Liquid Crystalline Phase Transition of a Semiflexible Polymer: (Acetoxypropyl)cellulose

Gunar V. Laivins and Derek G. Gray*

Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, Quebec H3A 2A7, Canada. *Received August 29, 1984*

ABSTRACT: (Acetoxypropyl)cellulose (APC) fractions form thermotropic mesophases and also form lyotropic mesophases in dibutyl phthalate (DBP). The liquid crystal to isotropic transitions of these mesophases are examined. The critical concentration for mesophase formation, $\phi_c^{\,i}$, increases markedly with temperature. This increase is caused primarily by the reduced stiffness of the chain; as calculated in the preceding paper, the axial ratio of the Kuhn segment decreases from 10.8 to 5.6 ± 0.4 in the temperature range from 25 to 150 °C. At room temperature, the volume fraction of APC in DBP needed for anisotropic phase separation is 0.52 ± 0.02, for chains with contour lengths from 10^2 to 10^3 nm. The ordered phase coexists with a more dilute isotropic phase up to a polymer volume fraction of 0.69 ± 0.04. The concentrations of both phases increase with that of the solution. The molar mass of the APC in the mesophase exceeds that in the isotropic phase. The enthalpy of the transition to an isotropic solution, measured by differential scanning calorimetry, decreases with a reduction in the APC concentration. The experimental results are interpreted in the light of recent theories for liquid crystalline phase separation. Theories introducing orientational anisotropic interactions between chains are used to explain the extended temperature or concentration range of the thermotropic and lyotropic APC mesophases. However, the variation in critical concentration can be roughly predicted over a very wide temperature range from the freely jointed segment model without anisotropic interactions.

Introduction

Polymers which possess asymmetric and relatively stiff segments may spontaneously form an anisotropic phase when dissolved in suitable solvents. The early phase separation theories for rodlike species[1-3] related the concentration at which the mesophase formed, $\phi_c^{\,i}$, to the axial ratio, n, of the molecule. According to these theories a dilute isotropic solution exists below a critical concentrations, $\phi_c^{\,i}$. At some higher polymer concentration, a second critical point, $\phi_c^{\,a}$, exists at which the last trace of the isotropic phase disappears. Within the intermediate two-phase region, the concentration of each of the phases must remain constant for a two-phase–two-component system. The ratio, Φ^a, of the anisotropic phase volume to the total volume increases across the two-phase region.

The calculated $\phi_c^{\,i}$ based upon Flory's lattice theory[3] reduces to the following approximation for athermal solutions with $n \geq 10$:

$$\phi_c^{\,i} \geq (8/n)(1 - 2/n) \qquad (1)$$

The concentration at which the isotropic phase disappears is $12.5/n$ for large n. The width of the two-phase region, $\phi_c^{\,a}/\phi_c^{\,i}$, is a function of the axial ratio of the polymer but approaches a limiting value of 1.56 for rods of infinite axial ratio in athermal equilibrium. Flory's theory, though including a term for the heat of mixing between polymer segments and solvent, relates the critical concentration for phase separation, $\phi_c^{\,i}$, to particle asymmetry.

Flory and co-workers subsequently extended the phase separation theory for athermal solutions of rodlike polymers to include polydispersity.[4-6] They predicted that fractionation should occur between the phases in the biphasic region. Rods with high axial ratios preferentially migrate to the anisotropic phase, while the shorter rods enter the isotropic phase. The smaller the volume fraction of the anisotropic phase Φ^a, the greater is the exclusion of short rods from the anisotropic phase. The volume fractions of polymer in both the isotropic phase and mesophase should increase with increasing Φ^a. The breadth of the biphasic region, although dependent upon the distribution function in the mixture,[6] is predicted to increase due to the polydispersity in the length of the rods.

The rigid rod phase separation theories adequantely describe the formation of the lyomesophases of biological materials which tend to be rather rigid and elongated such as the poly(benzyl glutamates),[7,8] poly(carbobenzoxylysine),[9] the polysaccharide schizophyllan,[10] and aromatic polyamides.[11] The formation of lyomesophases for systems involving more flexible polymeric chains such as the cellulosics[12-16] requires refinement of the rigid rod theories.

The concept of flexibility can be introduced into the rigid rod theories by considering a semiflexible molecule to be a freely jointed chain, envisioned as a series of shorter rigid rods. On the basis of his lattice model, Flory[17] showed that the critical concentrations $\phi_c^{\,i}$ and $\phi_c^{\,a}$, which characterize the phase separation behavior of freely jointed chains of contour length L and rigid rod segment length l, are dependent on the axial ratio of the segments, n' ($=l/d$, where d is the diameter of the segment), and not on the number of segments in the chain. As the chain is lengthened by increasing the number of rods it contains, the critical concentration for the onset of phase separation, $\phi_c^{\,i}$, minimally decreases while $\phi_c^{\,a}$ increases slightly.

The phase separation of a chain composed of freely jointed rods has also been studied theoretically by using models based on the second virial approximation.[18,19] The critical concentrations characterizing the onset, $\phi_c^{\,i}$, and end, $\phi_c^{\,a}$, of the two-phase region are related to the axial ratio of the freely jointed segments, n', by the following equations:

$$\phi_c^{\,i} = 3.25/n' \qquad (2a)$$

$$\phi_c^{\,a} = 4.86/n' \qquad (2b)$$

An alternative model for a semiflexible polymer molecule is the Kratky–Porod wormlike chain.[20] Khokhlov and Semenov[21] have derived relationships between the critical concentrations and chain contour length for wormlike chains

$$\phi_c^{\,i} = \tilde{d}\left[\frac{3.34 + 11.3\tilde{L} + 4.06(\tilde{L}^2)}{\tilde{L}(1 + 0.387\tilde{L})}\right] \qquad (3a)$$

$$\phi_c^{\,a} = \tilde{d}[12/(1 - (1 - \exp(-6\tilde{L}))/6\tilde{L})] \qquad (3b)$$

where the equivalent Kuhn segment length of the wormlike chain is k_w, the reduced diameter is $\tilde{d} = d/k_w$, and the reduced contour length $\tilde{L} = L/k_w$. The theory predicts

