# Photosensitive Polymers: Synthesis, Characterization, and Photocrosslinking Properties of Polymers with Pendant $\alpha$ , $\beta$ -Unsaturated Ketone Moiety

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ABSTRACT: Acrylate and methacrylate monomers with the photodimerizable  $\alpha,\beta$ -unsaturated ketone moiety, such as 4-cinnamoylphenyl, 4-(4-methoxycinnamoyl)phenyl, 4-(4-nitrocinnamoyl)phenyl, or 4-(4-chlorocinnamoyl)phenyl, were prepared and homopolymerized using benzoyl peroxide as the initiator at 70°C in methyl ethyl ketone. The poly(meth)acrylates were characterized by ultraviolet, infrared, <sup>1</sup>H-nuclear magnetic resonance (NMR), and <sup>13</sup>C-NMR spectra, and gel permeation chromatography. Their thermal properties were studied by thermogravimetric analyses in air and nitrogen, and differential scanning calorimetry. The photocrosslinking properties of the polymers were investigated as thin films and in solution in the presence and absence of sensitizer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2111–2120, 1998

**Key words:** photosensitive polymers;  $\alpha$ , $\beta$ -unsaturated ketone; photocrosslinking

## **INTRODUCTION**

In recent years the synthesis of polymers with reactive functional groups has been an active field of research in polymer science because it provides an approach to a subsequent modification of the polymer for the required application. Polymers having a photofunctional group that can be crosslinked by irradiation with ultraviolet (UV) light or electron beam and render the polymer insoluble, called "negative photoresists," have attracted much interest in microlithography,<sup>1</sup> photocurable coatings,<sup>2</sup> energy exchange materials,<sup>3</sup> etc. Most of the negative photoresists are based on cinnamate derivatives of polymers having hydroxy groups; for example, polyvinylalcohol, poly-(HEMA), etc. The Kodak KPR resist is mainly a cinnamic acid ester of polyvinylalcohol.<sup>4</sup> The synthesis and properties of a number of photocrosslinkable polymers have been reported.<sup>5–10</sup> Liquid crystalline polymers containing photocrosslinkable cinnamoyl units<sup>11,12</sup> and polyesters containing chalcone linkage as conducting polymers<sup>13</sup> were reported. The photochemistry involved in a number of photoresists and their technological applications have been reviewed.<sup>14–16</sup> Photosensitive polymers with a combination of properties such as high photosensitivity, good thermal stability, and good solubility are required for practical use as photoresists.

In continuation of our work<sup>17</sup> on photosensitive polymers, this article presents the synthesis, characterization, thermal stability, and photocrosslinking properties of polyacrylates and poly-

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methacrylates having a pendant  $\alpha,\beta$ -unsaturated ketone unit with either an electron withdrawing or donating substituent at the *para* position of the cinnamoyl aromatic ring. The presence of the pendant  $\alpha,\beta$ -unsaturated ketone moiety provides the advantage of converting them into photoconducting polymers.

# **EXPERIMENTAL**

#### Materials

4-Hydroxyacetophenone (HA), 4-methoxybenzaldehyde (MeOBA), 4-chlorobenzaldehyde (ClBA), 4-nitrobenzaldehyde (NBA), and benzaldehyde (BA) from Aldrich Co. (USA) were used as received. Acryloyl chloride and methacryloyl chloride (Aldrich) were vacuum-distilled. Benzoyl peroxide was recrystallized from a chloroform-methanol (1 : 1) mixture. All other chemicals were of analytical grade and used without further purification.

