

Copolymers of 4-(4'-Chlorocinnamoyl)phenyl Methacrylate and Methyl Methacrylate: Synthesis, Characterization and Determination of Reactivity Ratios

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ABSTRACT: 4-(4'-Chlorocinnamoyl)phenyl methacrylate (CCPMA) was synthesized and copolymerized with methyl methacrylate (MMA) in methyl ethyl ketone at 60°C using benzoyl peroxide as a free radical initiator. The copolymers were characterized by UV, IR, ¹H-NMR, and ¹³C-NMR spectroscopic techniques. The compositions of copolymers were determined by ¹H-NMR analysis. The reactivity ratios of the monomers were determined using the Finemann-Ross ($r_1 = 2.18$ and $r_2 = 0.72$) and Kelen-Tüdös ($r_1 = 2.11$ and $r_2 = 0.72$) methods. The molecular weights (M_w and M_n) of the copolymers were determined by gel permeation chromatography. Thermogravimetric analysis of the copolymers reveal that the thermal stability of the copolymers decreases with an increase in the mol fraction of MMA in the copolymers. Glass transition temperatures of the copolymers were found to increase with an increase in the mol fraction of CCPMA in the copolymers. The photo reactivities of the copolymers were investigated as thin films. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1412–1418, 2000

Key words: 4-(4'-chlorocinnamoyl)phenyl methacrylate; methyl methacrylate; copolymerization; reactivity ratio; photo conversion

INTRODUCTION

Many polymers with reactive functional groups are now being synthesized, tested, and used not only for their macromolecular properties but also for the properties of the functional groups.¹ Polymers with pendant cinnamoyl groups are well known, and have been used as photoresists.^{2,3} They find applications in microlithography,⁴ printing materials,⁵ energy exchange materials,⁶ etc. The synthesis and photochemical properties of poly (vinyl-*trans*-benzalacetophenone),⁷ poly (2-cinnamoyloxyethyl methacrylate)⁸, products of poly (4-vinylaceto-

phenone) with aryl aldehydes,⁹ and many other systems have been reported.^{10–15} Polymers with a combination of properties such as high photosensitivity, good thermal stability, and good solubility are required for practical use as a photoresist. Photocrosslinkable polymers obtained from the polymerization of vinyl monomers such as vinylphenyl cinnamates, vinylphenyl α -styryl acrylates, isopropenylphenyl cinnamates, isopropenylphenyl β -styryl acrylate, β -vinylxyethyl cinnamates, β -styrylacrylates, β -vinylxyethylxychalcones,¹⁶ and copolymers of 2-cinnamoyloxyethyl methacrylate¹⁷ have been reported.

The present research work was undertaken with a view to develop new photoresists based on the copolymers of 4-(4'-chlorocinnamoyl)phenyl methacrylate with methyl methacrylate. In the

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present article, the synthesis, characterization, thermal stability, and photosensitive properties of copolymers of 4-(4'-chlorocinnamoyl)phenyl methacrylate with methyl methacrylate and the reactivity ratios of the comonomers are reported.

EXPERIMENTAL

Materials

4-(4'-Chlorocinnamoyl)phenyl methacrylate (CCPMA) was prepared by reacting 4-(4'-chlorocinnamoyl)phenol with methacryloyl chloride in the presence of triethylamine in methyl ethyl ketone (MEK) by following the procedure described for the preparation of 4-cinnamoylphenyl methacrylate reported elsewhere.¹⁸ Benzoyl peroxide (BPO) was recrystallized from a 1 : 1 mixture of chloroform and methanol. Methyl methacrylate (MMA) was freed from the inhibitor by washing with 5% NaOH solution followed by distilled water, and after drying over anhydrous sodium sulphate it was distilled under vacuum. The solvents were purified by distillation.

Copolymerization

Copolymerization of CCPMA and MMA, having six different feed compositions, was carried out in MEK at 60°C using BPO as an initiator. Appropriate amounts of CCPMA, MMA, and MEK were mixed in a polymerization tube, purged with N₂ for 20 min, and kept at 60 ± 1°C in a thermostat. After the required time (≈2 h), the reaction mixture was added to excess methanol. The product was washed with methanol and purified by reprecipitation from a solution of the polymer in chloroform by methanol. Finally, the product was filtered and dried under vacuum.

