Gas Transport Phenomena in Hydroxypropyl Cellulose Solid Film Retaining Cholesteric Liquid Crystalline Order

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ABSTRACT: Two kinds of hydroxypropyl cellulose (HPC) films were prepared: one retained cholesteric liquid crystalline order (HPC-A), and another was amorphous (HPC-B). Gas transport phenomena in the HPC-A films were determined at 20°C, which is below the T_g of HPC, compared with those in the HPC-B films, by using mainly oxygen and nitrogen gases; herium and carbon dioxide gases were also used. The permeability coefficient P for the HPC-A films was smaller than that for the HPC-B films by approximately 10 times. The gas permselectivity, defined as the ratio of P for each gas, was affected by the liquid crystalline order, as follows: The permselectivity for the HPC-A films was greater than that of the HPC-B films. The trends of gas permeability and permselectivity for the liquid crystal-forming HPC films were the same as those reported for other liquid crystal-forming cellulosic films. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1465–1470, 1998

Key words: hydroxypropyl cellulose; cholesteric liquid crystal; amorphous films; gas permeability; gas permselectivity

INTRODUCTION

Recently, much attention has been given to the interesting properties of naturally occurring liquid crystalline polymers.[1–3] One of the applications of such liquid crystalline polymers was a gas or material-separation film.[4] We have prepared the cellulosic solid films retaining cholesteric liquid crystalline order (hereafter, CLCO solid films)[5–11] and determined the gas permeability in the ethyl cellulose (EC) solid films[12]; the CLCO EC solid films exhibited better permselectivity of oxygen and nitrogen gasses, compared with that of amorphous EC solid films. Our data suggested that the CLCO in the solid films results in a better permselectivity of gases.[12]

In this study, we tried to confirm the trend of the improved permselectivity for the CLCO EC solid films by using another cellulosic CLCO solid film, hydroxypropyl cellulose (HPC) solid film. We determined the characteristics of the gas permeability in the CLCO HPC solid film at 20°C by comparing with those of the gas permeability in an amorphous HPC solid film. HPC is crystalline and forms lyotropic liquid crystals in many kinds of solvent. Methanol was chosen for a liquid crystal-forming solvent. However, we failed to find suitable solvents in which HPC formed no liquid crystals. Consequently, the amorphous HPC solid film could not be prepared by the usual casting process with ease. The casting at an elevated temperature was adopted for the preparation of the amorphous HPC solid film in this study. The CLCO in the HPC solid films was ascertained by means of circular dichroism and polarized microscope. Gases used in this study were nitrogen, oxygen, carbon dioxide, and herium.

EXPERIMENTAL

Samples

HPC was used as supplied from Tokyo Kasei Ko-gyo Co. Ltd. The weight- and number-averaged molecular weights were 11.7×10^4 and 5.2×10^4, respectively. The molar substitution was 4.25. Methanol and triethylene glycol (Kanto Kagaku Co. Ltd.) were used as solvent. Both solvent systems form lyotropic liquid crystals above each given concentration. As the solvent for preparing the amorphous films, we chose triethylene glycol because of its relatively higher stability (no bubbling) at 70°C. The following four kinds of gases were used: helium (He, Japan Helium Co. Ltd.), nitrogen (N_2, Yamagata Oxygen Co. Ltd.), oxygen (O_2, Yamagata Oxygen Co. Ltd.), and carbon dioxide (CO_2, Yamagata Oxygen Co. Ltd.). N_2 and O_2 were mainly used.

Preparation of CLCO HPC Solid Films

The 50 wt % liquid crystalline solution of HPC in methanol was prepared at 25°C. The solution is fully liquid crystalline. This means that the solution has no isotropic phase because the 50 wt % is over the critical concentration C_b of the HPC–methanol system.[13] The solution was spread on a glass plate, then the plate was stored in a desiccator saturated with methanol vapor for 24 h,[11] followed by drying at room atmosphere (25°C and 65% relative humidity) for 72 h. The peeled films (approximately 80 μm thickness) were dried *in vacuo* and were stored in a desiccator over silica gel. The films are abbreviated as HPC-A films.

