Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Influence of molecular structure on the cholesteric liquid crystalline behaviour of ethyl-cyanoethyl cellulose/acrylic acid solutions

Guanqi Zhang[a]; Yong Huang[b]
[a] LCLC, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China, [b] LCLC, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China, & Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China,

Online publication date: 11 November 2010

To cite this Article Zhang, Guanqi and Huang, Yong(2002) 'Influence of molecular structure on the cholesteric liquid crystalline behaviour of ethyl-cyanoethyl cellulose/acrylic acid solutions', Liquid Crystals, 29: 2, 289 — 294
To link to this Article: DOI: 10.1080/02678290110099457
URL: http://dx.doi.org/10.1080/02678290110099457

LIQUID CRYSTALS, 2002, VOL. 29, NO. 2, 289–294

Influence of molecular structure on the cholesteric liquid crystalline behaviour of ethyl-cyanoethyl cellulose/acrylic acid solutions

GUANQI ZHANG† and YONG HUANG†‡*

†LCLC, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China

‡Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

(*Received 16 July 2001; accepted 28 August 2001*)

The liquid crystalline behaviour of (E-CE)C/AA solutions is connected with the (E-CE)C molecular structure and it was found that the critical concentration C_1 at which the cholesteric phase begins to appear decreases with increase in both (E-CE)C molecular mass and the degree of substitution with cyanoethyl. The pitch of the cholesteric phase decreased with increasing (E-CE)C/AA concentration, and was not influenced by the (E-CE)C molecular mass. The pitch, however, was dependent on the (E-CE)C molecular mass and the degree of substitution with cyanoethyl. It increased with increasing (E-CE)C molecular mass when the degree of substitition with cyanoethyl was unchanged. It decreased and then increased with increasing degree of substitution with cyanoethyl when the (E-CE)C molecular mass was unchanged. There was a minimum value of the pitch when the degree of substitution with cyanoethyl was about 0.25.

1. Introduction

Cellulose and its derivatives can form lyotropic liquid crystals in appropriate solvent systems when the concentration is high enough [1–3]. The molecular structure of cellulose and its derivatives, such as the molecular mass and its distribution, the chemical properties of the substituents and the degree of substitution and its distribution may greatly influence the behaviour of the liquid crystals. For some cellulose derivatives, it is reported that the critical concentration for LC formation decreases with increasing molecular mass [4–7], but for polydisperse derivatives, molecular mass has little effect on the critical concentration [8, 9]. The chemical properties of the substituents and the degree of substitution and its distribution may influence the spatial interaction between adjacent pyranoid rings, the intramolecular hydrogen bonding and steric interference, and thereby influence the rigidity of the macromolecular chains. For example, the dimensions of the undisturbed chains of acetylcellulose are increased with increase in the degree of substitution in dilute solutions [10]. The critical concentration of carbamoyl-ethyl cellulose decreases from 50 to 35 wt % when the degree of substitution with carbamoyl increases from 1.0 to 2.3 [11].

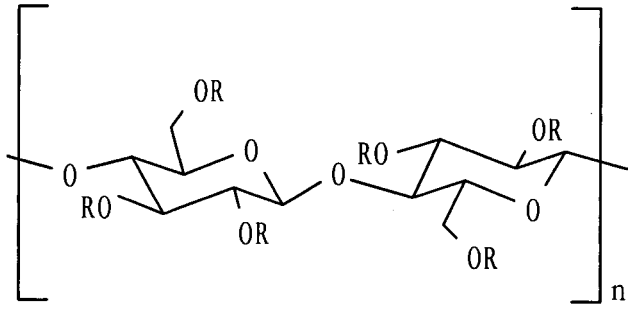
Ethyl-cyanoethyl cellulose, (E-CE)C, is a cellulose derivative with two kinds of ether groups and can form lyotropic liquid crystals in many solvents when the concentration is higher than the critical concentration [12]. (E-CE)C can be readily dissolved in acrylic acid (AA) and forms cholesteric liquid crystals [13]. In this work, the influence of the (E-CE)C molecular structure on the cholesteric liquid crystalline properties is studied and the relationships between the behaviour of the liquid crystals and the (E-CE)C molecular mass (M_w) and the degree of substitution (DS) with cyanoethyl are discussed.

