Ordered Phase Formation in Concentrated Hydroxypropylcellulose Solutions

Rita S. Werbowyj and Derek G. Gray*

Pulp and Paper Research Institute of Canada, and the Department of Chemistry, McGill University, 3420 University Street, Montreal, P.Q. H3A 2A7, Canada.

Received August 13, 1979

ABSTRACT: Optical, NMR, and X-ray evidence indicate that an ordered liquid-crystalline phase is formed in concentrated hydroxypropylcellulose (HPC) solutions. The concentration necessary to form an ordered phase depends on the solvent, but only slightly on the molar mass of the HPC samples investigated. Liquid-crystalline phases form at about 40 wt % polymer in water and at slightly higher concentrations in methanol and ethanol. The flexibility of the cellulosic chain appears to be the primary factor governing the concentration of polymer that is required for formation of the liquid-crystalline phase.

Hydroxypropylcellulose (HPC) forms an ordered liquid-crystalline phase with cholesteric structure in concentrated aqueous solutions.[1] The polymeric component is a highly-substituted cellulose ether prepared by the base-catalyzed reaction of propylene oxide with cellulose and is available commercially in a wide range of molecular weights.[2-4] An idealized structure is shown in Figure 1, which indicates that the propylene oxide may react with hydroxyl groups on either the anhydroglucose units or on previously attached hydroxypropyl substituents. The polymer is soluble in cold water, but when aqueous solutions of HPC are warmed to about 40 °C, a phase separation occurs with a sharp increase in turbidity and a decrease in viscosity.[2-4] Aqueous solutions are surface active;[2] a detailed study of the surface activity[5] showed that the steady-state surface tension for a range of high molecular weight samples remained virtually constant over a concentration change of five orders of magnitude, and the kinetics of the surface tension change were analogous to those of a diffusion-controlled two-dimensional crystallization. These results are compatible with the formation of an ordered monolayer at the solution surface. The activity of water vapor over concentrated HPC solutions was recently measured by gas chromatographic and static techniques.[6] The results were interpreted by assuming that the entropy of mixing was given by the Flory–Huggins theory in dilute solutions and by Flory's theory for rodlike mixing[7] at very high polymer concentrations.

In this paper, some further evidence for the formation of ordered solutions of HPC in water and other solvents is presented, and an attempt is made to relate the phase separation to the limited flexibility of the polymer chain.

Experimental Section

The hydroxypropylcellulose samples were obtained from Hercules Inc. and the Aldrich Chemical Co. The Hercules samples were labeled Klucel E, L, J, G, and H in order of ascending molar mass. Nominal values for $\bar{M}_w$ given in the product literature[2] are 60 000 for E, 100 000 for L, 300 000 for G, and 1 000 000 for H. The Aldrich samples had nominal $\bar{M}_w$ values of 100 000 and 1 000 000. Distilled water and Analar grade solvents were used directly to prepare concentrated solutions. Water for light scattering was carefully prepared in a closed nonboiling still, using an infrared lamp as the heat source. Viscosity measurements were performed conventionally with Ubbelohde viscometers in a well-thermostated bath. Some light-scattering measurements were attempted with a Sofica 42000 photogonio-diffusometer and also with a Chromatix KMX-6 low-angle laser-light-scattering photometer. Refractive index increments for aqueous HPC solutions were measured with a Hilger and Watts M154 interferometer; the average value for five different HPC samples was 0.131 ± 0.003 g/mL. Values for the molar masses of the polymers measured in aqueous solution appeared to be significantly larger than the nominal values listed above. Thus $\bar{M}_w$ for Klucel G measured with the Sofica instrument was apparently $\sim 0.8 \times 10^6$ g mol^{-1}. However, it was found that aggregation of the polymer was occurring. Measurements with the KMX-6 on aqueous solutions, which had been passed through a Millipore 0.45 μm filter, gave values of 0.41×10^6, 0.69×10^6, and 1.7×10^6 g mol^{-1} at time intervals of 24, 48, and 72 h after preparation, respectively. The nominal value of 0.3×10^6 g mol^{-1} thus seems a reasonable initial value.

