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Photoresponsive polymers having pendant chlorocinnamoyl moieties: synthesis, reactivity ratios and photochemical properties

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Abstract

New photoreactive homo- and copolymers containing pendant chlorocinnamoyl moieties were respectively synthesized by homopolymerization of corresponding acrylic monomer and copolymerization with glycidyl methacrylate. The diverse structures were characterized by different spectroscopic techniques. The thermal properties of the photosensitive polymers were investigated by thermogravimetric analysis in air and differential scanning calorimetry under nitrogen atmosphere. The compositions of polymers were determined by ^{1}H-NMR analysis. The reactivity ratios of both comonomers were calculated using the conventional linearization methods such as Fineman–Ross, Kelen–Tudos, extended Kelen–Tudos and a non-linear error-in-variables model (EVM) method using a computer program, RREVM, in order to optimize the reaction conditions for industrial applications. The photoreactivity of newly synthesized homo- and copolymers containing pendant chlorocinnamoyl moieties was investigated in solution as well as in thin films. The effects of solvent nature, concentration, temperature, copolymer compositions and photosensitizers on the rate of photocrosslinking of these new photoresponsive polymers were evaluated. Suitable conditions were discussed for using as negative photoresists in industries.

Keywords: Negative photoresists; Copolymerization; Reactivity ratios

1. Introduction

The synthesis and technological applications of polymers with photoresponsive groups have attained much attention during the past decades because of their wide range of applications in emerging fields such as advanced microelectronics [1], liquid crystalline display [2], photolithography [3], holographic head-up-display [4], non-linear-optical materials [5], integrated circuit technology [6], photocurable coatings [7], etc. UV radiation curing has been revealed as a powerful tool to crosslink rapidly heat sensitive polymers and to modify, selectively in the illuminated areas, their physico-chemical characteristics. Phototunable technology has found major openings in various industrial applications where its distinct advantages such as fast and selective curing at ambient temperature have allowed this environmentally friendly technology to outclass more conventional processing techniques. Polymers having α, β-unsaturated carbonyl groups either in the backbone or in pendant position undergo crosslinking upon UV irradiation and such polymers are regarded as negative-type photoresists. These polymers with the properties of high photosensitivity, film-forming ability, good solubility before irradiation, resistance towards solvents, plasmas and etching agents after crosslinking and good thermal stability are very important for commercial photoresist applications.

Polymers with photoresponsive groups such as cinnamic esters of poly(acrylate) derivatives [8,9], poly(vinyl alcohol) [10], poly(2-hydroxyethyl methacrylate) [11] and many other systems have been reported as negative photoresists. Most of the reported photoresists were mainly derived from grafting of photoactive groups along polymer chains or chemical modification of other types of existing photosensitive polymers. Alternatively, the synthesis of copolymers having known composition of photoactive monomers with other commercial monomers is an attractive and economic way to get tailor-made model macromolecules with well-defined structure of technical interest. There are only very few reports on photoresponsive copolymers having different

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compositions formed from newly synthesized photosensitive monomers and other commercial monomers. Copolymers of glycidyl methacrylate (GMA) with acrylic monomers are transparent in nature and have excellent thermosetting properties at low temperature [12]. The presence of oxirane groups in GMA units allows to further modify the copolymers for desired industrial applications such as binding of drugs, biomolecules and other phototunable molecules [13]. In order to make suitable materials for the aforementioned applications, it is necessary to know the exact composition of the comonomers present in a copolymer system. The reactivity ratios are important quantitative values for any starting feed in batch, semi-batch and continuous reactor and to understand the kinetic and mechanistic aspects of copolymerization. For the estimation of copolymer compositions, ^{1}H-NMR analysis has been used as a powerful technique [14,15].

The main aim of the present investigation is to develop new negative photoresist materials based on polymers with different compositions of photoresponsive units. In continuation of earlier work [16], this article deals with the synthesis, thermal stability and photochemical properties of new photoresponsive homo- and copolymers having chlorocinnamoyl moiety at pendant position. The reactivity ratios of photoresponsive monomer and GMA were estimated. The photoreactivity of the new homo- and copolymers and the influence of various factors on the rate of photocrosslinking were examined for practical utilization of these polymers as commercial negative photoresists.

2. Experimental

2.1. Materials

3-Chlorobenzaldehyde (Merck, Germany), glycidyl methacrylate (GMA, Acros, Belgium) were purified by reduced pressure distillation. 4-Hydroxyacetophenone (Merck, Germany) and benzoyl peroxide (BPO, Fluka, Switzerland) were recrystallized from ethanol and methanol-chloroform (1:1) mixture, respectively. Acryloyl chloride was prepared according to the method of Stempel et al. [17]. All the solvents were distilled prior to their use.

2.2. Synthesis

2.2.1. 4-Hydroxyphenyl-3′-chlorostyryl ketone (HPCSK) (*1*)

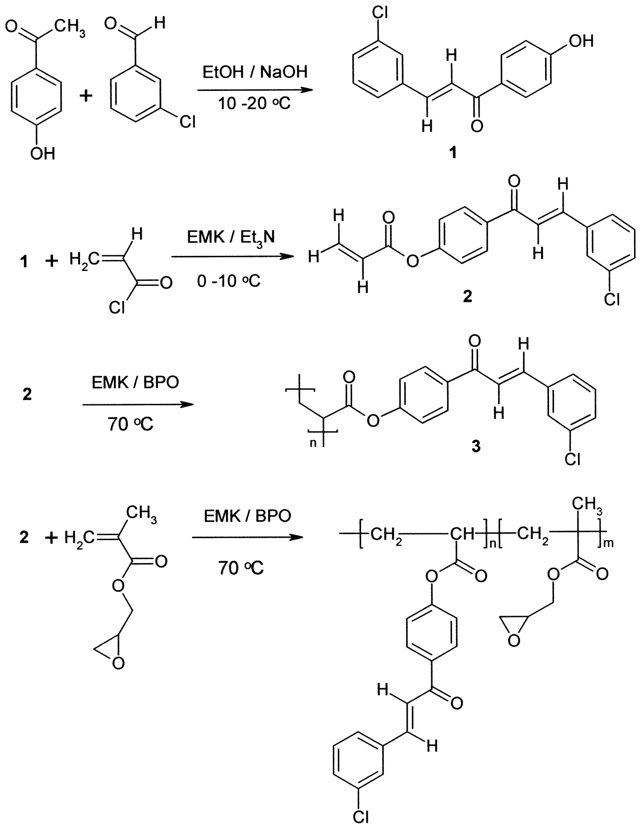
A solution of sodium hydroxide (8 g) in 40 ml of distilled water was added dropwise to the mixture of 4-hydroxyacetophenone (13.6 g, 0.1 mol) and 3-chlorobenzaldehyde (14 g, 0.1 mol) dissolved in 100 ml of ethanol and maintained at the temperature range of 18–20 °C. The mixture was stirred well for 12 h and the temperature was not allowed to exceed 25 °C. After 12 h, the reaction mixture was refrigerated overnight and neutralized with 2 M HCl to isolate the product. The yellow color solid was filtered off and washed several times with ice-cold water. The crude product was recrystallized from methanol to yield 20.1 g (73%) of yellow crystalline product, HPCSK (**1**) (Scheme 1); mp = 165 °C.

