

Synthesis and Characterization of Photosensitive Copolymers of 4-(4'-Nitrocinnamoyl)phenyl Acrylate and Glycidyl Methacrylate

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ABSTRACT: Copolymers of 4-(4'-nitrocinnamoyl)phenyl acrylate (NCPA) and glycidyl methacrylate (GMA) were prepared in a methyl ethyl ketone solution with benzoyl peroxide as the initiator at 70°C. They were characterized with UV, IR, ¹H-NMR, ¹³C-NMR, and gel permeation chromatography. Copolymer compositions were determined from ¹H-NMR spectra. The monomer reactivity ratios, de-

termined by the method of Kelen and Tüdös, were r_1 (NCPA) = 1.22 and r_2 (GMA) = 0.76. The initial decomposition temperatures of the copolymers were greater than 272°C, as observed by thermogravimetric analysis in air. The photocrosslinking properties of the polymer films were examined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3264–3270, 2002

INTRODUCTION

In recent years, the synthesis of polymers containing reactive functional groups in the pendant units has been an active field of research in polymer science because it provides an approach to the subsequent modification of polymers for required applications. Polymers containing α,β -unsaturated carbonyl groups undergo crosslinking upon irradiation with UV light or an electron beam, and such polymers are regarded as negative-type photoresists. They are being used in a variety of applications, such as photocurable coatings and energy-exchange materials, and in a variety of fields, such as microlithography and medicine.^{1–6} A number of polymers with photosensitive groups in the pendant units have been prepared and tested for their photoreactive properties.^{7–15} We reported the synthesis and photosensitive properties of polymers containing α,β -unsaturated ketone moieties with electron-donating or electron-withdrawing groups in the pendant.^{16,17} The curing of these polymeric films occurs within 60 s of irradiation with UV light in air in the absence of a sensitizer. The presence of an electron-withdrawing group (e.g., NO₂) in the cinnamoyl aromatic ring reduces the rate of photocrosslinking of the polymer.

High photosensitivity, thermal stability, and good solubility are very desirable properties for a photocrosslinkable polymer. The copolymerization of

monomers with different photofunctional groups is the best technique for tailor-made polymers with a range of properties for various applications. Copolymers based on glycidyl methacrylate (GMA) have versatile applications, such as photocurable or electron-beam-curable coatings and printing inks, because of the presence of reactive epoxy groups.¹⁸ The presence of both unsaturated carbonyl and epoxy functional groups in the polymer may provide some additional advantages in terms of photosensitivity, thermal stability, and solubility for coatings, films, and many other applications.

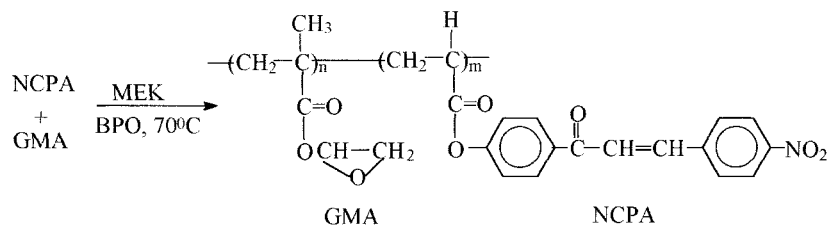
In a continuation of our work on photosensitive polymers,^{16,17} the synthesis, characterization, thermal stability, and photocrosslinking properties of copolymers of 4-(4'-nitrocinnamoyl)phenyl acrylate (NCPA) and GMA are reported in this article.

EXPERIMENTAL

Materials

GMA (Aldrich) was vacuum-distilled before use. Benzoyl peroxide (BPO) was recrystallized from a chloroform/methanol (1:1) mixture. NCPA was synthesized by the esterification reaction between 4-hydroxyphenyl-4'-nitrostyryl ketone (8.9 g, 0.033 mol) and methacryloyl chloride (4.08 g, 0.039 mol) in the presence of triethylamine (3.33 g) in methyl ethyl ketone at 0 to –5°C according to a procedure described elsewhere.¹⁷ All the other chemicals were analytical-grade samples and were used as received.