0024-9297/85/2218-1753$01.50/0

that the critical volume fraction for phase separation should increase as the chain length approaches the equivalent Kuhn length. Furthermore, ϕ_c^i is larger for wormlike chains than for freely jointed ones with the same Kuhn length. The breadth of the two-phase region is markedly smaller than for the Kuhn chain. The appearance of the phase diagram for the orientational ordering of polymers is thus very dependent on the flexibility distribution along the chain.[22]

The geometric theories for mesophase formation do not recognize intermolecular anisotropic attractive interactions. The other extreme viewpoint is that the nematic ordering results primarily from the anisotropy of the intermolecular attractive forces and that the intermolecular repulsions can be neglected. Mean field theories have been developed to describe nonpolymeric nematogens. Maier and Saupe[23,24] in their classical work surmise that the anisotropic dispersion interactions between nematic molecules create the orientational-dependent interactions which lead to the formation of a mesophase. For polymeric systems, Flory and Ronca have formulated the energy of a system of impenetrable rodlike molecules subject to orientation-dependent mutual attractions by considering the anisotropic parts of the polarizability tensors between pairs of segments in contact.[25] The intensity of the interactions is denoted by a characteristic temperature T^*, which increases with the intensity of the orientational interactions. The conclusions from this modified lattice theory are that the effects of molecular shape asymmetry are still of primary importance in the phase transition of nematic systems. Secondly, molecules with an axial ratio greater than the critical axial ratio of 6.42 are predicted to form stable nematic phases at all temperatures. Molecules with an axial ratio less than 6.42 can exhibit a nematic-to-isotropic transition provided that the orientational anisotropic forces are strong.

Ronca and Yoon[26,27] have developed a statistical theory of nematic systems for semiflexible wormlike polymers. As sharp bends do not occur in molecules, a finite cutoff length, L_c, is introduced into their theory. Their major conclusions are that isotropic–nematic phase transitions are predicted for semiflexible polymers even when orientational-dependent dispersion forces are absent. The degree of order in the nematic phase is low. A nematic phase of absolute stability at all temperatures is predicted for critical axial ratio $n_c = L_c/d$ exceeding 4.45. The values of the parameters approach the rodlike limit values calculated by Flory and Ronca[25] when bending of the chain is not permitted.

ten Bosch and Sixou have expressed the free energy of a homogeneous melt of namatic polymers as a function of the degree of polymerization, the inherent elasticity of the chain, and the quadrupolar mean field between monomers.[28] The polymer chain is described by a continuous elastic line with a given bending constant. The order parameter, the transition temperature, and the latent heat associated with the nematic–isotropic transition can be calculated as a function of chain length and flexibility. Extension of this theory from nematic thermotropic polymers to lyotropic systems requires the consideration of the role of the isotropic solvent, which dilutes the mean field interaction energy between the polymer molecules.[29]

In this paper, the phase behavior of (acetoxypropyl)cellulose (APC) in dibutyl phthalate (DBP), from a dilute isotropic solution through lyomesophase formation to the pure thermotropic polymer, is presented. The amounts, compositions, and molar masses of the isotropic and anisotropic phases within the two-phase region are characterized. Dibutyl phthalate was chosen as the solvent due to its low vapor pressure, which simplified handling at elevated temperatures. By means of the hydrodynamic theory developed by Yamakawa et al.[30,31] the Kuhn segment length and diameter for APC were determined in dimethyl phthalate from 25 to 150 °C.[32] The anisotropic–isotropic transition temperature for the APC–DBP system is studied as a function of concentration. Differential scanning calorimetric measurements of this transformation as a function of concentration are reported. The results are compared with the theories for the formation of liquid crystalline phases. (Acetoxypropyl)cellulose is an ideal polymer for this study. It exhibits both thermotropic and lyotropic behavior, so that the relative importance of the geometric factors and anisotropic interactions can be analyzed as a function of temperature.

APC, in common with all cellulose derivatives, forms cholesteric mesophases, whereas the phase separation theories consider nematic ordering. However, the pitch of the cholesteric structure increases with temperature and with diluent concentration,[33] and the small amount of twist should have a negligible effect on the phase separation behavior of what is essentially an almost untwisted nematic material.

Experimental Section

Preparation of the (Acetoxypropyl)cellulose–Dibutyl Phthalate Solutions. Dibutyl phthalate (Matheson) was purified by vacuum distillation and was added to accurately weighed samples (~1.5–2.0 g) of (acetoxypropyl)cellulose in 10-mL cylindrical vials. The details concerning the preparation and characterization of the (acetoxypropyl)cellulose polymer and fractions have been previously described.[32] In order to promote complete mixing, acetone was added to dissolve the APC and DBP. Once a homogeneous solution had formed, the acetone was allowed to evaporate slowly. Homogeneity was ensured by periodically inverting the vials and spinning in a centrifuge. A complete range of APC–DBP solutions ranging from pure polymer to pure solvent was prepared. The mixtures were allowed to equilibrate for 1–2 months prior to analysis.

A slightly different technique was employed to prepare solutions from the rather small amounts of fractionated (acetoxypropyl)cellulose. Thin slivers of the APC fractions which had been dried overnight at 70 °C under vacuum were introduced into 10–15-cm-long capillary tubes with one end flame sealed. A predetermined aliquot of dibutyl phthalate was added by syringe to the polymer sample. The contents were settled by centrifugation. The mixture was degassed twice and then the capillary tube was sealed under vacuum. The mixture was inverted and centrifuged a number of times to facilitate the formation of a homogeneous solution.

Determination of the Critical Concentration, ϕ_c^i, for the Formation of a Lyomesophase. A small portion of the solution, placed under a cover glass on a microscope slide, was examined under the polarizing microscope (Reichert) for birefringence. The samples in capillary tubes were placed in an immersion liquid to minimize distortion.