Elemental analysis for $C_{15}H_{11}O_2Cl$: calcd: C, 69.64%; H, 4.28%. Found: C, 69.51%; H, 4.24%. FT-IR (KBr, cm^{-1}): 3262 (OH), 1652 (>C=O), 1599 (>C=C<), 1564 (aromatic C=C stretching), 811 and 758 (C–H out-of-plane bending), 500 (C–Cl). ^{1}H-NMR ($CDCl_3$, δ in ppm): 10.20 (s, 1H, O–H), 8.11–7.22 (m, 8H, Ar-H), 6.92 and 6.84 (2d, 2H, –CH=CH–).

2.2.2. 4-Acryloyloxyphenyl-3′-chlorostyryl ketone (APCSK) (*2*)

The photoreactive monomer, APCSK was prepared by reacting HPCSK (15 g, 0.06 mol) with acryloyl chloride (5.4 g, 0.06 mol) in ethyl methyl ketone solvent adopting our reported procedure [18]. The crude monomer isolated was dissolved in CH_2Cl_2 and washed successively with very dilute NaOH solution, distilled water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the solid obtained was recrystallized in ethanol to get 14.3 g (70%) of pale yellow crystals, APCSK (**2**) (Scheme 1), mp = 80 °C.

Elemental analysis for $C_{18}H_{13}O_3Cl$: calcd: C, 69.12%; H, 4.18%. Found: C, 68.97%; H, 4.14%. FT-IR (KBr, cm^{-1}): 1733 (ester >C=O), 1661 and 1630 (ketone >C=O), 1601



Scheme 1. Synthesis of photoreactive monomer (APCSK, **2**) and its homopolymer (**3**) and copolymer with glycidyl methacrylate (GMA).

(aliphatic >C=C<), 1540 and 1506 (Ar, C=C), 798 and 754 (C–H out-of-plane bending), 511 (C–Cl). ^{1}H-NMR ($CDCl_3$, δ in ppm): 8.28–7.10 (m, 8H, Ar-H), 6.78–6.01 (m, 2H/3H, –CH=CH–/–CH_2=CH–). ^{13}C-NMR ($CDCl_3$, δ in ppm): 187.99 (keto C=O), 174.85 (ester C=O), 153.24–120.18 (Ar-C and –CH=CH–), 128.86 and 121.73 (–CH=CH–), 119.11 (=C–H), 113.61 (CH_2=).

2.2.3. Photoreactive homopolymer, poly(APCSK) (3)

Polymerization of the monomer APCSK was carried out as a 2 M solution in ethyl methyl ketone using BPO (0.25 wt% with respect to monomer) as a free radical initiator at 70 °C. The mixture of APCSK, BPO and the solvent were deaerated in a reaction vessel using oxygen-free nitrogen for 30 min and heated in a thermostat at 70 °C. After 12 h, the mixture was cooled and poured into excess methanol. The precipitated polymer was filtered off and purified by reprecipitation using methanol in DMF solution and finally dried in vacuum at 50 °C to get pure poly(APCSK) (**3**).

FT-IR (KBr, cm^{-1}): 3060 (Ar, C–H stretching), 1759 (ester >C=O), 1705 and 1669 (ketone >C=O), 1601 (–CH=CH–), 1527 and 1510 (Ar, C=C), 801 and 760 (C–H out-of-plane bending), 512 (C–Cl). ^{1}H-NMR ($CDCl_3$, δ in ppm): 8.28–6.16 (m, 8H/2H, Ar-H/–CH=CH–), 2.72–1.38 (m, 1H/2H, –CH–/–CH_2–). ^{13}C-NMR ($CDCl_3$, δ in ppm): 188.82 (keto C=O), 175.36 (ester C=O), 154.43–122.21 (Ar-C and –CH=CH–), 54.33 (backbone CH_2), 43.21 (backbone >C–H–).

2.2.4. Copolymers of APCSK and GMA

Copolymerization of APCSK and GMA having five different feed compositions (Table 1) was carried out at 70 °C in ethyl methyl ketone solvent using BPO (0.25 wt% with respect to monomers) as a free radical initiator. Predetermined amounts of APCSK, GMA, BPO and the solvent were mixed in a polymerization tube having inlet and outlet system, purged with nitrogen gas for 20 min and kept in a water bath at 70 °C. After the desired time (15–30 min), the copolymers of different comonomer composition were isolated by adding the reaction mixture into excess methanol. In order to obey the copolymer equation, the conversions were restricted to less than 10%. The precipitated copolymers were purified by repeated reprecipitation from chloroform solution using methanol as a non-solvent and dried in vacuum for 12 h.

Table 1
Composition data for the copolymerization of APCSK with GMA

Copolymer no.	M_1[a]	Conversion (%)	Intensities of protons		C[b]	m_1[c]
			I_{Ar+Oli}	$I_{Oth.ali}$		
1	0.1501	9.27	16.486	59.496	0.2771	0.2331
2	0.3507	9.02	30.787	48.060	0.6406	0.4423
3	0.5007	8.46	34.064	39.121	0.8707	0.5410
4	0.6532	9.19	36.007	32.381	1.1120	0.6253
5	0.8534	7.97	42.100	24.264	1.1735	0.7835

[a] Mole fraction of APCSK in the comonomer feed.

[b] $C = I_{Ar+Oli}/I_{Oth.ali}$.

[c] Mole fraction of APCSK in the copolymer.

^{1}H-NMR ($CDCl_3$, δ in ppm): 8.24–6.88 (m, 8H/2H, Ar-H/–CH=CH–), 4.20 and 3.63 (s, 2H, ester –CH_2O–), 3.08 (s, 1H, epoxy >CH–), 2.71 and 2.49 (d, 2H, epoxy –CH_2O–), 2.35–1.48 (broad, 2H/1H, backbone –CH_2–/>CH–), 1.42–0.69 (broad, 3H, α-CH_3). ^{13}C-NMR ($CDCl_3$, δ in ppm): 189.47 (keto C=O), 164.32 (ester C=O), 154.59–122.23 (Ar-C/–CH=CH–), 59.02 (ester –CH_2O–), 56.28 (epoxy –CH_2O–), 54.03–47.12 (backbone –CH_2–, >CH– and >C<), 18.92 (α-CH_3).