Measurements

Ultraviolet spectra of the polymers were recorded with an Hitachi UV-2000 spectrophotometer. Infrared spectra were obtained with a Hitachi 270-50 spectrophotometer using KBr pellets. ¹H- and ¹³C-NMR spectra in DMSO(d₆) solution were recorded on a JEOL JNX-100 FT-NMR spectrometer with tetramethylsilane (TMS) as an internal reference. Thermogravimetric analysis (TGA) was performed with a Mettler TA 3000 thermal analyser in air at a heating rate of 15°C min⁻¹. Molecular weights (\overline{M}_w and \overline{M}_n) of the polymers were determined by a Waters 501 gel permeation

chromatograph equipped with a differential refractive index detector. The molecular weights were calibrated against polystyrene standards using tetrahydrofuran as the eluent.

Photoreactivity Measurements

The photoreactivities of the copolymers were measured as thin films formed on a quartz plate from 2% solution in chloroform, and irradiated at room temperature in air with a high-pressure Hg lamp (Toshiba SHL-100 UV, 75 W) for different time intervals at a distance of 10 cm. After each exposure the UV spectrum of the polymer film was recorded at intervals and the rate of photocrosslinking was followed by a decrease in UV absorption intensity at 310 nm using the following expression.

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

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

RESULTS AND DISCUSSION

Copolymerization of CCPMA with MMA in MEK was studied for molar fractions of CCPMA ranging from 0.10 to 0.85 in the monomer feed. The reaction time was selected to give conversions less than 10% to satisfy the differential copolymerization equation.¹⁹ The data on the composition of feed and copolymer is presented in Table I. The copolymer monomeric units are shown in Scheme 1.

Solubility

As solubility is one of the important requirements for a photosensitive polymer, the solubilities of the copolymers in various organic solvents were tested. These were easily soluble in polar aprotic solvents such as dimethylformamide, *N*-methyl-2-pyrrolidone, dimethyl acetamide, dimethyl sulfoxide, tetrahydrofuran, etc., and chlorinated solvents such as chloroform and methylene chloride. These were insoluble in hydrocarbons such as benzene, toluene, xylene, and also in hydroxy group containing solvents such as methanol, ethanol, and 2-propanol.

Table I Composition, Molecular Weights, and Polydispersity Index Values of Polymers

M_1^a	Conversion (%)	C^b	m_1^c	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
0.10	10.20	0.47	0.14	5.42	2.75	1.97
0.20	8.34	1.05	0.28	5.47	2.94	1.86
0.35	9.60	2.45	0.48	4.93	2.70	1.82
0.50	7.25	3.58	0.57	5.26	3.02	1.74
0.65	8.35	9.63	0.78	3.91	2.45	1.59
0.85	9.25	36.33	0.93	—	—	—

^a The mol fraction of CCPMA in the feed.

^b The ratios of the integrated intensities of aromatic protons to that of methoxy protons in the ¹H-NMR spectra of copolymers.

^c The mol fraction of CCPMA in the copolymer.

UV Spectra

The ultraviolet spectra of the copolymers show an absorption maxima at 312 nm due to the $\pi-\pi^*$ transitions of $>C=C<$ of the pendant chalcone chromophore present in the CCPMA units.

Infrared Spectra

The strong absorptions at 1760 and 1640 cm^{-1} in the spectra of poly(CCPMA-co-MMA) [0.57: 0.43] (Fig. 1) are due to the carbonyl stretching of ester and keto groups, respectively. A strong band at 1620 cm^{-1} corresponds to the olefinic group flanked between the ketone and phenyl group of the pendant chalcone unit. The aromatic C=C stretching appears at about 1520 cm^{-1} . Peaks at 740–770 cm^{-1} may be assigned to the aromatic C—H out-of-plane bending, and those at 1445 cm^{-1} may be assigned to CH₃ bending vibrations.

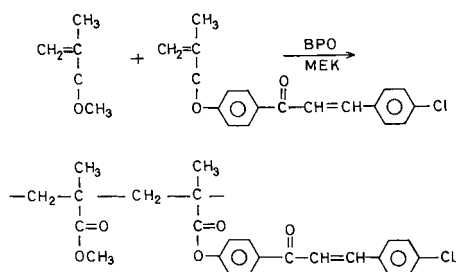
¹H-NMR Spectra

The ¹H-NMR spectrum of poly(CCPMA-co-MMA) [0.57: 0.43] is presented in Figure 2. Multiplet resonance absorptions at 8.11–7.23 ppm are due to the aromatic protons of CCPMA. Resonance signals at 6.43 (d) and 5.85 (d) ppm may be as-

signed to olefinic protons of the cinnamoyl group. The methoxy proton resonance of the MMA unit appears at 3.81 ppm. A broad signal centered at 1.76 ppm arises due to the backbone methylene protons. A broad signal centered at 1.01 ppm corresponds to the α -methyl protons of the both monomers units.