2. Experimental

(E-CE)C was prepared by the reaction of ethyl cellulose, of which the degree of substitution with ethyl was about 2.1, and acrylonitrile. The molecular formula of (E-CE)C is shown in figure 1. (E-CE)C with different molecular masses was prepared by using ethyl cellulose of different molecular mass values, which was degraded in hydrochloric acid at different concentrations and for different times. (E-CE)C with different degrees of substitution with cyanoethyl was prepared by controlling the conditions of the cyanoethyl etherification. The acrylic acid (AA) was a chemically pure reagent and was refined by vacuum distillation before use.

*Author for correspondence; e-mail: yhuang@cashq.ac.cn

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110099457



R=H, CH_2CH_3, CH_2CH_2CN

Figure 1. The molecular formula of (E-CE)C.

The (E-CE)C molecular mass, M_w, and its distribution were measured by gel permeation chromatography (GPC) (Waters ALC/244/GPC), with calibration by standards of polystyrene. The solvent for GPC was tetrahydrofuran. The degree of substitution (*DS*) with cyanoethyl was calculated from the nitrogen content of the (E-CE)C as measured by elemental analysis (Heraeus, CHN-O-RAPID). The critical concentration of the (E-CE)C/AA solutions, C_1, at which the cholesteric liquid crystalline phase began to appear, was determined by refractometry [14] and observation using a polarizing optical microscope (Leitz, Orthoplane-Pol). The cholesteric pitch of the (E-CE)C/AA liquid crystalline solutions was calculated from the maximum wavelength of the selective reflection, which was measured spectrophotometrically on (E-CE)C/AA liquid crystalline solutions placed in sample cells ($0.3 \times 15 \times 20\,mm^3$). The maximum wavelength of the selective reflection of the solutions was recorded using a UV-Vis spectrophotometer (Shimadzu, UV-2550).

3. Results and discussion

3.1. *The critical concentration and the (E-CE)C molecular structure*

Table 1 gives values for the (E-CE)C molecular mass (M_w), the *DS* with cyanoethyl and the critical concentration of (E-CE)C/AA solutions (C_1) at which the cholesteric liquid crystalline phase begins to appear. It can be seen from table 1 that C_1 decreases with increasing molecular mass of (E-CE)C. As an example, the *DS* of sample **c** is almost the same as that of sample **f**, but the M_w of sample **c** is 10.7×10^4 and that of sample **f** is 3.6×10^4. As a result, the C_1 of samples **c** and **f** are 38 and 44 wt %, respectively. The M_w of samples **a**, **b**, **c** and **d** are all higher than 10×10^4 and much bigger than those for samples **e** and **f**; and the C_1 of samples **a**, **b**, **c** and **d** are all smaller than those of sample **e** and **f**. Therefore, when there is much difference in (E-CE)C molecular mass, the solutions with higher molecular mass exhibit the lower critical concentrations. In other polymer liquid crystal systems, such as polypeptides and chitosan systems, a similar phenomenon has also been observed [15].

Table 1. Effect of (E-CE)C molecular mass and the degree of substitution with cyanoethyl on the critical concentration of (E-CE)C/AA.

Sample	*DS* for cyanoethyl	$M_w/10^4$	C^1/wt %
a	0.134	14.5	40
b	0.272	14.7	38
c	0.325	10.7	38
d	0.398	15.7	37
e	0.300	3.6	45
f	0.332	3.6	44

When the molecular masses are almost the same, the C_1 are influenced by the *DS* with cyanoethyl. For example, the molecular mass of sample **a** is almost the same as that of sample **b**, but the *DS* with cyanoethyl of sample **a** is 0.134 and of sample **b** is 0.272. The C_1 of samples **a** and **b** are now 40 and 38 wt %, respectively. The molecular mass of sample **e** is almost the same as that of sample **f**, but the *DS* values with cyanoethyl are 0.300 and 0.332 giving C_1 of 45 and 44 wt %, respectively. It can be concluded that the higher the *DS* with cyanoethyl, the lower is the C_1 when the molecular mass of the (E-CE)C is almost the same.

From the structure of the macromolecular chain of (E-CE)C (figure 1), it can be seen that the cyano groups on the (E-CE)C chains can form hydrogen bonds with the carboxyl groups of the acrylic acid and the hydroxy groups on the (E-CE)C chains (figure 2, A and B). The hydroxy groups on the (E-CE)C chains can also form hydrogen bonds with the carboxyl groups of acrylic acid (figure 2, C), and the hydroxy groups on the macromolecules can form hydrogen bonds with the oxygens of the pyranoid rings of (E-CE)C (figure 2, D). When the *DS* with canoethyl increases, the degree of hydrogen bonding of type A will be enhanced and that of hydrogen bonding of type C will be weakened. Assuming that the hydrogen bonds between cyano and carboxyl groups (hydrogen bonding A) are stronger than those between hydroxyl and carboxyl groups (hydrogen bonding C), then the intensity of hydrogen bonding between macromolecule chains and solvent molecules will be enhanced with increasing *DS* with cyanoethyl. Since the critical concentration is decreased with increasing interaction between macromolecular chains and solvent molecules [12], increasing the *DS* with cyanoethyl favours a decrease in the critical concentration of the (E-CE)C/AA solutions.

