isotactic polymer may be extracted with the atactic polymer into the hexane.

The results are very similar to those obtained[4] by Magagnini et al. for poly(1-eicosene), except for the solvent used to separate the fractions. As mentioned previously, several poly(1-alkene)s with long side chains display two melting points. The work of Magagnini et al. and the present work are in agreement that the two melting points are caused by the presence of atactic and isotactic fractions which independently exhibit their melting points. This suggestion has been confirmed for poly(1-octadecene) and poly(1-eicosene), but further work is needed to establish the nature of the transition in the other polymers.

The soluble Ziegler–Natta catalysts $V(acac)_3/AlEt_2Cl$,[16] Cp_2TiCl_2/methalumoxane, Cp_2ZrCl_2/methalumoxane, and Cp_2HfCl_2/methalumoxane[17–20] were identified as having the potential to polymerize 1-octadecene. So far, we have been unsuccessful in attempts to produce atactic PEBP26 using these catalysts, as only oligomers have been obtained.

Conclusion

A series of six new hydrocarbon side-chain polymers containing the biphenyl mesogen have been prepared with a $Et_3Al/TiCl_4$ catalyst. The polymers have high molecular weights and broad polydispersities. The yields of the polymers were low (5–15%), and unreacted monomer was recovered from the polymerization reactions. A sample of the polymer with a two-carbon tail and six-carbon spacer was also polymerized with the Chien catalyst in 36% yield. The tacticities of the polymers as determined by ^{13}C NMR were shown to range from 65% to 90% isotactic. The isotactic content seemed unusually high and may be due to some specific interaction between the incoming monomer and chain end or catalyst surface.

Aubrey and Barnatt have proposed previously that poly(1-octadecene) prepared with $Et_3Al/TiCl_4$ catalyst is composed of a mixture of atactic and isotactic polymers, which independently display their individual melting points. This suggestion has been confirmed in the present work by separating the isotactic and atactic fractions of poly(1-octadecene) with hexane and determining their tacticities by ^{13}C NMR. The hexane solubility or thermal properties of poly(1-octadecene) may thus be used to establish the tactic preferences of particular catalysts. The two melting points previously reported[8] for poly(1-alkene)s with side-chain lengths of 11–14 carbon atoms are probably due to the independent melting of the atactic and isotactic fractions. Preliminary experiments have not succeeded in finding a catalyst capable of polymerizing one of the new mesogenic monomers to polymers with high atactic content.

Acknowledgment. The support of the National Science Foundation for the Materials Research Laboratory is gratefully acknowledged.

Registry No. PEBP04, 115181-06-1; PEBP06, 115181-08-3; PEBP24, 118798-37-1; PEBP26, 115181-10-7; PEBP44, 115181-12-9; PEBP46, 115181-14-1; MgCl, 7786-30-3; Et_3Al, 97-93-8; $TiCl_4$, 7550-45-0; ethyl benzoate, 93-89-0; *p*-cresol, 106-44-5; poly(1-octadecene), 25511-67-5.

References and Notes

(1) Newman, B. A.; Frosini, V.; Magagnini, P. L. In *Mesomorphic Order in Polymers*; Blumstein, A., Ed.; ACS Symposium Series 74; American Chemical Society: Washington, DC, 1978; p 71.
(2) Hahn, B.; Wendorff, J. H.; Portugall, M.; Ringsdorf, H. *Colloids Polym. Sci.* **1981**, *259*, 875.
(3) Aubrey, D. W.; Barnatt, A. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 241.
(4) Magagnini, P. L.; Segre, A. L.; Andruzzi, F.; Lupinacci, D. *Macromolecules* **1981**, *14*, 1845.
(5) Magagnini, P. L.; Andruzzi, F.; Vergamini, P.; Benedetti, E. *Polym. Bull. (Berlin)* **1980**, *2*, 241.
(6) Magagnini, P. L.; Andruzzi, F.; Benetti, G. F. *Macromolecules* **1980**, *13*, 12.
(7) Magagnini, P. L.; Andruzzi, F.; Lupinacci, D.; Paci, M. *Polymer* **1982**, *23*, 277.
(8) Porter, R. S.; Wang, J.; Knox, J. R. *Polym. J. (Tokyo)* **1978**, *10*, 619.
(9) Mallon, J. J.; Kantor, S. W. *Macromolecules*, in press.
(10) Chien, J. C. W.; Kuo, C.-J. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 761.
(11) Mallon, J. J.; Kantor, S. W. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 43.
(12) Chien, J. C. W.; Kuo, C. I.; Ang, T. *J. Poly. Sci., Polym. Chem. Ed.* **1985**, *23*, 723.
(13) Breitmaier, E.; Voelter, W. *^{13}C NMR Spectroscopy*; Verlag Chemie: New York, 1978; Chapter 4.
(14) Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.
(15) Duran, R.; Gramain, P. *Makromol. Chem.* **1987**, *188*, 2001.
(16) Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, *12*, 814.
(17) Kaminsky, W.; Sinn, H. In *Advances in Organometallic Chemistry*; Academic Press: New York, 1980; Vol. 18, pp 99–149.
(18) Kaminsky, W.; Schlobohm, M. *Makromol. Chem., Makromol. Symp.* **1986**, *4*, 103.
(19) Kaminsky, W.; Herwig, J. *Polym. Bull. (Berlin)* **1983**, *9*, 464.
(20) Kaminsky, W.; Luker, H. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 275.

