

Homopolymer and Copolymers of 4-Methacrylamidophenyl-4-methoxystyryl Ketone with Methyl Methacrylate: Synthesis, Characterization, Reactivity Ratios, and Photocrosslinkable Properties

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ABSTRACT: 4-Aminophenyl-4-methoxystyryl ketone (APMSK) was prepared by reacting 4-aminoacetophenone and 4-methoxybenzaldehyde in the presence of sodium hydroxide as base catalyst. The methacrylamide monomer, 4-methacrylamidophenyl-4-methoxystyryl ketone (MPMSK), was synthesized by reacting APMSK with methacryloyl chloride in the presence of triethylamine. Free-radical solution polymerization technique was used to prepare the homo- and copolymers of different feed compositions of MPMSK with methyl methacrylate in methyl ethyl ketone solution at 70°C, using benzoyl peroxide as the initiator. The polymers were characterized by UV, IR, ¹H-NMR, and ¹³C-NMR spectral techniques. The reactivity ratios of both comonomers were calculated using Fineman–Ross, Kelen–Tüdös, extended Kelen–Tüdös, and a nonlinear error-in-variables model (EVM) method using a computer program, RREVM. The molecular weights

(\bar{M}_w and \bar{M}_n) and polydispersity indices of the polymers were determined using size exclusion chromatography. The glass-transition temperatures of the polymers were determined by differential scanning calorimetry. The thermal stability of the polymers was measured by thermogravimetric analysis in air. The photoreactivity of the polymers was studied in chloroform solutions in the presence and absence of various triplet sensitizers. The effect of concentration of homopolymer and composition of the copolymers on the rate of photocrosslinking of the polymers was investigated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2913–2925, 2006

Key words: copolymerization; thermal properties; NMR; crosslinking; photoresists

INTRODUCTION

The photocrosslinkable polymers carrying reactive functional groups has been widely studied and is of broad current interest. Such polymers are used in the preparation of photoresists for use in macro and microlithography,¹ liquid crystalline display,^{2,3} photocurable coatings,⁴ integrated circuit technology,⁵ photoconductors,⁶ energy-exchange materials,⁷ in the field of nonlinear optical materials,^{8,9} etc. UV radiation curing has been revealed as a powerful tool to rapidly crosslink the heat-sensitive polymers and modifies (selectively in the illuminated areas) the physicochemical characteristics of these polymers. Phototuneable technology has found major openings in various industrial applications where its distinct advantages, such as fast cure, selective cure, and ambient temper-

ature, have allowed this environmental friendly technology to outclass more conventional processing techniques.

A classical photosensitive moiety is the cinnamate group. This system is well studied and widely used in photocrosslinkable polymers because of the high sensitivity to UV radiation and the chemical resistance of the resultant polymers. However, another photoreactive unit, the chalcone group, is particularly useful for these purposes because of the higher overall photoreactivity of the chalcone unit compared with that of the classical cinnamate system. Polymeric materials that contain chalcone-type groups have existed since 1959.¹⁰ These species include macromolecules with chalcone-type groups in the side chain,^{11–13} in the main chain,^{14–18} and in epoxy resins.^{19–22} Because of the difficulties in solubility of polymers arising from the rigid rod nature of chalcone group in main chain, recently, emphasis has been on polymers with side-chain chalcone units. 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-denned structure of techni-

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cal interest. There are only very few reports on photosensitive copolymers having different compositions formed from newly synthesized photoresponsive monomers and other commercial monomers. 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 reactors and to understand the kinetic and mechanistic aspects of copolymerization. In the past few decades, the $^1\text{H-NMR}$ spectroscopic analysis has been established as a powerful tool for the determination of copolymer composition, tacticity, and sequence distribution because of its simplicity, rapidity, and sensitivity.²³⁻²⁷ The accurate estimation of copolymer composition and determination of monomers reactivity ratios are significant for tailor-made copolymer with required physical and chemical properties and in evaluating the specific end application of copolymers. The main aim in commercial copolymerization is to obtain a product having uniform composition. The knowledge about the monomer reactivity ratios would help in achieving this.

Although the photocrosslinking of polymers bearing side-chain chalcone units has been reported both in the open literature and in patents, use of methacrylamides bearing chalcone as pendant units is unexplored. The work described here involves the synthesis, characterization, and analysis of thermal and photocrosslinking properties of methacrylamide homo- and copolymers containing chalcone as pendant group. The reactivity ratios of photomonomer, 4-methacrylamidophenyl-4-methoxystyryl ketone (MPMSK), and methyl methacrylate (MMA) were determined. The effect of different concentrations of homopolymer and composition of copolymers of MPMSK on the rate of photocrosslinking was also assessed for using the polymers as negative resist materials.

EXPERIMENTAL

Materials

4-Aminoacetophenone (SRL, India) and 4-methoxybenzaldehyde (Merck, Darmstadt, Germany) were used as-received. Benzoyl peroxide (BPO, Fluka, Buchs, Switzerland) was recrystallized from a 1:1 mixture of chloroform and methanol. Methacryloyl chloride was prepared according to the method in literature.²⁸ MMA (SRL) was purified by reduced pressure-distillation. All other reagents were used without further purification. The solvents were distilled before use.

Synthesis of 4-aminophenyl-4-methoxystyryl ketone

4-Aminoacetophenone (7 g, 0.0517 mol) in 50 mL of ethanol and a solution of sodium hydroxide (2 g) in distilled water (20 mL) were taken in a three-necked flask and the contents were cooled in an ice bath. 4-Methoxybenzaldehyde (7 g, 0.0517 mol) dissolved in 40 mL of ethanol was added drop wise with constant stirring and the temperature was not allowed to exceed 20°C. After the mixture was stirred for 24 h at room temperature, the precipitate was filtered, washed successively with ice-cold water and methanol, dried, and recrystallized from ethanol to get pure MPMSK. Yield 12.5 g (83%); m.p. 167°C.

The structure of 4-aminophenyl-4-methoxystyryl ketone (APMSK) was confirmed by elemental analysis, IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectra.

Elemental analysis (%): C = 75.84 (found), 75.87 (calcd); H = 5.90 (found), 5.97 (calcd); N = 5.46 (found), 5.53 (calcd). IR (KBr, cm^{-1}): 3346 (NH stretching); 1655 (C=O); 1600 (olefinic and aromatic C=C); 1510 (NH bending and C=C aromatic); 1440 (C=C aromatic); 1170 (C—OCH₃); 822 (C—H out-of-plane bending of the aromatic nuclei); 675 and 534 (C=C out-of-plane bending). $^1\text{H-NMR}$ (DMSO, ppm): 8.11–7.26 (m, 8H, aromatic); 6.92 (d, 1H, CH—Ar); 6.54 (d, 1H, —CO—CH=); 3.70 (3H, —OCH₃); 3.33 (s, 2H, —NH₂). $^{13}\text{C-NMR}$ (DMSO, ppm): 186.88 (keto C=O); 114.06, 115.20, 126.30, 128.66, 131.12, 131.84, 154.55, and 161.72 (aromatic carbons); 142.26 (=CH—Ar); 120.42 (=CH—CO—); 56.17 (OCH₃).

Synthesis of MPMSK

Methacryloyl chloride was prepared from methacrylic acid and benzoyl chloride, using the procedure of Stempel et al.²⁸ In a 500-mL three-necked flask, APMSK (10 g, 0.0395 mol) and triethylamine (6 mL, 0.0395 mol) were dissolved in 250 mL of methyl ethyl ketone (MEK) and cooled between 0 and 10°C. Methacryloyl chloride (3.9 mL, 0.0395 mol) in 40 mL of MEK was then added drop wise with stirring. Then, the reaction mixture was stirred for 2 h at room temperature, and the precipitated quaternary ammonium salt was filtered off. The solvent, MEK, was removed in a rotary evaporator, and the residue was dissolved in diethyl ether and washed with distilled water. The organic layer was dried over anhydrous sodium sulfate. Then, the ether layer was evaporated to get solid methacrylamide monomer, MPMSK. It was recrystallized from methanol to get pure monomer. Yield 10.53 g (83%); m.p. 34–35°C.

The structure of the monomer, MPMSK, was confirmed by elemental analysis, IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectra.