In the same way, the intensity of hydrogen bonding B is enhanced and that of hydrogen bonding D is weakened with increasing *DS* with cyanoethyl of (E-CE)C. Assuming

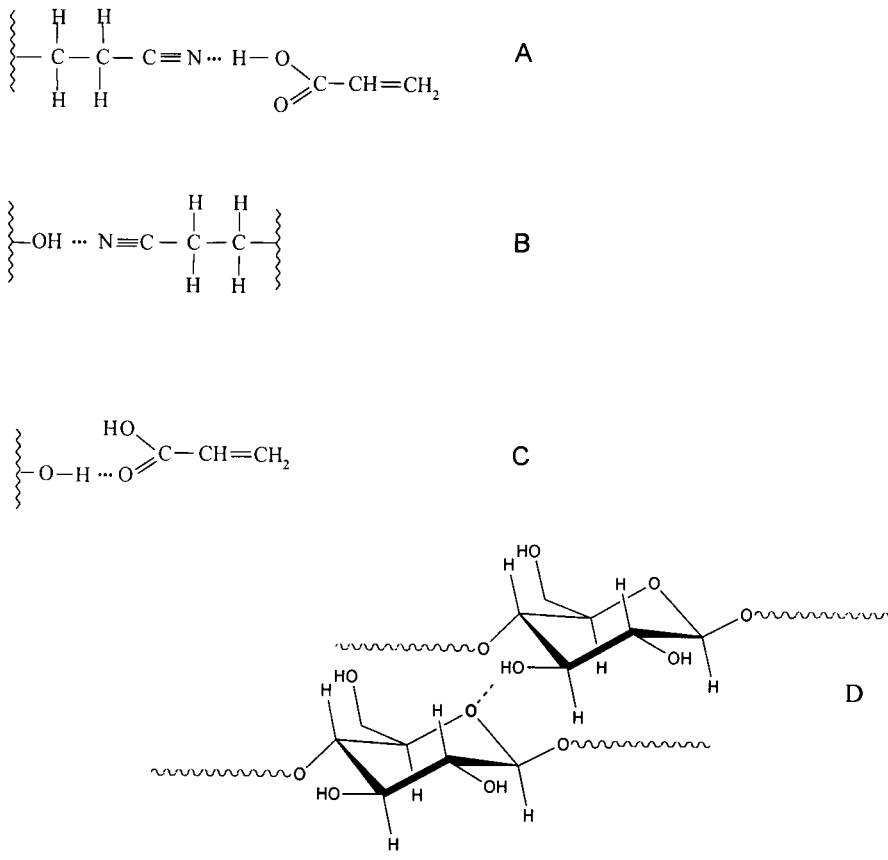


Figure 2. The schemes of hydrogen bonding in (E-CE)C/AA cholesteric liquid crystalline solutions.

that hydrogen bonding B is stronger than hydrogen bonding D, the intensity of hydrogen bonding between macromolecular chains will be enhanced with increasing *DS* with cyanoethyl. Therefore, the interaction between macromolecular chains is strengthened, and this is favourable for formation of the liquid crystalline phase, giving a critical concentration decrease with increasing *DS* with cyanoethyl.

3.2. *Variation of the concentration and the cholesteric structure*

The (E-CE)C/AA cholesteric phase has a planar texture in a certain concentration range [12] and the liquid crystalline solutions exhibit vivid colours because of the selective reflection of visible light from the cholesteric phase. The maximum wavelength of selective reflection λ_{max} is related to the cholesteric pitch P according to the following equation [16].

$$\lambda_{max} = nP \sin \varphi \qquad (1)$$

where n is the mean refractive index of the system and φ is the angle between the incident light and the molecular planes of the cholesteric phase.