The concentration of polymer required to form the ordered phase was found by preparing gravimetrically a series of solutions of known composition and examining them visually for cloudiness and with a polarizing microscope to detect birefringence. A period of several weeks was required between sample preparation and examination to achieve uniform composition. The iridescent colors of the samples vary with the method of viewing; colors in this paper refer to reflected colors at approximately normal incident and viewing angles. Quantitative measurements of reflection band wavelength were made with a JASCO ORD-UV5 spectropolarimeter and suitable thin glass or quartz cells.

The cloud points of dilute aqueous HPC solutions were estimated, using the Sofica instrument. The cloud point was arbitrarily taken as the temperature at which the light scattered at 90° to the incident beam went off-scale on the least sensitive photometer range. This temperature was within 2 °C of the first significant deviation from the base-line scattering when the temperature was raised at 0.2 °C/min. More precise measurements of the turbidity were made on concentrated solutions by sealing a thin layer of solution in a parallel-sided glass tube (0.4-mm microslides, Vitrodynamics, Inc.) and placing the tube, held between the heated plates of a Mettler FP5 microscope hot stage, in the laser beam of the Chromatix KMX-6 photometer.

For X-ray scattering, the mesophase was drawn into thin-walled quartz capillaries by gentle suction with a water aspirator, and the powder pattern was recorded photographically, using Cu Kα radiation. The X-ray pattern from fibers drawn from the mesophase was obtained through the courtesy of Dr. E. Atkins, University of Bristol.

The NMR spectra were kindly provided by Dr. U. Henriksson of the Royal Institute of Technology, Stockholm, using a Bruker B-KR322s pulsed spectrometer.

Results and Discussion

Phase Behavior in Water. (i) Formation of the Concentrated Isotropic Phase. On heating, dilute solutions of hydroxypropylcellulose turned an intense white at about 40 °C. The scattering of light was due to the separation of a polymer-rich phase, which under the microscope appears as roughly spherical particles with diameters of the order of 1 μm. Further heating caused the coagulation of the polymer-rich phase as a white gel.

No birefringence could be observed in the polymer-rich phase. It is assumed that this phase separation is analogous to that observed on heating many other mixtures of water with both polymeric and nonpolymeric solutes.

---

*Address correspondence to this author at McGill University.

0024-9297/80/2213-0069$01.00/0

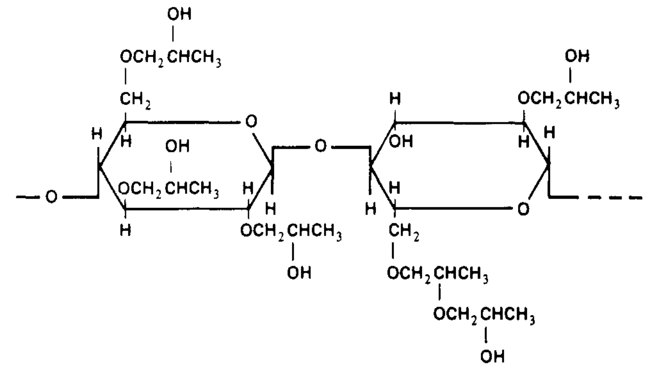

Figure 1. Idealized structure of hydroxypropycellulose with an average of three hydroxypropyl groups per anhydroglucose residue.

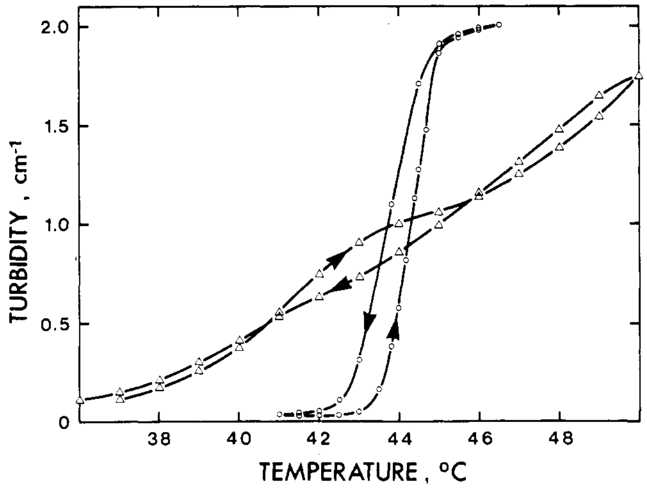

Figure 2. Turbidity of aqueous hydroxypropylcellulose (Aldrich 100 000) solutions as a function of temperature: (circles) 9 wt % solution; (triangles) 41 wt % solution. The rate of temperature change is 0.2 °C min^{-1}.

