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(4-Vinylbenzyl)cinnamate: A Useful Monomer for Water-Soluble Photopolymers

AMY S. CANNON AND JOHN C. WARNER

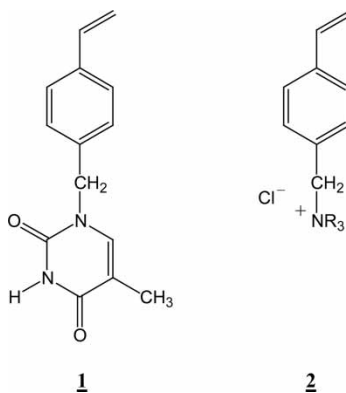
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*It was found that the (4-vinylbenzyl)cinnamate (VBC) (**3**) copolymers with (4-vinylbenzyl)triethylammonium chloride (VBA) (**4**) function similarly to (4-vinylbenzyl)thymine (VBT) (**1**) copolymers as water soluble photocrosslinking systems. Initial evidence indicates that the VBC:VBA copolymers are highly photosensitive systems. A matrix of twelve VBC:VBA copolymers was prepared in order to study the effects of molecular weight and polymer composition on the photoreactivity.*

Keywords photodimer, crosslink, green chemistry, polymer

Introduction

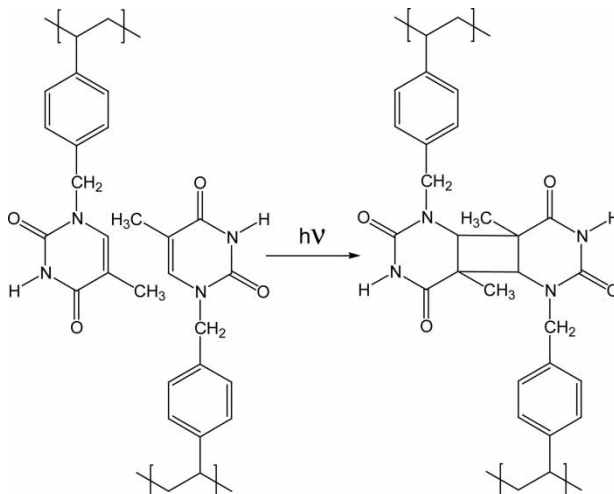
For several years, we have been interested in the photocyclodimerization of thymine as a mechanism to photocrosslink water soluble polymers (1). In these systems we have copolymerized (4-vinylbenzyl)thymine (**1**) with various trialkyl-(4-vinylbenzyl)-ammonium salts (**2**) in order to construct a water soluble copolymer. Irradiation with UV light induces a $2\pi + 2\pi$ photoreaction to occur, generating covalent cyclobutane dimers within the polymer matrix. This crosslinking increases the effective molecular weight of the polymer, and after a threshold number of crosslinks are created, renders the material water-insoluble.



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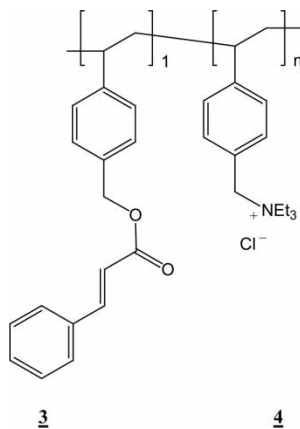
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There are several interesting properties of this system that we have proscribed to the hydrogen bonding afforded by the thymine ring (2). In order to experimentally differentiate the impact of the unique properties of the thymine heterocycle, we needed a "simpler" analog capable of undergoing a $2\pi + 2\pi$ photocyclodimerization reaction, but not display the complex behavior of the thymine monomer.



We turned to the cinnamate group as a well-known system that undergoes this type of photocyclodimerization reaction. Cinnamate containing polymers have been known in the literature for quite some time (3). In fact, poly(vinylcinnamate) is commercially available.

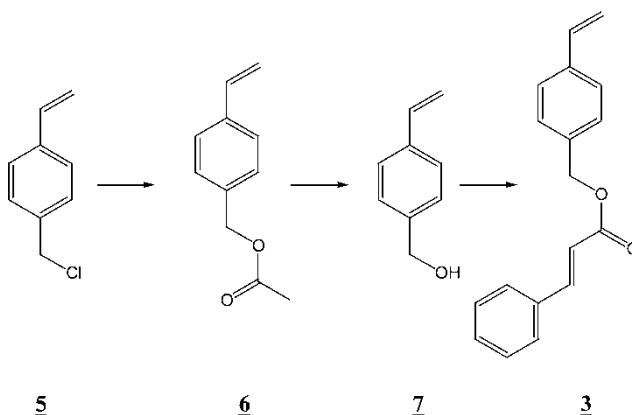
While it was found that (4-vinylphenyl)cinnamate had been reported previously in the literature (4), the best analog would be the (4-vinylbenzyl)cinnamate (**3**). With the exception of some references to this material within preformed polymers (5) we were unable to find any report of this monomer in the literature.