2.3. Instruments

Fourier Transform-Infrared (FT-IR) spectra of the polymers were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. Elemental analyses were performed using Perkin–Elmer C–H–N analyzer. The UV spectra were recorded with a Shimadzu UV-1601 UV–Visible spectrometer. ^{1}H-NMR spectra were run on a Bruker 400 MHz NMR spectrometer at room temperature with tetramethylsilane (TMS) as the internal reference in $CDCl_3$ solvent. The proton decoupled ^{13}C-NMR spectra were recorded on the same instrument operating at 125.77 MHz at room temperature. Molar mass distributions of the polymers were determined with a Waters 501 size exclusion chromatography (SEC) equipment using tetrahydrofuran as the eluent. A Mettler TA 3000 thermal analyser was used for TGA analysis. TG/DTG thermograms were recorded in air at a heating rate of 10 °C min^{-1}. Netzsch-Geratebau Gmbh DSC 204 calorimeter was used for recording the glass transition temperatures of the polymers over the temperature range of 30–250 °C at a heating rate of 10 °C min^{-1} in nitrogen atmosphere. The thickness of the polymer films was measured with a Sloan-Dektak 3030 surface profile measuring instrument.

2.4. Photoreactivity studies

A medium-pressure mercury lamp (Heber Scientific, 6 W) equipped with a filter to get a single emission line at 365 nm was used as UV source for the irradiation of the polymers in various organic solvents and also for the polymer films prepared from 5% solution in chloroform. The path length of the quartz cell used for polymer solution was 1 cm. Thin films having thickness of 1.5 ± 0.1 μm were prepared on a quartz plate. The polymer solutions and films were irradiated with a UV intensity of 33 mW cm^{-2} (distance of 10 cm from light source) for different intervals of time at room temperature in air. Immediately after each exposure interval, the UV spectra of the polymer solutions/films were recorded. The rate of disappearance of the photoactive cinnamoyl double bond was followed using the following expression:

$$\text{Extent of conversion (\%)} = (A_0 - A_T)100/(A_0 - A_\infty) \quad (1)$$

where A_0, A_T and A_∞ are the absorption intensities due to >C=C< double bond of the photosensitive group after irradiation times $t = 0$, $t = T$ and $t = \infty$, respectively.

3. Results and discussion

3.1. Synthesis of photoactive monomer and corresponding polymers

The new acrylate monomer, APCSK, containing photosensitive chlorosubstituted α, β-unsaturated carbonyl moieties and a free radical polymerizable acrylate group, was synthesized from newly prepared hydroxy chalcone, HPCSK, as outlined in Scheme 1. The structures were confirmed by elemental analysis, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral techniques. The photoactive homopolymer, poly(APCSK) and copolymers of APCSK with GMA having different compositions of photoresponsive unit were synthesized by varying the comonomer feed compositions (0.15–0.85) via solution polymerization technique using BPO as initiator. The copolymerization time was selected in trials to restrict conversions less than 10 wt% in order to satisfy the differential copolymerization equation [19]. The data on the composition of comonomers in the feed and in the resulting copolymers are given in Table 1.

3.2. Solubility

The solubility of the newly prepared photosensitive homo- and copolymers in various solvents was tested in room temperature for practical application of these polymers. They were easily soluble in chlorinated solvents such as $CHCl_3$, CH_2Cl_2 and polar aprotic solvents like DMF, DMSO, *N*-methyl pyrrolidone, THF and dioxane. They were insoluble in non-polar solvents such as benzene, toluene and xylenes and hydroxy group containing solvents like methanol, ethanol, propanol and water. The solubility test clearly shows that there is wide possibility for using different solvents required for photocurable coating applications.

3.3. Structure of polymers

Poly(APCSK) and poly(APCSK-co-GMA) [0.54:0.46] show UV absorption maxima in $CHCl_3$ solution at 296 and 300 nm, respectively, corresponding to the pendant photoactive chlorocinnamoyl group of APCSK units.

The FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral characterization of poly(APCSK) and ^{1}H-NMR and ^{13}C-NMR analysis of poly(APCSK-co-GMA) [0.54:0.46] (Figs. 1 and 2) (see Sections 2.2.3 and 2.2.4) confirmed the expected structure. The IR spectrum of poly(APCSK-co-GMA) [0.54:0.46] shows an absorption band at 3070 cm^{-1} due to the aromatic C–H stretching vibrations. The symmetrical and asymmetrical C–H stretching of methylene and methine groups are shown at 2935 and 2850 cm^{-1}. The ester and keto carbonyl stretching of the copolymers are observed at 1733 and 1662 cm^{-1}, respectively. A strong absorption band at 1600 cm^{-1} is assigned to the stretching vibration of photoactive ethylenic bond flanked between keto and phenyl group in the APCSK unit of the copolymers. The aromatic >C=C< stretchings are observed at 1502 and 1410 cm^{-1}. The peak at 1460 cm^{-1} may be due to the CH_3 bending vibrations. The symmetrical and asymmetrical stretchings of the epoxide group of the GMA unit in the copolymers appear at 1274 and 907 cm^{-1}, respectively. The band at 1216 cm^{-1} is attributed to the C–O stretching of the ester group. The band at 805 and 730 cm^{-1} may be assigned to the out-of-plane bending vibrations of the CH group of the benzene ring. The C–Cl present in the cinnamoyl moiety of APCSK units shows strong absorption at 515 cm^{-1}.

3.4. Molar masses of polymers

The mass-average (M_w) and number-average (M_n) molar masses and polydispersity indices (M_w/M_n) of poly(APCSK) as well as copolymers of different compositions of comonomers determined by SEC are listed in Table 2. The polydispersity indices of poly(APCSK) and poly(GMA) are 1.65 and 1.96, respectively. In the free radical polymerization of (meth)acrylate monomers, the polydispersity indices of the resultant polymers depends on the chain termination mechanism and the theoretical values of M_w/M_n for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively [20]. This suggests that the termination of the polymerization of APCSK might occur by radical recombination of growing chains. In the case of copolymers, the polydispersity indices range between 1.67 and 1.87. It is very clear that the polydispersity indices of the copolymers depend on the mole fractions of the comonomers in the polymer chain. The values of M_w/M_n of the copolymers suggest a strong

Table 2
Molar mass data for homo- and copolymers of APCSK and GMA

Polymer	m_1[a]	$M_w \times 10^{-4}$ (g mol^{-1})	$M_n \times 10^{-4}$ (g mol^{-1})	M_w/M_n
Poly(APCSK)	1.0000	3.78	2.29	1.65
Copolymer 1	0.2321	2.72	1.45	1.87
Copolymer 2	0.4423	2.78	1.54	1.81
Copolymer 3	0.5410	2.96	1.70	1.74
Copolymer 4	0.6253	3.25	1.93	1.68
Copolymer 5	0.7835	3.13	1.92	1.63
Poly(GMA)	0.0000	3.52	1.80	1.96

[a] Mole fraction of APCSK in the copolymer.

