CELLULOSE CHEMISTRY AND TECHNOLOGY

TRANSPORT PROPERTIES OF CHEMICALLY CROSSLINKED HYDROXYPROPYL CELLULOSE IN SOLVATED STATE

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Transport properties of chemically crosslinked hydroxypropyl cellulose (HPC) in the solvated state were investigated. Chemical crosslinking of HPC was performed by esterification of hydroxyl groups using adipoyl chloride as a crosslinker. The formation of a permanent network by the crosslinking was confirmed by limited swelling of the HPC film in acetone. Furthermore, the wide-angle X-ray scattering profile showed the crosslinked HPC retained the liquid crystalline supramolecular order even in the solvated state. The lyotropic liquid crystallinity in the solvated HPC film was affected by the solvents used. Furthermore, the permeability and diffusivity of neutral red through the crosslinked HPC membrane showed a marked contrast in the two types of solvents, i.e., ethanol and 1-propanol. This, in turn, suggests that the transport properties within the HPC film can be controlled by the lyotropic liquid crystalline order.

Keywords: hydroxypropyl cellulose, crosslinking, transport properties

INTRODUCTION

Cellulose and its derivatives have long and widely been utilized as raw materials for making fibers, films, and membranes for textile, packaging, and separation purposes. Among the cellulosic materials that have ever been developed and commercially utilized, hydroxypropyl cellulose (HPC) possesses versatile functionalities, which are not present in other cellulose derivatives. HPC is a thermoplastic polymer that shows solubility in many common solvents with variant polarities, such as water and dichloromethane. Moreover, HPC has the ability to form cholesteric liquid crystalline phase on heating or in its concentrated aqueous or organic solutions.[1-4] Various approaches have been proposed to control the liquid crystalline properties of HPC. For example, Nishio *et al.* investigated the effect of salt addition on the cholestericmesophase structure of concentrated aqueous solution of HPC.[5] Functionalization has also been performed by several researchers.[6-8]

Chemical crosslinking of cellulosic materials has been performed to regulate the swelling behavior and functionalities, such as drug releasing ability.[9] Crosslinking of HPC has also been attempted to enhance its mechanical strength and control its liquid crystalline phase transition behavior. Bhadani and Gray reported the preparation of a highly crosslinked cholesteric network of HPC.[10] In their study, crosslinking was performed by introducing a vinyl group as a side chain of HPC and then linking the vinyl termini by UV photoradical polymerization using acrylic acid as a monomer. Mitchell and his coworkers prepared crosslinked HPC using adipoyl chloride as a crosslinker, to which propionyl chloride was mixed in a variable ratio.[11] They further investigated the effect of the crosslinking degree on the high-order structure and swelling behavior of HPC. The effect of crosslinking on the thermal and mechanical properties of HPC was also investigated by Rials and Glasser.[12] Furthermore, crosslinking has been performed to retain the liquid crystalline order, which causes coloring due to selective light reflection.[13] Chiba *et al*. prepared a photo-crosslinked HPC network, which showed selective light reflection depending on the type and concentration of the ions added to the solution.[14] The HPC network reversibly responds to electric field changing its color. Other applications, such as making composites with polycarbonate urethane and inorganic particles,[15] drug releasing carrier,[16-18] and food packaging[19] have also been considered.

Aside from these previous studies, the effect of crosslinking on the transport properties of HPC, such as the permeability of small molecules, has not yet been clarified. In this study, we have investigated the permeability through the crosslinked HPC membrane in solvated state by using neutral red as probe substance. As a function of the solvent type and crosslinking degree, the permeability is evaluated and discussed in terms of the liquid crystalline order in the solvated state.

EXPERIMENTAL

Materials

Commercial HPC (Wako Chemical, Japan, 150-400cp) was used as received. The degree of substitution and of molar substitution of HPC, estimated by ^{1}H- and ^{13}C-NMR,[20] was 1.6 and 2.8, respectively. Weight-averaged molecular weight and polydispersity index, determined by GPC using tetrahydrofuran (THF) as an eluent, were 4.2×10^5 and 2.4, respectively. Commercial adipoyl chloride (Sigma-Aldrich Co., Milwaukee, WI, US) was used as received.

