

Chemical cross-linking of cholesteric liquid-crystalline hydroxypropyl cellulose with dialdehydes

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Cross-linking of the cholesteric liquid-crystalline order in a hydroxypropyl cellulose (HPC) aqueous solution was attempted and the swelling and mechanical (static and dynamic) properties of cast films were determined. HPC solid films cast from the liquid-crystalline aqueous solution with dialdehyde (glyoxal or glutaraldehyde) and hydrochloric acid were insoluble in water and retained the right-handed cholesteric liquid-crystalline order. The swelling and static tensile properties exhibited a general behaviour with respect to the concentration of the cross-linking agent and to the heat treatment. However, dynamic and loss moduli exhibited an opposite behaviour to the static tensile modulus. A cross-linking mechanism is proposed for HPC molecules and dialdehydes based on the swelling and mechanical properties of HPC films cast from two dialdehyde systems.

1. Introduction

The cross-linking of cholesteric liquid-crystalline order (CLCO) has been tried using liquid-crystal-forming polypeptides since the 1960s [1–4]. Very recently, the cross-linking of CLCO was applied to cellulosic cholesteric liquid crystals, i.e. hydroxypropyl cellulose (HPC), by a chemical cross-linking method [5, 6], by γ -irradiation method [7], and by a photo-initiation method [8]. The fixing of lyotropic CLCO in HPC has been attempted by a chemical cross-linking method [9–13]. However, the mechanism and topochemistry of cross-linking were still unclear. To understand the fundamental basis of the changes in properties caused by the cross-linking of CLCO, the problems above need to be evaluated.

In order to estimate the cross-linking mechanism of HPC, we attempted to make clear the effect of the chain length of the cross-linking agent on the mechanical properties of the cross-linked liquid-crystalline HPC films by using two kinds of dialdehydes, glyoxal and glutaraldehyde, with different chain lengths. The aqueous liquid-crystalline HPC system with an acid catalyst and a cross-linking agent was cast to form a cross-linking film retaining CLCO. The tensile and dynamic mechanical properties and swelling behaviour of the film were determined.

2. Experimental procedure

2.1. Samples

The HPC was the same as that used previously [9–13]. Glyoxal ((CHO)₂, Tokyo Kasei Kogyo Company Ltd), glutaraldehyde (CHO(C₃H₆)CHO, Tokyo Kasei Kogyo Company Ltd) and hydrochloric acid (HCl), acetic acid (CH₃COOH, Wako Pure Chemical

Industry Ltd) were used as cross-linking agents and as the catalyst, respectively. All samples were used as received. Deionized water prepared in our laboratory (hereafter water) was used as a solvent.

2.2. Preparation of the liquid-crystalline solution

An aqueous 50 wt % solution of HPC was prepared and aged in a refrigerator (ca. 7 °C) for ca. one month. Then, a given wt % of the cross-linking agent and 3 wt % acid were added to the solution and mixed with a glass rod. Air bubbles introduced when mixing were removed in a vacuum dessicator. The air-bubble-free solution with the cross-linking agent and acid was not cross-linked at room temperature for at least one year.

2.3. Preparation and measurement of solid films

The solution was cast on a glass plate at room temperature (ca. 20 °C). The cast process has been reported elsewhere in detail [9–13]. The film thickness was ca. 110 μ m. Some of the cast films were heated in vacuum at 60 °C for 24 h or 72 h. The cast films were stored in a dessicator at room temperature.

Solubility of solid film in water at 20 °C. Solid cast film (ca. 0.011 \times 1.3 \times 1.3 cm) was soaked in water for 24 h.

Measurement of the gel fraction. The soluble material of the solid film (ca. 0.011 \times 1.3 \times 1.3 cm) was extracted in water for 24 h using a Soxhlet apparatus. The extracted film was dried *in vacuo* at 60 °C. The gel

fraction was taken as the ratio of the weight of the extracted film to that of the non-extracted film.

Measurement of swelling. After vacuum drying at 60 °C for at least 24 h, the extracted film (its size is the same as that for the measurement of the gel fraction) was soaked in water at 20 °C for 10 h. Then, the surfaces of the swollen film were wiped with soft paper tissue and the swollen film was weighed. The swollen volume of the film was calculated using the density of HPC (1170 kg m⁻³) [14]. The surface area (width × length) of the swollen film was also determined.

