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Preparation and characteristics of cholesteric gel from pentyl ether of hydroxypropyl cellulose

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A new cellulose derivative, pentyl ether of hydroxypropyl cellulose (P-HPC), and its crosslinked gel (PG-HPC) were prepared in non-aqueous solution. The temperature dependence of the optical pitch for the thermotropic mesophases formed by P-HPC and PG-HPC was determined spectroscopically. PG-HPC displayed the cholesteric reflection colour at room temperature and its cholesteric order and structure were fixed on heating up to 90°C. The optical pitch of the redried gel of PG-HPC, after swelling in tetrahydrofuran (THF), was shifted to lower wavelength and the reflection band became narrower than that of the original, before swelling in THF.

(Keywords: hydroxypropyl cellulose; optical pitch; cholesteric gels)

Introduction

Cellulose and its derivatives readily form cholesteric mesophases in lyotropic[1-5] and thermotropic[6-12] systems. The cholesteric mesophases formed by cellulose derivatives show the selective reflection colour if the wavelength of the optical pitch ($\lambda_m = nP$) is in the visible wavelength region[13]. The wavelength of the reflection band of the cholesteric mesophase is strongly influenced by the concentration[1-5,14] in lyotropic systems and by temperature[6-11] in thermotropic systems. The fixation of cholesteric order and structure with its optical pitch in the visible region is desirable for applications including optical components and new displays. In this paper, the preparation is described of cholesteric gels with reflection colour based on cellulose by chemical crosslinking.

Hydroxypropyl cellulose (HPC) is the most popular cellulose derivative that forms cholesteric ordered mesophases in both aqueous solution[15] and organic solvents[14,16,17] and is easily modified to a thermotropic cholesteric by simple chemical treatments[7-10]. So HPC seems to be a suitable starting material for the preparation of cholesteric gel. Crosslinked HPC films with cholesteric ordered structure have been prepared by chemical[18-21], photoinitiated[22,23] and γ-ray irradiated[24] crosslinking methods. Suto and co-workers[19-21] have reported on the preparation and the gel properties of the chemical crosslinked HPC films, which were obtained by casting preformed liquid crystalline solutions of HPC in water and in alcohols, and then adding paraformaldehyde and HCl. However, the cholesteric film obtained did not display the reflection colour. The immobilization of cholesteric reflection colour displayed by the crosslinked film of a thermotropic HPC derivative has been reported by Bhadani and Gray[22]. However, they did not determine the swelling properties of the cholesteric gel. In this study, we aim to prepare a crosslinked gel based on cellulose with cholesteric colour. First, we prepare an HPC gel in non-aqueous solution and determine the swelling and mesophase properties of the gel.

Experimental

The cholesteric gel of pentyl ether of HPC was prepared from HPC (Hercules Inc., Klucel; $M_w = 60\,000$, molar substitution = 4.1 (ref. 25)), iodopentane (IP) and 1,6-diiodohexane (DIH), which is a crosslinking agent. The preparation of gel was carried out according to the modified method based on the preparation[26,27] of tri-*O*-(alkyl)cellulose. This method was characterized by adding IP and DIH to the reaction mixture before adding powdered NaOH[28]. A typical preparation for the crosslinked gel is described below.

HPC (1.0 g) was dissolved in 60 ml of dry dimethylsulfoxide at 50°C. Four-fifths (17.5 g) of the total amount of the mixture of IP and DIH (the DIH content is 1 mol%) was added dropwise to the solution. After stirring for 30 min at 55°C, powdered NaOH (4.5 g) was added and then the reaction mixture was heated at 65°C. Following stirring for 2 h, the remaining mixture of IP and DIH (4.4 g) was added dropwise and the reaction mixture was stirred at 65°C for 48 h. The reaction mixture was cooled to room temperature and then poured into 120 ml of methanol. The gel separated as a sticky mass. After repeated washing with methanol, the gel was purified by swelling in tetrahydrofuran (THF) and shrinkage in methanol four more times. The purified gel was dried on a hot stage at 70°C for 2 weeks. The final yield was 1.0 g of cholesteric gel that displayed a light yellow-green colour.

The degree of etherification was estimated by i.r. measurements. I.r. spectra were obtained on a Perkin-Elmer 580 spectrophotometer. I.r. spectra of the pentyl ether derivative and its gel showed a small peak at 3500 cm^{-1} corresponding to the hydroxyl group. This indicates that polymers in this study seem to be almost fully substituted derivatives. The pentyl ether derivative

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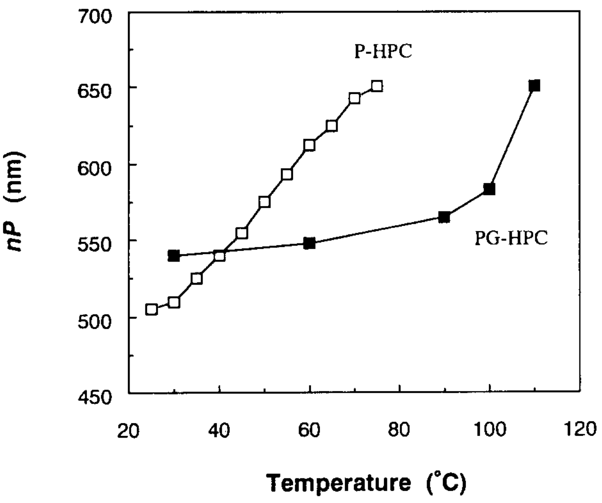

Figure 1 Temperature dependences of the optical pitch, *nP*, for P-HPC (□) and PG-HPC (■)

of HPC and its gel are represented by P-HPC and PG-HPC, respectively.

