

Preparation and Mechanical Properties of Chemically Cross-Linked Hydroxypropyl Cellulose Solid Films Retaining Cholesteric Liquid Crystalline Order*

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SYNOPSIS

Hydroxypropyl cellulose films were cast from liquid crystalline solutions with a cross-linking agent. The solubility test and the optical measurements of the resultant films were performed. The tensile, dynamic mechanical, and creep properties of the films were determined. The data of solubility in water determined that the cast films are cross-linked, and the data of circular dichroism spectra, that the cast films retain the cholesteric liquid crystalline order (right-handed sense). Both findings clarified that the cast films retain the cholesteric order fixed by cross-linking. The cross-linking depended on the pairs of the solvent-cross-linking agent. The mechanical properties also depended on the pairs: the tensile strength and moduli did not always increase with cross-linking. The creep resistance improved with cross-linking. The thermally activated Eyring process could be applied and the activated volumes were evaluated for water- and methanol-cast films. There were not clear phenomenological correlations between the mechanical properties of our films.

INTRODUCTION

Many cellulose derivatives are well known to form cholesteric liquid crystal. Hydroxypropyl cellulose (HPC) is the most useful model sample for investigating liquid crystalline behavior, because of its solubility in a relatively wide range of solvents.¹ However, unfortunately, the application of liquid crystalline HPC fibers or films to end use is less possible, because of its great solubility. One method to overcome the drawback of the HPC fibers or films is the fixing of the liquid crystalline order by cross-linking.

Samulski and Tobolsky,² Aviram,³ and Tanaka et al.⁴⁻⁶ have already reported the cross-linking of cholesteric liquid crystalline polypeptides. However, there were very few papers on the cross-linked cellulosic films retaining a liquid crystalline order. We

have reported the chemical cross-linking of HPC films by using mainly *p*-formaldehyde.⁷⁻¹¹ Rials and Glasser¹² described the cross-linked HPC films with toluylene diisocyanate. Very recently, the liquid crystalline order in HPC film was cross-linked by gamma radiation.¹³ However, many problems on cross-linking of liquid crystalline HPC remain unclear, although the cross-linking of cellulose has been reviewed.¹⁴

In this study, we prepared the cross-linked HPC films cast from liquid crystalline solutions by using four chemical cross-linking agents, identified the liquid crystalline order in the films by optical means, and determined the static tensile, dynamic mechanical, and tensile creep properties of those films. Those properties chosen in this study connected with the deformability of cross-linked polymers.

EXPERIMENTAL

Samples

HPC (Tokyo Kasei Kogyo Co.) was used after vacuum-drying at 40°C for 24 h. The weight-average

* Dedicated to Emeritus Professor Dr. Toshikazu Fujimura on the occasion of his 77th birthday in appreciation of his contribution to my knowledge of cross-linking (S. S.).

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and number-average molecular weights were 11.7×10^4 and 5.2×10^4 , and the molar substitution, 4.25.

All solvents (summarized in Table I) were of commercial reagent grade (Wako Pure Chemical Ind.), except for deionized water prepared in our laboratory (hereafter, "water").

Four commercial reagent grade cross-linking agents were used: *p*-formaldehyde (*p*-FA, Kanto), toluylene diisocyanate (TDI, Tokyo Kasei Kogyo), *N,N*-dimethylolurea (DMU, Tokyo Kasei Kogyo), and dimethylolthiourea (DMTU, Wako). As catalysts, commercial reagent grade di-*n*-butyltindilaurate (DBTDL, Tokyo Kasei Kogyo), hydrochloric acid (HCl, Kanto), and sodium hydroxide (NaOH, Kanto) were used. The cross-linking agent-catalyst pairs studied are shown in Table I. All samples noted above were used as supplied.

Preparation of Liquid Crystalline Solutions

The procedure was the same as that reported in our previous papers.⁷⁻¹¹ It must be emphasized that each liquid crystalline solution is single phase at 25°C: The HPC concentration is above C_b .

Preparation of Solid Films

Liquid crystalline solution was mixed with a cross-linking agent (3.5 wt %) and a catalyst (3.5 wt %)

by using a glass rod for 10 min. During the mixing, the solution was contaminated by air bubbles. To remove the air bubbles, the solution was centrifuged (2000 rev/min) for ca. 30 min. Then, the solution free from air bubbles was poured on a Teflon film, which was framed with a 180 μ m-thick adhesive tape on the edges, and the solvent was allowed to evaporate in a laboratory atmosphere (25°C). The resultant film was peeled from the Teflon film and was vacuum-dried at 40°C for 24 h. Then, the film was stored in a desiccator in the dark at room temperature.

Solubility of Solid Films

Solid-cast film (80 μ m thick \times 0.7 cm long \times 0.7 cm wide) was soaked in water for 24 h at room temperature.

Measurement of Gel Fraction

The soluble material of solid film (80 μ m thick \times 1.2 cm long \times 1.2 cm wide) was extracted in boiling water using a Soxhlet apparatus. It usually took ca. 24 h for the extracted film to attain constant weight.⁷ The extracted film was dried *in vacuo* at 60°C and the gel fraction was taken as the ratio of the weight of the extracted film to that of the nonextracted one.

Table I Solubility of HPC Solid Films Cast from Each Liquid Crystalline Solution with Cross-Linking Agent (3.5 wt %) and Catalyst (3.5 wt %)

LC Solution		Solubility					
Solvent	Conc (wt %)	<i>p</i> -FA + HCl	TDI + DBTDL	DMU + NaOH	DMU + HCl	DMTU + HCl	DMTU + NaOH
Water	45	Insol.	Sol.	Insol.	Insol.	Insol.	Sol.
Methanol	45	Insol.	Sol.	Insol.	Insol.	Insol.	Sol.
Ethanol	50	Insol.	Sol.	Insol.	Insol.	Insol.	—
Propanol	50	Insol.	Sol.	Insol.	—	—	—
Butanol	50	Insol.	Sol.	Insol.	Insol.	Insol.	—
Pentanol	55	Insol.	Sol.	Insol.	—	—	—
Benzylalcohol	40	Insol.	Sol.	Sol.	Sol.	—	—
<i>m</i> -Cresol	40	Sol.	Sol.	Sol.	—	Sol.	—
Morpholine	40	Sol.	Sol.	Sol.	—	—	—
DMAc	50	Sol.	Insol.	Insol.	Sol.	—	—
DMSO	50	Sol.	Insol.	Insol.	Sol.	—	Sol.
Pyridine	40	Sol.	Insol.	Insol.	—	—	—
Chloroform	50	Insol.	Insol.	—	—	—	—
THF	50	Insol.	Insol.	Insol.	—	—	—
Acetone	50	Insol.	Insol.	Insol.	—	—	—
Dioxane	50	Insol.	Insol.	Insol.	Insol.	Insol.	—

Measurement of Volume Swelling

After vacuum-drying at 60°C, the extracted film was soaked in water at 25°C and the swollen film was weighed. The swollen volume was calculated from the weight using the density of HPC (1.17 g/cm³).¹⁵ Figure 1 shows the volume swelling ratio against soaking time. This indicated that it takes ca. 40 min for swelling to reach equilibrium. However, in this study, we weighed the swollen film after 12 h.

Circular Dichroism (CD) of Solid Films

CD spectra of film (80 μm thick) between glass plates were determined with a Jasco J-40S spectropolarimeter (Japan Spectroscopic Co.) at room temperature.

Small-Angle Light Scattering (SALS) of Solid Films

Light-scattering patterns were obtained with a 15 mW He—Ne gas laser as a light source.

Scanning Electric Microscopy (SEM) of Solid Films

Scanning electron micrographs were obtained with a scanning electron microscope (Hitachi Seisakusho, S-415). Cast films were freeze-fractured by bending in liquid nitrogen on a plane parallel to that of the shear.

Measurement of Tensile Properties

The properties of film specimens (size: 3 cm long × 0.3 cm wide × ca. 0.009 cm thick) were determined by using a Tensilon VTM-IV-500 (Toyo Baldwin

Co.) at room atmosphere (ca. 18°C, 50% RH). An interval between chucks of 2 cm was chosen. The crosshead speed was 5 mm/min. Three measurements were performed and the mean was obtained for the films.

Measurement of Dynamic Mechanical Properties

The measurements of film specimens (size: 2.7 cm long × 0.3 cm wide × ca. 0.009 cm thick) were carried out with a Rheovibron DDV-II-C (Toyo Baldwin) in the temperature range from 10 to ca. 200°C at a heating rate of ca. 1.4°C/min and a constant frequency of 110 Hz.

Measurement of Tensile Creep

The creep data under reduced pressure (ca. 3.0 Pa) at 90°C were obtained using an apparatus designed and constructed in our laboratory. The apparatus and procedure are shown in detail elsewhere.¹⁶⁻¹⁸ Our main feature of creep measurement is an evaluation of an activated volume (*V*) on the basis of the Eyring activated process¹⁹: The value of *V* was evaluated by applying the approach proposed by Wilding and Ward.^{20,21} The size of the specimen was 4 cm long × 0.17 cm wide × ca. 0.005 cm thick.