Infrared spectroscopy of the solid films. Infrared (I.R.) spectra for the films were determined with IR-435 (Shimazu Seisakusho Company Ltd) at 20 °C.

Circular dichroism of solid films. Circular dichroism (CD) spectra for films were determined with a Jasco J-40S spectropolarimeter (Japan Spectroscopic Company Ltd) at room temperature.

Scanning electron microscopy of solid films. Scanning electron microscopy (SEM) was performed on a scanning electron microscope S-415 (Hitachi Seisakusho Ltd). Cast films were freeze fractured by bending in liquid nitrogen.

Measurement of the tensile properties. The properties were determined with a Tensilon VTM-IV-500 (Toyo Baldwin Company Ltd) at room temperature and atmosphere (ca. 20 °C and ca. 50% relative humidity). The size of the specimens was 3.0 × 0.3 × 0.011 cm. The cross-head speed was 5 mm min⁻¹. Five or six measurements were performed and the mean was obtained for the films.

Measurement of dynamic mechanical properties. The properties were determined with a Rheovibron DDV-II-C (Toyo Baldwin Company Ltd) in a temperature range from -100 to ca. 200 °C at a heating rate of ca. 1.4 °C min⁻¹ and at a constant frequency of 110 Hz. The sample size was the same as that for the tensile test.

3. Results

3.1. Identification of cross-linking

Table I shows solubility data for each cast film in water at 20 °C. The cast films were insoluble, except for the system with acetic acid. Fig. 1 shows the i.r. spectra for the films with and without heat treatment. Each spectrum of films was almost the same as that reported by Samuels [14] except for the peak at 1720 cm⁻¹ which corresponds to aldehyde. This showed that the chemical structure of HPC does not change during casting and heat treatment. Furthermore, the peak at 1720 cm⁻¹ became weak after heating. This suggested that cross-linking develops due to heating.

3.2. Identification of CLCO retained

Fig. 2 shows the CD spectra for HPC solid films cast from each system, and cast from p-formaldehyde for comparison [11, 13]. Each film exhibited a negative peak and the peak seemed to shift to lower wavelengths after heating. The shift in peak with heating suggested that the cholesteric pitch changes [11]. The data in Fig. 2 show that the films retain the right-handed cholesteric order. The texture of the cast film observed by polarized microscope was almost the same as that of the liquid-crystalline solution which was the starting solution for the casting process. This also confirmed that the solid films retain the CLCO.

In previous papers [10, 12, 13], it was reported that the HPC films cast from some solvent systems exhibited a band texture and the small-angle-light-scattering (SALS) pattern exhibited a -type, not a +type pattern. Fig. 3 shows the SALS patterns of each film with and without heat treatment. All films exhibited +type patterns. Recently, the same pattern for the HPC films was reported by Matsuo and Yanagida [15]. This showed that whether the SALS pattern does or does not exhibit +type is dependent on the existence of the band texture.

Consequently, our films cast from liquid-crystalline systems with dialdehyde retained the right-handed CLCO and the order was cross-linked. In a previous paper [13], three-dimensional cross-linking was reported, both between molecules in the same layer and between molecules cross-linked in adjacent layers. Cross-linking by dialdehydes will also be three-dimensional. The lack of a band texture in our solid films shows that cross-linking is performed after the CLCO reaches equilibrium.

3.3. Swelling behaviour

Table II shows the swelling ratio and gel content for each film. The swelling ratio decreased with increasing concentration of the cross-linking agent and the heat-treatment time. This thickness increase was greater than that of the surface (width or length) increase. This was the same as the trend reported by Qiansong *et al.* [8]. The ratio for the film cast from the glyoxal system was greater than that of the glutaraldehyde system. The swelling ratio for lower gel content was greater than that for higher gel content except for the swelling ratio for thickness. This is general for cross-linked polymers. Interestingly, the thickness swelling ratio for the films cast from the glutaraldehyde system increased with increasing gel content. This suggests that the gel is anisotropic: the degree of cross-linking between HPC molecules in the same layer is different from that between the molecules in an adjacent layer.

