Calorimetric Study of Aqueous Solutions of (Hydroxypropyl)cellulose

L. Robitaille, N. Turcotte, S. Fortin, and G. Charlet*

Department of Chemistry and Centre de Recherches en Sciences et Ingénierie des Macromolécules (CERSIM), Université Laval, Quebec City, Quebec, Canada G1K 7P4

Received August 29, 1990; Revised Manuscript Received December 3, 1990

ABSTRACT: Precise measurements of the temperature and enthalpy of phase separation in aqueous solutions of fractionated (hydroxypropyl)cellulose (HPC) have been performed, using a scanning Calvet calorimeter. In dilute solutions, the heats of demixing range from 22 to 33 J/g of polymer. With the exception of low molar mass samples ($M_w \leq 64$ kg·mol^{-1}), the solubility of HPC is essentially controlled by the extent of substitution, the temperature and the enthalpy of transition respectively decreasing and increasing when the average number of hydroxypropyl groups per anhydroglucose segment increases. For a given polymer, the enthalpy of phase separation is a linearly decreasing function of the polymer weight content. No discontinuity is observed at the isotropic–anisotropic critical composition. The thermal effect reflects only the changes occurring in the isotropic phase, which indicates that the formation of a cholesteric mesophase in aqueous HPC is a purely entropic phenomenon.

Introduction

(Hydroxypropyl)cellulose (HPC) is soluble in a wide variety of aqueous and organic solvents. Like most cellulose derivatives, its concentrated solutions are liquid crystalline. Numerous aspects of HPC properties in water have been investigated.[1-7] In a previous work,[1] the phase diagram of aqueous HPC was carefully examined. Phase separation was found to occur upon heating solutions at all concentrations. The reduced solubility at high temperature originates from the melting of the enhanced water structure built around the hydrophobic regions of the polymer molecule. Interestingly, cholesteric liquid crystals phase-separate at lower temperatures than isotropic solutions. A difference as large as 28 deg was observed for a low molar mass fraction. This behavior suggests that HPC chains display a more hydrophobic surface to the solvent in cholesteric phases than in isotropic solutions. The purpose of the present work is to assess the origin of the anomaly in the phase diagram, using precise measurements of the enthalpy associated with the transition. Commercial samples of HPC are synthesized by the reaction of propylene oxide on cellulose, giving lateral chains of variable length. The chemical structure of HPC is then characterized by the degree of substitution (DS), which represents the average number of oxygens of the original cellulose repeating unit bearing a substituent, and the molar substitution (MS), i.e., the average number of hydroxypropyl groups ($CH_2CH(CH_3)O$) per anhydroglucose segment. First, the effect of the molar mass and the structure of the polymer on temperatures and heats of transition will be investigated on carefully fractionated samples. The heat of transition as a function of polymer concentration will then be studied, in order to measure the effect of liquid-crystalline order on the phase separation.

Experimental Section

Materials. Two batches of (hydroxypropyl)cellulose with a nominal molar mass of 100 kg·mol^{-1} were obtained from Aldrich Chemical Co. Ethanol, heptane, and tetrahydrofuran (THF) were at least 99% pure and were used without further purification. Deionized water (resistivity ≥ 16 MΩ·cm) was prepared with a Sybron-Barnstead Nanopure II ion exchanger. Deuterated solvents were purchased from MSD Isotopes, Merck-Frosst, Canada.

Molar Mass Measurements. Size Exclusion Chromatography. Average molar masses and polydispersity ratios were evaluated by size exclusion chromatography (SEC; Waters, Model 590). The elution profiles of THF solutions were recorded at the output of the column (Ultrastyragel Linear P/W 10681) with a differential refractometer (Millipore, Model R401) and compared to those obtained for solutions of monodisperse polystyrene standards (Pressure Chemicals Co., Pittsburgh).

Viscosimetry. The specific viscosity of ethanol solutions of HPC (between 0.08 and 0.5 g·dL^{-1}) was measured at 25.00 ± 0.05 °C in an Ubbelhode viscosimeter (Cannon Instrument Co.).

Fractionation of the Polymer. The polymer was first dissolved in water at a weight fraction between 5 and 10%. The solution was filtered through glass microfiber filters (Whatman 934-AH, nominal retention 1.5 μm) under a nitrogen pressure of about 40 psi, in order to remove the insoluble materials (essentially silica powder, added as an anticaking agent, and polymer of a lower DS) that are generally present in the commercial polymer.[2] The polymer was then recovered from the clear solution by freeze-drying. Fractional dissolution in ethanol–heptane mixtures is generally applied to fractionate HPC.[8] The same solvent–nonsolvent pair was used, but fractional precipitation was preferred over dissolution because equilibrium conditions between the coexisting liquid phases at a given solvent composition could be achieved more easily and rapidly. Two series of fractions were collected, using different procedures.