#### Preparation of Cinnamoylphenols (1-4)

To a well-stirred mixture of 4-HA (6.8 g, 0.05 mol) and BA, MeOBA, ClBA, or NBA (0.05 mol) in ethanol (40 mL) was added dropwise NaOH solution (4 g in 25 mL water) at 15°C, and the mixture was stirred at room temperature for 10 h. The reaction mixture was then neutralized with dilute HCl to isolate the product. It was filtered, washed with an ice-cold water-ethanol mixture, and dried. 4-Cinnamoylphenol (CP), 4-(4-methoxycinnamoyl)phenol (MeOCP), 4-(4-chlorocinnamoyl)phenol (ClCP), and 4-(4-nitrocinnamoyl)phenol (NCP) were obtained by reacting HA with BA, MeOBA, ClBA, and NBA, respectively. After recrystallization from ethanol, the compounds were characterized by melting points and elemental analysis, infrared (IR), and <sup>1</sup>H-nuclear magnetic resonance (NMR) techniques.

## Preparation of Monomers (5-12)

A typical example for the preparation of 4-cinnamoylphenyl acrylate (CPA) is as follows. In a 250-mL three-neck flask, 4-CP (22.43 g, 0.10 mol), triethylamine (10.12 g), and methyl ethyl ketone (150 mL) were placed and cooled to -5 to 0°C. Acryloyl chloride (10.86 g, 0.12 mol) in 50 mL of methyl ethyl ketone was then added dropwise with stirring at the same temperature. After stirring at room temperature for 2 h, the quaternary ammonium salt was filtered off. The organic layer was washed with 5% aqueous sodium hydroxide solution followed by distilled water, dried over anhydrous sodium sulphate, and methyl ethyl ketone was evaporated. The solid CPA was recrystallized from ethanol.

Similarly, 4-(4-methoxycinnamoyl)phenyl acrylate, (MeOCPA), 4-(4-chlorocinnamoyl)phenyl acrylate (ClCPA), and 4-(4-nitrocinnamoyl)phenyl acrylate (NCPA) were prepared by reacting acryloyl chloride with MeOCP, ClCP and NCP, respectively; and 4-cinnamoylphenyl methacrylate (CPMA), 4-(4-methoxycinnamoyl)phenyl methacrylate (MeOCPMA), 4-(4chlorocinnamoyl)phenyl methacrylate (ClCPMA), and 4-(4-nitrocinnamoyl)phenyl methacrylate (NCPMA) were prepared by reacting methacrylate (NCPMA) were prepared by reacting methacryloyl chloride with CPMA, MeOCP, ClCP, and NCP, respectively. The monomers were characterized by melting points, elemental analyses, IR, and <sup>1</sup>H-NMR techniques.

#### **Polymerization**

Monomers **5–12** were polymerized as 2M solutions in methyl ethyl ketone using benzoyl peroxide (0.25 wt % of monomer) as initiator at 70°C under nitrogen. After a predetermined polymerization time (2, 4, 6, 8, or 10 h), the polymer was isolated in excess methanol, purified by reprecipitation into methanol from chloroform solution, and dried under vacuum.

## Measurements

Microelemental analyses were performed with a Perkin-Elmer C-H-N analyser. UV-visible spectra were recorded on a Hitachi UV-2000 spectrophotometer. IR spectra were obtained with a Hitachi 270-50 spectrophotometer as KBr pellet. <sup>1</sup>H-NMR spectra with a Bruker 270 MHz FT NMR spectrometer, and <sup>13</sup>C-NMR spectra with a CXP 22.64 MHz FT NMR spectrometer, were obtained in CDCl<sub>3</sub> with tetramethylsilane as an internal standard. A Mettler TA 3000 thermal analyzer at a heating rate of 15°C/min in air/N<sub>2</sub>; and a Perkin-Elmer DSC-7 thermal analyzer at a temperature rise of 10°C/min in air, were used for the measurements of the polymers' thermal properties. Molecular weights of the polymers were determined with a Waters 501 GPC with three ultrastyragel columns and differential refractive index detector. The molecular weights were calibrated with standard polystyrene samples using tetrahydrofuran (THF) as the mobile phase. The thicknesses of the polymer films, for photo-



