

Liquid Crystalline Phase-Formation Behavior of Cellulose Cinnamate

KENICHIRO ARAI* and HIDETOSHI SATOH

Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

SYNOPSIS

Cellulose cinnamates with degrees of substitution (*DS*) of up to 2.3 were prepared by a reaction of cellulose with cinnamoyl chloride in pyridine. The cellulose cinnamate was found to form a cholesteric liquid crystalline phase at the concentrations higher than a critical concentration in some organic solvents. The critical concentration showed tendencies to be higher for the cellulose cinnamate with higher *DS* and with higher degree of polymerization (*DP*). Influences of formation of liquid crystalline phase and of irradiation with UV light on the physical strength of the cellulose cinnamate film were investigated and both were found to make the breaking strength and modulus of elasticity of the film higher.

INTRODUCTION

Photoregulation of polymers containing photochromic moieties such as azobenzene, spiropyran, and stilbene has been a subject of numerous investigations.¹⁻⁵ In the previous article, we reported the preparation of cellulose *p*-phenylazobenzoate (AB-cellulose) and its application to an adsorbent for thin-layer chromatography.⁶

Many cellulose derivatives have been found to form cholesteric liquid crystalline phases. For example, liquid crystalline phase-forming behavior of hydroxypropylcellulose and its esters has been investigated, especially by Gray et al., in detail.⁷⁻¹² We also investigated the lyotropic crystalline phase-forming behavior of AB-cellulose in the dark and under irradiation with UV light and found that the AB-cellulose formed a liquid crystalline phase in some organic solvents at the concentrations higher than the critical concentration, and the critical concentration was regulated under irradiation with UV light at a certain concentration range of AB-cellulose.^{13,14}

In the present article, we deal with preparation of cellulose cinnamate and its lyotropic liquid crys-

talline phase-formation behavior. Preparations of cellulose cinnamate have already been reported by Frank and Mendrzyk¹⁵ and Minsk et al.,¹⁶ but properties of the product have scarcely been investigated. Cinnamates are well known to dimerize with opening the double bonds under irradiation with UV light. Influences of formations of intermolecular cross-linking due to the dimerization of the cinnamoyl moieties in the cellulose cinnamate under irradiation with UV light and of liquid crystalline phase on physical strength of the cellulose cinnamate films are also investigated.

EXPERIMENTAL

Materials

Three celluloses were used. Commercially available microcrystalline cellulose (Avicel, Asahi Kasei Co., Tokyo) was extracted with hot water in a Soxhlet extractor for 24 h and used as cellulose A. Dissolving pulp from coniferous trees was dissolved in cupric hydroxide-ethylenediamine aqueous solution and then poured into excess volume of water to obtain amorphous cellulose. The precipitate was filtered and washed with water thoroughly and used as cellulose B. Cellulose B was hydrolyzed in 2% sulfuric acid aqueous solution for 12 h under refluxing. The residue was filtered, washed with water, and used as

* To whom correspondence should be addressed.

cellulose C. These celluloses were finally washed with acetone to remove water, dried in vacuum, and offered to the esterification reaction with cinnamoyl chloride.

Pyridine and tetrahydrofuran (THF) were dehydrated in an usual manner. All other reagent grade chemicals, commercially available, including cinnamoyl chloride, were used without further purification.

Preparation of Cellulose Cinnamate

About 1.0 g cellulose was suspended in 70 mL anhydrous pyridine and 70 mL pyridine solution of cinnamoyl chloride (3.2 g) was added. The suspension was kept at 70°C with stirring. After a given time, the reaction mixture was added to excess volume of methanol and then filtered. The residue was extracted with methanol in a Soxhlet extractor and then dried under vacuum. Cellulose cinnamates with different degrees of substitution (*DS*) of up to 2.15 were prepared at a different reaction time and those with *DS* of up to 2.3 were obtained by repeating the same reaction once more. The *DS* was determined by elemental analysis.

Determination of Intrinsic Viscosity of Cellulose Cinnamate

Cellulose cinnamate was dissolved in chloroform at various concentrations and their viscosities were measured with an Ubbelohde type viscometer at 25°C. Intrinsic viscosity ($[\eta]$) was calculated from the plot of the data in the usual manner, as a measure of degree of polymerization (*DP*) of the cellulose cinnamate.

Optical Observation of Liquid Crystalline Phase

Cellulose cinnamate was dissolved in some organic solvents and placed between two slide glasses. The cellulose cinnamate was sheared by shifting the slide glasses parallel in one direction, and birefringence phenomena due to liquid crystalline phase were observed between crossed polarizers with a polarizing microscope. Photomicrography of liquid crystalline phase of cellulose cinnamate was taken in dichloromethane.

