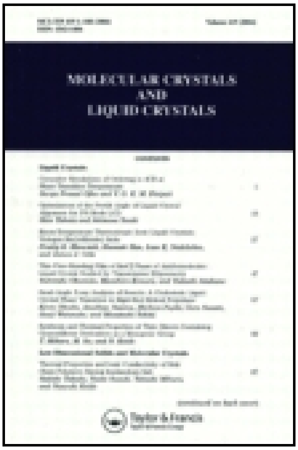

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Molecular Interactions in the Ethyl-cyanoethyl Cellulose/Dichloroacetic Acid Solution

Y. Huang [a] & J. He [b]

[a] Guangzhou Institute of Chemistry, Academia Sinica, Guangzhou, China

[b] Chinese National Analytical Center, Guangzhou, China

To cite this article: Y. Huang & J. He (1989): Molecular Interactions in the Ethyl-cyanoethyl Cellulose/Dichloroacetic Acid Solution, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 174:1, 11-19

To link to this article: http://dx.doi.org/10.1080/00268948908042691

Mol. Cryst. Liq. Cryst., 1989, Vol. 174, pp. 11–19
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Molecular Interactions in the Ethyl-cyanoethyl Cellulose/ Dichloroacetic Acid Solution†

Y. HUANG
Guangzhou Institute of Chemistry, Academia Sinica, Guangzhou, China

and

J. HE
Chinese National Analytical Center, Guangzhou, China

(Received September 23, 1988; in final form March 10, 1989)

The molecular interactions in the ethyl-cyanoethyl cellulose/dichloroacetic acid solution are studied by Fourier transform infrared spectroscopy (FTIR). It is found that the molecular interactions are related to the structures of the solution. The formation and destruction of hydrogen bonds during the transition between isotropic and anisotropic phases greatly affects the displacement of the IR bands. In the mesophase, the solvent molecules prefer the head-to-end state. There is another critical concentration above C_2^+ in the solution, over which the structure of the solution is nearly unchangeable and the infrared absorption bands of the various groups do not shift with concentration.

INTRODUCTION

Phase transitions of polymer liquid crystals are studied by such methods as DSC,[1] polarizing microscopy[2] and X-ray diffraction.[3] These methods can provide information about the phase transition temperatures, the textures and the morphological characteristics of the mesophase and the changes of the enthalpy and entropy in the phase transition. With these methods, however, it is difficult to acquire useful data about the molecular interactions which are directly related to the liquid crystalline phase transition and the variations of molecular chain conformation. Infrared spectroscopy can be used to obtain molecular information. Infrared absorption bands are very sensitive to the changes of microstructures caused by slight changes of molecular interactions and environment around the molecules. Information about the arrangement of molecular chains can be obtained from the changes of vibrational frequency, band shape and band intensity. This information is very important to understand the nature of the formation of liquid crystals. Until now, very few scientists have studied the formation of polymer liquid crystals by FTIR and the study is limited to only several kinds of thermotropic polymer liquid crystals.[4,5]

---

†Projects Supported by the Chinese Academy of Sciences.

We have used FTIR to study the lyotropic liquid crystals of ethyl-cyanoethyl cellulose ((E—CE)C). The (E—CE)C/dichloroacetic acid (DCA) solution can form a cholesteric mesophase when the concentration is high enough.[6] In the formation of liquid crystals the molecular interaction must vary. In this report we study the variation of the molecular interaction with the concentration in the formation of the liquid crystal by FTIR.

EXPERIMENTAL

The (E—CE)C was obtained by reaction of ethyl cellulose and acrylonitrile. The degree of substitution for ethyl was about 2.09 and for cyanoethyl was about 0.56 and $\overline{Mn}$ was about 38,000. The DCA was a chemically pure reagent. The (E—CE)C was mixed with the DCA at room temperature. The solution was sealed in a test-tube and was left over a week at room temperature after having been heated at 50°C for 10 hours.

The IR spectra of the samples were measured by a Nicolet FTIR system model 170SX. The samples were placed between two KBr crystals, the wavenumber accuracy was 0.01 cm^{-1} and the spectral resolution was 2 cm^{-1}. To improve the signal-to-noise, all samples and the background were scanned 100 times. The measure conditions and the instrument parameters were the same for every sample. The peak values of the absorption bands were typed directly on the IR spectra.