Elemental analysis (%): C = 74.69 (found), 74.75 (calcd); H = 5.92 (found), 5.96 (calcd); N = 4.28

(found), 4.36 (calcd). IR (KBr, cm^{-1}): 3274 (N—H stretching); 3062 ($\text{C}=\text{H}$ stretching); 2978 and 2840 (C—H stretching); 1658 (C=O), 1647 (C=O, amide band I); 1599 (olefinic and aromatic C=C); 1520 (N—H bending); 1489 (aromatic C=C); 1410 (=CH_2 scissoring); 1333 (C—N stretching); 1219 and 1030 (C—O—C asymmetric and symmetric stretching); 979 and 817 ($\text{=C}=\text{H}$ out-of-plane bending); 683 (NH wagging); 546 (C=C] out-of-plane bending). $^1\text{H-NMR}$ (CDCl_3 , ppm): 8.03–7.26, (m, 1H/8H/2H; NH/Ar—H/—CH=CH—); 6.90 and 6.65, 5.82 and 5.47 (dd, 2H; $\text{CH}_2=\text{C}$); 3.81 (s, 3H; — OCH_3). 2.04 (s, 3H, $\alpha\text{-CH}_3$). $^{13}\text{C-NMR}$ (DMSO, ppm): 189.16 (C=O, ketone); 167.01 (—CO—NH—); 142.18 ($\text{=CH}=\text{Ar}$); 120.56 ($\text{=CH}=\text{CO}$ —); 140.72 ([bond]C); 119.81 ($\text{CH}_2=\text{}$); 161.75, 144.50, 131.04, 130.86, 130.02, 129.87, 119.51, 114.50 (aromatic carbons); 55.44 (OCH_3); 18.74 ($\alpha\text{-CH}_3$).

Homopolymerization of MPMSK

MPMSK was polymerized as a 2M solution in MEK, using BPO as the initiator at 70°C. The predetermined quantities of MPMSK, the initiator (0.25 wt % of monomer), and solvent were placed in a polymerization tube and the mixture was flushed with a slow stream of nitrogen for 15 min. Then, the tube was closed and placed in the thermostated oil bath at 70°C. After 8 h, the reaction mixture was poured into excess methanol to precipitate the polymer, poly(MPMSK). The crude polymer was purified by dissolving in MEK and reprecipitated by methanol, filtered, washed with methanol, and dried under vacuum at 50°C. The yield of the polymer was 40%.

Synthesis of poly(MPMSK-co-MMA)

Copolymerization of MPMSK and MMA having six different feed compositions was carried out at 70°C in MEK solvent, using BPO (0.25 wt % with respect to monomers) as a free-radical initiator. Predetermined amounts of MPMSK, MMA, BPO, and the solvent were mixed in a polymerization tube having inlet and outlet system, purged with nitrogen gas for 20 min, sealed, and kept in an oil bath at 70°C. After specified time (ranging from 45 to 120 min), the copolymers were precipitated by adding the reaction mixture into excess methanol. The conversions were restricted to below 10%, to apply the copolymer equation. The precipitated copolymers were purified by repeated reprecipitation from chloroform solution using methanol as a nonsolvent and dried in vacuum for 12 h.

Measurements

Elemental analysis was performed with a Perkin-Elmer C—H—N analyzer. The UV spectrum was re-

corded in Hitachi UV-2000 spectrophotometer. Infrared spectra were obtained with a Hitachi 270–50 spectrophotometer as a KBr pellet. $^1\text{H-NMR}$ spectra were run on a Bruker 270 MHz FT-NMR spectrometer at room temperature, using CDCl_3 and TMS as the solvent and the internal standard, respectively. The proton-decoupled $^{13}\text{C-NMR}$ spectrum was run on the same instrument operating at 22.63 MHz at room temperature, and the chemical shifts were recorded under similar conditions. The molecular weights (\bar{M}_w and \bar{M}_n) were determined using Waters 501 gel permeation chromatograph. Tetrahydrofuran was used as the eluent, and the polystyrene standards were employed for calibration. Thermogravimetric analysis (TGA) was performed with a Mettler TA 3000 thermal analyzer in air atmosphere at a heating rate of 15°C/min. The glass-transition temperature was determined with a Perkin-Elmer DSC d7 differential scanning calorimeter at a heating rate of 10°C/min in air.

Solubility studies

Solubility of the polymers was tested in various polar and nonpolar solvents. About 5–10 mg of the polymer was added to about 2 mL of different solvents in a test tube and kept overnight, with the test tube tightly closed. The solubility of the polymers was noted after 24 h.

Photoactivity measurements

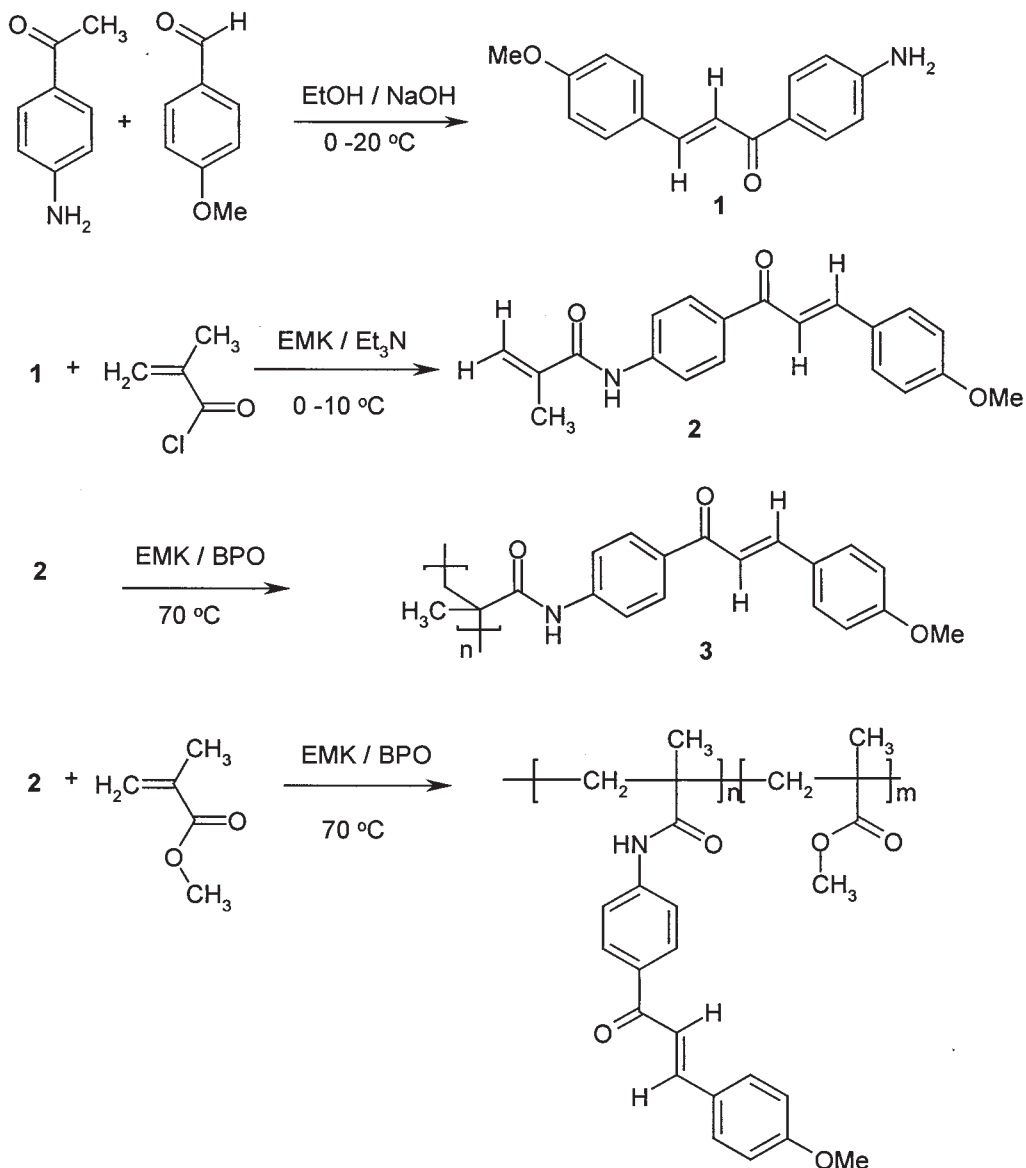
The photoactivity of the prepared polymers was studied by dissolving the polymers in chloroform solution and irradiated with a medium-pressure mercury lamp (Toshiba SHL-100 UV, 6 W, 254 nm) in air atmosphere. The quartz cell containing the polymer solutions was kept at a distance of 10 cm from the UV lamp for different time intervals of irradiation. The UV spectra of the polymer solution were recorded immediately after each exposure to UV light, and the rate of disappearance of the C=C double bond of the chalcone moiety of the polymer was followed by using the following expression.