Series A. A solution of 10 g of unfractionated polymer (A0) was prepared in 250 mL of anhydrous ethanol. *n*-Heptane was then added until phase separation occurs (heptane molar fraction $X_H = 0.355$). At this stage, the biphasic system was heated at 60 °C until the system became homogeneous again and cooled back to 25 °C. The temperature cycles were repeated several times, in an effort to reduce coprecipitation of low molar mass material. Finally, the system was allowed to stand at 25 °C in a temperature-controlled water bath until the two phases could be physically separated (a few days were generally required). The concentrated phase was recovered and dried in a rotating evaporator under reduced pressure. The resulting polymer was mixed with water and freeze-dried to give the first fraction (A1). More heptane was added to the dilute phase, and the above process was repeated to yield seven more fractions. The last fraction (A9) was prepared by pouring the final dilute phase in a large excess of heptane. Throughout the fractionation, the solvent composition was monitored, using the relative intensity of the hydroxyl and alkyl protons in the ^{1}H NMR spectrum of the mixture. This allowed us to correct for changes prompted by differences in relative evaporation rates and possible solvent segregation between the two phases in equilibrium. The precipitation conditions and some relevant physicochemical data for the fractions are gathered in Table I. Despite the thermal

0024-9297/91/2224-2413$02.50/0

Table I
Physicochemical Data on HPC Fractions Prepared by Fractional Precipitation in Ethanol–Heptane Mixtures

fraction	X_H[a]	M_w,[b] kg·mol^{-1}	M_w/M_n[b]	$[\eta]$,[c] dL·g^{-1}	molar substitution[d]		
					^{1}H $CDCl_3$[e]	^{1}H DMSO[f]	^{13}C D_2O[g]
A0		299	4.0	2.00			
A1	0.355	509	3.3				
A2	0.394	312	2.6				
A3	0.398	212	2.2	2.20			5.5 ± 0.3
A4	0.408	177	2.2	2.08	5.9 ± 0.7	5.5 ± 0.8	
A5	0.419	140	1.8	1.56	5.7 ± 0.5	5.9 ± 0.8	5.5 ± 0.3
A6	0.425	110	1.8	1.26	5.5 ± 0.6	5.3 ± 0.6	5.5 ± 0.3
A7	0.438	89	1.7			6.0 ± 0.8	
A8	0.451	64	1.7		5.8 ± 0.5	5.9 ± 0.4	5.8 ± 0.3
A9		28	2.0	0.45			6.2 ± 0.2
B0		513	3.6	4.77			
B4	0.348	1055	1.4	7.7	5.0 ± 0.5		4.0 ± 0.4
B5	0.365	718	1.7				
B6	0.372	413	1.8				
B7	0.387	461	1.7	5.05	4.9 ± 0.5		4.9 ± 0.4
B8	0.390	112	1.7				
B9	0.394	58	2.0				
B10	0.430	209	1.5	2.57	5.0 ± 0.4	5.0 ± 0.4	5.0 ± 0.3
B11	0.434	111	1.5				
B12		71	2.3				5.2 ± 0.3

[a] Molar fraction of heptane in the precipitating solvent. The listed compositions are in agreement with the solubility curve of HPC in ethanol–heptane, reported by Wirick and Waldmann.[8] [b] Measured by SEC in THF, using polystyrene standards. [c] Intrinsic viscosity in ethanol at 25 °C. The results fit satisfactorily to the Mark–Houwink equation $[\eta] = KM_2^a$. The calculated parameters $K = 1.077 \times 10^{-4}$ dl·g^{-1} and $a = 0.814$ compare favorably with literature data[8] obtained in a slightly different M_w range. [d] Average number of hydroxypropyl groups per anhydroglucose residue, MS. The listed uncertainties represent the standard deviation on several evaluations of the peak areas on a given spectrum. [e] Calculated by ^{1}H NMR spectroscopy of $CDCl_3$ solutions. [f] Calculation by ^{1}H NMR spectroscopy of solutions in DMSO-d_6 at 98 °C. [g] Calculated by ^{13}C NMR spectroscopy of D_2O solutions.

history imparted to the phase-separated systems, some coprecipitation occurred, as shown from the increase of polydispersity with molar mass. The SEC elution curves also confirm that the first fractions contain a significant proportion of shorter polymer chains. Only low molar mass samples (A5–A9) possess values of M_w/M_n lower than 2.0.