RESULTS AND DISCUSSION

The IR spectra of gaseous and liquid DCA and the (E—CE)C are shown respectively in Figures 1 to 3. The assignment of some bands are listed in Tables 1 and 2. The IR spectra of several different concentration (E—CE)C/DCA solutions have been measured and Figure 4 shows the spectrum of the 50 wt.% (E—CE)C/DCA solution.

From Figures 1 to 4, it can be seen that some IR bands of the (E—CE)C and the DCA in the solution shift as compared with those in the pure substances. In the solution, for example, the C═O stretching band of the DCA shifts to higher frequency and the C≡N stretching band of the (E—CE)C shifts to lower frequency as compared with that in the pure liquid DCA and in the pure (E—CE)C. In the gaseous DCA spectrum, however, both the C═O and C—Cl stretching bands shift to higher frequency compared with those in the liquid DCA spectrum. The IR spectroscopy specific vibrational frequency ν of a molecule can be expressed as[7]

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{f(m_1 + m_2)}{m_1 \cdot m_2}}$$

where c is the speed of light, m_1 is the mass of atom 1 and m_2 is the mass of atom 2, and f is the bond force constant, which expressed a bond strength or the energy level of a bond. From the formula, it can be seen that the IR absorption bands will shift if the bond strength in a molecule changes.

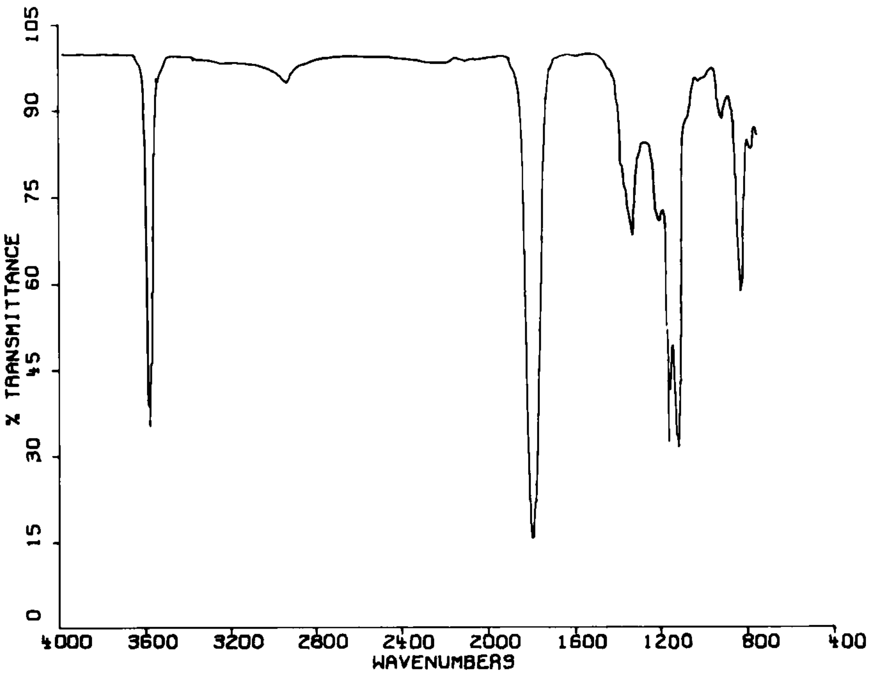

FIGURE 1 IR spectrum of the gaseous DCA.

