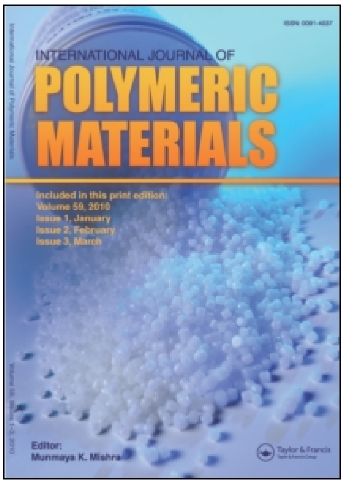

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Synthesis, Characterization, Reactivity Ratio and Photo Crosslinking Properties of the Copolymer of 4-Cinnamoyl Phenyl Methacrylate with Butyl Methacrylate

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Copolymers of 4-cinnamoyl phenyl methacrylate (4-CPMA) and n-butyl methacrylate (BMA) were prepared in a methyl ethyl ketone (MEK) solution with benzoyl peroxide (BPO) as an initiator at 70°C. They were characterized with UV, IR, ^{1}H-NMR, ^{13}C-NMR, TGA, DSC and gel permeation chromatography. Copolymers were prepared by using different feed ratio of monomers. The monomer reactivity ratios determined by the method of Kelen-Tudos (K-T) were r_1 (CPMA) = 2.32, r_2 (BMA) = 0.56. The glass transition temperature of the copolymer shows a single Tg indicating the formation of random copolymer for all of the monomer feed composition. Thermogravimetric analysis in air has shown that the initial decomposition temperature of the copolymer was above 220°C. The photocrosslinking properties of the copolymer were examined by UV irradiation with polymer film.

Keywords copolymerization, crosslinking, NMR, photoresists, reactivity ratio, UV irradiation

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INTRODUCTION

Technological applications of radiation-sensitive polymers have attained considerable interest and been applied to a wide research area in different fields such as photolithography [1–4], printing materials [5], and liquid crystalline [6–10] and nonlinear optical material [11–13]. The technological application of many photoresists has been reviewed in many research papers [14–16]. The polymers with a reactive functional group in their pendant unit give subsequent modification of the polymer for the required application. Polymers which consisting carbonyl group undergoes crosslinking upon irradiation with UV light are regarded as negative photoresist polymers [17–22]. Polymers with photosensitive groups such as the cinnamic esters of poly (acrylate and methacrylate) derivatives have been studied as photoresists [23–27]. Photolithographic patterning technology has made significant contributions to the microelectronics industry [28–30]. Photolithography is generally based on photocrosslinking reactions of polymeric photoresists. Resist materials need to be highly transparent in a visible region in order to be used as display device materials. In the past decade, we worked on several photosensitive polymers [31–32]. High photosensitivity, thermal stability and good solubility are the required properties for a photocrosslinkable polymer. For making a tailor-made polymer, a copolymerization of a monomer with a different photo functional group is the best technique, with a wide range of properties for various applications. In continuation of our previous research on photosensitive polymers, the synthesis, characterization, reactivity ratio and photo crosslinking properties of copolymers of 4-cinnamoyl phenyl methacrylate (4-CPMA) and BMA are reported in this article.

EXPERIMENTAL

Materials

BMA (CDH) was purified by washing successively with 5% NaOH solution and distilled water. Benzoyl peroxide (BPO) was recrystallized from a chloroform/methanol (1:1) mixture. 4-Cinnmoyl phenyl methacrylate (4-CPMA) was prepared by esterification reaction between 4-cinnamoyl phenol (22.4 g; 0.1 mol) and methacryloyl in the presence of triethylamine (10.1 g) in methyl ethyl ketone (EMK) at 0–5°C according to a procedure reported by Subramanian et al. [33]. All other chemicals were analytical grade samples and were used as received.

Copolymerization

Copolymers of 4-CPMA and n-butylmethacrylate (BMA) in five different compositions were prepared with a 2 M solution of monomer in methyl ethyl ketone in the presence of BPO (0.5% weight of monomer) as an initiator at 70°C. Appropriate amounts of monomer, solvent, and initiator were mixed in a polymerization tube, flushed with nitrogen gas for 20 min, and kept in a thermostat at 70°C. After a predetermined time (≈4 h) the reaction mixture was poured into an excess of methanol to isolate the copolymer. The copolymer was further purified by repeated reprecipitation into methanol from a solution of chloroform and finally dried in vacuum at 50°C.

