Studies on Photosensitive Homopolymer and Copolymers Having a Pendant Photocrosslinkable Functional Group

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Received 3 August 2001; accepted 10 December 2001

ABSTRACT: The methacrylate monomer 4-methyacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone (MPDMSK), having a free-radical polymerizable group and a photocrosslinkable functional group, was synthesized. The homopolymer and copolymers of MPDMSK with glycidyl methacrylate were synthesized by free-radical solution polymerization. The structures of the newly synthesized monomers, homopolymer, and copolymers were confirmed by different spectroscopic techniques. The average molecular weights of the polymers were determined by gel permeation chromatography. The thermal stability of the polymers was measured by thermogravimetric analysis in air and the glass-transition temperatures were determined by differential scanning calorimetry under nitrogen atmosphere. The copolymer compositions were determined by ^{1}H-NMR analysis. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman–Ross, Kelen–Tüdös, and extended Kelen–Tüdös methods. The photoreactivity of both the homopolymer and the copolymers having pendant chalcone moieties was studied in various solvents. The effects of various factors such as solvents, concentrations, copolymer ratios, and photosensitizers on the rate of photocrosslinking of the newly synthesized polymers were investigated and the results were discussed for using the polymers as negative photoresists.
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Key words: poly(4-methyacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone); copolymerization; photoresists; crosslinking; photoreactive effects

INTRODUCTION

In recent years, the synthesis of polymers having a photoreactive functional group 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.[1,2] Polymers that contain α,β-unsaturated carbonyl groups undergo crosslinking upon irradiation with UV light or an electron beam and are used as photoresists.[3–5] Crosslinking with ultraviolet light is an excellent method for obtaining articles with thick cross sections, with or without reinforcement, without significant heat build-up in the interior, which would damage the plastic.[6] Photosensitive polymers find applications in such fields as integrated circuit technology, printing technology, photocurable coatings,[7] photorecorders,[8] photolithography,[9] advanced microelectronics,[10] holographic head-up display,[11] energy exchange materials,[12] liquid crystalline display,[13,14] and nonlinear optical materials.[15,16] High photosensitivity, the ability to form films, good thermal stability, good solubility, and resistance toward solvents after crosslinking are essential requirements for practical use of the photopolymers as negative photoresist materials. Polymers with a pendant photofunctional group such as cinnamoyl esters of poly(2-hydroxyethyl methacrylate),[17] poly(vinylamine)[18] and polyvinyl alcohol,[19] poly(vinyloxy carbonyl chalcone),[20] poly(vinyloxyethyl cinnamate),[21] and many other groups[22–24] have been synthesized and tested for their photosensitivity. The technological applications of many photoresists and their photochemistry have been reviewed.[25–27]

Copolymers of glycidyl methacrylate (GMA) with methacrylic manomers are transparent in nature.[28] Epoxy group–containing compounds have excellent thermosetting properties at low temperatures.[29] Polymer supports based on GMA are found to have versatile applications because of the presence of an oxirane group.[30] The synthesis and photosensitivity of copolymers having pendant photosensitive groups have been reported.[18,22,31,32] The accurate estimation of copolymer composition and determination of reactivity ratios are significant for tailor-making copolymers with required physicochemical properties and in evaluating the end application of copolymers. In the past few decades, ^{1}H-NMR has been established as a powerful tool for the determination of tacticity and sequence distribution as well as for the estimation of copolymer composition because of its simplicity, rapidity, and sensitivity.[33–36]

The present work was undertaken to develop the new negative photoresists based on the homopolymer and copolymers of 4-methylacryloyloxyphenyl-3′,4′-

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Contract grant sponsor: CSIR, Government of India.

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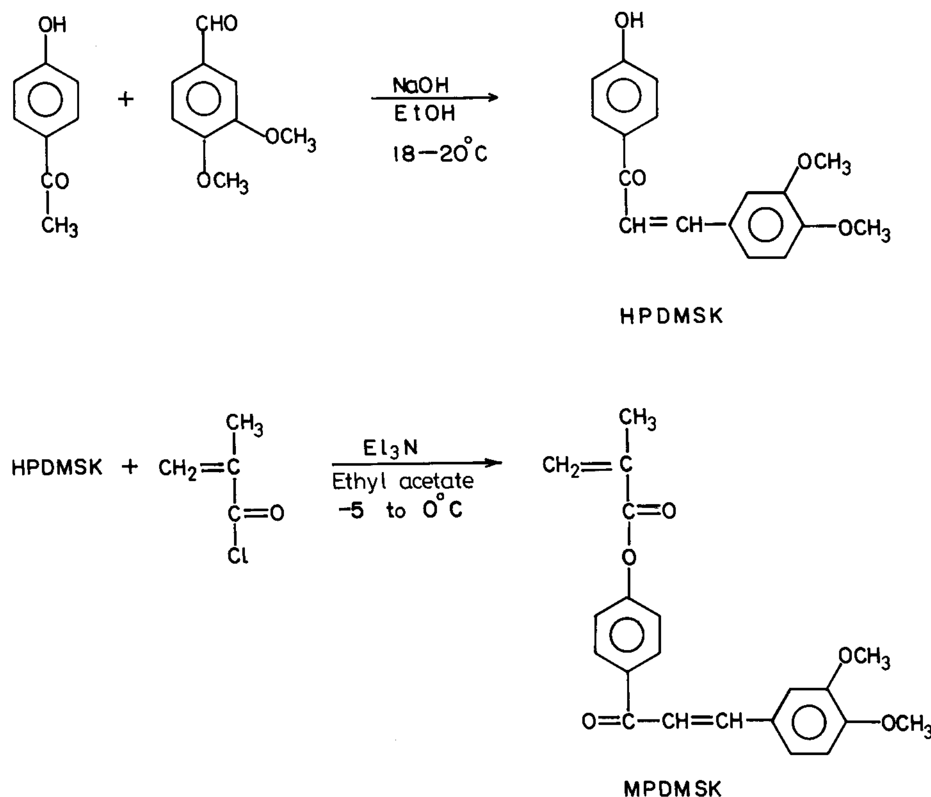


Scheme 1 Synthesis of HPDMSK and MPDMSK.

dimethoxystyryl ketone (MPDMSK) and GMA. The present study discusses the synthesis, characterization, thermal stability, and photocrosslinking properties of a new homopolymer and the copolymers having a pendant photosensitive chalcone group; the copolymer reactivity ratios are also reported. The effects of various factors on the rate of photocrosslinking of the polymers are assessed for using the polymers as negative photoresist materials.

EXPERIMENTAL

Materials

3,4-Dimethoxybenzaldehyde (Merck, Darmstadt, Germany) and 4-hydroxyacetophenone (Merck) were recrystallized from ethanol. GMA (Acros Chemicals, Belgium) was purified by distilling under reduced pressure. Benzoyl peroxide (BPO) was recrystallized from a chloroform–methanol (1 : 1) mixture. Methacryloyl chloride was prepared by reacting methacrylic acid with benzoyl chloride following the procedure of Stempel et al.[37] All the solvents were purified by distillation.

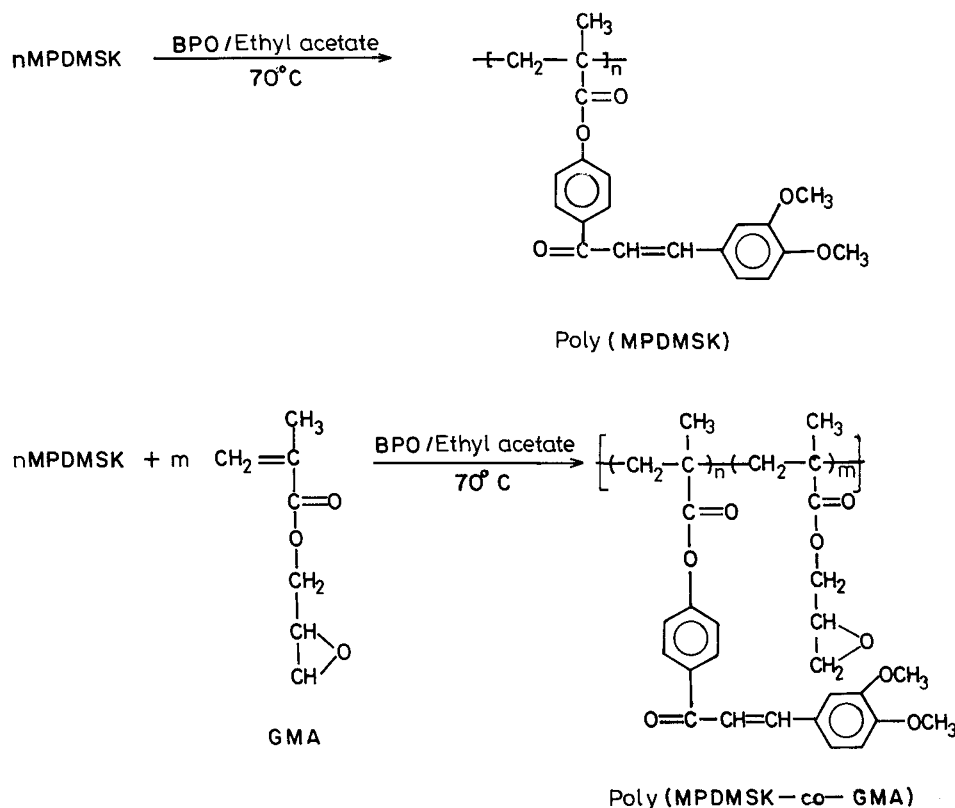
Synthesis of 4-hydroxyphenyl-3′,4′-dimethoxystyryl ketone (HPDMSK)