Table 2 gives the values of λ_{max} and the cholesteric pitch P, which is calculated from the λ_{max} of the (E-CE)C/AA liquid crystalline solutions at different concentrations. There are two systems with different (E-CE)C molecular masses in table 2, sample a ($M_w = 10.7 \times 10^4$, $DS = 0.325$) and sample b ($M_w = 4.0 \times 10^4$, $DS = 0.321$).

Table 2. The pitch of (E-CE)C/AA cholesteric liquid crystalline solutions having different concentrations.

Sample	C/wt %	λ_{max}/nm	P/nm
a	40.0	905	632
$M_w = 10.7 \times 10^4$	42.5	863	602
$DS = 0.325$	45.0	700	488
	47.5	626	436
	50.0	518	360
	52.5	454	315
	55.0	389	270
	60.0	358	248
b	45.0	566	394
$M_w = 40.0 \times 10^4$	46.0	578	402
$DS = 0.321$	47.0	533	371
	48.0	485	338
	49.0	444	309
	50.0	386	268
	51.0	391	272
	52.0	380	264
	53.0	340	236
	54.0	309	214

The variation of the pitch with (E-CE)C concentration in the (E-CE)C/AA cholesteric liquid crystalline solutions is shown in figure 3.

In both sample a and sample b, λ_{max} and the cholesteric pitch P decrease with increasing concentration of the (E-CE)C/AA solutions. It has been reported that the λ_{max} of chiral polyisocyanate/AA systems is first decreased and then increased with increasing concentration when the degree of polymerization of the chiral polyisocyanate is low [17]. However, in the (E-CE)C/AA system with low (E-CE)C molecular mass, the variation of the cholesteric pitch with the concentration is the same as that of the high molecular mass (E-CE)C systems and the pitch is only decreased with increasing the concentration.

In the liquid crystalline polymer/solvent lyotropic systems, the relationship between the concentration and the cholesteric pitch can be described as follows [18]:

$$\frac{M_A(1-C)}{2PdC} = \left(\frac{N\beta_A M_B}{M_A} - 2N\beta_{AB}\right)C + 2N\beta_{AB} \quad (2)$$

$$d = \frac{d_B}{1+(d_B/d_A - 1)C}$$

where M_A and M_B are the molecular masses of the polymer and the solvent, respectively, C is the weight fraction of the polymer, N is the Avogadro number. P is the cholesteric pitch and d_A and d_B are the density of the polymer and the solvent, respectively; β is the interaction parameter, the 'molecular twisting power', which is related to the molecular structure, the molecular mass and the temperature of the system. Equation (2) can be used to study the relationship between cholesteric pitch and concentration, temperature and molecular mass of a macromolecule. The relationship between $(1-C)/PdC$ and C is linear and molecular twisting powers can be obtained by extrapolation of the straight line to $C=1$.

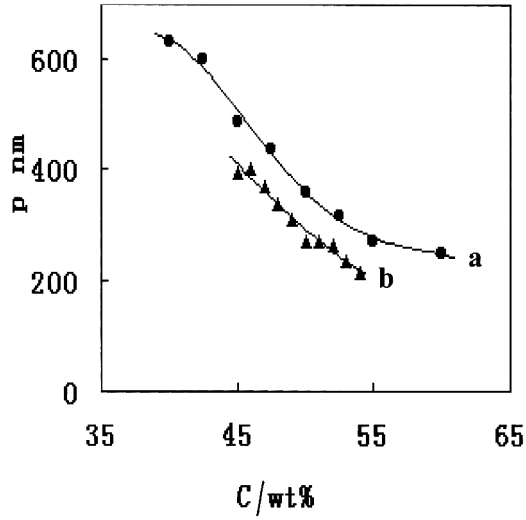


Figure 3. Plots of pitch vs. concentration for (E-CE)C/AA cholesteric liquid crystalline solutions: sample a and sample b—see table 2.

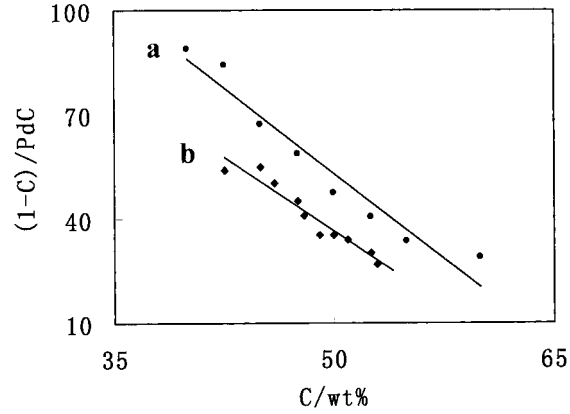


Figure 4. Relationship between $(1-C)PdC$ and C for (E-CE)C/AA liquid crystalline solutions. Curves a and b refer to the polymer series A and B, respectively, given in table 4

The plots of $(1-C)PdC$ vs. C for the (E-CE)C/AA cholesteric liquid crystalline solutions are shown in figure 4. It is clear that the relationship between $(1-C)/PdC$ and C is linear and that the variation of pitch with the concentration can be described by equation (2) for the (E-CE)C/AA liquid crystalline solutions.