Measurement of Film Strength

Breaking strength and modulus of elasticity of the cellulose cinnamate films containing and not containing liquid crystalline phase, before and after ir-

radiation with UV light, were measured using Tensilon (Toyo Measuring Instruments Co., Tokyo, UTM-II). The film not containing liquid crystalline phase was prepared with the method mentioned above, and the film containing liquid crystalline phase was prepared with standing the cellulose cinnamate 1,2-dichloroethane solution on a glass plate in a sealed vessel filled with 1,2-dichloroethane vapor to be dried slowly.

RESULTS AND DISCUSSION

Celluloses with different *DP*s were esterified by a reaction with cinnamoyl chloride in pyridine at 70°C. Figure 1 shows change in *DS* of the obtained cellulose cinnamate from cellulose A, with the reaction time. The *DS* is found to increase with the reaction time and then show a tendency to level off at *DS* of about 2.15. The cellulose cinnamate with *DS* of 2.15 was offered to the same reaction again to obtain those with *DS*s of up to 2.3. The *DS* of the obtained cellulose cinnamates at the same condition was in the order of those from cellulose C > cellulose A > cellulose B.

Formation behavior of liquid crystalline phase of the cellulose cinnamate was examined. The birefringence phenomenon was found at the concentrations higher than a critical concentration, which depends on the solvent, and *DS* and degree of poly-

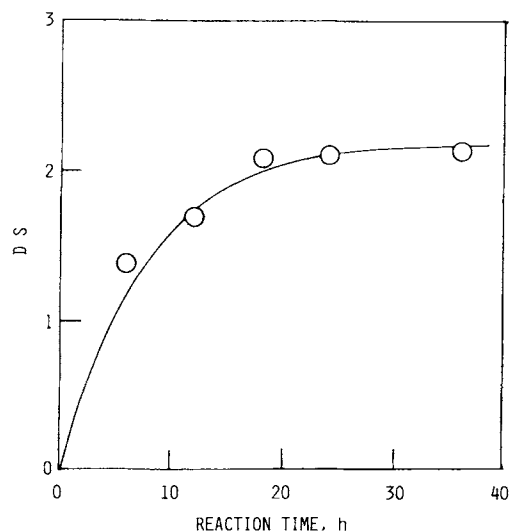


Figure 1 Change in *DS* in the reaction of cellulose A with cinnamoyl chloride in pyridine at 70°C, with reaction time. Cellulose, 6.6×10^{-2} mol L⁻¹ as anhydroglucose unit; Cinnamoyl chloride, 0.23 mol L⁻¹.

merization (DP) of the cinnamate. Figure 2 presents an example of photomicrography of the birefringence of cellulose cinnamate in dichloromethane, which clearly shows a fingerprint pattern, characteristic of cholesteric liquid crystalline phases, with a spacing size of about $20\ \mu\text{m}$.

Figure 3 shows plots of the critical concentration for formation of liquid crystalline phase of the cellulose cinnamate in chloroform, 1,2-dichloroethane, or THF against the DS . In each plot, the critical concentration is found to decrease with the increasing DS , which may be due to the increase in interaction between the solute molecules. The critical concentrations in the organic solvents at the same DS are in the order of those in THF > 1,2-dichloroethane > chloroform, the order being assumed to be in accord with that of the solubility; solubility parameters of THF, 1,2-dichloroethane, and chloroform are 9.90, 9.78, and 9.49,¹⁷ respectively, and that of cinnamoyl moiety in the cellulose cinnamate is inferred to be about 10.

Figure 4 shows a plot of the critical concentration of cellulose cinnamates from celluloses A, B, and C in THF against $[\eta]$ as a measure of DP of the cinnamate, where the DS s of the cinnamates are similar. It is found that the critical concentration decreases with increasing $[\eta]$ of the cinnamate, indicating that the cinnamate molecules with higher DP are more easily ordered, probably because of higher interaction among the molecules, thereby lowering the critical concentration.

