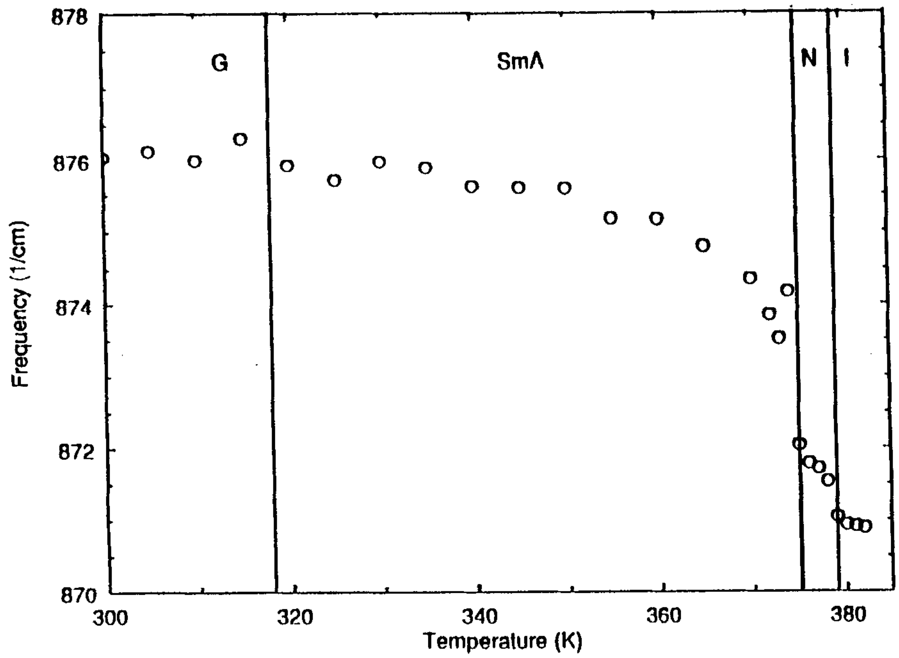

FIGURE 15 Vibrational frequency in cm^{-1} vs temperature, this band is assigned to C—C benzene ring out-of-plane deformation vibration.

achieved the ordering by stretching the elastomer. However, a value of 0.61 seems quite reasonable in view of the limitation of the surface alignment technique used by us.

Figure 7 shows the plot of the apparent value of the order parameter as a function of temperature for the C—C aromatic in plane vibrations which should lie along the long molecular axis. For this calculation, we have assumed $\bar{\Psi} = 0°$ as a first approximation, an average of angles between $\mathbf{p}_i$ and $\mathbf{L}$. However, we may reasonably expect a small average angle between the long molecular axis and the transition dipole moment. In Figure 8, we recalculate S_2 by assuming $\bar{\Psi} = 11°$ and $\bar{\Psi} = 25°$ and we find that the curve for the latter angle is almost coincident with that for the out of plane C—H stretch vibrations. It is therefore reasonable to conclude that the director makes a non-zero angle with the long molecular axis, this angle may lie in between 10° and 25°.

The CH_2 and CH_3 groups in the alkyl chain are approximately normal to the main body of the chain. The dichroism ratio for these deformations is used to calculate S_2. A plot of S_2 as a function of temperature for CH_2, CH_3 stretch vibrations is shown in Figure 9. The order parameter for these deformations is of the order of 0.14 for SmA phase and when compared to values of 0.61 for C—H out of plane vibrations, this value is exceedingly small. This shows that the alkyl chains of the macromolecules are relatively disordered. This is due either to their possible flexibility or due to the existence of several conformations of the molecule in which the chain lies in different positions. S_2 results for CH_2, CH_3 deformations are in agreement with those found on low molar mass liquid crystals using NMR. Guo and Fung[13] find S_2 for the alkyl chain in cyanobiphenyls and their value lies in between 0.10 and 0.15 depending on the carbon atom in the chain.

Vibrational Bond Frequencies Versus Temperature

We now examine the frequencies of the vibrational bands as a function of temperature. In Figure 10, frequency of the C—C aromatic, in-plane deformations, is plotted as a function of temperature. The total change in frequency over a temperature range of 100°C is 2.5 cm^{-1}. It is small but nevertheless it is a factor 10 higher than an accuracy of the measurements.

Frequency of the band was fitted to a standard program supplied by the manufacturers and the centre frequency was calculated from it. We observe a gradual fall-off of the frequency of SmA phase, with a tendency of some further drop from SmA to N phase transition.

In Figure 11, the plot of C—C aromatic stretch vibrations frequency as a function of temperature is shown. The behaviour is almost similar to that observed in Figure 10. Here again there is a gradual and a smooth reduction in the frequency of these vibrations in SmA phase, this is followed by a somewhat sudden drop at the nematic and isotropic phases. Figure 12 shows the plot for the frequency of C—H aromatic, out of plane deformation, as a function of temperature, the behaviour is almost similar to that observed in Figure 11. The most common feature of Figures 10–12 is that there is a considerable and a gradual drop in the frequency of the various vibrational bands in SmA phase. This shows a definite existence of the pre-transition effects. This may follow from a gradual softening up of the bonds with temperature which in turn follows from a gradual reduction in the intermolecular interactions. In the literature, frequency shifts of internal modes for a few low molar mass liquid crystals, as the phase transition is approached, have also been observed. Amer and Shen[14] reported such shifts in some cases so did Itoh *et al.*[15] for PAA.