To investigate the critical concentration for mesophase formation, the variation of the birefringence with temperature of the anisotropic samples was measured photometrically. The sample, sandwiched between a microscope slide and cover plate, was placed on a Mettler FP52 hot stage and examined with a Reichert polarizing microscope. A Mettler 18100 photocell replaced an ocular. The variation in light intensity transmitted through the crossed polars was monitored with the photocell and a Varian A25 strip chart recorder, while the sample was heated at 1 °C/min. The marked decrease in transmitted light intensity associated with the transformation of the birefringent anisotropic phase into the isotropic one occurred over a broad temperature range ~30 °C); the clearing temperature at which the anisotropic phase disappeared was noted.

Characterization of the Two-Phase Region. Solutions of APC with concentrations which just exceeded the critical concentration for mesophase formation separated into two distinct phases. After an 18-month equilibration period, the concentrations of each of the two phases were analyzed by infrared spectroscopy. The stretching band of the aromatic ring at 1600 cm^{-1} was used to quantify the DBP component. The APC component was measured by using a band at 830 cm^{-1}. DBP also absorbed slightly at 830 cm^{-1}, so the measured absorbance $A^{\mathrm{APC+DBP}}$ at this wavelength was corrected to eliminate this absorbance. The absorbance of DBP at 830 cm^{-1}, A_{830}^{DBP}, was related to the absorbance at 1600 cm^{-1}

$$A_{830}^{\mathrm{DBP}} = A_{1600}^{\mathrm{DBP}}(\epsilon_{830}^{\mathrm{DBP}}/\epsilon_{1600}^{\mathrm{DBP}}) \tag{4}$$

and thus

$$A_{830}^{\mathrm{APC+DBP}} = A_{830}^{\mathrm{APC+DBP}} - A_{1600}^{\mathrm{DBP}}(\epsilon_{830}^{\mathrm{DBP}}/\epsilon_{1600}^{\mathrm{DBP}}) \tag{5}$$

where ϵ is the molar absorptivity at the given wavelength. The quantity $\epsilon_{830}^{\mathrm{DBP}}/\epsilon_{1600}^{\mathrm{DBP}}$ was determined in a separate experiment using pure dibutyl phthalate.

Since the total volume and path length were identical for a given sample, the ratio of the absorbances of the components was proportional to their mass ratio. Isotropic solutions were used as calibrants by plotting the ratio of the masses, $g(\mathrm{APC})/g(\mathrm{DBP})$, against the ratio of the absorbances, $A_{830}^{\mathrm{APC}}/A_{1600}^{\mathrm{DBP}}$.

The spectra of the samples, smeared onto sodium chloride plates, were measured with a Nicolet 7000 series Fourier transform infrared spectrophotometer. The mesophase fraction was collected by carefully inserting a pipet through the upper isotropic phase into the denser mesophase. Gentle suction from a water aspirator was then used to draw the sample into the pipet. The concentration ratio of the components in the phases was determined by extrapolation of the calibration curve to the ratio of the absorbances of the components.

The molar mass of the polymer in each of the isotropic and anisotropic phases in the two-phase region was determined by low-angle laser light scattering photometry coupled with gel permeation chromatography. An accurately weighed sample of the APC–DBP solutions was diluted in 10 mL of HPLC grade tetrahydrofuran to give solution concentrations from 3 to 6 g/L. Each solution was stirred overnight. The APC content was verified by UV spectroscopy. A 500- or 750-μL volume of this solution was injected into the size exclusion chromatography–low-angle laser light scattering apparatus. The differential refractive index increment, dn/dc, used in the calculations was assumed to be that of the pure (acetoxypropyl)cellulose in tetrahydrofuran, 0.0565 g mL^{-1},[32] since the columns separate polymer and diluent molecules. The solvent flow rate was 1 mL min^{-1}.

The relative abundance of each of the phases within the biphasic region was measured on the vial with a ruler. As the major source of error (±~10%) was the indistinct boundary between the two phases, more precise methods of measurement were inappropriate.

Enthalpy Associated with the Liquid Crystal to Isotropic Transition. The thermal properties of the transition from the mesophase to isotropic phase of the thermotropic (acetoxypropyl)cellulose fractions were mreasured with a Perkin-Elmer DSC-2C differential scanning calorimeter. The concentration dependence of the heat evolution during the transition was obtained for the DBP–APC lyotropic samples. Accurately weighed samples, ~20 mg, were encapsulated in standard DSC volatile sample pans. The temperature scale of the instrument was calibrated with a high-purity indium sample. The samples were heated or cooled at 20 °C/min from 60 °C to 30 °C above the transition temperature. The breadth of the phase transition, coupled with the low heat output associated with the transition, created a large uncertainty in the latent heat value. This large uncertainty masked any effect of thermal pretreatments on the heat evolved during the phase transition.

X-ray Diffraction. A thin film of unfractionated (acetoxypropyl)cellulose was pressed and allowed to equilibrate for 24 h to remove any orientation effects. The Warhus flat-film camera chamber containing the sample and camera film was evacuated to remove air. A Philips PW1730 nickel-filtered Cu Kα (λ = 0.154 nm) X-ray generator was used. The voltage and current settings were 40 kV and 20 mA, respectively. The X-rays passed through a collimeter, inner diameter 0.02 in., through the sample and onto a "no-screen" film, Kodak NS-57, located 17.4 cm from the sample.

Table I
Critical Volume Fraction of (Acetoxypropyl)cellulose in Dibutyl Phthalate as a Function of Chain Length at 25 °C

$\bar{M}_w \times 10^5$, daltons	L,[a] nm	DP[b]	$\phi_c{}^i$
7.66	945	1835	[d]
4.32	533	1035	0.52 ± 0.02
2.80	345	671	0.515 ± 0.01
1.94	239	465	0.52 ± 0.01
1.33	153	317	0.52 ± 0.02
0.765	94	183	0.54 ± 0.01
2.29[c]	282	549	0.52 ± 0.015

[a] Assumes length of the anhydroglucose unit is 0.515 nm.[34] [b] Assumes molar mass of anhydroglucose unit is 423 daltons.[32] [c] Unfractionated (acetoxypropyl)cellulose. [d] Sample did not dissolve in dibutyl phthalate.