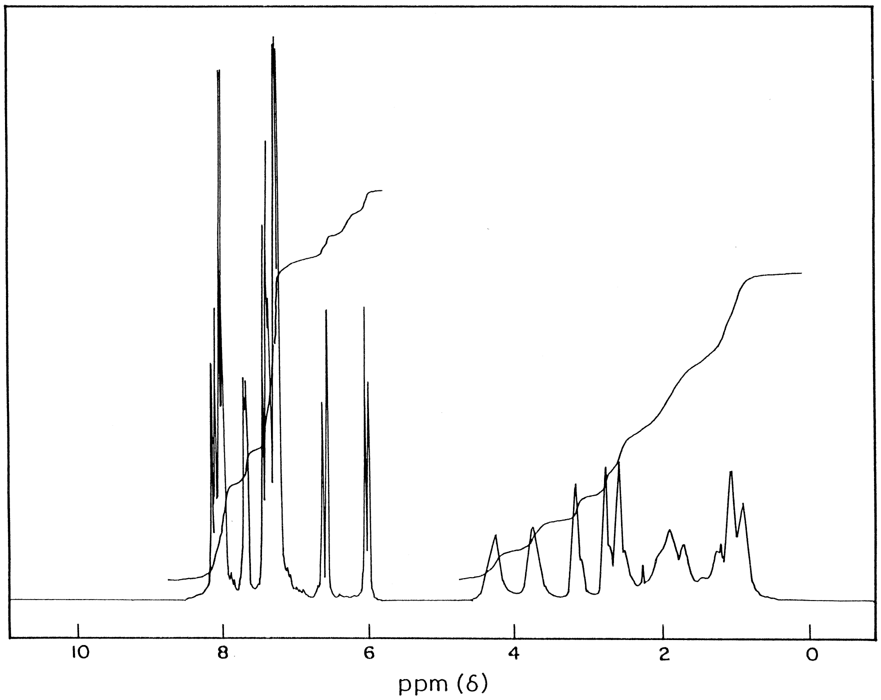


Fig. 1. ^{1}H-NMR spectrum of poly(APCSK-co-GMA) [0.54:0.46].

tendency for chain termination by disproportionation at high mole fraction of GMA and recombination at high mole fraction of APCSK in the feed.

3.5. Thermal properties

The glass transition temperatures (T_g) of the homo- and copolymers were determined by differential scanning calorimetry and are given in Table 3. The T_g value of poly(APCSK) is found to be 58 °C. All the copolymers show single T_g, indicating the absence of microphase separation at a length scale of tens of nanometers. The increase of GMA content in the copolymer leads to an increase of the T_g value of the copolymer sample. This suggests that the copolymerization of APCSK and GMA occurred rather randomly than with a tendency to

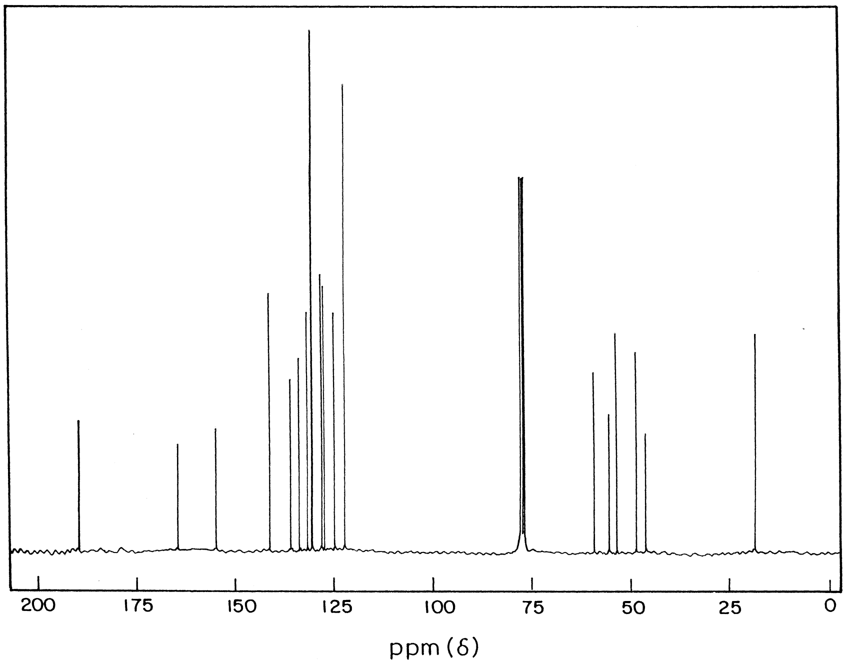


Fig. 2. ^{13}C-NMR spectrum of poly(APCSK-co-GMA) [0.54:0.46].

Table 3
Glass transition temperatures and TGA data for the homo- and copolymers of APCSK with GMA

Polymers	m_1[a]	DTR[b] (°C)			TWL[c] (%)					T_g[d] (°C)
		Stage 1	Stage 2	Stage 3	10	25	50	75	90	
Poly(GMA)	0.0000	206–480	–	–	254	275	302	360	381	74
Copolymer 1	0.2321	218–361	364–471	480–654	288	320	452	498	560	66
Copolymer 2	0.4423	233–370	376–480	485–675	302	338	475	540	565	65
Copolymer 3	0.5410	248–368	372–470	478–700	312	368	482	570	602	62
Copolymer 4	0.6253	265–370	374–481	483–698	318	351	489	540	601	61
Copolymer 5	0.7835	272–358	362–472	481–678	322	349	502	538	569	59
Poly(APCSK)	1.0000	278–340	352–440	450–640	328	382	512	554	578	58

[a] Mole fraction of APCSK in the copolymers.
[b] Decomposition temperature range.
[c] Temperature (°C) corresponding to the weight loss (%).
[d] Glass transition temperature as determined by DSC.

blockiness. This issue will be discussed in details in the two following paragraphs.

In order to investigate the thermal stability of new photosensitive homo- and copolymers for specific resist applications, the thermogravimetric analyses were carried out in air atmosphere in the range of 30–800 °C. The decomposition data of the polymers are presented in Table 3. Poly(APCSK) and copolymers undergo three decomposition stages whereas the poly(GMA) decomposes in a single stage. The initial decomposition temperatures of poly(APCSK), poly(APCSK-co-GMA) [0.54:0.46] and poly(GMA) are 278, 248, 206 °C, respectively. The homopolymer and poly(APCSK-co-GMA) [0.54:0.46] show 50% weight loss at 512 and 482 °C, respectively. The actual decomposition temperature range of copolymers depends on the composition and type of comonomer used. Incorporation of photomonomeric unit, APCSK in the copolymers increases the thermal stability of the copolymers. These results indicate that the homopolymer as well as copolymers having different compositions of photosensitive units have good thermal and thermal-oxidative stability required for the negative photoresist applications.