TABLE I Solubility of HPC solid film cast from each liquid-crystalline system

Sample	(cross., catalyst)	Glyoxal + HCl	Glutaraldehyde + HCl	Glutaraldehyde + CH ₃ COOH
HPC/H ₂ O	(0, 0)	Soluble	Soluble	Soluble
	(3, 3)	Insoluble	Insoluble	Soluble
	(5, 3)	Insoluble	Insoluble	Soluble
	(7, 3)	Insoluble	Insoluble	-
	(9, 3)	Insoluble	-	-

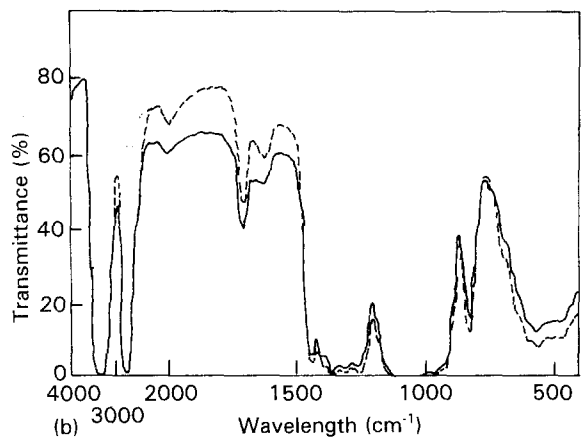
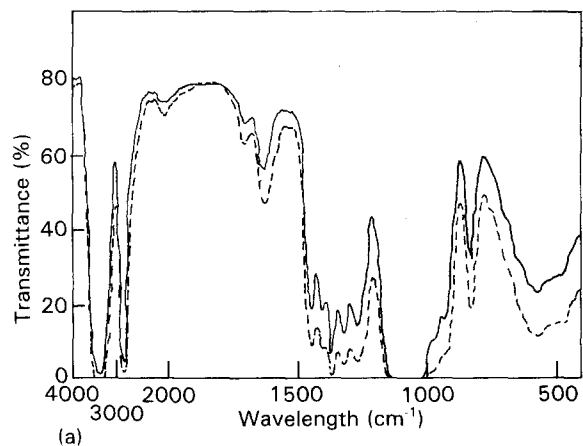


Figure 1 I.R. spectra for HPC solid films cast from a HPC/water system with (a) 3 wt % glyoxal or (b) 5 wt % glutaraldehyde. (---) as-cast, and (—) heat treated at 60 °C.

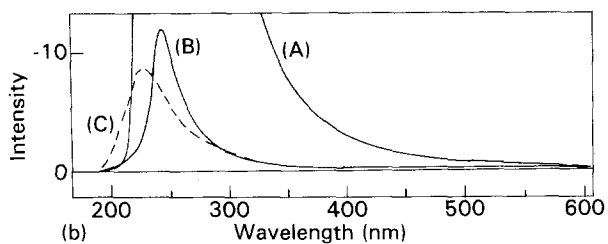
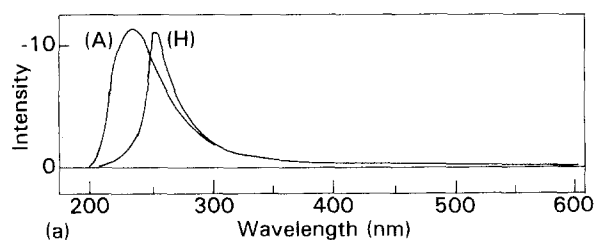


Figure 2 (a) CD spectra for HPC solid films cast from a HPC/water system with 3 wt % glutaraldehyde: (A) as-cast, and (H) heat treated at 60 °C. (b) CD spectra for HPC solid films cast from a HPC/water system with 3 wt % of each cross-linking agent: (A) glyoxal, (B) glutaraldehyde, and (C) p-formaldehyde.

Figure 3 SALS patterns for HPC solid films cast from the HPC/water system with 5 wt % glyoxal, (a) as-cast, and (b) heat treated at 60 °C; and with 5 wt % glutaraldehyde, (c) as-cast, and (d) heat treated at 60 °C.