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3:	Х		Cl (C	210	CP);			4:	Х	=	NO <sub>2</sub>	()	NCP)		
5:	Х		Н	&	R =	Н	(CPA);	6:	Х	175	Н	&	R = 0	CH 3	(CPMA)
7:	Х	==	OCH3	&	R =	Н	(MeOCPA);	8:	Х	=	OCH 3	&	R = 0	СНЗ	(MeOCPMA)
9:	Х		C1	&	R =	Η	(CLCPA);	10:	Х	222	Cl	&	R = 0	СН З	(CLCPMA)
11:	Х	=	NO <sub>2</sub>	&	R =	H	(NCPA);	12:	Х	==	NO <sub>2</sub>	&	R = 0	CH 3	(NCPMA)

**Scheme 1** Preparation of acrylate and methacrylate monomers with photodimerizable cinnamoyl group.

crosslinking reactions, were measured with a Sloan Dektat-3030 surface profile measuring instrument.

#### **Photoreactivity of Polymers**

A thin film (thickness =  $\sim 1.25 \ \mu$ m) of the polymer on a quartz plate was made from 2% CHCl<sub>3</sub> solution of the polymer by dipping into and evaporating the solvent. The polymer film or polymer solution was irradiated for selected time intervals using a high-pressure mercury lamp at a distance of 10 cm. The rate of disappearance of >C==C< of the pendant  $\alpha,\beta$ -unsaturated ketone unit of the polymer was followed by measuring the UV absorption intensity of the film/solution after each exposure interval using the following expression:

Rate of conversion (%) =  $(A_0 - A_T/A_0) \times 100$ 

where  $A_0$  and  $A_T$  are absorption intensities due to >C = < after irradiation times t = 0 and t = T, respectively.

#### **RESULTS AND DISCUSSION**

Acrylate and methacrylate monomers (5–12) containing a photodimerizable  $\alpha,\beta$ -unsaturated ketone moiety were prepared in two steps as outlined in Scheme 1. In the first step, cinnamoylphenols 1–4 were prepared by reacting 4-HA with para-substituted benzaldehydes in the presence of NaOH in aqueous ethanol medium. Then 1–4 were esterified with acryloyl chloride or methacryloyl chloride in presence of triethylamine in methyl ethyl ketone at -5 to 0°C to obtain monomers 5–12.

The elemental analysis data of the monomers were in good agreement with the calculated values for the assigned structures. The IR spectra of the monomers show characteristic strong absorptions at about 1735 and 1680 cm<sup>-1</sup> due to carbonyl stretchings of ester and ketone groups, respectively; and at about 1620 cm<sup>-1</sup> due to ethylenic double-bond stretchings. The <sup>1</sup>H-NMR spectra (Fig. 1) of the monomers show a multiplet at 8.25 to 5.80 ppm corresponding to aromatic as



**Figure 1** <sup>1</sup>H-NMR spectrum of 4-cinnamoylphenyl acrylate (CPA).

well as olefinic protons. In addition, methacrylate monomers exhibit a singlet at about 1.95 ppm due to methyl protons.

Polymer	UVmax	$\bar{M}_{m}$	$\bar{M}_n$	
Ňo.	(nm)	$ imes 10^{-4}$	$ imes 10^{''-4}$	$\bar{M}_w/\bar{M}_n$
13	311	4.24	2.62	1.61
14	311	6.12	3.50	1.75
15	339	4.76	3.11	1.53
16	340	4.03	2.42	1.86
17	313	6.84	4.38	1.56
18	316	4.89	2.55	1.92
19	311	3.94	2.68	1.47
20	313	3.72	2.18	1.70
16 17 18 19 20	340 313 316 311 313	4.03 6.84 4.89 3.94 3.72	$5.11 \\ 2.42 \\ 4.38 \\ 2.55 \\ 2.68 \\ 2.18$	1.53 1.86 1.56 1.92 1.47 1.70

Polyacrylates and polymethacrylates (13–20) with a pendant photodimerizable  $\alpha,\beta$ -unsaturated ketone group were prepared by free-radical polymerization of monomers **5–12** in methyl ethyl ketone at 70°C (Scheme 2). Table I gives the weight-  $(M_w)$  and number-average  $(M_n)$  molecular weights and polydispersity index values of the



Table IUV Spectral Data and MolecularWeights of Polymers



Figure 2 Infrared spectrum of poly(CPA).

polymers. The  $M_w/M_n$  values of the polymers are in the range of 1.47 to 1.92 dL/g.