In a three-neck flask equipped with a mechanical stirrer, thermometer, and a dropping funnel, a mixed solution of 4-hydroxyacetophenone (10.9 g, 0.08 mol) in 50 mL ethyl alcohol and sodium hydroxide (6 g) in distilled water (30 mL) was placed and cooled in an ice-water bath (18–20°C). Then a solution of 3,4-dimethoxybenzaldehyde (13.3 g, 0.08 mol) in 50 mL of ethyl alcohol was added dropwise with constant stirring, and the temperature was not allowed to exceed 25°C. The stirring was then continued for 14 h at room temperature and the mixture was kept in the refrigerator for about 12 h. The reaction mixture was then neutralized with dilute HCl to isolate the product (see Scheme 1). The precipitated solid product was filtered, washed with cold water, dried, and recrystallized from ethyl alcohol to get fluorescent yellow crystals. The product of 17.04 g was obtained with a yield of 75% (m.p. 194–195°C).

ANAL. calcd for $C_{17}H_{16}O_4$: C, 71.81%; H, 5.66%. Found: C, 71.78%; H, 5.65%. IR (KBr, cm^{-1}): 3169 (–OH), 1637 (>C═O),1604 (–CH═CH–), 1550 and 1440 (Ar, C═C stretching), and 833 and 810 (C—H out-of-plane bending). ^{1}H-NMR ($CDCl_3$, ppm): δ = 10.12 (s, 1H, O—H), 7.87–7.01 (m, 7H, Ar—H), 6.72 (2d, 2H, –CH═CH–), 3.78 (s, 6H, $2OCH_3$).

Synthesis of 4-methacryloyloxyphenyl-3′,4′-dimethoxystyryl ketone (MPDMSK)

The hydroxy chalcone HPDMSK (14.2 g, 0.05 mol) and triethylamine (5.06 g, 0.05 mol) dissolved in 200 mL of ethyl acetate were taken in a 500-mL three-neck flask



Scheme 2 Synthesis of poly(MPDMSK) and poly(MPDMSK-*co*-GMA).

equipped with a mechanical stirrer, thermometer, and pressure equalizer, and the temperature of the reactants was maintained in the range of −5 to 0°C. Methacryloyl chloride (5.2 g, 0.05 mol) dissolved in 25 mL of ethyl acetate was added dropwise to this solution with constant stirring and cooling. The temperature of the reaction mixture was allowed to rise to 30°C and the contents were stirred for an additional 1 h. The quaternary ammonium salt formed was filtered and the solvent was evaporated in a rotary evaporator, after which the crude monomer MPDMSK obtained was washed with 0.05% NaOH and recrystallized from methanol to get fluorescent shining yellow crystals (see Scheme 1). The product of 12.49 g was obtained with a yield of 71% (m.p. 99–100°C).

ANAL. calcd for $C_{21}H_{20}O_5$: C, 71.57%; H, 5.71%. Found: C, 71.12%; H, 5.65%. IR (KBr, cm^{-1}): 1727 (ester C=O),1655 and 1634 (ketone C=O), 1599 and 1571 (olefinic >C=C<), 1510 and 1441 (Ar, C=C stretching), 767 and 702 (out-of-plane bending of =C—H). ^{1}H-NMR ($CDCl_3$, ppm): δ = 8.20–6.85 (m, 7H/2H, Ar—H/CH_2=C), 6.40 and 5.82 (d, 2H, –CH=CH–), 3.92 (s, 6H, 2OCH_3), 2.08 (s, 3H, α-CH_3). ^{13}C-NMR ($CDCl_3$, ppm): δ = 189.45 (keto *C*=O), 170.84 (ester *C*=O), 152.20 (Ar—*C*—O), 149.82, 148.95, 145.43, 136.22, 127.84, 120.75, 118.56, 112.56, and 109.99 (other Ar—C), 145.3 (=C<), 129.85 and 122.64 (–CH=CH–), 112.82 (CH_2=), 18.54 (α-CH_3).

Synthesis of photoreactive homopolymer

Homopolymerization of the monomer MPDMSK was carried out as a 2*M* solution in ethyl acetate using BPO (0.5 wt % with respect to the monomer) as a free-radical initiator at 70 ± 1°C. Appropriate amounts of MPDMSK, BPO, and the solvent were mixed in a polymerization tube, flushed with oxygen-free nitrogen for 20 min, and kept in a thermostat at 70 ± 1°C. After 10 h, the contents were added to excess methanol to isolate the polymer (see Scheme 2). The crude polymer poly(MPDMSK) was purified by redissolving in chloroform, reprecipitated by methanol, filtered and washed with methanol, and dried under vacuum at 50°C. Yield was 45–50%.

IR (KBr, cm^{-1}): 3066 (Ar, C—H stretching), 1751 (ester C=O), 1661 (keto C=O), 1597 (–CH=CH–), 1510 (Ar, >C=C<), 802 and 765 (Ar, C—H out-of-plane bending). ^{1}H-NMR ($CDCl_3$, ppm) (see Fig. 1): δ = 8.28–6.40 (m, 7H and 2H, Ar—H and –CH=CH–), 3.87 (s, 6H, 2OCH_3), 1.70 (backbone –CH_2–), 1.46 and 1.25 (3H, α-CH_3). ^{13}C-NMR ($CDCl_3$, ppm) (see Fig. 2): δ = 189.20 (keto *C*=O), 175.94 (ester *C*=O), 154.05 (Ar—C—O), 151.95–110.82 (other Ar—C and –CH=CH–), 56.35 (OCH_3), 53.31 (backbone CH_2), 46.5 (>C<), 18.73 (α-CH_3).

Copolymerization

Copolymers of MPDMSK and GMA of five different compositions were synthesized by free-radical solu-

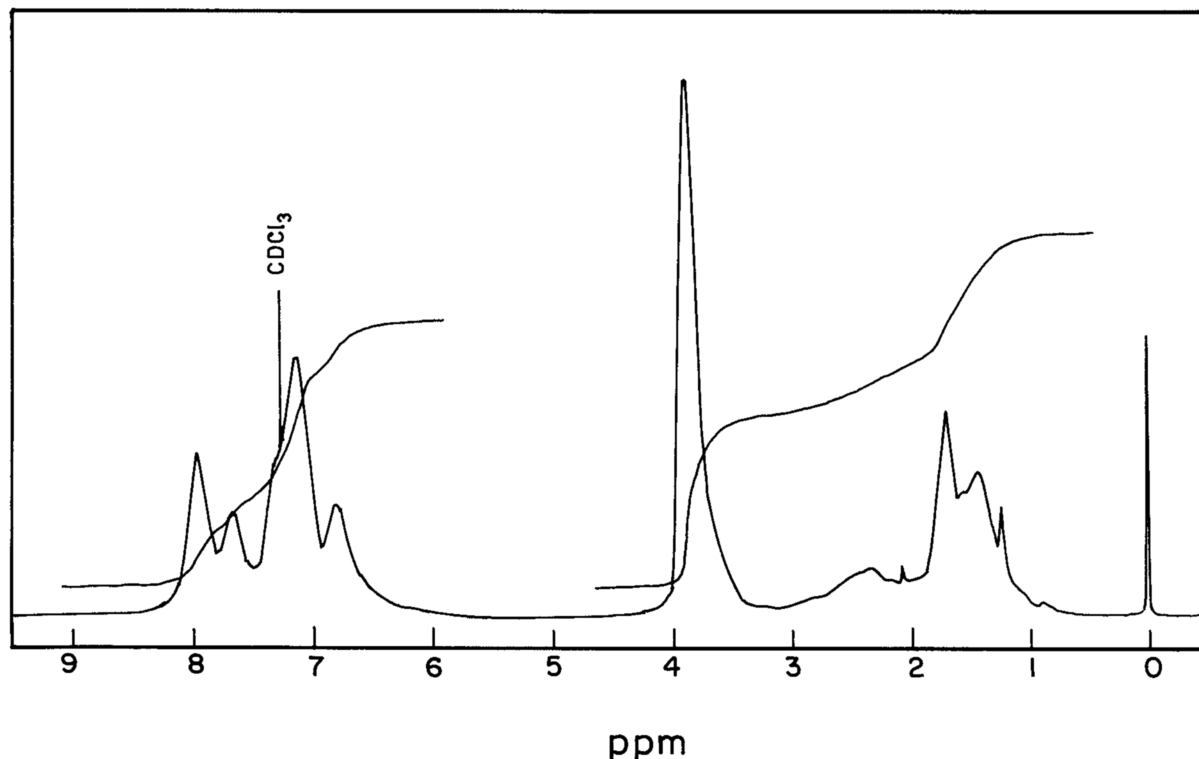


Figure 1 ^{1}H-NMR spectrum of poly(MPDMSK).

tion polymerization using BPO as initiator (0.25 wt % of monomer) at 70 ± 1°C. Predetermined quantities of MPDMSK, GMA, BPO, and ethyl acetate were taken in a standard reaction tube and the mixture was purged with nitrogen for 30 min. The tube was tightly sealed and immersed in a thermostated water bath maintained at 70 ± 1°C. The conversions were restricted to less than 10% to follow the copolymer equation. After the required time, the reaction mixture was poured into excess methanol; the precipitated polymer poly(MPDMSK-*co*-GMA) (see Fig. 2) was filtered off, purified by reprecipitation of the polymers from dimethyl formamide solution using methanol, and finally dried in a vacuum oven at 50°C for 24 h.