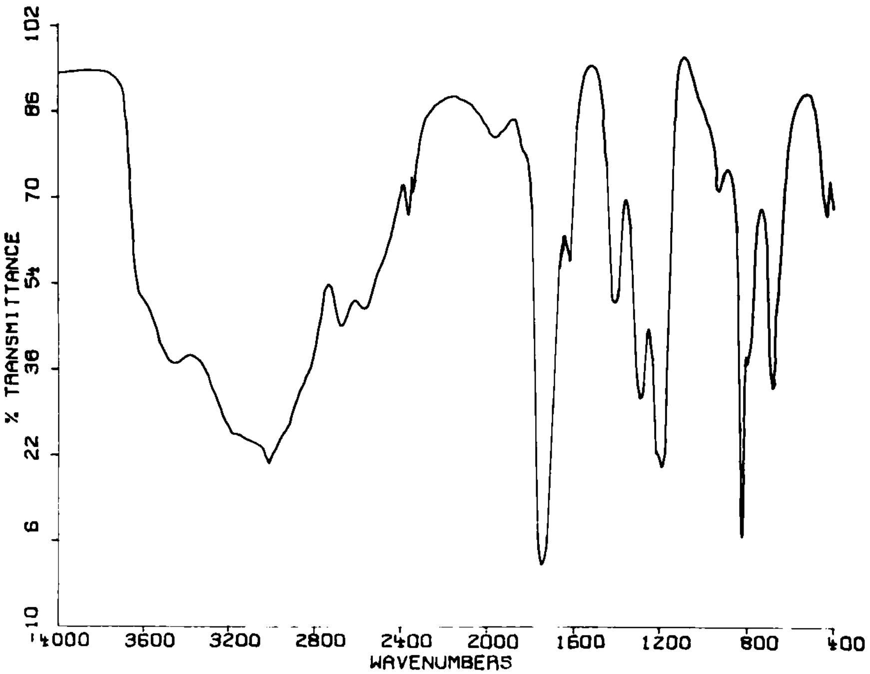

FIGURE 2 IR spectrum of the liquid DCA.

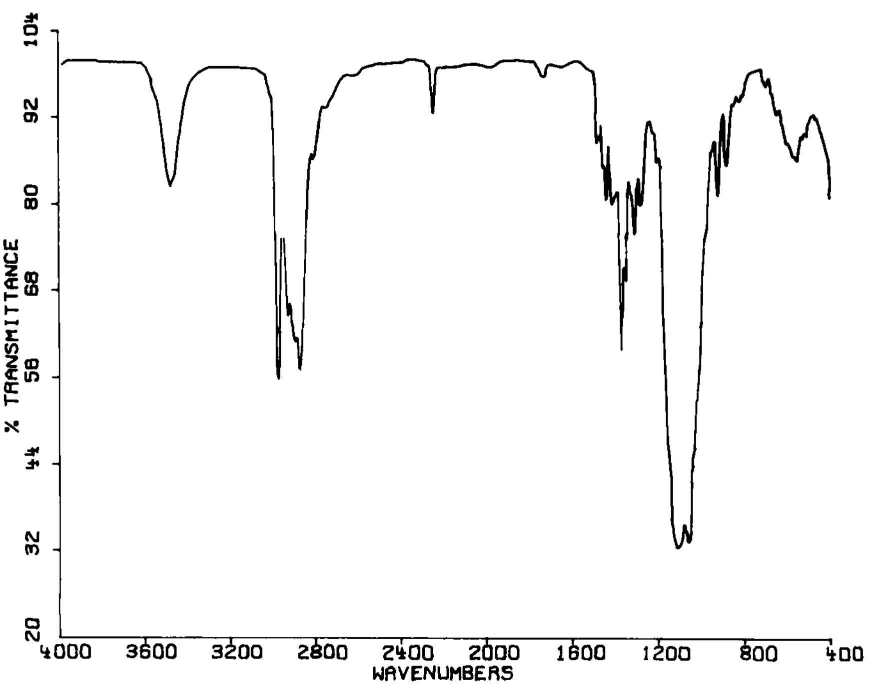

FIGURE 3 IR spectrum of the (E—CE)C.

There are C≡N and OH groups in the (E—CE)C chain and Cl and COOH groups in the DCA molecule. Several kinds of hydrogen bonds in the solution can exist (Figure 5). These hydrogen bonds greatly influence the bond strength of some

TABLE I

The assignment of IR absorption bands of liquid DCA (2400–700 cm^{-1})

Frequency (cm^{-1})	1744	1405	1289	1187	921	821
Intensity	strong	middle	middle	strong	weak	strong
Assignment†	C=O S	C—O—H B	C—O S	C—H B	O—H B	C—Cl S

†B: bending, S: stretching

TABLE II

The assignment of IR absorption bands of the (E—CE)C (2400–800 cm^{-1})

