

# Studies on photocrosslinkable copolymers of 4-methacryloyloxyphenyl-3',4'-dimethoxystyryl ketone and methyl methacrylate

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## Abstract

Copolymers with various contents of 4-methacryloyloxyphenyl-3',4'-dimethoxystyryl ketone (MPDSK) and methyl methacrylate (MMA) were prepared in methyl ethyl ketone solution using benzoyl peroxide as a free radical initiator at 70 °C. Characterization of the resulting polymers was done by UV, FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic techniques. The copolymer compositions were determined by <sup>1</sup>H NMR analysis. The monomer reactivity ratios were calculated using linearisation methods such as Finemann–Ross ( $r_1 = 0.4283$  and  $r_2 = 0.3050$ ), Kelen–Tudos ( $r_1 = 0.4264$  and  $r_2 = 0.2606$ ), and extended Kelen–Tudos ( $r_1 = 0.4022$  and  $r_2 = 0.2704$ ) methods as well as by a non-linear error-in-variables model (EVM) method using the computer program RREVM ( $r_1 = 0.4066$  and  $r_2 = 0.2802$ ). The molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) and the polydispersity index of the copolymers were determined by gel permeation chromatography. The thermal stability of the copolymers increases with increase in concentration of MPDSK. Glass transition temperatures were determined by differential scanning calorimeter under nitrogen atmosphere. The photoreactivity of the copolymers having pendant chalcone moieties was studied in chloroform solution.

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**Keywords:** 4-Methacryloyloxyphenyl-3',4'-dimethoxystyryl ketone; Methyl methacrylate; Photocrosslinkable polymers; Reactivity ratios; <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra

## 1. Introduction

Photoreactive materials have recently gained remarkable interest since the photochemical reaction in organic materials can induce many changes in physicochemical

properties such as solubility, absorbability of light, flexibility and elasticity [1–4]. Polymers containing unsaturated aromatic acid or ester units, for example the cinnamic acid and cinnamic ester derivatives, were used for the study of phototransformation phenomena that occur under UV irradiation [5,6]. Photosensitive polymers find applications in fields such as integrated circuit technology, energy exchange materials [7], photorecorders [8], photocurable coatings [9], advanced microelectronics [10], photolithography [11] and liquid

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crystalline displays [12]. Examples of photosensitive polymers containing chalcone units in the side chains include  $\beta$ -vinyloxyethyl cinnamates [13], poly(vinyl-4-methoxy cinnamate) [14], poly(vinylcinnamoxy acetate) [15], poly(vinyl cinnamate) [16], poly(4-vinylphenyl cyanate) [17], poly[4-(2-hydroxy ethyloxy)-*N*-(5-nitro-2-thienylmethylene)]aniline [18], and poly(2-(*N*-phthalimido)-2-methyl propyl acrylate) [19]. Apart from these a variety of photosensitive polymers containing pendant cinnamoyl groups such as vinylphenyl cinnamate, isopropenylphenyl- $\beta$ -styryl acrylate, and copolymers of 2-cinnamoyloxyethyl methacrylate [20] have been reported.

The chemical composition of the copolymers depends on the degree of incorporation of the comonomers, i.e., on the relative reactivity between them. Monomer reactivity ratios are very important quantitative values to predict the copolymer composition for any starting feed and to understand the kinetic and mechanistic aspects of copolymerization. In the past few decades,  $^1\text{H}$  NMR spectroscopic analysis 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 [21–24]. The accurate estimation of copolymer composition and determination of monomer reactivity ratios is significant for tailor-made copolymers with required physical and chemical properties and in evaluating the specific end application of the copolymers. The main aim in commercial copolymerization is to achieve a desirable product composition. Knowledge about the monomer reactivity ratios of the comonomers would help in achieving this. The present work is aimed to develop new photoresist materials based on the copolymers of 4-methacryloyloxyphenyl-3',4'-dimethoxystyryl ketone with methyl methacrylate. In this article, we report the synthesis, characterization, thermal stability, and photocrosslinking properties of copolymers of 4-methacryloyloxyphenyl-3',4'-dimethoxystyryl ketone (MPDSK) with methyl methacrylate (MMA) and determination of monomer reactivity ratios for the comonomers MPDSK and MMA.

## 2. Experimental

### 2.1. Materials

The methacrylate monomer, 4-methacryloyloxyphenyl-3',4'-dimethoxystyryl ketone was prepared by reacting 4-(3',4'-dimethoxycinnamoyl)phenol with methacryloyl chloride in the presence of triethyl amine in MEK following the procedure of Balaji and Nanjudan [25]. Benzoyl peroxide (BPO) was recrystallized from a 1:1 mixture of chloroform and methanol. Methyl methacrylate was purified by washing with 5% NaOH solu-

tion, followed by distilled water, dried over anhydrous sodium sulfate and distilled twice under reduced pressure. All other solvents were distilled before use.

### 2.2. Copolymerization

Copolymers of MPDSK and MMA of six different compositions were prepared in MEK solution using benzoyl peroxide as a free radical initiator at 70 °C. Appropriate quantities of MPDSK and MMA with MEK and BPO were placed in a standard reaction tube and the mixture was flushed with oxygen-free nitrogen for 15 min. The tube was then tightly sealed and immersed in a thermostatic oil bath at 70 °C. After the required time, the copolymers were precipitated in methanol, and purified by reprecipitation with methanol from a solution of the polymer in MEK. They were then filtered and dried in a vacuum oven at 40 °C for 24 h.