Measurements

Elemental analysis was performed with a Perkin–Elmer carbon–hydrogen analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT). The UV spectra were recorded in a Shimadzu UV-1601 UV-visible spectrometer (Shimadzu, Kyoto, Japan). Infrared spectra were obtained with a Nicolet Avatar 360 FTIR spectrophotometer (Nicolet Instruments, Madison, WI) as a KBr pellet. ^{1}H-NMR spectra were run on a Bruker 400 MHz FT-NMR spectrometer (Bruker Instruments, Billerica, MA) at room temperature using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The proton decoupled ^{13}C-NMR spectra were run on the same instrument operating at 125.77 MHz at room temperature, and the chemical shifts were recorded under similar conditions. Molecular weights ($\overline{M}_w$ and $\overline{M}_n$) of the polymers were determined by a Waters 501 gel permeation chromatograph (Waters Associates, Milford, MA) equipped with a refractometer index detector. Tetrahydrofuran was used as an eluent at a flow rate of 10 mL/min and polystyrene standards were employed for calibration. Thermogravimetric analysis (TGA) was performed using a Mettler (Schwerzenbach, Switzerland) TA 3000 thermal analyzer at a heating rate of 20°C/min in air. Glass-transition temperatures of the polymers were determined with a Netzsch-Geratebau GmbH DSC 204 thermal analyzer (Selb, Bavaria, Germany) at a heating rate of 10°C/min in nitrogen atmosphere.

Photoreactivity measurements

A mercury lamp (Heber Scientific Photoreactor-UV, 6 W, 254 nm; Chennai, India) was used as the UV source for studying the photoreactivity of the synthesized photosensitive polymers. The polymers were dissolved in chloroform and other solvents and irradiated (in quartz cell) at a distance of 10 cm from the light source for different intervals of time. After each exposure, the UV spectra were recorded at different intervals and the rate of photocrosslinking was followed by a decrease in UV absorption intensity at 358–360 nm using the following expression:

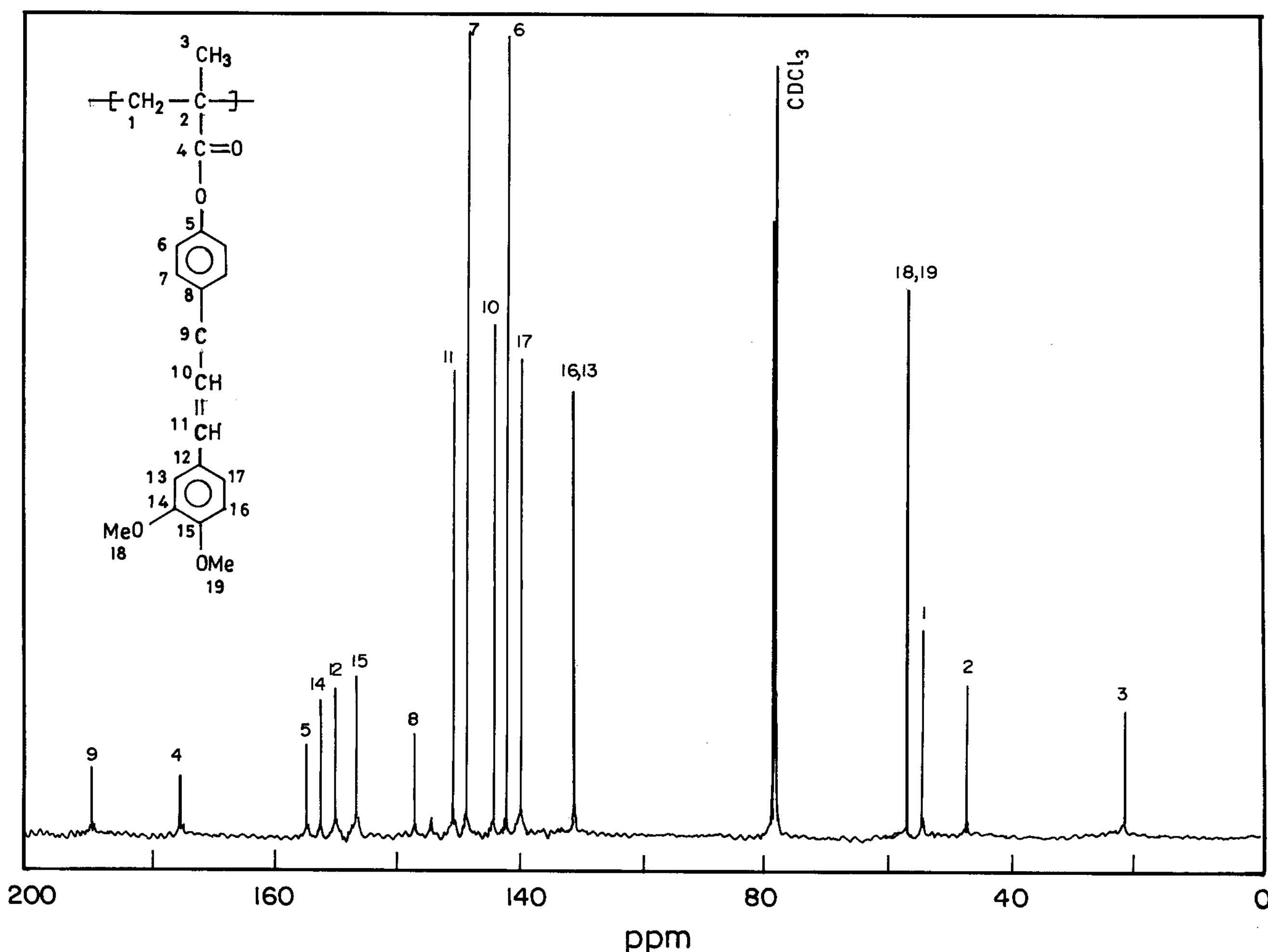


Figure 2 ^{13}C-NMR spectrum of poly(MPDMSK).

$$\text{Extent of conversion (\%)} = \frac{A_0 - A_T}{A_0 - A_\infty} \times 100$$

where A_0, A_T, and A_∞ are the absorption intensities after irradiation time $t = 0$, $t = T$, and $t = \infty$, respectively.

RESULTS AND DISCUSSION

Synthesis

The photosensitive methacrylate monomer MPDMSK, having a free-radical polymerizable olefinic group and a chalcone moiety as photosensitive group, was synthesized from HPDMSK as outlined in Scheme 1. The structures of HPDMSK and MPDMSK were confirmed by elemental analysis, FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The photoactive homopolymer poly-(MPDMSK) and copolymers of MPDMSK with GMA in ethyl acetate solution having different mole fractions of MPDMSK (0.15 to 0.85) in the feed were synthesized. The homopolymerization conversion was restricted to 45–50% to avoid any possibility of crosslinking at higher conversions. In the copolymerization of MPDMSK with GMA, the reaction time was initially selected to reach conversions lower than 10 wt % to satisfy the differential copolymerization equation.[17] The data of the compositions of the initial mixture of comonomers and of the resulting copolymers are presented in Table I.

Polymer characterizations

Because the solubility of photosensitive polymers is one of the important requirements for practical uses of these polymers, the solubility of the prepared homopolymer and copolymers was tested in various polar and nonpolar solvents. They were easily soluble in chloroform ($CHCl_3$), tetrahydrofuran, dichloromethane (CH_2Cl_2), dimethyl formamide (DMF), dioxane, and dimethyl sulfoxide (DMSO). They were insoluble in nonpolar solvents, such as benzene and toluene, and hydroxy group–containing solvents, such as methanol, ethanol, 2-propanol, and water. The solubility of poly(MPDMSK) was generally consider-

TABLE I
Composition Data of the Free-Radical Copolymerization of MPDMSK with GMA in Ethyl Acetate Solution at 70 ± 1°C

Feed composition[a] (M_1)	Conversion (%)	Intensities of protons		$C = \frac{I_{Ar+Oli}}{I_{oth \cdot ali}}$	Copolymer composition[a] (m_1)
		I_{Ar+Oli}	$I_{oth \cdot ali}$		
0.1501	9.64	18.481	81.519	0.2267	0.2584
0.3514	9.66	26.343	69.052	0.3815	0.4426
0.5073	9.06	29.587	65.084	0.4546	0.5320
0.6602	8.96	31.231	60.338	0.5176	0.6102
0.8598	9.53	36.434	57.658	0.6319	0.7551

[a] M_1 and m_1 are the mole fractions of MPDMSK in the feed and in copolymers, respectively.

ably less if the conversion was above 60%. After 21 h of homopolymerization (80% yield), the poly(MPDMSK) was completely insoluble in common organic solvents (even at boiling temperature). This might have been the result of crosslinking.

