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The influence of intramolecular hydrogen bonds on handedness in ethylcellulose /CH$_2$Cl$_2$ liquid crystalline mesophases

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This article shows that intramolecular hydrogen bonds formed at the three hydroxyl group positions of cellulosic glucose unit contribute in determining the handedness of chiral nematic mesophases ethylcellulose in CH$_2$Cl$_2$. Using two series of samples which differed only by increasing the ethyl substitution of the hydroxyl groups at either the C-6 or C-3 positions, the handedness of individual mesophase solutions was investigated using circular dichroism (CD). The CD spectra indicated that free hydroxyls at the C-6 position hindered dissolution in the solvent while hydroxyls at the C-3 position may play an important role in determining the handedness of the EC mesophase in CH$_2$Cl$_2$. Free hydroxyls at the C-3 position are known to easily form intramolecular hydrogen bonds, resulting in enhanced stiffness of the molecular chains. Therefore, these results lead to the conclusion that breaking intramolecular hydrogen bonds by increasing the substitution along the molecular chain causes it to become more flexible, which may account for the change in structural handedness. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: hydrogen bond; ethycellulose; liquid crystal)

INTRODUCTION

To date, we have investigated the formation of inter- and intramolecular hydrogen bonds in cellulosic molecules in various states ranging from films[1] and film blends[2–4] to gel[5] and amorphous phases[6] using two types of cellulose model compounds, 2,3-di-0-methylcellulose (23MC) and 6-0-methylcellulose (6MC[7,8]) which have every structural unit regioselectively and completely methylated. More specifically, 6-0 alkyl cellulose derivatives such as 6MC mainly exhibit two kinds of intramolecular hydrogen bonds[1] as shown in *Figure 1b*: one type may form between the hydroxyls at the C-3 position and an adjacent ether oxygen of the glucose ring while a second type can form between the ether oxygen at the substituted C-6 position and an adjacent hydroxyl at the C-2 position. Further, in 6MC samples there was a direct correlation between the physical properties observed and formation of the intramolecular hydrogen bonds which can be even maintained in solution[9]. The intramolecular hydrogen bonds were also found to have an influence on the enzymatic hydrolysis of 6MC[10,11]. We must add that these intramolecular hydrogen bonds also exist, of course, in pure cellulose as illustrated in *Figure 1c*.

Recently, we succeeded in preparing a series of methyl- and ethylcelluloses having a systematically controlled distribution of substitutents and DS (degrees of substitution)[7] These polymers would appear to form an ideal set of complete samples for determining what type of correlation exists between the physical properties and the distribution of substituents for alkylcellulose derivatives in terms of hydrogen bond formation. In this article, we focused on the effect of the substituent distribution on the liquid crystalline properties of EC. Many cellulose derivatives form lyotropic and thermotropic liquid crystals which normally exhibit cholesteric or chiral nematic structures[12–18]. The majority of cellulosic mesophases that have been studied to date are right-handed cholesterics, but a few left-handed systems were also reported[19–24]. Specifically, lyotropic ethylcellulose (EC) mesophases were observed to show both types of handedness depending on the polymer volume fraction and solvent[19,20]. Guo and Gray[23,24] reported that cholesteric liquid crystalline solutions of acetylated EC in chloroform exhibited a change in handedness from a left-handed to a right-handed helicoidal supermolecular arrangement with an increasing acetyl content in the EC. The twist sense of EC mesophases in chloroform and CH$_2$Cl$_2$ was also observed to change from left-handed to right-handed with an increasing degree of ethyl-substitution in EC[25,26]. However, the driving force for this structure reversal is still not clear. In this article, we report on the relationship between hydrogen bond formation and the reversal of handedness in EC mesophases in CH$_2$Cl$_2$. Using ethylcelluloses having a systematically controlled distribution of substitutents and DS as mentioned previously, the influence of intramolecular hydrogen bonds, within the same chiral backbone, in determining the handedness of these lyotropic mesophases was investigated.