Influences of formations of liquid crystalline phase and of intermolecular crosslinking due to dimerization of the cinnamoyl moieties on the physical

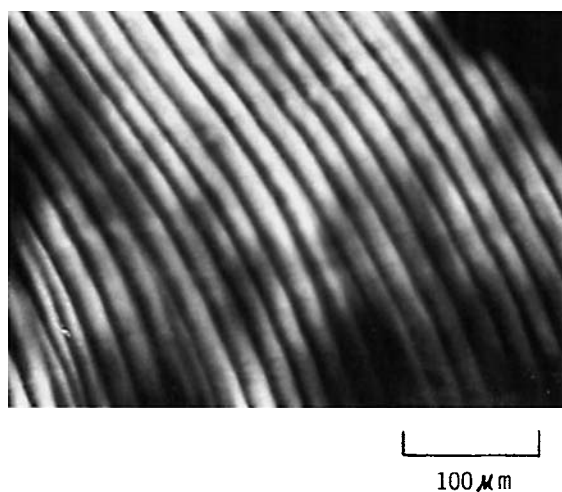


Figure 2 Typical photomicrography of liquid crystalline phase of cellulose cinnamate in dichloromethane, observed between crossed polarizers.

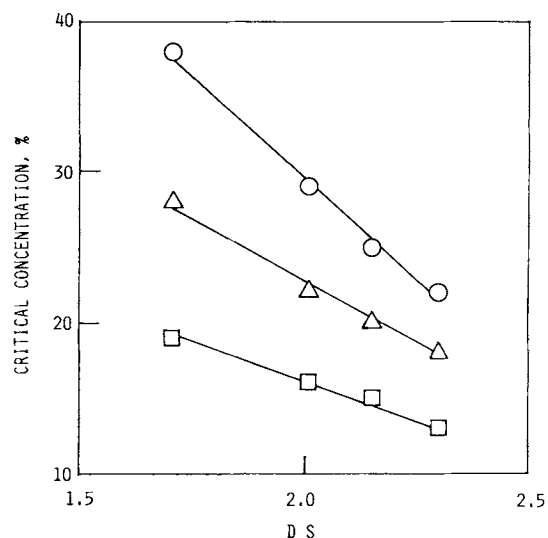


Figure 3 Plots of critical concentration for liquid crystalline phase formation of cellulose cinnamate in (□) chloroform, (△) 1,2-dichloroethane, and (○) THF against the DS .

properties of the cellulose cinnamate films were investigated. We have found that when cellulose cinnamate solution is stood in the solvent vapor to be dried slowly liquid crystalline phase is formed in the obtained film without applying stress, while when the solution is stood in open air to be dried quickly the obtained film does not contain any liquid crystalline phase; the liquid crystalline phase in the film slowly dried appears to be rather higher ordered than

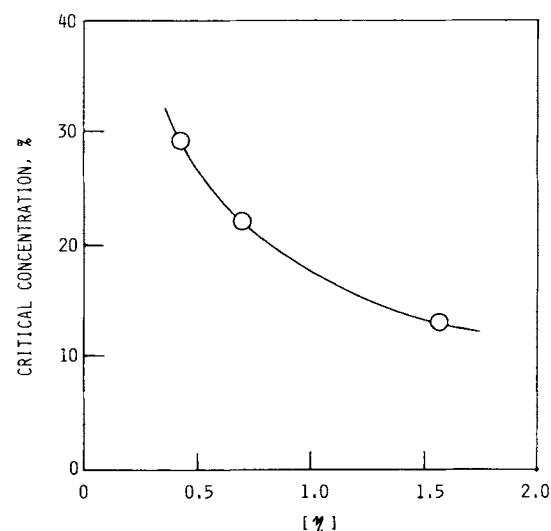


Figure 4 Plot of critical concentration for liquid crystalline phase formation of cellulose cinnamate from celluloses A, B, and C in THF, against their intrinsic viscosity ($[\eta]$). DS of cellulose cinnamates from cellulose A, B, and C, 2.30, 2.27, and 2.22.

Table I Breaking Strength and Modulus of Elasticity of Cellulose Cinnamate Films from Cellulose B before and after UV Light Irradiation

	Liquid Crystalline Phase			
	Not Formed		Formed	
	Before	After	Before	After
Breaking strength (MPa)	58.8	64.2	84.8	93.1
Modulus of elasticity (GPa)	1.72	2.24	3.22	4.12

that formed in the solution with applying stress. Thus, two films, one of which contains liquid crystalline phase and another that does not, were prepared from 1,2-dichloroethane solution of cellulose cinnamate from cellulose B. Breaking strength and modulus of elasticity of the films were measured before and after irradiation with UV light and are summarized in Table I. It is found that both breaking strength and modulus of elasticity of the film containing liquid crystalline phase are higher than those of the film not containing it. This may result from higher intermolecular interaction due to higher ordered structure of the molecules in the film containing liquid crystalline phase. Under irradiation with UV light, both breaking strength and modulus of elasticity of the films are found to increase. This is believed to result from the formation of intermolecular crosslinking due to the dimerization of the cinnamoyl moieties in the cellulose cinnamate.

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