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]

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

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

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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

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(ethyl)cellulose is a left-handed structure in the same solvent. The chirality of cholesteric liquid crystal polymers has been widely investigated for polypeptides[2-7] and polyesters,[8] and recently a reversal of pitch with solvent has been reported for cellulosics.[9] A reversal in the sense of cholesteric twist for lyotropic liquid crystals has been reported in three situations.

1. **Reversal in the Chirality of the Constituent Molecules.** The cholesteric sense of the liquid crystals of poly(γ-benzyl L-glutamate) is opposite to that of its mirror (D) isomer. An equal mixture of the two isomers, whose twisting power falls to zero, is called a compensated nematic structure.[2,3]

2. **Change of Solvent.** Some lyotropic liquid crystal polymers form right-handed cholesterics in some solvents and left-handed cholesterics in others, even though the chirality of the polymer apparently remains the same and the solvents themselves are achiral. Compensation also occurs at the appropriate ratio of the two solvents.[2-4,9]

3. **Change with Temperature.** The cholesteric sense of some lyotropic liquid crystals reverses handedness on heating. The twist drops to zero at the compensated temperatures.[2,5-7]

By analogy with these three cases, there must exist a compensated state with a critical degree of acetylation at which (acetyl)(ethyl)cellulose behaves as a compensated nematic in a given solvent. In the present paper, we examine the chiroptical properties of AEC with various degrees of acetylation. The effect of acetyl DS on the temperature dependence of cholesteric pitch is also investigated for AEC solutions in chloroform.

The changes in handedness reported here are presumed to be characteristic of polymer and solvent. The concentration of polymer will of course influence the magnitude of the observed pitch, but to date no evidence for a change of sign of pitch with concentration has been reported.

Experimental Section

The AEC samples were synthesized and characterized as previously described.[1] The (ethyl)cellulose starting material had an ethyl DS of 2.5, and the acetyl DS's of the products are AEC-1, 0.05; AEC-2, 0.06; AEC-3, 0.08; AEC-4, 0.11; AEC-5, 0.13; AEC-6, 0.17; AEC-7, 0.19; AEC-8, 0.25; AEC-9, 0.30; AEC-10, 0.42; AEC-11, 0.50. For comparison, a sample of (ethyl)cellulose (EC) was subjected to the same treatment as for acetylation,[1] but without the acetylation agent. Reagent-grade chloroform was used without further purification.

The dilute (5% by weight) isotropic solutions were prepared conventionally and transferred to a 10-mm-path length stoppered quartz spectrophotometric cell for optical rotatory dispersion (ORD) measurement.

The liquid crystalline samples for UV-visible reflection measurement were prepared by placing powdered polymer and chloroform in rectangular glass capillary tubes, 0.4-mm path length (Vitrodynamics Inc.), to give a polymer concentration of 45% by weight. The capillaries were then sealed with epoxy resin. The solutions were well mixed by centrifuging back and forth in the capillaries and were allowed to equilibrate for 2 weeks. The relative fluidity of the 45% (by weight) polymer solutions was estimated from the time required for the meniscus to move a given distance (2 cm) when the vials were tilted through 30°. The liquid crystalline samples for CD were prepared by sandwiching lyotropic solution between a microscope slide and cover slide.[1] Sealed capillary tubes could not be used because the samples were too thick and gave off-scale CD signals. However, the exact concentration of the solutions between the slides is unknown because of the rapid evaporation of chloroform during the preparation of the samples. The sample concentration is thus not given for the CD measurements but is in the range 40–60% by weight polymer.

Circular dichroism spectra were recorded with a Jasco J-500C spectropolarimeter. The samples were placed in a microscope hot stage (Mettler FP52) mounted in the spectrometer beam and heated at a rate of 0.2 °C/min. The mean refractive index of lyotropic samples (45% by weight) was measured with an Abbê refractometer (Carl Zeiss Model 44159) at 25 °C. Microscopic observations were made with a Reichert Zetopan polarizing microscope, and fingerprint spacings were measured from photomicrographs.