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

where A_0 , A_T , and A_∞ are absorption intensities due to C=C after irradiation times $t = 0$, $t = T$ and $t = \infty$, respectively.

RESULTS AND DISCUSSION

The new methacrylamide monomer, MPMSK, containing photosensitive α,β -unsaturated carbonyl moiety and a free-radical polymerizable olefinic group,



Scheme 1 Synthesis of MPMSK and its homo- and copolymers with MMA.

was synthesized from newly prepared aminochalcone, APMSK, and methacryloyl chloride. The structure of the monomer was confirmed by elemental analysis, FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectral techniques. The photoactive homopolymer was synthesized by free-radical solution polymerization of MPMSK. The copolymers of MPMSK with MMA having different compositions of photoresponsive unit were synthesized by varying the comonomer feed compositions (0.1–0.9) via solution polymerization technique, using BPO as the initiator. The copolymerization time was selected in trials to restrict conversions up to 10 wt % to satisfy the differential copolymerization equation.²⁹ Synthesis of the acrylamide monomer, MPMSK, and its homo- and copolymers with MMA is shown in Scheme 1.

Solubility

One of the important requirements for a photosensitive polymer is its solubility in different organic solvents. The solubility of the newly prepared photosensitive homo- and copolymers in various solvents were tested in room temperature for practical application of these polymers. The polymers were easily soluble in the polar aprotic solvents viz. chloroform, methylene chloride, dimethylformamide, *N*-methyl-2-pyrrolidone, and dimethylacetamide, but insoluble in hydrocarbons (e.g., benzene, toluene, xylene) and hydroxy group-containing solvents such as methanol, ethanol, and 2-propanol. The solubility test clearly shows that there is wide possibility for using different solvents required for photocurable coating applications. How-

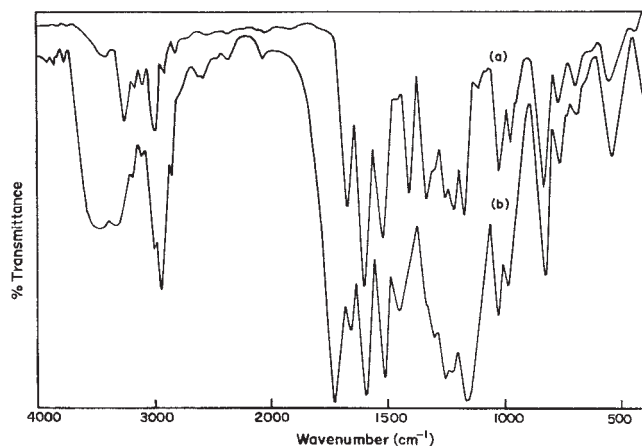


Figure 1 IR spectra of (a) poly(MPMSK) and (b) poly(MPMSK-co-MMA).

ever, at conversions of above 50%, the solubility of the polymers obtained generally decreased with increase in conversion, and the polymers obtained at about 70% conversion were completely insoluble even at the boiling temperature of the solvents. This might be due to crosslinking. However, the infrared spectra of both the soluble and insoluble polymers are identical, which does not prove the presence or absence of crosslinking. This might be due to the fact that crosslinking density might be below the detection

limit. However, swelling experiments prove the presence of crosslinks in these polymers.

Characterization of homopolymer

Infrared spectrum

The infrared spectrum of the homopolymer, poly(MPMSK), is shown in Figure 1(a). The polymer shows an absorption peak at 3436 cm^{-1} that corresponds to the NH stretching vibrations. The $=\text{C}-\text{H}$ stretching is observed at 3094 cm^{-1} . The symmetrical and asymmetrical C—H stretchings are observed at 2984, 2930, and 2836 cm^{-1} . The carbonyl absorption due to the amide (amide band I) overlaps with that of the keto group in the pendant chalcone unit and is observed at 1650 cm^{-1} . In the polymer, there is a shifting of the amide band I to higher frequency due to loss of conjugation with the double bond after polymerization. The strong bands at 1594 cm^{-1} correspond to the pendant olefinic group, which is flanked by keto and phenyl groups. The strong absorption observed at 1512 cm^{-1} is due to the amide band II caused by NH bending. The aromatic C=C stretching vibrations can be observed at 1594 and 1415 cm^{-1} . Bands at 1301 cm^{-1} may be attributed to the aromatic C—N stretching vibrations. Peaks at 1251 and 1028 cm^{-1} may be assigned to the asymmetric and symmetric Ar—O—C stretching vibra-

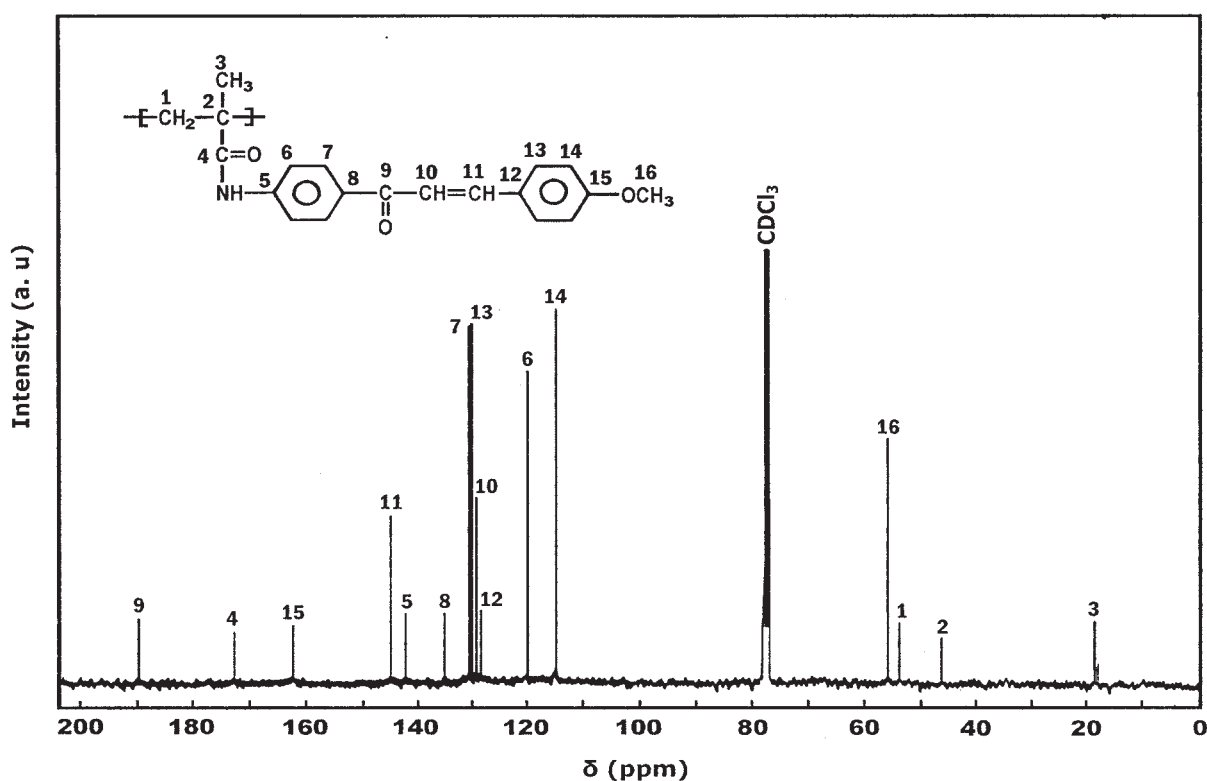


Figure 2 Proton-decoupled ^{13}C -NMR spectrum of poly(MPMSK).

