

# Interpenetrating Polymer Networks of Photocrosslinkable Cellulose Derivatives

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## SYNOPSIS

A series of interpenetrating polymer networks has been prepared from two cellulose derivatives, one of which contains cinnamate groups and the other containing randomly substituted cinnamate and allyl groups. The latter derivative forms a crosslinked network in less than 5 min on exposure to ultraviolet radiation and can be used to make amorphous interpenetrating polymer networks containing 50% by weight loading level of crosslinked vinyl polymers. The syntheses of both derivatives and the thermal properties and film morphologies of their interpenetrating polymer networks are discussed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

In past decades, interpenetrating polymer networks (IPNs) of "organic-organic" polymers such as poly(*n*-butyl acrylate) with polystyrene,<sup>1,2</sup> styrene-butadiene with polystyrene,<sup>3,4</sup> and polyurethane with epoxy or unsaturated polyesters,<sup>5</sup> and "organic-inorganic" polymers such as polyurethane with polysiloxane<sup>6</sup> and polystyrene with polyphosphazene<sup>7,8</sup> have been extensively studied. In most cases, IPNs provide better physicochemical properties over the individual polymers used to make the IPNs. In spite of their potential for numerous applications, all IPN systems investigated thus far have been limited to synthetic polymers. Although extensive studies on grafting of cellulose<sup>9</sup> have been performed, there are surprisingly no reports on IPNs made from cellulose (especially surprising in light of its superior mechanical properties and ready availability from natural resources). Nevertheless, a number of synthetic hydrogels of cellulose esters constituting semiinterpenetrating polymer networks with polyacrylamide have recently been developed to mimic some aspects of the behavior of biological composites.<sup>10,11</sup> Cellulose IPNs have a distinct potential for yielding light weight and high strength

materials. The mechanical properties of such systems are expected to be far superior to those obtained by grafting, since the former involves two intermeshed three-dimensional networks.

Years ago, due to insufficient knowledge of proper solvents to dissolve cellulose, cellulose derivatives were synthesized under heterogeneous conditions that produced nonuniform substitutions. Among these, cellulose derivatives containing photocrosslinkable group such as cinnamate were made.<sup>12</sup> Recently, McCormick and Callais<sup>13</sup> discovered a solvent system, *N,N*-dimethylacetamide containing 9% LiCl, for cellulose dissolution. Consequently, a number of cellulose derivatives such as ethers, esters, and carbamates have been prepared under homogeneous reaction conditions.<sup>14</sup> Degrees of substitution ranging from 2.5 to 3 have been achieved by controlling reaction conditions. However, regioselective synthesis of cellulose derivatives containing cinnamate groups has not been attempted thus far. In this paper we present the properties of IPNs derived from photocrosslinkable cellulose derivatives and common vinyl monomers.

## EXPERIMENTAL

### Instrumentation

FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer. Ultraviolet spectra

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were taken on a Perkin-Elmer Lambda-19 spectrophotometer. The thermogravimetric analyses were performed on a Perkin-Elmer Thermal analyzer Series 7 instrument. Elemental analysis was carried out on a Perkin-Elmer 2400 elemental analyzer. SEM photographs were obtained with a digital scanning microscope (Jeol T-300).

### Materials

Cellulose was purchased from Aldrich and used directly after pretreatment by a solvent-exchange technique.<sup>13</sup> Allyl bromide, cinnamoyl chloride, and lithium chloride were obtained from Aldrich and used without further purification. *N,N*-Dimethylacetamide (DMAc), dioxane, triethylamine, pyridine, styrene, 1,4-divinylbenzene (DVB), methylmethacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), and vinyl acetate (VA) were obtained from Aldrich and distilled under nitrogen before use. AIBN was purchased from Eastman Kodak and used as received.