Series B. The previous fractionation already constitutes a fairly good separation of HPC, quite comparable to the results obtained by fractional precipitation.[8] A second procedure was however designed for the preparation of larger quantities (10–20 g) of material of both high molar mass and low polydispersity, while keeping the volume of solutions to moderate values (less than 4 L). A different batch of the commercial polymer (B0) was used to prepare a solution in pure ethanol (72.6 g in 0.86 L). Heptane was added until a molar fraction $X_H = 0.394$. Equilibrium conditions were ascertained in a similar fashion as in the preparation of series A, and the coexisting phases were physically separated. The dilute solution yielded fraction B1. The polymer recovered from the concentrated phase was dissolved again in pure ethanol. Phase separation was performed upon addition of heptane at $X_H = 0.378$. Fractions B2 and B3 were recovered from the dilute and concentrated phases, respectively. The three samples were fractionated again by using the following procedure. To an ethanol solution of B1, B2, or B3 was added heptane up to a molar fraction equal to 0.434, 0.390, and 0.365, respectively. Fractions B12, B9, and B6 were recovered from the respective dilute phases. Finally, the polymer extracted from the concentrated phases was fractionated in a solvent richer in ethanol, yielding, for instance, fractions B4 and B5 from the phase previously in equilibrium with a dilute solution of B6. As shown in Table I, this two-stage procedure led to samples exhibiting a molar mass dependence of polydispersity opposite to that of series A. Therefore, the use of both methods enabled the preparation of fairly monodisperse samples in a wide range of M_w.

Structural Characterization of the Fractions. Several solution NMR methods have been proposed in the literature for the assessment of HPC structural parameters. The complete substitution pattern of a sample, including the distribution of the various substituted anhydroglucose units, could in principle be determined by ^{13}C NMR of the product of a methanolysis reaction.[9,10] The reaction was conducted on fractions A3, B4, B7, and B10. In all cases, an unknown but sizable quantity of bicyclic acetals was formed, which prevented a complete quantitative evaluation. Rather, three methods using the polymer directly were used. Their results are summarized in Table I.

^{1}H NMR of $CDCl_3$ Solutions. Ho and Klosiewicz[11] proposed the use of a ^{1}H NMR analysis of HPC solutions in $CDCl_3$. The MS can be calculated from the ratio of methyl protons over protons linked to secondary and tertiary carbons. The spectra for solutions containing 10–20 mg·mL^{-1} were recorded at 200 MHz on a Varian XL-200 spectrometer. The results are given in Table I. The method lacks sensitivity for highly substituted samples, since any extra hydroxypropyl substituent equally contributes to both types of protons. At MS = 6, for instance, a 2% uncertainty on the experimental ratio translates into an uncertainty equal to 0.7 on the molar substitution.

^{1}H NMR of HPC Solutions in Deuterated Dimethyl Sulfoxide (DMSO) at 98 °C. NMR spectroscopy of DMSO solutions has been mentioned[12] as a method for the characterization of HPC. Spectra recorded at 98 °C exhibit a peak at a chemical shift of 4.4 ppm, which can be attributed to the anomeric proton. Heating is required, because, at room temperature, the chemical shift of the hydroxyl protons is also about 4.3–4.4 ppm. The molar substitution of the sample can be calculated from the relative intensity of the peaks due to the anomeric and methyl protons ($0.9 \leq \delta \leq 1.2$ ppm). Measurements were carried out on selected fractions, using the same experimental conditions as for chloroform solutions. Again, the uncertainty on the result is rather large (Table I), this time because of the small size of the peak of the anomeric proton.

^{13}C NMR in Deuterated Water. The ^{13}C NMR spectrum of HPC in aqueous solution has been thoroughly studied by Lee and Perlin.[13] Signals in the 17–19 ppm range and at 20.0 ppm originate from methyl carbons located inside and at the extremity of the hydroxypropoxy pending chain, respectively. Their relative areas allow for the calculation of the average length of the lateral chain. The molar substitution can be evaluated from a comparison of the methyl peaks with that of the anomeric carbon (δ = 104.2 ppm). Spectra of D_2O solutions containing 2–3 mg·mL^{-1} polymer were obtained at 100.6 MHz with a Bruker WH-400 spectrometer (20 000–50 000 collections with a delay of 1.6 s). As shown in Table I, the method provides the best results in terms of the uncertainty on MS, probably because of the higher resolution of the instrument. For comparison purposes, some measurements on more concentrated solutions (20–30 mg·mL^{-1}) were also performed at 50.3 MHz on the Varian XL-200