### 2.3. Measurements

FT-IR spectra were recorded on a Hitachi 270-50 spectrophotometer using KBr pellets for solid samples. High-resolution  $^1\text{H}$  NMR spectra were run on Bruker 270 MHz spectrometer and the spectra were recorded at room temperature as 15–20% (w/v) solutions in  $\text{CDCl}_3$ . The same instrument was used to record  $^{13}\text{C}$  NMR spectra in  $\text{DMSO}-d_6$  at room temperature using tetra methyl silane (TMS) as an internal standard. Ultra-violet spectra of the polymers were recorded with a Hitachi UV-2000 spectrophotometer. The number-average molecular weight ( $\bar{M}_n$ ) and weight-average molecular weight ( $\bar{M}_w$ ) were determined by a Waters 501 gel permeation chromatograph equipped with three ultra styragel columns and a differential refractive index detector. Tetrahydrofuran was used as the eluent and polystyrene standards were employed for calibration. Thermogravimetric analysis (TGA) curves were recorded with a Mettler TA 3000 thermal analyzer in air at a heating rate of 15 °C/min. The glass transition temperature ( $T_g$ ) was determined using a Perkin-Elmer DSC d7 differential scanning calorimeter (DSC) at a heating rate of 10 °C/min in nitrogen atmosphere.

### 2.4. Photoreactivity measurement

A low-pressure mercury lamp (Heber Scientific photo reactor-UV, 6 W, 254 nm) was used as the UV source for the irradiation of the polymers in solution. The polymer dissolved in chloroform was kept at a distance of 10 cm from the UV lamp for different time intervals of irradiation. The UV spectra of the polymer in solution were recorded immediately after each exposure, and the rate of disappearance of the  $>\text{C}=\text{C}<$  double bond

of the chalcone moiety of the polymer was measured using the expression.

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

where  $A_0$ ,  $A_T$  and  $A_\infty$  are the absorption intensities due to  $>\text{C}=\text{C}<$  after irradiation times  $t = 0$ ,  $t = T$  and  $t = \infty$ , respectively.

### 3. Results and discussion

#### 3.1. Synthesis of copolymers of MPDSK and MMA and their characterization

The copolymerization of MPDSK with MMA in MEK solution was studied in a wide range of compositions with the mole fractions of MPDSK ranging from 0.10 to 0.85 in the feed. The copolymerization was restricted to below 10% conversion in order to satisfy the requirements of the copolymerization equation for reactivity ratio determination. The synthesis of the copolymers of 4-methacryloyloxyphenyl-3',4'-dimethoxystyryl ketone with MMA is outlined in Scheme 1.

One of the important requirements for a photosensitive polymer is its solubility in different organic solvents. The solubility of the prepared copolymers was tested in various polar and non-polar solvents. These were easily soluble in polar aprotic solvents like dimethylformamide (DMF), dimethylsulfoxide (DMSO), dimethylacetamide, *N*-methyl-2-pyrrolidone, tetrahydrofuran (THF) and chlorinated solvents like chloroform ( $\text{CHCl}_3$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), etc. They were insoluble in aliphatic and aromatic hydrocarbons (e.g. benzene, toluene, xylene), and hydroxy group containing solvents such as methanol, ethanol and 2-propanol. The solubility of the polymer obtained generally decreased with

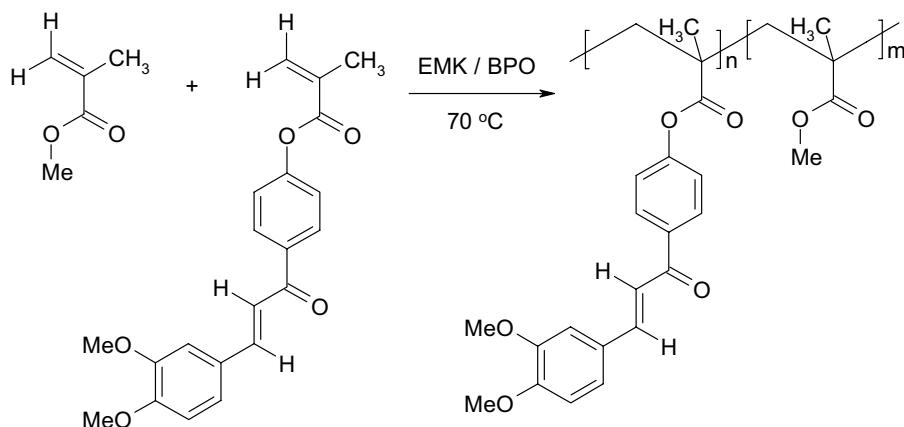
increasing conversion. At higher conversion the polymer was completely insoluble in most of the organic solvents, which might be due to the result of crosslinking. The infrared spectra of both the soluble and insoluble portion of the polymer were almost identical and hence did not prove any crosslinks due to an obviously very small crosslinking density. However, swelling studies performed with dry polymer samples and MEK as the solvent verified the presence of crosslinks in the insoluble polymer.

#### 3.2. UV spectra

The copolymers exhibit UV absorption maxima at 359 nm due to the  $\pi-\pi^*$  transitions of  $>\text{C}=\text{C}<$  of the pendant chalcone moiety present in the MPDSK units. The bathochromic shift (blue shift) of UV absorption maxima in the polymer occurs on the higher wavelength side and this might be attributable to the presence of the electron donating methoxy group at the 3',4'-position of the aromatic ring of the styryl unit.