The twisting power between macromolecules, $N\beta_A$, and that between macromolecules and solvent molecules, $N\beta_B$, calculated from equation (2), are shown in table 3. The data indicate that the interaction between macromolecules is much stronger than that between macromolecules and solvent molecules. It can also be seen that the twisting power between macromolecules with higher molecular masses is stronger than for those with lower molecular masses. Stronger interactions between the macromolecules are favourable for liquid crystalline phase formation, and therefore (E-CE)C/AA liquid crystalline solutions with higher (E-CE)C molecular masses have the lower critical concentration.

3.3. *Cholesteric pitch and the molecular structure of (E-CE)C*

Table 4 gives the cholesteric pitches of the 45 wt % (E-CE)C/AA liquid crystalline solutions with different (E-CE)C molecular mass and *DS* with cyanoethyl. It

Table 3. The twisting power between macromolecules ($N\beta_A$) and that between macromolecules and solvent molecules ($N\beta_{AB}$) in (E-CE)C/AA solutions.

M_w of (E-CE)C	$N\beta_{AB}$/cm^2	$N\beta_A$/cm^2
10.7×10^4	0.581	0.210
4.0×10^4	1.66×10^3	2.14×10^2

Table 4. Molecular mass, degree of substitution with cyanoethyl and pitch of (E-CE)C/AA cholesteric liquid crystalline solutions.

Sample	$M_w/10^4$	*DS* for cyanoethyl	*P*/nm
A1	14.5	0.134	511
A2	26.8	0.211	477
A3	13.1	0.225	485
A4	14.7	0.272	478
A5	10.7	0.325	488
A6	9.9	0.342	502
A7	15.7	0.398	577
B1	4.00	0.212	393
B2	3.92	0.219	357
B3	3.95	0.244	349
B4	3.60	0.300	386
B5	4.00	0.321	386

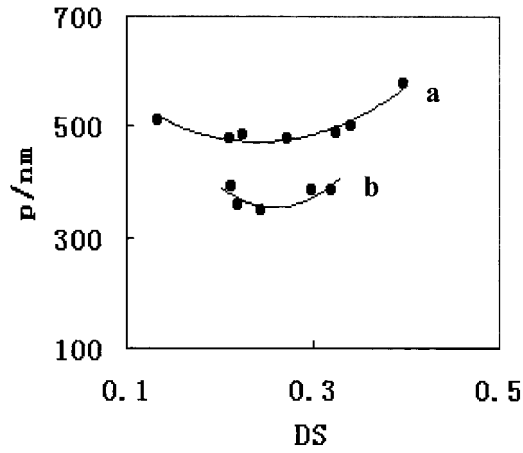


Figure 5. Plots of the pitch vs. the *DS* with cyanoethyl for (E-CE)C/AA cholesteric liquid crystalline solutions. Curves a and b refer to the polymer series A and B, respectively, given in table 4.

can be seen that the cholesteric pitch depends on the (E-CE)C molecular mass. The *DS* with cyanoethyl of sample A2 is almost the same as that of sample B1, 0.211 and 0.212, respectively. However, their pitches are 477 and 393 nm, respectively, because the molecular masses are very different, 26.8×10^4 (A2) and 4.0×10^4 (B1). The *DS* with cyanoethyl of samples A5 and B5 are 0.325 and 0.321, respectively. Their molecular masses are 10.7×10^4 and 4.0×10^4, and the pitches are 488 and 386 nm, respectively. Therefore, when the degrees of substitution with cyanoethyl units are almost the same, the pitch of the cholesteric phase is increased with increasing the (E-CE)C molecular mass. It has been reported that the pitch of the cholesteric phase of cellulose tricarbanilate rapidly changes with *DS* at low molecular mass [8].