¹³C-NMR Spectra

The proton decoupled ¹³C-NMR spectrum of copoly(CCPMA-MMA) is shown in Figure 3. The chemical shift assignments were made from the off-resonance decoupled spectra of the copolymers. The resonance signals at 193.2 and 174.3 ppm are due to the keto and ester carbonyl carbons, respectively. The signal at 154.2 ppm is assigned to the aromatic carbon attached to the esteric oxygen. The group of signals at 144.6–122.3 ppm arises from other aromatic carbons and olefinic carbons of the pendant cinnamoyl phenyl groups in the CCPMA unit. The methoxy carbon signal of MMA unit is observed at 58.4 ppm. The signal at 18.9 ppm corresponds to the α -methyl carbon of both types of monomer units.



Scheme 1

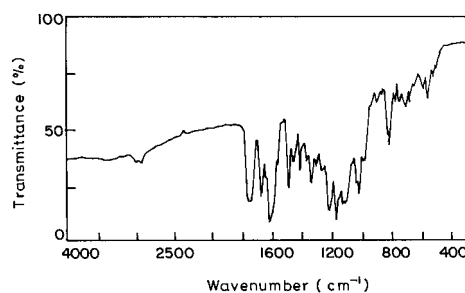


Figure 1 Infrared spectrum of poly(CCPMA-co-MMA) [0.57 : 0.43].

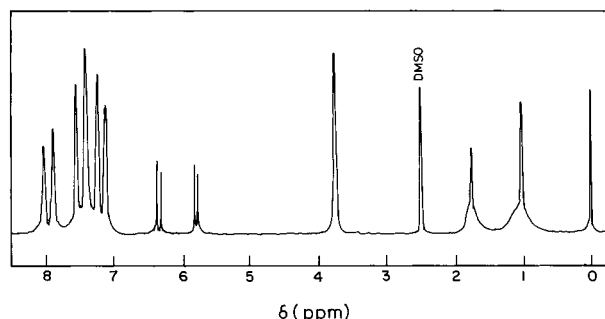


Figure 2 $^1\text{H-NMR}$ spectrum of poly(CCPMA-co-MMA) [0.57 : 0.43].

Copolymer Compositions

The $^1\text{H-NMR}$ technique is well established as a simple, rapid, and accurate method for the determination of copolymer composition.^{20–22} The assignment of resonance peaks in the $^1\text{H-NMR}$ spectrum allow accurate determination of both kinds of monomeric units incorporated into the copolymers. Thus, the mol fraction of CCPMA in the copolymer was determined from the integrated intensities of aromatic protons (8.11–7.23 ppm) and methoxy protons (3.86 ppm) using the following expression.

$$\text{Mol fraction of CCPMA } (m_1) = \frac{3C}{8 + 3C}$$

where C is the ratio of the integrated intensities of aromatic protons to that of methoxy protons in the $^1\text{H-NMR}$ spectrum of copolymer. Table I gives the values of C and the corresponding mol fractions of CCPMA in the copolymer samples.

Copolymerization Reactivity Ratios

The copolymerization behavior of the comonomers can be better understood by the determination of reactivity ratios. From the monomer feed ratios and the copolymer compositions, the reactivity ratios of CCPMA and MMA were determined by the application of Finemann-Ross (F-R) and Kelen-Tüdös (K-T) methods. In the latter method, all the data are weighed equally, and thus the method is insensitive to transposition of data.^{23–25} The significance of parameters of F-R and K-T equations are presented in Table II.

The reactivity ratios were determined by a least-squares fit through the H-G points or ξ - η points. Figure 4 gives the ξ vs. η plot due to the

K-T method. The reactivity ratios obtained from the F-R and K-T methods are: F-R method— r_1 (CCPMA) = 2.18 and r_2 (MMA) = 0.72; K-T method— r_1 (CCPMA) = 2.11 and r_2 (MMA) = 0.72.

The product of r_1 and r_2 indicates that the system copolymerizes statistically. The reactivity of growing radicals of both CCPMA and MMA as measured by the values of $1/r_1$ and $1/r_2$ strongly suggests that the growing radicals of both monomeric ends prefer to add to the CCPMA monomer, thus leading to the formation of a copolymer with a higher content of CCPMA.

Molecular Weights

The number- and weight-average molecular weights of poly(CCPMA) and five different samples of copolymers, determined by gel permeation chromatography, are presented in Table I. The polydispersity index of the copolymers ranges between 1.59 to 1.97. The theoretical values of $\overline{M}_w/\overline{M}_n$ for polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively.²⁶ In the homopolymerization of MMA, the radicals undergo termination mainly by disproportionation. The value of $\overline{M}_w/\overline{M}_n$ in copolymerization is also known to depend on chain termination in the same way as in homopolymerizations.²⁷ The values of $\overline{M}_w/\overline{M}_n$ of these copolymers suggest a strong tendency for chain termination by disproportionation at high mole fractions of MMA and recombination at high mole fractions of CCPMA in the feed.