The exposure time was 30 min. The diameter of the X-ray halo was measured with a double-beam recording microdensitometer (Joyce, Loebl and Co. Ltd.).

Results and Discussion

Dependence of the Critical Concentration $\phi_c{}^i$ on the Molar Mass. For rigid molecules, the critical concentration at which an anisotropic phase spontaneously forms depends on the length of the molecule.[1,3] For freely jointed chains, the critical concentration for mesophase formation should not exhibit a dependence on the chain length.[17,19] The Kratky–Porod wormlike chain behaves as the freely jointed chain in the limit of high molar mass. However, as the wormlike chain becomes shorter, a dependence of the critical concentration on the contour length is predicted.[21]

The variation of the critical concentration with the chain contour length is shown in Table I. The critical volume fraction of (acetoxypropyl)cellulose in dibutyl phthalate is independent of the chain contour length. It should, however, be noted that the range of contour lengths of the (acetoxypropyl)cellulose fractions is not very broad. The lowest molar mass fraction exhibits a slightly higher critical concentration for mesophase formation than do the other fractions. This trend, if real, is in accord with the results reported for some other cellulosics. A marked increase was observed for low molar mass fractions of the benzoic acid ester of (hydroxypropyl)cellulose[12] and of (hydroxypropyl)cellulose in dichloroacetic acid[35] and to a lesser extent in dimethyl acetamide.[16] A more pronounced decrease in the critical concentration for lyomesophase formation with increasing chain length has been reported for the less substituted cellulose derivatives such as cellulose acetate[14,36-39] and cellulose itself.[40]

The critical volume fraction of 0.52 ± 0.02 at 25 °C for the formation of the anisotropic phase for the (acetoxypropyl)cellulose–dibutyl phthalate system is higher than that exhibited by most other cellulosic systems. Comparison of the critical concentrations of different cellulosics in the literature is difficult because the values depend on the degree of polymerization, the degree of substitution, and the solvent. However, the range of critical concentration values at which lyotropic mesophases are formed at room temperature for various derivatives is 20–35% by weight for cellulose,[40] 16–45% for cellulose diacetate,[36] 34–46% for cellulose acetate butyrate,[36] 22–26% for cellulose triacetate,[14] 28–39% for ethylcellulose,[36] 35% for cellulose triacetate,[36] 19–40% for the (hydroxypropyl)cellulsoe mesophases,[12,16,36,41] 30–35% for the propanoate ester,[42] and ~40% for the benzoic acid ester of (hydroxypropyl)cellulose.[12] As the bulkiness of the side chains surrounding the cellulosic backbone increases, the critical concentration for anisotropic phase formation tends to

Table II
Segment Axial Ratio of (Acetoxypropyl)cellulose in Dimethyl Phthalate as a Function of Temperature[32]

temp, °C	k_w(Y-F),[a] nm	ax. ratio[b]	k_w(B),[c] nm	ax. ratio[b]
25	11.8	10	13.5	11.5
105	8.4	7	9.3	7.8
150	6.3	5.2	7.1	6.0

[a] From Yamakawa–Fujii theory. [b] Chain diameter taken as 1.2 nm. [c] From Bohdanecky

increase. The dependence of ϕ_c^i on the side chains can be attributed to an increasing diameter, and hence a decreasing axial ratio.

The invariant critical concentration for mesophase formation with the contour length of the (acetoxypropyl)cellulose molecule is characteristic of long semiflexible molecules.

Temperature Dependence of the Segment Axial Ratio. The Kuhn segment lengths and diameters of the (acetoxypropyl)cellulose chain at 25, 105, and 150 °C were calculated from dilute solution viscosity measurements according to the hydrodynamic theories of Yamakawa and co-workers[30,31] and Bohdanecky,[43] as described in the preceding paper.[32] A temperature-independent diameter of 12.0 Å was used in the calculation of the axial ratio. This value is consistent with the calculated hydrodynamic diameter from the Bohdanecky theory at 25 and 105 °C of 11.5 Å,[32] as well as with the average intermolecular spacing of 12.2 Å determined by X-ray analysis. The temperature dependence of the axial ratio according to each hydrodynamic theory is indicated in Table II.

The solvent used for the dilute solution viscosity measurements was dimethyl phthalate. The lyotropic mesophases are (acetoxypropyl)cellulose–dibutyl phthalate solutions. Dimethyl phthalate was used for the viscosity experiments instead of dibutyl phthalate because the oxidative degradtion of cellulosic esters is substantially lower in dimethyl phthalate than in the butyl derivative at 150 °C.[44] A 4.5% difference in the limiting viscosity number resulted for the unfractionated (acetoxypropyl)cellulose molecule at 105 °C when dibutyl phthalate was used as the solvent instead of dimethyl phthalate. This uncertainty is within the range of axial ratios for the APC polymer.

Comparison of Experimental ϕ_c^i with Theoretical Predictions. The dependence of the critical concentration on the contour length of a wormlike chain is given according to Khokhlov and Semenov by eq 3. For short wormlike chains, the increase in the critical concentration with a decrease in the chain length is pronounced. However, for long chains the critical concentration attains a limiting value; $\phi_c^i = 10.48/n'$. For a value of $n' = 10$ (Table II) this gives nonphysical values for the critical volume fraction. This is shown in Figure 1, broken curve, which is included to illustrate the predicted length dependence for the wormlike chain. (According to this theory, an axial ratio, k_w/d, greater than 11.39 is required for a mesophase to form.)