Frequency (cm^{-1})	2251	1375	1109	1058	922	883
Intensity	weak	middle	strong	strong	weak	weak
Assignment†	C≡N S	CH_3 S.D.	C—O—C S	C—O S	CH_3 B	CH_3 B

†B: bending, S: stretching, S.D.: symmetrical deformation

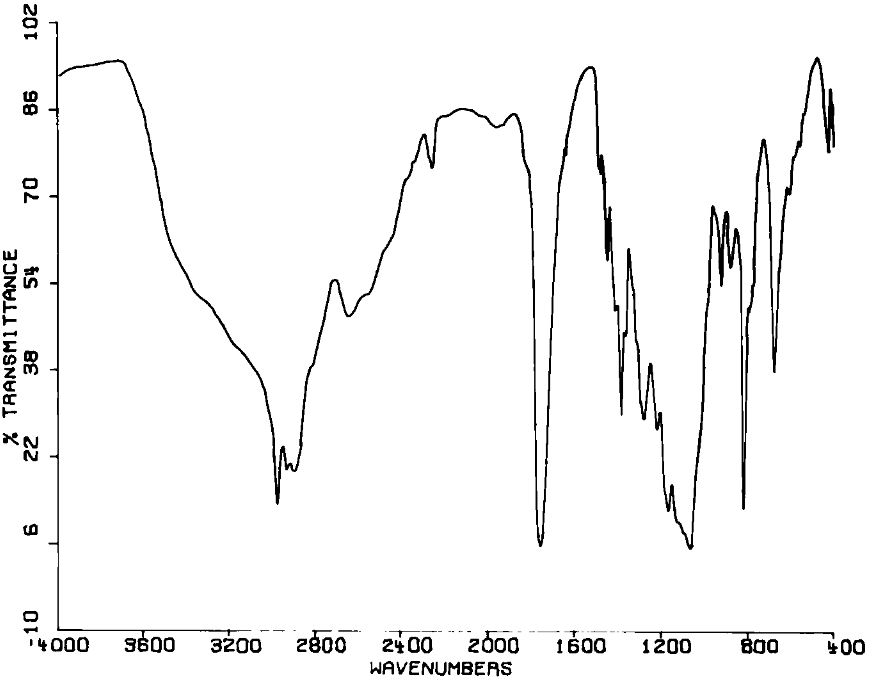

FIGURE 4 IR spectrum of the 50 wt.% (E—CE)C/DCA solution.

bonds in the solvent molecule and in the polymer and cause some bands in the IR spectra to shift.

1. C=O stretching band

The C=O stretching vibration band in the spectrum of the solution belongs to the DCA molecule. In Figures 1 and 2, it can be seen that the $\nu_{C=O}$ of gaseous DCA is 1797 cm^{-1} and of liquid DCA is 1744 cm^{-1}. The gaseous $\nu_{C=O}$ is 53 cm^{-1} higher than the liquid $\nu_{C=O}$. As a general rule,[8] condensed fatty acids exist as dimers (Figure 5A). Because of forming hydrogen bonds in the liquid state, the strength of C=O double-bond is weakened and $\nu_{C=O}$ is reduced. The molecules in the gaseous state, however, are mainly present in nonassociated form and there is no hydrogen bond between them. Thus, the $\nu_{C=O}$ in the gaseous DCA is much higher than that in the liquid DCA. It can be said that the $\nu_{C=O}$ of the DCA shifts to higher frequency when the associated state of the DCA is removed.

In the (E—CE)C/DCA solution, the $\nu_{C=O}$ shifts to higher frequency with increasing concentration and the shifting rate *dv/dC* changes its value at concentrations of about 20, 31 and 40 wt.%, respectively (Figure 6). The reasons that the $\nu_{C=O}$ shifts to higher frequency with increasing concentration are the increase of the hydrogen bond (D) and the decrease of the hydrogen bond (A). Because the hydrogen bond (D) weakens the C=O double-bond less than hydrogen bond (A) does, the strength of the C=O bond increases and the $\nu_{C=O}$ shifts to higher frequency with increasing concentration.