3.6. Copolymer compositions

^{1}H-NMR technique is a simple, rapid and accurate method for the determination of copolymer compositions. The assignment of resonance peaks in the ^{1}H-NMR spectra of polymers allows for accurate determination of both kind of monomeric units incorporated into the copolymers. As described under characterization of copolymers by ^{1}H-NMR analysis (see Section 2.2.4), poly(APCSK-co-GMA) exhibits distinct resonance signals for both monomeric units. From the ^{1}H-NMR spectra of all copolymer samples the copolymer compositions were determined by measuring the integrated intensities of aromatic and olefinic proton signals of APCSK unit and the other aliphatic proton signals of the two monomeric units. The following expression was derived to determine the copolymer compositions. Let m_1 be the mole fraction of APCSK and $(1 - m_1)$ be that of GMA in the copolymer. There are eight aromatic protons, two olefinic protons and three other aliphatic protons in APCSK unit. The GMA unit contains 10 aliphatic protons. Therefore,

$$C = \frac{\text{Intensities of down field protons } (I_{\text{Ar}} + I_{\text{Ole}})}{\text{Intensities of aliphatic protons } (I_{\text{Oth.ali}})}$$

$$C = \frac{10m_1}{3m_1 + 10(1 - m_1)} \tag{2}$$

On simplification this gives,

$$m_1 = 10C/10 + 7C \tag{3}$$

Thus, the mole fraction of APCSK (m_1) in the copolymers were determined from Eq. (3) by measuring the intensities of down field proton signals and other aliphatic proton signals from ^{1}H-NMR spectra of all five copolymer samples. In the determination of intensity of down field protons and the other aliphatic protons, a correction is carried out to exclude the value due to the residual proton signals of $CDCl_3$ by recording the ^{1}H-NMR spectrum of the pure solvent with the same volume of polymer solution. The values of C and corresponding mole fractions in the copolymers are given in Table 1. The kinetic behavior of the copolymer system was determined by plotting the mole fractions of APCSK in the feed (M_1) versus that in the copolymer (m_1) and the curve (Fig. 3) indicates that the system exhibits azeotropic polymerization when the mole fraction of APCSK in the comonomer feed was 0.593.

3.7. Reactivity ratios

In commercial copolymerization, the main aim is to achieve as narrow composition distribution as possible. A knowledge about the reactivity ratios of the comonomers would help in achieving desired quality product. A uniform product can be obtained by working nearer to the azeotropic compositions whenever possible. Considering these import-

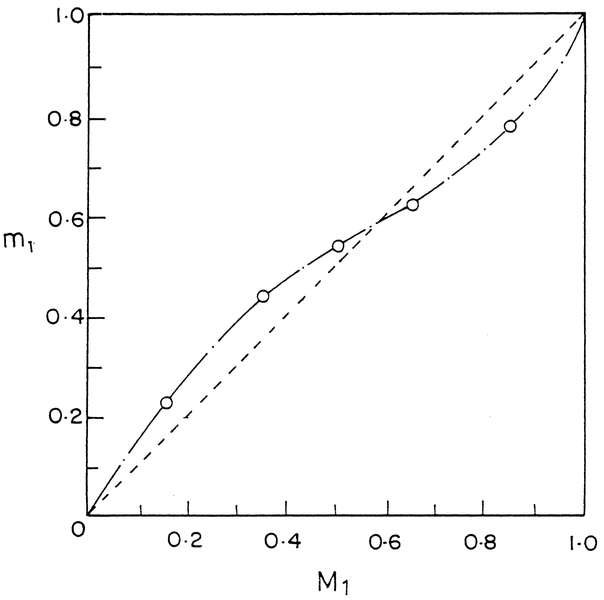


Fig. 3. Composition diagram of APCSK-GMA copolymer system.

ant points in mind, the reactivity ratios of comonomers, APCSK (r_1) and GMA (r_2) in the photoreactive copolymers were determined by the application of conventional linearization methods such as Fineman–Ross (F–R) [21], Kelen–Tudos (K–T) [22] and extended Kelen–Tudos (Ext. K–T) [23] methods. The results from the analysis of F–R, K–T and Ext. K–T (Fig. 4) are presented in Table 4. The monomer reactivity ratios determined by conventional linearization methods can be utilized for non-linear parameter estimation schemes for getting accurate values.

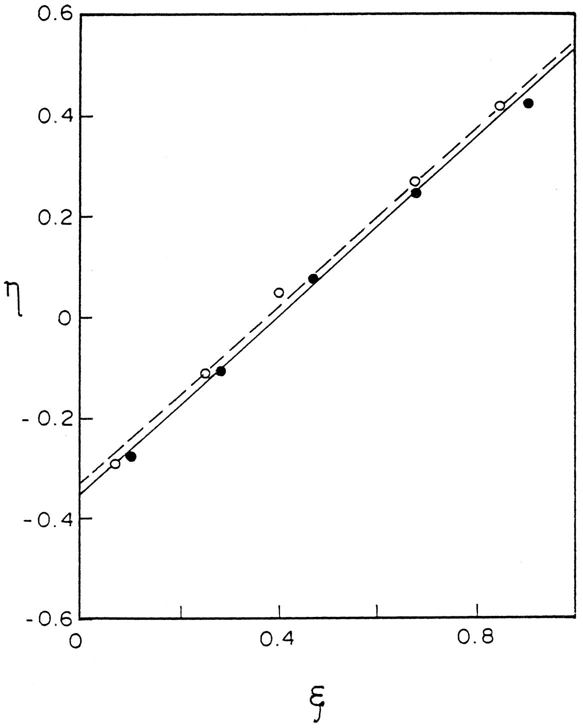


Fig. 4. Kelen–Tudos (solid line) and extended Kelen–Tudos (dotted line) plots for the poly(APCSK-co-GMA) system.

Several non-linear methods have been attempted to evaluate the reactivity ratios of comonomers [24–26]. In the present study, a non-linear error-in-variables model (EVM) method is used utilizing the computer program, RREVM [24] to determine more reliable values of reactivity ratios of APCSK (r_1) and GMA (r_2). The r_1 and r_2 values obtained by both linear and non-linear methods are presented in Table 5. The r_1 and r_2 values obtained by EVM method are 0.62 and 0.44, respectively. The 95% joint confidence region for the determined r_1 and r_2 values using EVM method is shown in Fig. 5. Since r_1 and r_2 values are lower than 1, this system gives rise to azeotropic composition at a particular composition of the monomers which is calculated using the following equation,

$$N_1 = (1 - r_2)/(2 - r_1 - r_2) = 0.593 \tag{4}$$

When mole fraction of the monomer APCSK in the feed (M_1) is 0.593, the copolymer formed will also have the same composition as that of the feed. When M_1 is lower than 0.593, the copolymer composition in APCSK unit is relatively higher than that in the feed. At the same time, if M_1 is above 0.593, the copolymer is richer in GMA units. The value of product of r_1 and r_2 is much lower than 1, indicating that the copolymer system shows a strong alternating tendency. The reactivity of growing radicals associated with APCSK and GMA as measured by the values of $1/r_1$ and $1/r_2$ strongly suggests that the growing radicals with both monomeric ultimate units prefer to add either APCSK or GMA depending on the feed ratio, leading to the formation of different types of copolymers.