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Scheme 1 Preparation of the copolymers of NCPA with GMA.

Copolymerization

Copolymers of NCPA and GMA in six different compositions were prepared with 2M solutions of the monomers in methyl ethyl ketone in the presence of BPO (0.5 wt % monomers) as an initiator at 70°C. Suitable amounts of the monomers, initiator, and solvent were mixed in a polymerization tube, flushed with oxygen-free nitrogen for 20 min, and kept in a thermostat at 70°C. After a predetermined time (≈ 1 h), the copolymer was isolated in excess methanol, purified by reprecipitation into methanol from a chloroform solution, and finally dried in vacuo.

Instruments

UV spectra were recorded with a Hitachi UV-2000 spectrophotometer (Kyoto, Japan). IR spectra were obtained with a Hitachi 270-50 spectrophotometer with KBr pellets (Kyoto, Japan). $^1\text{H-NMR}$ spectra with a Bruker 270 MHz spectrometer Bruker 270 MHz spectrometer (Silberstreifen, Germany) and $^{13}\text{C-NMR}$ spectra with a CXP 22.64 MHz FT NMR spectrometer were obtained in CDCl_3 solutions with tetramethylsilane as an internal reference. Thermogravimetric analysis (TGA) was performed in air with a Mettler TA 3000 thermal analyzer Mettler TA 3000 thermal analyzer (Switzerland) at a heating rate of $15^\circ\text{C min}^{-1}$. Glass-transition temperatures (T_g 's) of the polymers were determined with a PerkinElmer DSC D7 PerkinElmer DSC D7 (Uberlingen, Germany) at a heating rate of $15^\circ\text{C min}^{-1}$ in air. A Waters 501 HPLC instrument Waters 501 HPLC instrument (Milford, MA) equipped with three Ultrastaygel columns and an RI-401 detector was used for the determination of the molecular weights of the polymers. The molecular weights were calibrated against polystyrene standards with tetrahydrofuran as the mobile phase. The thicknesses of the polymer films were measured with a Solan Dektak 3030 surface profile measuring instrument.

Photoreactivity of the polymers

The photoreactivity of the polymers was measured as follows. A thin film ($1.25 \pm 0.1 \mu\text{m}$ thick) of the polymer on a flat quartz plate was made with a 2%

solution of the polymer in chloroform by the dipping and evaporation of the solvent. Then, the film was irradiated for selected time intervals with a high-pressure (75-W) mercury lamp at a distance of 10 cm. After each exposure time, the UV spectrum of the film was recorded, and the disappearance rate of >C=C< of the pendant α,β -unsaturated ketone unit was calculated with the following expression:

$$\text{Rate of conversion (\%)} = (A_0 - A_T)/(A_0 - A_\alpha) \times 100$$

where A_0 , A_T , and A_α are absorption intensities due to the >C=C< group after the irradiation times $t = 0$, $t = T$, and $t = \alpha$ (maximum irradiation time), respectively. The data presented are the averages of three experiments. The standard deviation between the experiments was $\pm 2\%$.

RESULTS AND DISCUSSION

Photocrosslinkable polymers containing different amounts of pendant α,β -unsaturated ketone and epoxy groups were prepared by the free-radical copolymerization of NCPA and GMA in a methyl ethyl ketone solution with BPO as the initiator at 70°C (Scheme 1). The copolymerization proceeded in a homogeneous solution for all the compositions of the monomer feeds. Table I gives the data of the molar compositions of the initial mixtures of the comonomers used and of the resulting copolymers.

Solubility

Because solubility is one of the most important requirements for a photosensitive polymer, the solubility of the copolymers was tested in various organic solvents. All the copolymers were easily dissolved in aprotic polar solvents such as *N*-methyl-2-pyrrolidone, dimethylformamide, dimethylacetamide, dimethylsulfoxide, and tetrahydrofuran and in chlorinated solvents such as chloroform and methylene dichloride. They were insoluble in hydrocarbons such as benzene, toluene, and xylene and in protic solvents such as methanol, ethanol, and 2-propanol.

