Colloid Polym Sci 279:1139–1143 (2001)
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SHORT COMMUNICATION

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Effects of pressure on the behavior of (hydroxypropyl)cellulose in aqueous solution

Received: 14 March 2001
Accepted: 3 May 2001

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Abstract The effects of pressure and temperature on the phase behavior of aqueous solutions of (hydroxypropyl)cellulose (HPC) were investigated at low and high concentrations. In dilute solutions, the transition temperature (T_t) as measured by apparent light scattering increased with an increase in pressure at lower pressures, but decreased with increasing pressure above 100 MPa. At lower temperatures, the transition pressure (P_t) increased slightly with increasing temperature, but decreased with at temperatures above 10–15 °C. Both T_t and P_t showed a moderate polymer-concentration dependence and they also showed strong concentration dependence on salt; T_t and P_t decreased with increasing concentrations of KCl and K_2SO_4, whereas the addition of KI or KSCN increased T_t and P_t. The apparent absorbance of concentrated solutions (62.5%) of HPC, in a cholesteric (chiral nematic) mesophase, was also measured. The spectrum shifted to a longer wavelength under high pressure. These results could be explained by assuming that the helicoidal pitch was increased under elevated pressure, probably due to a decrease in the angle between the two semiflexible and twisted HPC molecules in adjacent planes under high pressure.

Key words Pressure effects · Phase behavior · (Hydroxypropyl)cellulose · Liquid-crystal

Introduction

Aqueous solutions of (hydroxypropyl)cellulose (HPC) and its homologues are known to show characteristic phase properties [1–7]. At lower concentrations, they dissolve at higher temperatures into (micro)crystal solvates, and at higher concentrations they form a cholesteric type of mesophase (chiral nematic).

The physicochemical properties of the phase-transition of thermoresponsive synthetic polymers, such as poly(*N*-isopropylacrylamide) (polyNIPAM) and poly(*N*-vinylisobutyramide) (polyNVIBA), have been studied [8–12]. We have investigated the effects of pressure on their behavior and showed that the pressure effects were highly interactive with the effects of inert salts. Furthermore, these results can be generally explained in terms of hydration and dehydration processes, and the effects of pressure on them.

The apparent transition properties and light scattering behavior of these polymers upon a variation in temperature are similar to those of dilute solutions of HPC. Furthermore, Nishio et al. [13] reported that the maximum reflectance of concentrated aqueous HPC solution in a cholesteric (chiral nematic) mesophase is highly influenced by the presence of inert salt; salting-in (lyotropic) anions such as SCN^- shifted the apparent peak wavelength of the reflectance spectrum toward a longer wavelength, whereas a salting-out anion (Cl^-)

resulted in a blueshift in the peak. The results can be explained by the cholesteric pitch of the liquid crystal affected by both temperature and the anions added.

In this study, we investigated the effects of pressure on the phase behavior of HPC in both dilute and concentrated aqueous solutions. We found that pressure strongly affects the dissolution temperature and the light-reflecting properties over two concentration ranges, respectively, and that the pressure effects are strongly interactive with added inert salts.

Experimental

HPC was obtained from Tokyo Kasei Co. [Tokyo, Japan; H0474: 6–10 cps (2% in water at 20 °C), MS = 3.2, $M_n \sim 60$ kDa].

The cloud points for aqueous solutions of HPC were determined by observing light transmission or light scattering. The light transmission (or absorbance) of the sample was measured under controlled pressure using an inner-cell-type high-pressure optical cell with two sapphire windows (Teramecs, Kyoto, Japan), which was placed in a single-beam spectrophotometer (Multispec 1500, Shimadzu, Kyoto, Japan). The temperature of the sample solution in the cell was controlled by a Peltier-type thermoregulator and was monitored using a Pt resistance thermometer.

For the measurements of apparent light scattering, another type of high-pressure optical cell with three sapphire windows and a quartz inner optical cell (Teramecs Co.) was placed inside a conventional fluorophotometer (RF5000, Shimadzu Co., Kyoto, Japan). The apparent light scattering at the same excitation and emission wavelengths (363 nm) was then recorded. In this apparatus, thermostated water containing ethylene glycol as the antifreeze was circulated through the cellblock, and the temperature of the solution inside the cell (just outside the inner cell) was monitored using a Cu–constantan thermocouple.

In both cases, the extraneous pressure was applied by a high-pressure hand pump equipped with an intensifier (ratio 8.5:1) (Teramecs Co.). The pressure was mediated by deionized water and was measured using a Bourdon-tube-type pressure gauge. The temperature and pressure scanning rates were approximately 0.5 °C/min and 5 MPa/min, respectively.