### Cellulose Dissolution

Homogeneous solutions of cellulose were obtained following a procedure described by McCormick and Callais.<sup>13</sup> In a typical procedure, lithium chloride (18 g) was dissolved in 200 mL of DMAc at 100°C. The solvent was then allowed to cool to room temperature and 6.6 g of pretreated cellulose (which contains about 4 g of dry cellulose) was then added under a nitrogen atmosphere. The mixture was stirred for approximately 2 h at room temperature to get a clear solution.

### Synthesis of Cellulose Cinnamate(1)

To 100 mL of the above cellulose solution 11.1 g (0.11 mol) triethylamine in 25 mL DMAc was added.

A solution of 18.3 g (0.11 mol) cinnamoyl chloride in 25 mL DMAc was then added dropwise over a period of 1 h. After stirring overnight at room temperature the product was precipitated by pouring the reaction mixture into water, washed with water and methanol, and dried at 50°C under vacuum to constant weight (~ 6.3 g). Analysis: C, 63.95%; H, 4.73%; (degree of substitution = 2.9). IR (KBr): 1578 (aromatic C—C stretching), 1633 (C=C stretching), and 1702 (carbonyl stretching) cm<sup>-1</sup>. Ultraviolet ( $\lambda_{\max}$ ): 284 nm (dioxane).

### Synthesis of Allyl Cellulose Cinnamate(2)

To 100 mL of the cellulose solution 8.1 g (0.08 mol) of triethylamine in 25 mL DMAc was added. A solution of allyl bromide (9.7 g, 0.08 mol) in 25 mL DMAc was added dropwise under nitrogen over a period of 1 h. The stirring was continued overnight at room temperature, after which a solution of cinnamoyl chloride (13.3 g, 0.08 mol) and triethylamine (8.1 g, 0.08 mol) in 25 mL of DMAc was added slowly at 0°C. After stirring overnight at room temperature the product was precipitated by pouring the reaction mixture into water, washed with water and methanol, and dried at 50°C under vacuum to constant weight (~ 4.1 g). Analysis: C, 62.33%; H, 5.69%. IR (KBr): 1578 (aromatic C—C stretching), 1635 (C=C stretching), and 1715 (carbonyl stretching) cm<sup>-1</sup>. Ultraviolet ( $\lambda_{\max}$ ) = 277 nm (dioxane); 287 nm (film).

### Preparation of IPNs

IPNs were made by heating a mixture of one of the above photocrosslinkable cellulose derivatives, a monomer, a crosslinker, and AIBN followed by exposure to ultraviolet light. The composition of each IPN is shown in Table I. In a typical procedure, monomer (1 g), crosslinker (0.3 g), and AIBN (0.03

**Table I** Composition of IPNs

IPN	Cellulose Derivative		Monomer			Crosslinker		AIBN
	1	2	Styrene	MMA	VA	DVB	EGDMA	
I	X		X			X		X
II		X	X			X		X
III	X			X			X	X
IV		X		X			X	X
V	X				X		X	X
VI		X			X		X	X

g) were heated at 80°C for 20 min to obtain a viscous solution. The cellulose derivative (1.06 g) in 10 mL dioxane was added and the mixture sonicated for 10 min prior to film casting. The film was allowed to dry at room temperature overnight and then baked at 80°C for 10 h. The film was then photocrosslinked by irradiation at 254 nm for 15 min to obtain IPNs.

## RESULTS AND DISCUSSION

In this study two photocrosslinkable cellulose derivatives, **1** and **2**, were synthesized under homogeneous conditions (Fig. 1). One derivative, cellulose cinnamate (**1**), which was previously synthesized in a heterogeneous condition,<sup>12</sup> was prepared by reacting a homogeneous solution of cellulose with cinnamoyl chloride in the presence of a base such as

triethylamine. The other derivative, allyl cellulose cinnamate (**2**), was made by reacting cellulose with allyl bromide followed by reaction with cinnamoyl chloride. Both products were isolated as pale yellow flakes. Elemental analysis was used for the determination of the degree of substitution and indicated a high degree of substitution, e.g., the value for **1** was calculated at 2.9. Although both derivatives were found soluble only in dioxane, derivative **2** showed greater solubility over derivative **1**.