Poly(MPDMSK) and poly(MPDMSK-*co*-GMA) [0.53 : 0.47] exhibit UV absorption maxima in chloroform solution at 358 and 360 nm, respectively, corresponding to the pendant chalcone group. The bathochromic shift of UV absorption maxima in the polymers occurs on the higher wavelength side and this might be attributable to the presence of the electron-donating methoxy group at the *para* position of the aromatic ring of the cinnamoyl group.

The IR spectrum of poly(MPDMSK-*co*-GMA) [0.53 : 0.47] shows an absorption peak at 3065 cm^{-1} attributed to the aromatic C—H stretching vibrations. The peaks at 2936 and 2837 cm^{-1} are attributed to the C—H stretching of the methyl and methylene groups. The strong absorption band at 1745 cm^{-1} corresponds to the ester carbonyl stretching. A stronger peak at 1659 cm^{-1} and a weaker peak at 1630 cm^{-1} are assigned to the ketonic carbonyl group. The stretching vibrations of the ethylenic bond flanked between keto and a phenyl group in the MPDMSK unit are shown at 1598 cm^{-1}. The peaks at 1511 and 1417 cm^{-1} are assigned to the aromatic >C═C< stretchings. The peak at 1459 cm^{-1} may be assigned to CH_3 bending vibrations. The absorption peaks at 1263 and 843 cm^{-1} are attributed to the symmetrical and asymmetrical stretching of the epoxide group, respectively. The band at 1205 cm^{-1} is attributed to the C—O stretching of the ester group. The polymers also exhibit a strong peak at 1161 cm^{-1} attributed to the methoxy stretchings. Bands at 763 and 728 cm^{-1} may be ascribed to the out-of-plane bending vibrations of the CH groups of the benzene ring.

The ^{1}H-NMR spectrum of poly(MPDMSK-*co*-GMA) [0.53 : 0.47] (see Fig. 3) is consistent with its chemical structure. The multiplet signals between 8.03 and 6.55 ppm are attributed to the aromatic protons overlapped with that of the pendant ethylene group (–CH═CH–) of MPDMSK units in the coploymer. The methylenoxy protons of the ester group of the GMA unit show a signal at 4.15 and 3.64 ppm. The resonance signal at 3.78 ppm is attributed to the methoxy protons. The ring methyne (>CH–) proton of the GMA unit shows a signal at 3.02 ppm. The signals at 2.58 and 2.35 ppm correspond to the methylenoxy protons of the epoxy group in the GMA unit. The backbone methylene protons of the two comonomer units are observed between 2.20 and 1.47 ppm. The signals between 1.46 and 0.65 ppm are attributed to the methyl protons of the MPDMSK and GMA units in the copolymer.

The proton-decoupled ^{13}C-NMR spectrum of poly(MPDMSK-*co*-GMA) [0.53 : 0.47] is shown in Figure 4. Chemical shift assignments were made from the off-resonance decoupled spectra of the polymers. The ketone carbonyl carbon resonances are observed at 189.35 ppm. In general the ketone carbonyl carbon

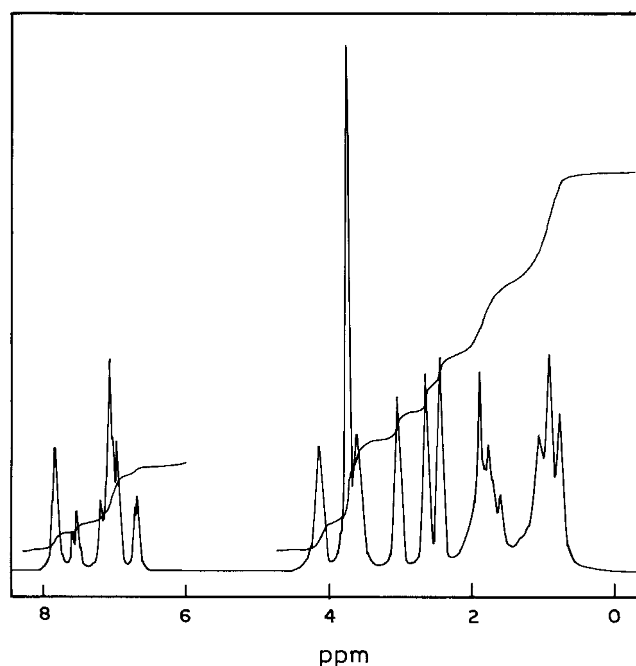


Figure 3 ^{1}H-NMR spectrum of poly(MPDMSK-*co*-GMA) [0.53 : 0.47].

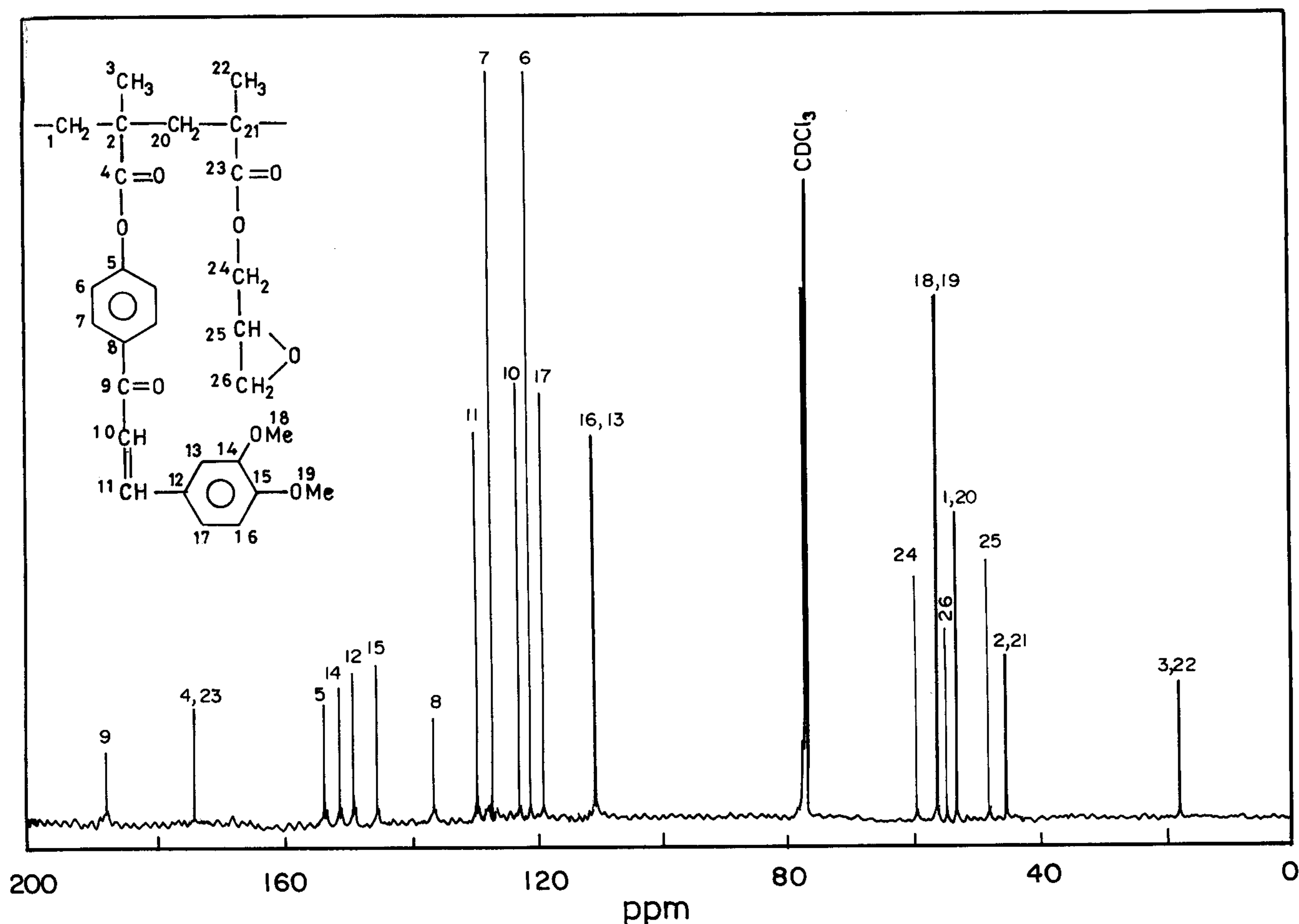


Figure 4 ^{13}C-NMR spectrum of poly(MPDMSK-*co*-GMA) [0.53 : 0.47].

appears at about 200 ppm. The small upfield shift of the ketone carbonyl carbon in this system may be attributable to the presence of extended conjugation. The extent of the chemical shift depends on the extent of conjugation with electrons and the π-system on the substituent.[38] The signal at 175.85 ppm corresponds to the ester carbonyl carbon. The aromatic carbon attached to the ester oxygen atom is observed at 154.15 ppm. The resonances of other aromatic and ethylenic (>C═C<) group carbons are observed between 151.85 and 110.78 ppm. The methylenoxy carbon of the ester group of the GMA unit appears at 59.86 ppm. The methoxy carbons attached at the *meta* and *para* positions of the phenyl ring of the cinnamoyl group are observed at about 56.35 ppm. The signal at 55.02 ppm is ascribed to the methylenoxy carbon of the epoxy group in the GMA unit. The backbone methylene group (–CH_2–) and tertiary (>C<) carbons of both monomeric units in the copolymer are observed at 53.30 and 46.46 ppm, respectively. The methyne (>CH–) carbon of the GMA unit is observed at 48.36 ppm. The α-methyl carbons of the MPDMSK and GMA units in the copolymer appear at 18.73 ppm.