Preparation and Liquid Crystalline Properties of (Acetyl)(ethyl)cellulose

Jian-Xin Guo and Derek G. Gray*

Pulp and Paper Institute of Canada and Department of Chemistry, McGill University, 3420 University Street, Montreal, PQ, Canada H3A 2A7. *Received April 22, 1988*

ABSTRACT: (Acetyl)(ethyl)cellulose (AEC) samples with a range of acetyl contents were made from (ethyl)cellulose (EC) with a degree of substitution of 2.5. The products formed cholesteric liquid crystals in chloroform, dichloromethane, aqueous phenol, *m*-cresol, dichloroacetic acid, and acetic acid. The acetyl degree of substitution (DS) ranged from 0.0 to 0.5 and strongly influenced the thermal behavior of the polymers in the solid state, with the higher acetyl DS giving higher melting points and heats of fusion. The AEC liquid crystals with high acetyl contents in chloroform, *m*-cresol, aqueous phenol, and acetic acid were right-handed cholesterics, in contrast to the handedness of the original unsubstituted EC in the same solvents. However, in dichloroacetic acid, both AEC and EC were right-handed.

Introduction

Most cellulosic liquid crystals are cholesteric, possessing the exceptionally high optical rotatory power characteristic of the helicoidal supramolecular arrangement.[1–6] The handedness of the mean chain orientation around the helicoidal axis may be deduced from the chiroptical

0024-9297/89/2222-2082$01.50/0

Table I
Acetylation Conditions for (Ethyl)cellulose

sample	reagent, mL	temp, °C	time, h	catalyst, g	acetyl DS
AEC-1	6.0	40	0.5	0	0.05
AEC-2	6.0	40	1.0	0	0.06
AEC-3	6.0	40	2.0	0	0.08
AEC-4	9.0	40	3.0	0	0.11
AEC-5	9.0	40	4.0	0	0.13
AEC-5	12.0	40	5.0	0	0.17
AEC-7	12.0	40	6.0	0	0.19
AEC-8	12.0	25	12.0	0	0.25
AEC-9	12.0	25	18.0	0	0.30
AEC-10	12.0	25	12.0	0.5	0.42
AEC-11	12.0	25	12.0	1.0	0.50

properties of the liquid crystals.

Early observations indicated that most cellulosics seemed to form right-handed cholesterics. However, (ethyl)cellulose (EC) dissolved in acetic acid (AA) forms left-handed cholesteric liquid crystals,[7] whereas EC dissolved in DCA forms right-handed cholesteric structures.[8] (Ethyl)cellulose in chloroform, aqueous phenol, and *m*-cresol forms left-handed cholesteric liquid crystals,[9] as does cellulose acetate[10] and triacetate[11] in trifluoroacetic acid, and (methyl)cellulose in trifluoroacetic acid and dichloroacetic acid.[12] (No handedness was derived from the circular dichroism measurements in ref 10. The apparent positive Cotton effect in ref 11 was incorrectly attributed to a right-handed arrangement.) This solvent dependence of handedness has long been observed for polypeptide solutions.[13-18] The relationship between the handedness of the supramolecular helicoidal structure and the molecular structure of cellulose derivatives and solvents is not at all understood.