The cloud point was measured as a function of concentration and molar mass for a series of HPC samples with the Sofica apparatus. The heating rate was 0.2 °C/min. Within the rather large (±2 °C) errors of the method, there was no dependence of cloud point on polymer concentration in the range 10^{-6}–2×10^{-2} g/mL. Furthermore, there was no systematic variation with molar mass. Klucel types G, L, and E all gave cloud points of 44 and 41 °C on heating and cooling, respectively. For Klucel types H and J, the corresponding temperatures were 41 and 37 °C. The different grades of HPC may differ in the degree of substitution, and this may be responsible for variations in the cloud point.

Some more precise measurements of this phase separation process at higher polymer concentrations were made by sealing a thin layer of solution in a parallel-sided glass tube and placing the tube, held between the heated plates of a microscope hot stage, in the laser beam of the Chromatix KMX-6 photometer. The sensitive photomultiplier and wide dynamic range of this instrument enabled the transmitted light intensity to be measured over several orders of magnitude. Figure 2 shows the change in turbidity (uncorrected for scattering at the cell faces) as a function of temperature. The 9% HPC solution showed a sharp rise in scattering over a relatively narrow temperature range, as did solutions with lower concentrations. Some hysteresis was evident on cooling. However, the 41% HPC solution showed a more complex behavior. The scattering increased in two steps over a much broader temperature range. The concentration of this solution is close to that at which an anisotropic phase separates (see below), so the turbidity may reflect some nonequilibrium behavior involving two concentrated phases. At higher concentrations, the anisotropic phase displays cholesteric colors, which on heating turn an increasingly intense white over a wide temperature range. However, the cholesteric color remains detectable and returns instantly on cooling.

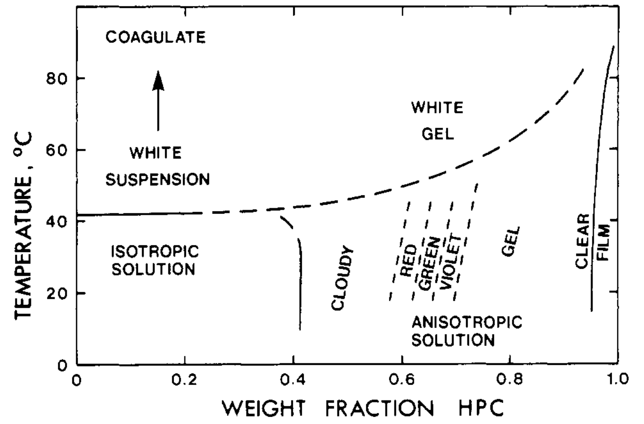

Figure 3. Sketch indicating the appearance of the hydroxypropylcellulose–water system as a function of temperature and concentration.

(ii) Formation of the Concentrated Anisotropic Phase. At room temperature, very concentrated aqueous HPC solutions form an anisotropic, liquid-crystalline phase, which is turbid or iridescent in appearance, and which shows birefringence under crossed polars.[1] The critical concentration necessary for the formation of this phase was found to be 42 and 41 wt % for Klucel L and E, respectively. For the highest molecular weight sample, Klucel H, birefringence was initially observed for samples containing as little as 31 wt % polymer, but it disappeared with time, and thus was ascribed to the effects of shear orientation during preparation of the microscope slide. A concentration of 39 wt % Klucel H was necessary for stable birefringence.

No observable change in the concentration necessary for anisotropic phase formation was detected when observations were repeated at 30 and 35 °C. However, at 40 °C anisotropic phase formation seemed to take place at somewhat lower polymer concentrations.