RESULTS AND DISCUSSION

Identification of Cross-Linking

Solubility in Water at Room Temperature

Table I shows the solubility of HPC film cast from each system. Many cast films were insoluble in wa-

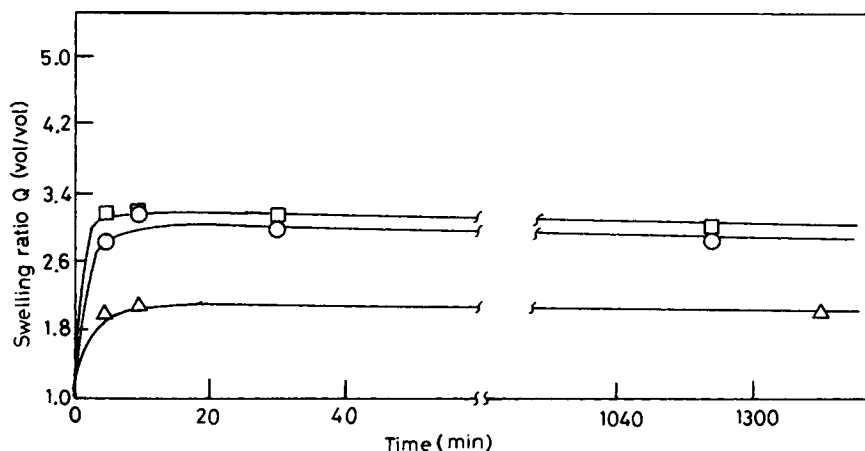


Figure 1 Soaking time dependence of swelling ratio for extracted HPC film cast from each system with 3.5 wt % *p*-FA; solvent: (○) water; (△) methanol; (□) ethanol.

Table II Volume Swelling of Extracted Liquid Crystalline HPC Solid Films

Solvent	Crosslink, Catalyst (wt %, wt %)	Gel Contents (%)	Swelling Ratio Q (vol/vol)
Water	<i>p</i> -FA, HCl: (3.5, 3.5)	89.6	2.7
	DMU, NaOH: (3.5, 3.5)	90.0	2.8
Methanol	<i>p</i> -FA, HCl: (3.5, 3.5)	58.0	4.0
	"	88.0	3.6
	"	95.0	1.8
DMAc	DMU, HCl: (3.5, 3.5)	66.1	7.5
	DMU, NaOH: (3.5, 3.5)	72.8	10.6
	TDI, DBTDL: (3.5, 3.5)	93.1	6.8

ter. This finding clearly indicated that the insolubility of HPC film is greatly dependent on the species of solvent, cross-linking agent, and catalyst. All films cast from the solution with only HCl or NaOH (without cross-linking agent) were easily soluble in water as expected.

Volume Swelling

Table II shows the data of swelling and gel content for HPC cast films. In the case of the methanol system with *p*-FA, the swelling ratio decreased with increasing gel content. This was the same as the general trends for cross-linked polymers. Another feature shown in Table II is that the swelling is dependent on the cross-linking agent: For DMU, the swellings were relatively great, compared to those for other cross-linking agents. Our results noted above show that the insolubility of HPC films cast from many systems is due to cross-linking.

In our previous papers,⁸⁻¹¹ we did not show whether the intercross-linking occurs between two adjacent HPC molecules in the same layer or between the molecules in two adjacent layers. Here, following the method proposed by Tsutsui and Tanaka,⁶ we try to estimate the dimension of intercross-linking: the intercross-linking between molecules in one layer (two dimensional) or between molecules in other layers (three dimensional). Tsutsui and Tanaka⁶ reported that the cholesteric pitch (S) is expressed in terms of the swelling ratio (Q) and proposed the equations for three-dimensional and two-dimensional swelling for cross-linked cholesteric polymer: For the simplest case:

$$S/S_0 = Q^{1/3} \quad \text{for three-dimensional} \quad (1)$$

$$S/S_0 = Q^{1/2} \quad \text{for two-dimensional} \quad (2)$$

De Vries²² derived an equation for the cholesteric pitch to wavelength of the selective reflection (λ):

$$S = n \cdot \lambda \quad (3)$$

$$S_0 = n_0 \cdot \lambda_0 \quad (3')$$

where n is mean birefringence, and S_0 , n_0 , and λ_0 denote S , n , and λ for the unswollen state, respectively. From eqs. (1), (2), (3), and (3'), we can derive the following equations:

$$S/S_0 = n/n_0 \cdot \lambda/\lambda_0 = Q^{1/3} \quad (1')$$

$$= Q^{1/2} \quad (2')$$

Here, we assume that $n_0 = n$; then, we finally can derive the equations

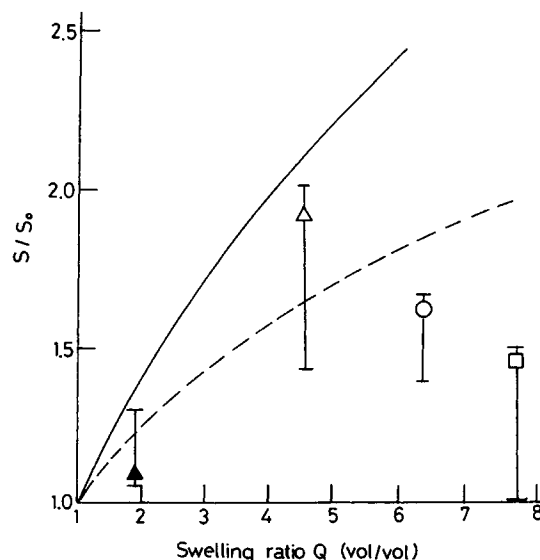


Figure 2 S/S_0 vs. swelling ratio for each HPC film. Cast system: (O) water with 3.5 wt % DMU; (Δ) methanol with 3.5 wt % DMU; (\square) DMAc with 3.5 wt % DMU; (\blacktriangle) methanol with 3.5 wt % *p*-FA. The broken and solid lines represent three-dimensional and two-dimensional swelling, respectively.

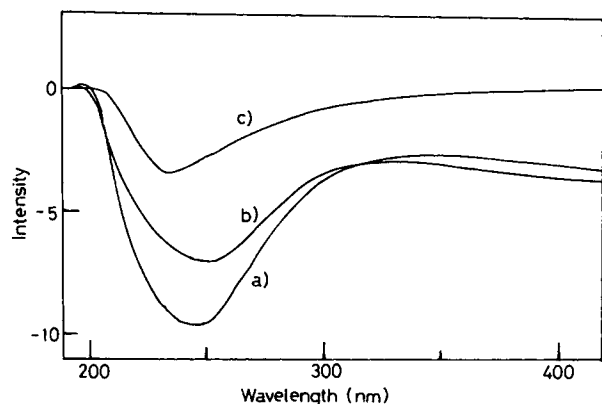


Figure 3 CD spectrum for HPC film cast from the methanol system: (a) with no cross-linking agent; (b) with 3.5 wt % *p*-FA; (c) with 3.5 wt % DMU.

$$S/S_0 = \lambda/\lambda_0 = Q^{1/3} \quad (1'')$$

$$= Q^{1/2} \quad (2'')$$

We determined λ and λ_0 with the CD spectra for the swollen and unswollen films, respectively. Figure 2 shows the pitch vs. swelling ratio for cross-linked HPC films. The broken and the solid lines in Figure 2 represent the three-dimensional and two-dimensional swelling based on the eqs. (1'') and (2''), respectively. Our experimental data were lower than the curve indicating the three-dimensional swelling, except for the methanol system with DMU. Our finding suggested that the three-dimensional cross-linking preferentially performs between HPC mol-

ecules: both between molecules in the same layer and between molecules in the adjacent layers.

Identification of Cholesteric Order

We have described the way of how the cholesteric liquid crystalline order in the cast film is evidenced by polarized microscopy on the basis of the existence of band texture.⁸ For all films in this study, the textures for cast films were almost the same as those for the starting liquid crystalline solutions. This strongly suggested that our cast films retain the cholesteric order. Here, in order to corroborate the cholesteric order in the cast films, we will show the data on the CD. Furthermore, we will add also the data on SALS and SEM.