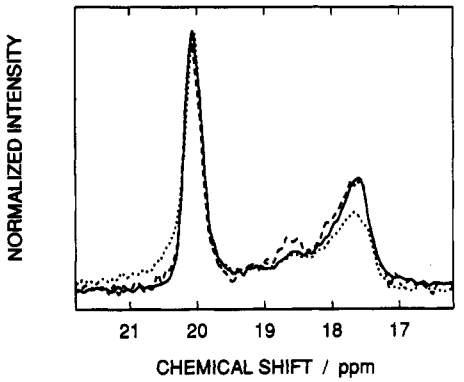

Figure 1. ^{13}C NMR spectra of D_2O solutions of HPC in the region characteristic of methyl carbons: fraction A5 (MS = 5.5; M_w = 140 kg·mol^{-1}) (full line), fraction A9 (MS = 6.2; M_w = 28 kg·mol^{-1}) (dashed line), and fraction B10 (MS = 5.0; M_w = 209 kg·mol^{-1}) (dotted line). The intensity scales have been adjusted so that the total area under the curve between 17 and 21 ppm is the same for all specimens. The peak at $\delta \simeq 18.7$ ppm in the spectrum of fraction A9 can be attributed to a carbon atom located in the middle of a lateral chain containing three 2-hydroxypropoxy groups.

instrument (12–36-h accumulation; no delay). Figure 1 gives the typical spectra recorded for three fractions in the region characteristic of methyl carbons. The intensity scales have been adjusted so that the total area under the curve between 17 and 21 ppm is the same for all specimens. An identical trend is observed in the relative size of the two methyl peaks (Figure 1) and in the values of MS (Table I), calculated by either of the three above methods. The occurrence of a peak at $\delta \simeq 18.7$ ppm in the spectrum of the most substituted sample indicates that, despite an average MS equal to 6.2, lateral chains containing three hydroxypropoxy groups are present in a sizable quantity. This in turn suggests that the fractions may contain polymer molecules that possess a fairly broad distribution of lateral chain length.

Enthalpy of Phase Separation. The heat associated with the phase separation of HPC–water systems was measured by scanning microcalorimetry, using a Calvet calorimeter (SETARAM C80, Lyon, France). The instrument is essentially composed of three parts. The cell containing the sample is a stainless steel cylinder (17-mm o.d.; 15-mL capacity). It is placed at the center of a massive cylindrical metal block that acts as a heat sink. The only exchange between the cell and the calorimetric block is provided through a crown of several hundred thermocouples whose junctions are in contact alternatively with the block and the cell wall. At a constant temperature of the block, the occurrence of a thermal event in the cell produces a difference in temperature dT between the cell and the sink. For a given thermocouple i, characterized by a thermoelectric constant ϵ and a thermal conductance γ, this temperature difference is responsible for both an electromotive force e_i

$$e_i = \epsilon\, dT \tag{1}$$

and a heat flux $(\partial Q/\partial t)_i$

$$(\partial Q/\partial t)_i = \gamma\, dT \tag{2}$$

As all the thermocouples are linked in series, the total electromotive force E, which is the parameter experimentally measured, is

$$E = \sum e_i \tag{3}$$

or

$$E = \sum \left[\frac{\epsilon}{\gamma}\left(\frac{\partial Q}{\partial T}\right)_i\right] \tag{4}$$

By design, all junctions are identical and the calorimeter is carefully assembled while maintaining the cylindrical symmetry of the thermocouples around the cell well. Consequently, E is proportional to the total heat transfer between the cell and the calorimetric block:

$$E = \frac{\epsilon}{\gamma}\sum\left(\frac{\partial Q}{\partial t}\right)_i \tag{5}$$

Any change in the temperature of the heat sink itself, e.g., when the calorimeter is operated in the scanning mode, will generate an undesired signal. A two-cell assembly is then used, in which two identical crowns of thermocouples surrounding the cells are connected in opposition. The proportionality constant between E and the heat flux is determined by providing a known amount of energy to a resistor placed in the cell.

Mixtures of water and HPC at a weight fraction $0.01 \le w \le 0.75$ were allowed to dissolve at room temperature for at least a week. An amount of solution containing 50–150 mg of polymer was placed into the calorimetric cell, which was subsequently sealed by using a Teflon O-ring. The cell was heated in the calorimeter between 21 and 90 °C at a rate of 0.1 deg·min^{-1}. In order to check reproducibility, the thermograms of all solutions was recorded a second time under the same conditions, after rapid cooling and thorough agitation.