The appearance of cholesteric colors in white light required higher polymer concentrations. A red iridescence became apparent at about 60 wt % polymer, and the colors moved to the violet end of the spectrum with increasing polymer content. The colors were sensitive to temperature; heating the mesophase resulted in the color moving toward the red end of the spectrum. From the temperature dependence of preliminary optical rotatory dispersion measurements, the wavelength of the reflection band colors increased with increasing temperature by about 1.5 nm/°C. A detailed study of the optical properties of the mesophase is in progress.[8]

The visual appearance of the HPC–water system is summarized schematically in Figure 3. The precise behavior for solutions containing more than 40 wt % HPC at temperatures close to 40 °C was difficult to discern, because of the turbidity and slow rate of equilibration of these highly viscous solutions. It was also difficult to detect, by optical methods, the composition at which the last of the isotropic phase disappears.

NMR of the Ordered Phase. In dilute solution, ^{1}H NMR spectroscopy has been employed to characterize HPC samples.[9] Dr. U. Henriksson kindly provided broadline NMR spectra at higher concentrations in D_2O. The proton signal from the viscous isotropic solution was

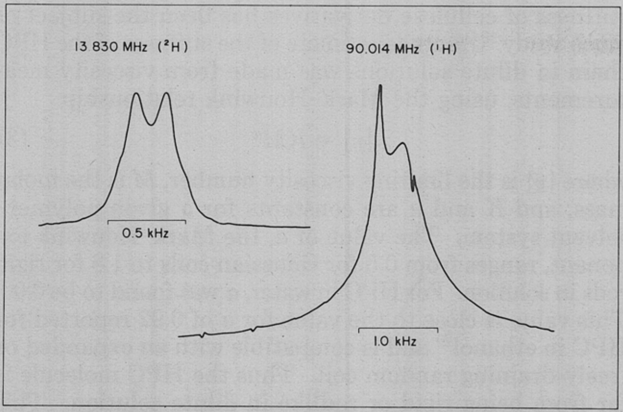

Figure 4. Proton and deuteron magnetic resonance spectra for a blue-green mesophase of Klucel J (~65 wt %) in D_2O.

poorly resolved. In the mesophase region, the signal showed a single relatively sharp component superimposed on a very broad peak (Figure 4). The sharp peak was attributed to HDO in the solvent, either as an impurity or due to hydrogen exchange with the polymer. The HPC protons gave a broad, non-Lorentzian peak similar to that observed for many low molar mass lyomesophases.[10] The ^{2}H spectra were more significant. In soap mesophases made with D_2O, Lawson and Flautt[11] observed quadrupole splitting of the deuteron resonance, which was attributed to partial orientation of the water molecules and to exchange between water deuterons and deuterons bound to the amphiphile.[10,11] A similar phenomenon was observed for the HPC–D_2O system. Dilute solutions showed a single sharp line, but at concentrations in the mesophase region a broad doublet of characteristic shape was observed (Figure 4). The magnitude of the splitting increased with increasing concentration of polymer and with decreasing temperature. This suggests that local ordering of the solvent increases at low temperatures and at high HPC concentrations.

X-ray Diffraction. The most characteristic feature of the X-ray diffraction patterns from the aqueous HPC mesophase was a single diffuse ring, with a *d* spacing ranging from 1.2 to ~1.35 nm, which increased with decreasing concentration of the mesophase. For example, a blue-green sample of Klucel J containing ~64 wt % polymer gave $d = 1.24$ nm. An isotropic aqueous HPC solution containing ~35 wt % polymer showed no diffuse ring in this angular region.

An examination of a dry fiber of HPC drawn from the mesophase provided some useful information. A diffraction pattern, kindly provided by Dr E. Atkins, is shown in Figure 5. The pattern indicates that the HPC molecule exists in the fiber as a rodlike threefold helix. The fiber repeat distance is 1.506 nm, which corresponds to three anhydroglucose units per repeat. The rods are parallel but are randomly translated relative to each other, resulting in the strong ill-defined spot on the equator with $d = 1.11$ nm, from which an average center-to-center distance for the hexagonally-packed rods of $1.11 \times 2/3^{1/2} = 1.28$ nm may be estimated. These results are in accord with the measurements of Samuels,[12] who examined in detail the properties of water-cast and oriented HPC film and concluded that the polymer crystallized as an irregular threefold helix.