#### 3.3. IR spectra

The IR spectrum of poly(MPDSK-*co*-MMA) [0.5599:0.4401] is shown in Fig. 1. It exhibits absorption at 3071–3004  $\text{cm}^{-1}$  corresponding to aromatic C–H stretching. The carbonyl stretching due to the ester groups of MPDSK and MMA units is seen at 1749  $\text{cm}^{-1}$ . The peak at 1659  $\text{cm}^{-1}$  is due to the keto carbonyl stretching. The aromatic C=C stretching is observed at 1596 and 1510  $\text{cm}^{-1}$ . The peak at 1455  $\text{cm}^{-1}$  is due to the bending of the methyl group. The absorption band at 1263–1203  $\text{cm}^{-1}$  is due to the methoxy group stretching. The peak at 801  $\text{cm}^{-1}$  is due to C–H out of plane bending vibrations of the aromatic nuclei. The  $>\text{C}=\text{C}<$  out of plane bending vibration is observed at 587  $\text{cm}^{-1}$ .



Scheme 1. Synthesis of poly(MPDSK-*co*-MMA).

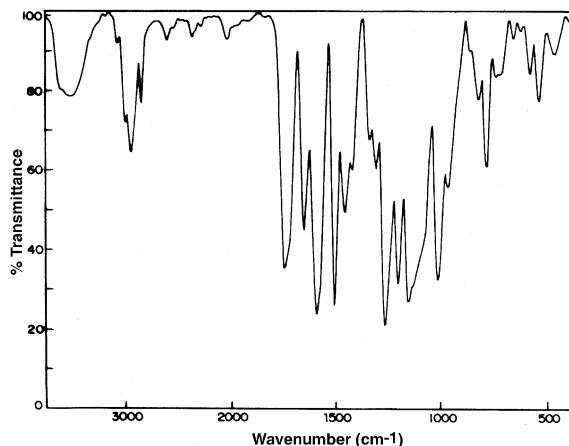


Fig. 1. FT-IR spectrum of poly(MPDSK-*co*-MMA) (0.5599:0.4401).

### 3.4. $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectrum of poly(MPDSK-*co*-MMA) [0.5599:0.4401] is shown in Fig. 2. The aromatic protons show multiplet resonance signal between 8.15 and 7.20 ppm. The signal at 6.90 ppm (d) may be attributed to one of the olefinic protons of the cinnamoyl group. The other olefinic proton signal is overlapped with that of aromatic protons. The methoxy proton resonance of the MPDSK and MMA units appears at 3.94 and 3.61 ppm, respectively. The backbone methylene pro-

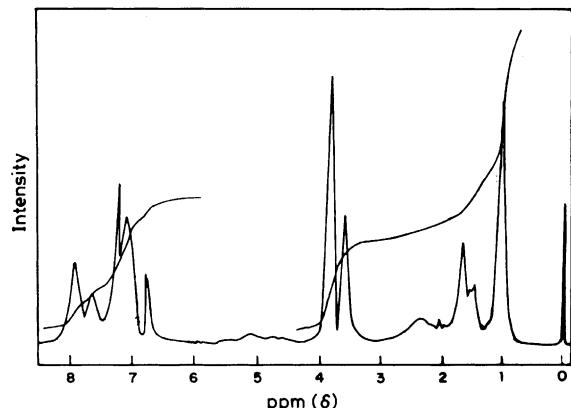


Fig. 2.  $^1\text{H}$  NMR spectrum of poly(MPDSK-*co*-MMA) (0.5599:0.4401).

tons of the two comonomer units are observed between 2.85 and 1.25 ppm. A broad signal centered at 1.07 ppm corresponds to the  $\alpha$ -methyl protons of both monomeric units.

### 3.5. $^{13}\text{C}$ NMR spectra

The proton-decoupled  $^{13}\text{C}$  NMR spectrum of poly(MPDSK-*co*-MMA) [0.5599:0.4401] is shown in Fig. 3. Chemical shift assignments were made from the off-resonance decoupled spectra of the copolymers. The ketone carbonyl carbon and ester carbonyl carbon

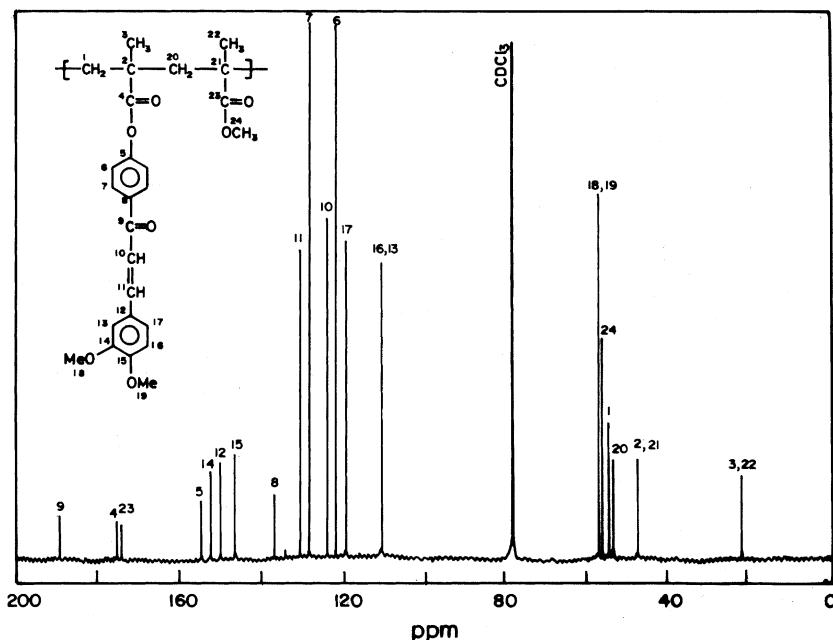


Fig. 3.  $^{13}\text{C}$  NMR spectrum of poly(MPDSK-*co*-MMA) (0.5599:0.4401).

resonance is observed at 189.6 and 175.6 ppm, respectively. The signal at 154.4 ppm is assigned to the aromatic carbon attached to the esteric oxygen. The group of resonance signals between 136.8 and 121.9 ppm arises from other aromatic carbons and olefinic carbons of the pendant cinnamoyl phenyl groups in the MPDSK unit. The methoxy signals of MPDSK and MMA units are observed at 56.7 ppm and 54.9 ppm, respectively. The backbone methylene carbon gave resonance signals at 52.68 and 51.36 ppm, whereas the tertiary carbon gave signal at 47.51 ppm. The signal at 19.7 ppm corresponds to the  $\alpha$ -methyl carbon of both types of monomer units.