Phase Diagram. Turbidimetry. Solutions were prepared in sealed parallel-sided glass tubes (Vitro Dynamics, 0.4 × 4 mm i.d.), as described previously.[1] Phase separation temperatures were taken as the point of sharp increase of turbidity upon heating, as measured from the light transmitted by the tube in an optical microscope (heating rate 1 deg·min^{-1}) or the absorbance of the solution at 700 nm in a UV–visible Hewlett-Packard 8450A diode array spectrophotometer (isothermal measurements every 1–3 deg).

Calorimetry. The onset of phase separation is much less sharp on the thermograms than on the cloud-point curves. An unambiguous, reproducible temperature can be nevertheless measured from the integral of the heat-flow trace. The transition was defined as the temperature at which 5% of the total heat had been absorbed by the solution.

Results and Discussion

Effect of Molar Mass and Substitution on the Phase Transition. Isotropic solutions of HPC in water separate into a cholesteric phase and an infinitely dilute solution around 45 °C.[1] The transition temperature shows only a very small dependence on concentration, which indicates that only the immediate solvent environment of the polymer controls its solubility behavior. This is in accord with a model for the reduced aqueous solubility of HPC at high temperature, which involves melting of the enhanced water structure built around hydrophobic regions of the chain. Presumably, the solvent structure, hence the temperature and the heat of transition, should be very sensitive to the substitution of HPC. The calorimetric trace of dilute solutions (w = 0.01) of fractions A9, B4, and A3 is given in Figure 2. Phase separation appears to be endothermic, as expected from the above interpretation. The onset of the heat effect, which is in excellent agreement with cloud point measurements, varies with the polymer fraction. This is also the case for the enthalpy (measured from the area under the calorimetric trace). Most interestingly, the manner in which the solution absorbs the heat of transition differs significantly from one sample to another, as seen from the shape of the heat flow as a function of temperature. The same features are observed throughout the isotropic range (w less than 35–45% depending on M_w). At the transition, there is no significant change in the heat capacity or the temperature dependence of the heat capacity of the system. The effects of molar mass and structure on the temperature and the enthalpy of transition are represented in Figure 3 and Figure 4, respectively. The transition temperature observed for fractions B4, B7, and B10 (MS = 4.9–5.0; $209 \le M_w \le 1055$ kg·mol^{-1}) does not depend on M_w. The same feature is true for samples A3, A5, and A6 (MS = 5.5; 110

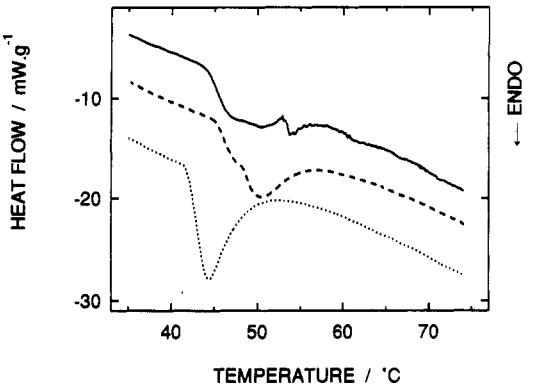

Figure 2. Thermograms of aqueous solutions (1% polymer by weight) of fractions A9 (MS = 6.2; M_w = 28 kg·mol^{-1}) (full line), B4 (MS = 4.9; M_w = 1055 kg·mol^{-1}) (dashed line), and A3 (MS = 5.5; M_w = 212 kg·mol^{-1}) (dotted line). The calorimetric signal, expressed in terms of heat flow per unit mass of polymer in the sample, was recorded upon heating at 6 deg·h^{-1}. The curves have been shifted along the vertical axis for clarity, but no baseline subtraction has been performed.

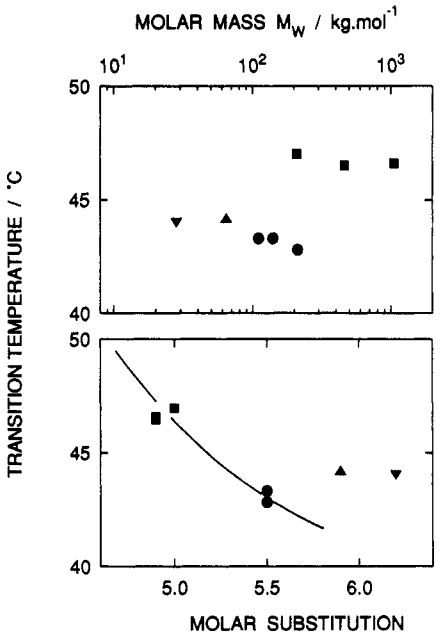

Figure 3. Temperature of the onset of phase separation in dilute solutions of HPC (w = 0.01) as a function of the molar mass and the molar substitution of the polymer: (■) fractions B4, B7, and B10 (MS = 4.9–5.0; 209 ≤ M_w ≤ 1055 kg·mol^{-1}); (●) fractions A3, A5, and A6 (MS = 5.5; 110 ≤ M_w ≤ 212 kg·mol^{-1}); (▲) fraction A8 (MS = 5.8; M_w = 64 kg·mol^{-1}); (▼) fraction A9 (MS = 6.2; M_w = 28 kg·mol^{-1}).