Preparation of crosslinked HPC (HPC-c)

Crosslinking of HPC was performed by esterification of HPC using adipoyl chloride as a crosslinker. THF solution of HPC with varying concentration was cast onto a Teflon® petri dish, to which adipoyl chloride solution in THF was added dropwise. The petri dish placed in a separable flask was kept under nitrogen atmosphere at the ambient temperature until the solution lost its fluidity and a free-standing film of HPC was formed. The formation of the gel-like HPC film took place in 3 to 4 days. Crosslinking of HPC was confirmed by limited swelling of the film in acetone. The reactants remaining in the crosslinked HPC were removed by washing the film in water and further in acetone. After the washing, the crosslinked HPC film was vacuum dried for 1 day at 100 °C. In the following sections of this paper, the crosslinked and uncrosslinked HPCs are abbreviated as HPC-c and HPC-u, respectively.

Wide-Angle X-ray Scattering (WAXS)

WAXS patterns of HPC films were acquired using a Rigaku RINT-2500 system, operating at 40 kV and 200 mA. Measurements were performed on a Bragg-Brentano type goniometer in the transmission mode. Scans were performed in the 2θ range from 5 to 45° at 2° min^{-1}. The crystallinity of the HPC films was calculated as the ratio of integrated peak intensities against the entire scattering intensity.

Diffusion measurement of neutral red through HPC-c film

The transport properties of the HPC-c film were investigated by diffusion experiments of neutral red (NR) dissolved in ethanol or 1-propanol. The diffusion experiments were carried out on a laboratory-made apparatus, as shown in Figure 1.[21,22] In this apparatus, the HPC-c film with an effective channel area of 2.0 cm^2 was placed between a reservoir and a sink. The reservoir and the sink were filled with 0.1 mM NR solution in the alcohols and the corresponding alcohol, respectively. The diffusion of the NR molecule across the HPC-c film was monitored by UV-vis measurement (Varian Inc., Cary-3 UV-vis spectrophotometer, Palo Alto, CA) by periodically taking up 1-mL solution samples from the sink. After the UV-vis measurement, the solution was immediately returned to the sink. The concentration of NR was estimated from the absorbance by using a linear calibration line prepared in the concentration ranges up to 12 μM. Previous to the diffusion measurement of NR, the perfection of the membrane (no cracks or holes) was confirmed by measuring the diffusion of 0.1% (v v^{-1}) toluene in hexane. No emission of toluene from the reservoir to the sink was detected.

RESULTS AND DISCUSSION

Effect of crosslinker and polymer concentration on gelation behavior of HPC

We first investigated the effect of HPC concentration and amount of adipoyl chloride on the gelation behavior of HPC in THF. Table 1 summarizes the final state of the reaction mixture after the addition of adipoyl chloride. Gelation occurred when the HPC concentration and the amount of adipoyl chloride exceeded 5% (w w^{-1}) and 25% (mol (mol OH)$^{-1}$ in HPC), respectively. Among them, the smoothest, flattest, and most transparent film of HPC-c was obtained from 5% (w w^{-1}) HPC solution to which 40% (mol (mol OH)$^{-1}$ in HPC) of adipoyl chloride was added. Increasing the amount of adipoyl chloride to 50% gave a similar result to the addition of 40%adipoyl chloride. Investigations of physical properties were performed using these HPC-c films.

Figure 2 shows WAXS profiles of HPC-u and HPC-c. In both samples, a diffraction peak at about $2\theta = 9°$ arising from interchain spacing of HPC is observed.[23-26] The appearance of a small-angle diffraction peak in HPC-c suggests that the mesomorphic order of HPC-u is retained after the crosslinking. The structural difference of the HPC-c film in ethanol and 1-propanol is obviously reflected in the WAXS profiles shown in Figure 3.