EXPERIMENTAL

Ethylcellulose samples

Two series (A and B) of ethylcellulose samples were used in this experiment to cover the entire range of hydroxyl substitutions possible in EC.

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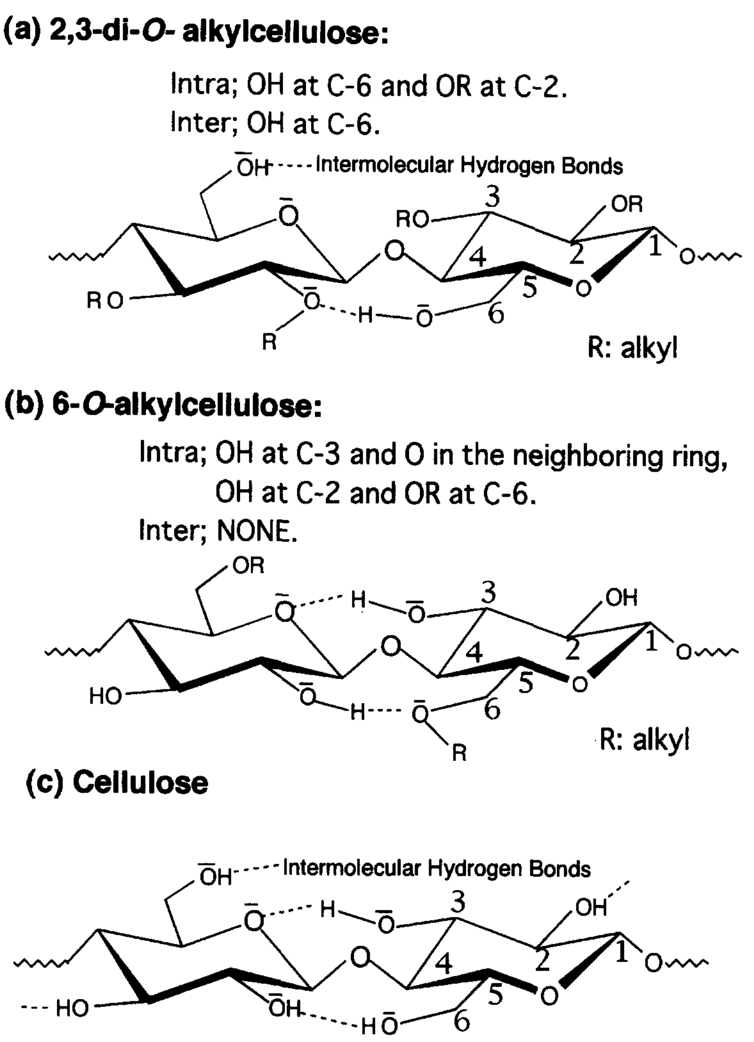

Figure 1 Possible hydrogen bonds formed at the individual C-2, C-3 and C-6 positions of the glucose ring in typical alkylcelluloses (a and b) and cellulose (c)

Series A (2,3-O-ethylcellulose: Preparation from 2,3-di-O-ethylcellulose(23EC). Series A consisted of 9 samples. The starting material with an average degree of polymerization (DP) of 200 was 2,3-di-O-ethylcellulose (23EC), prepared as reported previously[7], having ethoxyl groups at both C-2 and C-3 positions of the glucose unit (*Figure 1a*). The 23EC was then ethylated 8 times to yield 8 different samples of 2,3-di-O-ethyl-6-0-partially ethylated cellulose having different DS at the C-6 position as schematically shown in *Figure 2I*. The 23EC was added to 60 ml of DMSO with 2.0 g of pulverized NaOH powder and differing amounts of ethyl iodide. After 30 min of stirring under a nitrogen atmosphere at room temperature, the temperature was raised to 70°C and maintained there for 1 h for the first 5 samples and 3 h for the remaining three samples. The reaction mixture was then cooled to room temperature and poured into a 95% methanol solution. The resulting products were then precipitated and washed thoroughly with a 95% methanol solution and subsequently with distilled water. The average yield for each preparation was approximately 85% to 90%. The final products had a DP of 200 indicating that significant depolymerization of the products did not occur during alkylation[7].