### 3.6. Copolymer composition

The  $^1\text{H}$  NMR technique is a well established method for the determination of copolymer composition [26,27]. The composition of the MPDSK and MMA units in the copolymer was determined from the assignment of distinct and well separated resonance peaks in the  $^1\text{H}$  NMR spectra. Thus, the mole fraction of MPDSK in the copolymer was determined from the integrated peak area of aromatic protons of MPDSK and total protons of MPDSK and MMA units.

Let  $m_1$  be the mole fraction of MPDSK and  $m_2 = (1 - m_1)$  be that of MMA units.

$$C = \frac{\text{Integral peak area of aromatic protons } (I_{\text{Ar}})}{\text{Integral peak area of total protons } (I_{\text{Tot}})} \\ = \frac{7m_1}{20m_1 + 8(1 - m_1)} \quad (1)$$

On simplification;

$$m_1 = \frac{8C}{7 - 12C} \quad (2)$$

The value of  $C$  and the corresponding mole fractions of MPDSK in the copolymer are given in Table 1. The plot of mole fraction of MPDSK ( $M_1$ ) in the feed vs that in the copolymer ( $m_1$ ) is shown in Fig. 4.

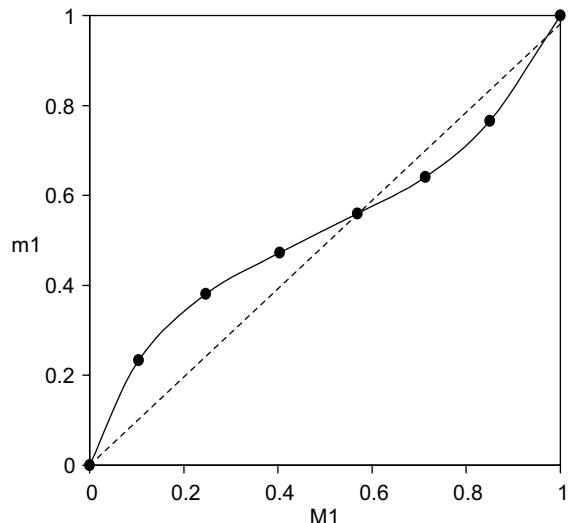


Fig. 4. Copolymer composition diagram of poly(MPDSK-*co*-MMA) system.

### 3.7. Monomer reactivity ratios

To understand the copolymerization behavior, the monomer reactivity ratios of MPDSK and MMA were estimated first by graphical methods according to Fine-mann–Ross [F–R] [28], Kelen–Tudos (K–T) [29], and extended Kelen–Tudos (Ext. K–T) [30] methods. Reactivity ratios were determined by a linear least-squares fit. The parameters of F–R and K–T equations are presented in Table 2 and those for Ext. K–T are shown in Table 3. The values from the F–R, K–T, Ext. K–T plots and RREVM are presented in Table 4. The reactivity ratios obtained from F–R (Fig. 5), K–T and Ext. K–T (Fig. 6) methods are: F–R method— $r_1(\text{MPDSK}) = 0.4283$  and  $r_2(\text{MMA}) = 0.3050$ ; K–T method— $r_1(\text{MPDSK}) = 0.4264$  and  $r_2(\text{MMA}) = 0.2606$ ; Ext. K–T method— $r_1(\text{MPDSK}) = 0.4022$  and  $r_2(\text{MMA}) = 0.2704$ . The monomer reactivity ratios determined by conventional linearisation methods are

Table 1  
Composition data for free radical copolymerization of MPDSK (1) with MMA (2) in EMK solution at 70 °C

Copolymer	$(M_1)^a$	Conversion (%)	Intensities of protons		$C$	$(m_1)^a$
			$I_{\text{Ar}}$	$I_{\text{Tot}}$		
1	0.1038	6.93	6.521	43.043	0.1515	0.2338
2	0.2467	8.13	14.318	67.506	0.2121	0.3808
3	0.4035	7.19	18.387	75.948	0.2421	0.4729
4	0.5691	9.23	12.146	45.610	0.2663	0.5599
5	0.7132	8.17	14.742	51.563	0.2859	0.6408
6	0.8498	6.42	16.691	53.530	0.3118	0.7655

<sup>a</sup>  $M_1$  and  $m_1$  are the mole fractions of MPDSK in the feed and in the copolymer, respectively.