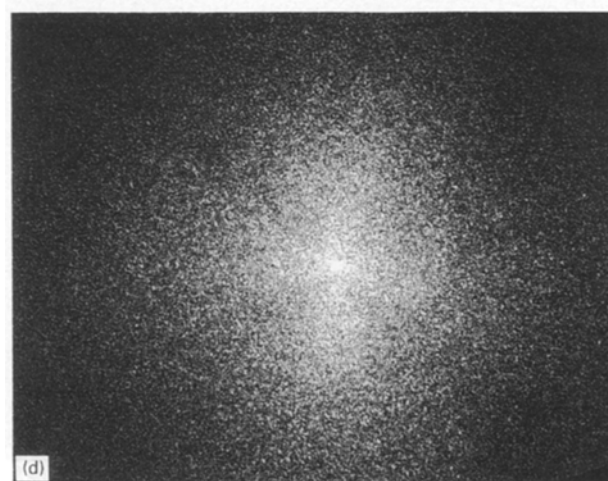
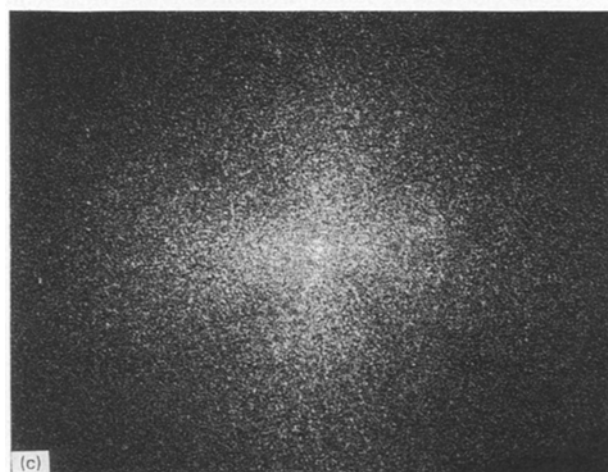
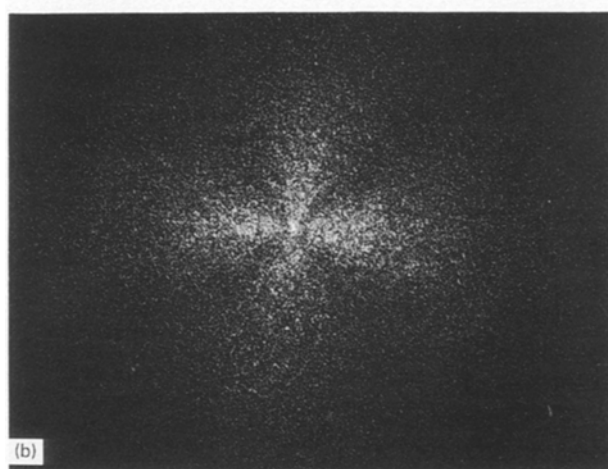
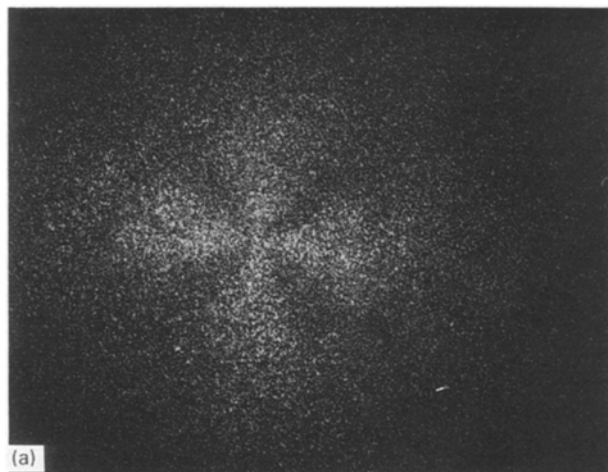


TABLE II Swelling ratio of extracted cross-linked HPC solid films

Sample	Thickness (μm)	Gel content (wt %)	Swelling ratio			
			In weight	In volume	In thickness	Surface area
Glyoxal 3%	100	93.5	4.81	5.08	3.32	1.53
Glyoxal 5%	100	94.3	3.24	3.58	2.52	1.42
Glutaraldehyde 3%	110	93.8	1.43	1.49	1.13	1.32
Glutaraldehyde 5%	105	94.1	1.36	1.42	1.17	1.21
Glutaraldehyde 3% ^a	110	94.3	1.35	1.40	1.18	1.19
Glutaraldehyde 5% ^a	110	97.5	1.32	1.37	1.23	1.11

^a Heat treated at 60°C for 72 h.