Preparation of Amorphous HPC Solid Films

The 30 wt % isotropic solution of HPC in triethylene glycol was prepared. The solution system forms liquid crystal at higher concentrations and room temperature. The solution was spread on a stainless steel plate, and the plate was heated at 70°C for 48 h and then quenched. The peeled films (approximately 80 μm thickness) were dried *in vacuo* and were stored in the desiccator. The films are abbreviated as HPC-B films.

Optical Measurements

Both kinds of the cast HPC solid films were observed by means of an Olympus polarized microscope (POM). Circular dichroism (CD) spectra of both kinds of the HPC films were determined with a Jasco J-40S spectropolarimeter (Japan Spectro-scopic Co.). Both measurements were done at room atmosphere (approximately 25°C; approximately 65% relative humidity). The free-surface and fractured planes of the films were observed with a scanning electron microscope S-415 (SEM, Hitachi Seisakusho Ltd.). The films were freeze-fractured by bending in liquid nitrogen.

Gas Transport in HPC Solid Films

Gas transport coefficients were determined at 20°C for approximately 600 min by using equipment in our laboratory.[12] At least three determinations for each film were done at a given pressure. The gas leak rate in the equipment was less than 1% in comparison with the gas permeation rate. Consequently, we ignored the gas leak. Permeability coefficient P is estimated by using equation (1), as follows:

$$P = V \cdot (\Delta p/\Delta t)_s \cdot 273/(273 + T)$$
$$\cdot 1/76 \cdot L/A \cdot 1/p_1 \quad (1)$$

where V is volume of the downside tank (22.85 cm^3), $(\Delta p/\Delta t)_s$ is the slope of the steady state, T is the temperature, L is the film thickness (approximately 80 μm), A is the area of film (1.58 cm^2), and p_1 is pressure at upperstreamside.

Further details on the apparatus and procedure were shown elsewhere.[12] The permselectivity is defined as the ratio of pure gas permeabilities.

RESULTS AND DISCUSSION

Morphological Observations

The HPC-B films exhibited no texture in the polarized microscopy and no peak in CD, as shown in Figures 1 and 2, respectively; those showed that the HPC-B films are amorphous. Consequently, we succeeded in preparing the amorphous HPC films as a reference standard HPC film. On the other hand, the HPC-A films exhibited a typical texture for the cholesteric liquid crystals in the polarized microscopy and exhibited a negative peak around 220 nm in CD, as shown in Figures 1 and 2; those showed that the films retain the cholesteric liquid crystalline order. The CLCO solid films should exhibit a laminated pattern.[14,15] For the confirmation of the CLCO in the HPC-A films, scanning electron microscopy (SEM) observation for the HPC-A and -B films was done. As opposed to our expectation, no clear
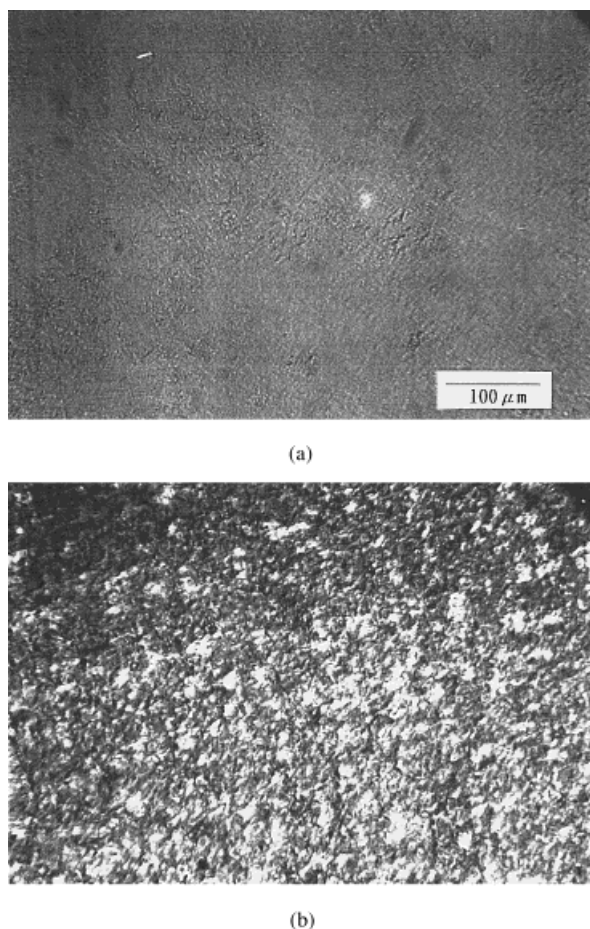
(a)