In the (E—CE)C/DCA solution, a cholesteric mesophase can form when the

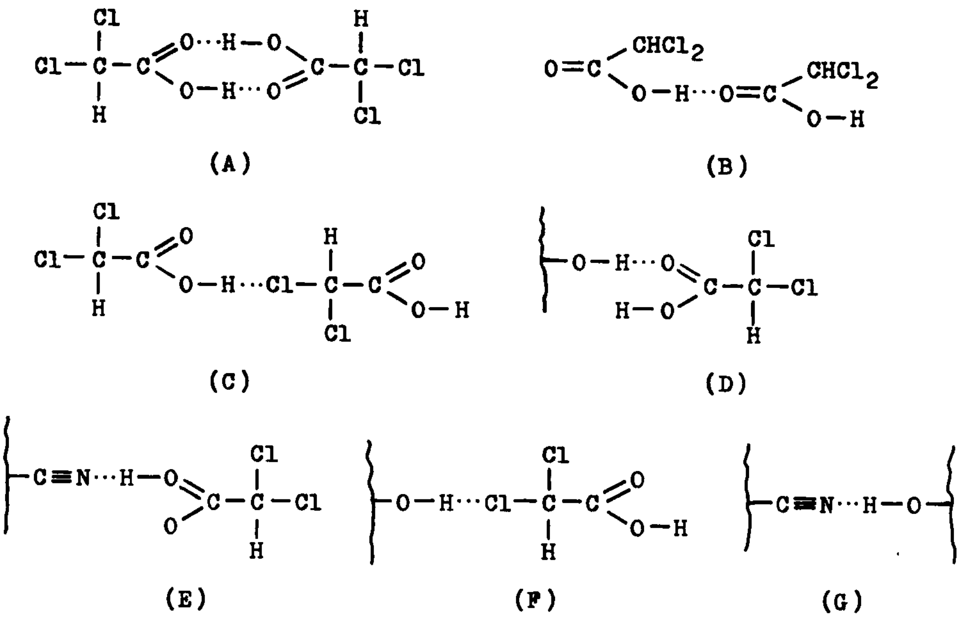

FIGURE 5 Schemes of the hydrogen bonds in the (E—CE)C/DCA solution.

concentration is high enough.[6] At room temperature, the critical concentrations are $C_1^+ = 20\text{–}25$ wt.%, $C_2^+ = 30\text{–}35$ wt.%. There is a biphasic solution between the C_1^+ and C_2^+. The changes of the $d\nu/dC$ with concentration reflect the changes of the solution structures.

When $C < C_1^+$, macromolecules are dispersed homogeneously in the solution. When the macromolecules, which act as a diluent to the DCA dimers, increase in

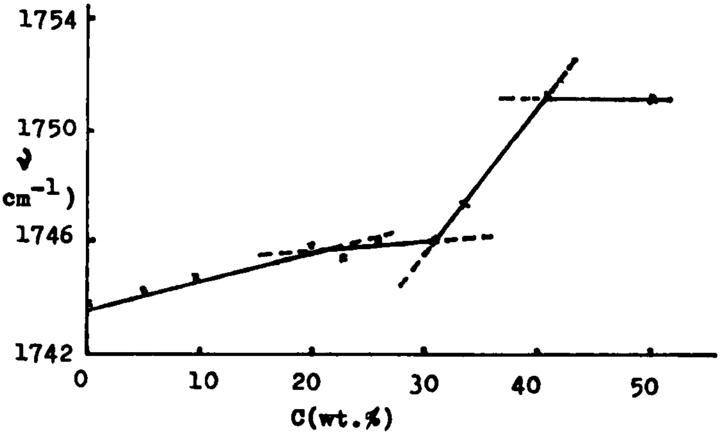

FIGURE 6 The frequency of the C═O stretching band vs. the concentration of the (E—CE)C/DCA solution.

the solution, the hydrogen bond (A) decreases, the hydrogen bond (D) and (E) increase and the strength of the C=O bond increases. The $\nu_{C=O}$, therefore, shifts to higher frequency at a constant rate.

When $C_1^+ < C < C_2^+$, there are two phases, isotropic and anisotropic phases, in the solution. With increasing concentration, the polymer chains change from a random state to an ordered state. In the mesophase, the interaction between the polymer chains are strengthened, the hydrogen bond (G) forms and the chance of forming the hydrogen bond (D) and (E) decreases. Now, not all the macromolecules in the solution act as a diluent to the DCA dimers. With increasing concentration, therefore, the rate of the destruction of the hydrogen bond (A) is less than that when the solution is isotropic and the $\nu_{C=O}$ shifts to higher frequency at a lower speed.