#### **Characterization of Polymers**

The polymers obtained in up to 45% conversion were easily soluble in polar aprotic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), DMAc, NMP, THF, etc., and chlorinated solvents, such as chloroform, methylenedichloride, etc. They were insoluble in hydrocarbons (e.g., benzene, toluene, xylenes) and such protic solvents as methanol, ethanol, and isopropanol. However, at conversions of above 50%, the polymer solubility decreases gradually with the increase of conversion; and the polymers obtained after 70% conversion were completely insoluble even at the boiling temperature of the polar aprotic as well as chlorinated solvents. This might be due to crosslinking through the pendant  $\alpha,\beta$ -unsaturated carbonyl unit. The IR spectra of both the soluble and insoluble polymers were, however, identical and do not prove the presence or absence of crosslinkings because the crosslinking density might be below the detection limit.

The UV-visible spectra of the polymers show an absorption band between 311 and 340 nm (Table I) due to  $\pi \rightarrow \pi^*$  transitions of the  $C = C \langle$  of the pendant cinnamoylphenyl moiety. The presence of an electron-donating methoxy (OCH<sub>3</sub>) group at the para-position of cinnamoyl aromatic ring in polymers 15 and 16 causes a bathochromic shift, and the UV band was observed at 340 nm. The IR spectra of all the polymers show almost identical features, except for small differences corresponding to the substitution at the para position of the cinnamoyl aromatic ring. The polymers show a strong band at around  $1750 \text{ cm}^{-1}$ due to ester carbonyl stretchings. The ketonic carbonyl stretching band was observed as a doublet, with the stronger peak at about 1680  $\text{cm}^{-1}$  and the weaker peak at about 1660  $\text{cm}^{-1}$  (Fig. 2). This may be due to the presence of *s*-*cis* and *s*-*trans* isomeric structures in the pendant cinnamoyl units,<sup>18</sup> as shown in Structures I and II. A sharp characteristic band at about 1610  $cm^{-1}$  can be assigned to >C=C< stretchings of the pendant cinnamoyl moiety. In addition, strong absorption bands are observed at 1530 and 1350  $\text{cm}^{-1}$  due to the nitro group in polymers 19 and 20, at 1195  $cm^{-1}$  due to the methoxy group in polymers 15 and 16, and at  $640 \text{ cm}^{-1}$  for polymers 17 and 18 due to C-Cl stretchings.



Structure I (s-trans)

Structure II (s-cis)

The <sup>1</sup>H-NMR spectra of the polymers show a number of doublets corresponding to the pendant cinnamoylphenyl unit due to the existence of s-cis and s-trans isomers. Poly(CPA) and poly(CPMA) exhibit a multiplet at 8.15 to 7.31 ppm corresponding to the protons of mono- and disubstituted aromatic rings, and two doublets at 6.70 and 6.10 ppm due to the ethylenic protons of the cinnamoyl unit (Fig. 3). The spectra of polymers 15-20 show eight doublets, centered at 8.08, 7.80, 7.61, 7.40, 7.29, 6.93, 6.65, and 6.03 ppm in polymers 15 and 16; at 8.11, 7.80, 7.59, 7.50, 7.40, 7.31, 6.65, and 6.08 ppm in polymers 17 and 18; and at 8.33, 8.13, 7.94, 7.81, 7.65, 7.35, 6.67, and 6.01 ppm in polymers 19 and 20, due to the protons of the two symmetrically disubstituted aromatic rings of the pendant cinnamoylphenyl group. All the polyacrylates show broad signals at 2.10 to 1.70 ppm due to backbone methylene and



Figure 3  $^{1}$ H-NMR spectra of the cinnamoylphenyl region of (a) poly(CPA) and (b) poly(MeOCPA).

methine protons. Polymethacrylates exhibit a group of signals at 1.28 to 0.88 ppm due to  $\alpha$ -methyl protons, thus indicating the presence of conformational tacticity. Besides, poly(MeOCPA) and poly(MeOCPMA) show an additional singlet at about 3.85 ppm, which is assignable to the methoxy (OCH<sub>3</sub>) protons at the 4-position of the pendant cinnamoyl aromatic ring.