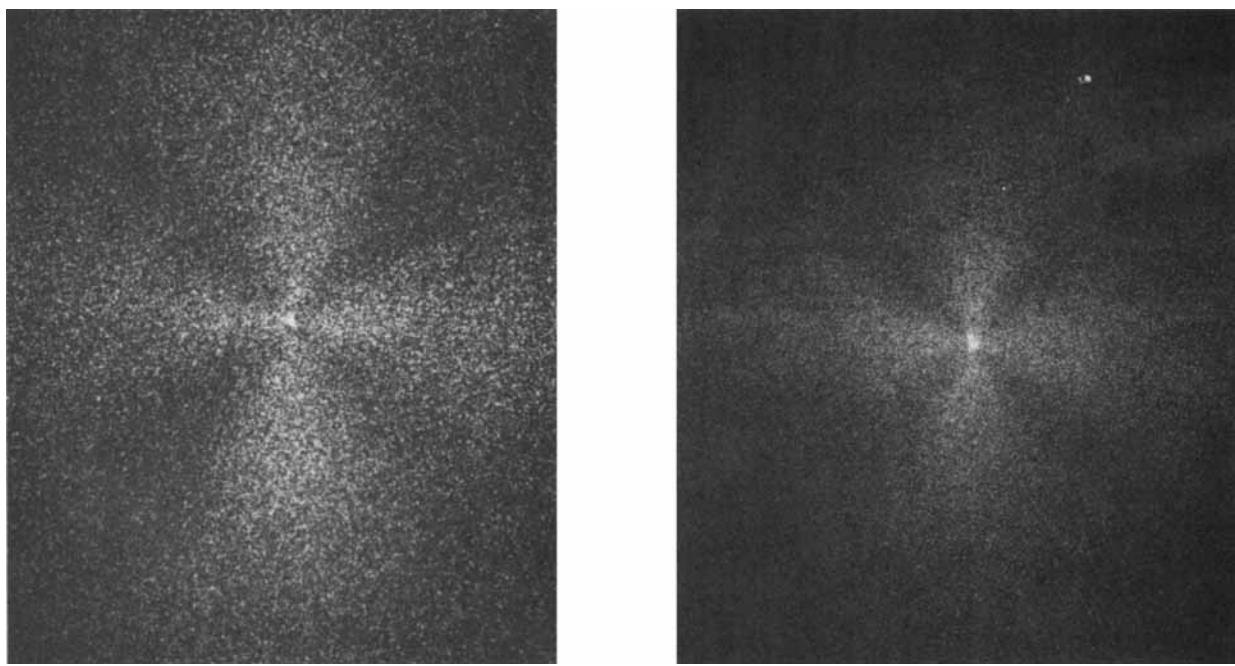
CD Spectra

Figure 3 shows the typical CD spectra for the HPC films cast from the methanol system. Films cast from the systems with *p*-FA, DMU, and no cross-linking agent exhibited a negative peak. Table III shows the maximum wavelength (λ) of the cast films. The values of λ were about 240 nm, although some films showed greater values of λ . Effects of addition of the cross-linking agent and of extraction of films on the value of λ were not distinct. The cholesteric sense of the cast films was right-handed regardless of solvent and cross-linking agent species. Our finding clearly indicated that our films retain the cholesteric order.

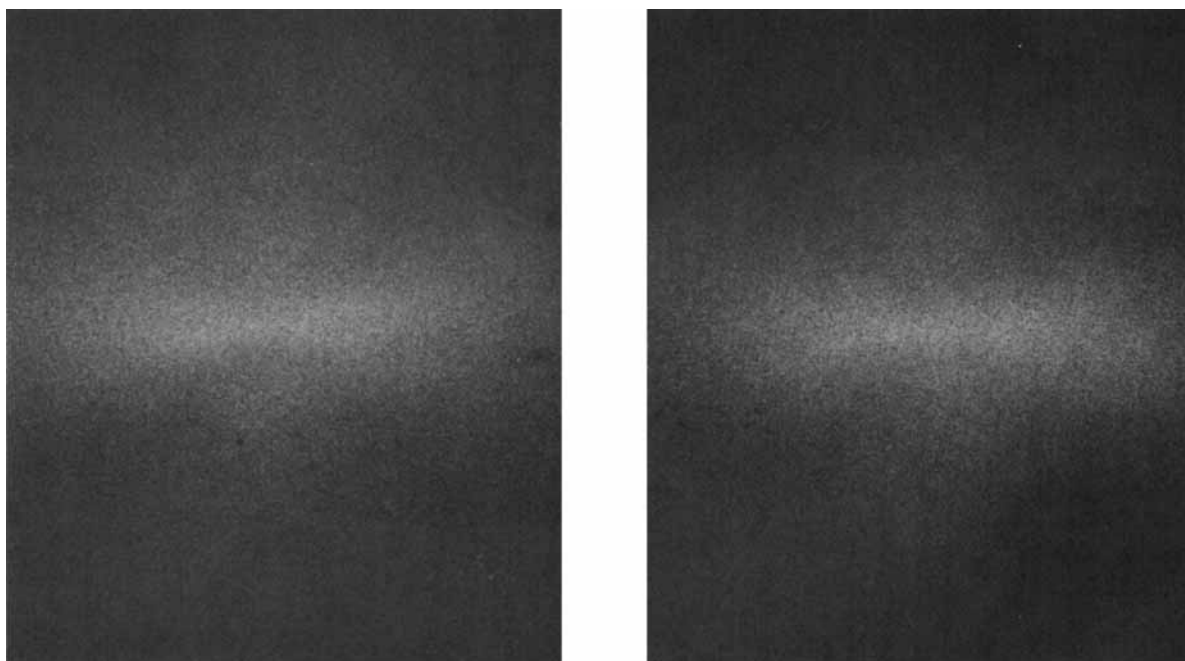
Table III Maximum Wavelength of CD Spectrum for Each HPC Solid Film

Solvent	Noncross-Linked	<i>p</i> -FA	<i>p</i> -FA _{ex}	TDI	TDI _{ex}	DMU	DMU _{ex}	DMTU	DMTU _{ex}
Water	230	238	243			243	420	334	320
Methanol	245	235	230			234	342	284	251
Ethanol	211	290	260			234		515	512
Propanol		243							
Butanol	214	217							
Pentanol	364								
Benzylalcohol	270								
<i>m</i> -Cresol	470								
Morpholine	230								
DMAc	311			308	307	367	485		
DMSO	240			313					
Pyridine	410								
Chloroform	248								
THF	244								
Acetone	250			345					
Dioxane	223	309	335	309		565		277	

ex: extracted film.

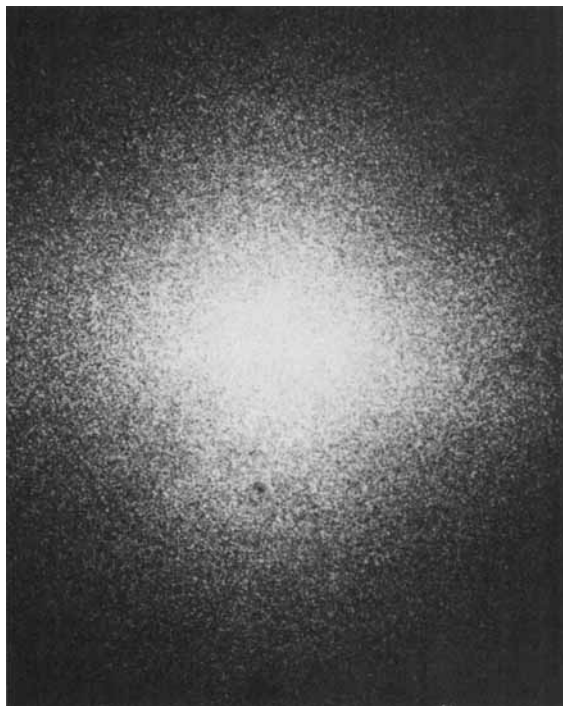


(a)



(b)

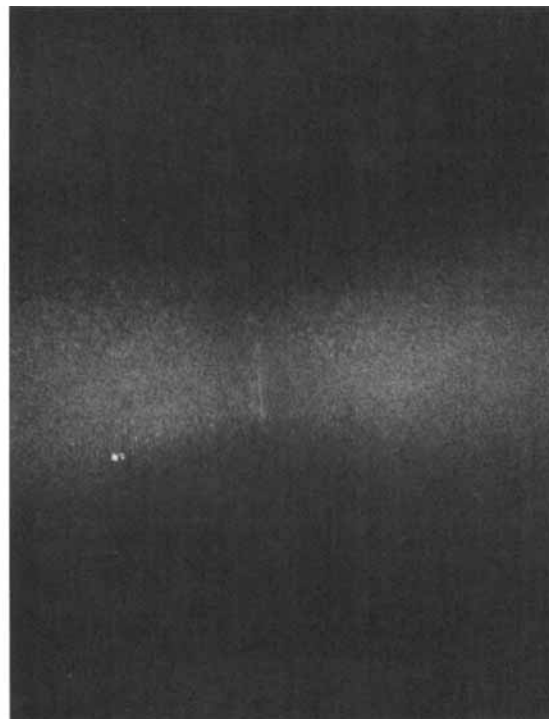
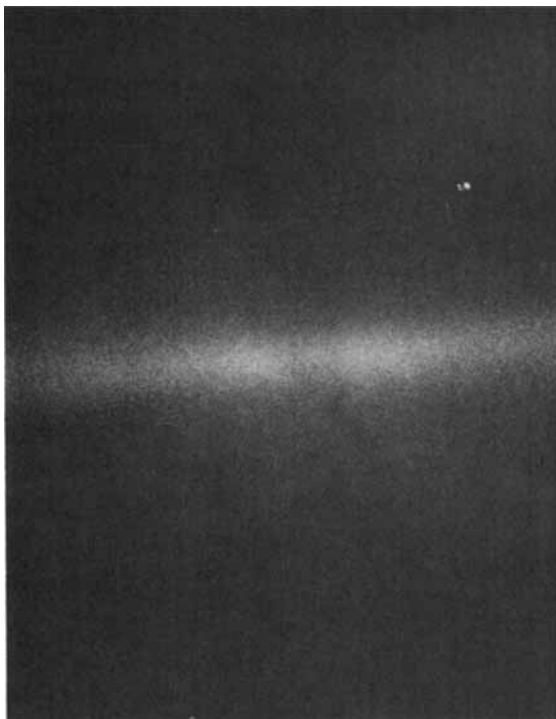
Figure 4 H_v SALS patterns for HPC films cast from each system: (a) water with no (left) and 3.5 wt % p -FA (right); (b) methanol with no (left) and 3.5 wt % p -FA (right), with band texture; (c) methanol with 3.5 wt % p -FA, with no band texture; (d) dioxane with no (left) and 3.5 wt % p -FA (right).