Table 2

F–R and K–T parameters for the copolymerization of MPDSK with MMA

Copolymer	$F = M_1/M_2$	$f = m_1/m_2$	$H = F^2/f$	$G = F(f-1)/f$	$\eta = G/(\alpha + H)$	$\xi = H/\alpha + H$
1	0.1158	0.3051	0.0439	-0.2637	-0.3767	0.0627
2	0.3275	0.6150	0.1744	-0.2050	-0.2468	0.2100
3	0.6764	0.8972	0.5099	-0.0775	0.0664	0.4373
4	1.3207	1.2722	1.3710	0.2826	0.1394	0.6763
5	2.4867	1.7839	3.4664	1.0927	0.2650	0.8408
6	5.6578	3.2644	9.8060	3.9246	0.3751	0.9373

$$\alpha = (H_{\max} \times H_{\min})^{1/2} = 0.6561.$$

Table 3

Extended K–T parameters for MPDSK–MMA copolymer systems

Parameters	Copolymer system					
	1	2	3	4	5	6
$\zeta_2$	0.0470	0.0553	0.0585	0.0952	0.1095	0.1075
$\zeta_1$	0.1238	0.1038	0.0776	0.0917	0.0785	0.0620
$Z$	2.7453	1.9265	1.3400	0.9614	0.7049	0.5628
$F$	0.1111	0.3192	0.6696	1.3233	2.5307	5.8003
$H$	0.0405	0.1657	0.4997	1.3764	3.5902	10.3061
$G$	-0.2531	-0.1998	-0.0767	0.2831	1.1120	4.0234
$\eta$	-0.3001	-0.2063	-0.0589	0.1299	0.2531	0.3622
$\xi$	0.0480	0.1711	0.3836	0.6316	0.8173	0.9277

$$\alpha = (F_{\max} \times F_{\min})^{1/2} = 0.8028.$$

Table 4

Copolymerization reactivity ratios for the free radical copolymerization of MPDSK with MMA

Methods	$r_1^a$	$r_2^a$	$r_1 r_2$
Finemann–Ross	0.4283	0.3050	
Kelen–Tudos	0.4264	0.2606	
Ext. Kelen–Tudos	0.4022	0.2704	
RREVM	0.4066	0.2802	0.1139

<sup>a</sup>  $r_1$  and  $r_2$  are the reactivity ratios for MPDSK and MMA, respectively.

only approximate and are usually employed as good starting values for non-linear parameter estimation schemes.

Several non-linear methods have been attempted to determine monomer reactivity ratios [31–36]. To determine more reliable values of monomer reactivity ratios a non-linear error-in-variables model (EVM) method is used utilizing the computer program, RREVM [32]. The  $r_1$  and  $r_2$  values obtained by the RREVM method are  $r_1 = 0.4066$  and  $r_2 = 0.2802$ . The 95% joint confidence region for the determined  $r_1$  and  $r_2$  values using RREVM is shown in Fig. 7. Since both  $r_1$  and  $r_2$  values are less than unity the system gives rise to an azeotropic polymerization at a particular composition. When the composition of MPDSK in the feed is less than that of the azeotropic composition, the copolymer composition

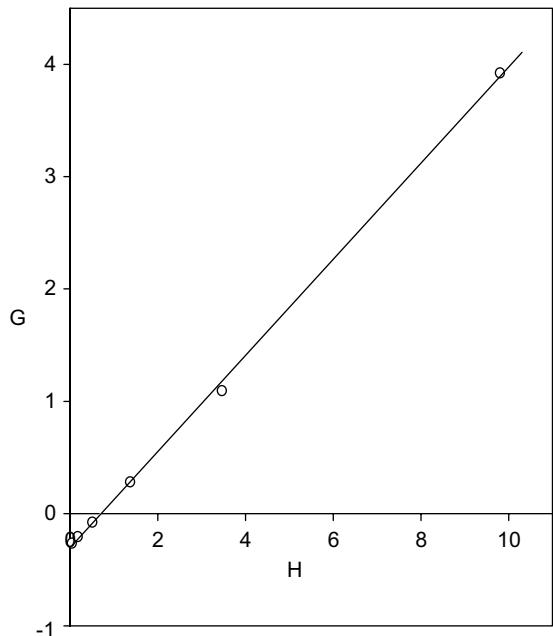


Fig. 5. Finemann–Ross plot for poly(MPDSK-*co*-MMA) system.

of MPDSK will always be higher than that in the feed. On the other hand, when the composition of MPDSK

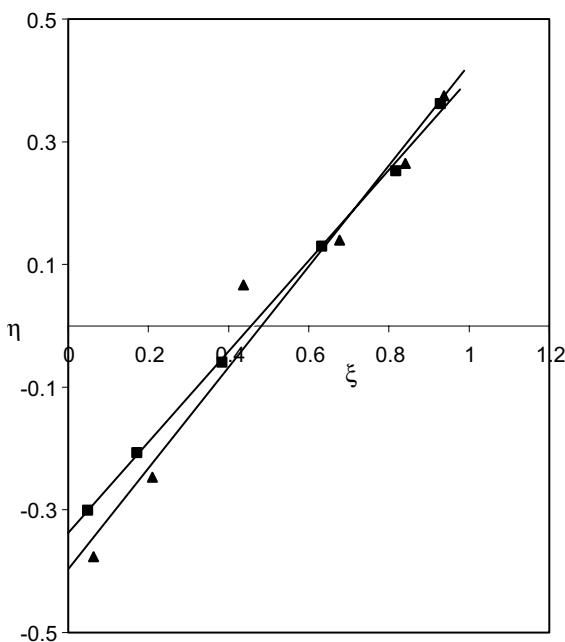


Fig. 6. K-T (▲) and Ext. K-T (■) plots for poly(MPDSK-*co*-MMA) system.