Results and Discussion

(4-Vinylbenzyl)cinnamate (**3**) was synthesized in three steps. The requisite (4-vinylbenzyl)-alcohol (**7**) was prepared following a procedure similar to that of Corson (6) through the

conversion of (4-vinylbenzyl)chloride (**5**) to (4-vinylbenzyl)acetate (**6**). The acetate was then hydrolyzed to (4-vinylbenzyl)alcohol (**7**). The alcohol was then condensed with cinnamoyl chloride to form (4-vinylbenzyl)cinnamate (**3**). This monomer was found to be very reactive and unstable, with a half life of several hours under ambient conditions. After 3 days of storage in a vial for light-sensitive materials, the NMR spectra indicated the monomer had polymerized, and showed no evidence of the vinyl peaks at δ 5.80 and δ 5.30.



The (4-vinylbenzyl)cinnamate monomer (**3**) had a UV absorbance that extended into longer wavelengths. Figure 1 shows that the spectra of thymine monomer **1** tails off at around 300 nm, while the cinnamate derivative **3** extended past 320 nm.

With the cinnamate monomer in hand, a series of water-soluble polymers were prepared. (4-Vinylbenzyl)cinnamate (VBC) (**3**) was copolymerized along with

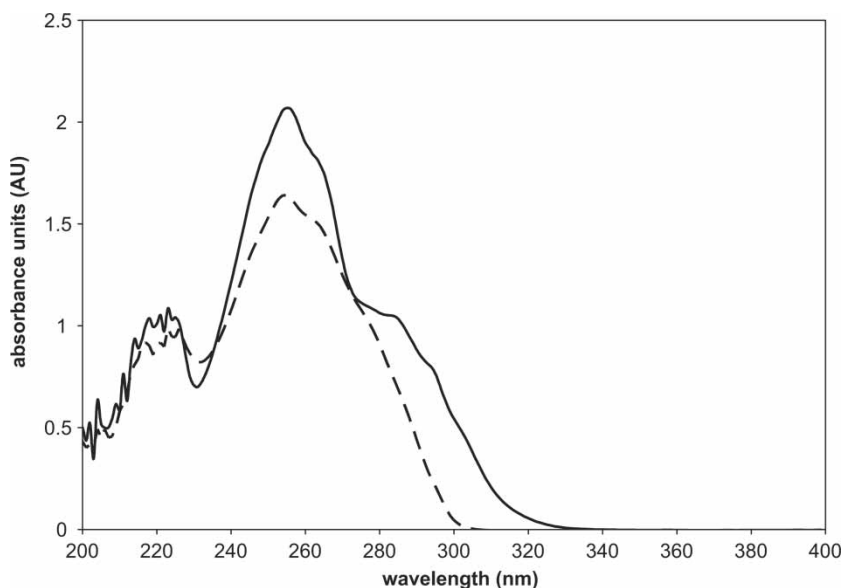
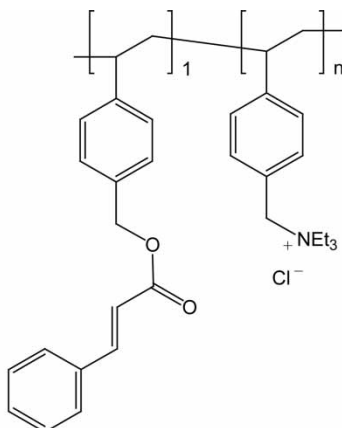


Figure 1. UV-vis spectra of VBT (**1**) (---) and VBC (**3**) (—) monomers (0.05 mM solution in isopropanol).

(4-vinylbenzyl)-triethylammonium chloride (VBA) (**4**) using azobisisobutyronitrile (AIBN) as the thermal initiator.



8: $n = 1$, **9**: $n = 2$, **10**: $n = 4$, **11**: $n = 8$

Monomer ratios of 1:1, 1:2, 1:4 and 1:8 were prepared, holding the amount of cinnamate monomer constant and varying the stoichiometric amount of the water-solubilizing cationic monomer accordingly. The matrix of reaction conditions for the various copolymerizations are summarized in Table 1. The amount of AIBN was varied from (a) 1% by total mass, (b) 2% by total mass and (c) 4% by total mass.