Thin films of the photocrosslinkable derivatives were made by either solution casting or by spin casting from solutions containing ~ 2% by weight of the derivative. Derivative **1** formed opaque crystalline or somewhat phase-segregated films after evaporation of the solvent. Similar behavior was reported by another group,<sup>15</sup> which subsequently made an amorphous transparent film by coderivatizing with trimethylsilyl chloride. In light of this, we partially

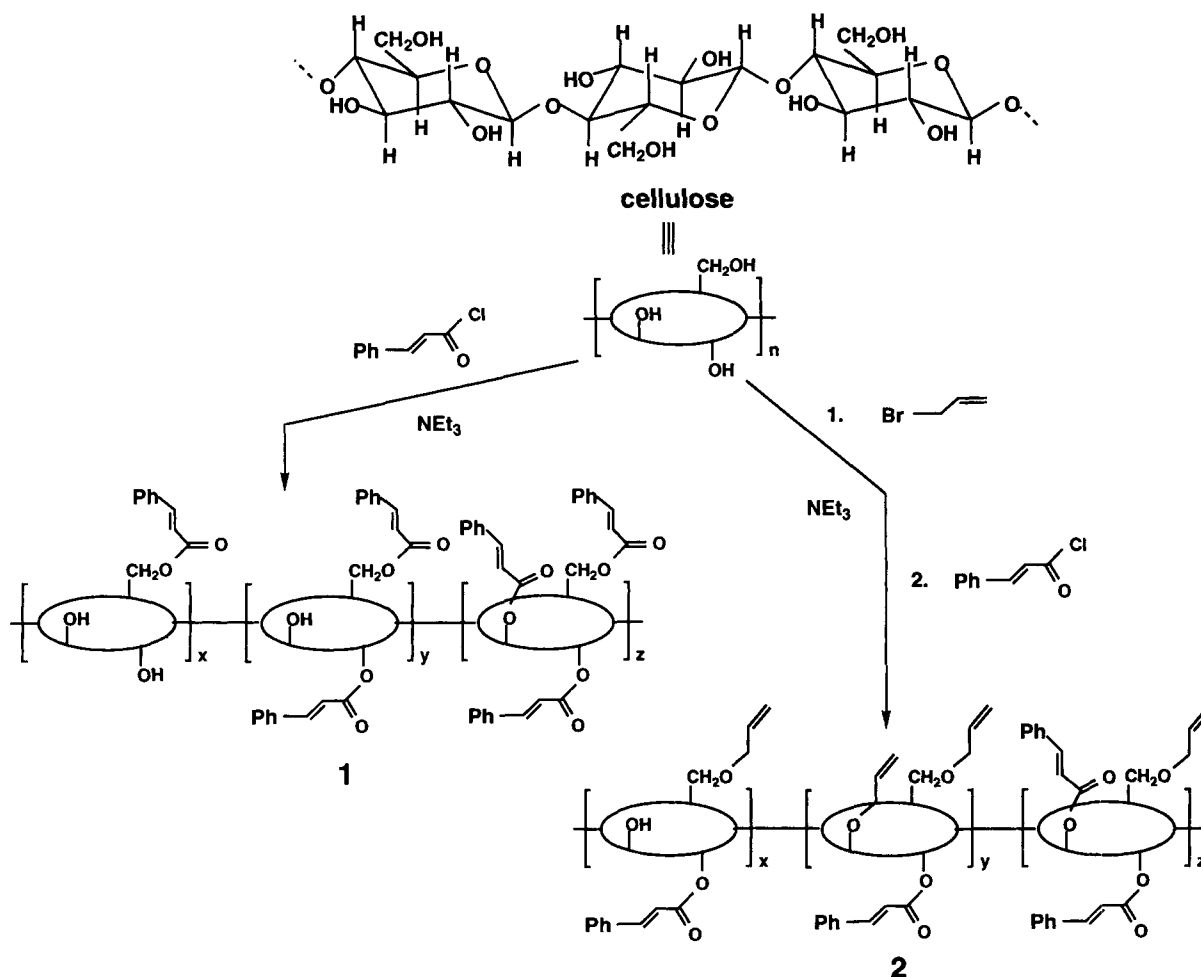


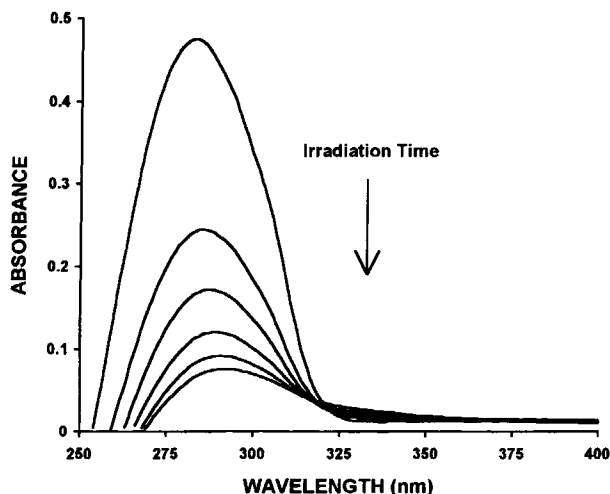
Figure 1 Synthesis of photocrosslinkable cellulose derivatives.

derivatized cellulose with allyl groups prior to functionalization with cinnamate groups. Indeed, the coderivatized product **2** formed transparent films that can be removed from a glass surface as tough, free-standing films.