In order to measure concentrated HPC solutions, the sample solution was sandwiched between two glass slides, covered with plastic film, and then placed in the sample chamber inside the optical cell of the absorbance (transmittance) observation system, perpendicular to the incident light beam. The cell was later filled with distilled water and sealed with a rubber cap. This system is different from that used in a previously reported study on the pressure effect of HPC [14]. In the latter case, a bottle-type sample cell filled with HPC solution was used, and the reflection from the sample close to the cell wall only was measured.

Results

Dilute aqueous solutions

The turbidity change of a dilute (1 w/w%) solution of HPC was measured by temperature-scanning at constant pressure or by pressure-scanning at constant temperature. In each case, a sudden spike in the scattering which depended on the other variable was observed. These apparent transition points (T_t and P_t) are plotted on the T–P plane in Fig. 1. At lower pressures, the transition temperature increased with an increase in pressure, but above 100 MPa it decreased with increasing pressure. At lower temperatures, the transition pressure increased slightly with increasing temperature, but above 10–15 °C, it decreased with increasing temperature. Hence, we observed two extremes; one maximum T_t at around 100 MPa and one maximum P_t at around 15 °C.

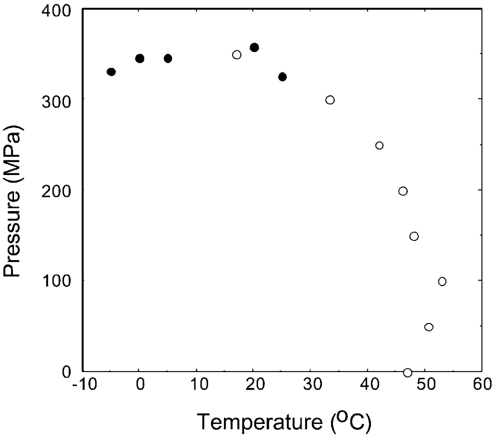

Fig. 1 Diagram of the transition temperatures and the transition pressures of a 1 w/w% aqueous solution of (hydroxypropyl)cellulose (*HPC*) in the *T–P* plane.The *open symbols* represent data obtained by temperature-scanning, and the *closed symbols* represent data obtained by pressure-scanning. The temperature- and pressure-scanning rates were approximately 0.5 °C/min and 5 MPa/min, respectively

The temperature-induced HPC transition in the low-concentration range has been described as almost independent of the polymer concentration; in other words, the phase diagram in the concentration–temperature plane showed a phase boundary almost parallel to the concentration axis. Figure 2, however, shows the concentration dependence of T_t and P_t measured up to 5 w/w%, and they actually showed a moderate concentration dependence. When compared to the results for the thermoresponsive vinylpolymers, these concentration dependencies are quite evident.

T_t and P_t showed a much greater dependence on the concentration of added salt (anion), as illustrated in Fig. 3. Both T_t and P_t decreased with increasing concentrations of KCl and K_2SO_4, whereas the addition of KI or KSCN increased T_t and P_t. T_t of polyNVIBA or polyNIPAM solution in the presence of K_2SO_4 and KCl decreased almost linearly with increasing salt concentrations over a range similar to that used here [9]. For a divalent anion (SO_4^{2-}), T_t of HPC dropped sharply with an increase in the salt concentrations, and the KCl results cannot be explained in terms of ionic strength; the slope for K_2SO_4 is more than 5 times that for KCl. In contrast, with the addition of I^- or SCN^-, an upward shift in T_t was first observed with an increase in the salt concentration and then T_t levels off. These

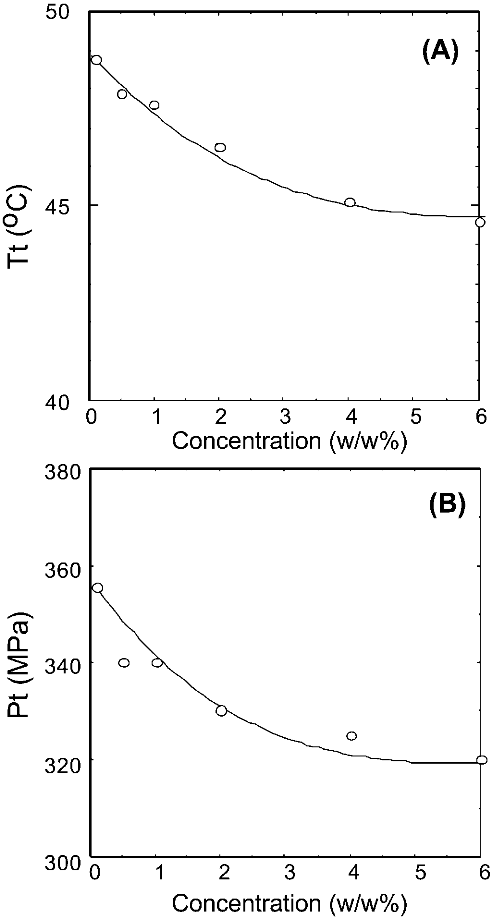

Fig. 2 Concentration dependence of **A** the transition temperature and **B** the transition pressure of aqueous solutions of HPC. **A**: 0.1 MPa; **B**: 20 °C