The polymers were then coated on PET film, irradiated with short-wave UV light, washed and toned with an anionic dye to visualize the crosslinking of the cinnamate groups in the polymer. The test of crosslinking and toning the polymer showed that the VBC:VBA polymers underwent sufficient crosslinking and solubilization to record patterns with less than 600 $\mu\text{J}/\text{cm}^2$ of exposure to UV. Figure 2 illustrates the result of a typical patterning experiment.

Table 1
Matrix of reaction conditions for (VBC)(VBA)_n copolymers

	VBC:VBA ratio	VBC (mmol)	VBA (mmol)	AIBN (g)	Yield (%)
8a	1:1	11.4	11.4	0.059	76
8b	1:1	11.4	11.4	0.118	78
8c	1:1	11.4	11.4	0.176	70
9a	1:2	7.5	15.0	0.059	100
9b	1:2	7.5	15.0	0.117	100
9c	1:2	7.5	15.0	0.234	86
10a	1:4	5.7	22.8	0.073	93
10b	1:4	5.7	22.8	0.145	100
10c	1:4	5.7	22.8	0.290	98
11a	1:8	3.79	30.32	0.087	100
11b	1:8	3.79	30.32	0.174	97
11c	1:8	3.79	30.32	0.348	96

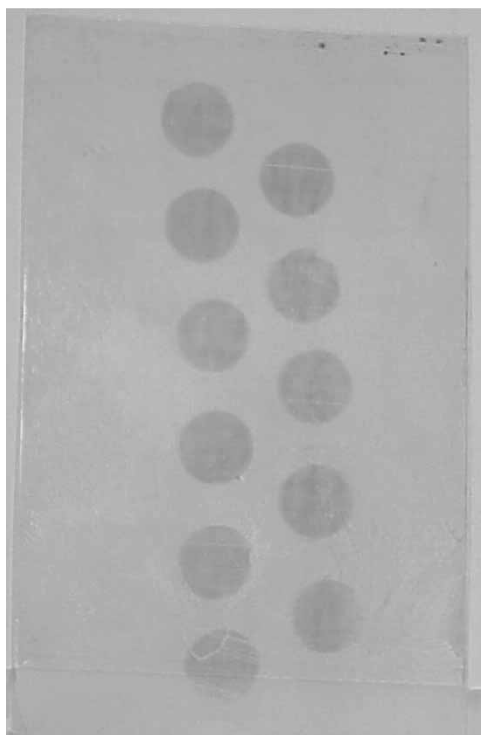


Figure 2. VBC:VBA copolymer patterned on PET film.

There are some trends that are evident in these polymer systems, as can be seen in Table 2. In all cases, the highest molecular weight polymers (with 1% AIBN) were too viscous to coat under simple draw-down techniques. Also, the polymers with the highest amount (1 : 1) of VBC were also too viscous to coat. Comparing the behavior of the (6) remaining polymers provides some mechanistic insight.

As can be seen by the data, the photosensitivity of the polymers is increased with the higher quantities of the photoreactive (VBC) **3** monomer. Also, the photosensitivity seems to increase with molecular weight, where the polymers derived from the lowest amount initiator were the most reactive. Both of these observations are consistent with a mechanism where the water soluble photopolymer increases its effective molecular weight upon photoinduced crosslinking up to the point where the polymer is no longer

Table 2
Qualitative photoreactivity of VBC:VBA polymers

	VBC:VBA	1% AIBN (a)	2% AIBN (b)	4% AIBN (c)
8	1 : 1	—	—	—
9	1 : 2	—	high	high
10	1 : 4	—	high	medium
11	1 : 8	—	low	low

(— indicates that the polymer was too viscous to coat).

soluble. The greater the amount of photoreactive monomer, the more efficient this process should be. Furthermore, the longer the polymer chains are to begin with, the less additional mass through crosslinking should be required to induce insolubility.

Experimental

All starting materials were purchased from Aldrich Chemical Company or ACROS and used without further purification. NMR spectra were taken of all polymers to ensure that no residual monomers were present. Proton NMR spectra were taken using a 300 MHz Bruker AC300 Spectrometer. Melting points were taken using a Mel-Temp melting point apparatus by Laboratory Devices. Elemental analysis was performed using the classical modified Pregl/Dumas technique on an Exeter Analytical 240 analyzer at University of Massachusetts Amherst. UV irradiation was performed with a Fisher Biotech Electrophoresis UV Hand Lamp, FBVLS-80 (Spectronics).