Molecular weights

The weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights and the polydispersity indexes ($\overline{M}_w/\overline{M}_n$) of homopolymers as well as copolymers were determined by gel permeation chromatography and are presented in Table II. The polydispersity index values of poly(MPDMSK) and poly(GMA) are 2.03 and 1.96, respectively. The theoretical value of $\overline{M}_w/\overline{M}_n$ for polymers produced by radical combination and disproportionation are 1.5 and 2.0, respectively.[39] In the free-radical homopolymerization and copolymerization of (meth)acrylate monomers, the polydispersity index value of the resultant polymer depends on the chain-termination mechanism.[40,41] The polydispersity indices of poly(MPDMSK) and poly(GMA) obtained using benzene as solvent are 1.99 and 1.96, respectively. This shows that poly(MPDMSK) and poly(GMA) might be produced by termination of the growing chain by disproportionation.

In the case of copolymers, the polydispersity index values range between 1.95 and 2.01, values that suggest that the chain termination occurs more predomi-

TABLE II
Molecular Weight Data for the Homopolymer and Copolymers of MPDMSK and GMA

Polymer	m_1[a]	Molecular weight		
		$\overline{M}_w \times (10^{-4})$	$\overline{M}_n \times (10^{-4})$	$\overline{M}_w/\overline{M}_n$
Poly(MPDMSK)	1.0000	2.85	1.40	2.03
Poly(MPDMSK-*co*-GMA)	0.7551	3.02	1.51	1.99
	0.6102	3.12	1.55	2.01
	0.5320	3.06	1.57	1.95
	0.4426	2.94	1.48	1.96
	0.2584	3.25	1.66	1.96
Poly(GMA)	0.0000	3.52	1.80	1.96

[a] m_1 is the mole fraction of MPDMSK in the polymers.

nantly by disproportionation than by radical recombination and that the close value of the polydispersity index for the copolymers is not attributed to chain transfer to the solvent.

Thermal properties

The thermal stability of poly(MPDMSK), poly(GMA), and different copolymer samples was studied in air by estimating the percentage weight loss of the polymers on thermal decomposition. The TGA and DTG traces of poly(MPDMSK), poly(GMA), and poly(MPDMSK-*co*-GMA) [0.53 : 0.47] are shown in Figure 5 and the data are presented in Table III. The poly(MPDMSK) and copolymers undergo a three-stage decomposition, whereas the poly(GMA) decomposes in a single stage. The actual decomposition temperature range of the copolymer samples depends on the composition of the constituent monomeric units in the copolymers. The initial decomposition temperature of poly(MPDMSK) is 250°C and that of poly(MPDMSK-*co*-GMA) [0.53 : 0.47] and poly(GMA) are 221 and 206°C, respectively. Incorporation of the MPDMSK unit in the copolymer chain increases the thermal stability of the copolymers. A 50% weight loss of poly(MPDMSK) and poly(MPDMSK-*co*-GMA) [0.53 : 0.47] occurs at 410 and 398°C, respectively, showing the very good thermal stability required for the photosensitive polymers.

The glass-transition temperatures (T_g's) of poly(MPDMSK), poly(GMA), and the copolymer samples were determined by differential scanning calorimetry and are given in Table III. The T_g value of poly(MPDMSK) is found to be 137°C. All the copolymer samples show a single T_g value, thus indicating the absence of formation of a mixture of homopolymers or block copolymers. The T_g values of the copolymers range between 94 and 125°C and depend on the copolymer compositions. The increase of MPDMSK content in the copolymer increases the T_g value of the copolymer sample. These high T_g values of poly(MPDMSK) and the copolymers may be attributable to the inflexible and bulky pendant chalcone units and the presence of short side chains (–CH_3), which facilitate the chain entanglement.

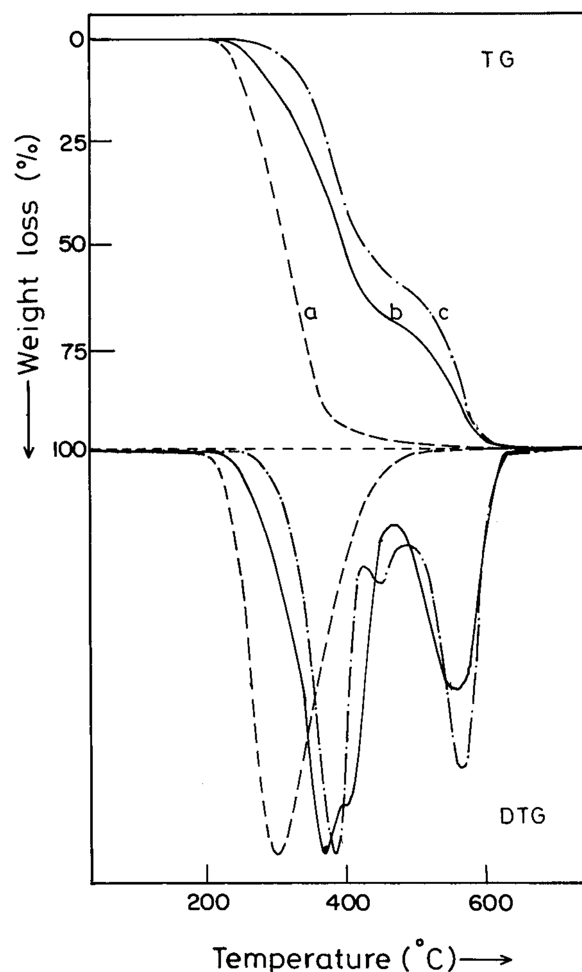


Figure 5 TGA and DTG traces of (a) poly(GMA), (b) poly(MPDMSK-*co*-GMA) [0.53 : 0.47], and (c) poly(MPDMSK).

TABLE III
Glass-Transition Temperature and TGA Data for the Homopolymer and Copolymers of MPDMSK and GMA

Polymer	m_1[a]	T_g[b] (°C)	DTR[c] (°C)			TWL[d,e] (%)				
			Stage 1	Stage 2	Stage 3	10	25	50	75	90
Poly(MPDMSK)	1.00	137	250–400	410–474	480–625	304	352	410	535	565
Poly(MPDMSK-*co*-GMA)	0.76	125	242–395	398–482	488–630	310	374	408	526	584
	0.61	117	235–396	397–491	504–675	321	367	410	562	601
	0.53	112	221–392	394–470	476–642	298	352	398	525	572
	0.44	107	216–325	330–486	498–628	298	309	418	498	579
	0.26	94	209–318	320–467	471–610	274	292	366	452	544
Poly(GMA)	0.00	74	206–480	—	—	254	275	302	360	381

[a] Mole fraction of MPDMSK in copolymers.
[b] Glass-transition temperature.
[c] Decomposition temperature range.
[d] Temperature (°C) corresponding to the weight loss (%).
[e] Figures in parameters indicate weight loss (%) during the temperature range stated.

Copolymer compositions

Because the general chemical structure of the copolymer may be represented as in Scheme 2, the average compositions of copolymer samples were determined from the corresponding ^{1}H-NMR spectra. The assignment of the resonance peaks in the ^{1}H-NMR spectrum allows for the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. The copolymers of MPDMSK with GMA show distinct resonance absorptions for both monomer units in the ^{1}H-NMR spectra. Thus, the mole fraction of MPDMSK in the copolymer was determined from the integrated intensities of aromatic and olefinic protons of the MPDMSK unit and other aliphatic protons of MPDMSK and GMA units in the copolymer.

The following expression was applied to the copolymers. Let m_1 be the mole fraction of MPDMSK and $(1 - m_1)$ be that of GMA. There are 7 aromatic protons, 2 olefinic protons, and 11 other aliphatic protons in MPDMSK. The GMA unit contains 10 aliphatic protons. Therefore,

$$C = \frac{\text{Intensities of aromatic and olefinic protons } (I_{\text{Ar}} + I_{\text{Oli}})}{\text{Intensities of other aliphatic protons } (I_{\text{oth·ali}})} = \frac{7m_1 + 2m_1}{11m_1 + 10(1 - m_1)} \quad (1)$$

which on simplification gives

$$m_1 = \frac{10C}{9 - C} \quad (2)$$

Based on eq. (2), the mole fraction of MPDMSK in all of the copolymers was calculated by measuring the intensities of the aromatic and olefinic proton signals and other aliphatic proton signals from the spectra of all the copolymer samples. Table I shows the values of C and the corresponding mole fractions in the copolymers. The kinetic behavior of the copolymer system was determined by plotting the mole fractions of MPDMSK in the feed (M_1) versus that in the copolymer (m_1), and the curve (see Fig. 6) indicates that the system forms an azeotropic polymer when the mole fraction of MPDMSK in the feed was 0.554.