In this paper, we describe the effects of a simple acetylation of the residual hydroxyl groups in a sample of (ethyl)cellulose. The product, (acetyl)(ethyl)cellulose (AEC), has already been prepared by Huang and shown to form liquid crystalline solutions in acetic, dichloroacetic, and trifluoroacetic acids.[19] Our samples, with a range of acetyl contents, also form liquid crystalline solutions in chlorinated and phenolic solvents. Furthermore, it was found that the acetylation of unsubstituted hydroxyl groups in EC can change the sense of the helicoidal cholesteric twist from *left-handed* for the initial EC solution to *right-handed* for the highly substituted (acetyl)(ethyl)cellulose solution in the *same* solvent (e.g., chloroform, *m*-cresol). Some of the effects of increasing acetyl group content on the physical properties of AEC will be presented.

Experimental Section

Synthesis of AEC. (Ethyl)cellulose (3 g) (Aldrich Co., ethoxyl content 48%, viscosity (5%) 300 cP) was dissolved in 50 mL of pyridine to give a clear, homogeneous, viscous solution. Acetic anhydride was added to the solution with stirring under nitrogen. The acetylated products were isolated by pouring the reaction mixture into a large amount of cooled water, filtering, and washing several times with distilled water to remove excess reagent and solvent. The products were redissolved in tetrahydrofuran (THF) and reprecipitated in distilled water. Final products were dried under vacuum at 65 °C. The acetyl content depended on the reaction temperature, time, and amount of reagent, as shown in Table I.

Samples for X-ray measurement were prepared by compressing EC and AEC samples (40 mg) into disks at a pressure of 10^4 kg/cm^2.

The lyotropic liquid crystal samples to be studied by optical microscopy, CD, and optical rotation were prepared by mixing appropriate weights of AEC or EC and solvent in glass vials. Once homogeneous, the liquid crystalline solutions were sandwiched between microscope slide and cover glass and sealed with epoxy resin to prevent solvent loss.

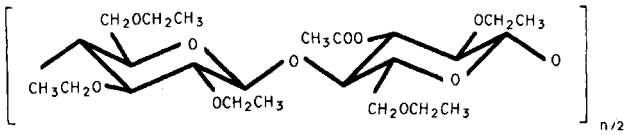

Figure 1. Idealized structure of AEC with ethyl DS = 2.5 and acetyl DS = 0.5.

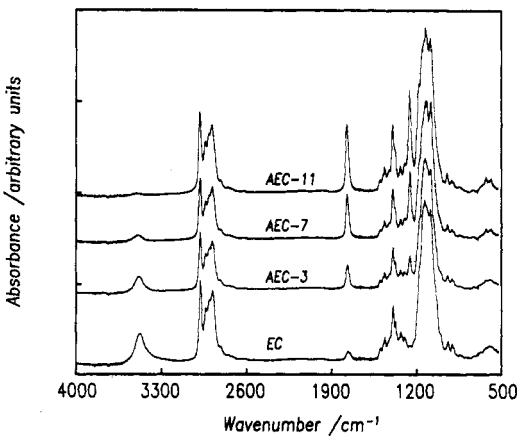

Figure 2. Infrared spectra for (ethyl)cellulose and three (acetyl)(ethyl)cellulose samples.

General Analysis. IR spectra of the films were recorded with a Mattson Cygnus FT-IR spectrophotometer at room temperature. Liquid crystalline textures were observed with a Reichert polarizing microscope. DSC curves were recorded with a Perkin-Elmer DSC-2C differential scanning calorimeter from 350 to 580 K in a N_2 atmosphere. Wide-angle X-ray diffraction was performed with a Philips PW 1730 nickel-filtered Cu Kα (λ = 0.154 nm) X-ray generator. The voltage and current settings were 40 kV and 20 mA, respectively. Photometer curves were recorded with a double-beam recording microdensitometer (Joyce Loebl and Co. Ltd.). Circular dichroism (CD) spectra were recorded with a Jasco J-500C spectropolarimeter at room temperature. Optical rotations were measured with a Jasco DP-140 digital polarimeter (λ = 589 nm) at room temperature.