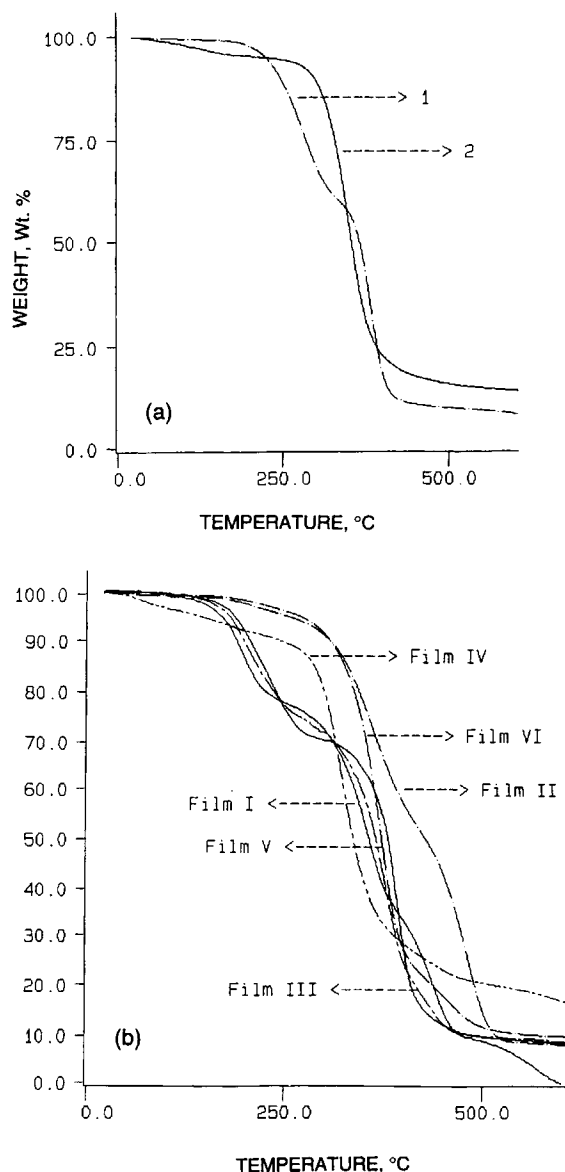
Although the two derivatives possess similar chromophores they differ slightly in their infrared and ultraviolet spectra. For instance, the C=O stretching in derivative **1** was observed at  $1702\text{ cm}^{-1}$  and that of derivative **2** at  $1715\text{ cm}^{-1}$ . Other absorption frequencies due to C=C stretching ( $1633\text{ cm}^{-1}$ ) and the cellulose residue were found to be similar for both derivatives.<sup>16</sup> The absorption maximum ( $\lambda_{\text{max}}$ ) due to the cinnamate groups of **1** and **2** appeared at 284 and 277 nm, respectively, in dioxane solution. A red-shift of 10 nm was observed when a thin film of **2** was measured.