3.4. Static tensile properties

Fig. 4 shows the stress-strain curves for each film. The observed values of each property are shown in Table III. Some trends were observed: (i) with increasing concentrations of the cross-linking agent, the Young's modulus and strength increase, but the elongation decreases; (ii) with heat treatment, the Young's modulus and strength increase, but the elongation decreases; (iii) comparing the films cast from glyoxal and glutaraldehyde, the Young's modulus, strength and elongation for the film cast from the glyoxal system were greater than those for the film cast from the glutaraldehyde system.

3.5. Dynamic mechanical properties

Fig. 5 shows the dynamic modulus, E' , loss modulus, E'' , and loss tangent, $\tan \delta$, for the films cast from both systems with 5 wt % of the cross-linking agent. The features shown in Fig. 5 are: (i) both moduli decrease with heat treatment, (ii) no significant difference in the moduli of the films cast from both cross-linking systems is observed. Furthermore, though the data is not shown in Fig. 5, these moduli decreased with increasing concentrations of cross-linking agent.

4. Discussion

In Table IV the data are summarized. Generally, with increasing concentration of cross-linking agent, the gel fraction should increase and the swell should decrease; the Young's modulus and tensile strength should increase and the elongation should decrease. Therefore, the experimental data shown in Table IV for the dependence of gel content, swell, and tensile properties on the concentration of the cross-linking agent exhibited a general tendency, as expected. The effect of heat treatment on the properties noted above can be explained on the basis of the development of cross-linking. Furthermore, with respect to the decrease in cholesteric pitch, the free-ordering of liquid crystals is restricted by the cross-linking, the crosslinking causes the molecules in two adjacent layers to tighten.

There are two interesting features in Table IV. First, the effects of the concentration of the cross-linking agent and the heat treatment on the Young's modulus were different to those on the dynamic modulus. Secondly, the properties for the film cast from the glyoxal system were greater than those for the film

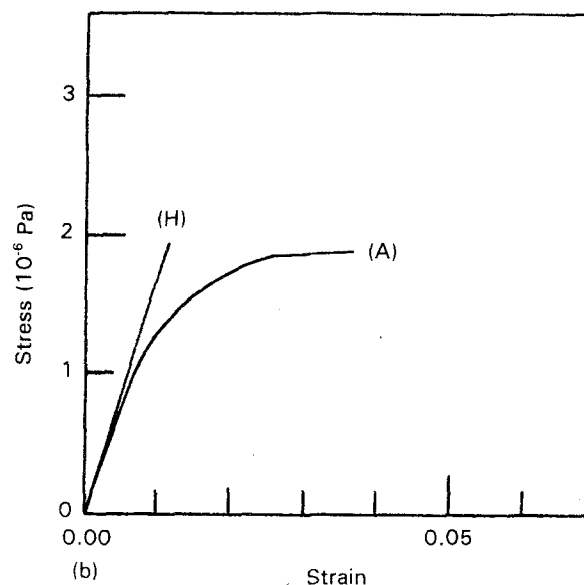
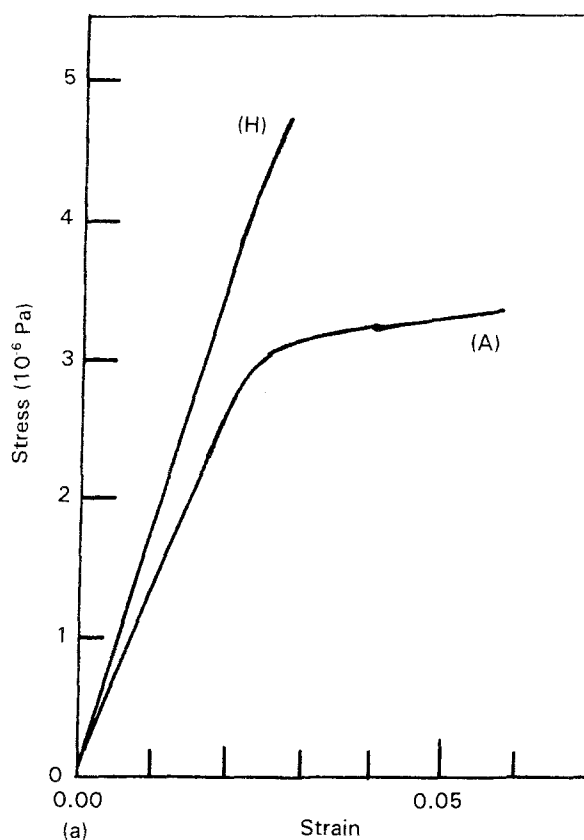


Figure 4 Stress-strain curves for HPC solid films cast from HPC/water system with (a) 5 wt % glyoxal, (A) as-cast, and (H) heat treated at 60°C and (b) with 5 wt % glutaraldehyde, (A) as-cast, and (H) heat treated at 60°C.