Results and Discussion

Polymer Characterization. An ethoxyl content of 48% corresponds to a degree of substitution of 2.5. Thus, there is about one free hydroxyl group for every two anhydroglucose units available for acetylation. An idealized structure for the acetylated (ethyl)cellulose is shown in Figure 1.

In order to clarify how the degree of substitution influences the properties of AEC, a range of acetyl contents was prepared by selecting different reaction conditions as shown in Table I. IR spectra of the corresponding AEC products are presented in Figure 2. The absorption bands around 3650–3350 and 1850–1700 cm^{-1} are due to OH and C=O stretching vibrations, respectively. The small carbonyl peak for the (ethyl)cellulose sample is presumably due to adventitions oxidation of the cellulose during manufacture. The intensity of the hydroxyl peak decreases and that of the carboxyl peak increases with increasingly severe acetylation from AEC-1 to AEC-11. No other changes are apparent. The absence of hydroxyl peak in the IR spectrum of AEC-11 indicates that the free hydroxyl groups of EC were completely substituted by acetyl groups when perchloric acid was used as a catalyst during acetylation.

If the acetyl degree of substitution (DS) of product AEC-11 is taken equal to 0.5, then column 6 of Table I

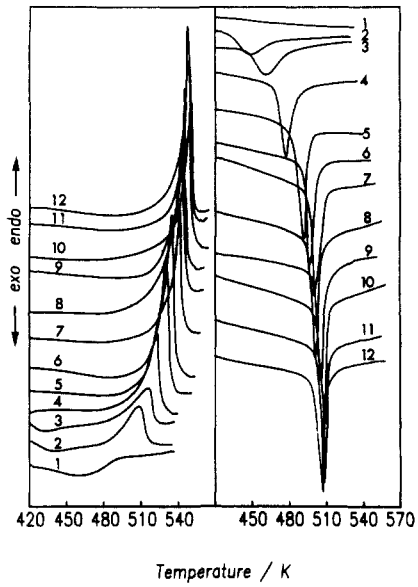

Figure 3. DSC traces of the initial (ethyl)cellulose sample (curve 1) and the acetylated samples, in order of increasing acetyl content (curves 2–12). Heating (left) and cooling (right) at 20 K/min.

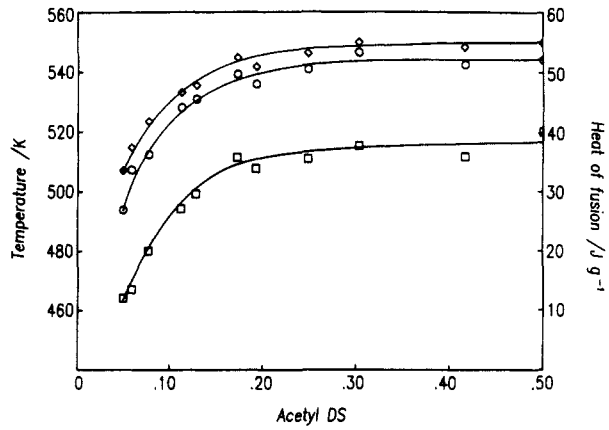

Figure 4. Effect of degree of acetyl substitution on DSC endotherm on heating at 20 K/min. (○) Temperature of endotherm onset; (◇) temperature of peak maximum; (□) heat of fusion.

shows the results calculated for the acetyl DS of all samples based on

$$(\mathrm{DS})_x = 0.5(I^{\mathrm{C=O}}/I^{\mathrm{OH}})_x(I^{\mathrm{C=O}}/I^{\mathrm{OH}})_{\mathrm{AEC\text{-}11}} \qquad (1)$$

where $I^{\mathrm{C=O}}$ and I^{OH} are the maximum intensities of carboxyl and hydroxyl peaks, respectively, and subscript x indicates the sample under consideration.