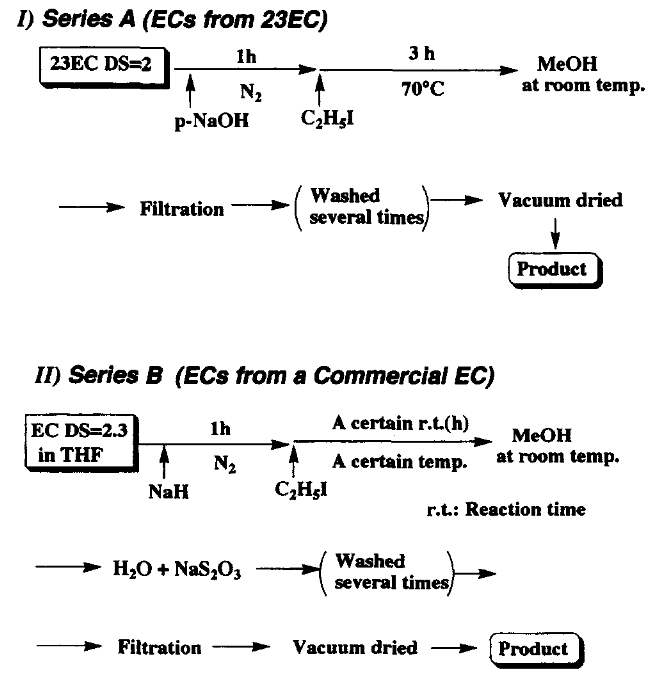

Figure 2 Preparation schemes for 2 series (A and B) of ethylcellulose samples with different distribution patterns for the ethyl substituents

Series B (2,6-0-ethylcellulose): Preparation from a commercial ethylcellulose. This second series of samples were prepared following the Budgell method[25,26], as shown in *Figure 2II*. The starting, material was a commercial EC obtained from Aldrich Ltd and had a DS of 2.3 and a mass average molar mass of 65 000. Dried EC, 5 g, was dissolved in 60 ml of tetrahydrofuran under nitrogen. Sodium hydride (NaH), 0.7 g, was then added and the solution was stirred for 1 h before the dropwise addition of ethyl iodide as the alkylating agent. The temperature ranged from 40 to 60°C, the reaction time and the amount of ethyl iodide added were varied to give samples with ethyl DS of 2.3 to 3.0. After cooling, 50 ml of methanol were slowly added to the reaction mixture to remove any unreacted NaH and the polymer was precipitated by pouring into 200 ml of water containing 1 g of NaS_2O_3. It was then thoroughly washed with water and dried under vacuum at 60°C. Degradation of the polymer during the ethylation was not severe since the samples had molar masses similar to that of the starting, EC.

Characterization of the distribution of ethyl substituents.

The distribution of ethyl groups in the EC samples was determined by acid hydrolysis and subsequent analysis of the components as partially ethylated alditol acetates by gas-liquid chromatography[7,9]: The samples were treated with 4% sulfuric acid at 120°C for 1 h. Following neutralization to pH 5.5, the acid-hydrolyzates were subjected to reduction with $NaBH_4$ for overnight and dried completely for the subsequent acetylation with acetic anhydride. Then the alditol acetates in acetone were injected into the gas chromatograph.

Analysis

Thin samples of EC and dichlorometane (CH_2Cl_2) were prepared for optical measurements by flame-sealing one end of a 0.4 mm thick glass microslide (Vitro Dynamics Inc). The slide was packed with a known mass of polymer and predetermined mass of solvent was injected with a microsyringe. The sample was then cooled in liquid nitrogen and the other end of the microslide was flame-sealed. CD measurements were performed on polymer concentrations ranging, from 40 to 50 wt% where the EC solutions in CH_2Cl_2 formed chiral nematic mesophases exhibiting reflection colours. However, since CH_2Cl_2 is very volatile the exact concentrations could not be determined with complete accuracy even using the above procedure. Centrifugation was used to promote mixing, in the microslides. Then, the CD spectra were recorded by placing, the microslides in the spectropolarimeter beam path.