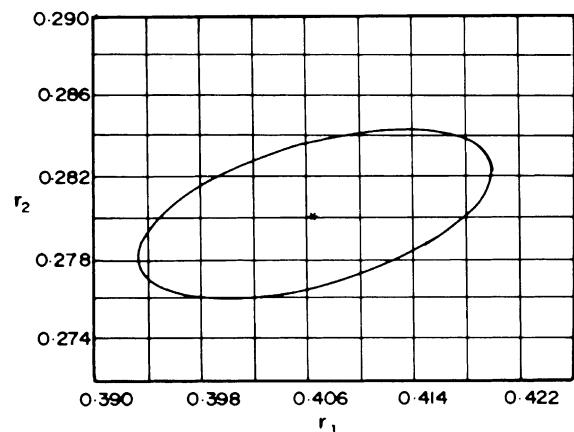


Fig. 7. 95% Joint confidence region of  $r_1$  and  $r_2$  values by RREVM for MPDSK-*co*-MMA copolymer system.

in the feed is higher than that of the azeotropic composition, then the composition of MPDSK in the copolymer will be less than that in the feed. The product  $r_1 r_2$  is much less than 1 suggesting that the system shows strong alternating tendency. The azeotropic composition in terms of the mole fraction of MPDSK in the feed is given by the relation,

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

and it is equal to 0.5481.

### 3.8. Molecular weights

The number-average molecular weight ( $\bar{M}_n$ ) and weight-average molecular weight ( $\bar{M}_w$ ) of six different samples of copolymers determined by gel permeation chromatography, are presented in Table 5. The polydispersity indices ( $\bar{M}_w/\bar{M}_n$ ) of the copolymers range between 1.88 and 1.97. The theoretical value of polydispersity indices for polymers produced by radical combination and disproportionation are 1.5 and 2.0, respectively [37]. In the free radical homopolymerization of MMA, the radicals undergo termination mainly by disproportionation. The value of  $\bar{M}_w/\bar{M}_n$  for poly(MPDSK) also suggests that in the free radical homopolymerization of MPDSK, the radicals undergo termination mainly by disproportionation. The value of  $\bar{M}_w/\bar{M}_n$  in copolymerization is also known to depend on chain termination in the same way as in homopolymerization [38]. The values of  $\bar{M}_w/\bar{M}_n$  of these copolymers suggest a strong tendency for chain termination by disproportionation and this tendency increases with an increase in the mole fraction of MPDSK in the feed.

### 3.9. Glass transition temperature

The glass transition temperature ( $T_g$ ) of the polymers was determined by differential scanning calorimeter and is given in Table 6. All the copolymers show a single  $T_g$ , showing the absence of formation of a mixture of homopolymers or a block copolymer. The  $T_g$  values of poly(MPDSK), poly(MPDSK-*co*-MMA) [0.5599: 0.4401] and poly(MMA) are 137 °C, 130 °C and

Table 5  
Molecular weight data for the copolymers of MPDSK with MMA

Copolymers	$m_1^a$	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$M_w/M_n$
Poly(MMA)	0.2338	4.78	2.60	1.84
Poly(MPDSK- <i>co</i> -MMA)	0.3808	3.21	1.71	1.88
	0.4729	3.33	1.75	1.90
	0.5599	3.54	1.83	1.93
	0.6408	3.68	1.89	1.95
Poly(MPDSK)	0.7655	3.52	1.79	1.97

<sup>a</sup>  $m_1$  is the mole fraction of MPDSK in the copolymer.

Table 6

TGA and DSC data for MPDSK–MMA copolymer system

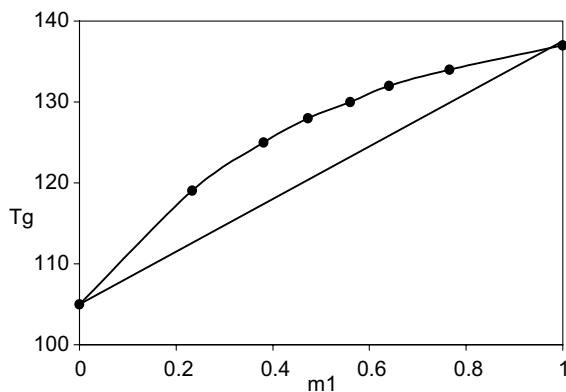
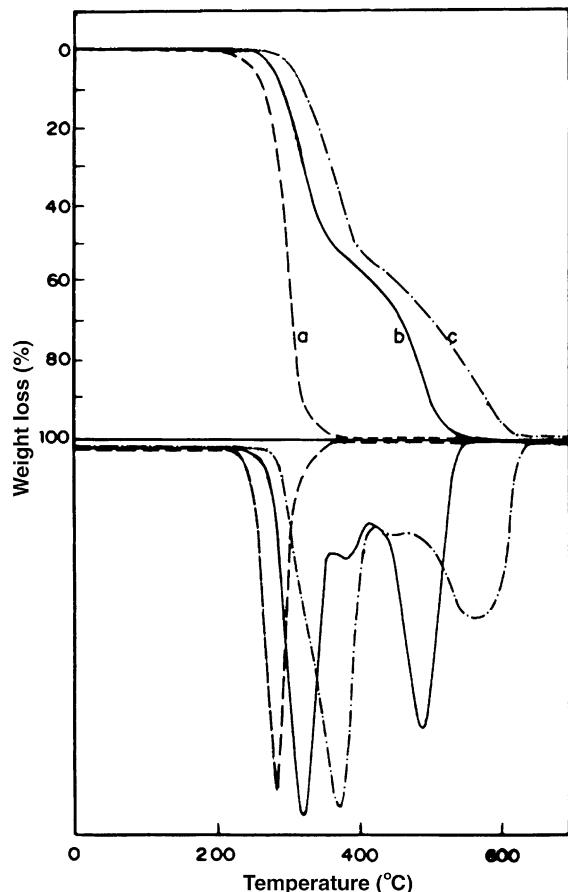
$m_1^a$	$T_g^b$ (°C)	DTR <sup>c</sup> (°C)			Temperature <sup>d</sup> (°C) at wt loss (%)				
		Stage 1	Stage 2	Stage 3	10%	30%	50%	70%	90%
Poly(MPDSK)	137	258–415	421–471	484–628	324	363	411	515	584
0.7655	134	250–363	371–458	463–574	309	347	400	495	537
0.6408	132	246–358	363–453	458–553	302	339	382	476	516
0.5599	130	243–347	356–415	421–544	295	326	370	463	476
0.4729	128	240–337	340–411	415–516	287	311	342	437	476
0.3808	125	236–326	332–390	396–471	280	305	329	392	439
0.2338	119	231–305	314–373	381–432	276	295	305	355	399
Poly(MMA)	105	224–374	—	—	271	284	295	305	314

<sup>a</sup> Mole fraction of MPDSK in copolymers.<sup>b</sup>  $T_g$ —Glass transition temperature (°C).<sup>c</sup> Decomposition temperature (°C) range.<sup>d</sup> Temperature (°C) corresponding to the weight loss (%).