Figure 4 shows the proton-decoupled <sup>13</sup>C-NMR spectrum of poly(CPA). Table II gives the <sup>13</sup>C-NMR chemical shift data of all the polyacrylates. Chemical shift assignments were made from the off-resonance decoupled spectra of the polymers by comparing with the calculated values for the given structures. All the polymers show resonance signals at about 190 and 171 ppm corre-



**Figure 4** Proton-decoupled <sup>13</sup>C-NMR spectrum of the cinnamoylphenyl region of poly(CPA).

sponding to ketone and ester carbonyl carbons, respectively. The aromatic and olefinic carbon resonances are observed at 162.1 to 121.1 ppm. In

Table II	<sup>13</sup> C-NMR	Chemical	Shift	Data
of Polyac	rylates			

	Chemical Shift (ppm) of Polymer					
Carbon No.	13	15	17	19		
C1	171.23	170.82	171.15	171.85		
C2	154.41	154.15	154.23	155.25		
C3	121.75	121.97	121.98	121.11		
C4	130.07	130.14	130.22	129.41		
C5	134.76	133.25	133.99	132.93		
C6	189.28	189.52	190.71	189.88		
$\mathbf{C7}$	145.02	145.24	145.13	144.31		
C8	130.58	130.55	130.42	130.77		
C9	135.50	130.14	142.28	136.79		
C10	128.44	127.79	129.01	138.42		
C11	128.93	114.72	123.82	128.95		
C12	127.88	162.03	148.30	132.17		
$OCH_3$		55.86	—	_		



**Figure 5** TGA traces in air and  $N_2$  atmospheres of poly(CPA).

polymethacrylates, backbone  $CH_2$  and quaternary carbon (—C—) and  $\alpha$ -CH<sub>3</sub> carbon resonances appeared at 48.61, 45.29, and 18.5 ppm, respectively. In addition, the methoxy carbon  $(OCH_3)$  resonances in polymers **15** and **16** are observed at about 55.8 ppm.

#### **Thermal Properties**

The thermal stability of the polymers was studied by thermogravimetric analysis (TGA) under thermal and thermal oxidative conditions. Figure 5 shows the TGA traces of poly(CPA) in air and nitrogen atmospheres. The differential TGA data of all the polymers are given in Table III. Polymers 13–18 decompose in a single stage in  $N_2$  and in two stages in air, but polymers 19 and 20 decompose in two stages in both  $\mathrm{N}_2$  and air. The initial decomposition temperatures of the polymers are above 250°C in air as well as nitrogen. In a nitrogen atmosphere the polymer decomposes rapidly in a single stage, but in air, after an initial weight loss of about 60%, the decomposition becomes slow for an increase of 20 to 40°C and then takes place rapidly. In the case of polymers 19 and 20, more weight loss (>50%) occurred in the first-stage decomposition in nitrogen and in the second-stage decomposition in air.

The glass transition temperatures ( $T_g$ s) of the polymers are shown in Table III. Poly(NCPMA) possesses the highest  $T_g$  (155°C) and poly-(MeOCPA) has the lowest (122°C). The  $T_g$  values