After $C > C_2^+$, nearly all macromolecules in the solution have ordered to form liquid crystalline phase. Now, with increasing concentration, the density of the polymer chains in the solution increases and the polymer chains are packed more closely. In this phase, the DCA molecules are dispersed between the layers of the ordered polymer chains, the association of the DCA dimers disintegrates and the hydrogen bond (A) content is rapidly reduced. Therefore, the $\nu_{C=O}$ shifts to higher frequency faster after $C > C_2^+$. The $d\nu/dC$, however, becomes nearly zero after $C = 40$ wt.%. This is because that the association of the most DCA dimers has been removed and the hydrogen bond (A) content is very low. The influences on the strength of the C=O bond with increasing concentration are very weak. This suggests that the structure of the solution is nearly unchangeable with increasing concentration. In this phase, however, it can be seen that $\nu_{C=O}$ is still much lower than that in the gaseous DCA spectrum, which indicates that there are many hydrogen bond (B) and (D) in the solution.

2. C—Cl stretching band

The ν_{C-Cl} in the gaseous DCA spectrum is 822 cm^{-1} and in the liquid DCA spectrum is 821 cm^{-1}. The ν_{C-Cl} in the liquid DCA is 1 cm^{-1} lower than that in the gaseous DCA (Figures 1 and 2). This is because there are some hydrogen bonds (C) in liquid DCA and the strength of the C—Cl bond is weakened. In the (E—CE)C/DCA solution, the ν_{C-Cl} also shifts with concentration. But it does not shift to higher frequency with increasing concentration like the $\nu_{C=O}$. It shifts to lower frequency. When $C = C_2^+$, the $d\nu/dC$ changes its value, too (Figure 7).

When the concentration is increased, the association of the DCA dimers is gradually removed. This is advantageous to the formation of the hydrogen bond (C) besides the hydrogen bond (B). Therefore, the C—Cl bond is weakened and the ν_{C-Cl} shifts to lower frequency. When $C < C_1^+$, the macromolecules act as the diluent to the DCA dimers. The shifting speed of the ν_{C-Cl} is constant. When the solution is biphasic, the shifting speed of the ν_{C-Cl} to lower frequency does not change, which indicates that the hydrogen bond (C) can form in both isotropic and anisotropic phases. After $C > C_2^+$, the DCA molecules are dispersed, layer by layer, between the layers of the ordered polymer chains and hydrogen bond (A) is rapidly destroyed with increasing concentration, which is advantageous to the

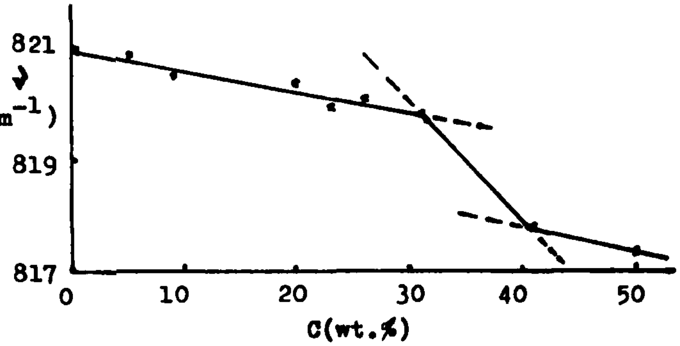

FIGURE 7 The frequency of the C—Cl stretching band vs. the concentration of the (E—CE)C/DCA solution.

formation of the hydrogen bond (C). Hence, the $\nu_{C—Cl}$ shows a sudden change when the concentration goes to this range. These results indicate that in the mesophase the DCA molecules are preferentially oriented in the head-to-end state. After the concentration is over 40 wt.%, the structure of the solution becomes nearly unchangeable with increasing concentration and the shifting rate of the $\nu_{C—Cl}$ becomes slower than before. These results are in agreement with the case of the C═O stretching band.