Only quantitative analyses were possible because of the previously described concentration problems caused by the CH_2Cl_2 volatility and thus only the mesophase cholesteric twist sense was noted. The handedness and wavelength of the cholesteric reflection bands at 25°C were measured with a Jasco J-500C spectropolarimeter.

RESULTS AND DISCUSSION

Characterization of the two polymer series.

Series A-starting material 23EC. *Figure 3* shows the charge in DS for the ethyl groups at each position (C-2, C-3 and C-6 position) of the glucose unit for the entire set of 9 samples in this series. For this set of samples, all hydroxyl groups at the C-2 and C-3 positions were almost completely ethylated and only the ethyl DS at the C-6 position hydroxyl was increased systematically with increasing sample code number. As already reported in previous articles[1,5,6], the hydroxyls at the C-6 position in cellulosics easily form intermolecular hydrogen bonds, resulting in poor sample solubility in many solvents. In this series as seen in *Figure 3*, samples 1–4 which had a DS at the C-6 position of less than 0.78 did not give clear CH_2Cl_2 solutions even at concentrations of 1 wt%. A high degree of substitution at the C-6 position was required for the polymer to dissolve in CH_2Cl_2.

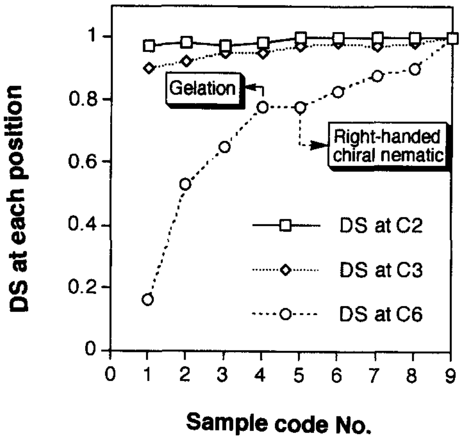

Figure 3 Change in the degree of substitution (DS) pattern at the individual C-2, C-3 and C-6 positions for series A samples prepared from synthesized 23EC

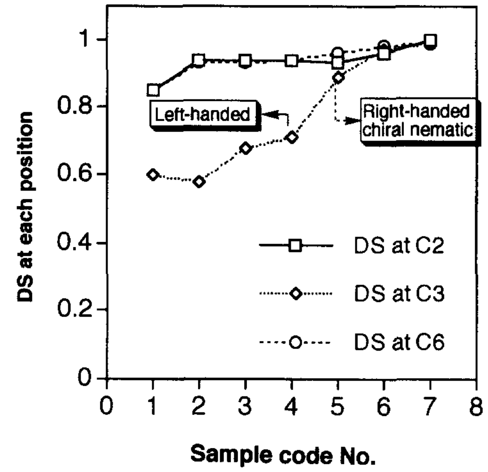

Figure 4 Change in degree of substitution (DS) pattern at the individual C-2, C-3 and C-6 positions for series B samples prepared from a commercially available EC

Series B-starting material a commercial ethylcellulose. The distribution of ethyl substituents for the starting material (sample 1 in *Figure 4*) was 0.85, 0.6 and 0.85 for the C-2, C-3 and C-6 positions, respectively. The DS at the C-3 position was somewhat lower than that for the other positions. The C-2 and C-6 hydroxyl groups were easily and completely ethylated to give a saturated point with a DS of 1.0. Thus only the ethyl DS for the C-3 hydroxyls was individually increased up to a limit of 1.0. In contrast to series A, the C-6 position hydroxyl groups in series B were almost completely ethylated and all samples dissolved in CH_2Cl_2 at 1 wt% to yield clear solutions.

Handedness of EC lyotropic liquid crystals.