Reactivity ratios

Determination of the reactivity ratios of monomers participating in the copolymer will provide the copolymerization behavior of the corresponding monomer pair. From the copolymer compositions and monomer

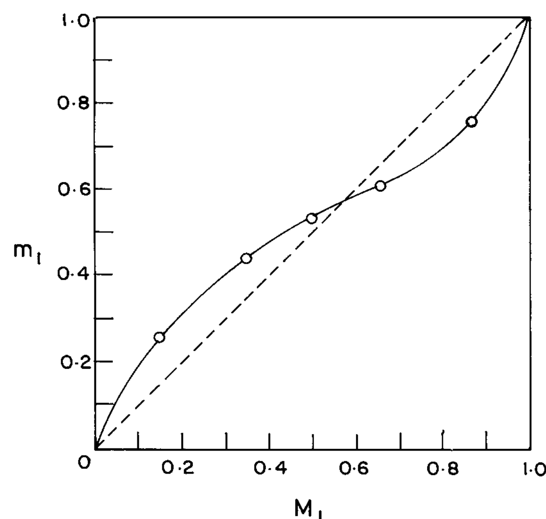


Figure 6 Composition diagram of the MPDMSK–GMA copolymer system.

TABLE IV
F-R, K-T, and Ext. K-T parameters for the Copolymerization of MPDMSK with GMA

		F-R Parameters		K-T Parameters		Ext. K-T Parameters	
$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$[a]	$\xi = H/(\alpha + H)$[a]	$\eta = G^1/(\alpha^1 + H^1)$[b]	$\xi = H^1/(\alpha^1 + H^1)$[b]
0.1763	0.3484	−0.3297	0.0842	−0.2852	0.0874	−0.2676	0.0774
0.5396	0.7940	−0.1399	0.3667	−0.1078	0.2826	−0.1028	0.2642
1.0123	1.1367	0.1217	0.9015	0.0664	0.4920	0.0646	0.4761
1.8814	1.5654	0.6795	2.2612	0.2128	0.7084	0.2087	0.7014
5.4729	3.0833	3.6978	9.7145	0.3473	0.9125	0.3348	0.9145

[a] α is equal to 0.9308.
[b] α^1 is equal to 0.9818.

feed ratios, the reactivity ratios of MPDMSK and GMA were determined by the application of the Fineman–Ross (F-R),[42] Kelen–Tüdös (K-T),[43] and extended Kelen–Tüdös (ext. K-T)[44] methods. The K-T and ext. K-T methods were superior to the F-R method, given that the experimental values distribute symmetrically between 0 and 1. Reactivity ratios were determined by a least-squares fit method. The significance of the parameters of F-R and K-T equations is presented in Table IV. The reactivity ratio values of MPDMSK (r_1) and GMA (r_2) obtained from the F-R plot (see Fig. 7) and the K-T and ext. K-T plots (see Fig. 8) are presented in Table V. Given that the r_1 and r_2 values are less than 1, this system gives rise to azeotropic composition at a particular composition of the monomers, which is calculated using the equation

$$N_1 = \frac{1 - r_2}{2 - r_1 - r_2} = 0.554 \quad (3)$$

When the mole fraction of the monomer MPDMSK in the feed is 0.554, the copolymer formed will have the same composition as that of the feed. When the mole fraction of the feed is less than 0.554 with respect to MPDMSK, the copolymer is relatively richer in this monomer unit than that in the feed. When the mole fraction of the monomer MPDMSK in the feed is greater than 0.554, the copolymer is relatively richer in GMA unit than that in the feed. The value of the product $r_1 \times r_2$ is considerably less than 1, indicating that the copolymer system shows a strong alternating tendency.

Photocrosslinking properties

The photocrosslinking properties of poly(MPDMSK) and the copolymer samples having a photosensitive chalcone moiety have been examined in various solvent solutions with concentration ranges of 23–154

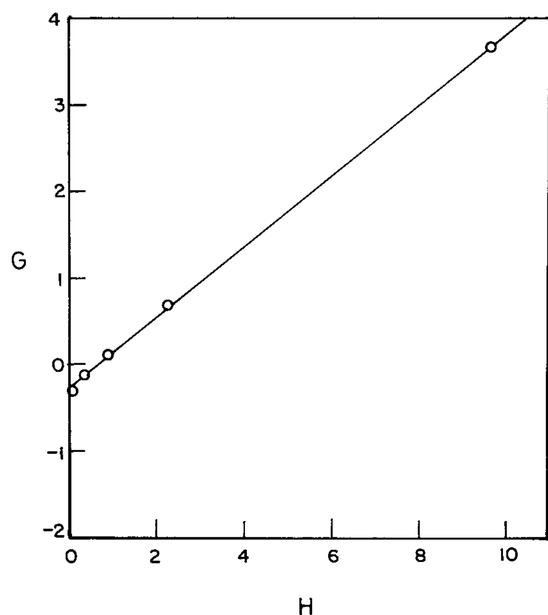


Figure 7 Fineman–Ross plot for the MPDMSK–GMA copolymer system.

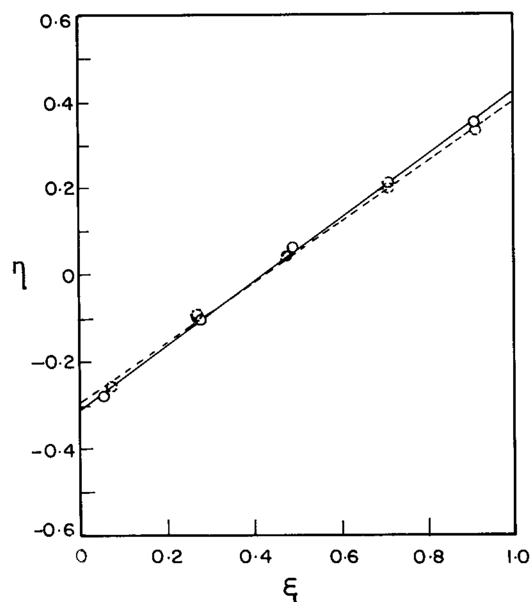


Figure 8 Kelen–Tüdös (—) and extended Kelen–Tüdös (– – –) plots for the MPDMSK–GMA copolymer system.

TABLE V
Copolymerization Parameters for the Free-Radical Copolymerization of MPDMSK with GMA

Method	r_1[a]	r_2[b]	$r_1 \times r_2$	$1/r_1$	$1/r_2$
Fineman–Ross	0.41	0.27	0.111	2.439	3.704
Kelen–Tüdös	0.42	0.28	0.117	2.381	3.571
Ext. Kelen–Tüdös	0.41	0.29	0.119	2.434	3.448
Average	0.41	0.28	0.116	2.420	3.574

[a] Reactivity ratio for MPDMSK.
[b] Reactivity ratio for GMA.

mg/L in the presence and the absence of photosensitizers. Polymer solutions were irradiated with a mercury lamp (UV source) at room temperature in the presence of air. Poly(MPDMSK) and the copolymer samples in chloroform solution show UV absorption bands at 360 and 358 nm, respectively, attributed to the π– π* transitions of >C=C< of the pendant cinnamoyl groups. The effect of irradiation on the photosensitive polymers was studied by measuring the changes in the UV absorption intensity at various time intervals. The changes in the UV spectral patterns of poly(MPDMSK) and poly(MPDMSK-*co*-GMA) [0.53 : 0.47] in chloroform solutions for different time intervals of irradiation at room temperature are presented in Figure 9 and Figure 10, respectively. Initial irradiation showed a *trans–cis* isomerization of the double bond, as was evident by the appearance of an isobestic point at 242 nm. Further irradiation results in a rapid decrease in absorption at 360 or 358 nm and it disappears almost completely within 10 min of irradiation. This behavior clearly indicates the formation of the cyclobutane ring by the $2\pi + 2\pi$ addition of pendant chalcone units of polymers, as shown in Scheme 3, which destroys conjugation in the entire π-electron system and thus results in a decrease in UV absorption intensity attributed to the chalcone unit. Thus, poly(MPDMSK) and the copolymer samples react photochemically according to a mechanism similar to that found for cinnamic acid and its derivatives.[45–47]

Chloroform solutions of the polymers at higher concentrations (520–550 mg/L) were irradiated for 3–4 h and the solvent was evaporated. The residue obtained was found to be insoluble in the organic solvent, in which these were soluble before irradiation. The infrared spectra of the irradiated polymers show the shifting of the carbonyl peak to a higher wavelength: 1720 cm^{-1} attributed to the loss of conjugation in the photocrosslinkiing reactions and the absence of an absorption peak at 1598 cm^{-1} attributed to the olefinic bonds in the chalcone moiety.