TABLE I
Composition and Molecular-Weight Data for the Copolymerization of NCPA with GMA

M_1	Conversion (%)	C	m_1	$M_w \times 10^{-4}$	M_w/M_n
0.10	8.14	0.14	0.19	5.02	1.97
0.20	9.16	0.20	0.28	4.12	1.89
0.35	10.21	0.34	0.49	3.88	1.83
0.50	10.26	0.48	0.75	3.51	1.79
0.65	9.25	0.52	0.82	3.05	1.76
0.85	8.55	0.57	0.92	2.29	1.75
1.00	—	—	—	3.94	1.47

M_1 and m_1 are the molar fractions of NCPA in the feed and copolymer, respectively.

Molecular weights

Table I gives the weight-average molecular weight (M_w) and polydispersity index [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values for poly[4-(4'-nitrocinnamoyl)phenyl acrylate] (PNCPA) and copolymer samples. The M_w values of the copolymers range from 2.29 to 5.02×10^4 Da, with polydispersity index values of 1.75–1.97, the normal molecular weight distribution expected for the free-radical polymerization of (meth)acrylate monomers.

IR spectra

The IR spectra (Fig. 1) of the copolymers apparently show more prominent absorptions of NCPA units because the absorptions due to GMA overlap those of NCPA. Strong absorptions at about 1760 cm^{-1} correspond to the ester carbonyl stretchings. A doublet with a strong peak at 1680 cm^{-1} and a weak peak at 1640 cm^{-1} may be assigned to the ketonic carbonyl group in the NCPA unit.¹⁷ A strong band at 1620 cm^{-1}

corresponds to the pendant olefin group, which is flanked by the ketone and phenyl groups in the NCPA unit. The aromatic >C=C< stretchings and C—H out-of-plane bending vibrations can be observed at 1510 and 760 cm^{-1} , respectively. Absorptions at 990 and 810 cm^{-1} are due to the epoxy group of the GMA unit.¹⁹ A strong peak at 1360 cm^{-1} is due to the —NO_2 group stretchings.

¹H-NMR spectra

The ¹H-NMR spectrum (Fig. 2) of copoly(NCPA-GMA) contains distinct signals for both NCPA and GMA units. Signals at 8.40–6.94 ppm are due to aromatic protons, and those at 6.36 and 6.08 ppm are assignable to the ethylenic protons of the pendant chalcone moiety of the NCPA unit.¹⁷ The GMA unit is characterized by resonance signals at 4.35 and 3.83 ppm due to the methyleneoxy (CH_2O) protons of the ester and epoxy ring, respectively, and at 3.23 ppm due to the methyne (CH) proton of the epoxy group.¹⁹ The resonance signals at 2.68 and 2.06 ppm are assign-