≤ M_w ≤ 212 kg·mol^{-1}). Therefore, the solubility of HPC in dilute solution depends essentially on the structure of the polymer, the temperature of phase separation decreasing when MS increases. This is in qualitative agreement with literature results on unfractionated samples.[14] The decrease of solubility when MS increases can be understood in terms of the hydrophobic character of the polymer, as measured for instance by C/O, the ratio of number of carbon over oxygen atoms in the molecule. The latter increases with the molar substitution, from 1.88 at MS = 3 to 2.25 at MS = 7. At high C/O values, a larger entropy loss occurs upon dissolution, as a larger structure enhancement is required from the solvent. Accordingly, the enthalpy of demixing (Figure 4) for the same fractions (M_w > 64 kg·mol^{-1}) increases with MS.

The results for fractions A8 and A9 reflect a higher solubility due to their low molar mass (M_w < 64 kg·mol^{-1},

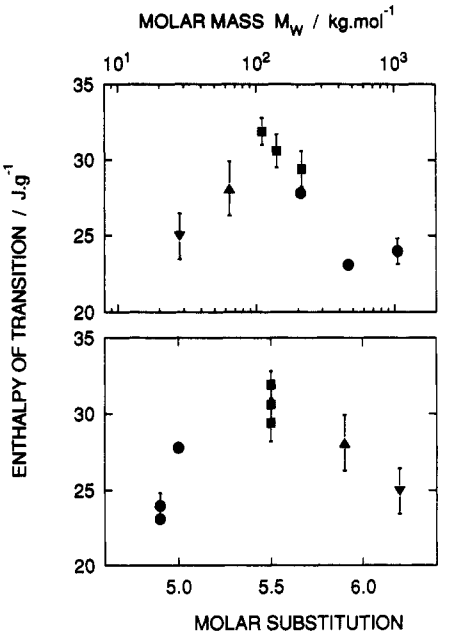

Figure 4. Enthalpy of phase separation in dilute solutions of HPC (w = 0.01) as a function of molar mass and molar substitution: (■) fractions B4, B7, and B10 (MS = 4.9–5.0; 209 ≤ M_w ≤ 1055 kg·mol^{-1}); (●) fractions A3, A5, and A6 (MS = 5.5; 110 ≤ M_w ≤ 212 kg·mol^{-1}); (▲) fraction A8 (MS = 5.8; M_w = 64 kg·mol^{-1}); (▼) fraction A9 (MS = 6.2; M_w = 28 kg·mol^{-1}). The error bars represent the standard deviation on values calculated by using different baselines and integration limits.

i.e., a degree of polymerization lower than 130), which increases the combinatorial entropy of mixing. Commercial HPC is prepared heterogeneously from cellulose and propylene oxide. Low molar mass species, which dissolved first in the course of the reaction, tend to be the most substituted. This is clearly apparent in Table I (see for instance B12, as compared to B10, or A9 and A8, as compared to A5). In view of the results of Figures 3 and 4, lowering M_w *and* increasing MS act in an opposite fashion on the solubility. Therefore, solutions of unfractionated HPC, which contain low molar mass material, have unpredictable phase transition parameters, from which no reliable structural information can be gathered. Indeed, literature data on the heat of transition of aqueous solutions of unfractionated commercial samples have been reported.[15] Values ranging from 30 to 50 J·g^{-1} were observed, but no consistent trend with M_w or MS could be emphasized, probably because some low molar mass material with a higher substitution was present in the samples. Similarly, measurements performed in our laboratory on a variety of commercial Klucel (E, G, LF, JF, M, and H) and Aqualon polymers (GF) showed that the spread of the endotherm (i.e., the difference between the temperatures at which 95% and 5% of the enthalpy of transition had been absorbed by the solution) was surprisingly constant, around 8–10 deg. The shape of the endotherm was, however, observed to vary with the polymer, as already noted for the fractions (Figure 2). It could be used to characterize HPC, provided further work is undertaken to relate it to the distribution of molar mass and molar substitution in the sample.