The replacement of free hydroxyl groups by acetyl groups should give rise to changes in physical properties. Figure 3 shows some preliminary results on the thermal behavior of EC and AEC with increasing acetyl content. Differential scanning calorimetry shows very weak evidence of crystallization for the (ethyl)cellulose sample, but acetyl substitution results in markedly larger peaks. The magnitude and temperature of the transition peaks for crystallization increase with the acetyl content of the polymer; the endotherm and exotherm peak temperatures increase with increasing acetyl content, leveling out for acetyl DS over 0.25. Plots of onset point, maximum temperature, and heat of fusion for the endothermic peaks against acetyl DS are presented in Figure 4. A similar effect of the degree of substitution on thermal behavior has been observed for partially and completely substituted (acetoxypropyl)cellulose[20] and (benzyl)cellulose.[21] It has been suggested[21] that the increase in crystallinity results from

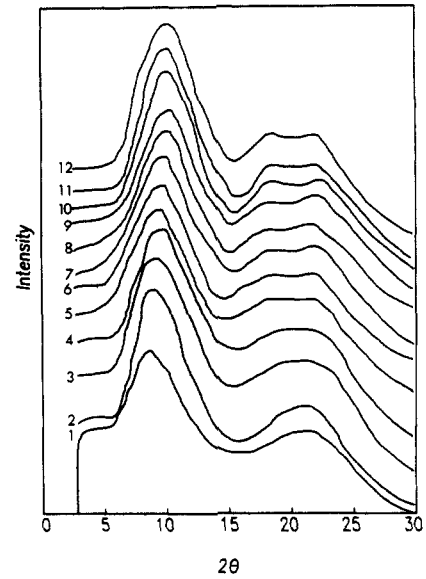

Figure 5. Densitometer traces across semiequators of X-ray diffraction patterns for (ethyl)cellulose and 11 (acetyl)(ethyl)-cellulose samples, in order of increasing acetyl content (bottom to top).

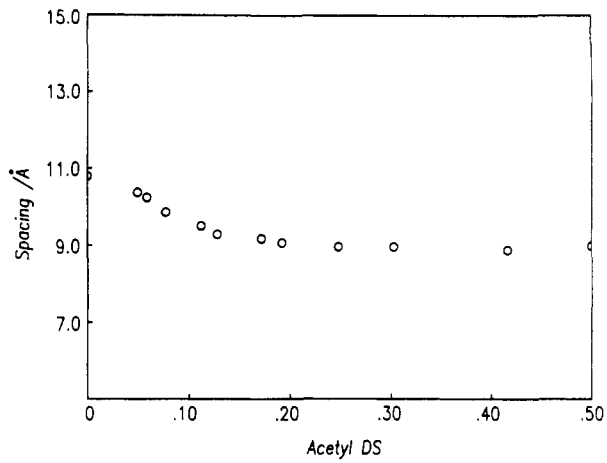

Figure 6. Spacing corresponding to largest peak of Figure 5 as a function of acetyl DS.

the increase in chain regularity with increasing DS. In our system, the increase in crystallinity with acetyl content is in accord with the increase in heat of fusion and the extremely sharp exothermic peaks on cooling (Figure 3). The acetoxy group is obviously more compatible with crystallization than the hydroxyl group that it replaces. On cooling from the melt, AEC shows strong birefringence under crossed polars; no birefringence was observed for EC.

Introduction of the acetyl substituent also modifies the X-ray diffraction patterns. Figure 5 shows densitometer traces of the diffraction from a series of AEC samples with different acetyl contents. All samples exhibit diffuse halos. An additional halo appears at intermediate angles with increasing acetyl DS, indicative of a more ordered packing structure. The same pattern has been observed for the acetate derivatives; cellulose triacetate is more crystalline than secondary cellulose acetate.[22] The d values for the longest spacings were calculated from the Bragg equation and are plotted against acetyl DS in Figure 6. The values decrease slightly with increasing acetyl DS.

AEC Lyotropic Liquid Crystals. The introduction of acetyl groups influences the solubility of AEC and affects the properties of the mesophase solutions. Although solutions of both EC and AEC can form liquids crystals,

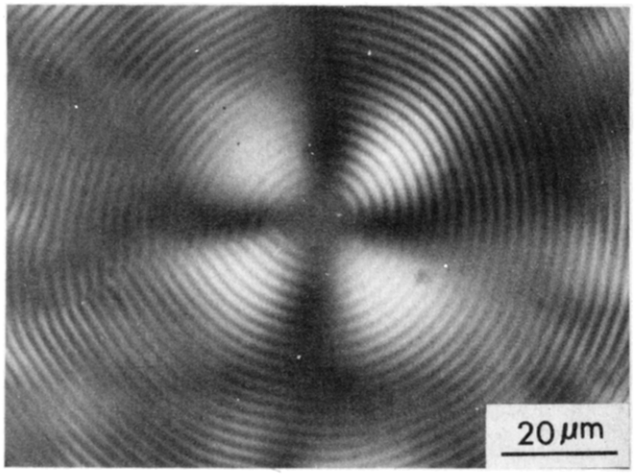

Figure 7. Photomicrograph (crossed polars) of fingerprint texture for AEC-9 (47% by weight) in aqueous phenol.

the acetylated polymers dissolve more readily to form liquid crystalline phases in a given solvent, possibly because the replacement of hydroxyls by acetoxy groups inhibits interchain hydrogen bonding.