TABLE III Tensile properties of as-cast HPC films

Sample	Young's modulus ($\times 10^{-8}$ Pa)	Tensile strength ($\times 10^{-6}$ Pa)	Elongation (%)
Glyoxal 3%	2.80	3.10	400
Glyoxal 3% ^a	3.26	3.67	195
Glyoxal 5%	2.46	3.26	335
Glyoxal 5% ^a	3.40	4.57	218
Glutaraldehyde 3%	1.88	1.42	293
Glutaraldehyde 3% ^a	3.26	2.13	170
Glutaraldehyde 5%	2.45	1.88	255
Glutaraldehyde 5% ^a	3.31	1.92	136

^a Heat treated at 60 °C for 24 h.

TABLE IV Summary of each property of cross-linked HPC film

	Cholesteric pitch	Swell	Gel	Tensile properties			Dynamic property E'
				E	σ	ε	
Increase in cross-linking agent	Increase	Decrease	Increase	Increase	Increase	Decrease	Decrease
Heat treatment at 60 °C	Decrease	Decrease	Increase	Increase	Increase	Decrease	Decrease
Glyoxal	Long	Great	≡	Great	Great	Great	≡
Glutaraldehyde	Short	Small	≡	Small	Small	Small	≡

cast from the glutaraldehyde system. Both features are discussed below.

4.1. Effects of the concentration of the cross-linking agent and heat treatment on the moduli

Although the Young's modulus (a tensile, static, mechanical property) and the dynamic modulus (a tensile, dynamic, mechanical property) are both elastic characteristics of materials, the two moduli were differently affected by the cross-linking-agent concentration and heat treatment: both factors increased the Young's modulus, but decreased the dynamic modulus. When a material exhibits an anomalous behaviour, generally the behaviour is a result of the texture of the material. Scanning electron photomicrographs of the fractured plane for cross-linked solid films are shown in Fig. 6. A photograph for a non-cross-linked film is also shown to compare with the cross-linked films. There was a characteristic point in the texture where the cross-linked films exhibit a so-called skin-core-type texture. A uniform and dense phase at the skin and a relatively disordered piled texture in the core can be seen. The different responses in the moduli to the applied static or dynamic tensile (extensional and compressive) strain seem to be partially due to the skin-core texture.

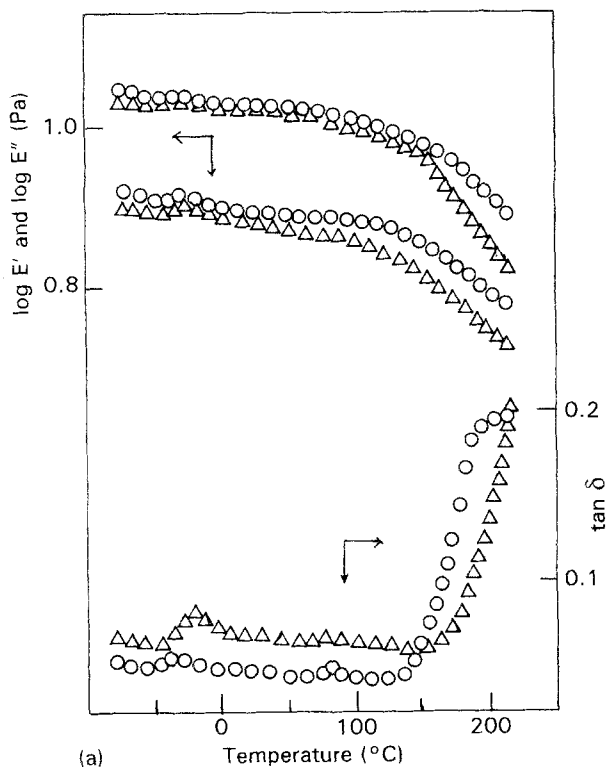
4.2. Effect of the chain length of the cross-linking agent on the properties

When the chemical structures of the two dialdehydes are compared, glutaraldehyde has a longer chain than glyoxal. Then, assuming the same cross-linking density