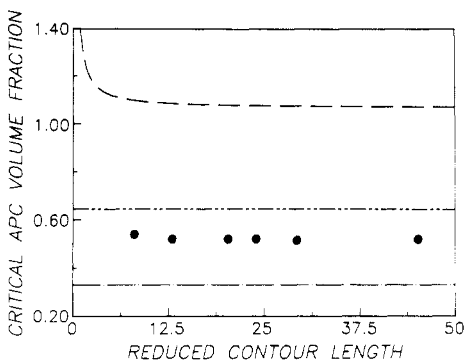

Figure 1. Comparison of the critical concentration of APC, ϕ_c^i, in dibutyl phthalate at 25 °C with limiting models for chain flexibility as a function of reduced chain contour length. The circles are experimental points. The curves are culculated for an axial ratio n' of 10 (see text).

In contrast, the phase separation theories developed for freely jointed chains[11,18] predict that the critical concentration does not depend on the contour length, once the Kuhn segment length has been exceeded. In Figure 1, the volume fraction at which the anistropic phase first appears for the (acetoxypropyl)cellulose–dibutyl phthalate system at 25 °C (points) is compared to those predicted for freely jointed chains. The lowest line is calculated from eq 2 according to Khokhlov et al.[18,19] and the upper one from Figure 4 of Flory and Ronca.[45] The freely jointed chain models predict the formation of anisotropic phases at concentrations lower (Khokhlov et al.) and at slightly higher concentrations (Flory and Ronca) than those experimentally observed. The observed critical volume fraction is independent of the chain length, within the range of contour lengths studied, as predicted by the theories.

The segment axial ratio of the (acetoxypropyl)cellulose molecule is temperature dependent (Table II).[32] The critical concentration for APC mesophase formation in DBP is also temperature cdependent. The critical concentrations are compared with the theoretical predictions at three temperatures in Table III. The experimental values for the critical volume fraction lie between the theoretical values predicted by the freely jointed chain models and are rather closer to the values predicted by Flory and Ronca, especially with the axial ratios calculated from Bohdanecky's theory. Thus, the phase separation behavior of lyotropic (acetoxypropyl)cellulose solutions is reasonably well predicted by a lattice model where the molecule is represented by a freely jointed chain over the temperature range from 25 to 150 °C. The critical volume

Table III
Critical Volume Fractions for Anisotropic Phase Formation: Comparison of Theoretical and Experimental Values

		crit vol fract, ϕ_c^i			
		freely jointed chain		wormlike chain	
temp, °C	ax. ratio[a] n'	Flory[b]	Khokhlov[c]	Khokhlov[d]	exptl value
25	11.5	0.62	0.28	0.91	0.52
	10.0	0.65	0.33	isotropic	
105	7.8	0.85	0.42	isotropic	0.71
	7.0	0.93	0.46	isotropic	
150	6.0	isotropic	0.54	isotropic	0.86
	5.2	isotropic	0.62	isotropic	

[a] Upper value, Bohdanecky;[43] lower value, Yamakawa and co-workers.[30,31] See text. [b] Lattice theory, interpolated from Figure 4 of Flory and Ronca.[25] [c] Khokhlov et al.,[18,19] eq 2. [d] Khokhlov et al.,[21,22] eq 3.

Table IV
Variation in Phase Composition for (Acetoxypropyl)cellulose (APC) in Dibutyl Phthalate at Ambient Temperatures

overall mass frac of polymer in sample[a]	volume frac of phase in sample Φ^a	mass frac of APC in phase[b]	$\bar{M}_w \times 10^4$, daltons
	Anisotropic Phase		
0.50	0		
0.55	0		
0.60	0.40	0.600	8.5 ± 0.2
0.62	0.60	0.621	9.7 ± 0.1
0.64	0.50	0.640	6.75 ± 0.05
0.664	0.82	0.674	11.6 ± 1.5
0.683	0.84	0.693	9.1 ± 0.2
0.754	1.00	0.754	10.5
0.86	1.00	0.86	18
1.00	1.00	1.00	23
	Isotropic Phase		
0.50	1.00	0.50	8.0 ± 0.3
0.55	1.00	0.55	8.2 ± 0.2
0.60	0.60	0.594	6.9 ± 0.2
0.62	0.40	0.607	5.2 ± 0.1
0.64	0.50	0.628	4.9 ± 0.1
0.664	0.18	0.638	5.3 ± 0.1
0.683	0.16	0.658	5.9 ± 0.2
0.754	0		
0.86	0		
1.00	0		

[a] Prepared gravimetrically. [b] Measured by IR spectroscopy.

Table V
Comparison of the Weight Fraction of (Acetoxypropyl)cellulose in the Sample before and after Phase Separation

wt frac of APC				
init gravimetric comp	mesophase[a]	isotropic[a]	calcd[b]	% error
0.598	0.600	0.594	0.598	−0.07
0.623	0.621	0.607	0.616	−2.2
0.640	0.640	0.628	0.634	−1.6
0.664	0.675	0.638	0.668	+2.0
0.682	0.693	0.658	0.688	+2.5

[a] Measured by infrared spectroscopy. [b] Calculated from IR data and relative amounts of the two phases.

Table VI
Enthalpy of the Anisotropic-to-Isotropic Transition as a Function of Molar Mass for (Acetoxypropyl)cellulose Fractions

molar mass × 10^5, daltons	DP	enthalpy of trans, cal/g
7.7	1835	0.61 ± 0.09
6.5	1540	0.8 ± 0.1
2.8	671	0.71 ± 0.06
2.1[a]	490	0.65 ± 0.05
1.9	465	0.74 ± 0.05
1.3	317	0.75 ± 0.05
0.76	183	0.66 ± 0.05
~0.03	~70	no endotherm

[a] Unfractionated (acetoxypropyl)cellulose.

fraction $\phi_c{}^i$, for the (acetoxypropyl)cellulose system increases with the temperature. This increase can be attributed primarily to the decreasing rigidity of the polymer as quantified by the decrease in the equivalent Kuhn length of the polymer chain.