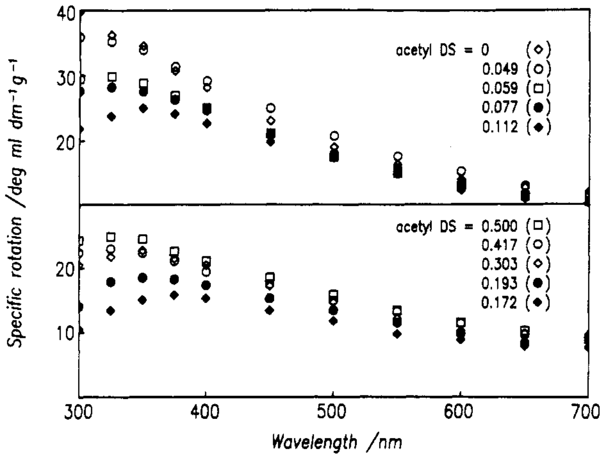

Figure 1. ORD curves for (ethyl)cellulose and (acetyl)(ethyl)cellulose dilute solution in chloroform (5% by weight) at room temperature.

Results and Discussion

Dilute Solution. The optical rotatory dispersion curves for dilute (5%) solutions of EC and AEC in chloroform are shown in Figure 1. The most significant observation is that the specific rotations of these solutions are all positive and the shapes of the curves are similar except at short wavelengths. This implies that there is no fundamental change in chain or local chirality with increasing substitution; both EC and AEC have apparently similar conformations in dilute solution.

Stipanovic and Stevens[10] investigated the vacuum ultraviolet CD for dilute solutions of cellulose acetate and found a negative dichroism (at 190–210 nm) for the carbonyl electronic transition. The ellipticity increased with increasing acetyl DS. The low-energy tail of the corresponding ORD Cotton effect should appear as a negative contribution to the optical rotation at short wavelengths. Thus, the introduction of acetyl groups may be responsible for the observed change in shape at short wavelengths of the ORD curves for dilute AEC solutions. The results in Figure 1 also show that acetylation decreases the specific rotation over the whole wavelength range up to an acetyl DS of ~0.18. Further acetylation then increases the specific rotation. A decrease in optical activity with increasing acetylation has been observed for cellulose acetate dilute solution in some solvents.[11] It remains unclear why the trend reverses above DS ≃0.18.

Acetyl DS Dependence of Twisted Sense in Concentrated Solution. The cholesteric helicoidal structure for (ethyl)cellulose in chloroform is left-handed, whereas that of highly substituted (acetyl)(ethyl)cellulose in the same solvent is right-handed.[1] There must therefore be a critical acetyl content where the anisotropic AEC solution is a compensated nematic structure.

Figure 2 shows a series of CD curves for AEC lyotropic solutions of various acetyl DS's. The curves illustrate the apparent dichroism that results from the selective reflection of circularly polarized light from the cholesteric samples. For acetyl DS below about 0.18 (curves 2–6), the solutions display positive ellipticity like that of the initial EC solution (curve 1), corresponding to left-handed helicoidal structures. When the acetyl DS is over 0.2, negative

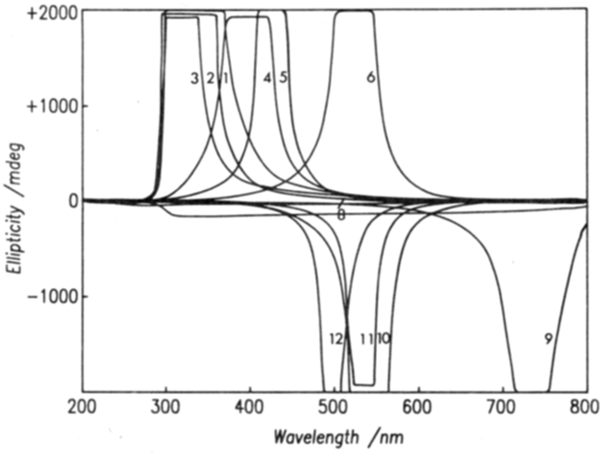

Figure 2. CD spectra of (ethyl)cellulose and (acetyl)(ethyl)cellulose lyotropic solutions in chloroform. The solvent was allowed to evaporate to give reflection bands in the UV–visible range (concentration range, 40–60% by weight polymer.) Curve 1, (ethyl)cellulose: curves 2–12 correspond to samples AEC-1–AEC-11, respectively.