Glass Transition Temperatures

The glass transition temperatures (T_g) of copolymers were determined by differential scanning calorimetry, and the data are presented in Table

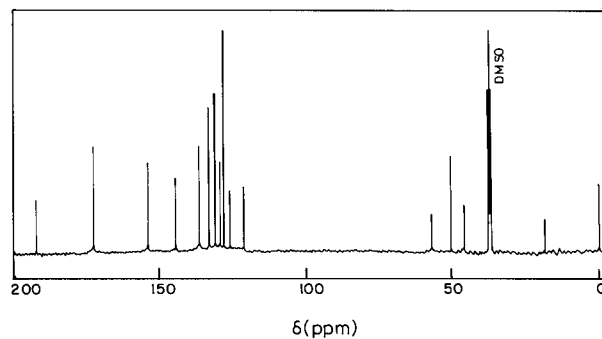


Figure 3 $^{13}\text{C-NMR}$ spectrum of poly(CCPMA-co-MMA) [0.57 : 0.43].

Table II F-R and K-T Parameters for the Copolymerization of CCPMA with MMA

$F = M1/M2$	$f = M1/M2$	F-R Parameters		K-T Parameters	
		$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
0.11	0.16	-0.57	0.07	-1.17	0.15
0.25	0.38	-0.40	0.16	-0.70	0.28
0.53	0.92	-0.04	0.30	-0.05	0.42
1.00	1.32	0.24	0.75	0.20	0.64
1.85	3.54	1.32	0.96	0.96	0.70
5.66	13.28	5.23	2.41	1.85	0.85

α is equal to 0.41.

III. The T_g of poly(CCPMA) is 127°C, and that of poly(MMA) is 105°C. The results clearly indicate that the T_g values of copolymers depend on the composition of comonomers and decrease with decreasing CCPMA content in the polymer chain.

Thermogravimetric Analysis

Thermal stability of the copolymers was measured by TGA under thermooxidative conditions, and the data are presented in Table III. The copolymers underwent decomposition in two distinguished stages similar to poly(CCPMA) in air. The actual decomposition temperature range of the two stages as well as the initial decomposition temperature (IDT) of the copolymers depend on the copolymer composition and the IDT shifts towards higher temperature with an increase in the CCPMA content. However, one important observation is that as the CCPMA content in the copolymer decreased, the weight loss increased in the first stage and decreased in the second stage for all the copolymers. The total weight loss was about 98%.

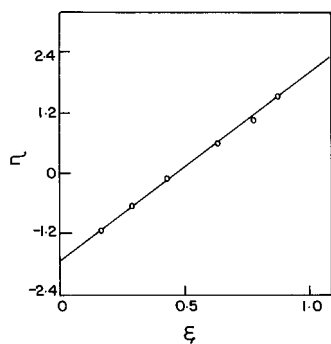


Figure 4 Kelen-Tüdös plot for the CCPMA-MMA copolymer system.

Photocrosslinking Properties

Poly(CCPMA) and the copolymers were cast as thin films with the thickness of $1.5 \pm 0.2 \mu\text{m}$ from chloroform solutions on quartz slides, and the photocrosslinking properties have been examined by irradiating the cast film with a high-pressure Hg lamp and measuring the UV-absorption intensity due to the pendant cinnamoyl group of CCPMA. The UV absorption spectra of the copolymers before and after irradiation are shown in Figure 5. The rate of disappearance of the chalcone double bond with irradiation time is shown in Figure 6. An isobestic point at 264 nm was observed in the initial irradiation, and this can be attributed to the *trans-cis* isomerization of the pendant chalcone units after irradiation. Further irradiation for 20–30 s causes another isobestic point at 232 nm. The UV absorption intensity at 311 nm decreases with further irradiation time. This behavior clearly indicates the formation of the cyclobutane ring by the 2+2 addition of pendant chalcone units of the polymer, which destroys conjugation in the entire π -electron system and, hence, results in a decrease in UV absorption intensity due to the chalcone units.^{28,29} The photoconversions for poly(CCPMA) were about 30 and 38% after an irradiation time of 30 and 60 s, respectively, and in the case of copolymers, the photoconversion rate of the chalcone double bond depends on the copolymer composition, and it increases with increased CCPMA content in the chain (Fig. 6). The copolymers are insoluble after about 45 s of irradiation, thus indicating the high photoreactive nature of the cinnamoyl phenyl group of CCPMA. The IR spectra of the photocrosslinked polymers obtained after 45 s of irradiation did not show the band at 1620 cm^{-1} corresponding to the conjugated olefinic group.