3.8. Photochemical properties

The photochemical properties of newly prepared poly(APCSK) and copolymers having different compositions of

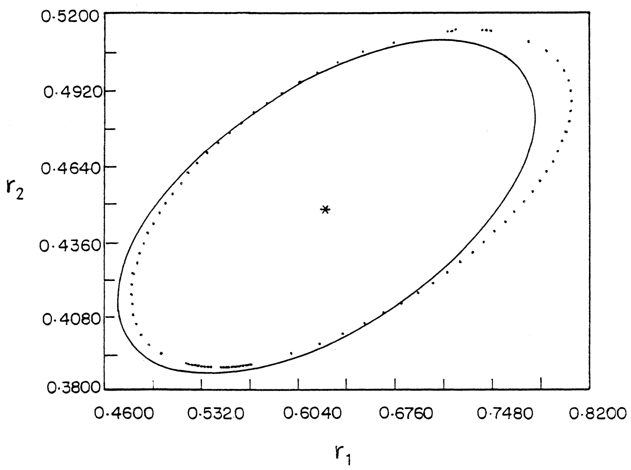


Fig. 5. 95% Joint confidence region of r_1 and r_2 values by EVM for APCSK-GMA copolymer system (solid line for approximate ellipse and dotted line for contour diagram)

Table 4
Fineman–Ross (F–R), Kelen–Tudos (K–T) and extended Kelen–Tudos (Ext. K–T) parameters for the copolymerization of APCSK with GMA

Copolymer no.	F–R parameters		K–T parameters		Ext. K–T parameters	
	$G = F(f-1)/f$[a]	$H = F^2/f$[a]	$\eta = G/(\alpha + H)$[b]	$\xi = H/(\alpha + H)$[b]	$\eta^1 = G^1/(\alpha^1 + H^1)$[c]	$\xi^1 = H^1/(\alpha^1 + H^1)$[c]
1	−0.4075	0.1031	−0.2808	0.0988	−0.3648	0.0895
2	−0.1405	0.3654	−0.1076	0.2800	−0.1030	0.2628
3	0.1511	0.8440	0.0847	0.4732	0.0825	0.4570
4	0.7438	2.0599	0.2477	0.6867	0.2433	0.6784
5	4.0285	8.5631	0.4239	0.9011	0.4144	0.9007

[a] $F = M_1/M_2$ and $f = m_1/m_2$.
[b] $\alpha = 0.9396$.
[c] $\alpha^1 = 0.9874$.

photoreactive chlorocinnamoyl moieties have been examined in various solvents with concentration range of 18–155 mg l^{-1} as well as in thin films, in the presence and absence of photosensitizers. Poly(APCSK) and the copolymer samples show UV absorption bands around 296 and 300 nm, respectively, attributed to the ($\pi \rightarrow \pi^*$) transitions of >C=C< of the pendant chlorocinnamoyl moiety. The influence of irradiation on the photoresponsive polymers was examined by measuring the changes in the UV absorption intensity at various intervals of irradiation time. Figs. 6 and 7 show the changes in the UV spectral patterns of poly(APCSK) and poly(APCSK-co-GMA) [0.54:0.46], respectively, in chloroform solutions in the absence of photosensitizers. Upon irradiation, an isobestic point is observed around 270 nm. Obviously enough, its occurrence is related to the progressive disappearance of the conjugated photoreactive moieties, and the simultaneous formation of non-conjugated aromatic structures absorbing at shorter wavelength (around 240 nm). Further irradiations of the homo- and the copolymers result in a rapid decrease in absorption intensity at 296 or 300 nm and it disappears almost completely within 10 min of irradiation. This behavior clearly indicates the formation of the cyclobutane ring by the [$2\pi + 2\pi$] cycloaddition of pendant cinnamoyl units of the polymers, which destroys conjugation in the entire π-electron system. Thus, these polymers reacted photochemically according to a mechanism similar to that found for cinnamic acid and its derivatives, in which cyclobutane structures [8–11,27] were formed (Scheme 2). An almost similar phenomenon was observed upon irradiation of thin films of the polymers.

In general, the photosensitivity of polymers containing an α, β-unsaturated carbonyl group (for example cinnamoyl moiety) is assessed in terms of rate of disappearance of >C=C< group of photoresponsive units with irradiation time. In chloroform solution, poly(APCSK) shows photoconversions of 23, 50 and 81% after 5, 35 and 135 s of irradiation time, respectively, and about 98% conversion occurs within 5 min of irradiation (Fig. 8). The effect of concentration of the photoresponsive homo- and copolymers was examined in chloroform solution with concentration range of 18–155 mg l^{-1}. In both cases, the increase of concentration of polymers enhances the rate of photocrosslinking, because of availability of more photoresponsive units. Although *trans–cis* isomerization cannot be ruled out, photocrosslinking through intermolecular cycloaddition takes precedence over the latter mechanism as there is no ordered arrangement or aggregation of the chromophores in dilute solution. However, photocycloaddition between two neighboring cinnamoyl groups located on the same polymer chain is likely to proceed to some extent, and such a competitive intramolecular process is useless for

Table 5
Copolymerization parameters for poly(APCSK-co-GMA) system

Methods	r_1[a]	r_2[a]	$r_1 \cdot r_2$	$1/r_1$	$1/r_2$
Fineman–Ross	0.51	0.32	0.16	–	–
Kelen–Tudos	0.54	0.33	0.18	–	–
Ext. Kelen–Tudos	0.55	0.32	0.17	–	–
EVM	0.62	0.44	0.27	1.61	2.27

[a] r_1 and r_2 are the reactivity ratios of APCSK and GMA, respectively.

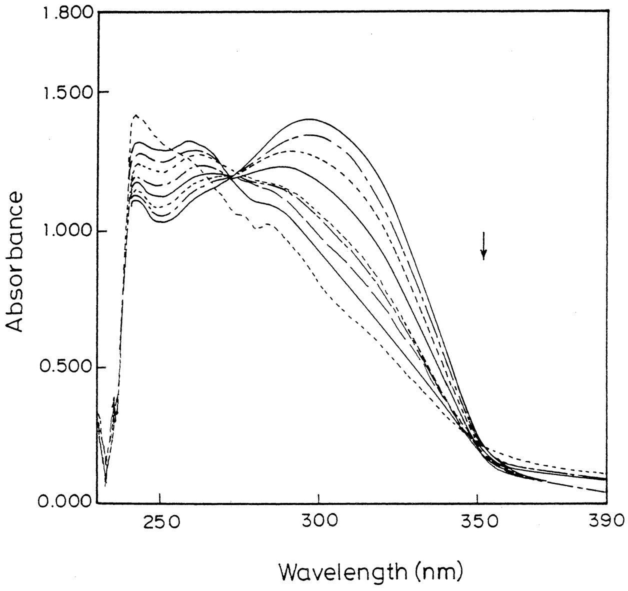


Fig. 6. Changes in the UV spectral patterns of poly(APCSK) in chloroform solution at a concentration of 155 mg l^{-1} upon UV irradiation (top to bottom, after irradiation time $t = 0$, 5, 10, 40, 60, 90, 120, 300 and 600 s).