(c)

SALS Patterns

Figure 4 shows the H_v SALS patterns of HPC cast films. Films cast from the water system with and without a cross-linking agent exhibited the plus (+)-type pattern, regardless of cross-linking species. This pattern was similar to those of HPC films reported by Samuels,¹⁵ Hashimoto et al.,²³ and Takahashi et al.²⁴ However, films cast from methanol and dioxane systems exhibited the minus (-)-type pattern. Those films exhibited the band texture, and the direction of the elongated pattern was normal to the band texture. Film cast from DMAc, which exhibited no band texture, exhibited the (+)-type pattern.¹⁷ This suggested that the pattern seems to depend on the existence of band texture. Then, we tried to prepare the methanol-cast film with no band texture, controlling the evaporation rate of methanol. Such a film exhibited the (+)-type pattern shown in Figure 4(c). Therefore, films with no band texture exhibited the (+)-type pattern, whereas films with band texture exhibited the (-)-type pattern. Those patterns were independent of the cross-linking.



(d)

Figure 4 (Continued from the previous page)

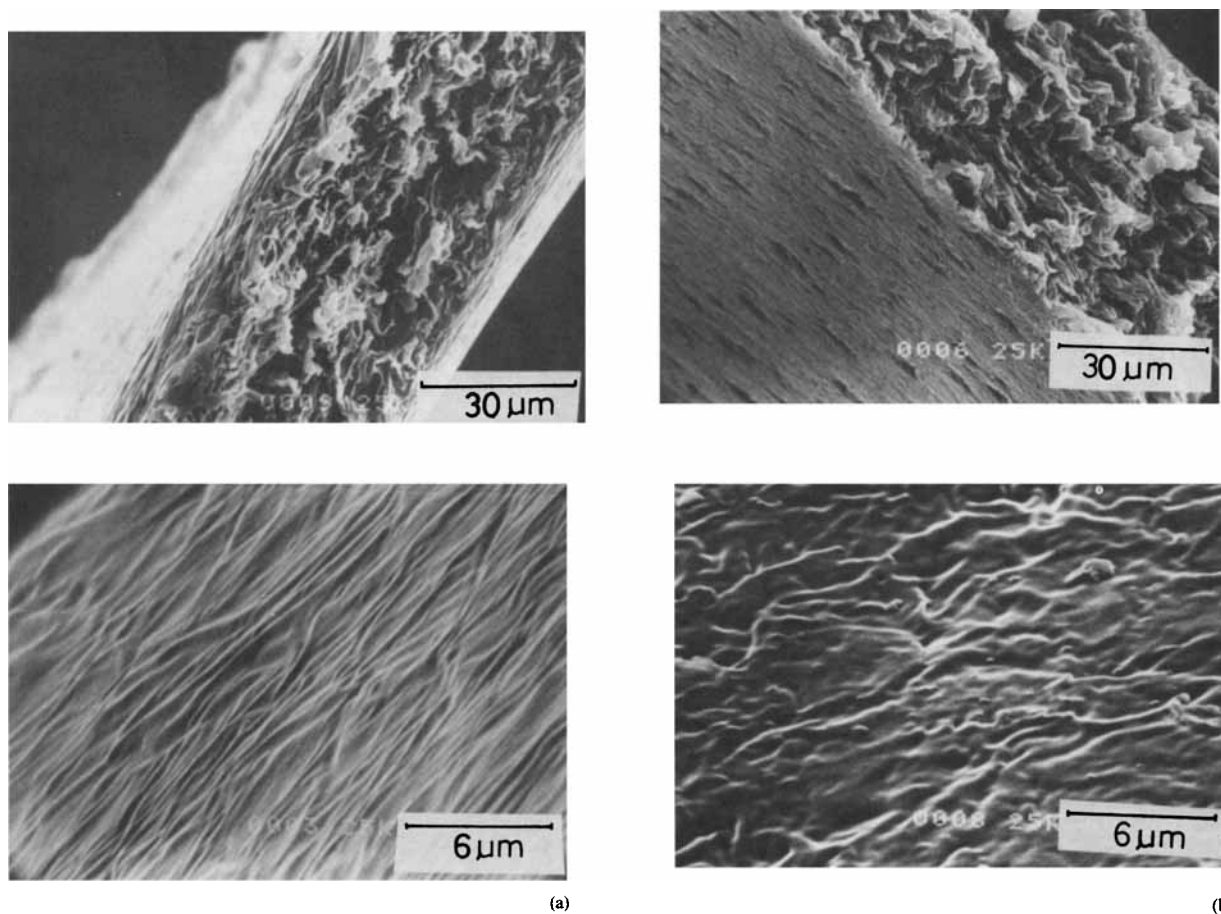


Figure 5 Scanning electron photomicrographs of fracture plane (upper) and free-surface plane (lower) for HPC films cast from each system: (a) water with no cross-linking; (b) water with 3.5 wt % DMU; (c) methanol with no cross-linking agent; (d) methanol with 3.5 wt % DMU; (e) DMAc with no cross-linking agent; (f) DMAc with 3.5 wt % DMU.

SEM

Figure 5 shows the microphotographs of the fractured or free-surface plane for cast films with and without a cross-linking agent. The texture of the fractured or free-surface plane was not smooth and was almost independent of solvent and cross-linking. In the fractured plane, fluffy morphology was observed. In the free-surface plane, wrinkles formed in a wavy pattern. The wrinkled texture for the free-surface plane was similar to that for the Teflon film plane.

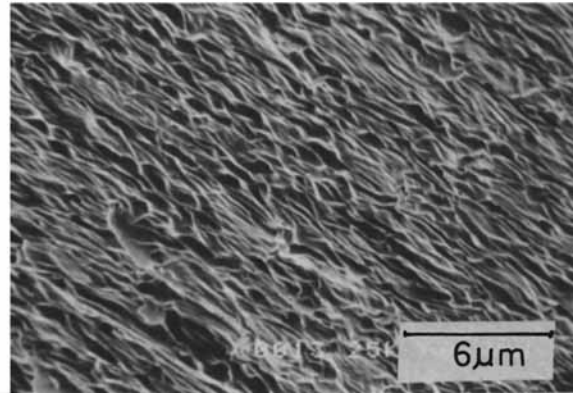
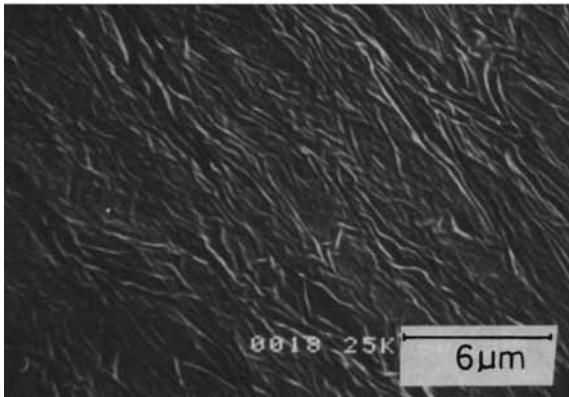
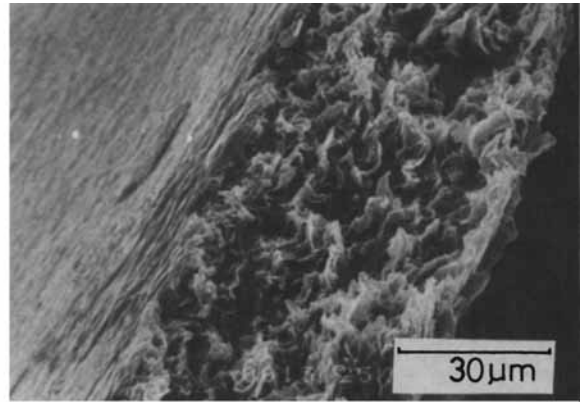
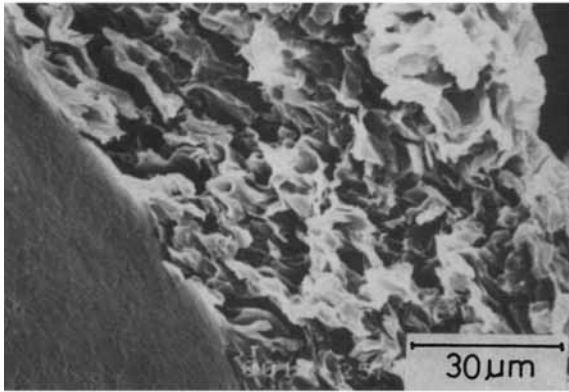
In summarizing the findings noted above, the three-dimensional cross-linking of HPC was performed and was dependent on the solvent-cross-linking agent pairs. The cross-linked HPC-cast films retained the cholesteric liquid crystalline order. That indicated that we can prepare the solvent cast films in which liquid crystalline order was fixed by cross-linking. The SALS patterns for the films were independent of cross-linking and were only dependent on the existence of band texture. The morphologies

in films and on the film surface seemed to be independent of solvent-cross-linking agent pairs.