Photoreactivity characteristics were studied with a film obtained from derivative **2**, since derivative **1** produced phase-segregated films. An ultraviolet lamp which emitted maximum intensity of light at 254 nm was used to irradiate the sample. 2 + 2 Photodimerization between two cinnamate double bonds was very rapid as indicated by a sharp decrease in absorption at 287 nm in less than 5 min due to depletion of double bonds leading to formation of cyclobutane rings (Fig. 2).<sup>17</sup>

Both derivatives **1** and **2** were used to produce IPN films using vinyl monomers. Three common vinyl monomers, styrene, MMA and VA, and two well-known crosslinkers, DVB and EGDMA, were used to generate network polymers. Table I describes the combination of monomer and crosslinker used

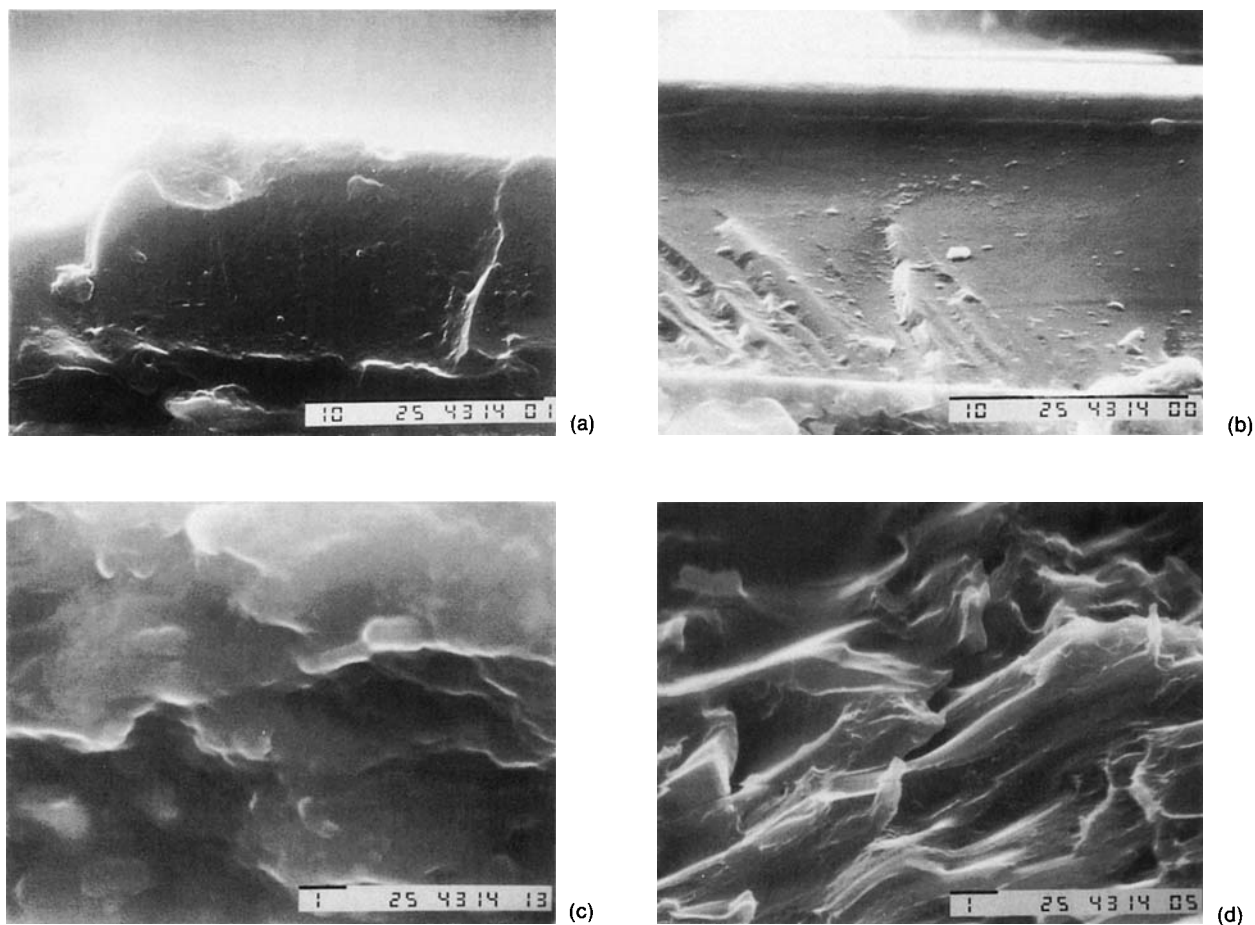


**Figure 2** Change in absorption maximum due to cinnamate chromophores under exposure to ultraviolet light [wavelength of irradiation 254 nm; irradiation time (min): 1, 2, 3, 5, 7, 11].



**Figure 3** TGA thermograms of (a) photocrosslinkable cellulose derivatives and (b) IPN films derived from photocrosslinkable cellulose derivatives (heating rate of  $20^{\circ}\text{C}/\text{min}$  under nitrogen).

with the cellulose derivative. AIBN was used as an initiator to polymerize all vinyl monomers. Initially a semi-IPN film was made by polymerizing an appropriate monomer and crosslinker with a cellulose derivative. The film was converted into an IPN by irradiating at 254 nm for 15 min. The resulting films contained an equal composition (50 : 50) of cellulose derivative and crosslinked vinyl polymer. Derivative **2** forms compatible films with all three crosslinked vinyl polymers in both semi-IPN and IPN stages as indicated by their visual transparency. Derivative **1**, on the other hand, formed translucent to phase