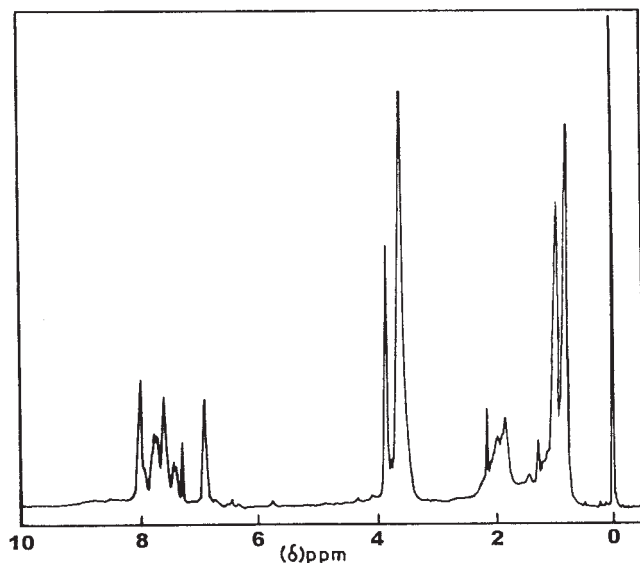


Figure 3 $^1\text{H-NMR}$ spectrum of poly(MPMSK-co-MMA) [0.2124 : 0.7876].

tions of poly(MPMSK). Absorptions at 820 and 708 cm^{-1} are due to the C—H out-of-plane bending of the aromatic nuclei and that at 690 cm^{-1} is due to out-of-plane NH wagging. The peak at 525 cm^{-1} is attributed to the C=C out-of-plane bending.

$^1\text{H-NMR}$ spectrum

The $^1\text{H-NMR}$ spectrum of the homopolymer, poly(MPMSK), exhibits multiplet resonance signals between 8.04 and 7.27 ppm due to the aromatic protons, NH proton, and olefinic ($-\text{CH}=\text{CH}-$) protons of the pendant chalcone group. The methoxy proton resonance signal of the poly(MPMSK) is observed at 3.87 ppm. The backbone methylene ($-\text{CH}_2-$) protons are observed as broad signals at 2.09–1.62 ppm, indicating the presence of conformational tacticity. The methyl protons give a resonance signal at 1.26 ppm.

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

The proton-decoupled $^{13}\text{C-NMR}$ spectrum of poly(MPMSK) is shown in Figure 2. The chemical shift assignments were made from the off-resonance decoupled spectrum of the polymer. The keto carbonyl carbon resonance of the pendant chalcone unit appears at 189.79 ppm. The amide carbonyl carbon of the polymers is observed at 173.02 ppm. The signals between 162.41 and 115.17 ppm are due to the aromatic and olefinic carbons. The resonance peaks at 145.21 and 129.27 ppm are attributed to the olefinic carbons attached to the aromatic ring and ketone group, re-

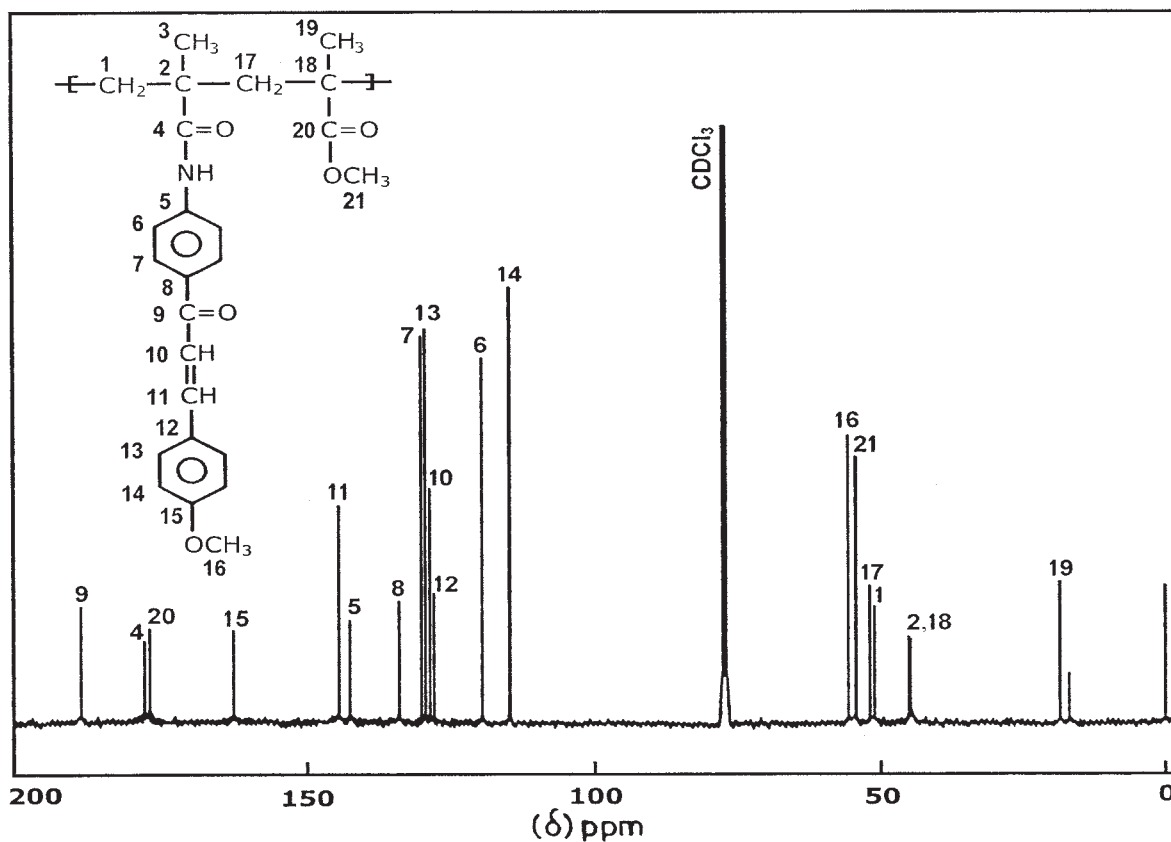


Figure 4 Proton-decoupled $^{13}\text{C-NMR}$ spectrum of poly(MPMSK-co-MMA) [0.4696 : 0.5304].

spectively. Resonance signals of backbone methylene carbons and tertiary carbons appear at 54.48 and 46.31 ppm, respectively. The methoxy carbon shows signal at 56.11 ppm. The series of signals between 18.40 and 18.29 due to the α -methyl carbon indicates the presence of tacticity in the polymer.

Characterization of the copolymers

Infrared spectrum

The infrared spectrum of the copolymer, poly(MPMSK-co-MMA), is shown in Figure 1(b). The IR spectrum of the copolymer shows strong absorption at 3449 cm^{-1} due to the NH stretching vibrations. The $=\text{C}-\text{H}$ stretching is observed at 3087 cm^{-1} . The ester carbonyl stretching vibrations of MMA units are observed at 1730 cm^{-1} . The peak at 1658 cm^{-1} is assigned to the carbonyl stretching of the keto group and the amide carbonyl group (amide band I). The peak at 1516 cm^{-1} is assigned to the amide band II due to the N-H bending. The strong band at 1597 cm^{-1} corresponds to the olefinic group flanked between keto and phenyl groups of pendant chalcone unit. The aromatic $\text{C}=\text{C}$ stretching vibrations appear at 1598 and 1448 cm^{-1} . The $\text{Ar}-\text{O}-\text{C}$ stretching of MPMSK unit of the copolymer shows absorption band at 1254 and 1027 cm^{-1} . The $\text{C}-\text{O}$ group stretching vibrations of MMA units are observed at 1166 and 1168 cm^{-1} . The peak at 1312 cm^{-1} is due to the $\text{C}-\text{N}$ stretching vibration. The $\text{C}-\text{H}$ out-of-plane bending vibrations and the out-of-plane N-H wagging are observed at 820 and 677 cm^{-1} , respectively. The out-of-plane bending vibrations of $\text{C}=\text{C}$ of benzene ring appears at 525 cm^{-1} .