Synthesis of (4-vinylbenzyl)acetate (**6**): 4-Vinylbenzyl chloride (**5**) (20 mL, 142 mmol) and potassium acetate (15.4 g, 157 mmol) were added to concentrated acetic acid (100 mL). The reaction was heated to reflux for 15 hours. The reaction was cooled to room temperature. A white solid (potassium chloride) was filtered from the solution and washed with acetic acid. The reaction mixture was poured into water (100 mL) and extracted with toluene (3 × 100 mL). The toluene layers were collected and washed with water (2 × 100 mL). The toluene layer was dried over magnesium sulfate. The solvent was evaporated to yield a clear liquid (20.567 g, 91.5% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 7.407 (dd, J₁ = 35.15 Hz, J₂ = 26.95 Hz, 4H, Ar H), 6.711–6.806 (m, 1H, CH), 5.804 (d, J = 17.87 Hz, 1H, CH), 5.309 (d, J = 10.84 Hz, 1H, CH), 5.134 (s, 2H, CH₂), 2.147 (s, 3H, –OCH₃).

Synthesis of (4-vinylbenzyl)alcohol (**7**): 4-Vinylbenzyl acetate (**6**) (16.0 g, 90.9 mmol) was added slowly over three hours to an ethanol/NaOH solution (50 mL, 3.33M NaOH in 20/80 H₂O/ethanol with 0.0012 mol/L of hydroquinone) while stirring. After the addition of the acetate, the reaction was heated gently for an additional hour. The reaction was cooled to room temperature. The solution was poured into water (100 mL), and then extracted with toluene (3 × 50 mL). The toluene layers were collected and washed with water (2 × 50 mL). The toluene layer was dried over magnesium sulfate. The magnesium sulfate was filtered out of the solution. The solvent was then evaporated to afford a slightly yellow liquid (8.196 g, 67.3% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 7.395 (dd, J₁ = 38.38 Hz, J₂ = 21.98 Hz, 4H, Ar H), 6.812–6.717 (m, 1H, CH), 5.800 (d, J = 17.58 Hz, 1H, CH), 5.298 (d, J = 10.84 Hz, 1H, CH), 4.684 (s, 2H, CH₂), 2.313 (s, 1H, –OH).

Synthesis of (4-vinylbenzyl)cinnamate (**3**): Sodium hydride (60% dispersion in mineral oil) (2.15 g, 54 mmol) was dissolved in diethyl ether (50 mL). The reaction was stirred and cooled in an ice bath for 10 min. 4-Vinylbenzyl alcohol (**7**) (7.2 g, 54 mmol) was added slowly over 15 minutes to the cooled diethyl ether. Cinnamoyl chloride (9.0 g, 54 mmol), dissolved in ether (50 mL) was added via addition funnel to the sodium hydride solution, while stirring. The ice was removed, and the reaction was allowed to warm to room temperature. The reaction was allowed to stir for two more hours at room temperature. The reaction was poured into methylene chloride (100 mL), and then extracted with water (3 × 50 mL). The methylene chloride layers were collected and dried over magnesium sulfate. The magnesium sulfate was filtered. The solvent was evaporated to yield a yellow liquid, which later crystallized upon cooling. The crude solid was re-crystallized in hexanes (8.022 g, 56.3% yield), mp

116.5–118.5°C. ¹H-NMR (300 MHz, CDCl₃, δ): 7.828 (d, J = 16.12 Hz, 1H, CH), 7.61–7.303 (m, 9H, Ar H), 6.812–6.718 (m, 1H, CH), 6.503 (d, J = 15.82 Hz, 1H, CH), 5.800 (d, J = 17.58 Hz, 1H, CH), 5.297 (d, J = 10.84 Hz, 1H, CH), 4.716 (s, 2H, CH₂).

General procedure for the synthesis of VBC:VBA copolymers: (4-Vinylbenzyl)cinnamate (**3**) and (4-vinylbenzyl)triethylammonium chloride (**4**) were added to 40 mL of isopropanol in the appropriate proportions described in Table 1. The solution was heated to 65°C, and then azobisisobutyronitrile was added to the mixture. The reaction was allowed to heat and stir at 65°C for 21 h. The solution was allowed to cool to room temperature. The reaction mixture was concentrated by 50% of the total volume by rotary evaporation. The polymer was precipitated using acetone. A white solid was collected and washed with copious amounts of acetone.

General procedure for photoreactivity studies for the VBC:VBA copolymers: A 10% (w/w %) aqueous solution was prepared for each VBC:TEQ polymer. The polymer solution was coated on poly(ethylene terephthalate) (PET) film using a #3 Meyer coating rod (6.86 microns wet thickness). The films were allowed to air dry for 30 min. The films were irradiated with short UV light for one minute at a distance of one centimeter from the surface of the film. The films were then washed with water, and then placed in a dye solution (0.1 g FD&C green #3 in 500 mL of water) for one minute. The dyed film was washed with water. The color was then observed and assessed visually. The results of the photoreactivity study are summarized in Table 2.

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