Mechanical Properties

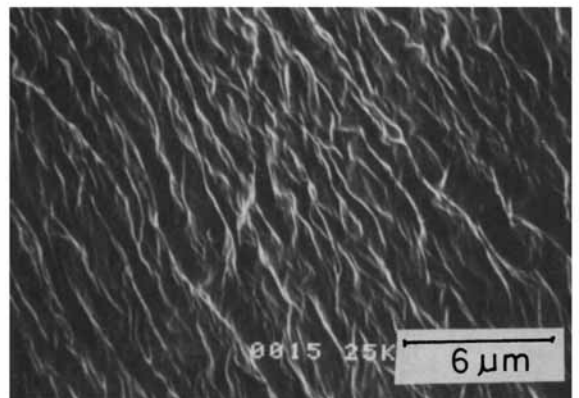
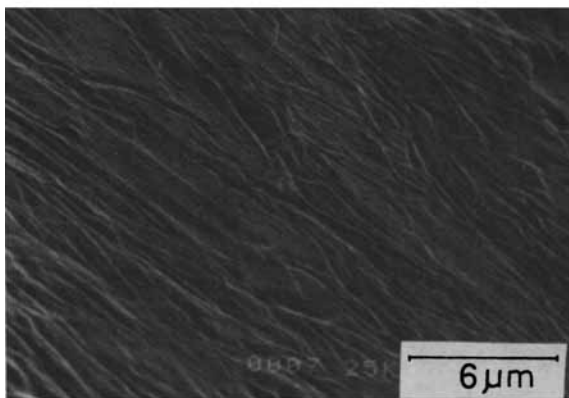
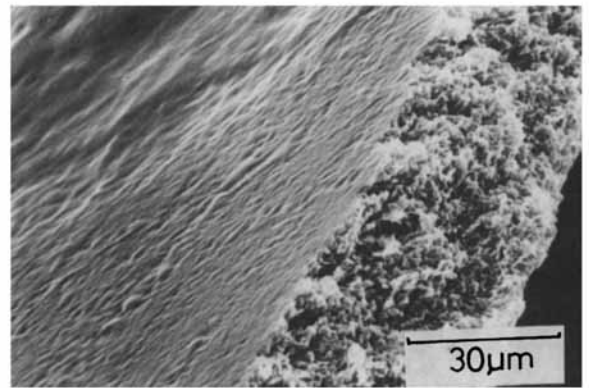
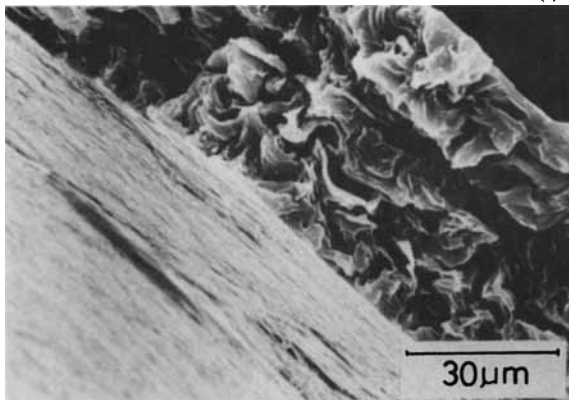
Tensile Properties

Figure 6 shows the stress-strain curves for HPC films cast from water, methanol, and DMAc systems with and without each cross-linking agent. All films exhibited no marked yield behavior regardless of cross-linked or uncross-linked films. In the case of the system with *p*-FA, Young's modulus and tensile strength increased and elongation decreased with cross-linking. After extraction of the cross-linked film, Young's modulus and tensile strength decreased and elongation increased, but the elongation was still smaller than that for uncross-linked film. The findings for water and methanol systems with *p*-FA were almost the same as those for ethanol and butanol systems with *p*-FA.⁹ The tensile behavior for the cross-linked films with DMU and TDI was



(c)

(d)



(e)

(f)

Figure 5 (Continued from the previous page)

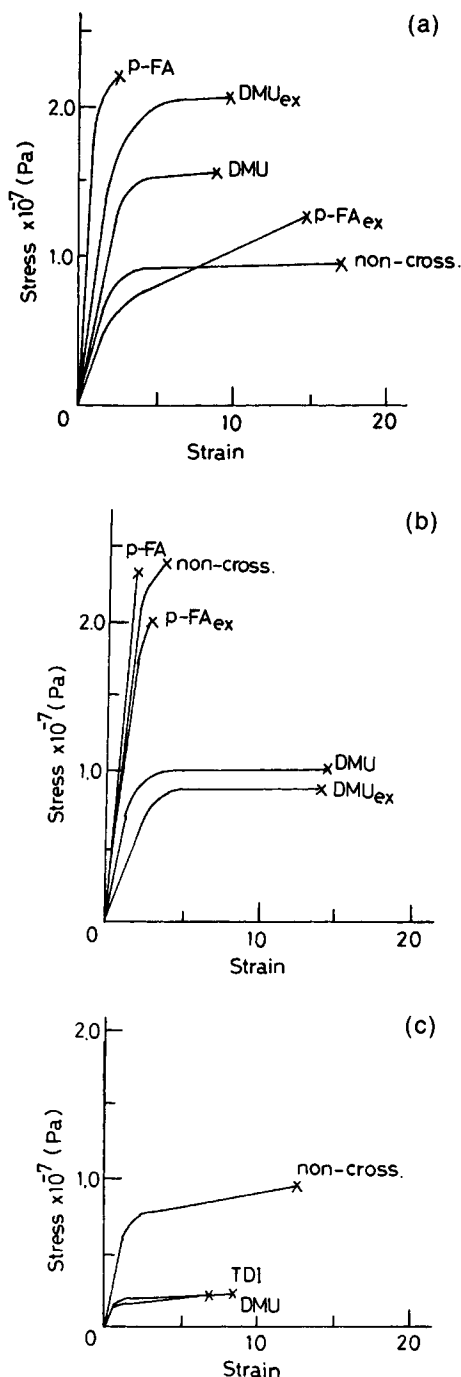


Figure 6 Stress-strain curves for HPC films cast from each system: (a) water; (b) methanol; (c) DMAc. Cross-linking agent was noted in the figures. The subscript "ex" in the figures is used to designate the data for the extracted film.

different from that for the films with *p*-FA. Except for the water system, Young's modulus and strength decreased and elongation increased with cross-linking. For cross-linked cellulose fibers, for example,

cotton, Young's modulus increases and strength and elongation decrease with cross-linking.¹⁴ Our findings suggested that the properties depend on the cast conditions.

As shown in Table II, the swelling of cross-linked films depended on the species of the cross-linking agent. This qualitatively demonstrates that the films cast from different cross-linking agent systems have different cross-linking structures that could not be observed by SEM. Here, we took up the averaged molecular weight per cross-linked unit (\bar{M}_c) as a measure of cross-linked structure. Flory²⁵ described the relation between the swelling ratio and \bar{M}_c :

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{V/V_1 \cdot \{\ln(1 - V_2) + V_2 + \chi_1 \cdot V_2^2\}}{\{(V_2)^{1/3} - 1/2(V_2)\}} \quad (4)$$

where \bar{M}_n is number-average molecular weight of HPC; V , the specific volume of HPC ($1/1.17 = 0.855 \text{ cm}^3/\text{g}$)¹⁵; V_1 , the molar volume of solvent at 25°C; χ_1 , the interaction parameter between solvent and HPC (0.55)²⁶; and V_2 , the volume fraction of the equilibrium swelling polymer. As is well known, eq. (4) is for an isotropic rubber. Therefore, in a strict sense, eq. (4) may not be valid for our anisotropic films. However, for convenience, we will estimate \bar{M}_c from the swelling data by applying eq. (4) and will compare the tensile properties of each film based on the \bar{M}_c . (Note: The actual magnitude of \bar{M}_c for each film is not so meaningful.)

Table IV shows the tensile properties for each film, together with the data of gel content and \bar{M}_c . For the films cast from the methanol system, Young's modulus and tensile strength decreased and elongation increased with increasing \bar{M}_c . This was the behavior as expected, because cross-linking generally reduces the mobility of molecules.²⁷ However, for the films cast from the water system, the relation between tensile properties and \bar{M}_c was not general. The effect of extraction on the tensile properties for the films cast from the water system is also not clear now.