Two of the primary optical methods for studying chiral nematic (cholesteric) liquid crystals are optical rotatory dispersion (ORD) and circular dichroism (CD). In this study, we used only CD to determine the handedness of the cholesteric structure by the sign of the induced CD band which results from the selective reflection of circularly polarized light. A positive CD band corresponds to a left-handed cholesteric twist, while a negative CD band corresponds to a right-handed twist.

Figure 5 shows the induced CD spectra for anisotropic CH_2Cl_2 solutions of EC 4, 5 and 7 in series B which has an increasing ethyl DS at the C-3 position hydroxyl. The positive CD band for EC 4 indicates that the liquid crystal is left-handed while the negative CD bands for EC 5 and 7 indicate right-handed twists. The change in cholesteric handedness for all the series B samples is illustrated in *Figure 4*. The concentration range for the anisotropic phases was between 40% and 50% by weight of polymer. This suggests that the introduction of more ethyl groups into the C-3 hydroxyl position leads to a change in the cholesteric handedness in this particular solvent, CH_2Cl_2.

Samples from series A, as shown in *Figure 3*, showed a totally different behaviour in cholesteric handedness from that of series B samples. Series A samples which were prepared from 23EC have free hydroxyls only at the C-6 position. As the sample code number increases, the free hydroxyl groups at the 6 position are gradually replaced by ethyl groups. As already noted, hydroxyl groups at the C-6 position in cellulosics contribute favourably to the formation of intermolecular hydrogen bonds and this results in poor solubility of the polymer. This can be seen for samples 1–4 in *Figure 3* which do not dissolve completely even in very dilute solution. Instead, they were found to swell and form gels. Samples with a DS of more than 0.8 at the C-6 position, namely samples 5–9, show induced CD spectra for concentrated anisotropic solutions from 40 to 50 wt% polymer (*Figure 3*) and all are right-handed chiral nematic liquid crystals.

These results suggest strongly that the distribution of ethyl substituents among C-2, C-3, and C-6 positions of the anhydroglucose unit in EC samples can affect the cholesteric handedness of their anisotropic solutions. In particular, the substitution of hydroxyl groups at the C-3 position may play an important role in determining the handedness, while hydroxyl groups at the C-6 position are important and contribute to the solubility of the sample in various solvents. Recently, we reported that the intramolecular hydrogen bonds formed between hydroxyls at the C-3 position and adjacent ether oxygens of the glucose ring (*Figure 1b* and *c*) are fairly strong[1,4] and may even be maintained in the solution state[9]. Further, it is recognized that intramolecular hydrogen bonds should have a strong influence on the physical properties[9,27,28] of the polymer. In other words, intramolecular hydrogen bonds at the C-3 position may play a role in determining the conformation of the extended glucose chain structure causing greater chain stiffness. Therefore in the present study, once the hydroxyl groups at the C-3 position are highly substituted, then the intramolecular bonds must be cut (*Figure 1a* type), and the glucose unit is now freer and may rotate easily to alter the torsion angle between two consecutive units and as a result the molecular chain will be more flexible. In fact, T_1 relaxation time of the C-1 carbon in a glucose unit in cellulose derivatives whose hydroxyl groups at the C-3 position remains unsubstituted is longer than that for 2,3-*O*-substituted cellulosics even in the solution state. ^{13}C-NMR chemical shifts and relaxation time at the C-1 carbon also change after deuteration of the hydroxyl groups in the same system[29]. These results indicates not only the engagements of the intramolecular hydrogen bonds in the solution state, but also the positive contribution of the interaction to the molecular chain stiffness. For all samples in series A, the hydroxyl groups at the C-3 position are assumed to be almost fully substituted and thus as long as the sample is dissolved, the anisotropic solution shows right-handedness. As shown in *Figure 4* (series B), the samples with an ethyl DS more than 0.9 at the C-3 position, EC 5–9, form a lyotropic right-handed chiral nematic mesophase. In relating the intramolecular hydrogen bonds at the C-3 position with chain stiffness, the above results indicate that the less stiff the chain is, the more favourably the right-handed chiral nematic structure is formed.