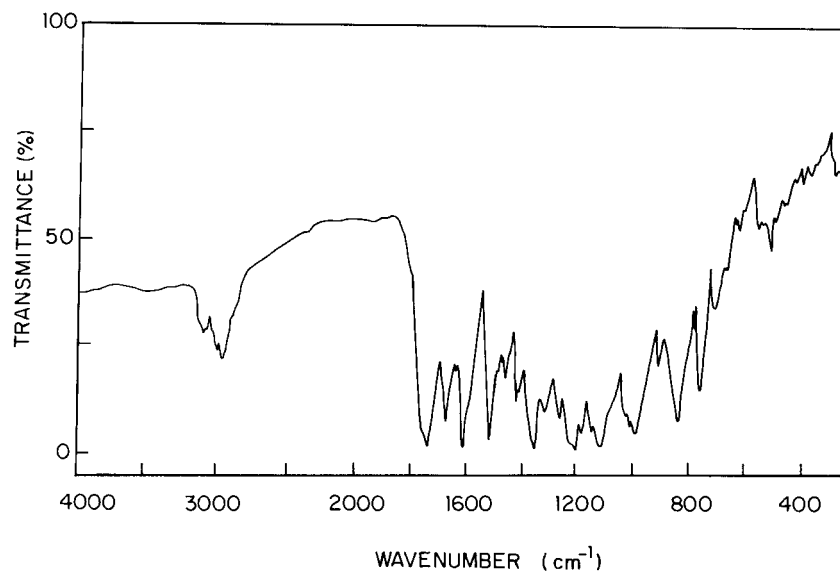


Figure 1 IR spectrum of poly(NCPA-co-GMA) (molar fraction of NCPA = 0.75).

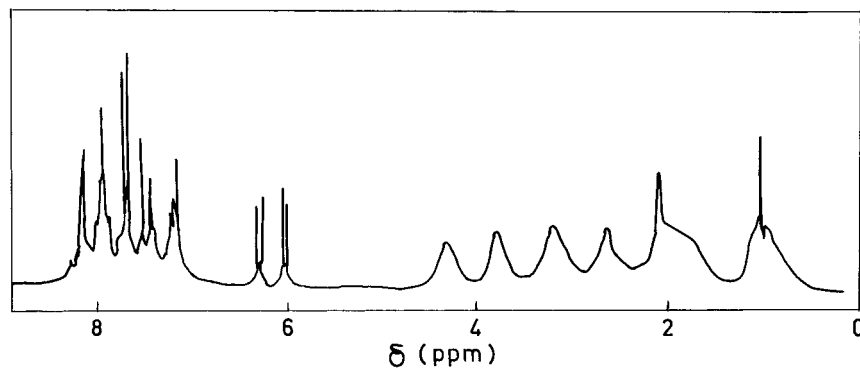


Figure 2 $^1\text{H-NMR}$ spectrum of poly(NCPA-co-GMA) (molar fraction of NCPA = 0.75).

able to the backbone methyne and methylene protons of both monomeric units. The methyl protons of the GMA unit can be observed at 1.15 ppm.

$^{13}\text{C-NMR}$ spectra

Figure 3 shows the proton-decoupled $^{13}\text{C-NMR}$ spectrum of copoly(NCPA-GMA). Chemical-shift assignments were made from the off-resonance decoupled spectra of the copolymers. The ketonic carbonyl carbon resonances of the pendant chalcone unit of NCPA appears at 190.4 ppm.¹⁷ The ester carbonyl carbons of both monomeric units can be observed at 176.9 and 175.5 ppm and are interchangeable. The aromatic carbon that is attached to the esteric oxygen atom gave resonance signals at 150.3 ppm. The other aromatic carbons gave signals at 142.3, 130.8, 129.5, 127.2, 125.5, 124.7, 125.6, and 122.5 ppm, and the olefinic carbons gave signals at 119.6 and 118.5 ppm. The signals due to pendant ester methyleneoxy ($-\text{OCH}_2$), epoxy ring methyleneoxy ($-\text{OCH}_2$), and methyne ($-\text{OCH}$) carbons of the GMA unit can be seen at 58.9, 55.1, and 53.4 ppm, respectively.¹⁹ Resonance signals of backbone methylene ($-\text{CH}_2$), methyne ($-\text{CH}$), and tertiary carbons appear between 48.1 and 45.1 ppm. A

group of signals at 18.5 ppm due to α -methyl carbon of GMA indicates the presence of configurational tacticity.