The AEC synthesized here was found to form liquid crystals in chloroform, dichloromethane, aqueous phenol, and *m*-cresol as well as in acetic, dichloroacetic, and trifluoroacetic acids. Mesomorphic solutions (~30–60% by weight) in dichloroacetic acid, chloroform, and dichloromethane display the brilliant iridescent reflection colors characteristic of cholesteric liquid crystals, with pitch values corresponding to the wavelengths of visible light.

Observation of the texture of these lyotropic solutions was carried out at room temperature with a polarizing microscope. Planar textures were observed for AEC in dichloroacetic acid and dichloromethane. Typical fingerprint textures were observed for AEC in aqueous phenol and in *m*-cresol. An example is shown in Figure 7. The distance between alternating dark and bright lines (half of the cholesteric pitch) was greater than 2 μm. In contrast, EC solutions in the same solvents displayed iridescent colors, indicating that their pitch values were smaller than the AEC solution. Thus, the introduction of acetyl groups affects the pitch of the cholesteric solution. The relationship between the pitch and acetyl DS will be considered in the following paper in this issue.[23]

The textures of AEC solutions in chloroform are more complicated. Planar, oily streak, or fingerprint textures are observed, depending in part on the acetyl DS. Furthermore, there is evidence of the coexistence of liquid crystalline and crystalline phases (Figure 8). Crystallization from polymer mesophases has been observed for polybenzamide (PBA)[24-28] and for cellulose carbanilate.[7] A more detailed investigation of AEC crystallization from the mesophase is in progress.

Cholesteric liquid crystals display high optical rotation and selective light reflection. de Vries[29] developed a theory relating these properties to the helicoidal structure of cholesterics. The optical rotations given by

$$\alpha = \pi(\Delta n)^2 P/4\lambda^2[1 - (\lambda/\lambda_0)^2] \qquad (2)$$

where α is the optical rotation, P is the helicoidal pitch (taken as positive for a right-handed helicoid), and Δn is the birefringence of the nematic layer. The wavelength of reflected light in air, λ_0, is given by $\lambda_0 = nP$, where n is the mean refractive index of the cholesteric mesophase. With $\lambda_0 \gg \lambda$, eq 2 reduces to

$$\alpha = \pi(\Delta n)^2 P/4\lambda^2 \qquad (3)$$

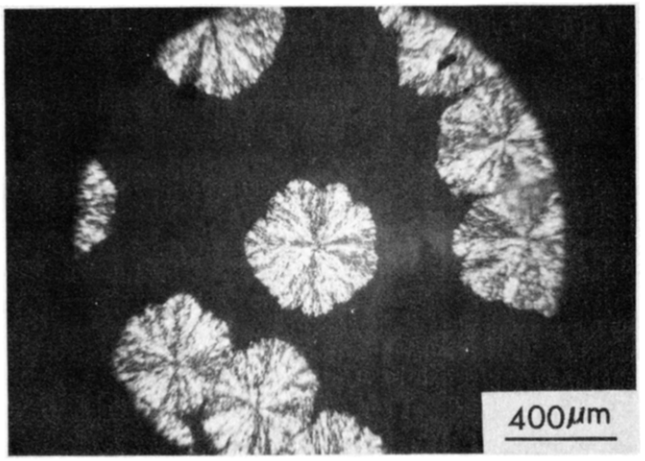

Figure 8. Photomicrograph (crossed polars) of deformed spherulites crystallizing from an AEC/chloroform liquid crystalline phase at room temperature.