In (E-CE)C/AA cholesteric liquid crystalline solutions, the (E-CE)C macromolecules are arranged and oriented in one direction in each plane. The orientation of the macromolecules is of course twisted through a definite angle between adjacent planes. When hydrogen bonding of types B and D is formed between adjacent cholesteric planes, there must be an angle between two (E-CE)C macromolecules because of the steric hindrance of the substituent. The angle between the orientations of adjacent cholesteric planes is therefore a balance between interaction and steric hindrance of the substituent between the macromolecules of two planes. With increasing (E-CE)C molecular mass, the interaction between macromolecules of adjacent planes becomes stronger (table 3). Therefore the angle between the orientations of adjacent planes is decreased and the number of planes in one periodicity is increased, resulting in the increase in the cholesteric pitch with increasing (E-CE)C molecular mass.

Figure 5 gives plots of the cholesteric pitch vs. the degree of substitution with cyanoethyl groups for (E-CE)C/AA liquid crystalline solutions. Curve a shows the variation of the pitch with *DS* for high (E-CE)C molecular masses and curve b shows the variation of the pitch with *DS* for lower (E-CE)C molecular masses. The data suggest that the pitch of the (E-CE)C/AA cholesteric phase is greatly influenced by the *DS* with cyanoethyl. The pitch is first decreased and then increased with increasing *DS* when the molecular mass is almost the same. For instance, the (E-CE)C molecular masses of the samples B (see table 4 and curve b in figure 5) are similar and the value of the cholesteric pitch is a minimum when the degree of substitution with cyanoethyl is about 0.25.

4. Conclusions

The critical concentration for an (E-CE)C/AA cholesteric liquid crystalline solution depends on the (E-CE)C molecular mass and is decreased by increasing the *DS* with cyanoethyl groups. The pitch of the (E-CE)C/AA cholesteric liquid crystalline phase is decreased with increasing concentration, which is not influenced by the (E-CE)C molecular mass. The cholesteric pitch is larger in the (E-CE)C/AA cholesteric liquid crystalline solutions with higher (E-CE)C molecular mass than it is for those with lower molecular mass, when the *DS* with cyanoethyl groups is the same. When the molecular mass is almost the same, the pitch of the cholesteric phase is first decreased and then increased with increasing *DS* with cyanoethyl. There is a minimum value in the cholesteric pitch when the *DS* with cyanoethyl groups is about 0.25.

Financial support by the National Natural Science Foundation of China and the National Key Projects for Fundamental Research 'Macromolecular Condensed State', Ministry of Science & Technology of China is gratefully appreciated.

References

[1] Gilbert, R. D., and Patton, P. A., 1988, *Prog. Polym. Sci.*, **9,** 115.

[2] Panar, M., and Willcox, O. B., 1977, *Ger. Offen.* 2 705 382.

[3] Gray, D. G., 1983, *Appl. polym. Symp.*, **37,** 179.

[4] Godinhox, M. H., Searin, M. J., and Massia, P., 1989, *Liq. Cryst.*, **5,** 1711.

[5] Werbowyj, R. S., and Gray, D. G., 1980, *Macromolecules*, **13,** 69.

[6] Laivins, G. V., and Gray, D. G., 1985, *Macromolecules*, **18,** 1753.

[7] Dong, Y. M., and Hong, Z. Z., 1996, *Chem. J., Chin, Univ.*, **17,** 993.

[8] Zhang, G. H., Huang, Y., and Yang, Y. Q., 1991, *Polym. Mater. Sci & Eng (Chin)*, **5,** 52.

[9] Wang, L. F., Pearce, E. M., and Kwei, T. K., 1991, *Polymer*, **32,** 249.

[10] Navard, P., and Huadin, J. M., 1981, *J polym Sci, polym Lett.*, **19,** 319.

[11] Patel, D. L., and Gilbert, R. D., 1983, *J polym Sci, polym Phys.*, **21,** 1079.

[12] Huang, Y., Chen, M. C., and Li, L. S., 1988, *Acta Chimica Sinica*, **46,** 367.

[13] Jiang, S. H., and Huang, Y., 1993, *J appl polym Sci.*, **50,** 607.

[14] Huang, Y., and Li, B. T., 1987, *Acta Polym. Sinica*, 52.

[15] Dong, Y. M., and Wang, J. W., 1999, *Acta Polym. Sinica*, 431.

[16] Wang, X. J., 1991, *Physics (Chin)*, **19,** 685.

[17] Georg, M., Sabine, M., and Rudolf, Z., 1999, *Macromolecules*, **32,** 5747.

[18] Shiau, C. C., and Labes, M. M., 1989, *Macromolecules*, **22,** 328.