Copolymer compositions

The copolymer compositions were determined by analysis of the $^1\text{H-NMR}$ spectra of the copolymers. The assignment of resonance peaks in the $^1\text{H-NMR}$ spectrum of the copolymer allows the accurate determination of the copolymer composition.¹⁹⁻²² The molar fraction of NCPA in the copolymer was determined by the measurement of the integrated intensities of downfield protons (aromatic + olefinic = 10) at 8.40–6.08 ppm of the nitrocinnamoylphenyl group in the NCPA unit and the total protons (22 H) from both monomers with the following expression:

$$\text{Molar fraction of NCPA} = 10 - C / (10 - 3C)$$

where C is the ratio of the integrated intensities of downfield protons to that of total protons in the $^1\text{H-NMR}$ spectrum of the copolymer. Table I gives the values of C and the corresponding molar fractions of NCPA in the copolymer samples. Table I clearly indi-

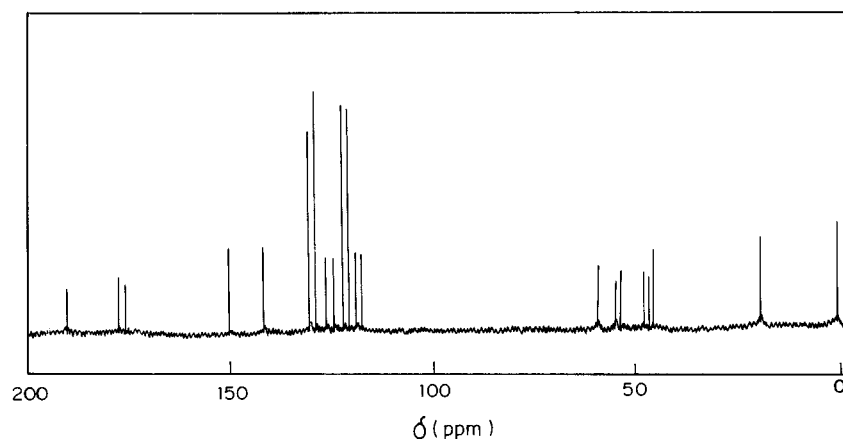


Figure 3 Proton-decoupled $^{13}\text{C-NMR}$ spectrum of poly(NCPA-co-GMA) (molar fraction of NCPA = 0.75).

TABLE II
 T_g 's and TGA Data for Copolymers of NCPA with the GMA System

m_1	m_2	T_g (°C)	RDT (°C)		T_{d10} (°C)
			Stage 1	Stage 2	
0.00	1.00	74	200–416 (96)	—	260
0.19	0.81	—	274–491 (75)	510–653 (23)	343
0.28	0.72	—	281–485 (64)	505–665 (34)	359
0.49	0.51	88	284–485 (50)	512–689 (47)	361
0.75	0.25	102	284–383 (33)	405–689 (65)	367
0.82	0.18	112	288–384 (26)	408–689 (72)	374
0.92	0.08	—	290–371 (21)	391–689 (78)	378
1.00	0.00	155	262–369 (40)	380–645 (56)	331

m_1 and m_2 are the molar fractions of NCPA and GMA, respectively, in the copolymer. RDT = range of decomposition temperature; T_{d10} = temperature at which 10% weight loss of polymer occurred.

icates that for all the monomer feed compositions, the copolymer contains more NCPA.

Monomer reactivity ratios

Monomer reactivity ratios are important quantitative values for predicting the copolymer composition for any starting feed in batch, semibatch, or continuous reactors and for understanding the kinetic and mechanistic aspects of the copolymerization. The reactivity ratios of NCPA and GMA were determined from the monomer feed and the resultant copolymer composition by the application of the Kelen–Tüdös method, the linear method of r_1 and r_2 determination in which all data are weighted equally and which is insensitive to the transposition of data.^{23,24} The reactivity ratio values obtained from the Kelen–Tüdös plot are as follows: r_1 (NCPA) = 1.22, r_2 (GMA) = 0.76, and r_1r_2 = 0.92. The product of the reactivity ratios (r_1r_2 = 0.92), which is less than 1, indicates a random distribution of the comonomers in the polymer chain. The value of $1/r_1$ (0.82) suggests that the reactivity of growing radicals with NCPA ends appears to be a little higher toward its own monomer molecule. Conversely, the reactivity of growing radicals with GMA ends, as observed by the value of $1/r_2$ (1.31), seems to be less toward its own monomer and higher toward the comonomer (NCPA). These observations clearly suggest that the probability of the NCPA unit entering the copolymer chain is somewhat more than that of GMA.