(b)

Figure 1 Polarized microphotograph of the free surface for (a) HPC-B film and (b) HPC-A film.

texture for the fractured planes of the HPC-A films was observed, as shown in Figure 3(a). This suggested that the preparation of test specimens for SEM observation with liquid nitrogen is not suitable: The fractured planes of the test specimens dissolved somewhat. Therefore, we prepared the chemically crosslinked HPC-A films,[11] of which the fractured planes did not dissolve. Figure 3(b) shows the SEM observation of the fractured plane of the crosslinked HPC-A films. This revealed that the crosslinked HPC-A films are nonporous and show a laminated wavy pattern. This pattern corresponded to the order of cholesteric liquid crystals; the spacing of the laminations is half of the cholesteric pitch.[14] We presume that the HPC-A films exhibit the same texture as that of the crosslinked HPC-A films.[15]

Gas Transport Phenomena in HPC Films

Dependence of Coefficients on Upperstreamside Pressure

Figure 4 shows the dependence of the permeability coefficient P on upperstreamside pressure p_1. For the HPC-B films, the order of P was 10^{-10}–10^{-11} [cm^3 (STP) · cm/cm^2 · s · cm Hg], and was the same as those reported for other cellulose derivatives, such as nitro cellulose,[16] cellulose acetate,[17] cellulose acetate butyrate,[18] and ethyl cellulose,[12,16] in the literature. On the other hand, the order of P for the HPC-A films was 10^{-9}–10^{-10} and was smaller than that for the HPC-B films. The trend in smaller P for the liquid
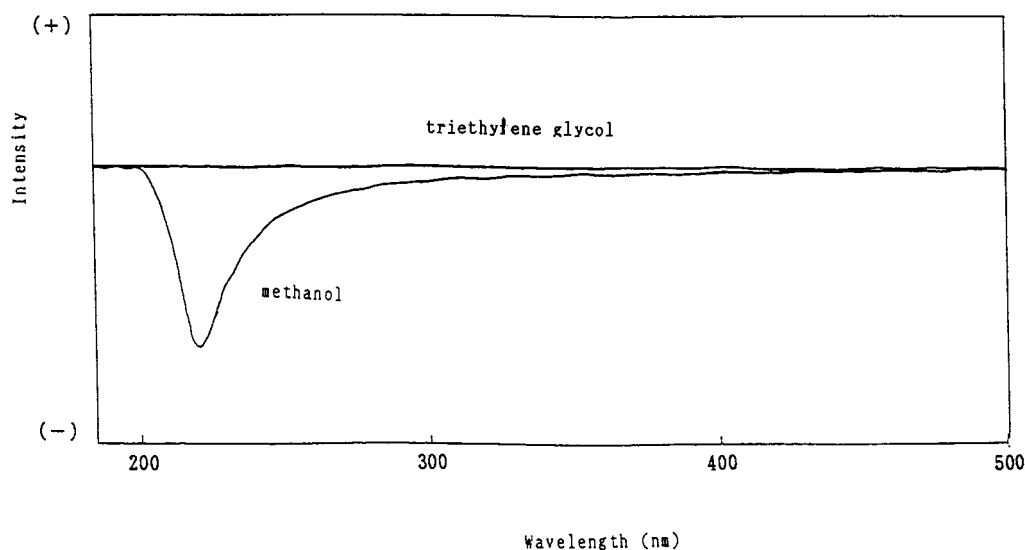