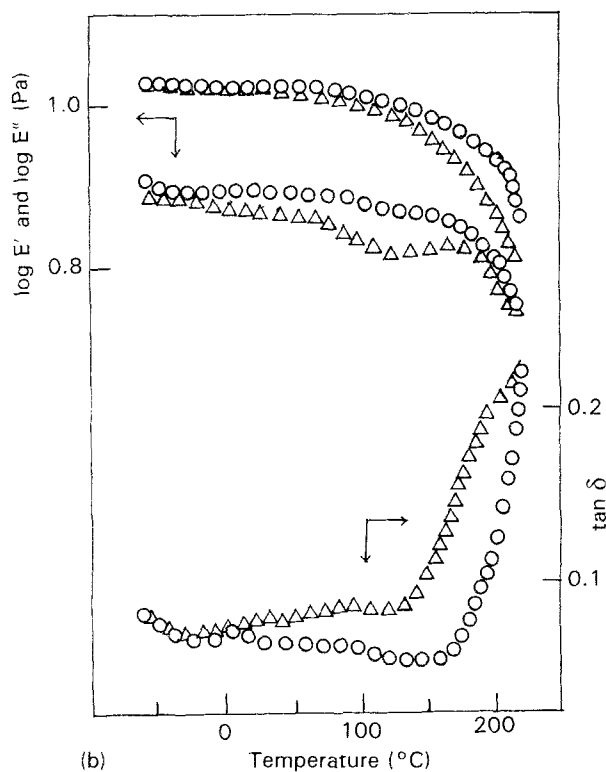
for each film, the length of the cross-linking bridge between molecules for the glutaraldehyde case is expected to be longer than that for the glyoxal case. If this expectation is true, the films cast from the glutaraldehyde system should exhibit a smaller modulus, a greater elongation, a greater swelling, and a longer cholesteric pitch than the films cast from the glyoxal system. However, as shown in Table IV, this expectation is not always true; experimental data, except for the Young's modulus, exhibited the opposite trend to this expectation. It was assumed that the cross-linking is performed by dialdehyde as shown in Fig. 7. Following the scheme in Fig. 7, the length of the cross-linking bridge between molecules for glutaraldehyde should be longer than that for glyoxal; the swelling data for the films cast from the glutaraldehyde system should be greater than that for the glyoxal system. However, our data suggested that the scheme in Fig. 7 is not always true. Then the scheme shown in Fig. 8 was proposed. If the cross-linking is performed as shown in Fig. 8, glutaraldehyde has longer branching than glyoxal. Then, compact cross-linking between molecules is possibly performed for glyoxal. The trends of our mechanical and swelling data can be explained on the basis of the scheme in Fig. 8 rather than the scheme in Fig. 7.

5. Conclusions

The HPC films cast from the cholesteric liquid-crystalline aqueous solutions with dialdehyde (glyoxal or glutaraldehyde) and hydrochloric acid were insoluble in water. The insoluble HPC films retained the CLCO.



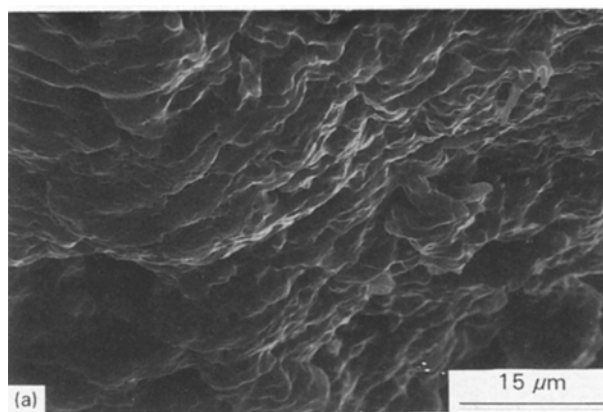
(a)



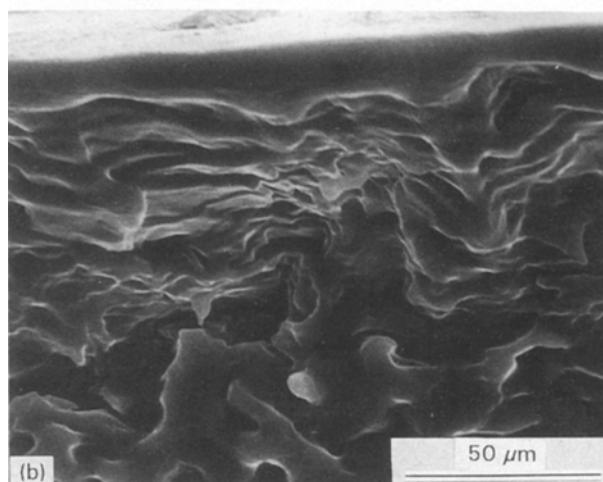
(b)