The textures were observed under a polarizing microscope (Olympus BH-2) equipped with a hot stage (Mettler FP-52). The reflection spectra of the cholesterics were measured with an automatic control of the monochromator and of the light intensity.

Results and discussion

P-HPC is a sticky mass, slightly blue in colour and showing birefringence under cross-polarized light at room temperature. On the other hand, PG-HPC is a gum of light yellow-green colour which swells well in THF. The temperature dependences of the optical pitch on heating for P-HPC and PG-HPC are shown in *Figure 1*. The wavelength of maximum reflection of P-HPC increases smoothly with temperature and the optical pitch response of the mesophases to changes in temperature is reversible. The wavelength of maximum reflection of PG-HPC does not change significantly in the temperature range 30–90°C. However, it increases rapidly with elevating temperature over 100°C, as shown in *Figure 1*. It is obvious that the cholesteric order and structure of PG-HPC are maintained and the helical pitch is insensitive to the temperature change, at least up to 90°C. The PG-HPC heated above 100°C does not show the reflection colour again, even when it is cooled to room temperature. The optical pitch response of PG-HPC to temperature change is irreversible. It seems that the unreacted end group of crosslinking agent (DIH) that remains in the gel reacts on heating and forms crosslinked networks to fix the structure.

The transition temperature from anisotropic to isotropic phase, T_i, is determined by polarizing microscope. The T_i of PG-HPC might be expected to be higher than that of P-HPC due to the fixation of cholesteric structure by crosslinking. However, the T_i of PG-HPC is 140°C, which is lower than that of P-HPC ($T_i = 150°C$). The reason for this is not clear, but it is suggested that a part of DIH reacts only in one end group, not in both ends, and PG-HPC has a DIH side chain which probably acts as a plasticizer to lower T_i.

Birefringence is observed in the gel of PG-HPC swollen in THF as well as in the dry gel before swelling. It is noteworthy that the concentration of PG-HPC in the swollen gel is about 10 wt%, which is much lower than the critical concentration for formation of lyotropic mesophase for cellulose derivatives. The critical concentration for HPC derivatives has been reported to be 30–35 wt%[7,9]. The anisotropic arrangement of the liquid crystal seems to be augmented by crosslinking. The same phenomenon has been reported on the crosslinked polypeptide gel with a long cholesteric pitch[29].

The dry PG-HPC displays a light yellow-green colour. The colour disappears on swelling in THF, but gradually reappears by evaporating THF from the swollen gel and drying. Comparison of the optical pitch spectra between the original gel and the gel after swelling is shown in *Figure 2*. The wavelength and reflection band of the cholesteric colour of completely dried PG-HPC after swelling in THF are lower and narrower than those of the original before swelling in THF. The swelling behaviour in the cholesteric network structure is not clear. However, it is speculated to be the same as the dilution effect of cholesteric lyotropic systems. By increasing the portion of solvent in the gel, the distance between the molecules becomes larger and the twist angle between neighbouring molecular layers becomes smaller, thus the cholesteric pitch is increasing. Contrary to the swelling, the shrinking behaviour of swollen gel may be the same as the effect of increasing the concentration of polymer in a lyotropic system. The distance between the molecular layers becomes smaller and the twist angle becomes larger to make the cholesteric pitch smaller. Therefore, the wavelength of the cholesteric colour of redried gel of PG-HPC may become lower due to the increment of twist angle by an excess of torque generated about the cholesteric axis on shrinking.

In conclusion, a new cellulose derivative, pentyl ether of HPC, and its crosslinked gel were prepared. The gel displayed the cholesteric reflection colour, and its cholesteric order and structure were fixed on heating up to 90°C. The optical pitch, λ_m, of the redried gel was shifted to lower wavelength on shrinking.

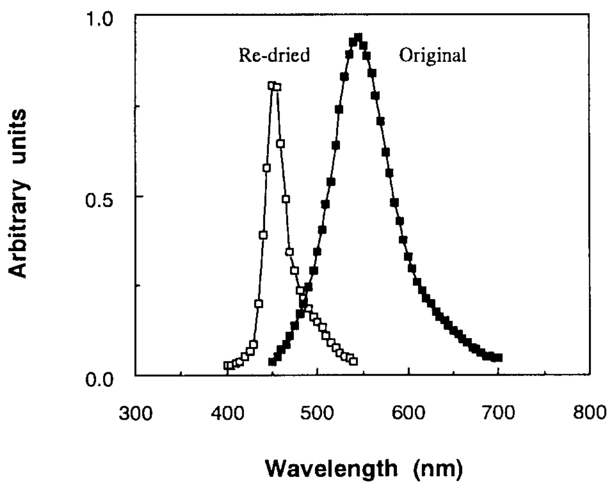

Figure 2 Reflection spectra of PG-HPC at 25°C: ■, original gel before swelling; □, redried gel after swelling in THF

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