In series B samples, as the polymer concentration was increased from an isotropic solution to a film, there was no appearance of visible reflection colours or of liquid crystalline fingerprint textures as viewed under cross polarizers in the microscope. This suggests that the mesophase is in the untwisted nematic state[25,26]. As shown in *Figure 6*, both left-handed (EC 1) and right-handed (EC 8) mesophases in CH_2Cl_2 show similar behaviour in their relationship between the reflection wavelength and the concentration; the lower the polymer concentration, the longer the reflection wavelength. For planar chiral nematic liquid crystals the pitch, *P*, of the supermolecular helicoidal assembly of molecular chains is

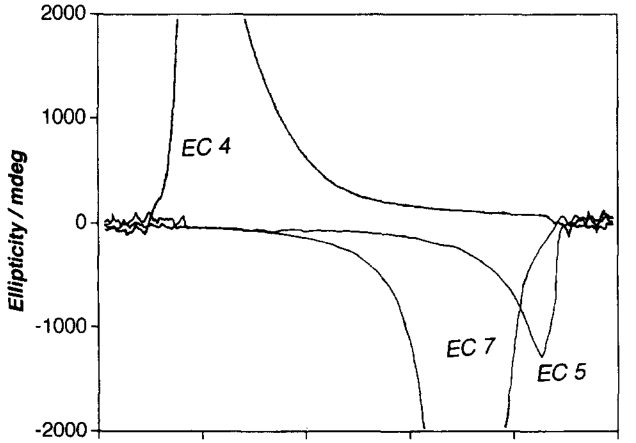

Figure 5 Induced CD spectra for mesophase of EC4, EC5 and EC7 (series B) in CH_2Cl_2 at 25°C

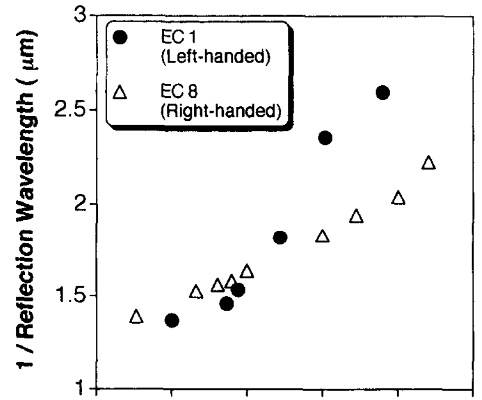

Figure 6 Dependence of maxmum reflection wavelength on concentration for left- and right-handed mesophases of EC (series B ECI and EC8, respectively) in CH_2Cl_2 at 25°C

related to the maximum reflection wavelength, λ_0, by de Vries equation[30], $\lambda_0 = nP$, where n is the average refractive index of the mesophase. Therefore, the concentration dependence trend is explained by the decrease in pitch of the cholesteric structure with increasing polymer concentration irrespective of the handedness. Unfortunately we could not examine the temperature dependence of the reflection wavelength because of experimental difficulties in the system at present.

CONCLUSION

Using two series of samples, in which degree of substitution (DS) at the individual hydroxyl groups at the C-2, C-3 and C-6 positions of the glucose unit were systematically changed, the dependence of the chiral nematic handedness of EC mesophases on the regioselectivity of the DS was investigated. As reported previously[5,6,9] free hydroxyl groups at the C-6 position interfered with the solubility of the samples in CH_2Cl_2. When the C-3 position hydroxyl groups were highly substituted by ethyl groups, the mesophase in CH_2Cl_2 exhibited a right-handed twist. Samples with a DS of less than 0.71 at the C-3 position in CH_2Cl_2 formed lefthanded mesophases with reflection colours. The hydroxyl groups at the C-3 position are known to easily form intramolecular hydrogen bonds with neighbouring ring oxygens. Therefore, we concluded that intramolecular hydrogen bonds formed between the C-3 position hydroxyls and the 0-5 position oxygens may have a strong, influence on the handedness of the cholesteric or chiral nematic supermolecular arrangement in EC. In addition, as chain stiffness arising from the intramolecular hydrogen bonds decreases a twist reversal for the mesophase can occur-specifically we found that as the DS of the EC increases samples with flexible chains caused by high ethyl substitution at the C-3 position (*Figure 1a* type) exhibited right-handed supermolecular arrangement in CH_2Cl_2, while left-handed mesophases of EC were found in samples with lower DS where rather stiff molecular chains had more intramolecular hydrogen bonds. These results indicate that the contribution of intramolecular hydrogen bonds should be considered when trying to explain or account for the chiroptical properties of cellulosic mesophases.