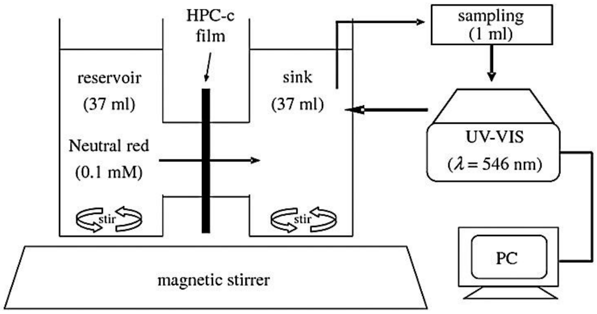

Figure 1: Scheme of the apparatus for measuring diffusivity of neutral red solution through crosslinked HPC (HPC-c) film

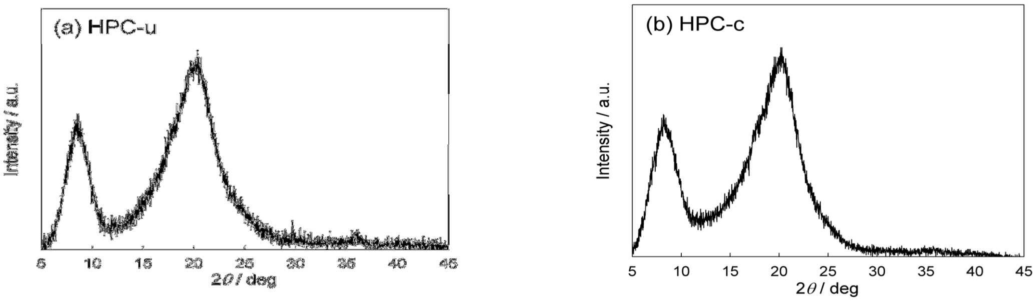

Figure 2: Wide angle X-ray scattering patterns of (a) HPC-u and (b) HPC-c (crosslinker: 40%(mol (mol OH)$^{-1}$ in HPC)) in dried state

Table 1
Effect of polymer concentration and adipoyl chloride on gelation behavior of HPC

Feed ratio of adipoyl chloride (%, mol (mol OH)$^{-1}$)[a]	Concentration of HPC (%, w w^{-1})			
	1	2	5	7
15	sol	sol	sol	sol
25	sol	sol	gel	gel
40	sol	sol	gel	gel

[a] molar percentage relative to that of hydroxyls in HPC

Namely, the WAXS profile of HPC-c in ethanol is rather broadened and the small-angle diffraction peak at $2\theta = 10°$ is shifted toward larger angles. This suggests that the HPC-c is quite swollen in ethanol and thus less ordered. On the other hand, the WAXS profile of HPC-c in 1-propanol shows sharper peaks than in ethanol, suggesting that the liquid crystalline order is better retained.

Transport properties of HPC-c film

The diffusion of NR through two kinds of HPC-c films at room temperature was investigated and analyzed on the basis of our previous studies.[21,22] Figure 4 shows the concentration of NR in the sink, C_s, as a function of time, *t*. In the case of diffusion in ethanol, the increase of C_s occurred slowly after a short lag time. In contrast, in the case of diffusion in 1-propanol, C_s steeply increased after a relatively long lag time.

The lag time t_0 was estimated as t-intercept of the linear regression line of the C_s – t plot.

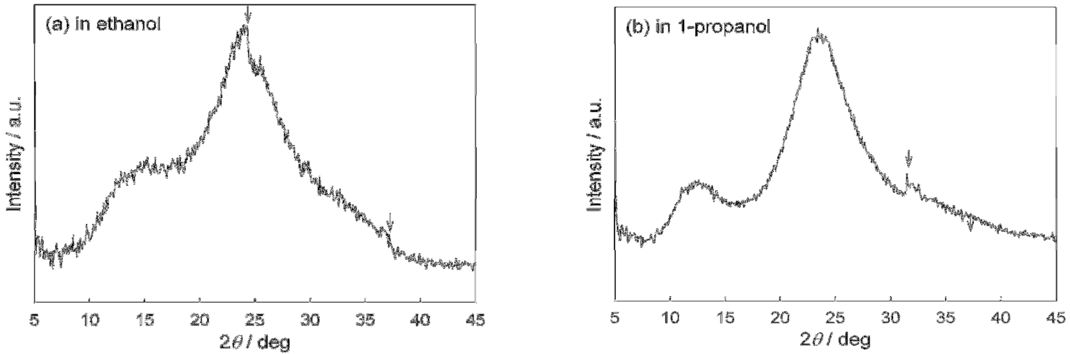

Figure 3: WAXS profiles of HPC-c films (crosslinker: 40%(mol (mol OH)$^{-1}$ in HPC)) swollen in (a) ethanol and (b) 1-propanol. Steep changes in intensity marked by arrows are artifacts caused by sample deformation during the measurements