^1H -NMR spectrum

The ^1H -NMR spectrum of poly((MPMSK-co-MMA) [0.2124:0.7876] is shown in Figure 3. The multiple resonance signals between 8.00 and 7.29 ppm are due to the aromatic protons, olefinic protons, and the NH proton. The resonance signals due to the methoxy protons of the MPMSK and MMA units appear at 3.84 and 3.59 ppm, respectively. The backbone methylene protons of both the monomer units are observed between 2.29 and 1.82 ppm. A broad signal at 1.26–0.84 ppm corresponds to the α -methyl protons of both the monomer units.

^{13}C -NMR spectrum

The proton-decoupled ^{13}C -NMR spectrum of poly(MPMSK-co-MMA) [0.4696 : 0.5304] is shown in Figure 4. The chemical shift assignments were made from the off-resonance decoupled spectrum of the copolymers. The keto carbonyl carbon and amide car-

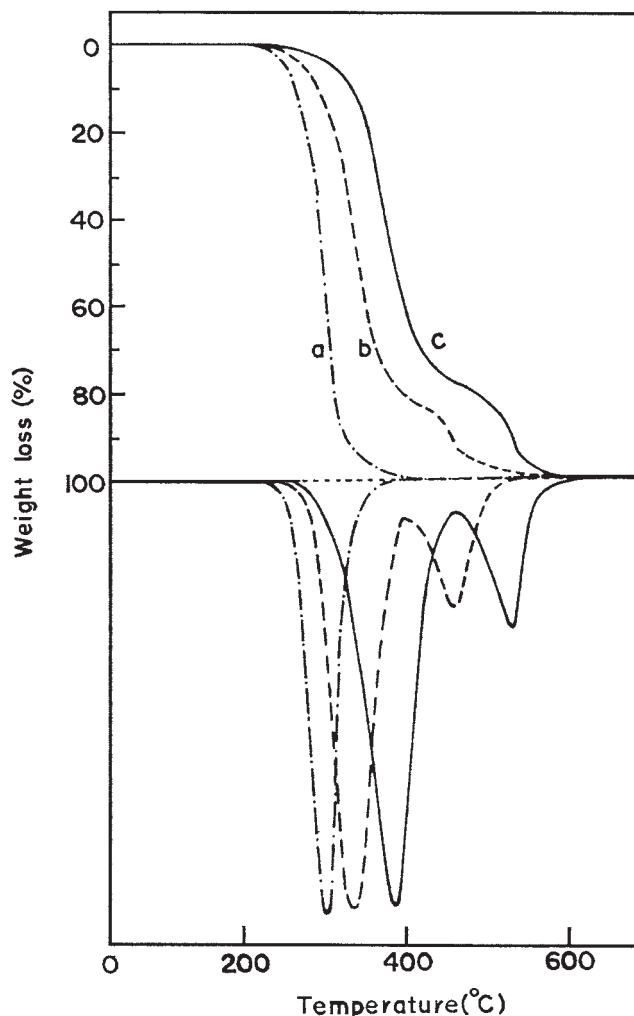


Figure 5 TGA and DTG traces of (a) poly(MMA), (b) poly(MPMSK-co-MMA) [0.4696 : 0.5304], and (c) poly(MPMSK) in air.

bonyl carbon resonance signals are observed at 189.19 and 178.11 ppm, respectively. The ester carbonyl carbon of MMA unit is observed at 177.44 ppm. The group of resonance signals between 162.67 and 114.47 ppm arises from aromatic carbons and olefinic carbons of the pendant chalcone moiety in the MPMSK unit. The methoxy proton signals of MPMSK and MMA units are observed at 55.43 and 54.02 ppm, respectively. The backbone methylene carbons are observed at 52.14 and 51.53 ppm. The backbone tertiary carbons gave resonance signals at 45.38 and 45.23 ppm, respectively. The signals at 18.91–18.85 ppm correspond to the α -methyl carbons of both monomer units.

Molecular weights

The weight-average molecular weights (\bar{M}_w), the number average molecular weights (\bar{M}_n), and the polydispersity index (\bar{M}_w/\bar{M}_n) of the polymer were

TABLE I
TGA and DSC Data for MPMSK-MMA Copolymer System

m_1	T_g (°C)	IDT ^a (°C)	DTR ^b (°C)		% Weight loss at different temperature (°C)				
			Stage I	Stage II	10	30	50	70	90
PMMA	105	244	244–374	—	271	284	295	305	326
0.0807	73	247	247–358	352–417	277	302	312	333	383
0.2124	55	249	249–382	382–449	288	316	329	347	418
0.3273	47	251	251–407	407–505	298	333	340	375	460
0.4696	42	254	254–418	418–516	305	340	358	382	474
0.6529	38	257	257–424	424–526	319	351	365	404	484
0.8057	36	259	259–435	435–533	326	358	379	414	502
Poly(MPMSK)	35	261	261–456	457–561	340	371	389	428	537

^a IDT denotes the initial decomposition temperature of the polymers.

^b DTR denotes the decomposition temperature range.

determined by gel permeation chromatography. For the homopolymer, poly(MPMSK) $\bar{M}_w = 5.03 \times 10^4$ g/mol, $\bar{M}_n = 2.54 \times 10^4$ g/mol, and $\bar{M}_w/\bar{M}_n = 1.98$. For poly(MPMSK-co-MMA) having different compositions, \bar{M}_w ranges from 3.84×10^4 to 3.98×10^4 g/mol, \bar{M}_n ranges from 2.00×10^4 to 2.13×10^4 g/mol, and \bar{M}_w/\bar{M}_n ranges from 1.87 to 1.97. The theoretical values of \bar{M}_w/\bar{M}_n for polymer produced via radical recombination and disproportionation are 1.5 and 2.0, respectively.^{30,31} The polydispersity index value of poly(MPMSK) suggests that in homopolymerization of MPMSK chain termination takes place mainly by disproportionation. The polydispersity indices for different compositions of poly(MPMSK-co-MMA) suggest that chain termination by disproportionation is predominant than dimerization and this tendency increases with increase in MPMSK content in the copolymer.

Thermogravimetric analysis

TGA was used to estimate the percent weight loss of the polymers in air atmosphere. The TGA-DTG curves of polymers and the data are presented in Figure 5 and Table I, respectively. Poly(MPMSK) and the copolymers undergo

decomposition in two stages, whereas poly(MMA) decomposes in a single stage. The initial decomposition temperatures of poly(MPMSK), poly(MPMSK-co-MMA) [0.4696:0.5304], and poly(MMA) are 261, 251, and 244°C, respectively. The homopolymer and poly(MPMSK-co-MMA) [0.4696:0.5304] show 50% weight loss at 389°C and 358°C, respectively. The actual decomposition temperature range of copolymers depends on the composition and type of comonomers used. Incorporation of photomonomeric unit, MPMSK, 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.

Glass-transition temperature

The glass-transition temperature (T_g) of the polymers was determined by differential scanning calorimetry in nitrogen and is given in Table I. T_g value of poly(MPMSK) is found to be 35°C. All the copolymers show a single T_g , showing the absence of formation of mixture of homopolymers or a block copolymer. The presence of inflexible and bulky pendant chalcone

TABLE II
Composition Data for Free-Radical Copolymerization of MPMSK (1) with MMA (2) in EMK Solution at 70°C

Copolymer no.	Feed composition (M_1) ^a	Conversion (%)	Integrated peak area of protons		$C = I_{Df}/I_{Tot}$	Copolymer composition (m_1) ^a
			I_{Df} ^b	I_{Tot} ^b		
1	0.1498	6.4	1.6469	16.485	0.0998	0.0807
2	0.3508	8.7	3.5995	15.927	0.2260	0.2124
3	0.5016	9.9	5.0080	16.134	0.3104	0.3273
4	0.6488	8.1	5.8142	14.817	0.3924	0.4696
5	0.8013	7.7	7.4338	15.713	0.4731	0.6529
6	0.9004	6.8	8.2141	15.628	0.5256	0.8057

^a M_1 and m_1 are the mole fractions of MPMSK in the feed and in the copolymer, respectively.