Figure 2 CD spectra for HPC films. The following solvents denoted in the figure are cast solvent: triethylene glycol (HPC-B) and methanol (HPC-A).
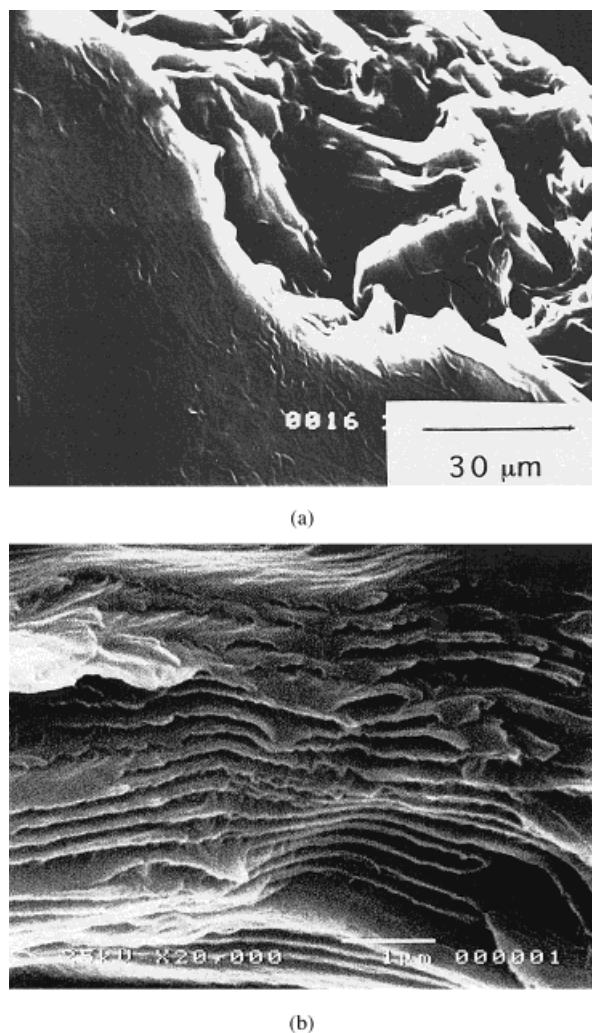
Figure 3 Scanning electron microphotograph of the fracture plane for (a) HPC-A film and (b) crosslinked HPC-A film.

crystalline films was the same as that observed in the ethyl cellulose[12] and nematic liquid crystalline films.[19–29]

P for both films tended to decrease with p_1. This is a typical behavior for the gas permeability in polymeric films below T_g.[30] Our determining temperature was 20°C and was below the T_g of HPC. The following was confirmed by dynamic mechanical determination of the HPC-A films: Tan δ exhibited two peaks around 40 and 110°C; the lower relaxation was associated with the amorphous phase, and the higher one was done with the liquid crystalline phase.[31–33]

Effect of CLCO on Transport Phenomena

P of N_2 and O_2 gases depended on the film texture. Compared with those coefficients for the

HPC-B films, the HPC-A films exhibited a smaller P. This suggested that the CLCO reduces P. As noted above, the trend of P was the same as those for EC liquid crystalline film[12] and the nematic liquid crystalline films.[19–29]

Weinkauf and Paul[21,22] proposed a gas transport mechanism in polymeric nematic liquid crystalline films; gases transport in less-ordered boundary regions and do not transport in the
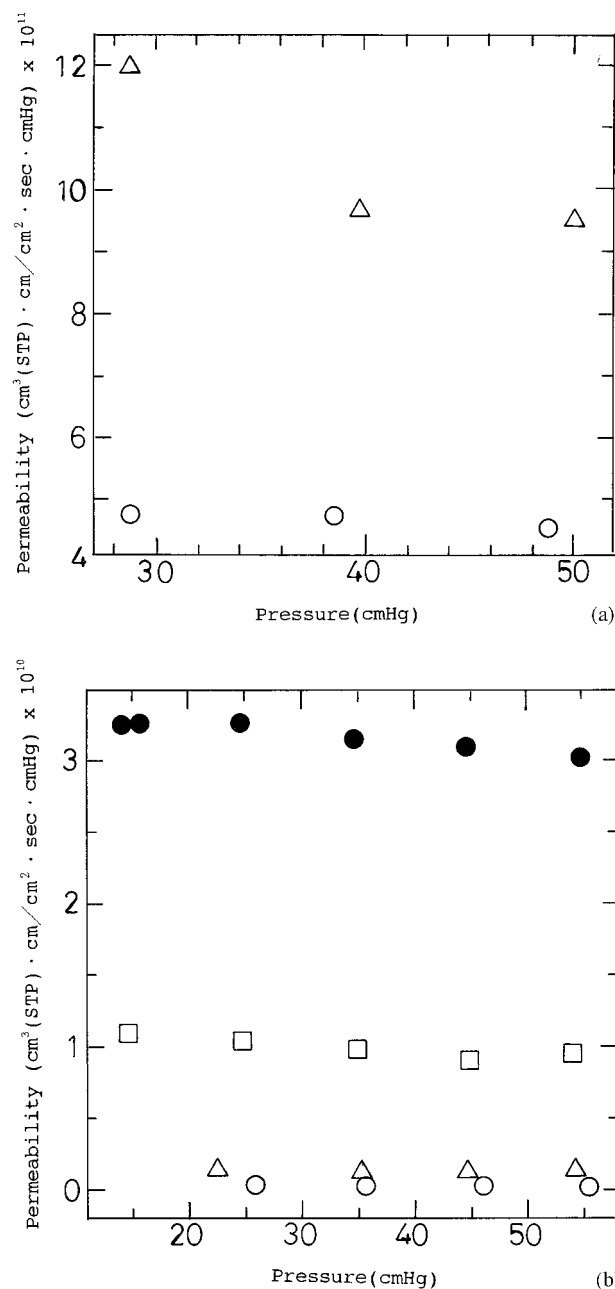