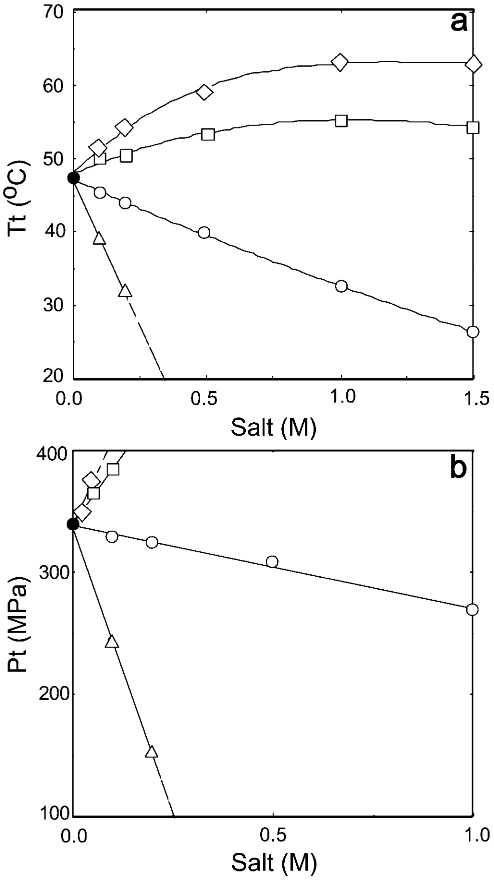

Fig. 3 Salt (anion) concentration dependence of **a** the transition temperature and the transition pressure of aqueous (1 w/w%) solutions of HPC. KCL: ○, K_2SO_4: △, KI: □, KSCN: ◇. **a**: 0.1 MPa; **b**: 20 °C

results from the different effects depending on the anionic species seem to be in line with the lyotropic series or Hofmeister series of anions. Anions with very low lyotropic numbers induced a linear decrease in T_t, whereas those with very high numbers showed an apparent maximum T_t with changes in the concentration.

The effects of the addition of these salts on the pressure behavior (P_t) were similar to the effects on T_t, but the characteristics of the ionic species were more clearly observed. The measuring temperature was set at 20 °C, taking the lowered T_t under high salt concentrations into account. The addition of SO_4^{2-}caused a sharp and simple downward shift of the transition pressure for both polymers. At 0.2 M, P_t decreased to almost 150 MPa, about 200 MPa less than the control. Again the difference due to KCl cannot be explained in terms of the ionic strength alone. Upward shifts were observed upon the addition of anions with very high lyotropic numbers (such as I^- and SCN^-) and resulted in a distinct increase in the transition pressure beyond the range of our equipment limit at about 0.1 M. These values did not return to the measurable range over the concentration range studied here (below 1.5 M).

Concentrated solutions

Concentrated HPC solutions (60–75%) are known to show characteristic colors owing to their selective reflectance of visible light. The peak in the apparent absorbance (reflectance) spectrum showed redshifts upon an increase in pressure from atmospheric pressure. The spectral change was rather slow and converged to form a single peak at a longer wavelength after several hours. The recovery of this shifted peak after the release of the applied high pressure was comparatively fast; the peak shifted back to its original position after 90 min following the release of the 200-MPa pressure. The pressure dependence of the reflectance peaks measured at 20 and 30 °C after incubating the sample under each

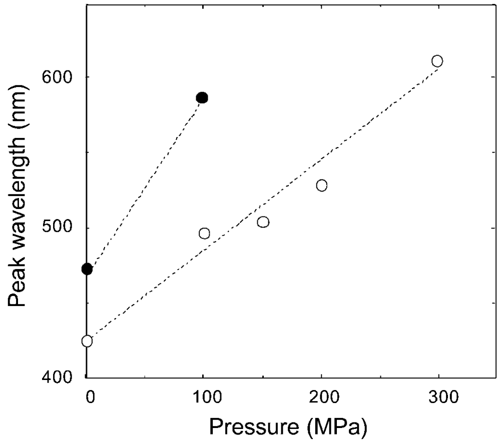

Fig. 4 Pressure dependence of the apparent peak wavelength of the reflectance spectrum of a 62.5% (w/w) HPC aqueous solution at 20 (○) and 30 °C (●)

pressure for 6 h is shown in Fig. 4. At each temperature, the peak shifted to a longer wavelength at higher pressures, and the shift per increment in pressure seemed to be steeper at the higher temperatures.