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REFERENCES

1. Kondo, T. J., *Polym. Sci. B Polym. Phys.*, 1994, **32**, 1229.
2. Kondo, T., Sawatari, C., Manley, R. St-J. and Gray, D. G., *Macromolecules*, 1994, **27**, 210.
3. Kondo, T. and Sawatari, C., *Polymer*, 1994, **35**, 4423.
4. Kondo, T. and Sawatari, C., *ACS Symposium Series*, in press.
5. Itagaki, H., Takahashi, I., Natsume, M. and Kondo, T., *Polym. Bull.*, 1994, **32**, 77.
6. Kondo, T. and Sawatari, C., *Polmer*, 1996, **37**, 393.
7. Kondo, T. and Gray, D. G., *Carbohydr. Res.*, 1991, **220**, 173.
8. Kondo, T., *Carbohydr. Res.*, 1993, **238**, 231.
9. Kondo, T. J., *Polym. Sci. B Polym. Phys.*, 1997, **35**, 717.
10. Kondo, T. and Nojiri, M., *Chem. Lett.*, 1994, 1003.
11. Nojiri, M. and Kondo, T., *Macromolecules*, 1996, **29**, 2392.
12. Werbowyj, R. S. and Gray, D. G., *Mol. Cryst. Liq. Cryst.*, 1976, **34**, 97.
13. Panar, M. and Willcox, 0. B., Offenlegungsschrift, German Federal Republic Patent 2705381, 1977.
14. Maeno, J. United State Patent No. 4132464, 1979.
15. Bheda, J., Fellers, J. F. and White, J. L., *Coll. Polym. Sci.*, 1980, **258**, 1335.
16. Yamagishi, T., Fukuda, T., Miyamoto, T. and Watanabe, J., *Polym. Bull.*, 1988, **20**, 373.
17. Gilbert, R. D. and Patton, P. A., *Progr. Polym. Sci.*, 1983, **9**, 115.
18. Gray, D. G., *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 1983, **37**, 179.
19. Vogt, U. and Zugenmaier, P., *Ber. Bunsen-Ges. Phys. Chem.*, 1985, **89**, 1217.
20. Zugenmaier, P. and Haurand, P., *Carbohydr. Res.*, 1987, **160**, 369.
21. Ritcey, A. M., Holme, K. R. and Gray, D. G., *Macromolecules*, 1988, **21**, 2914.
22. Pawlowski, W. A., Gilbert, R. D., Fornes, R. E. and Purrinaton, S. T., *J. Polym. Sci. B Polym. Phys.*, 1987, **25**, 2293.
23. Guo, J. -X. and Gray, D. G., Macromolecules, 1989, 22, 2082.
24. Guo, J. -X. and Gray, D. G., *Macromolecules*, 1989, **22**, 2086.
25. Budgell, D. R. and Gray, D. G. in *Polymer and Fiber Science: Recent Advances*, ed. R. E. Fornes and R. D. Gilbert, 1992, pp. 145.
26. Budgell, D. R. Ph.D. thesis, McGill University, Montreal, Canada, 1989.
27. Tashiro, K. and Kobayashi, M., *Polym. Bull.*, 1985, **14**, 213.
28. Tashiro, K. and Kobayashi, M., *Polymer*, 1991, **32**, 1516.
29. Nojiri, M. and Kondo, T., unpublished data.
30. de Vries, H. I., *Acta Crystallogr.*, 1951, **4**, 219.