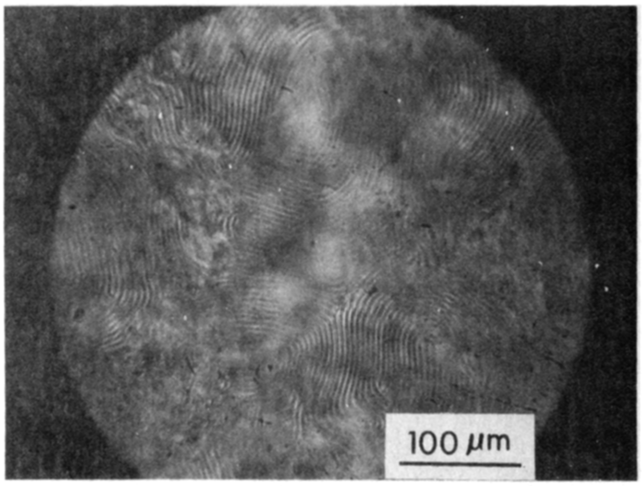

Figure 3. Fingerprint texture of AEC-6/chloroform solution (45% by weight) at room temperature.

ellipticity appears (curves 9–12), indicating a change to right-handed cholesterics. The absence of reflection bands for AEC mesophases with acetyl DS values around 0.18–0.20 indicates that the cholesteric pitch is beyond the wavelength of visible light. The long pitch for these samples was confirmed by the observation of fingerprint texture by optical microscopy (Figure 3). Unfortunately, due to the difficulty of controlling acetylation precisely, it was not possible to make a sample which showed purely nematic properties at a given solution concentration. Nevertheless, the critical degree of acetylation must be close to 0.2 for this solvent, concentration, and temperature.

The reversal of handedness with solvent composition and temperature has been observed for polypeptides[2-7] and recently for cellulosics.[9] It is striking that a small change in the number of substituents can lead to a change in the handedness of the supramolecular helicoidal structure. The incorporation of one acetyl group for every five anhydroglucose units can reverse the handedness. The optical properties of cholesteric liquid crystals are thus sensitive to chemical structure in addition to temperature and solvent.

Effect of Acetyl DS on Cholesteric Pitch. The pitch of cholesteric liquid crystals depends on many factors such as concentration, temperature, applied electromagnetic fields, pressure, composition, and polymer molar mass.

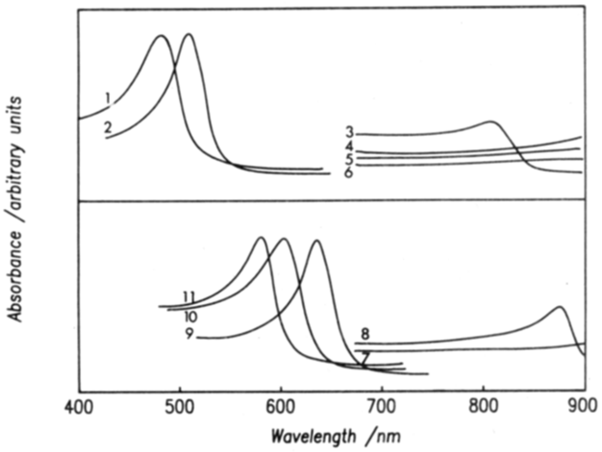

Figure 4. UV–visible spectra of AEC/chloroform solutions (45% by weight) at 30 °C. Curves 1–11 correspond to samples AEC-1–AEC-11.