Mesophase Formation in Other Solvents. Hydroxypropylcellulose is soluble in a wide range of organic solvents,[2,3] in several of which we have observed the formation of ordered phases. The concentration of polymer required for ordered phase formation in some solvents is listed in Table I; a marked dependence on the nature of the solvent is apparent.

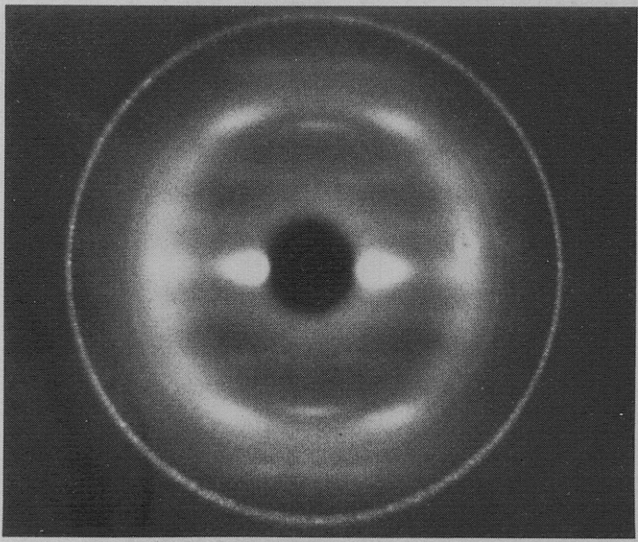

Figure 5. X-ray diffraction from HPC fibers drawn from the Klucel J mesophase. The sharp rings are calibrant for determination of spacings.

Table I
Minimum Hydroxypropylcellulose Concentrations Required for Mesophase Formation in Various Solvents

sample	solvent	polymer content: wt %	polymer content: vol fraction[a]
E	water	41	0.37
L	water	42	0.38
H	water	39	0.35
L	methanol	43	0.33
L	ethanol	47	0.37

[a] Calculated assuming additivity of component volumes and a HPC density of 1.20 g/mL.

Several significant conclusions may be drawn from Table I. In the previous note,[1] it was suggested that the amphiphilic nature of HPC in water might be related to the formation of the mesophase. This now seems incorrect, because the ordered phase also forms with organic solvents in which HPC is not surface active. Second, the volume fraction of polymer required to form an ordered phase depends to some extent on the solvent but is relatively insensitive to the molar mass of the polymer. This is contrary to theory[7] and observations[13,14] of rigid rod systems, in which the axis ratio of the rods is the critical factor governing phase separation. Flory has shown that both flexibility[15,16] and polydispersity[17] can influence the phase separation behavior. It will be shown that the phase separation of HPC in water and organic solvents is primarily governed by chain flexibility.

Chain Flexibility. The effect of chain flexibility on phase separation was considered in Flory's lattice theory,[15] in which the polymer molecules in the isotropic phase were characterized as having a fraction *f* of pairs of adjacent bonds with bent configurations, the remainder being collinear. The energy of the bent configuration was taken to be greater than that of the linear configuration by an amount ϵ, so that the degree of chain bending in the isotropic phase was

$$f = (z - 2)e^{-\epsilon/kT}/[1 + (z - 2)e^{-\epsilon/kT}] \qquad (1)$$

where *z* is the lattice coordination number. The molecules in the anisotropic phase were assumed to be linear, with $f = 0$. According to this model, the volume fractions of

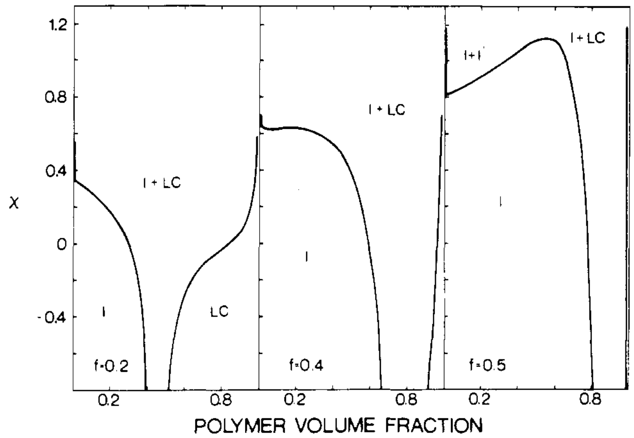

Figure 6. Predicted effect on the phase diagram of changing the flexibility *f* for a semirigid polymer chain of $x = 100$ segments. I and I′ are dilute and concentrated isotropic phases, respectively, and LC is the ordered liquid-crystalline phase.