3. C≡N stretching band

The variation of frequency for the C≡N stretching band with concentration is shown in Figure 8. Because the content of the C≡N bond is very low, the C≡N stretching vibration band is nearly not seen in the spectra when the concentration is lower than 20 wt.%. Above this concentration, the C≡N stretching band shifts to lower frequency with increasing concentration. Similar to the $\nu_{C═O}$ and $\nu_{C—Cl}$, the shifting speed of the $\nu_{C≡N}$ increases when $C = C_2^+$.

In the (E—CE)C/DCA solution, the hydrogen bonds related to the C≡N group

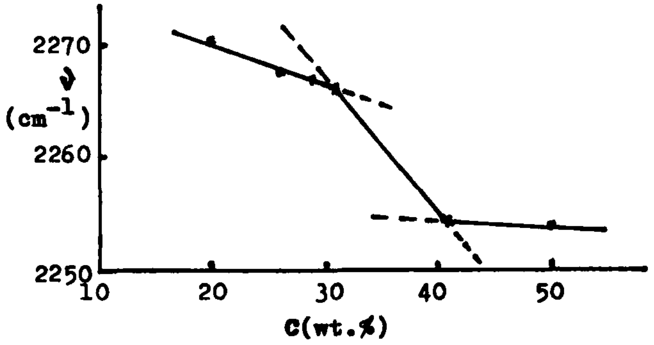

FIGURE 8 The frequency of the C≡N stretching band vs. the concentration of the (E—CE)C/DCA solution.

are hydrogen bonds (E) and (G), which weaken the triple-bond characteristics of the C≡N and cause the $\nu_{C\equiv N}$ to shift to lower frequency. When the solution is biphasic, the polymer chains are in disorder in the isotropic phase, which is advantageous to the formation of the hydrogen bond (E). In the anisotropic phase, the polymer chains are ordered and oriented, which is very advantageous to the formation of the hydrogen bond (G). Therefore, the $\nu_{C\equiv N}$ shifts to lower frequency with increasing concentration. After $C > C_2^+$, almost all polymer chains have been ordered. Now, with increasing concentration, the density of the polymer chains in the solution increases, which is more advantageous to the formation of the hydrogen bond (G). Therefore, the $d\nu/dC$ of the $\nu_{C\equiv N}$ increases when $C = C_2^+$. When the concentration is over 40 wt.%, the structure of the solution is nearly constant and $\nu_{C\equiv N}$ becomes nearly unchangeable with increasing concentration.

CONCLUSIONS

In the (E—CE)C/DCA solution, there are several kinds of hydrogen bonds, which change with the structures of the solution and influence the frequency of the infrared absorption bands of the solution. In the isotropic phase, the hydrogen bonds are mainly between the DCA molecules and between the DCA molecule and the (E—CE)C chain. The more polymer chains there are in the solution, the more the hydrogen bonds are between the solvent molecule and the polymer chain and the less DCA dimers there are in the solution. The macromolecules in the isotropic phase act as a diluent to the DCA dimers. In the anisotropic phase, polymer chains can form hydrogen bonds with each other besides forming the hydrogen bonds with the DCA molecules. The DCA molecules in the anisotropic are preferentially ordered in the head-to-end state (Figure 5C and B). When the concentration is over 40 wt.%, the structure of the solution is nearly unchangeable with increasing concentration.

References

1. G. Galli, E. Chiellini, C. Ober and R. W. Lenz, *Makromol. Chem.*, **183**, 2693 (1982).
2. H. Sachmann and D. Demus, *Mol. Cryst. Liq. Cryst.*, **41**, 269 (1978).
3. L. V. Azaroff, *Mol. Cryst. Liq. Cryst.*, **10**, 31 (1970).
4. P. P. Wu and S. L. Hsu, *Preprints of the Symposium on Fine Polymers* (Guangzhou, China), 305 (1986).
5. Z. C. Wen, D. Y. Shen, Q. F. Zhou and H. M. Li, *The Symposium on Polymer Liquid Crystals* (Shanghai, China), 1987, paper 35.
6. Y. Huang, M. C. Chen and L. S. Li, *Acta Chimica Sinica*, **46**, 367(Ch) (1988).
7. K. Nakanshi and P. H. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day, Inc., 1977.
8. Z. M. Wang, X. X. He and D. Q. Sun, *Applied Infrared Spectroscopy*, Petroleum Industry Press, 1982, P211(Ch).