Effect of Concentration on the Phase Separation. Concentrated aqueous solutions of HPC are liquid crystalline. Like in the isotropic region, phase separation occurs upon heating, but the cloud point is strongly dependent on the polymer content. Figure 5 gives the transition temperatures measured by turbidimetry for solutions of fraction B10 (●). The phase diagram exhibits

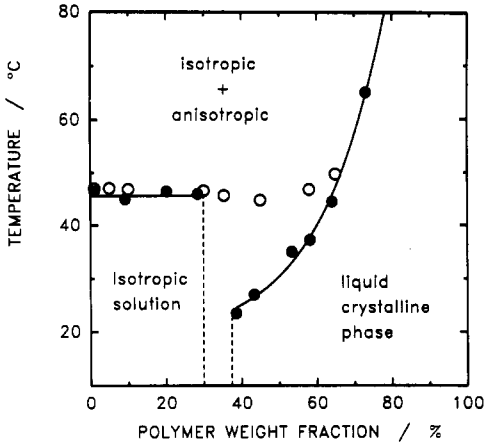

Figure 5. Phase diagram of aqueous solutions of polymer fraction B10 (MS = 5.0; M_w = 209 kg·mol^{-1}). The onset of phase separation was determined by turbidimetry (●). The transition temperatures calculated from the calorimetric traces are also plotted for comparison (○).

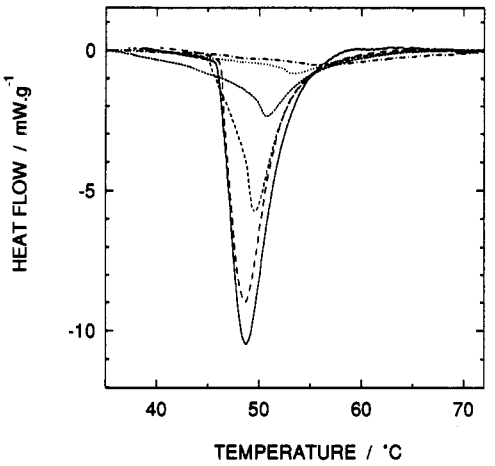

Figure 6. Thermograms of aqueous solutions of fraction B10 (MS = 5.0; M_w = 209 kg·mol^{-1}) at different concentrations: w = 0.01 (full line), w = 0.10 (long-dashed line), w = 0.30 (medium-dashed line), w = 0.45 (short-dashed line), w = 0.58 (dotted line), w = 0.65 (dashed-dotted line). Measurements were performed upon heating at 6 deg·h^{-1}. The plotted curves are the result of baseline subtraction and normalization to a unit mass of polymer.

the same features as already reported,[1] including (i) a single biphasic range throughout the normal liquid range of the solvent and (ii) a lower solubility of the most dilute mesomorphic solutions. The main difference in the phase diagram of the various fractions is in the critical polymer concentration, needed to form a liquid-crystalline solution. In contrast with previous observations[6] on unfractionated HPC, it changes considerably, for instance, from about 30% for fraction B10 to 42% for fraction A5. These variations reflect differences in M_w, which should play the crucial role in the critical concentration, in agreement with theoretical predictions.[16,17] The results of calorimetric measurements as a function of concentration are presented in Figure 6. Only a minor decrease of the onset temperature of the endotherm is observed as the concentration is increased from the isotropic ($w \leq 0.30$) to the cholesteric range ($w \geq 0.45$). As shown in Figure 5, the temperatures calculated by calorimetry (○) are in sharp contrast with the cloud points (●). There is no heat effect associated with the changes imparted to the anisotropic solutions below 47 °C. As a matter of fact, the formation of an isotropic solution ($w \simeq 30\%$) from the anisotropic solution ($w \geq 45\%$), as well as the subsequent increase in the amount of isotropic phase when the composition of

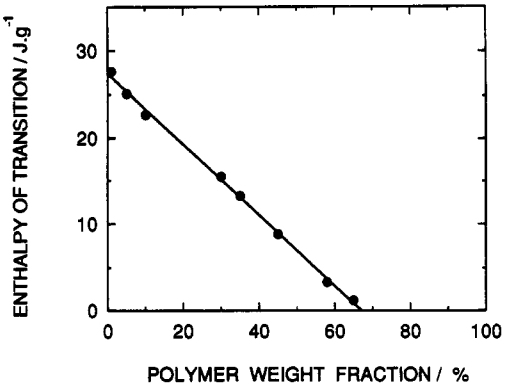

Figure 7. Enthalpy of phase separation in aqueous solutions of fraction B10 (MS = 5.0; M_w = 209 kg·mol^{-1}) as a function of concentration. The points have been obtained by integration of the thermograms of Figure 6.