Dynamic Mechanical Properties

Figure 7 shows the temperature dependence of storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) for HPC films cast from water, methanol, and DMAc systems. For films cast from water and DMAc systems, E' and E'' decreased with cross-linking over the whole range of temperature. On the other hand, for films cast from the methanol system,

Table IV Tensile Properties, Gel Content, and \bar{M}_c of Cross-Linked HPC Solid Films

Sample	(Cross-Link, Catalyst) (wt %, wt %)	Gel Contents (%)	\bar{M}_c	Test Temp (°C)	Tensile Property		
					E (Pa)	σ (Pa)	ϵ (%)
HPC/water	(0, 0)	0		25	4.4×10^8	0.93×10^7	17.3
<i>p</i> -FA	(3.5,3.5)	89.6		25	17.0	2.20	2.7
<i>p</i> -FA	(3.5,3.5)ex	100	2,490	25	3.8	1.26	15.7
DMU	(3.5,3.5)	91.4		25	4.8	1.54	9.2
DMU	(3.5,3.5)ex	100	16,300	21	8.6	2.05	9.9
HPC/me-OH	(0, 0)	0		18	12.4	2.40	3.5
<i>p</i> -FA	(3.5,3.5)	95.0		18	15.5	2.25	1.8
<i>p</i> -FA	(3.5,3.5)ex	100	1,960	18	11.7	2.00	2.4
DMU	(3.5,3.5)	66.1		25	4.5	1.06	14.3
DMU	(3.5,3.5)ex	100	4,540	21	3.1	0.91	14.1
HPC/DMAc	(0, 0)	0		30	5.7	0.9	12.6
DMU	(3.5,3.5)	72.8	33,350 ^a	30	2.3	0.23	7.0
TDI	(3.5,3.5)	93.1	20,700 ^a	30	2.7	0.23	8.5

ex: extracted film.

^a The value of extracted film.

E' for the cross-linked film with *p*-FA was greater than that for the uncross-linked one and E' for the cross-linked film with DMU was also greater above ca. 90°C.

Figure 8 shows the dynamic properties as a function of gel content for films cast from the methanol and dioxane systems. E' for methanol-cast films increased with gel content. However, E'' for methanol-cast films and E' and E'' for dioxane-cast films did not depend markedly on the gel content.

Now, we must describe the most remarkable feature shown in Figure 7: the marked decrease in E' and E'' around 40°C for some films. This behavior has been reported by Rials and Glasser.¹² They have described three effects accounting for the behavior: cross-linking, solvent evaporation, and crystallization. Generally, cross-linking reduces crystallinity of polymers.²⁷ Then, after cross-linking, crystallization is presumed less possible and we exclude the effect of crystallization on the behavior. For the cast films, there is a possibility of residual solvent in the films. However, uncross-linked films cast from the water and methanol systems did not exhibit such behavior. Therefore, we think that there is less possibility of an effect of the residual solvent, except for DMAc-cast films, in which DMAc remains in the film due to its high boiling point. Next, we tried to anneal the cast films at 80°C in vacuum. Figure 9 shows the effect of annealing time on the properties for the films cast from water and DMAc systems. For DMAc-cast films, the decrease in E' and E''

around 40°C became insignificant and finally disappeared with increasing annealing time and the same trend was also seen for the water-cast films. In those figures, the data for the extracted films were also shown. This was because the extraction is a kind of annealing. The extracted films did not exhibit the decrease in E' and E'' .

If the liquid crystalline order in solution decreased upon cross-linking, some events will be detected by CD. Then, in Figure 10, we show the CD spectra for the annealed films cast from both systems noted above. The width of the peak became narrow with annealing. This suggested that the liquid crystalline order strengthens with annealing. Consequently, the decrease in E' and E'' around 40°C for films cast from water and methanol with a cross-linking agent was attributed to the disorder of liquid crystal upon cross-linking and the decrease for films cast from DMAc was done to both the disorder and the residual solvent.

With respect to $\tan \delta$, there were two relaxation processes for some films within our temperature range. The lower relaxation process corresponded to T_g .²⁸ Generally, cross-linking increases the T_g of polymers.²⁷ However, in our study, the increase in T_g with cross-linking was not significant, even in the dioxane system. We had no definite reason why the T_g of cast films did not increase with cross-linking. Rials and Glasser¹² reported the higher relaxation process to arise from the liquid crystalline phase.

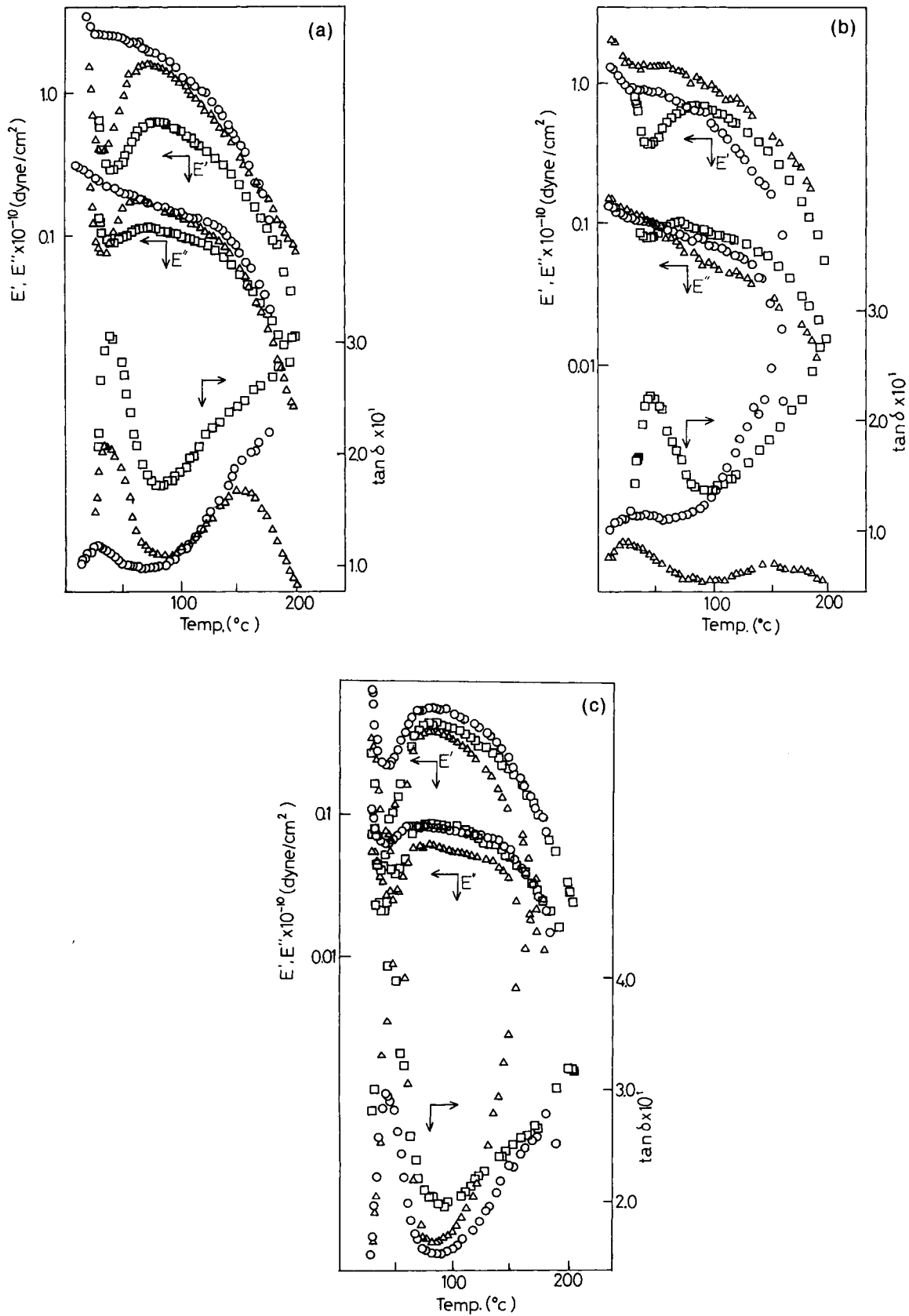


Figure 7 Temperature dependence of dynamic mechanical properties for HPC film cast from each system: (a) Water, cross-linking agent concentration (wt %): (○) 0; (△) *p*-FA (3.5); (□) DMU (3.5). (b) methanol, cross-linking agent concentration (wt %): (○) 0, (△) *p*-FA (3.5), (□) DMU (3.5). (c) DMAc, cross-linking agent concentration (wt %): (○) 0; (△) TDI (3.5); (□) DMU (3.5).