The photosensitivity of poly(MPDMSK) and the copolymer samples containing the α,β-unsaturated carbonyl groups is generally measured in terms of the rate of disappearance of the >C=C< group with irradiation time. In the chloroform solution, poly(MPDMSK) shows photoconversions of 22, 59, and 79% after 5, 30, and 90 s of irradiation time, respectively, and about 94% conversion occurs within 5 min of irradiation (presented in Fig. 11). In the copolymers, the photoconversions for poly(MPDMSK-*co*-GMA) [0.53 : 0.47] in chloroform are shown in Figure 12 and the values are about 30, 55, and 80% after an irradiation time of 5, 30, and 150 s, respectively. It is observed that within 5 min of irradiation, about 97% of conversion takes place. In solution, although the photoisomerization cannot be ruled out, the question of

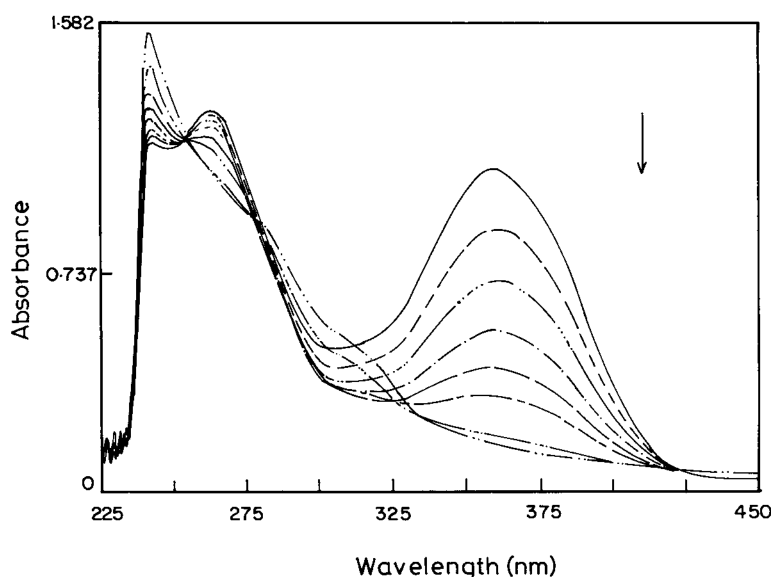


Figure 9 Changes in the UV spectral pattern of poly(MPDMSK) in chloroform solution upon irradiation. Top to bottom, after irradiation time $t = 0, 5, 15, 30, 60, 120, 300$, and 600 s.

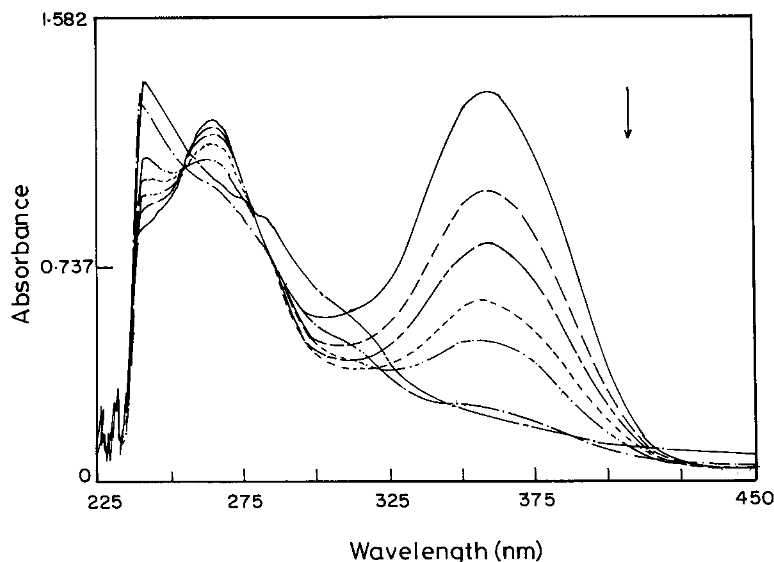


Figure 10 Changes in the UV spectral pattern of poly(MPDMSK-*co*-GMA) [0.53 : 0.47] in chloroform solution upon irradiation. Top to bottom, after irradiation time t = 0, 5, 15, 50, 110, 300, and 600 s.

disruption of the chromophore aggregate does not arise because there is no ordered arrangement of the chromophores in solution, and thus photodimerization takes precedence over *trans–cis* isomerization.

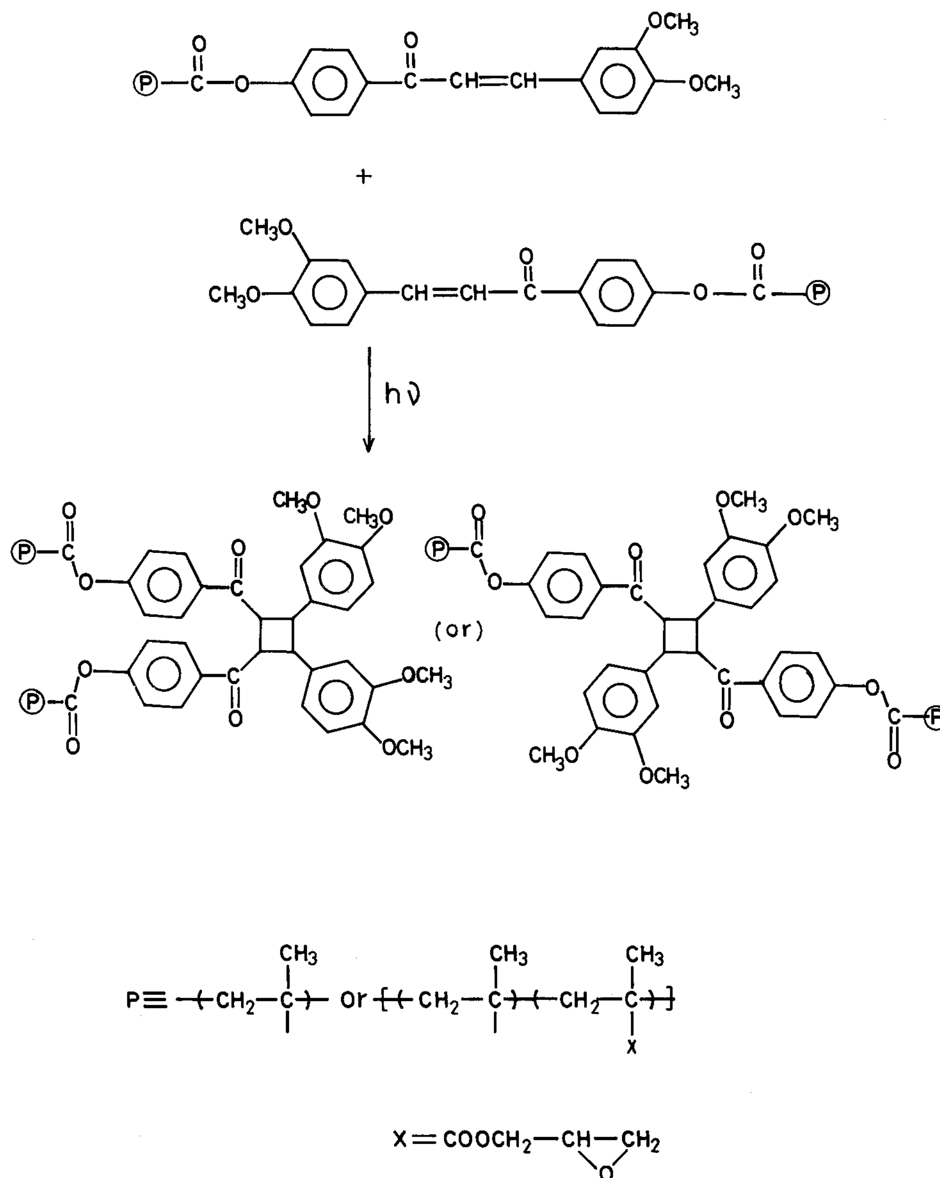
The effect of various solvents on the rate of photocrosslinking in poly(MPDMSK) and poly(MPDMSK-*co*-GMA) [0.53 : 0.47] was studied and the results are shown in Figure 11 and Figure 12, respectively. The rate of photocrosslinking of the polymers in chloroform is faster than that in the other solvents. The crosslinking rate of poly(MPDMSK) in various solvents is in the following order: $CHCl_3 > CH_2Cl_2 >$ dioxane > DMF > DMSO; in the case of copolymers, the rate of crosslinking of poly(MPDMSK-*co*-GMA) [0.53 : 0.47] is in the following order: $CHCl_3 > CH_2Cl_2$ > dioxane > DMSO > DMF. This indicates that the type of solvent used also has some significant effect on the rate of crosslinking of polymers in solution.

In copolymers, the photoconversion rate of the chalcone double bond depends on the copolymer compositions. The effect of copolymer compositions on the rate of crosslinking was studied in chloroform solution and are presented in Figure 13. The increase in the percentage of MPDMSK in the copolymers was found to decrease the rate of photocrosslinking, which results from the presence of more free space between the photoactive chalcone units in the copolymers of lower compositions. This illustrated that the copolymer composition plays an important role in the rate of photocrosslinking.