^b I_{Df} and I_{Tot} are integrated peak area of down field protons and total protons, respectively, in ¹H-NMR spectra of the copolymers.

units in the homopolymer and the α -methyl groups, which facilitate chain entanglement, tend to increase the T_g value, but the terminal methoxy group, due to its free rotation, pushes the polymer chains away, reduces chain entanglement, increases the free volume of the polymer, and thus, tends to decrease the overall T_g value. Introduction of MMA units in the copolymer increases the chain entanglement due the α -methyl groups, and hence, the T_g value of the copolymers increase with increase in MMA content in the copolymer.

Copolymer compositions

The composition of the copolymers was determined using $^1\text{H-NMR}$ spectral data. The assignment of resonance peaks in the $^1\text{H-NMR}$ spectra of polymers allows for accurate determination of both kind of monomeric units incorporated into the copolymers. As described under the characterization of copolymers by $^1\text{H-NMR}$ analysis (see Experimental section), poly(MPMSK-co-MMA) exhibits distinct resonance signals for both monomeric units. From the $^1\text{H-NMR}$ spectra of all copolymer samples, the copolymer compositions were determined by measuring the integrated peak area of downfield protons (aromatic, olefinic, and NH) of MPMSK unit and the total 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 MPMSK and $(1 - m_1)$ be that of MMA in the copolymer,

$$C = \frac{\text{Integrated peak area of down field protons}(I_{\text{Ar+NH+Ole}})}{\text{Integrated peak area of total protons}(I_{\text{Tot}})} \quad (1)$$

$$C = \frac{11m_1}{19m_1 + 8(1 - m_1)}$$

On simplification it gives,

$$m_1 = \frac{8C}{11 - 11C} \quad (2)$$

Using eq. (2), the mole fraction of the monomer units in the copolymer is determined. Table II gives the values of C and the corresponding mole fractions of MPMSK in the copolymer samples. The plot of mole fraction of MPMSK in the copolymer chain (m_1) against that in the monomer feed (M_1) is shown in Figure 6. It indicates that the composition of MMA unit in the copolymer is always higher than that in the monomer feed.

Monomer reactivity ratios

The instantaneous chemical composition of a copolymer depends exclusively on the concentration of

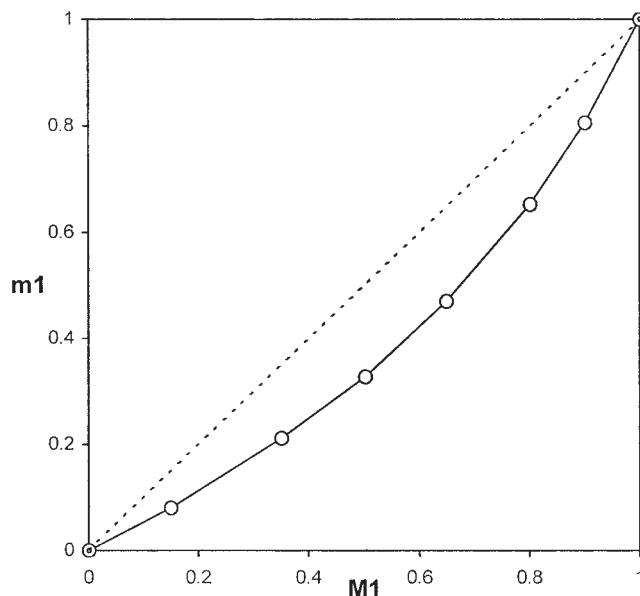


Figure 6 Composition diagram for MPMSK-MMA system.

monomers and their reactivity ratios as per the copolymer eq. (3).

$$\frac{m_1}{m_2} = \frac{r_1[M_1]^2 + [M_1][M_2]}{r_2[M_2]^2 + [M_1][M_2]} \quad (3)$$

where $[M_1]$ and $[M_2]$ are the mole fractions of the monomers in the feed; m_1 and m_2 are the mole fractions of the monomers 1 and 2 in the copolymer; and r_1 and r_2 are the respective monomer reactivity ratios. From the monomer feed ratios and the copolymer compositions, the monomer reactivity ratio of MPMSK and MMA were determined by conventional linearization methods such as Fineman-Ross (F-R),³² Kelen-Tüdös,³³ and extended Kelen-Tüdös (Ext. K-T).³⁴ The F-R, K-T, and Ext. K-T parameters for the copolymers are presented in Table III. The F-R plot is shown in Figure 7 and the K-T and Ext. K-T plots are shown in Figure 8. As the monomer reactive ratios determined by these methods are only approximate, a number of nonlinear methods have been proposed to obtain correct values of monomer reactivity ratios.³⁵⁻³⁷ However, the approximate values of monomer reactivity ratios determined by conventional linearization methods are usually employed as good starting values for nonlinear parameter estimation schemes.³⁸ In this study, a nonlinear error-in-variables model (EVM) method using the computer program, RREVM,³⁹ is used to determine reliable values of the monomer reactivity ratios. The r_1 and r_2 values from all methods are presented below.

$$\text{Fineman-Ross} : r_1=0.448; r_2=1.977$$

TABLE III
F-R, K-T, and Ext. K-T Parameters for Poly(MPMSK-co-MMA)

m_1	F-R parameters		K-T parameters		Ext. K-T parameters	
	$H = F^2/f$	$G = F(f-1)/f$	ξ	η	ξ'	η'
0.0807	0.3536	-1.8306	0.1181	-0.6115	0.2206	-1.1184
0.2124	1.0828	-1.4633	0.2909	-0.3931	0.4709	-0.6150
0.3273	2.0819	-1.0623	0.4409	-0.2250	0.6370	-0.3102
0.4696	3.8546	-0.2391	0.5935	-0.0368	0.7630	-0.0454
0.6529	8.6458	1.8888	0.7661	0.1674	0.8791	0.1835
0.8057	19.7085	6.8601	0.8819	0.3070	0.9428	0.3145

$\alpha = (H_{\min} \times H_{\max})^{1/2}$, $\xi = H/(\alpha + H)$ and $\eta = G/(\alpha + H)$.
 $\alpha' = (F_{\min} \times F_{\max})^{1/2}$, $\xi' = H/(\alpha' + H)$ and $\eta' = G/(\alpha' + H)$.
 m_1 is the mole fraction of MPMSK in the copolymer.

Kelen-Tudos : $r_1=0.449$; $r_2=1.977$

Ext. Kelen-Tudos : $r_1=0.371$; $r_2=1.780$

RREVM : $r_1=0.451$; $r_2=1.981$; $r_1r_2=0.893$

The product of r_1 and r_2 was <1 , indicating that the polymerization got preceded through the random pathway. The value of r_1 is <1 and that of r_2 is >1 , which indicates the presence of larger proportion of MMA units in the copolymer than that in the feed. The 95% joint confidence region for the determined r_1 and r_2 values using RREVM is shown in Figure 9.

Photocrosslinking properties

The photosensitivity of poly(MPMSK) and poly(MPMSK-co-MMA) were measured by irradiation of

the polymer solution with a medium-pressure mercury lamp in air. The irradiation was carried out in polymer solutions in the presence and absence of photosensitizer. The changes in the UV spectral pattern of poly(MPMSK) and poly(MPMSK-co-MMA) during the photocrosslinking of the polymers in solution with concentration 21 mg/L at various intervals of time at room temperature are shown in Figures 10 and 11, respectively. Poly(MPMSK) and copolymer samples show UV absorption bands at 346 and 344 nm, respectively, due to the $\pi-\pi^*$ transitions of C=C of the pendant chalcone moiety (C=C) of the polymers. Upon irradiation, an isobestic point appears at 307 or 305 nm for poly(MPMSK) and copolymer samples, respectively, which can be attributed to the decrease in the conjugated system upon irradiation, with a con-

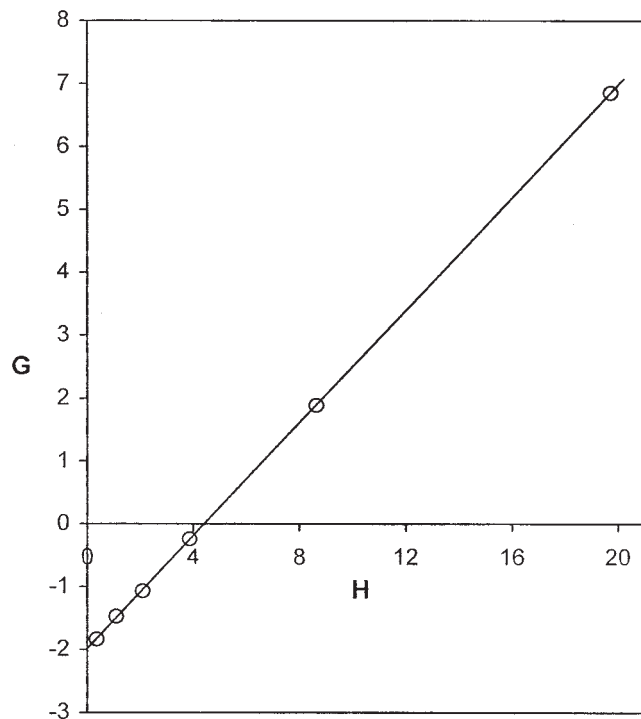


Figure 7 F-R plot for MPMSK-MMA copolymer system.