105 °C, respectively. The high  $T_g$  value of poly(MPDSK) and its copolymers may be due to the inflexible and bulky pendant chalcone units and the short methyl chains, which facilitate chain entanglement. The  $T_g$  of the copolymer decreases with decrease in MPDSK content in the polymer chain. The variation of  $T_g$  with copolymer composition is shown in Fig. 8.

### 3.10. Thermogravimetric analysis

Thermal stability of different copolymer samples was studied in air by TGA. The TGA traces of poly(MPDSK), poly(MPDSK-*co*-MMA) [0.5599:0.4401] and poly(MMA) are shown in Fig. 9. Table 6 gives the TGA data of the copolymers. The copolymers undergo a three-stage decomposition. The actual decomposition temperature range depends on the composition of the constituent monomeric units in the copolymer chain. Poly(MPDSK) and poly(MPDSK-*co*-MMA) [0.5599:0.4401] show 50% weight loss at 411 and 370 °C, respectively. The initial decomposition temperature (IDT) and

Fig. 8. Variation of  $T_g$  with copolymer composition.Fig. 9. TGA curves for (a) poly(MMA), (b) poly(MPDSK-*co*-MMA) [0.5599:0.4401] and (c) poly(MPDSK).

thermal stability of the copolymer increase with increase in the amount of MPDSK units in the copolymer. These thermal studies strongly indicate that the copolymers

have very good thermal stability required for negative type photoresists.

### 3.11. Photocrosslinking properties

The photocrosslinking properties of the copolymer samples having a photosensitive chalcone moiety have been examined in chloroform solution with concentration of 24 mg/L in the presence and absence of photosensitizers. Polymer solutions were irradiated with a mercury lamp (UV source) at room temperature in the presence of air. The UV absorption spectra of the copolymers before and after irradiation are shown in Fig. 10. Initially, the polymer shows a UV absorption band at 359 nm due to the  $\pi-\pi^*$  transitions of  $>\text{C}=\text{C}<$  of the pendant chalcone moiety. On irradiation an isosbestic point was observed at 284 nm and the intensity of

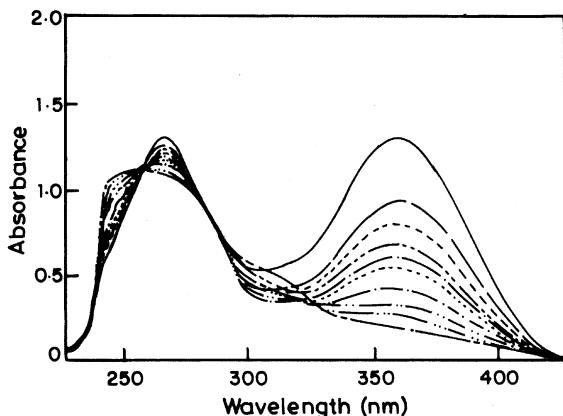
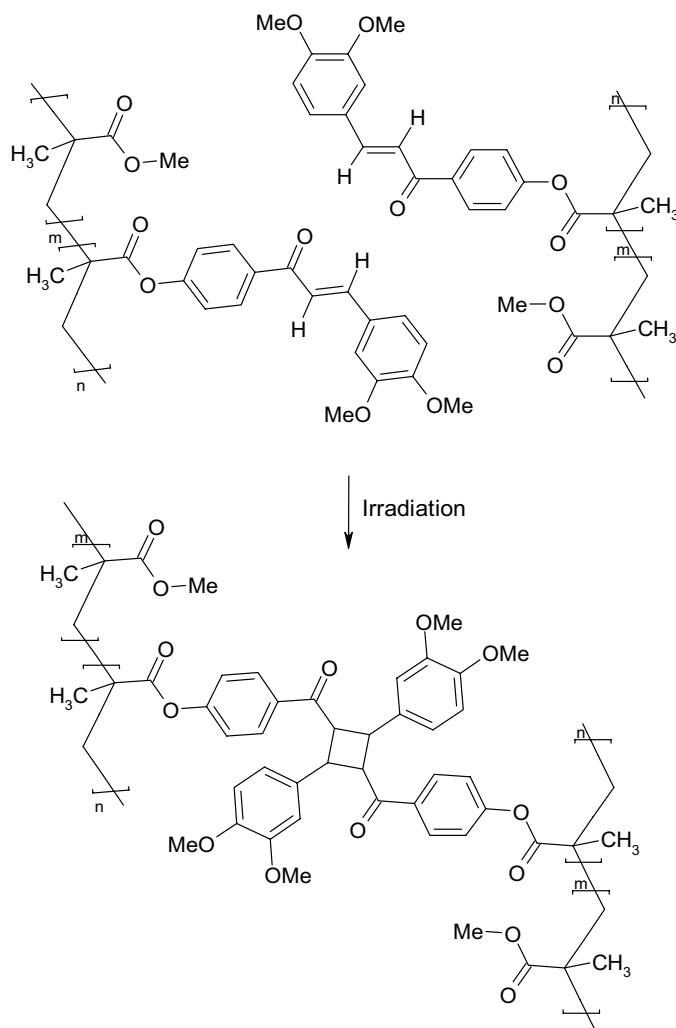


Fig. 10. UV absorption spectra of poly(MPDSK-*co*-MMA) (0.5599:0.4401) before and after irradiation.