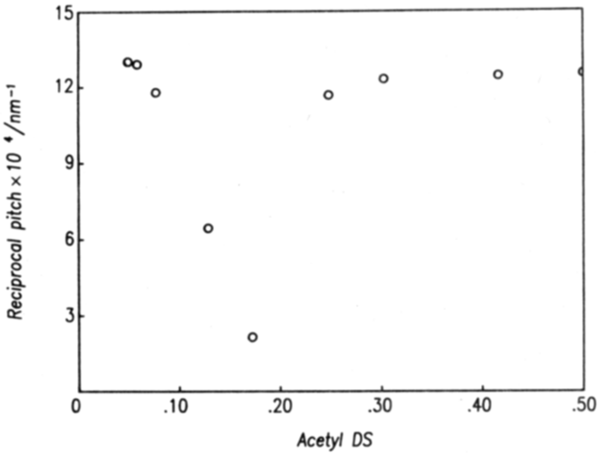

Figure 5. Magnitude of reciprocal pitch of AEC/chloroform solutions (45% by weight) as a function of acetyl DS.

Sealed samples of cholesteric AEC solutions in chloroform (45% by weight) display visible reflection colors which are also dependent on acetyl content. A series of samples with increasing acetyl DS display colors in the following sequence: violet → green → red → no color (fingerprint texture) → red → green → violet.

Figure 4 shows UV–visible spectra of these solutions. The wavelength of the reflection peak maximum, λ_0, and hence the cholesteric pitch, increases with increasing acetyl content to a maximum at the critical degree of acetylation, DA*, and then decreases with further increases in acetyl content. The corresponding pitch was calculated from de Vries' equation,[12] $\lambda_0 = nP$, where n is the average refractive index of the mesophase, measured with an Abbé refractometer, and λ_0 corresponds to the wavelength of the reflection peak maximum in Figure 4. A plot of reciprocal pitch against the acetyl DS of the AEC is presented in Figure 5. The pitches of samples AEC-5 and AEC-6 were directly measured as twice the distance between the dark and bright fingerprint lines observed with the optical microscope.

Acetyl Content and Flow. The flow properties of cholesteric solution are related to the magnitude of the pitch.[13,14] Figure 6 illustrates the dependence of an empirical flow time on the acetyl DS for the series of AEC solutions. Clearly, the overall flow time of the solution depends on the acetyl content. The flow time decreases with increasing pitch and reaches a minimum at the acetyl DS where the pitch is very long. Further increases in acetyl content cause an increase in flow time. Superimposed on

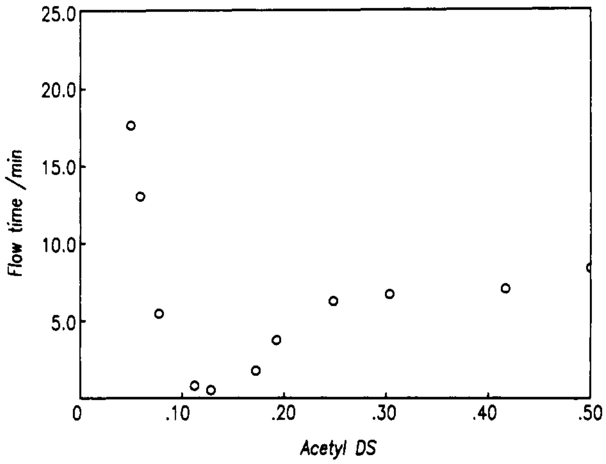

Figure 6. Flow time for AEC/chloroform solutions (45% by weight) as a function of acetyl DS at 28 °C (flow time for the corresponding EC solution is greater than 10 h).

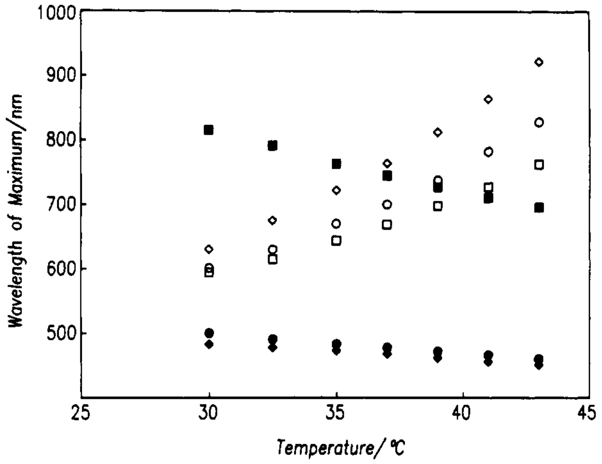

Figure 7. Temperature dependence of the wavelength of maximum reflection, determined from UV-visible spectra, for AEC-1 (◆), AEC-2 (●), AEC-3 (■), AEC-9 (◇), AEC-10 (○), and AEC-11 (□) in chloroform (45% by weight).