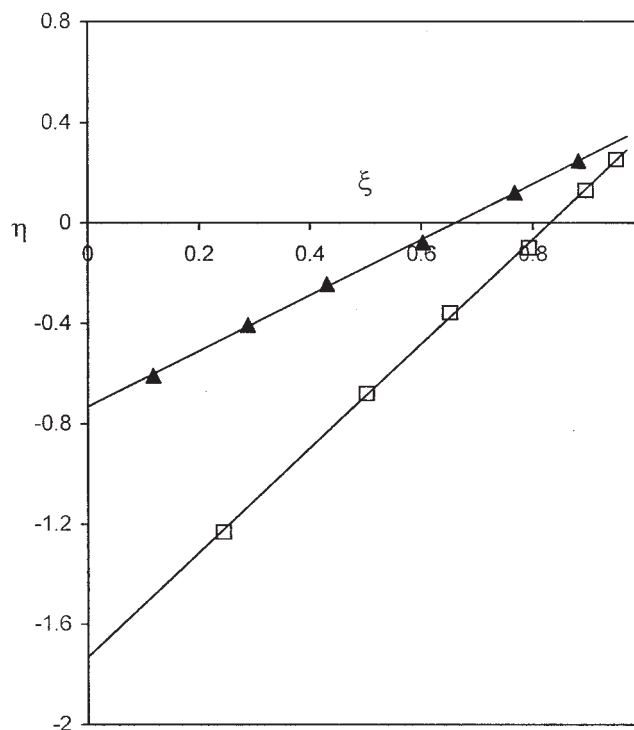


Figure 8 K-T (▲) and Ext. K-T (□) plot for MPMSK-MMA copolymer system.

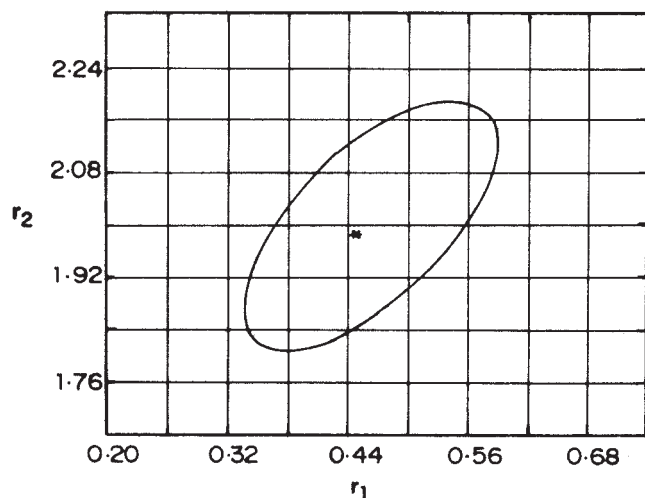


Figure 9 The 95% of joint confidence region of r_1 and r_2 values by RREVM for MPMSK-MMA copolymer system.

comitant increase in the absorbance at a shorter wavelength due to single bond formation in the cyclobutane ring via $2\pi + 2\pi$ cycloaddition of the C=C group of the pendant chalcone unit of the polymers as shown in Scheme 2. This ring formation destroys the conjugated π -electron system and, hence, results in a decrease in the UV absorption intensity. For poly(MPMSK) and the copolymers, the absorption band at 346 or 344 nm decreased very rapidly and disappeared almost completely within 2 min of irradiation. Thus, the polymer responded to irradiation similarly as found for cinnamic acid and its derivative.^{40,41}

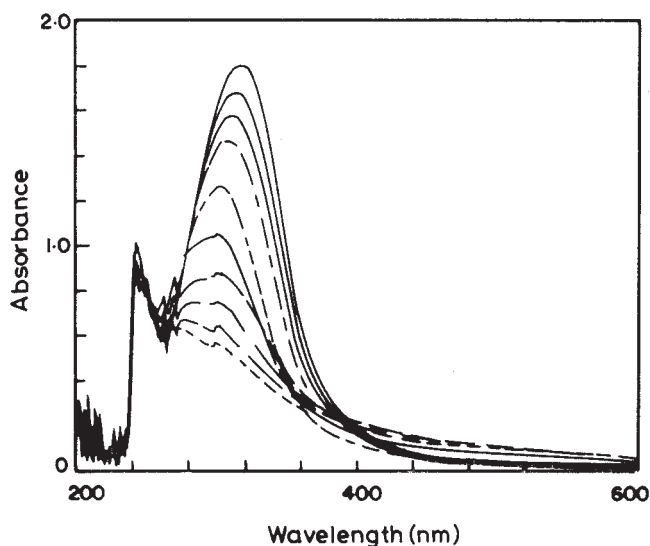


Figure 10 Changes in the UV spectral pattern of poly(MPMSK) in chloroform upon irradiation. Top to bottom: irradiation times $t = 0, 5, 10, 20, 40, 60, 80, 110, 120,$ and t_∞ s.

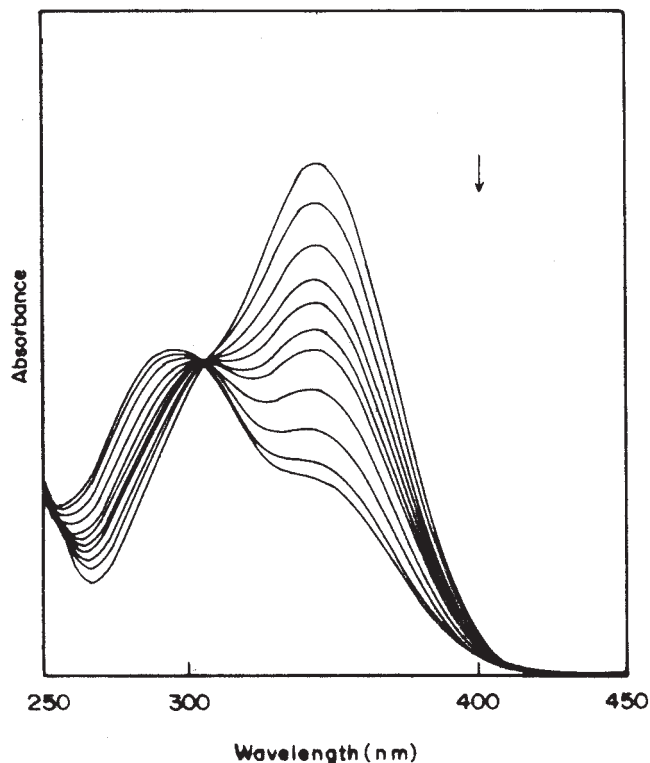
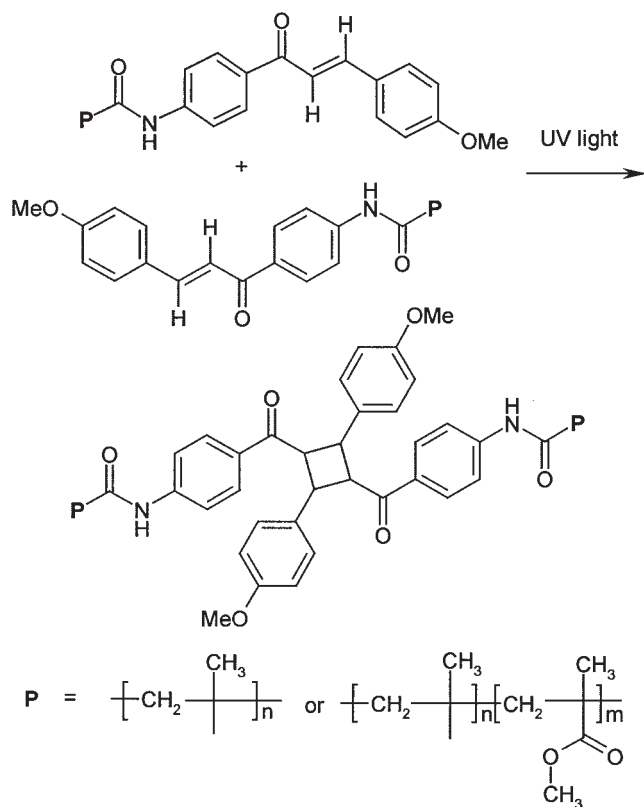


Figure 11 Changes in the UV spectral pattern of poly(MPMSK-co-MMA) (0.4696:0.5304) in chloroform upon irradiation. Top to bottom: irradiation times $t = 0, 5, 15, 25, 35, 45, 60, 90, 120,$ and t_∞ s.