On comparing our results of phase transitions with those determined by DSC or polarising microscopy, we find that the phase transitions are not restricted to the transition temperatures alone but start happening at temperatures before these are reached.

Figure 13 shows the plot of CH_3 symmetric stretching vibration frequency and here again the trend is more or less similar to that observed in Figures 10–12. Figure 14 shows a plot of a CH_2 asymmetric stretching vibration frequency vs. temperature. Here the frequency increases with temperature, there is relatively a big increase in the frequency observed for SmA to N phase transition and this trend extends into the I phase. This plot shows an exception to the general rule that frequency should decrease with an increase in temperature. It is conceivable that this particular vibrational frequency is related to the disorder in the system. The vibrational frequency is related to the force constant (k) and the reduced mass of vibration (μ) by the relation

$$\bar{\nu} \sim \sqrt{\frac{\langle k \rangle}{\mu}}$$

$\langle k \rangle$ is an averge value over the intermolecular interactions. The value of $\langle k \rangle$ depends on a delicate balance between the attractive and repulsive forces. If attractive forces are greater than the repulsive ones, $\langle k \rangle$ is small and $\bar{\nu}$ decreases. The opposite is true when attractive forces are weaker than the repulsive ones. Nevertheless, in real molecular systems the situation is much more complicated but investigation of vibrational frequency provides us with the information about interactions between molecules. Frequencies for the C=O and C—O stretching vibrations of the ester group ($\bar{\nu}$ at 1732 and 1250 cm^{-1}, respectively) linked to the benzene group also tend to shift to higher wavenumber for SmA to N phase transitions. This phenomenon might reflect changes in the molecular geometry which results in a higher conjugation between the π-electrons of the benzene ring and C=O bond or interactions with the lone pair electrons of the ether oxygen.

Figure 15 shows an unambiguous sudden decrease in the C—C benzene out-of-plane deformation vibrational frequency at SmA to N phase transition, followed by a similar trend at N to I transition. Figures 10–15 show that the phase transitions in liquid crystalline materials can also be studied by vibrational IR spectroscopy.

CONCLUSIONS

IR spectroscopy is found to be an extremely useful technique for the study of the localized ordering in a side chain liquid crystalline polymer (l.c.p.). The sample is aligned using the surface alignment techniques. The order parameter has been determined in its glass, SmA, N and I phases.

The average angle between the transition dipole moment of the C—C aromatic in-plane vibrations and the long molecular axis of l.c.p. is found to lie in between 10° and 25°. We observe variations in frequencies of the vibrational modes with phase transitions, which reflect variations in the intermolecular interactions. Pre-transition effects are also noted especially for SmA phase. As can normally be expected, the intermolecular interactions start changing even before the transition temperature is reached, this behaviour is reflected in a gradual variation in frequencies observed for the glass and SmA phases as a function of temperature.

Variations in frequencies of the vibrational modes at the transition temperatures show that the phase transitions are affected by the intermolecular interactions and to some extent these effect the internal vibrational bond frequencies.

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References

1. W. Mayer, G. Englert and B. J. Bulkin, *Z., Elektrochemie*, **64**, 68 (1960).
2. B. J. Bulkin, T. Kennelly and W. B. Lok, "Liquid Crystals and Ordered Fluids," J. F. Johnson, R. S. Porter (Eds.) NY, Plenum Press, 1974, Vol. 2, p. 85–95.
3. A. Gruger, F. Romain and N. LeCalve, *Mol. Cryst. Liq. Cryst.*, **116**, 85 (1984).
4. A. Gruger, F. Romain and N. LeCalve, *Mol. Cryst. Liq. Cryst.*, **116**, 57 (1984).
5. N. Kirov and P. Simova, "Vibrational Spectroscopy of Liquid Crystals," Publishing House of the Bulgarian Academy of Sciences, Sofia, 1984.
6. M. Zgonik, M. Rey-Lafon, C. Destrade, C. Leon and H. T. Nyuyen, *J. Phys.*, France, **51**, 2015, (1990).
7. C. David and D. Baeyens-Volant, *Liquid Crystals*, **6**, 247 (1989).
8. R. Zentel and G. Reckert, *Makromol. Chemie*, **187**, 1915 (1986).
9. V. D. Neff, L. W. Gulrich and G. H. Brown, in "Liquid Crystals," (G. H. Brown, G. J. Dienes and M. M. Labes, Eds.) Gordon and Breach, NY, 1967, pp. 21–35.
10. W. Maier and A. Saupe, *Z Naturforsch*, **16**a, 816 (1961).
11. A. Kocot, R. Wrzalik, G. Kruk and J. K. Vij, *Mol. Mater.*, **1**, 273 (1992).
12. J. Schätzle and H. Finkelmann, *Mol. Cryst. Liquid Crystals*, **142**, 85 (1987).
13. W. Guo and B. M. Fung, *J. Chem. Phys.*, **95**, 3917 (1991).
14. N. M. Amer and Y. R. Shen, *J. Chem. Phys.*, **56**, 2654 (1972).
15. H. Itoh, H. Nakatsuka and M. Matsuoka, *J. Phys. Soc. Jap.*, **34**, 841 (1973).