Table III Glass Transition Temperature and TGA Data for CCPMA-MMA Copolymers

m_1^a	T_g^b (°C)	DTR ^c (°C)		TWL ^{d,e} (%)				
		Stage 1	Stage 2	10	25	50	75	90
1.00	127	271–497 (71)	525–653 (28)	356	394	391	518	571
0.93	—	325–503 (67)	522–629 (28)	343	384	431	552	581
0.78	122	319–491 (71)	520–617 (25)	338	372	414	508	566
0.57	116	300–497 (74)	515–617 (18)	331	369	410	506	559
0.48	110	288–497 (80)	512–611 (15)	329	369	404	438	549
0.28	—	266–485 (82)	522–593 (6)	328	338	397	431	547
0.14	—	235–497 (92)	522–593 (6)	319	394	388	431	444

^a Mol fraction of CCPMA in copolymers.^b Glass transition temperature (°C).^c Decomposition temperature (°C) range.^d Temperature (°C) corresponding to the weight loss (%).^e Figures in parameters indicate weight loss (%) during the temperature range stated.

CONCLUSIONS

Poly(CCPMA) and the copolymers of CCPMA with MMA were synthesized by solution polymerization using a free radical initiator. The copolymers were characterized by IR, ¹H-NMR, and ¹³C-NMR spectroscopic techniques. The solubilities of the polymers were tested in different organic solvents. Copolymer compositions were determined by ¹H-NMR analysis. The reactivity ratios were calculated using Finemann-Ross and Kelen-Tüdös methods, and the values strongly suggest that the growing radicals of both monomeric ends prefer to add to CCPMA monomer resulting in the formation of copolymers with higher content of CCPMA than in the feed. Gel permeation chromatograph data showed that the values of \bar{M}_w/\bar{M}_n of the copolymers range between 1.59–1.97, which suggest a strong tendency for chain termination by disproportionation at high mol fractions

of MMA and recombination at high mol fractions of CCPMA in the feed. TGA results indicated that the initial decomposition temperature (IDT) shifts towards higher temperatures with the increase of CCPMA content in the copolymers. The photocrosslinking properties of copolymers were examined as thin polymer films by irradiation with a high-pressure Hg lamp, and changes in the UV absorption intensity were monitored at specific time intervals immediately after each irradiation. The photoconversion rate for poly(CCPMA) were about 30 and 38% after 30 and 60 s of irradiation time, respectively, and in the case of copolymers, the photoconversion rate of the chalcone double bond depends on the copolymer composition, and it was observed that the conversion rate was more at higher mol fractions of CCPMA in the copolymer. The copolymers were found to be

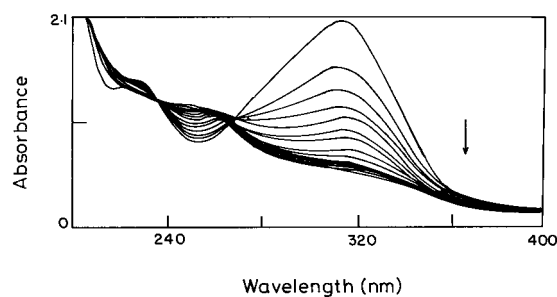


Figure 5 Changes in the ultraviolet spectra upon irradiation of poly(CCPMA-co-MMA); $m_1 : m_2$; 0.48:0.52); after 0, 0.25, 0.5, 1.5, 2.5, 4.5, 6.5, 9, 12, 16, 20, 25, and 30 min of irradiation.

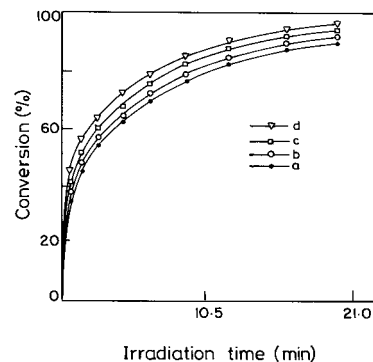


Figure 6 The rate of disappearance of the double bond (>C=C<) of poly(CCPMA-co-MMA); $m_1 : m_2$; (a) 0.28:0.72, (b) 0.48:0.52 (c) 0.57:0.43, (d) 0.78:0.22).

insoluble after about 45 s of irradiation, indicating the high photoreactive nature of the cinnamoyl phenyl group of CCPMA.

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