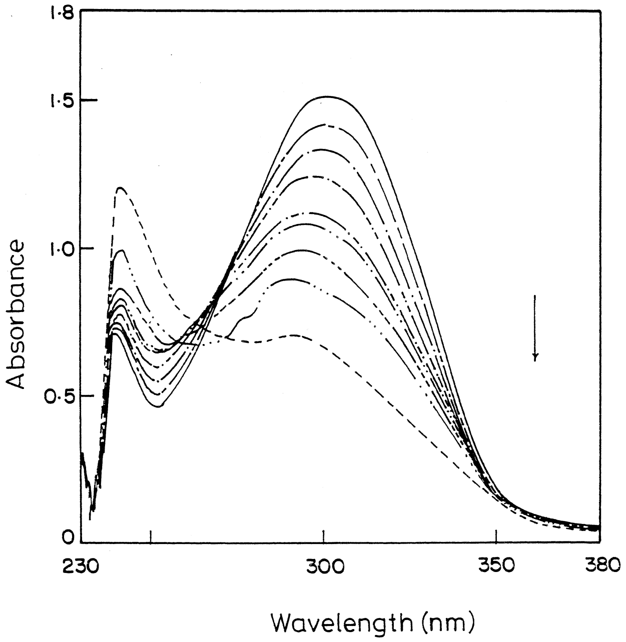


Fig. 7. Changes in the UV spectral pattern upon irradiation of poly(APCSK-co-GMA) [0.54:0.46] in chloroform solution at a concentration of 142 mg l^{-1} (top to bottom, after irradiation time $t = 0$, 5,10, 20, 30, 60, 100, 120, 140, 200, 300 and 600 s).

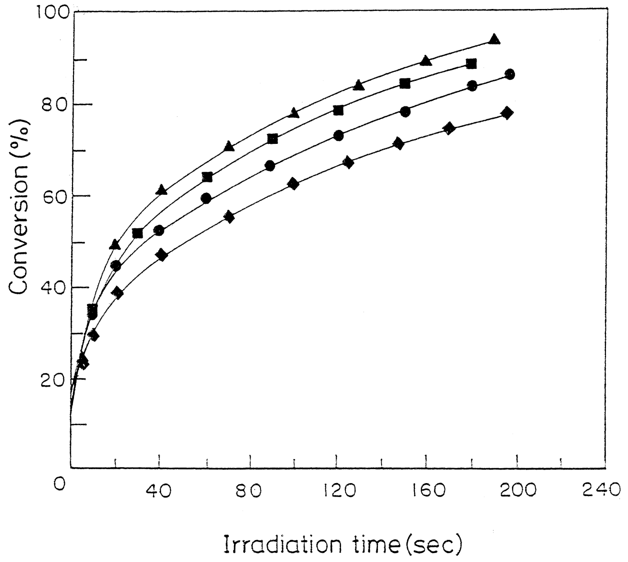
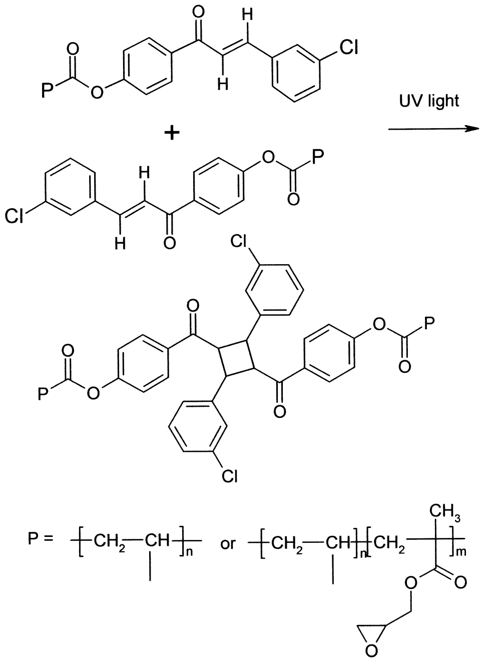


Fig. 8. Rate of disappearance of >C=C< associated with poly(APCSK) in chloroform solution at different concentrations: (▲) 155 mg l^{-1}; (■) 98 mg l^{-1}; (●) 53 mg l^{-1} and (◆) 26 mg l^{-1}.

photoresist applications, as it does not lead to crosslinking. The role of copolymer composition on the photoconversion rate was studied in chloroform solution in the absence of photosensitizers (Fig. 9). The copolymer with the lowest composition of photomonomer units (APCSK) ($m_1 = 0.23$) show photoconversions about 50 and 70% after 40 and 180 s of irradiation time, respectively. At the same irradiation times, the copolymer with the highest chromophore composition ($m_1 = 0.78$), displays higher conversions around 60 and 90%, respectively. These results clearly indicate that the photoconversion rate depends on the composition of photoresponsive units in the copolymers. Even though the chromophore concentration is low, the copolymers may show high rate of crosslinking which directs the significant usage of these copolymers as negative photoresists effectively.



Scheme 2. Photocycloaddition of poly(APCSK) and copolymer of APCSK and GMA.

The effect of various solvents on the rate of photo-crosslinking of homo- and copolymers was studied in $CHCl_3$, CH_2Cl_2, dioxane, DMSO and DMF solutions. The

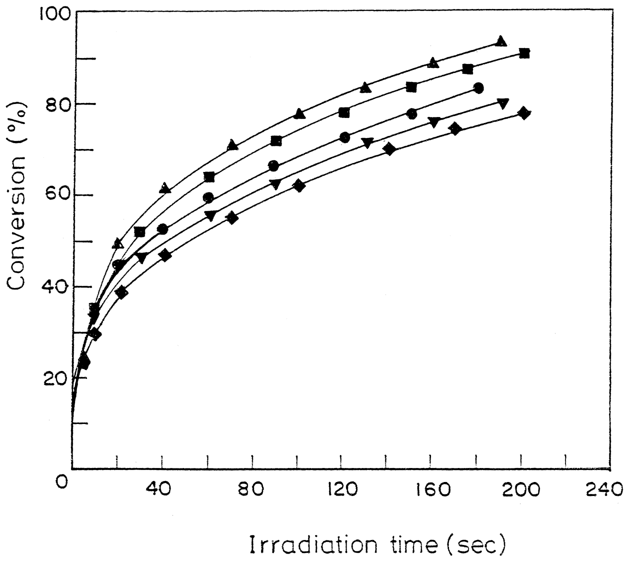


Fig. 9. Rate of disappearance of >C=C< associated with poly(APCSK-co-GMA) system in chloroform at a concentration of 142 mg l^{-1} (m_1 and m_2): (▲) 0.78:0.22; (■) 0.63:0.37; (●) 0.54:0.46; (▼) 0.44:0.56 and (◆) 0.23:0.77.

results indicate that there is no clear and regular difference in the photocrosslinking rate of polymers in chlorinated solvents and polar aprotic solvents.

The effect of temperature on the photocrosslinking of the homopolymer (Fig. 10) and copolymers was studied in DMF at different temperatures (30, 50, 70, 90 and 100 °C) at a constant concentration (45 mg l^{-1}). The results clearly indicate that the crosslinking rate decreases with increasing temperature. This might be attributed to a non-negligible contribution of side reactions with the medium during the photochemical reaction process, at high temperature.