the anisotropic solution evolves along the phase line, is an athermal phenomenon. This is a strong indication that the formation of the cholesteric phase from the isotropic solution, at constant temperature and composition, is also athermal. The endotherm observed upon heating cholesteric solutions occurs at about the same temperature as the transition in dilute solutions. It is therefore associated with phase separation happening in the isotropic phase in equilibrium with the cholesteric solution. Figure 6 shows that the enthalpy associated with phase separation decreases rapidly as the polymer concentration increases. The plot of the enthalpy as a function of polymer content is perfectly linear, as shown in Figure 7. No discontinuity occurs at the critical concentration, in accord with a thermal phenomenon limited to the isotropic phase. The enthalpy of transition extrapolates to zero at w = 67%, i.e., the minimum composition from which anisotropic solutions never form a concentrated isotropic solution upon heating (Figure 5). The heat associated with the transition of 1 g of polymer dissolved in an infinitely large quantity of water is 27.4 J·g^{-1}. For a fraction having MS = 5, this value represents about 3 kcal/mol of anhydroglucose segment, i.e., is of the order of the enthalpy needed to break 1 mol of hydrogen bonds/mol of polymer repeating unit.[18] The overall changes in the structure of the solvating water are therefore limited in magnitude, despite their dramatic effects on the polymer solubility. The absence of the heat of formation of the isotropic phase upon heating the most dilute anisotropic solutions between 25 and 47 °C indicates that there is no significant difference between the structure of water in both phases. The isotropic–anisotropic transition is driven by entropic factors alone, as predicted for semirigid polymers.[17]

Conclusions

Calorimetric measurements of the phase separation occurring in dilute aqueous solutions of HPC have shown that, at a sufficiently high molar mass (M_w > 64 kg·mol^{-1}), the solubility of the polymer is essentially controlled by the extent of substitution. The temperature and enthalpy of transition respectively decrease and increase when MS increases. For well-fractionated samples, calorimetry could be a useful tool for the characterization of HPC. Caution should however be exerted when interpreting results gathered on unfractionated polymers, as competing effects obscure the data. For a given HPC specimen, the enthalpy of phase separation is a linearly decreasing function of the polymer weight content. No discontinuity is observed at the isotropic–anisotropic critical composition and the thermal effect reflects only changes in the isotropic

phase. All results concur to indicate that the isotropic–cholesteric transition in aqueous HPC is a purely entropic phenomenon.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Thanks are due to Dr. A. S. Perlin for his helpful advice regarding the NMR characterization of HPC fractions.

References and Notes

(1) Fortin, S.; Charlet, G. *Macromolecules* **1989**, *22*, 2286.
(2) Charlet, G.; Gray, D. G. *J. Appl. Polym. Sci.* **1989**, *37*, 2517.
(3) Kyu, T.; Mukherjee, P. *Liq. Cryst.* **1988**, *3*, 631.
(4) Marsano, E.; Carpaneto, L.; Ciferri, A. *Mol. Cryst. Liq. Cryst.* **1988**, *158B*, 267.
(5) Winnik, F. M. *Macromolecules* **1987**, *20*, 2745.
(6) Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1984**, *17*, 1512.
(7) Conio, G.; Bianchi, E.; Ciferri, A.; Tealdi, A.; Aden, M. A. *Macromolecules* **1983**, *16*, 1264.
(8) Wirick, M. G.; Waldmann, M. H. *J. Appl. Polym. Sci.* **1970**, *14*, 579.
(9) Lee, D. S.; Perlin, A. S. *Carbohydr. Res.* **1983**, *124*, 172.
(10) Lee, D. S.; Perlin, A. S. *Carbohydr. Res.* **1984**, *126*, 101.
(11) Ho, F. F.-L.; Klosiewicz, D. W. *Anal. Chem.* **1980**, *52*, 913.
(12) Aden, M. A.; Bianchi, E.; Ciferri, A.; Conio, G.; Tealdi, A. *Macromolecules* **1984**, *17*, 2010.
(13) Lee, D. S.; Perlin, A. S. *Carbohydr. Res.* **1982**, *106*, 1.
(14) Klug, E. D. *J. Polym. Sci., Part C* **1971**, *36*, 491.
(15) Medved, Z. N.; Petrova, N. I.; Tarakanov, O. G.; Rotenberg, I. M. *Polym. Sci. USSR* **1985**, *27*, 1795.
(16) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.
(17) Flory, P. J. *Macromolecules* **1978**, *11*, 1141.
(18) Franks, F.; Reid, D. S. In *Water, A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1973; p 102.