The photosensitivity of polymers containing α,β -unsaturated carbonyl groups is generally measured in terms of the rate of disappearance of C=C group of photosensitive unit with irradiation time. In the chloroform solution, poly(MPMSK) shows photoconversions of 14%, 33%, and 55% after 5, 20, and 60 s of irradiation time, respectively, and about 66% conversion occurs within 90 s. The effect of concentration on the extent of photoconversion of the photoresponsive homopolymer studied in chloroform solution with concentration range of 21–166 mg/L is shown in Figure 12. For the copolymers, the rate of photoconversion of the chalcone double bond depends on the copolymer composition, and it increased with increase in MPMSK content in the copolymer chain as shown in Figure 13. In both cases, the increase in concentration of the polymers enhances the rate of photocrosslinking, because of the availability of more photosensitive units.⁴² The photoconversion of poly(MPMSK-co-MMA) (0.3273 : 0.6727) is about 42% and 56% after 35 and 60 s of irradiation time, respectively. Even though the concentration of photoresponsive unit is diluted, the copolymers show high rate of crosslinking, which directs the significant usage of these copolymers as negative photoresist, effectively.

When chloroform solutions of the polymers at higher concentration (520 mg/L) were irradiated for



Scheme 2 Photocycloaddition of homo- and copolymers of MPMSK and MMA.

3 h and the solvent was evaporated, the residue obtained was found to be insoluble in the organic solvent, in which the original polymers were easily soluble before irradiation. The FTIR spectrum of the ir-

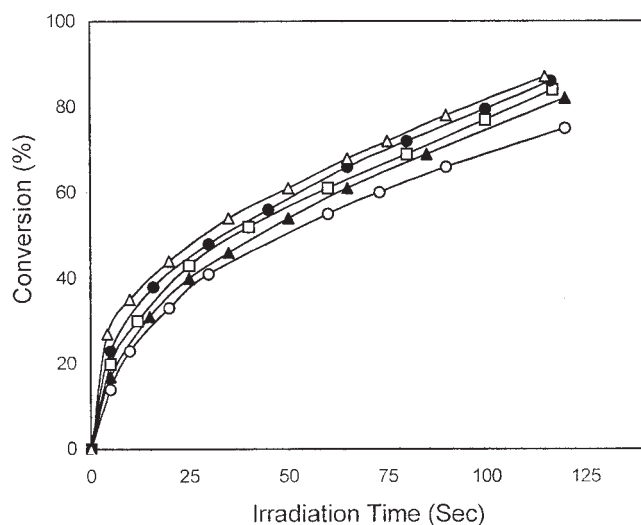


Figure 12 Rate of disappearance of chalcone double bond of poly(MPMSK) having different concentration with irradiation with UV light. (○) 21 mg/L; (▲) 44.2 mg/L; (□) 92.4 mg/L; (●) 124.2 mg/L; (Δ) 166.0 mg/L.

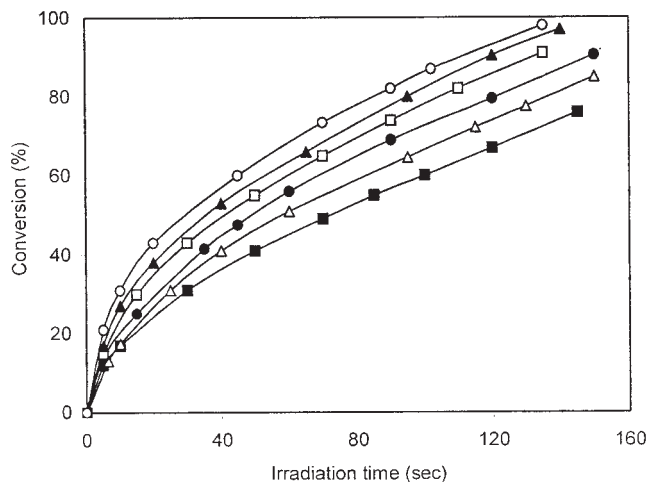


Figure 13 Rate of disappearance of chalcone double bond of poly(MPMSK-co-MMA) having different composition with irradiation with UV light. (■) 0.0807:0.9193; (Δ) 0.2124:0.7876; (●) 0.3273:0.6727; (□) 0.4696:0.5304; (▲) 0.6529:0.3471; (○) 0.8057:0.1943.

radiated polymer shows the shifting of the carbonyl peak to a higher wavelength (1685 cm^{-1}) that is attributed to the loss of the extended conjugation (with olefinic and the *p*-methoxyphenyl groups) after the photocrosslinking reactions. The decrease in the intensity of absorption peak at 1599 cm^{-1} after the photocrosslinking reactions is attributed to the disappearance of olefinic bonds of the chalcone moiety. These observations are an indirect proof for the formation of a cyclobutane ring after irradiation.

The photocrosslinking reactions of poly(MPMSK) and poly(MPMSK-co-MMA) 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 $\text{C}=\text{C}$ of the chalcone units of the polymers. It was found that there was no sensitizing effect on the rate of disappearance of $\text{C}=\text{C}$ of the photosensitive groups. This behavior is similar to that reported for some other photosensitive polymers such as α -phenylmaleimide⁴³ and α -cyanocinnamic ester,⁴⁴ which possess 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.⁴³ Thus, poly(MPMSK) and the copolymers with a pendant methoxycinnamoyl moiety possess high rate of crosslinking, leading to insolubility even in the absence of sensitizer, which are essential properties for using these polymers as negative photoresists for photolithography and protective coating applications.

CONCLUSIONS

Poly(MPMSK) and poly(MPMSK-co-MMA) having different compositions were synthesized by free-radical polymerization in solution, using BPO as initiator. The synthesized polymers were characterized by the UV, IR, ¹H-NMR, and ¹³C-NMR spectral techniques. The solubility of the polymers was tested in different organic solvents and the polymers were found to be soluble in polar aprotic solvents and insoluble in the hydrocarbon and hydroxy group-containing solvents. The polydispersity indices of the polymers obtained from GPC data indicated that in the homopolymerization of MPMSK the chain termination mainly takes place by disproportionation. In the copolymerization of MPMSK with MMA, chain termination by disproportionation outweighs radical combination and this tendency increased with increase in MPMSK content in the feed. The TGA result clearly shows that the polymers possess very good thermal and thermo-oxidative stability required for negative photoresist applications. T_g value of poly(MPMSK) is found to be lower than that of poly(MMA) and that of the copolymers increased with increase in MMA content. The photosensitivity of the homo- and copolymers were studied in chloroform solution by irradiation with a medium-pressure mercury lamp, and the spectral changes in the UV absorption intensity was recorded at predetermined time intervals immediately after each irradiation. The rate of photoconversion increases with increase in concentration of the polymers and with increase in mole fraction of the photomonomer unit in the copolymer. The photocrosslinking reactions of the polymers carried out in the presence of a triplet photosensitizer showed no significant changes in the rate of disappearing of C=C. Thus, the polymers with a pendant chalcone unit possess higher rate of photocrosslinking even in the absence of sensitizer, leading to insolubility of the polymer. It is expected that this type of polymer might be useful as a negative photoresist for various applications.

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