T_g

Table II gives the T_g values of PNCPA, poly(glycidyl methacrylate) (PGMA), and three copolymer samples. The T_g values for PNCPA and PGMA are 155 and 74°C, respectively. The copolymers exhibit a single T_g , thereby indicating the formation of random copolymers for all the monomer feed compositions. The T_g value of the copolymers depends on the copolymer

composition and increases with an increase in the NCPA content in the polymer chain. This may be attributed to the increase in the amount of stiff and bulky aromatic pendant groups (chalcone moieties) introduced into the system.

TGA

TGA is the most favored technique for the rapid evaluation of the thermal stability of polymeric materials. It is especially useful in comparing the thermal stabilities of various copolymers. Table II shows the differential TGA data for two homopolymers and for all the copolymer samples. The initial decomposition temperatures (IDTs) of PNCPA and PGMA are 262 and 200°C, respectively. The IDT of the copolymers depends on the composition of constituent monomers and increases with an increase in the NCPA content in the copolymer. PGMA decomposes in a single stage in the temperature range of 200–416°C, with a weight loss of about 96%. PNCPA undergoes thermooxidative decomposition in two stages, the first one at 262–369°C with a weight loss of about 40% and the second one at 380–645°C. The copolymers also decompose in two stages similarly to PNCPA. Copolymers with higher GMA contents undergo rapid decomposition in the first stage. As the NCPA content in the copolymer increases, the weight loss decreases in the first stage (274–371°C) and increases in the second stage in the temperature range of 400–650°C. The total weight loss of the copolymers in both decomposition stages is about 97%.

Photocrosslinking properties

The photoreactivity of the polymers was studied by the irradiation of the polymer films with a high-pressure mercury lamp and by the measurement of the UV absorption intensity due to >C=C< of the pendant nitrocinnamoyl group of the NCPA unit. Typical changes in the UV spectral pattern of the copolymer

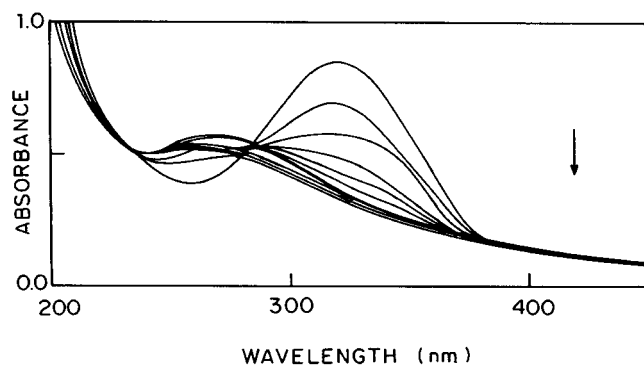


Figure 4 Changes in the UV spectra of a thin film of poly(NCPA-co-GMA) (molar fraction of NCPA = 0.75) after 0, 0.17, 0.5, 1.5, 2.5, 4.5, 6.5, 9, 12, 16, 20, and 25 min of irradiation (from top to bottom).

film for different time intervals of irradiation are presented in Figure 4. The copolymers show an absorption band at about 310 nm due to the $\pi-\pi^*$ transitions of the pendant nitrocinnamoyl group of the NCPA unit. The initial irradiation causes a trans-cis isomerization of the nitrocinnamoyl group, as evident from the appearance of an isobestic point at 272 nm. The absorption intensity at 310 nm decreases rapidly with the irradiation time, and the band disappears almost completely within 30 min of irradiation. The copolymer became insoluble in polar aprotic and chlorinated solvents, in which it was easily soluble before irradiation, within 60 s of irradiation. The decrease in the UV absorption intensity due to the pendant chalcone unit and the insoluble nature of the copolymers are due to the crosslinking of polymer chains through $2\pi + 2\pi$ cycloaddition of the >C=C< group of the pendant nitrocinnamoylphenyl unit,^{16,17} as shown in Scheme 2. The $2\pi + 2\pi$ cycloaddition destroys the entire π -electron system and results in a decrease in the UV absorption intensity of the double bond of the pendant nitrocinnamoyl unit with the irradiation time.^{25,26}