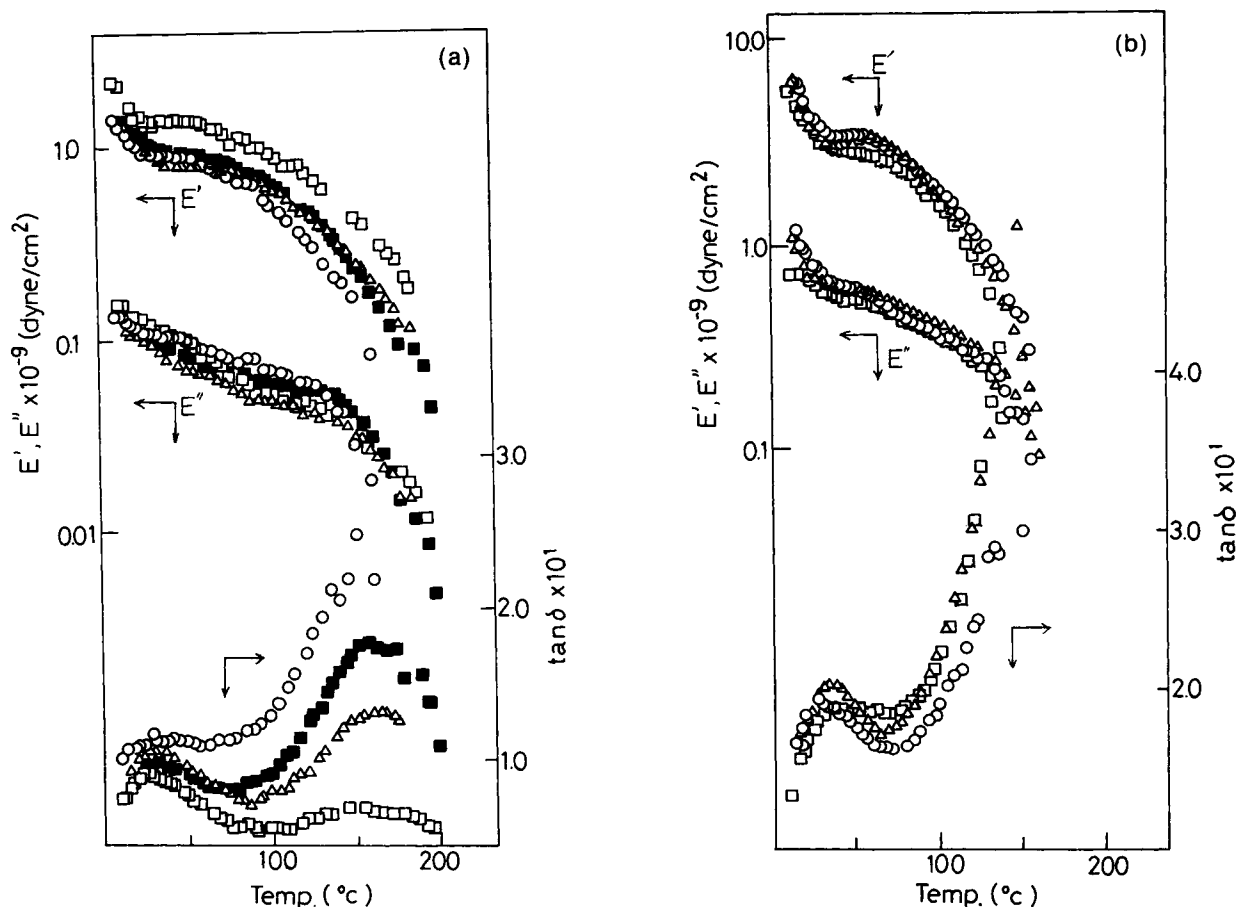


Figure 8 Dynamic mechanical properties as a function of gel content for HPC film cast from each system with *p*-FA at 110 Hz. (a) Methanol; gel concentration (%): (○) 0; (△) 58; (□) 95. Open mark: nonextracted film; closed mark: extracted film. (b) dioxane; gel concentration (%): (○) 0; (△) 95; (□) 100.

Creep Properties

The creep strain for all films increased with time and stress, and after given initial times, strain rate decreased with strain and finally attained a constant level.¹⁷⁻²¹ The constant plateau strain rate $\dot{\epsilon}_p$ for films cast from water and methanol with DMU was plotted against stress in Figure 11. The $\dot{\epsilon}_p$ increased with stress and showed a linear logarithmic dependence on stress. This confirms that the thermally activated Eyring process can be applied to the creep behavior of our films^{20,21}:

$$\log \dot{\epsilon}_p = \log(\dot{\epsilon}_0/2) - \Delta U/2.3kT + \sigma \cdot V/2.3kT \quad (5)$$

where σ is the applied stress; V , the activated volume; $\dot{\epsilon}_0$, a constant; k , Boltzmann's constant; and T , absolute temperature. The slope shown in Figure 11 was used to evaluate the value of V . The value

of V for each film is summarized in Table V. Clearly shown in Figure 11 (a) is that there are two processes for uncross-linked film cast from water: process 1 at a lower stress level and process 2 at a higher stress level. Our findings show that for water-cast films the values of V of process 2 is independent of cross-linking, but for methanol-cast films, the value of V for uncross-linked film is greater than that for the cross-linked one. This finding is inconsistent with those for polyethylene by Wilding and Ward^{20,21} and Hikmet et al.²⁸

Ward and Wilding²¹ showed that the activated volume V depends on the degree of crystal continuity: V decreases with increasing degree of crystal continuity. Hikmet et al.²⁸ determined that cross-linking may be expected to increase the V , because the cross-linking reduces the crystal continuity. However, as Ward and Wilding²¹ noted, cross-linking performs in an amorphous region and may act

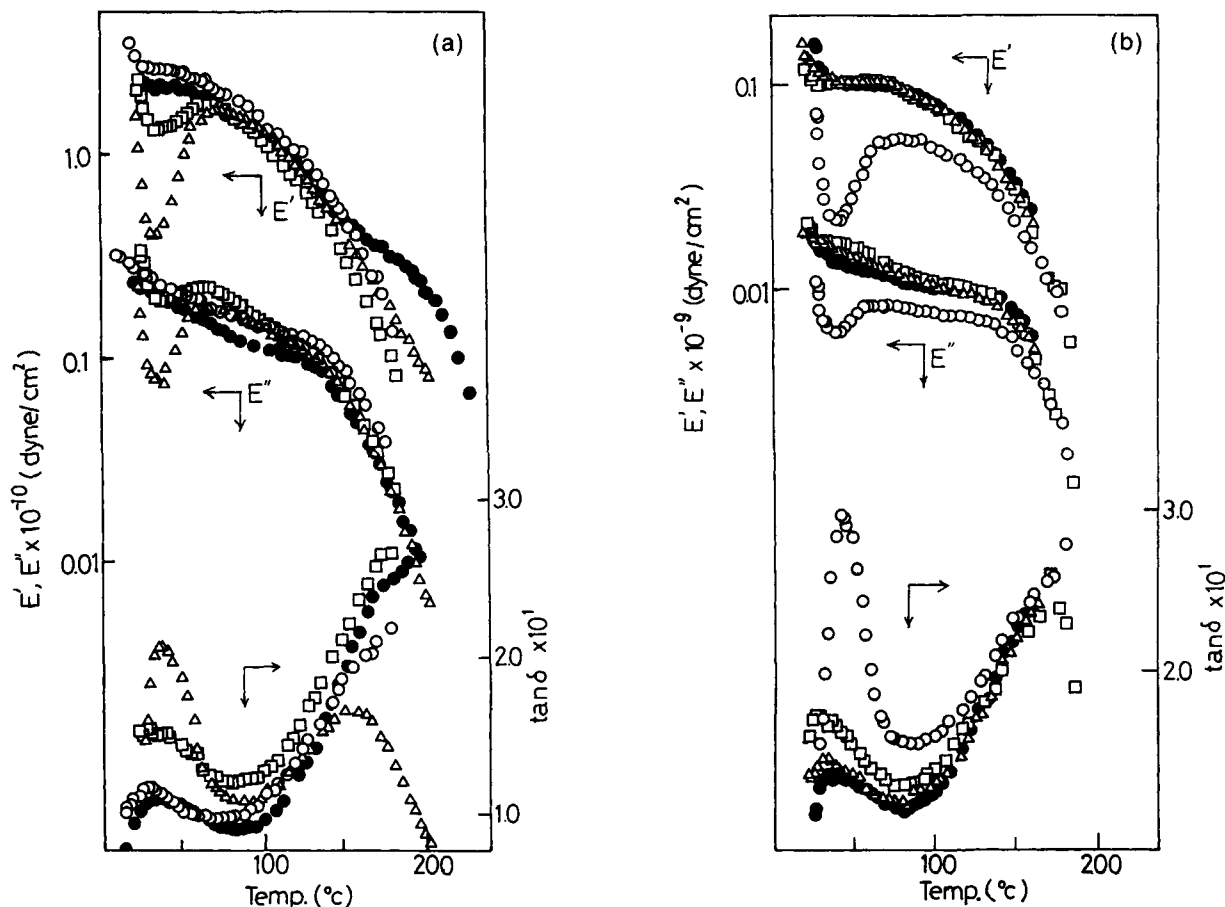


Figure 9 Effect of annealing on the dynamic mechanical properties for HPC film cast from each system. (a) Water with 3.5 wt % *p*-FA; annealing time (h): (Δ) 0; (\square) 7. (\circ) film with no cross-linking agent; (\bullet) extracted film. (b) DMAc with no cross-linking agent; annealing time (h): (\circ) 0; (Δ) 5; (\square) 7; (\bullet) 24.

as an intercrystalline bridge that induces the crystalline continuity. Hence, there may be a possibility that the cross-linking reduces the V , as in our finding for HPC film cast from methanol with DMU. It is noteworthy that the cross-linking for liquid crystalline polymers appears to be different from that for crystalline polymers: For the former, the cross-linking can occur in the liquid crystalline phases; whereas for the latter, the cross-linking can occur only in the amorphous regions. Clearly, our data are not sufficient to describe the effect of cross-linking on the V for HPC films. Furthermore, if the cross-linking reduces the V , the cross-linking should increase modulus.²¹ This was not true in this study: The cross-linked HPC film cast from the methanol system with DMU exhibited lower E and E' than the uncross-linked one. It seemed that the cross-linking with DMU produces a loose polymer network and may not markedly increase the V . This sugges-

tion is confirmed by the greater swelling of cross-linked HPC films with DMU rather than that of the film with *p*-FA.