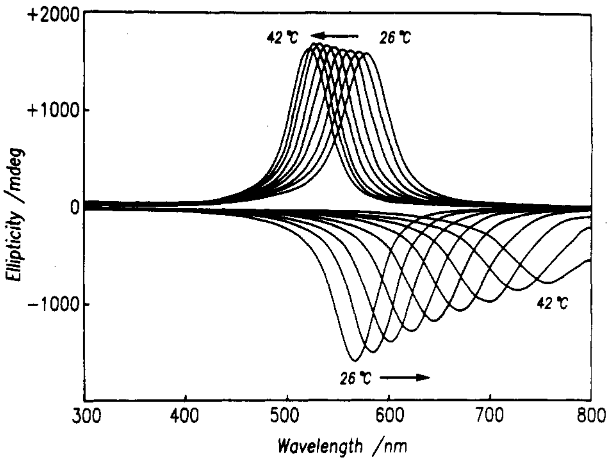

Figure 8. CD spectra as a function of temperature for left-handed sample AEC-2 (positive curves) and for right-handed sample AEC-11 (negative curves).

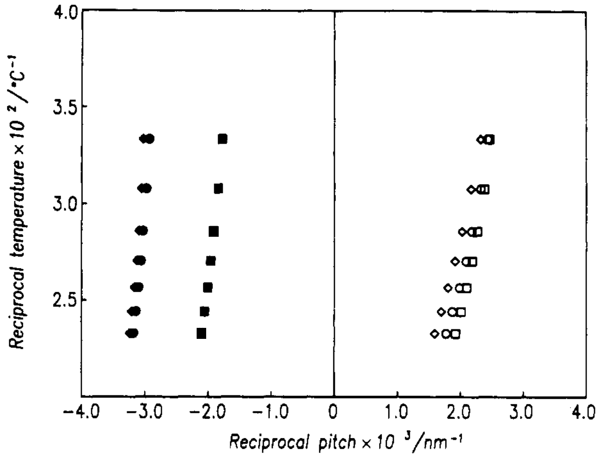

Figure 9. Reciprocal pitch as function of reciprocal temperature for AEC-1 (◆), AEC-2 (●), AEC-3 (■), AEC-9 (◇), AEC-10 (○), and AEC-11 (□) in chloroform. Negative values of the pitch correspond to left-handed helicoidal arrangements.

this effect is the overall decrease in flow times with increasing acetyl content. The flow time for the nonacetylated (ethyl)cellulose is more than 2 orders of magnitude greater than for the fully substituted AEC sample. Patel and DuPré[14] found that there is a general correlation of resistance to flow with inverse pitch in cholesteric mixtures of PBLG and PBDG solutions, except for the racemic mixture where the viscosity is anomalously high. Their results for the mixture of optical isomers resemble the AEC results, except that no precisely compensated AEC solution with high viscosity was observed in our experiments.

Temperature Dependence of Pitch. The pitch of cholesteric liquid crystals is sensitive to temperature. The temperature dependence of pitch has been measured for polymeric thermotropic[15-19] and lyotropic cholesteric liquid crystals.[2,5-7,9,20-23] A positive temperature dependence of the cholesteric pitch was observed for most thermotropic systems (low molar mass cholesterics show the opposite dependence), but for lyotropic systems, both negative and positive temperature dependences were observed, depending on solvent and temperature range.