Figure 4 Upperstreamside pressure dependence of the permeability coefficient. (a) HPC-B film: (○) N_2; (△) O_2. (b) HPC-A film: (○) N_2; (△) O_2; (□) CO_2; and (●) He.

Table I Upperstreamside Pressure Dependence of Permselectivity for HPC Films and Ethyl Cellulose Film

p_1 (cm Hg)	50	40	30	Reference
HPC-A	8.0	6.3	6.3	This work
HPC-B	2.1	2.1	2.5	This work
EC	—	—	3.5	Suto et al.[12]

liquid crystalline phase (the gas transport in the liquid crystalline phase is nearly negligible relative to the boundary phase). Our cellulosic cholesteric liquid crystalline films exhibit the polydomain textures and have many boundary regions, which envelop the liquid crystalline phase.[34,35] Therefore, their model[21,22] appears to be applicable to the gas transport phenomena in our cholesteric liquid crystalline films. However, the molecular packing in the liquid crystalline phase for our cellulosic liquid crystals is not always the same as that for the nematic Vectra-type liquid crystals; cellulosic molecules are semirigid and worm-like in the liquid crystalline phase, whereas Vectra molecules are rigid and rod-like. Consequently, the concept that the gas is permeable in the liquid crystalline phase is not necessarily excluded for the gas transport in the cellulosic cholesteric liquid crystals in this stage.

Gas Permselectivity of HPC Films

Table I shows the permselectivity of gases for the HPC-A and HPC-B films. The permselectivity for N_2 and O_2 was approximately 2 for the HPC-B films and it was approximately 6.5 for the HPC-A films. The permselectivity for the HPC-A films was approximately threefold greater than that for the HPC-B films. Furthermore, the permselectivity for N_2 and O_2 for the HPC-A films was approximately twofold greater than that for the liquid crystalline ethyl cellulose films reported in our previous article.[12] Both the HPC-A films and EC films that exhibit the greater permselectivity retained CLCO. Our HPC films data confirmed that the films that retained CLCO show the improved permselectivity. The HPC molecules in the cholesteric liquid crystalline phase orient parallel to the surface of films, and the orient direction twists layer by layer. The order, perpendicular to the surface of films, is often characterized by the cholesteric pitch (P). The pitch estimated from the SEM observation was approximately 0.36 μm, which was almost the same as that estimated

from the CD database on the following equation: $P = \bar{n} \cdot \lambda$, where $\bar{n}$ is the averaged refractive index, and λ is the wavelength at the CD peak. The pitch for the EC cast films was approximately 0.44 μm (our data of $\bar{n}$ for cast EC films at 20°C were approximately 1.47).[12] Consequently, the difference in the permselectivity for N_2 and O_2 between the EC and HPC-A films was inferred from the difference in the pitch; the permselectivity tended to increase as the pitch decreased. The validity of this inference will be verified when we definitely establish the pathway of the gases in the liquid crystalline films.

CONCLUSIONS

CLCO in the HPC-A films reduced the permeability of N_2 and O_2 gases compared with the amorphous HPC films. CLCO in the HPC-A films improved the gas permselectivity. Those trends were the same as those previously found in EC liquid crystalline films.

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