isotropic and anisotropic phases in equilibrium are given by

$$(x - 1)\phi_2 + (x - 2) \ln (1 - f) - \ln (zx/2) - \chi_1(\phi'_2 - \phi_2) \times [(x - 1)(\phi_2 + \phi'_2) - 2x] = \ln \{(1/\phi_2) \exp[\chi_1(\phi'^2_2 - \phi_2^2)] - [(1 - \phi_2)/\phi_2] \exp[(1 - 1/x)\phi_2]\}$$

and

$$\chi_1 = \{\ln[1 + \phi'_2/x(1 - \phi'_2)] + \ln (1 - \phi_2) + (1 - 1/x)\phi_2\}/(\phi'^2_2 - \phi_2^2) \quad (2)$$

where ϕ_2 and ϕ'_2 are the volume fractions of polymer in the isotropic and anistropic phases, respectively, x is the number of segments in the polymer, and χ is the polymer–solvent interaction parameter, assumed to be the same in both phases. When $f = 0$, these equations reduce to those for rodlike molecules.[7]

Equations 2 were solved by iteration, and some results are shown in Figure 6. Increasing the flexibility, *f*, shifts the onset of the anisotropic region to higher volume fractions of polymer, as required by the data in Table I. At the same time, the broad two-phase region is extended to higher positive values of χ. For *f* values greater than ~0.45, the formation of a polymer-rich isotropic phase is indicated, corresponding to that predicted by the conventional Flory–Huggins theory at positive χ values. Comparison of Figure 6 with Figure 3 illustrates the good qualitative agreement of Flory's theory with observations on the HPC water system; it should be noted that in this system, the χ values are large and positive and increase with increasing polymer concentration.[6] However, the theoretically predicted width of the two-phase region seems too broad. Although we have not succeeded in making unequivocal measurements of the compositions at which the isotropic phase disappears, it seems physically improbable that the isotropic phase could coexist with an anisotropic phase whose color changes with composition. The two-phase region must therefore be restricted to the "cloudy" area in Figure 3. A quantitative comparison between theory and experiment is also hindered by the polydispersity of the HPC and by the difficulty in relating the lattice-dependent parameter *f* to conventional measurements of chain flexibility. (A value of $f = 0.5$ on a cubic lattice with $z = 6$ implies that half of the chain elements are perpendicular to each other. More realistic values of *f* may result if bent but parallel orientations are allowed in the ordered phase.[18])

The flexibility of hydroxypropylcellulose thus seems to be a key factor in the phase separation. The flexibility or stiffness of cellulose derivatives has been the subject of much study.[19] A crude estimate of the stiffness of the HPC chain in dilute solutions was made from viscosity measurements, using the Mark–Houwink relationship

$$[\eta] = KM^a \quad (3)$$

where $[\eta]$ is the limiting viscosity number, M is the molar mass, and K and a are constants for a given polymer–solvent system. The value of a, the Mark–Houwink exponent, ranges from 0.5 for Gaussian coils to 1.8 for rigid rods in solution. For HPC in water, a was found to be 0.90. This value is close to the value for a of 0.92 reported for HPC in ethanol[20] and is compatible with an expanded or freely-draining random coil. Thus the HPC molecule is far from being rigid or rodlike in dilute solution. This conclusion is supported by a recent note[21] which considers viscometric and sedimentation measurements for a wide range of polymers; HPC in water behaves as a typical cellulosic derivative, intermediate between rodlike molecules and random coils.