Biphasic Region. The biphasic gap at room temperature begins at an (acetoxypropyl)cellulose volume fraction of 0.52 and ends at a volume fraction of 0.69. The ratio of limiting concentrations of the anisotropic and isotropic phases is 1.33 as compared to a predicted value of 1.23 for monodisperse rods with an axial ratio of 10.[45] The breadth of the biphasic gap for the unfractionated APC is not increased substantially by the large polydispersity, $\bar{M}_w/\bar{M}_n = 1.94$.[32] Conio et al. suggest that since a critical length which is much shorter than the contour length controls the mesophase formation for semiflexible molecules, these systems should behave as if they were monodisperse.[16]

The polymer weight fractions, molar masses, and relative abundances of each phase within the biphasic region are compiled in Table IV. The concentration of (acetoxypropyl)cellulose in the anisotropic phase exceeds that in the isotropic phase for every biphasic solution. The concentration of polymer in both phases increases as the relative volume fraction of the anisotropic phase, Φ^a, increases. A comparison of the initial concentration of (acetoxypropyl)cellulose introduced into the system, which was determined gravimetrically, with the calculated (acetoxypropyl)cellulose concentration in the system following phase separation is shown in Table V. The total polymer concentration was calculated from the relative volume fractions of the phases in equilibrium and from the individual concentrations measured by infrared spectrophotometry. The agreement between gravimetric and spectrophotometric measurements is excellent.

The data in Table IV show that the weight-average molar mass of the APC molecules in the anisotropic phase exceeds that of the coexisting isotropic solution, indicating that weak fractionation had occurred for this semiflexible polymer. The lack of reduction in the polydispersity despite fractionation is attributed to an unexpected degradation of the APC chain when in DBP solution. The molar mass of unfractionated (acetoxypropyl)cellulose is 2.3 × 10^5 daltons. The measured molar mass of a 1:1 mixture of APC and DBP after standing for 2 years has decreased to 8.0 × 10^4 daltons. The degradation seems more severe as the concentration of dibutyl phthalate increases (Table IV). The calculated overall weight-average molar mass, assuming a monodispersity in each phase and using the rleative volume fraction data of the phases in equilibrium, approximately corresponds to the molar mass value of the unfractionated (degraded) (acetoxypropyl)cellulose. This lends credence to the values of the measured molar masses in each phase. The relative amounts of the phases in equilibrium reflect of course the current rather than the initial molar mass of the polymer. The degradation hinders quantitative comparison between the biphasic samples.

Fractionation has been observed in the biphasic regions of lyotropic polydisperse rigid rod systems.[10,46-49] These systems generally confirm the predictions of Flory and Frost[6] concerning the biphasic region. Results similar to those reported in this paper concerning the biphasic region of another semiflexible molecule, (hydroxypropyl)cellulose in dimethylacetamide, have been reported.[16] The authors suggest that nonequilibrium effects, due to the centrifugation process used to facilitate phase separation, may be responsible for the observed fractionation. The APC–DBP solutions were mixed and allowed to equilibrate for at least a year, during which time the spontaneous fractionation process occurred, so nonequilibrium effects are unlikely in this case. It is not clear why fractionation should be observed in the biphasic region when for the same system the fractions all show the onset of the liquid crystalline phase at the same critical concentration (Table I).

Orientational Anisotropic Interactions. A latent heat is associated with the transformation of (acetoxypropyl)cellulose from a mesophase to the isotropic phase at 182 °C (see Table VI). This may indicate[25] the exist-

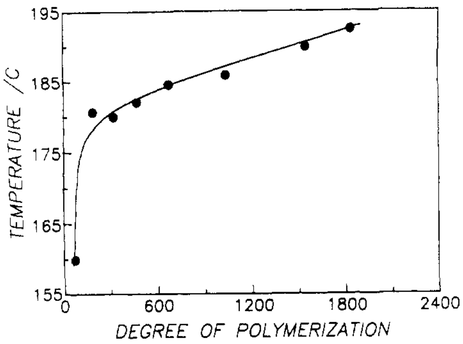

Figure 2. Dependence of the mesophase-to-isotropic transition temperature of thermotropic (acetoxypropyl)cellulose fractions on the degree of polymerization.

ence of an anisotropic interchain force which favors parallel chain orientation (or almost parallel orientation in the case of cholesteric materials).

The Kuhn segment length of (acetoxypropyl)cellulose varied linearly with temperature (Table II). Extrapolation to the transition temperature, T_{ni}, of the polymer (182 °C) gave segment axial ratios of 4.6 (Bohdanecky) or 4.0 (Yamakawa and co-workers) at the transition temperature. (We use the subscript ni because the theories refer to the nematic–isotropic transition. APC should show a cholesteric–isotropic transition, but the cholesteric properties are unimportant near the phase transition.) The reciprocal reduced temperatures, $\tilde{T}_{ni}^{-1}$, were determined to be 1.7 and 2.23 for axial ratios of 4.6 and 4.0, respectively, from the theory of Flory and Ronca for thermotropic rigid rods with orientational-dependent interactions (from Figure 1 of ref 25). The characteristic temperature T^* is given by

$$T^* = T_{ni}/(n\tilde{T}_{ni}) \tag{6}$$

It measures the intensity of the anisotropic interactions between segments for the thermotropic polymer. The value of T^* varies from 170 to 260 K, depending on the set of axial ratios used in the extrapolation. This may imply a weak orientational interaction between APC segments at the transition temperature.

The characteristic temperatures should be the same for all fractions. For a chain of Kuhn segments, the transition temperature to the isotropic state should not depend on the contour length of a semiflexible polymer. The dependence of the transition temperatures of the (acetoxypropyl)cellulose fractions on chain length is shown in Figure 2. Although the plot has not reached the plateau which is observed for some cellulosics,[12] a marked slowdown in the rate of increase of the transition temperature with molar mass occurs.