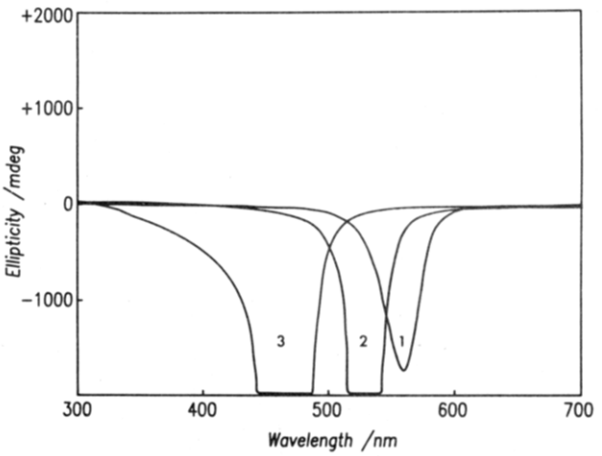

Figure 9. Apparent CD spectra for AEC-10 in (1) dichloroacetic acid, (2) chloroform, (3) methylene chloride at room temperature.

The sign of α for $\lambda < \lambda_0$ determines the handedness of the cholesteric structure, with $\alpha > 0$ for a right-handed twist and $\alpha < 0$ for a left-handed one.

The handedness of a cholesteric structure can be also determined from the sign of the apparent circular dichroism (CD) band which results from the selective reflection of circularly polarized light. A positive CD band corresponds to left-handed twist, and a negative CD band corresponds to right-handed.

Figure 9 shows the apparent CD spectra of anisotropic AEC solutions in dichloroacetic acid, chloroform, and dichloromethane. The negative CD bands indicate that these three liquid crystals are right-handed. The handedness of AEC liquid crystalline solutions in glacial acetic acid, *m*-cresol, and aqueous phenol was determined by measuring the optical rotation with a digital polarimeter. This is possible because the pitch values for these liquid crystalline solutions are much longer than the wavelength of UV–visible light, as discussed above. The rotations of AEC/acetic acid, AEC/*m*-cresol, and AEC/aqueous phenol at $\lambda = 598$ nm are all positive, indicative of a right-handed twist, according to eq 3.

Perhaps the most interesting observation is that the introduction of acetyl group into EC leads to a change of cholesteric handedness in a given solvent. EC liquid crystals in chloroform, *m*-cresol, and aqueous phenol are left-handed,[9] but AEC liquid crystals in the same solvents are right-handed. On the other hand, both EC and AEC liquid crystals in dichloroacetic acid remain right-handed. The apparent handedness of EC and AEC lyotropic cho-

Table II
Handedness of (Ethyl)cellulose and (Acetyl)(ethyl)cellulose Cholesteric Phases in Various Solvents

solvent	EC	AEC-9[a]
chloroform	left[9]	right
dichloromethane	left[9]	right
m-cresol	left[9]	right
aqueous phenol	left[9]	right
acetic acid	left[8]	right
dichloroacetic acid	right[8]	right

[a] Acetyl DS = 0.30.

lesteric liquid crystals is summarized in Table II.

Most cellulose derivatives with bulky substituents are right-handed. Left-handed cholesterics have been observed for (ethyl)cellulose,[7,8] cellulose acetate,[10] cellulose triacetate,[11] and (methyl)cellulose.[12] To date, only EC displays the solvent dependence of handedness,[7,8] which is commonly observed for polypeptides.[18] The reason is not clear. But the fact that the introduction of acetyl groups changes the twist from left-handed to right-handed in the same solvent (chloroform, *m*-cresol, or aqueous phenol) implies that the contribution to handedness is related to the structure of the side chain and the interaction between the side chain and solvent. In fact, a small change in acetyl DS (about 0.2) leads to a large change in chiroptical properties, as discussed in the following paper.[23]

Acknowledgment. We thank the Natural Sciences and Engineering Council of Canada for support. J.-X. Guo thanks the Chinese Government for a visiting scholarship.

Registry No. AEC, 37228-10-7; EC, 9004-57-3.