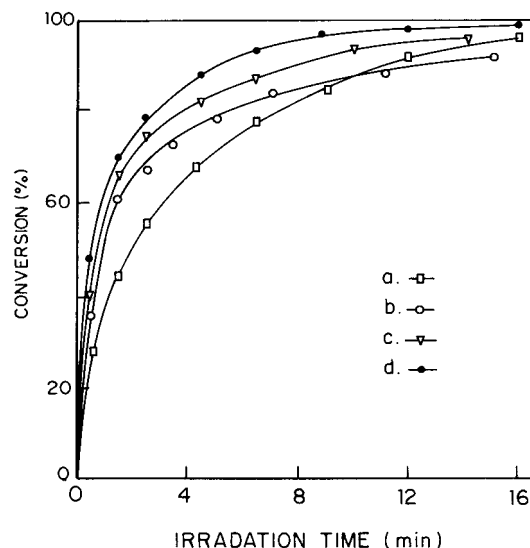
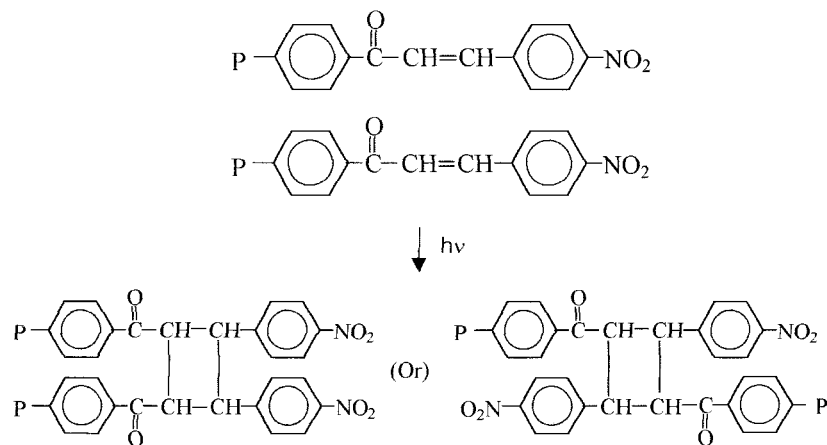


Figure 5 Disappearance rate of the pendant chalcone double bonds (>C=C<) of the copolymers with UV irradiation for the following molar fractions of NCPA: (a) 0.28, (b) 0.49, (c) 0.75, and (d) 0.82.

The disappearance rate of the double bonds of the pendant nitrocinnamoyl group in PNCPA and four copolymer samples with the irradiation time is shown in Figure 5. Interestingly, the photoconversion rate for the copolymers is faster than that of PNCPA and increases with an increase in the NCPA content in the copolymer chain. The higher rate of photoconversion in the copolymers may be due to the presence of epoxy groups.

CONCLUSIONS

Copolymers of NCPA with GMA were synthesized and characterized with UV, IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and gel permeation chromatography. The composition data and reactivity ratios of the monomers clearly suggest a random distribution of comonomers in the



Scheme 2 Photocrosslinking of the copolymers.

copolymer chain. The copolymers show a single T_g , thereby indicating the formation of random copolymers. The copolymers possess good thermooxidative stabilities, with IDTs greater than 270°C, as observed with TGA in air. The rate of photocrosslinking of the copolymer films increases with an increase in the NCPA content in the copolymer chain. The curing of the copolymers occurs within 60 s of irradiation in the absence of a sensitizer. Because the copolymers exhibit good photocrosslinking properties, even in the absence of a photosensitizer, they can find applications as photoresists and coatings.

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