			DTR		
Polymer No	N <sub>2</sub> /Air	$T_g$ (°C)	Stage 1	Stage 2	$T_{ m d10}~(^{ m oC})$
13	$N_2$		352-650 (96)	_	426
	Air	136	315-500 (55)	572-719 (41)	402
14	$N_2$		264-575 (95)		330
	Air	147	272-533 (76)	553-659 (19)	307
15	$N_2$		278-655 (96)	_	370
	Air	122	281-459 (46)	470-675 (53)	366
16	$N_2$		286-612 (97)		357
	Air	138	248-520 (69)	535-660 (27)	330
17	$N_2$		268-635 (98)		351
	Air	123	257-515 (59)	524-671 (39)	359
18	$N_2$		268-575 (96)		341
	Air	140	271-487 (71)	512-655 (24)	356
19	$N_2$		258-472 (57)	490-760 (42)	323
	Air	144	262-368 (40)	380-645 (56)	331
20	$N_2$		264-442 (52)	462-735 (42)	306
	Air	155	272-441 (31)	470-765 (65)	343

Table III TGA Data and Glass Transition Temperatures of the Polymers

Figures in parentheses are the weight loss (%) that occured in the temperature range cited. DTR, decomposition temperature range.  $T_{d10}$ , temperature of 10% weight of polymer.



**Figure 6** Changes in the UV absorption spectrum of thin film of poly(CPA) upon irradiation with high-pressure Hg lamp. Top to bottom: after irradiation time t = 0, 0.17, 0.34, 0.84, 2, 4, 8, 12, 23, and 30 min, respectively.

of polymethacrylates are higher by about 10 to 20°C than the polyacrylates with the corresponding pendant cinnamoylphenyl group. It may be appropriate to mention here that poly(methyl acrylate) has a  $T_g$  of about 10°C, whereas poly(methyl methacrylate), which contain an  $\alpha$ -methyl group, has very high  $T_g$  of about 110°C. However, the relatively smaller differences in the  $T_g$  values between polyacrylates and polymethacrylates in the present case may be due to the presence of the bulky pendant  $\alpha,\beta$ -unsaturated ketone unit, which greatly influences the  $T_g$  of the polymer.

#### **Photoreactive Properties**

The photoreactivities of the polymers were examined by irradiating the polymer films and polymer solutions in presence and absence of a photosensitizer with a high-pressure Hg lamp and measuring the UV absorption intensity due to the pendant cinnamoyl group.

Figure 6 shows the changes in the UV spectral pattern of poly(CPA) thin film for different time intervals of irradiation in the absence of sensitizer. The polymer shows an absorption band at 311 nm due to the  $\pi \rightarrow \pi^*$  transitions of >C==C< of the pendant cinnamoyl moiety. The initial irradiation causes a trans-cis isomerization, as was evident by the appearance of an isobestic point at about 270 nm. Further irradiation results in a fast decrease in absorption, and the band disappears almost completely within 25 min of irradiation. The polymer became insoluble in polar aprotic as well as chlorinated solvents (in which it was soluble before being subjected to irradiation) within 45 s of irradiation. This behavior indicates the crosslinking of polymer chains by  $2\pi + 2\pi$  cyclodimerization of the >C=C< group of pendant cinnamoylphenyl units as shown in Scheme 3. The  $2\pi + 2\pi$  cyclodimerization destroys conjugation in the entire  $\pi$ -electron system and hence results in a decrease in the UV absorption intensity with exposure time.<sup>19,20</sup> An almost similar phenomenon was observed upon irradiation of thin films of the other polymers (**14–20**), and hence their spectra are not presented.

In general, the photoreactivity of polymers containing an  $\alpha,\beta$ -unsaturated carbonyl group is measured in terms of the rate of disappearance of the >C=C< with irradiation time. Figure 7 compares the rate of disappearance of the >C=C < ofpolyacrylates, which have a different kind of substituent (H, OCH<sub>3</sub>, Cl, or NO<sub>2</sub>) at the para-position of the cinnamoyl aromatic ring. The rates of disappearance of >C=C< of polymethacrylates almost overlap with those of the polyacrylates having the corresponding pendant photosensitive cinnamoylphenyl moiety. Depending upon the nature of the substituent, a conversion of 24 to 58% was achieved within 120 s of irradiation. The photoreactivity decreases in the following order:  $poly(CPMA) \approx poly(CPA) > poly(MeOCPMA)$  $\approx$  poly(MeOCPA) > poly(NCPMA) > poly(NCPA) > poly(ClCPMA)  $\approx$  poly(ClCPA). It is explicit



 $(\mathbb{P})$  = Polymer Chain

Scheme 3 Photocrosslinking of the polymers.