Plots of the maximum wavelengths of reflection (λ_0) for a series of AEC solutions as a function of temperature are shown in Figure 7. This family of liquid crystals exhibits both kinds of temperature dependence. For lyotropic solutions of AEC with acetyl contents below DA* (with left-handed helicoidal structure), the pitch decreases with temperature; for AEC with acetyl contents greater than DA*, the pitch of the right-handed helicoidal structure increases with temperature. Thus, the introduction of acetyl groups into (ethyl)cellulose influences both the handedness and the temperature dependence of the pitch. These two effects are well illustrated by the apparent CD spectra shown in Figure 8; AEC-2 and AEC-11 are representative of AEC polymers with low and high acetyl contents, respectively.

The twisting power (inverse pitch) may be calculated from the data in Figure 7 and the mean refractive indices of the solutions. Results are shown in Figure 9. As predicted by Kimura et al.[24] (eq 1), there is a linear relation between reciprocal pitch and reciprocal temperature

$$1/P = C(T_N/T - 1) \qquad (1)$$

where C is a temperature-independent function of the solution concentration and the geometry of the molecular helix, and T_N is the compensation temperature, defined as the temperature at which the pitch of the cholesteric structure is infinite.

The different slopes in Figure 9 indicate different sensitivities to temperature for these lyotropic solutions: for the left-handed samples, the pitch for solutions of AEC with high acetyl DS is more sensitive to temperature than with low acetyl content; in contrast, the pitch of right-handed samples of AEC with high acetyl DS is less sensitive to temperature than of those with low acetyl DS. The reason is not clear at present. Extrapolation of these

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lines to infinite pitch ($1/P = 0$) suggests that the compensation temperature is below -50 °C for the left-handed samples and over the boiling point of chloroform for the right-handed samples. It is difficult to achieve these temperatures experimentally. However, if the trends shown in Figure 9 are maintained at intermediate acetyl contents, a thermally induced reversal of pitch is to be expected for long-pitch samples with acetyl contents near DA* at this concentration. So far, no temperature-induced reversal of handedness has been observed for any lyotropic or thermotropic liquid crystal derived from cellulose.[25]

Concluding Remarks

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 these AEC solutions. 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. The significant dependence of chiroptical properties on apparently minor changes in acetyl content suggests that molecular properties influencing chain conformations may play a dominant role in governing the cholesteric properties of these cellulosic polymers. This inference is supported by the recent observation[26] that formation of trifluoroacetate esters on the cellulosic backbone cause a reversal of handedness for cellulose acetate mesophases in trifluoroacetic acid.

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Chain Propagation/Step Propagation Polymerization. 5. Telechelomer Polymerization via Alanine Mediation

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ABSTRACT: The polyesterification of a monodisperse poly(oxyethylene-*b*-pivalolactone) telechelomer, having M_n of 2700 and containing –OH and –COOH end groups, is described. Polymerizations were attempted with no success using selected (a) activating agents, (b) dehydrating agents, and (c) esterification catalysts, wherein the reactions were monitored by size-exclusion chromatography, viscometry, and nuclear magnetic resonance. Success was achieved with titanium tetrabutoxide catalysis in the presence of alanine to give high molecular weight polymers. A 5-fold increase in viscosity was observed as the alanine-mediated polyesterification progressed, and the $\bar{M}_{GPC}$ of the polymer obtained was 31 000. Reaction conditions could be optimized to avoid side reactions. The function of alanine in the esterification reaction is not yet clear; however, functions include (a) acting as a dehydrating agent, (b) acting as a template, and (c) increasing the effectiveness of titanium tetrabutoxide catalyst.

Introduction

Research in the field of multiphase segmented copolymers, although some 30 years old, remains quite active,[1,2] in part due to the wide range of physical behavior exhibited by these copolymers, ranging from impact resistance to elasticity. Poly(urethane ether)s and poly(ester ether)s are particularly interesting examples of these copolymers. As true elastomers, however, poly(ester ether)s are deficient in terms of the physical properties that are demanded in many applications, particularly when they are melt processed.[3] Specifically, the elastic properties that are deficient in melt-shaped segmented polyester ethers

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