The flexibility of a polymer chain may be quantified by the length, l', of the Kuhn statistical segment,

$$l' = \langle r_0^2 \rangle / nl \quad (4)$$

where $\langle r_0^2 \rangle$ is the mean square unperturbed end-to-end distance of a chain consisting of n links of length l. The Kuhn length l' is thus the length of a *freely-jointed* segment in a hypothetical chain of nl/l' segments with the same end-to-end distance as the real chain. The Kuhn length may be estimated from light-scattering and viscosity data on polymer fractions. Wirick and Waldman[20] tabulate values of $\{r_0^2\}/\bar{n}$ as a function of $\bar{n}$, where $\bar{n}$ is the z average degree of polymerization, for HPC in ethanol and also for hydroxyethylcellulose in water. If the length l of an anhydroglucose link is taken as 0.545 nm,[22] then the values of l' calculated from eq 4 and the data of Wirick and Waldman[20] are markedly dependent on the degree of polymerization, increasing from ~13 nm for the fraction with the highest DP to ~21 nm for the fraction with DP = 575. (This latter nevertheless corresponds to a high molar mass material, with a tabulated $\bar{M}_z$ of 250 000.) These values for the Kuhn length are of the same order as those observed for other cellulose ethers in water; combined data for (ethyl)(hydroxyethyl)cellulose, methylcellulose, and hydroxyethylcellulose in water gave $l' = 18.2$ nm.[19] (However, it must be noted that some highly substituted cellulose derivatives show much shorter Kuhn lengths in organic solvents.[19])

Phase Separation and Flexibility. Phase separation of rodlike molecules is predicted to occur in athermal solutions at volume fractions given by Flory's well-known equation,[7]

$$\phi_2^* \simeq (8/x)(1 - 2/x) \quad (5)$$

where ϕ_2^* is the volume fraction of rods required for phase separation, and x is the axis ratio of the rods. The data in Table I would require that the axis ratio of rods range from about 19 to 21 in water. Obviously if HPC were rodlike, its axis ratio would be much larger than these values and would of course depend on the molar mass of the polymer. If, however, the polymer may be viewed as a set of freely-jointed rods, each with an axis ratio x, then in this case Flory has shown[16] that the axis ratio x and not the number, n, of such segments governs the phase separation (e.g., changing n from 1 to ∞ for $x = 20$ increases ϕ_2^* by less than 4%).

The X-ray data discussed above indicate a center-to-center distance for HPC of 1.28 nm. The Kuhn segment length is of the order of 17 ± 4 nm. Thus the axis ratio of rodlike segments is approximately 13 ± 3, which corresponds to volume fractions of polymer from 0.44 to 0.64. These are of the correct order of magnitude but are somewhat higher than the values observed in Table I. Replacing the Kuhn length by the persistence length, as suggested by Flory,[16] increases the discrepancy. In view of the theoretical and experimental difficulties associated with the use of the Kuhn segment length, and the use of the solid-state helix center-to-center distance as the diameter of the HPC molecule in solution, the agreement between the estimated segment axis ratio ($x = 13 \pm 3$) and that required by eq 5 ($x = 20$ for $\phi_2{}^* = 0.36$) is probably as good as can be expected.

Concluding Remarks

Optical, X-ray, and NMR evidence shows that hydroxypropylcellulose forms an ordered cholesteric mesophase in water and in several organic solvents. The ready availability of the polymer and its solubility in a wide range of solvents suggest that HPC and other polysaccharide-based mesophases may be a class of model polymer mesophases as useful as the much studied synthetic polypeptides.[13,14] The phase separation of the relatively flexible HPC molecule is predicted by a model in which rigid rods are replaced by freely-jointed rods whose length equals the Kuhn equivalent segment length of the polymer chain.

This latter point has some practical consequences. If chain stiffness is solely responsible for phase separation, then cellulose and its derivatives might be expected to form ordered solutions in many solvents. Some evidence to support this is given in a recent patent application[23] which covers a wide range of cellulose derivatives. However, in some of the examples claimed therein, it is necessary to shear the concentrated solution in order to observe a time-dependent orientation. Our feeling at present is that moderate chain stiffness is a necessary but not sufficient condition for ordered phase separation and that kinetic parameters must also be important at the very high polymer concentrations. The role of flexible side chains may be to allow the chains to slip past each other at high volume fractions, rather than to increase solubility. (The hydroxypropyl groups are rather hydrophobic and *lower* the affinity of the polymer for water.) Without such side groups, the polymers either crystallize or become locked into an unoriented concentrated gel. In some mesophase systems, species that strongly solvate the main chain may play the same role as flexible side chains.