**Figure 7** Rate of disappearance of C = C with irradiation time of thin films of (a) poly(CPA), (b) poly-(MeOCPA), (c) poly(NCPA), and (d) poly(ClCPA). Open symbols: polymer in solution; filled symbols: polymer thin films.

from this observation that the presence of either of the electron-withdrawing (NO<sub>2</sub>, Cl) or -donating (CH<sub>3</sub>O) group at the para-position of the cinnamoyl aromatic ring decreases the photoreactivity rate of the >C=C< bond.

Photocrosslinking of the polymers was also carried out in the presence of various triplet sensitizers, such as benzophenone, Michler's ketone, or benzoin. It was observed that there was no sensitizing effect on the rate of disappearance of >C=C< of the pendant cinnamoyl moiety of the polymers by the addition of 2 to 10 wt % of the sensitizers. This behavior is similar to that reported for polymers with the units of  $\alpha$ -cyanocinnamic ester,<sup>21</sup>  $\alpha$ -phenylmaleimide,<sup>22</sup> and styrylpyridinium,<sup>23</sup> which have high photosensitivity but cannot be sensitized. The results strongly suggest that photocrosslinking of polymers **13–20** might not be taking place through the triplet state but, alternatively, through singletstate electrons leading to a one-step, concerted  $(2\pi)$ +  $2\pi$ ) cyclodimerization.<sup>24</sup>

The solid-state <sup>13</sup>C-NMR spectrum of irradiated polymer film shows new resonance peaks at 64.5 and 66.2 ppm corresponding to the cyclobutane ring, and at 196.4 ppm due to the ketone carbonyl group. The downfield shift of ketone carbonyl carbon can be attributed to the loss of extended conjugation on cyclization. In the solidstate <sup>1</sup>H-NMR spectrum, the irradiated polymer film exhibits new peaks at 4.55 to 4.40 ppm due to the protons of the cyclobutane ring, which is formed upon photoirradiation. The IR spectra of the irradiated films show a very weak band at about 1615 cm<sup>-1</sup> due to ethylenic >C==C< stretchings, and a strong new peak at 1695 cm<sup>-1</sup> due to a ketonic carbonyl group without conjugation.

The rate of disappearance of >C=C< of polymers in solution (Fig. 7) was faster than that of thin films. This may be due to the fact that in solution, although photoisomerization cannot be ruled out, the question of disruption of chromophore aggregate does not arise because there is no ordered arrangement of the chromophores. Hence, photodimerization takes precedence over *trans-cis* isomerization and results in the rapid decrease of UV absorption intensity.<sup>25</sup> However, the order of photoreactivity of the polymers in solution was similar to that observed for thin films, thus reflecting that the photoreactivity is mainly related to the chemical nature of the pendant  $\alpha,\beta$ -unsaturated ketone moiety.

## **CONCLUSIONS**

Polyacrylates and polymethacrylates having cinnamoylphenyl moiety as the pendant exhibit good solubility, thermal and thermooxidative stabilities, and higher rates of photocrosslinking leading to insolubility of the polymer within 30 to 45 s of irradiation in the absence of a sensitizer. The presence of either an electron-withdrawing or -donating group at the para-position of the phenyl ring of the cinnamoyl unit causes a little decrease in the photoreactivity of the polymer. There was no sensitizing effect on the rate of photocrosslinking of the polymers by the addition of 2 to 10 wt %of the sensitizers. The photocrosslinking of the polymers taking place through the singlet-state electrons led to a one-step, concerted  $(2\pi + 2\pi)$ cycloaddition. Because the polymers have good rates of photocrosslinking leading to insolubilization, it could be expected that they can be used as photocurable polymers in coating, electronic, and other applications.

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