Figure 5 Temperature dependence of dynamic mechanical properties at 110 Hz for HPC solid films cast from the HPC/water system with (a) 5 wt % glyoxal, (○) as-cast, (△) heat treated at 60 °C; and (b) 5 wt % glutaraldehyde, (○) as-cast, and (△) heat treated at 60 °C.

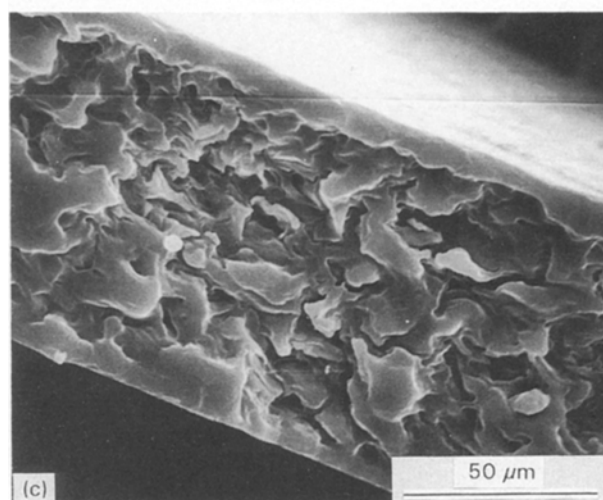
Swelling and static tensile behaviour for those HPC films was general, for increasing concentrations of the cross-linking agent and with heat treatment, the swelling ratio decreases and the Young's modulus and tensile strength increase. The dynamic and loss moduli decreased with increasing concentrations of the cross-linking agent and with heat treatment. This was an



(a)



(b)



(c)

Figure 6 Scanning electron photomicrographs of the fractured plane for HPC solid films: (a) no cross-linking agent and heat treated at 60 °C, (b) 5 wt % glutaraldehyde and as-cast, and (c) 5 wt % glutaraldehyde and heat treated at 60 °C.

opposite trend to the static tensile property (Young's modulus). The different trend seems to be partially due to the skin-core texture of the films. The films cast from the glyoxal system exhibit greater swelling and tensile properties than the films cast from the glutaraldehyde system. Based on the differences in the swelling and mechanical behaviour of the HPC films cast from glyoxal and glutaraldehyde systems, a cross-linking mechanism was proposed for HPC molecules and dialdehydes.

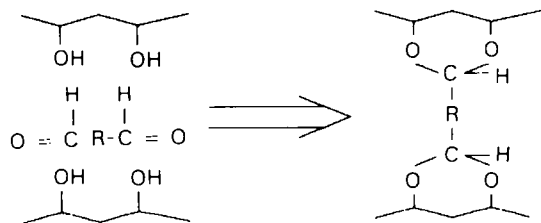


Figure 7 Scheme for dialdehyde cross-linking for glyoxal as an example. $R = (\text{CH}_2)_n$; $n = 0$ for glyoxal and $n = 3$ for glutaraldehyde.

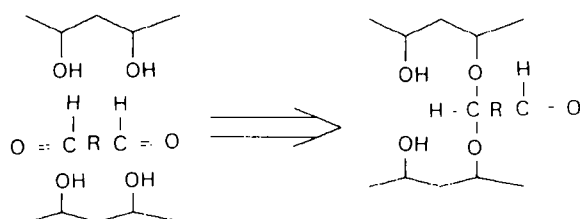


Figure 8 Proposed cross-linking scheme. $R = (\text{CH}_2)_n$; $n = 0$ for glyoxal and $n = 3$ for glutaraldehyde.

Acknowledgement

We are deeply indebted to Professor Masaru Matsuo, Faculty of Home Economics, Nara Women's University, for valuable suggestions for glyoxal cross-linking.

This work was partly supported by the Grant-in-Aid from the Ministry of Education Science and Culture, Japan (Grant No. 02650637)

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Received 8 April 1992

and accepted 3 February 1993