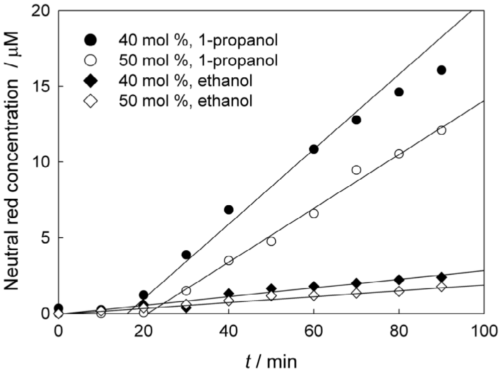

Figure 4: Diffusion of neutral red through HPC-c films with different crosslinking degrees

Table 2

Diffusivity and permeability parameters of neutral red in HPC-c films

Solvent	Adipoyl chloride (%mol (mol OH)$^{-1}$ in HPC)	t_0 (s)	L_m (µm)	$\overline{D}$ (cm^2 s^{-1})	dC_S/dt (mM s^{-1})	N (molcm^{-2} s^{-1})	$\overline{P}$ (cm^2 s^{-1})	$\overline{K}$ (-)
Ethanol	40	83	227	1.03×10^{-6}	4.78×10^{-4}	8.85×10^{-9}	2.00×10^{-5}	19.4
	50	147	189	4.07×10^{-7}	3.20×10^{-4}	5.91×10^{-9}	1.12×10^{-5}	27.5
1-Propanol	40	966	195	6.57×10^{-8}	4.12×10^{-3}	7.62×10^{-8}	1.49×10^{-4}	2264
	50	1255	199	5.23×10^{-8}	2.96×10^{-3}	5.48×10^{-8}	1.09×10^{-4}	2080

Furthermore, the diffusion coefficient, $\overline{D}$, the flux, N, the permeation coefficient, $\overline{P}$, and the partition coefficient, $\overline{K}$, of NR in the HPC-c film were calculated by the following equations:

$$\overline{D} = \frac{{L_m}^2}{6t_0} \tag{1}$$

$$N = \frac{dC_s}{dt} \cdot \frac{V_s}{A_m} \tag{2}$$

$$\overline{P} = N \cdot \frac{L_m}{(C_R - C_S)} \tag{3}$$

$$\overline{K} = \frac{\overline{P}}{\overline{D}} \tag{4}$$

where L_m, A_m, C_R, and V_s are thickness and effective area of the HPC-c membrane, concentration of NR in the reservoir and the volume of the solution in the sink, respectively. The calculated parameters are listed in Table 2. In this calculation, the value of $C_R - C_S$ was regarded constant (0.1 mM) throughout the experiment, because the estimated C_S was sufficiently smaller than C_R. The values of $\overline{D}$, N, $\overline{P}$ and $\overline{K}$ were larger in the HPC-c with 40% adipoyl chloride content(mol (mol OH)$^{-1}$ in HPC) than in that with 50% (mol (mol OH)$^{-1}$in HPC). This result shows that, as the crosslinking degree becomes higher, the permeability and diffusivity of NR is lowered in the HPC-c film. A detailed discussion on the parameters is given in the following section.

Effect of solvent type on the permeability and diffusivity in HPC-c film

The permeation and diffusion of NR in the HPC-c films showed a marked contrast depending on the type of solvent used: in ethanol, NR diffused rapidly, but permeated slowly; in 1-propanol, NR diffused slowly, but permeated rapidly. These differences are reflected in the parameters shown in Table 2, in which larger $\overline{D}$ and smaller $\overline{P}$ were estimated in ethanol, and vice versa.