The latent heats associated with the anisotropic-to-isotropic transformation for the (acetoxypropyl)cellulose fractions are independent of the contour length (Table VI). Thus, the intensity of the orientational interactive forces between the APC segments, T^*, is independent of the number of segments, as required by theory.[45]

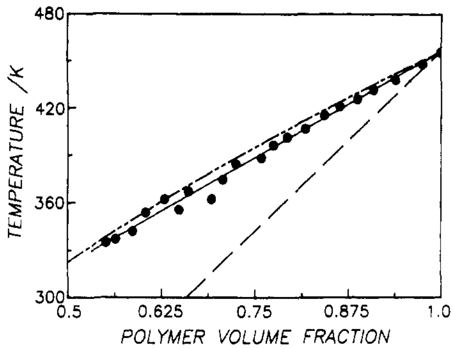

Figure 3. Clearing temperature for lyotropic (acetoxypropyl)cellulose–dibutyl phthalate as a function of concentration: lower line, eq 8; upper line, eq 7; points, experimental data.

Table VII
Temperature Dependence of the Intermolecular Anisotropic Dispersion Interactions for (Acetoxypropyl)cellulose

temp, °C	n'^{a}	ϕ_c^{i}(exptl)	T^*, K
25	10	0.52	78
105	7	0.71	122
150	5	0.86	195
182	4	1.00	254

[a] From the Yamakawa–Fujii theory.

According to Fried et al.,[29] the orientational-dependent interactions in an isotropic solvent are diluted by a factor given by the volume fraction ϕ_p occupied by the polymers. For molecules which can be represented by deformable elastic chains and whose Kuhn segment length is temperature independent, the relationship between the nematic-to-isotropic transition temperature of a lyotropic solution, $T_{ni}(\phi_p)$, is given by

$$T_{ni}(\phi_p) = \phi_p T_{ni} \tag{7}$$

where T_{ni} is the nematic-to-isotropic transition temperature of an undiluted mesophase. However, when the Kuhn segment length is inversely proportional to the thermal energy, kT, the relation is given by

$$T_{ni}(\phi_p) = \phi_p^{1/2} T_{ni} \tag{8}$$

The transition temperatures for the (acetoxypropyl)cellulose–dibutyl phthalate system are plotted as a function of polymer volume fraction in Figure 3. The temperature dependence of the Kuhn segment length is demonstrated by the closer agreement with the square root relationship, although the data in Table II suggest that the segment length is linearly dependent on the temperature and not inversely proportional, as assumed in this theory.

The phase separation theory for thermotropic systems with orientation-dependent interactions developed by Flory and Ronca[25] has been extended by Warner and Flory[50] to the situation where the molecules are dispersed in a diluent. This theory was tested on the APC–DBP data. The phase diagrams for lyotropic systems of rods of several axial ratios have been calculated by Warner and Flory[50] and Conio et al.[16] These diagrams were used to estimate T^* from the experimental values of ϕ_c^{i} and the appropriate APC *segment* axial ratio ($n' = 10$ at 25 °C, $n' = 7$ at 105 °C, $n' = 5$ at 150 °C). The results are shown in Table VII. The introduction of anisotropic soft-core interactions stabilizes a mesophase, thus allowing it to exist at extended concentration or temperature ranges. Through the inclusion of these ansiotropic forces along with the measured change in chain stiffness, the athermal value of the critical volume fraction for phase separation, ϕ_c^{i}, of the (acetoxypropyl)cellulose–dibutyl phthalate system (Table III) was lowered to the experimental value. The values of T^* required to bring the calculated ϕ_c^{i} into line with the experimental ϕ_c^{i} values are not constant with temperature. However, application of this phase separation model to the APC–DBP system may be simplistic. The model considers independent rods rather than freely jointed rods. Although joining the rods makes little difference when geometric factors alone are considered,[17] the difference may be significant when anisotropic interactions are present. Furthermore, the freely jointed rod model is at best an ap-

Table VIII
Observed Heats of the Anisotropic-to-Isotropic Transition as a Function of Concentration

concn, g of APC/g of soln	T_{ni},[a] °C	ΔH	
		cal/g of soln	cal/g of polymer
1.000	182	0.65 ± 0.05	0.65 ± 0.05
0.95	160	0.53 ± 0.08	0.56 ± 0.08
0.90	143	0.45 ± 0.04	0.50 ± 0.04
0.85	127	0.21 ± 0.06	0.25 ± 0.07
0.80	103	0.14 ± 0.03	0.165 ± 0.04

[a] Peak maximum of the DSC thermogram.

proximation to the cellulose backbone conformation. For example, the flexibility may be more evenly distributed along the chain to give a wormlike conformation. Changes in this flexibility distribution with temperature may affect the apparent T^* value.

It is important to note that the large temperature dependence of the critial volume fraction cannot be attributed to the anisotropic interactions alone. For example, it is predicted that for temperature-independent values of $T^* = 78$ K and $n' = 10$, the value of the critical volume fraction only increases from 0.52 to 0.56 over the temperature range from 25 to 150 °C. Experimentally, the critical volume fraction increase from 0.52 to 0.86 over this temperature range. The large dependence of the critical concentration for the formation of the mesophase on the temperature therefore results from the temperature dependence of the axial ratio of the Kuhn segment length rather than from the anisotropic interactions. The predominance of geometric factors over anisotropic intermolecular interactions in the formation of the mesophase, especially for large axial ratios, is predicted by Flory and Ronca.[25]

The temperature and latent heat of the transition from the mesophase to the isotropic phase are given as a function of concentration in Table VIII. The large uncertainties in the reported latent heats of transition reflect the irreproducibility of the heats in repeated experiments. The transition is extremely broad. The factors which may be responsible for the breadth of the transition for cellulose acetate–trifluoroacetic acid solutions have been previously analyzed by Navard et al.[53] The enthalpies of Table VIII may be overestimated because a straight base line between the beginning and end of the peak has been assumed. (The heat capacities of the mesophase and isotropic solution are significantly different.)

The latent heat associated with the transition decreases rapidly with decreasing polymer concentration and appears to be nonexistent for solutions whose polymer weight fraction is less than 0.75–0.80. A similar decrease was also noted by Navard et al. for cellulose acetate–trifluoroacetic acid solution.[51] These results suggest that the orientational interactive forces become diluted as an isotropic solvent is added. The weakening anisotropic orientational forces are no longer important for the more dilute mesophases, and geometric factors predominate.