**Figure 4** SEM micrographs of (a) film-II, (b) film-II at a higher magnification, (c) film-IV, and (d) film VI.

segregated films with the vinyl crosslinked polymers, quite similar to the film obtained from derivative **1** alone.

Thermal properties of both photocrosslinkable derivatives and their IPN films have been studied by thermogravimetric analysis. Derivative **2** showed much greater thermostability compared to derivative **1** [Fig. 3(a)]. The high thermostability of derivative **2** is probably due to facile thermal crosslinking and/or polymerization in contrast to derivative **1**, which is more hindered due to the presence of a large number of bulky cinnamate groups. Thermal behavior of the IPN films is shown in Figure 3(b). Higher thermal stability of IPN films prepared from derivative **2** was also observed.

SEM micrographs of fractured surfaces of all films derived from derivative **2** are shown in Figure 4. The IPN with polystyrene showed homogeneous single phase morphology [Fig. 4(a)]. This is more clearly revealed at higher magnification [shown in Fig. 4(b)]. The fractured surfaces of IPNs obtained

from polymethylmethacrylate and polyvinylacetate showed no significant crystalline domains but irregular stress propagation across the films.

## CONCLUSION

A new processable cellulose derivative containing allyl and cinnamate groups has been synthesized. This derivative forms compatible IPNs with common crosslinked vinyl polymers at equal masses of each component. The compatibility and thermal stabilities of these IPNs are better in comparison to similar IPNs of cellulose cinnamate. Further investigation of the mechanical properties of the IPNs as well as of the composites fabricated with glass fiber are under progress.

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