The effect of concentration of the photosensitive polymers on the rate of photocrosslinking in poly(MPDMSK) and poly(MPDMSK-*co*-GMA) [0.53 : 0.47] was studied in chloroform solution with the concentration range 23–154 mg/L. The results on rate of disappearance of >C=C< of chalcone units of poly(MPDMSK) are shown in Figure 14. In the case of both the homopolymer and the copolymers, the increase in concentration of the polymers reduces the rate of photocrosslinking. The rate of photocrosslinking of the polymers appears to be very rapid in dilute solution (less concentration) because of the availability of more free volume for pendant group rotation in dilute solution.[48]

The photocrosslinking reactions of poly(MPDMSK) and the copolymer samples were carried out in the presence of various triplet sensitizers such as benzoin, benzophenone, and Michler's ketone, to observe the effect of sensitizers on the rate of disappearance of >C=C< of the chalcone units of the polymers; it was observed that there was no sensitizing effect on the rate of disappearance of >C=C< of the photosensitive groups. This behavior is similar to that reported for some other photosensitive polymers[49,50] that have a high photosensitivity but cannot be sensitized. This behavior of the polymers strongly indicates that the photocrosslinking might not be taking place through the triplet (T) state, but rather through the singlet-state electrons leading to a one-step, concerted $(2\pi + 2\pi)$ cycloaddition.[51]

Thus, these polymers with a pendant chalcone moiety have a high rate of photocrosslinking, even in the absence of sensitizers, leading to insolubility of the polymers. It is expected that this type of polymers might be useful as negative photoresists for various applications.



Scheme 3 Photocycloaddition scheme of poly(MPDMSK) and poly(MPDMSK-*co*-GMA) upon irradiation.

CONCLUSIONS

Poly(MPDMSK) and its copolymers (with GMA), having pendant photoactive groups, were synthesized by free-radical solution polymerization and confirmed by spectral characterization. The polymers were easily soluble in polar aprotic solvents and chlorinated solvents. GPC data clearly indicate that poly(MPDMSK) was produced through termination by disproportionation, and in the copolymers chain termination also occurs mainly by disproportionation. TGA results clearly indicate that poly(MPDMSK) and the copolymers have very good thermal stability as required for negative photoresists. The incorporation of the MPDMSK unit in the copolymer chains increased the thermal stability of the copolymers. The polymers show a high T_g value, which may be attributable to the presence of rigid and bulky pendant chalcone units. The copolymer compositions were calculated from the ^{1}H-NMR spectra of the copolymers. The reactivity ratios of the comonomers determined by F-R, K-T, and ext. K-T are in good agreement. The r_1 and r_2 values obtained are less than 1, which indicates that the system gives rise to azeotropic polymerization at a particular composition of the feed. The value of the product $r_1 \times r_2$ suggests that the copolymer system shows a greater alternating tendency. The photoreactivity studies of polymers in various solvents strongly suggest the rapid conversion of the photoactive groups of the polymers during UV irradiation, as required for a photopolymer. The rate of photocrosslinking of the homopolymer and copolymers in chloroform solution were extremely rapid because of the free movement of

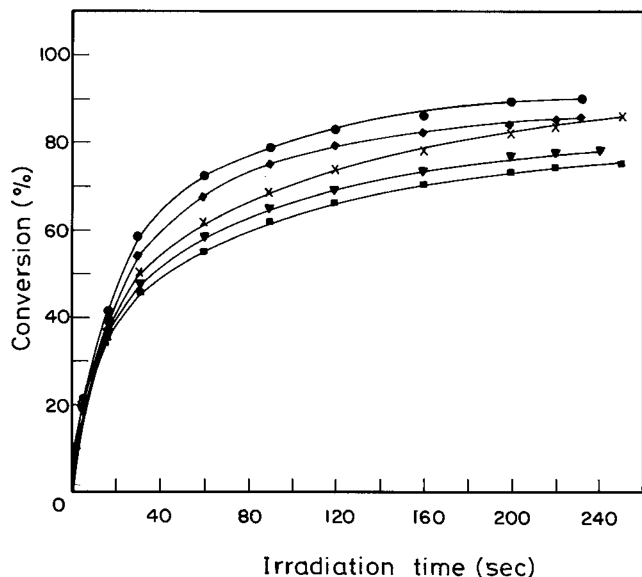


Figure 11 Disappearance rate of photosensitive >C=C< of poly(MPDMSK) with irradiation time in different solvents: (●), $CHCl_3$; (◆), CH_2Cl_2; (×), dioxane; (▼), DMF; (■), DMSO.

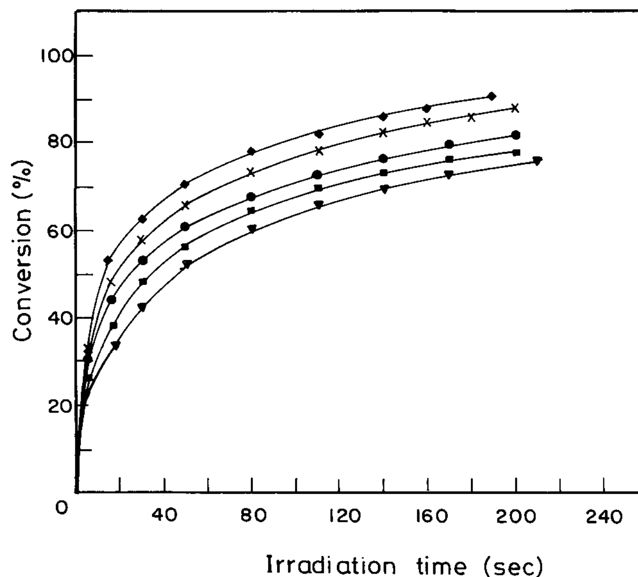


Figure 13 Rate of disappearance of the double bond (>C=C<) of poly(MPDMSK-*co*-GMA) in chloroform (m_1 : m_2): (◆), 0.26 : 0.74; (×), 0.44 : 0.56; (●), 0.53 : 0.47; (■), 0.61 : 0.39; (▼), 0.76 : 0.24.

the pendant unit. The rate of disappearance of the >C=C< of the chalcone unit of the polymers depended on factors such as solvents, concentration, and copolymer composition, and the rate was very rapid at lower concentration and at lower copolymer compositions because of the availability of more space between the chalcone units. The type of solvent has some significant effect on the rate of crosslinking. The photocrosslinking in the presence of triplet sensitizers showed no significant changes in the rate of disappearance of >C=C< of the chalcone unit. Because these polymers with a pendant chalcone moiety have a high rate of photocrosslinking, even in the absence of sensitizer, it might be expected that these polymers can be useful as good negative photoresists for photocurable coating systems.

R. Balaji acknowledges the CSIR, Government of India for providing financial assistance in the form of SRF for this research work.

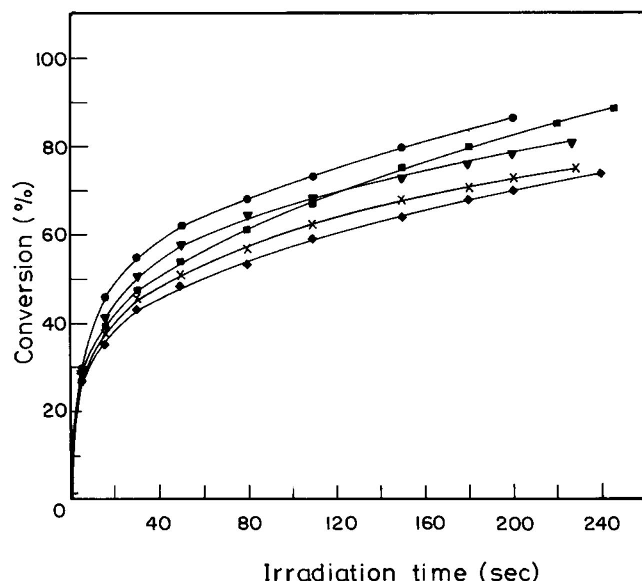


Figure 12 Disappearance rate of C=C of the chalcone unit of poly(MPDMSK-*co*-GMA) [0.53 : 0.47]: (●), in $CHCl_3$; (▼), in CH_2Cl_2; (■), in dioxane; (×), in DMSO; (◆), in DMF.

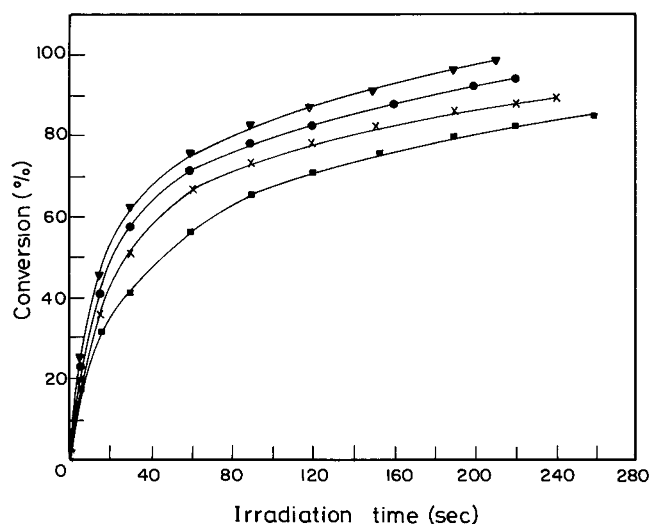


Figure 14 Disappearance rate of >C=C< of poly(MPDMSK) in chloroform solution at different concentrations: (▼), 23 mg/L; (●), 46.2 mg/L; (×), 94.6 mg/L; (■), 154 mg/L.

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