In conclusion, the effects of temperature on the critical concentration for APC mesophase formation primarily reflect a decrease in the chain stiffness with increasing temperature. However, anisotropic interchain interactions may influence phase separation at high polymer concentrations and elevated temperatures.

Acknowledgment. G.V.L. thanks the Government of Quebec for a graduate fellowship. The support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

References and Notes

(1) L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1979).
(2) A. Isihara, *J. Chem. Phys.*, **18**, 1446 (1950); **19**, 1142 (1951).
(3) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **234**, 73 (1956).
(4) P. J. Flory and A. Abe, *Macromolecules*, **11** (6), 1119 (1978).
(5) A. Abe and P. J. Flory, *Macromolecules*, **11** (6), 1122 (1978).
(6) P. J. Flory and R. S. Frost, *Macromolecules*, **11** (6), 1126 (1978).
(7) I. Uematsu and Y. Uematsu, *Adv. Polym. Sci.*, **59**, 38 (1984).
(8) J. H. Rai and W. G. Miller, *J. Phys. Chem.*, **76**, 1081 (1972).
(9) W. G. Miller, C. C. Wu, E. L. Wee, G. L. Santee, J. H. Rai, and K. G. Goebel, *Pure Appl. Chem.*, **38**, 37 (1974).
(10) K. Van and A. Teramoto, *Polym. J.*, **14** (12), 999 (1982).
(11) S. P. Papkov and V. G. Kulichikhin, "Liquid-Crystalline State of Polymers", Khimie, Moscow, 1977.
(12) S. N. Bhadani, S.-L. Tseng, and D. G. Gray, *Makromol. Chem.* **184**, 1727 (1983).
(13) S. M. Aharoni, *J. Macromol. Sci., Phys.*, **B21** (1), 105 (1982).
(14) S. Dayan, P. Maissa, M. J. Vellutini, and P. Sixou, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 33 (1982).
(15) R. S. Werbowyj, Ph.D. Thesis, McGill University, 1982.
(16) G. Conio, E. Bianchi, A. Ciferri, A. Tealdi, and M. A. Aden, *Macromolecules*, **16** (8), 1264 (1983).
(17) P. J. Flory, *Macromolecules*, **11** (6), 1141 (1978).
(18) A. R. Khokhlov, *Phys. Lett. A*, **68**, 135 (1978).
(19) A. Yu. Grosberg and A. R. Khokhlov, *Adv. Polym. Sci.*, **41**, 53 (1981).
(20) O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).
(21) A. R. Khokhlov and A. N. Semenov, *Physica (The Hague)*, **112A**, 605 (1982).
(22) A. R. Khokhlov and A. N. Semenov, *Physica (The Hague)*, **108A**, 546 (1981).
(23) W. Maier and A. Saupe, *Z. Naturforsch., A*, **14A**, 882 (1959).
(24) W. Maier and A. Saupe, *Z. Naturforsch., A*, **15A**, 287 (1960).
(25) P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 311 (1979).
(26) G. Ronca and D. Y. Yoon, *J. Chem. Phys.*, **76** (6), 3295 (1982).
(27) G. Ronca and D. Y. Yoon, *Physics (Long Island City, N.Y.)*, **80**, 925 (1984).
(28) A. ten Bosch, P. Maissa, and P. Sixou, *J. Phys. Lett. (Paris)*, **44** (3), 105 (1983).
(29) F. Fried and P. Sixou, *J. Polym. Sci., Polym. Chem. Ed.*, **22** (1), 239 (1984).
(30) H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128 (1974).
(31) H. Yamakawa and T. Yoshizaki, *Macromolecules*, **13**, 633 (1980).
(32) G. V. Laivins and D. G. Gray, preceding paper in this issue.
(33) G. V. Laivins and D. G. Gray, *Polymer*, in press.
(34) K. H. Meyer, *High Polym.*, **4**, 301 (1950).
(35) M. A. Aden, E. Bianchi, A. Ciferri, G. Conio, and A. Tealdi, *Macromolecules*, **17**, 2010 (1984).
(36) J. Bheda, J. F. Fellers, and J. L. White, *Colloid Polym. Sci.*, **258**, 1335 (1980).
(37) S. M. Aharoni, *Mol. Cryst. Liq. Cryst. Lett.* **56**, 237 (1980).
(38) G. H. Meeten and P. Navard, *Polymer*, **24**, 815 (1983).
(39) D. C. Patel and R. D. Gilbert, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1079 (1983).
(40) H. Chanzy, A. Peguy, S. Chaunis, and P. Monzie, *J. Polym. Sci., Polym. Phys. Ed.*, 18, 1137 (1980).
(41) R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
(42) S.-L. Tseng, G. V. Laivins, and D. G. Gray, *Macromolecules*, **15**, 1262 (1982).
(43) M. Bohdanecky, *Macromolecules*, **16**, 1483 (1983).
(44) G. C. de Croes and J. W. Tamblyn, *Mod. Plast.*, **29** (2), 127 (1952).
(45) P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 289 (1979).
(46) G. Conio, E. Bianchi, A. Ciferri, and A. Tealdi, *Macromolecules*, **14**, 1084 (1981).
(47) S. M. Aharoni and E. K. Walsh, *Macromolecules*, **12** (2), 271 (1979).
(48) S. L. Kwolek, P. W. Morgan, J. R. Schaefgen, and L. W. Gulrich, *Macromolecules*, **10** (6), 1390 (1977).
(49) T. I. Bair, P. W. Morgan, and F. L. Killian, *Macromolecules*, **10** (6), 1396 (1977).
(50) M. Warner and P. J. Flory, *J. Chem. Phys.*, **73** (12), 6327 (1980).
(51) P. Navard, J. M. Haudin, S. Dayan, and P. Sixou, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 379 (1981).