Another feature in Figure 11 is that the ϵ_p for cross-linked films is smaller than that for uncross-linked ones. This clearly showed the improvement of creep resistance by cross-linking.

Comparison of Mechanical Properties

We showed three mechanical properties independently. When the cholesteric liquid crystalline order fixed by cross-linking is not destroyed at relatively small strain, there seems to exist qualitative interrelations among the mechanical properties. Here, we will attempt to compare qualitatively the data of E' at 18°C and Young's modulus (E) and of E'' at 18°C and ϵ_p . Comparison of the data shown in Table IV and Figure 7 was made.

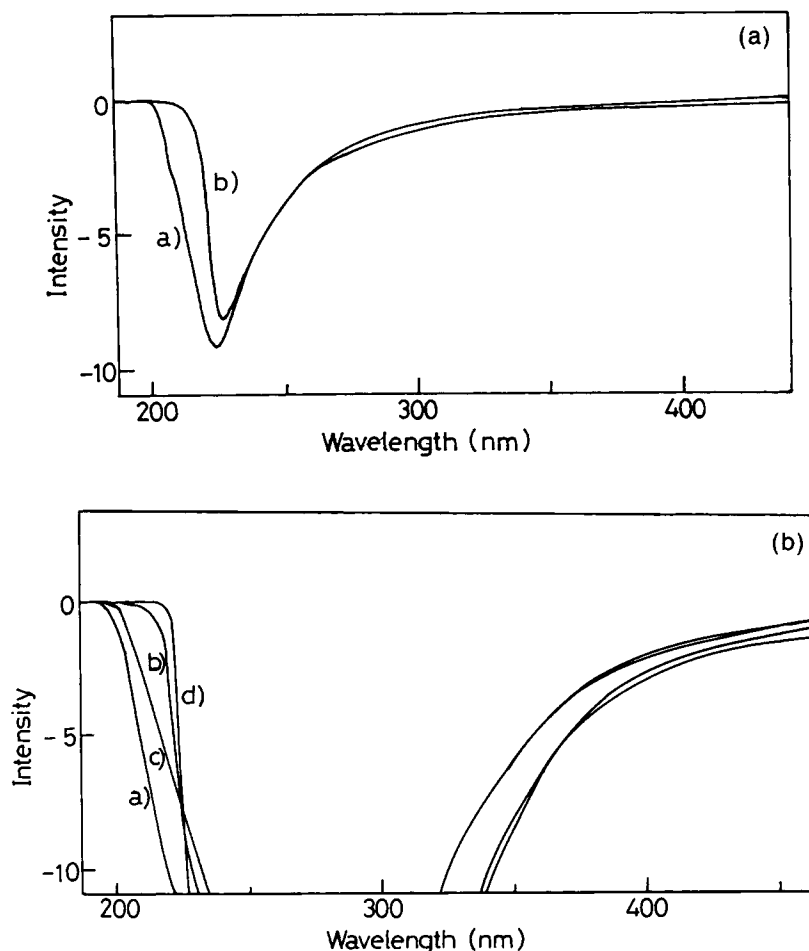


Figure 10 Effect of annealing on CD spectrum for HPC film cast from each system. (a) Water with 3.5 wt % *p*-FA; annealing time (h): (a) 0; (b) 7. (b) DMAc with no cross-linking agent; annealing time (h): (a) 0; (b) 5; (c) 7; (d) 24.

E' and Young's Modulus (*E*)

Both parameters are measures of elasticity. Then, we expect a certain correlation between them. For water-cast films with *p*-FA and DMU, cross-linked films exhibited higher *E*, but did not exhibit higher *E'*. On the other hand, for methanol- and DMAc-cast films, the cross-linked film with *p*-FA exhibited higher *E* and *E'* and the cross-linked film with DMU or TDI exhibited smaller *E* and *E'*. The comparison of the elastic parameters suggested that there qualitatively existed a correlation, except for water-cast films.

E'' and ϵ_p

Both parameters are measures of the viscosity component. For water-cast films with DMU, the cross-linked film exhibited smaller *E''* and smaller ϵ_p than those for the uncross-linked one. For methanol-cast

film with DMU, the cross-linked film showed smaller ϵ_p but had almost the same values of *E''* as those for the uncross-linked one. Our comparison did not necessarily show a qualitative correlation between them.

Table V Activated Volume for Liquid Crystalline HPC Solid Films

Solvent	Cross-link, Catalyst (wt %, wt %)	Stress Range (MPa)	<i>V</i> (Å ³)
Water	(0, 0)	< 1.3	23,900
	(0, 0)	2.0-3.2	3,150
Methanol	DMU, NaOH(3.5, 3.5)	2.0-4.0	3,170
	(0, 0)	2.3-2.8	4,210
	DMU, NaOH(3.5, 3.5)	2.3-3.0	3,670

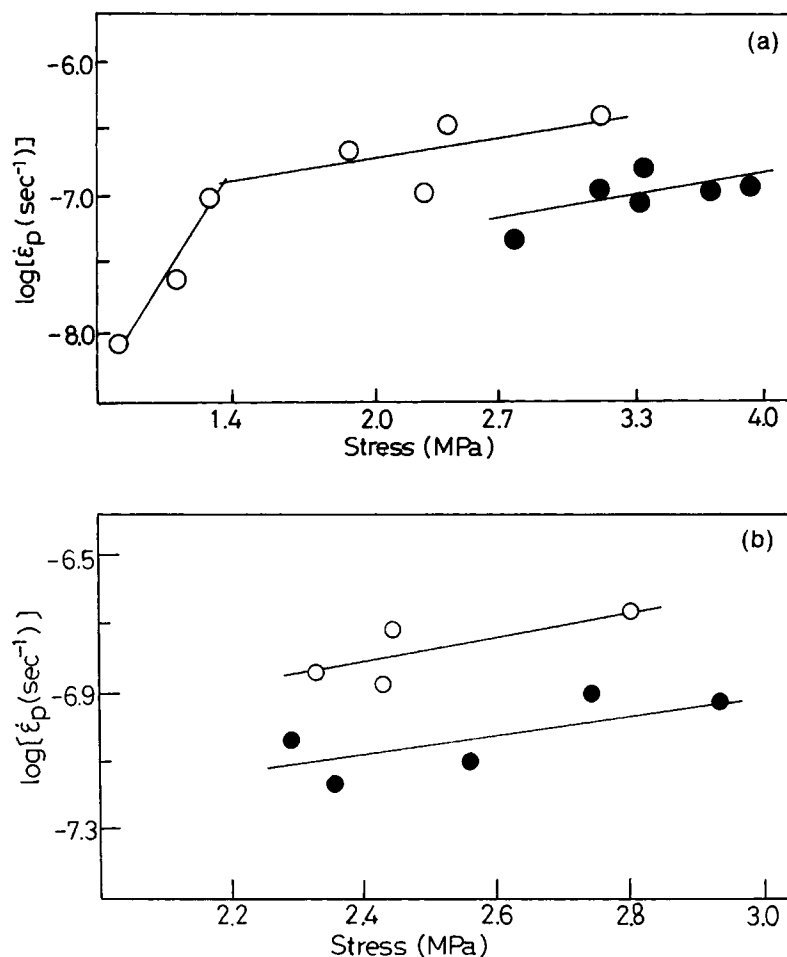


Figure 11 $\log \dot{\epsilon}_p$ vs. stress for HPC film cast from each system. (a) water; DMU concentration (wt %): (○) 0; (●) 3.5. (b) Methanol; DMU concentration (wt %): (○) 0; (●) 3.5.

The comparisons noted above clearly indicated no clear correlations that are valid for our all films. This was partially because the cross-linking is greatly dependent on the conditions (solvent, cross-linking agent, and annealing). Then, we need more detailed studies on the relation between the cross-linked texture and properties.

CONCLUSIONS

Both solubility test and optical measurements including circular dichroism of our solvent-cast films revealed that the resultant cast films retain the cholesteric liquid crystalline order (right-handed sense) fixed three-dimensionally by chemical cross-linking. The cross-linking and fixed liquid crystalline texture depended on the pairs of cross-linking agent-solvent. The cross-linking with DMU seemed to be looser than that with *p*-FA. The mechanical prop-

erties of the cast films also depended on the pairs of cross-linking agent-solvent. For water- and methanol-cast films with *p*-FA, Young's modulus and tensile strength increased and elongation decreased, but for films with DMU, Young's modulus and strength decreased and elongation increased, with cross-linking. The temperature dependence of E' and E'' for water-cast films was also different from that for methanol-cast films. The creep resistance improved with cross-linking. The thermally activated Eyring process could be applied to our films and the activated volume could be evaluated. For water-cast films, the value of V was almost independent of cross-linking with DMU, but for methanol-cast films, the value of V for cross-linked films with DMU was smaller than that for the uncross-linked ones. The clear correlation between mechanical properties could not be obtained. We need further mechanical data to conclude the more definite descriptions of the correlation.

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