The photochemical reactions of poly(APCSK) and copolymer samples were carried out in the presence of various triplet sensitizers such as benzophenone, Michler's ketone and nitroaniline in $CHCl_3$, to identify their effect on the rate of disappearance of photoactive >C=C< of cinnamoyl moiety. It has been observed that there is no sensitizing effect on the rate of disappearance and this behavior is similar to other reported photoactive polymers [28], which have high photosensitivity but cannot be sensitized. This strongly indicates that the photocrosslinking of these polymers takes place through the excited state electrons, leading to a one-step concerted $[2\pi + 2\pi]$ cycloaddition, and not through the triplet state [29].

In order to identify the suitable conditions and behavior of these photoresponsive polymers for various industrial applications, the photocrosslinking properties of poly(APCSK) and the copolymer samples have been investigated as thin films casted on quartz slides with the thickness of 1.5 ± 0.1 μm (in the absence of photosensitizers). In the copolymer films, the rate of conversion of photoresponsive double bonds depends on the composition of photoactive units in the copolymer chains. The rate of crosslinking increases with increasing the composition of cinnamoyl units, and it is slightly faster in solution than in bulk (Fig. 11). More than 70% photoconversion of photoactive double bond is observed within 6–7 min of irradiation in films. After only 40–80 s of irradiation (25–35% conversion), the polymer films are found to be insoluble in all organic solvents, even at boiling temperature of solvents in which they were soluble at room temperature before irradiation. The energy needed to achieve insolubilization of photoresponsive copolymers corresponds to 1320–2640 mJ cm^{-2}. This behavior is due to the formation of rigid three-dimensional networks through intermolecular photoinduced cycloaddition of pendant chlorocinnamoyl units (Scheme 2). These results suggest the high photosensitivity of these copolymers compared with other reported systems [8,9]. Hence, poly(APCSK) and copolymers with a pendant chlorocinnamoyl moiety have high rate of photocrosslinking, even in the absence of photosensitizer, which are essential properties for using these polymers as negative photoresists for photolithography and protective coating applications.

4. Conclusions

Poly(APCSK) and poly(APCSK-co-GMA) copolymers having different compositions of photoresponsive chlorocinnamoyl moiety were synthesized and their structures were confirmed by spectral studies. The solubility of these polymers in a wide range of solvents directs more chance for using different solvents required for practical industrial applications. The molar mass data obtained from SEC suggest that the termination of polymerization of APCSK might occur via radical recombination and in the case of copolymers the termination mechanism depends on the

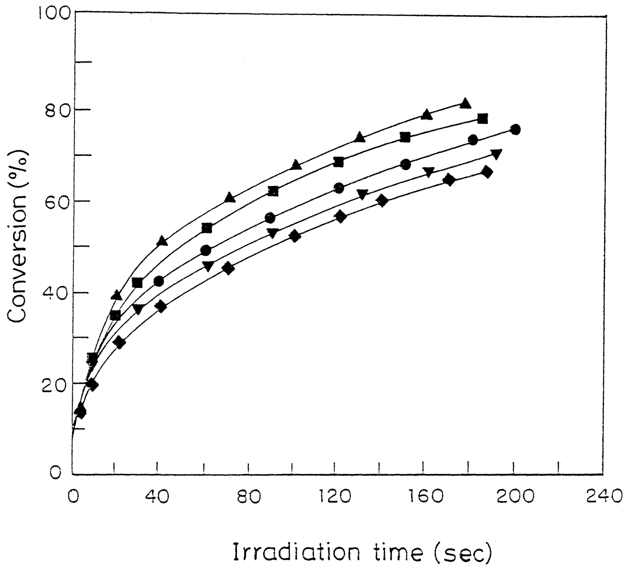


Fig. 10. Effect of temperature on the disappearance rate of photosensitive groups of poly(APCSK) in DMF at: (▲) 30 °C; (■) 50 °C; (●) 70 °C; (▼) 90 °C and (◆) 100 °C.

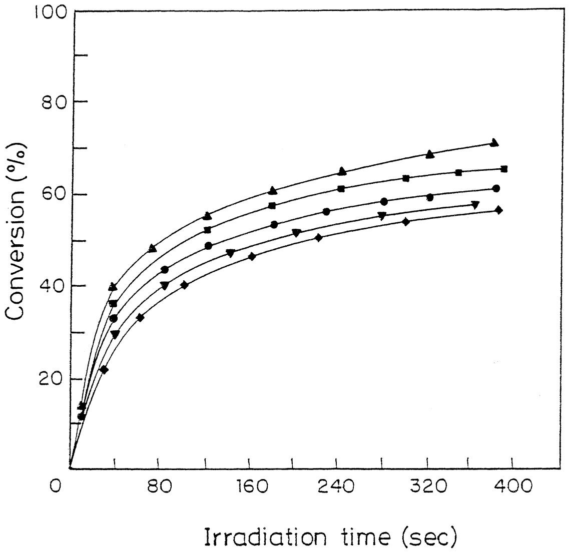


Fig. 11. Disappearance rate associated with >C=C< of poly(APCSK-co-GMA) as thin film: (m_1 and m_2): (▲) 0.78:0.22; (■) 0.63:0.37; (●) 0.54:0.46; (▼) 0.44:0.56 and (◆) 0.23:0.77.

nature and composition of comonomers. Thermal analysis clearly indicates that poly(APCSK) and the copolymers have very good thermal and thermo-oxidative stability as essential properties for negative photoresists. The incorporation of photoresponsive units in the copolymer chains increases the thermal stability of the copolymers. The copolymer compositions were calculated using ^{1}H-NMR spectroscopy. The reactivity ratios of comonomers (r_1 and r_2) determined by linear and non-linear methods are in good agreement. The values of r_1 and r_2 are lower than 1, indicating that the copolymer system gives azeotropic copolymers at a particular composition of the feed. The results give enough knowledge about the reactivity of new photoresponsive monomer, APCSK, with GMA, which help to design desired types of photopolymers with exact composition of comonomers for required industrial applications.

The photoreactivity studies of homo- and copolymers in solution and in thin films strongly suggest that these polymers have high photosensitivity, as required for negative photoresists. The rate of photoconversion of these polymers depends on various factors such as concentration, temperature, copolymer composition, and the conversion rate was very rapid at low temperature and high concentration. In the case of copolymers, the rate of crosslinking was significant, even for low composition of photomonomeric units, suggesting that the copolymers in the whole range of compositions might be useful for different types of applications. However, the fact that the photoinduced cycloaddition proceeds slightly faster in solution than in bulk argues in favor of a competitive intramolecular process, provided that the UV absorbance is comparable in both systems. This side reaction may be a non-negligible way of consumption of the pendant cinnamoyl groups upon UV exposure, especially in dilute solution.

The newly synthesized polymers possess high photosensitivity—even in the absence of sensitizers—, good thermal stability, and good solubility before irradiation and resistance towards solvents after crosslinking, which concludes their effective application as negative photoresists. Further chemical modification of photoresponsive copolymers through oxirane unit of GMA for phototunable applications as well as study of the effect of GMA content on stiffness and stability of copolymer films are under progress.

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