References and Notes

(1) Werbowyj, R. S.; Gray, D. G. *Mol. Cryst. Liq. Cryst.* **1976**, *34*, 97.
(2) Tseng, S.-L.; Valente, A.; Gray, D. G. *Macromolecules* **1981**, *14*, 715.
(3) Onogi, Y.; Fellers, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 663.
(4) Meeten, G. H.; Navard, P. *Polymer* **1983**, *4*, 815.
(5) Sixou, P.; Femetre, J.; Ten Bosch, A.; Gilli, J.-M.; Dayan, S. *Mol. Cryst. Liq. Cryst.* **1983**, *91*, 277.
(6) Patel, D. L.; Gilbert, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1231.
(7) Vogt, U.; Zugenmaier, P. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1217.
(8) Zugenmaier, P.; Haurand, P. *Carbohydr. Res.* **1987**, *160*, 369.
(9) Budgell, D. R.; Gray, D. G., unpublished results.
(10) Lematre, J.; Dayan, S.; Sixou, P. *Mol. Cryst. Liq. Cryst.* **1982**, *84*, 267.
(11) Meeten, G. H.; Navard, P. *Polymer* **1982**, *23*, 1727.
(12) Guo, J.-X.; Gray, D. G., unpublished results.
(13) Robinson, C. *Trans. Faraday Soc.* **1956**, *52*, 571.
(14) Robinson, C.; Ward, J. C.; Beevers, R. B. *Discuss. Faraday Soc.* **1958**, *25*, 29.
(15) Robinson, C. *Tetrahedron* **1961**, *13*, 219.
(16) Robinson, C. *Mol. Cryst.* **1966**, *1*, 467.
(17) Patel, D. L.; DuPré, D. B. *J. Chem. Phys.* **1980**, *72*, 2515.
(18) Uematsu, I.; Uematsu, Y. *Adv. Polym. Sci.* **1984**, *59*, 37.
(19) Huang, Y., private communication.
(20) Laivins, G. V.; Sixou, P.; Gray, D. G. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2779.
(21) Isogai, A.; Ishizu, A.; Nakano, J. *J. Appl. Polym. Sci.* **1984**, *29*, 2097.
(22) Fisher, J. W. In *Recent Advance in Chemistry of Cellulose and Starch*; Honeyman, J., Ed.; Heywood: London, 1959; Chapter 7.
(23) Guo, J.-X.; Gray, D. G. *Macromolecules*, following paper in this issue.
(24) Papkov, S. P. In *Mesomorphic Order in Polymers and Polymerization in Liquid Crystalline Media*; Blumstein, A., Ed.; ACS Symposium Series 74; American Chemical Society: Washington, DC, 1978; p 97.
(25) Krigbaum, W. R.; Ciferri, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 253.
(26) Balbi, C.; Bianchi, E.; Tealdi, A. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2037.
(27) Ciferri, A.; Krigbaum, W. R. *Mol. Cryst. Liq. Cryst.* **1981**, *69*, 273.
(28) Papkov, S. P. *Adv. Polym. Sci.* **1984**, *59*, 75.
(29) de Vries, H. *Acta Crystallogr.* **1951**, *4*, 219.

Chiroptical Behavior of (Acetyl)(ethyl)cellulose Liquid Crystalline Solutions in Chloroform

Jian-Xin Guo and Derek G. Gray*

Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, 3420 University Street, Montreal, PQ Canada H3A 2A7.
Received April 22, 1988

ABSTRACT: Cholesteric liquid crystal solutions of (acetyl)(ethyl)cellulose (AEC) in chloroform exhibit an unusual optical property, changing from a left-handed to a right-handed helicoidal structure with increasing acetyl content. The change occurs at a critical degree of acetylation, DA*, of around 0.18–0.20 for AEC solutions at room temperature. The acetyl content of AEC also strongly influences the magnitude of the cholesteric pitch and its temperature dependence. For acetyl contents below DA*, the cholesteric solutions are left-handed, with pitches which increase with acetyl content and decrease on heating. For acetyl contents above DA*, the solutions are right-handed, and the pitches decrease with increasing acetyl content and increase on heating. However, dilute solutions of all the AEC samples in chloroform show positive optical activity, independent of acetyl content.

Introduction

As described in the preceding paper in this issue,[1] the acetylation of an (ethyl)cellulose (EC) sample with a degree of substitution (DS) of 2.5 gives a product, (acetyl)-(ethyl)cellulose (AEC), whose physical properties are quite different from the original material. In particular, the replacement of hydroxyl substituents by acetoxyl groups reverses the handedness of the cholesteric structure of the liquid crystalline solutions. (Acetyl)(ethyl)cellulose forms a right-handed helicoidal structure in chloroform, while

0024-9297/89/2222-2086$01.50/0