The solubility of HPC in ethanol and 1-propanol, which is considered as a factor affecting the permeation and diffusion of NR in the HPC-c film, is discussed by employing the concept of Hansen solubility parameters (HSP).[27] In HSP theory, Hildebrand solubility parameter δ is divided into three components by the following equation:

$$\delta^2 = \delta_D{}^2 + \delta_P{}^2 + \delta_H{}^2 \qquad (5)$$

In Eq. (5), the subscripts D, P, and H denote the dispersive force, polarity, and hydrogen bonding, respectively. The reported values of HSPs for ethanol, 1-propanol and commercial HPCs are listed in Table 3. Because there is little difference in δ_D, a comparison of the data can be made by plotting δ_H versus δ_P, as shown in Figure 5. In this plot, both ethanol and 1-propanol are located in the 'interaction circle' of each HPC, implying that both alcohols act as good solvents for the HPCs. However, there is a slight difference in the 'goodness' of both alcohols for each HPC, as indicated by the distance between the center of each circle and points for each alcohols. This suggests that the interaction of HPC with the solvents is affected by the polarity and hydrogen bonding ability of each HPC. Molecular properties, such as degree of substitution, molar substitution, and molecular weight of HPC, may also influence these interactions.

Table 3
Hansen solubility parameters (literature data) of commercial HPCs and solvents used

	δ^a ((MPa)$^{1/2}$)	$\delta_D{}^b$ ((MPa)$^{1/2}$)	$\delta_P{}^c$ ((MPa)$^{1/2}$)	$\delta_H{}^d$ ((MPa)$^{1/2}$)	R^e ((MPa)$^{1/2}$)
Ethanol[f]	26.5	15.8	8.8	19.4	-
1-Propanol[f]	24.6	16.0	6.8	17.4	-
HPC (Exxon)[g,h]	25.6	17.6	10.2	15.3	9.4
HPC (Dow)[g,h]	23.9	17.2	9.8	13.5	7.3

[a]Total solubility parameter (Hildebrand solubility parameter); [b]Dispersive term; [c]Polarity term; [d]Hydrogen bonding term; [e]Radii of interaction circle; [f]Ref. 27; [g]Ref.28; [h] The original values in the cited literature are given in (cal cm^{-3})$^{1/2}$

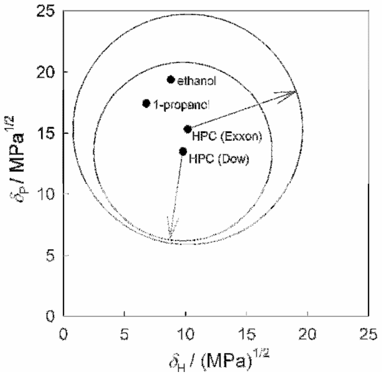

Figure 5: Plot of Hansen solubility parameters of commercial HPCs, ethanol and 1-propanol

Following the above-mentioned discussions, the differences in permeability and diffusivity in ethanol and 1-propanol are interpreted as follows: in ethanol, the highly swollen HPC-c film offers space for NR to diffuse, resulting in high diffusivity, but the distribution coefficient is lower than in the 1-propanol system, thus resulting in low permeability. In contrast, less space is given for NR to diffuse and retain in the 1-propanol-swollen HPC-c film, in which more of the liquid crystalline order remains. This leads to low diffusivity, but there is a higher permeability, because the equilibrium distribution coefficients of NR in the 1-propanol-swollen films are much larger than in the ethanol-swollen films. These findings further show that the transport properties of HPC can be controlled by altering the liquid crystalline order through the interaction with the surrounding media.

CONCLUSION

The effect of chemical crosslinking of HPC by adipoyl chloride on the thermomechanical, liquid crystalline and transport properties of the former are summarized as follows. Crosslinked HPC, HPC-c, was successfully prepared from 5% (w w^{-1}) HPC solution in THF, to which more than 40% (mol (mol $OH)^{-1}$ in HPC) of adipoyl chloride was added as a crosslinker. HPC-c retained the lyotropic liquid crystalline structural order even in the solvated state. The permeability and diffusivity of HPC-c, as probed by neutral red, were controlled by the crosslinking degree and the type of the solvent used. In particular, the type of the solvent significantly affected the permeation and diffusion behavior by altering the liquid crystallinity of HPC-c in the swollen state.

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