Werbowyj and Gray [4] analyzed the effects of sample thickness and the angle of the incident beam on the relationship between the apparent peak of the reflectance spectrum and the structure of a liquid crystal. For a thin-layered sample placed perpendicular to the incident light beam, as in the present study, the de Vries theory [15] can be applied,

$$\lambda_0 = \tilde{n}P \ , \tag{1}$$

where λ_0 is the wavelength of the normally reflected light in air, $\tilde{n}$ is the average refractive index of the mesophase, and P is the helicoidal pitch. In a thicker sample, the shorter wavelengths of light will be reflected and thus the peak will become less pronounced. Although the sample thickness could not be controlled under high pressure, it probably became thinner under atmospheric pressure. Indeed, the peak became sharper with increasing pressure, and the apparent reflectance intensity became smaller.

Discussion

HPC has the ability to form hydrogen bonds with water and also to cause structural changes in the solvent water because of its nonpolar methyl and methylene groups. In thermoresponsive vinyl polymers, the phase transitions occur owing to dehydration and the strengthening of hydrophobic interactions among the side chains, as well as the structural deformation of water around the hydrophobic groups. These changes are caused by both increasing temperature and increasing pressure.

Hydrophobic interactions among alkyl chains have been found to produce slightly positive volume changes [16]. Recent theoretical analyses of the effects of pressure on hydrophobic interactions among simple carbohydrates also suggested that solvent-separated species were favored at higher pressures [17]. At least up to a certain pressure, therefore, the pressure increased the coil-collapse transition temperature in thermoresponsive polymers, in a manner similar to salting-in ions. Similar to the thermoresponsive vinyl polymers and proteins, a turning point in this pressure-dependent behavior was observed at medium pressure for HPC. The compressibility of bulk water is greater than hydrophobically hydrated water, and thus the situation previously described can be inverted by increasing the pressure. Above 200 MPa, hydrophobic interactions are favored again.

In many different examples (from oligopeptides to synthetic water-soluble polymers), the effectiveness of salt addition (especially that of anions) follows the Hofmeister or lyotropic series [18–20]. In a study on the higher-order structure of proteins such as ribonuclease A, it was demonstrated that anions with higher lyotropic numbers (salting-in ions) caused the denaturation of proteins into coil-like structures, whereas those with lower lyotropic numbers (salting-out ions) induced native and ordered structures (globule state) [21]. The effects of salt on the transition properties of these vinyl polymers can be explained in a similar context [11, 12]. Salting-in anions such as SCN^- may disrupt the structure of bulk water and stabilize the hydrophobic hydration, thus favoring coil-like structures. In contrast, salting-out anions act as structure makers for water molecules, effectively strengthening the hydrophobic interactions that promote the collapse state in polymers.

In a concentrated HPC solution, pressure simply increased the apparent helicoidal pitch. The effects of salt on the reflective properties of the HPC mesophase as reported by Nishio et al. [13] can be interpreted in terms of the stabilization of the hydrophobic hydration (salting-in ions) and the strengthening of hydrophobic interactions (salting-out ions). The effects of pressure observed on the apparent helicoidal pitch are phenomenologically similar to the effects of salting-in ions.

The refractive index is known to be pressure-dependent [22], but the effects of pressure on normal liquids and solutions have been reported to be less than 3%. The wavelength shift observed in the present experiment reached 40% of that at atmospheric pressure; however, changes in the solution density or concentrations alone cannot explain the apparent results. Thus, the present results are best explained by an increase in the actual helicoidal pitch under elevated pressure.

Hydrogen-bonding properties, on the other hand, have been reported to be strengthened by pressure [23], and this might contribute to a change in the configuration of the twisted structure of HPC and may result in a modified arrangement of the adjacent chains. The linearity of the polymer chains may favor the formation of intramolecular hydrogen bonds, and the association of water molecules is very strong in the single anisotropic phase. Under these high concentrations, only about two water molecules are present per oxygen of the polymer, and thus a considerable amount of water will be fixed, leaving a reduced amount of free water. Therefore, HPC chains display a more hydrophobic surface to the solvent in the cholesteric phase and this enhancement of the water structure around them minimizes any unfavorable contact with the neighboring chains.

The semiflexible or stiff-chain structure of HPC, coupled with its roughly helical- or twisted-chain configuration, produces a macroscopic helicoidal structure characteristic of the cholesteric state. The helical pitch of such a planar cholesteric structure is determined by the distance between the polymers in adjacent planes and by the angle between them. The apparent elongation of the helical pitch observed under high pressure is best explained by a reduction in the angle between the two semiflexible and twisted HPC molecules in adjacent planes under high pressure.

Acknowledgements The authors wish to acknowledge Y. Nishio of Tokyo A&T University, Koganei, Japan, and R. Lange of INSERM U128, Montpellier, France, for their useful advice and helpful discussions. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan to S.K.

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