In the discussion to this point, it has been assumed that the stiffness, characterized by f or l', is an intrinsic property of the polymer chain in a given solvent. However, as pointed out by Frenkel,[24] the stiffness may vary with χ and with external fields. This leads to a slightly different picture of the phase separation of HPC in water. As observed previously, χ for this system increases with polymer concentration, and so polymer–polymer contacts become increasingly favored over water–polymer contacts, resulting in the formation of an intramolecularly hydrogen-bonded helix, which is sufficiently stiff to cause phase separation of the resultant rodlike species. Although the HPC molecule certainly exists as a helix in dry fibers and films, there is as yet no evidence that a helical molecular conformation is a prerequisite for the formation of the ordered liquid phase. Without clear evidence for a concentration-dependent change in conformation, it seems simpler to explain phase separation in terms of dilute solution conformation and volume fraction of chains.

Acknowledgment. We thank Drs. E. Atkins and U. Henriksson for their cooperation and patience. The Natural Sciences and Engineering Council of Canada provided a Scholarship for R.S.W. and partial support for this work. A grant from Hercules Inc. is gratefully acknowledged.

References and Notes

(1) R. S. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, **34**, 97 (1976).
(2) "Hydroxypropyl Cellulose: Chemical and Physical Properties", Hercules Inc., Wilmington, Del., 1971.
(3) E. D. Klug in "Encyclopedia of Polymer Science and Technology", Vol. 15, N. M. Bikales, Ed., Wiley-Interscience, New York, 1971, p 307.
(4) E. D. Klug, *J. Polym. Sci., Polym. Symp.*, **36**, 491 (1971).
(5) S. A. Chang and D. G. Gray, *J. Colloid Interface Sci.*, **67**, 255 (1978).
(6) J. S. Aspler and D. G. Gray, *Macromolecules*, **12**, 562 (1979).
(7) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **234**, 73 (1956).
(8) R. S. Werbowyj and D. G. Gray, unpublished results.
(9) F.-L. Ho, R. R. Kohler, and G. A. Ward, *Anal. Chem.*, **44**, 178 (1972).
(10) Å. Johansson and B. Lindman in "Liquid Crystals and Plastic Crystals", Vol. 2, G. W. Gray and P. A. Winsor, Eds., Ellis Horwood, Chichester, England, 1974, pp 192–230.
(11) K. D. Lawson and T. J. Flautt, *J. Phys. Chem.*, **72**, 2066 (1968).
(12) R. J. Samuels, *J. Polym. Sci. Part A-2*, **7**, 1197 (1969).
(13) C. Robinson, *Trans. Faraday Soc.*, **52** 571 (1956).
(14) W. G. Miller, *Annu. Rev. Phys. Chem.*, **29**, 519 (1978).
(15) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **234**, 60 (1956).
(16) P. J. Flory, *Macromolecules*, **11**, 1141 (1978).
(17) P. J. Flory and A. Abe, *Macromolecules*, **11**, 1119 (1978).
(18) W. R. Krigbaum and F. Salaris, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 883 (1978).
(19) W. Brown in "Cellulose and Cellulose Derivatives", Part IV, N. M. Bikales and L. Segal, Eds., Wiley, New York, 1971, pp 557–601.
(20) M. G. Wirick and M. H. Waldman, *J. Appl. Polym. Sci.*, **14**, 579 (1970).
(21) L.-O. Sundelöf and B. Nyström, *J. Polym. Sci., Polym. Lett. Ed.*, **15**, 377 (1977).
(22) N. Yathindra and V. S. R. Rao, *Biopolymers*, **9**, 783 (1970).
(23) For example, see M. Panar and O. B. Willcox, Demande de Brevet d'Invention, No. 7703473, Paris, France, 1977.
(24) S. Frenkel, *J. Polym. Sci., Polym. Symp.*, **44**, 49 (1974).