Scheme 2. Photocrosslinking reaction of poly(MPDSK-*co*-MMA).

the band at 359 nm decreases very rapidly with irradiation time, disappearing almost completely within 10 min of irradiation. The copolymer became insoluble within 90 s of irradiation time in polar aprotic and chlorinated solvents, in which it was easily soluble before subjecting it to irradiation. This is clearly due to the crosslinking of the polymer chains through  $2\pi + 2\pi$  cycloaddition, which destroys conjugation in the entire  $\pi$ -electron system [39,40]. The photocrosslinking reaction of poly(MPDSK-*co*-MMA) is shown in Scheme 2. In chloroform solution, poly(MPDSK) shows photoconversions of 22%, 41% and 59% after 5, 15 and 30 s of irradiation time, respectively, and about 94% conversion occurs within 300 s of irradiation. In the copolymers, the photoconversion rate of the chalcone double bond depends on the copolymer composition, and it increases with increase in MPDSK content in the chain (Fig. 11).

When chloroform solutions of the polymers at higher concentration (520 mg/L) were irradiated for 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 FT-IR spectrum of the irradiated polymer shows the shifting of the carbonyl peak to a higher wavelength,  $1685\text{ cm}^{-1}$  that is attributed to the loss of the extended conjugation (with olefinic and the dimethoxyphenyl groups) after the photocrosslinking reactions. The decrease in the intensity of absorption peak at  $1599\text{ cm}^{-1}$  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 (Scheme 2, Figs. 10 and 11).

In order to observe the effect of sensitizers on the rate of disappearance of  $>\text{C}=\text{C}<$  of the chalcone unit of the copolymer, the photocrosslinking reactions were carried out in the presence of various triplet sensitizers such as benzoin, benzophenone, etc., but they are not effective in increasing the sensitivity further. This behavior is similar to that reported for photosensitive polymers having units such as  $\alpha$ -cyanocinnamic ester [41] and  $\alpha$ -phenylmaleimide [42], which have high photosensitivity but cannot be sensitized. This behavior of the polymer strongly indicates that the photocrosslinking might not be taking place through the triplet (T) state, but alternatively through singlet state electrons leading to a one step, concerted (2 + 2) cycloaddition [43]. As these polymers with a pendant chalcone moiety have good photo-reactivity and become insoluble after exposure to UV light, it might be expected that they could be used for negative photoresist applications.

#### 4. Conclusions

Six copolymers of MPDSK and MMA were prepared using BPO as initiator in MEK at  $70\text{ }^\circ\text{C}$ . FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy reveals the presence of both monomeric constituents in the copolymer. The solubility of the copolymers was tested in different organic solvents. The copolymer compositions were determined by  $^1\text{H}$  NMR method. The monomer reactivity ratios were obtained by the F-R, K-T and Ext. K-T methods, as well as by a non-linear error-in-variables model (EVM) method using the computer program RREVM. The values of  $r_1$  and  $r_2$  are less than unity indicating that the system gives rise to an azeotropic polymerization at a particular composition. The value of the product  $r_1r_2$  indicates a strong tendency to alternation. Gel permeation chromatography data showed that the values of polydispersity index of the copolymers range between 1.88 and 1.97. This suggests a strong tendency for chain termination by disproportionation and the tendency increased with increase in MPDSK content in the feed. TGA analysis indicated that the initial decomposition temperature increases with increase in MPDSK content in the copolymers. The photosensitivity of the copolymer was studied in chloroform solution by irradiation with a high pressure Hg lamp, and the spectral changes in the UV absorption intensity were recorded at predetermined time intervals for each exposure to irradiation. The photoconversion rates of poly(MPDSK) were about 22%, 41% and 59% after 5, 15 and 30 s of irradiation time, respectively, and in the case of copolymers, the extent of photoconversion of the chalcone double bond depends on the copolymer composition. It was observed that the conversion rate was higher at larger mole fractions of MPDSK in the copolymer. Copolymers were found to be insoluble after

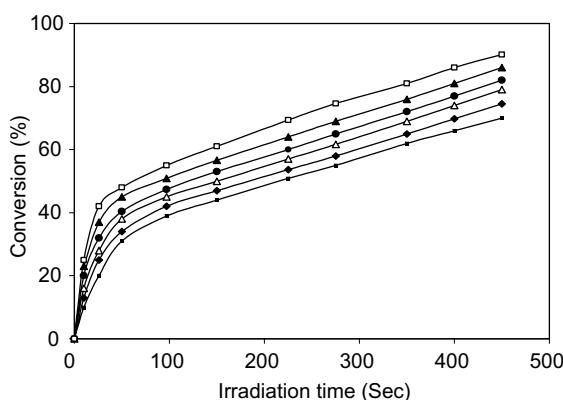


Fig. 11. Rate of disappearance of chalcone double bond of poly(MPDSK-*co*-MMA) having different composition with irradiation with UV light. (■) (0.2338:0.7662), (◆) (0.3808:0.6192), (△) (0.4729:0.5278), (●) (0.5599:0.4401), (▲) (0.6408:0.3592), (□) (0.7655:0.2345).

45 s of irradiation, indicating the high photoreactive nature of the MPDSK unit.

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