Instruments

UV spectra were recorded with a Hitachi UV-2000 spectrophotometer. IR spectra were obtained from a Hitachi 270-50 spectrophotometer using KBr pellet. ^{1}H-NMR spectra were recorded on a Bruker 270 MHz/90 MHz FT-NMR spectrophotometer at room temperature using a 10–15% solution of $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C-NMR spectra were recorded on a Bruker CXP22.64 MHz FT-NMR spectrometer. Thermogravimetric analysis (TGA) was carried out using a Mettler TA 3000 thermal analyzer. TG traces were recorded on 10 mg samples in a nitrogen/air atmosphere at the heating rate of 15°C-min^{-1}. The glass transition temperature (Tg) of the polymer was determined by a Mettler TA-3000 differential scanning calorimeter. A Waters 501 HPLC instrument equipped with three ultrastyragel columns and an RI-401 detector was used for the determination of molecular weight of the polymers. Polystyrene was used as a standard for calibration of molecular weight with tetrahydrofuran as the mobile phase. The thickness of the polymer films were measured with a Solan Dektak 3030 surface profile measuring instrument.

Photoreactivity of the Polymer

The photoreactivity of the polymer was measured as follows. A thin film ($1.25 \pm 0.1\,\mu m$ thickness) of the polymer on a flat quartz plate was made with a 2% solution of polymer in chloroform by the spreading and evaporation of the solvent. Then the film was irradiated for a selected time interval with a high-pressure (75-w) mercury lamp kept at a distance of 10 cm. After each exposure, the UV spectrum of the film was recorded and the disappearance rate of >C=C< of the pendant α, β-unsaturated ketone unit was calculated using the following expression.

$$\text{Rate of Conversion (\%)} = (A_0 - A_T)/(A_0 - A_\alpha) \times 100$$

where A_0, A_T and A_α are absorption intensities due to the C=C group after the irradiation times $t = 0$, $t = T$ and $t = \alpha$ (maximum irradiation time), respectively.

RESULTS AND DISCUSSION

Photo polymers with appropriate amounts of pendant α, β- unsaturated ketone and butyl ester groups are prepared by the free radical copolymerization of 4-CPMA and BMA in a methyl ethyl ketone solution with benzoyl peroxide (BPO) as an initiator at 70°C (Scheme 1). For all the composition of the monomer feed, the copolymerization proceeded in a homogeneous solution. Table 1 gives the data of the molar composition of the mixture of the comonomer used and the resulting copolymers.

Solubility

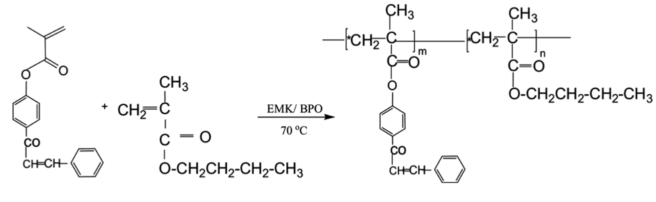
An important criterion that should be satisfied by most of the photosensitive polymers is solubility. The solubility of the copolymer was tested in various organic solvents. The copolymer was easily dissolved in aprotic polar solvents such as N-methyl-2-pyrolidene, dimethylformamide, dimethylacetamide, dimethylsulfoxide and tetrahydrofuran and chlorinated solvents such as chloroform and methylene dichloride. They were insoluble in hydrocarbons such as benzene, toluene and xylene and in protic solvents such as methanol, ethanol and 2-propanol.

IR- Spectra

The IR spectra (Figure 1) of the copolymer poly (4-CPMA-co-BMA) show more prominent 4-CPMA units due to the overlap of absorption of BMA monomer units. The absorption at 1750–1740 cm^{-1} is due to ester carbonyl stretching. The ketone carbonyl of the pendant chalcone unit of the photomonomer shows a strong peak at 1680 cm^{-1}. A strong absorption peak between 1620–1610 cm^{-1} corresponds to the olefinic double bond lying between the ketone and phenyl groups of a photoresist monomer. The aromatic –C=C– stretching and C–H out of plane bending vibrations are observed at 1510 and 760 cm^{-1}.

^{1}H-NMR Spectra

The 1H-NMR spectrum (Figure 2) of the copolymer poly (4-CPMA-co-BMA) shows distinct signals for both 4-CPMA and BMA units. The aromatic



Scheme 1: Copolymerization of 4-CPMA with BMA.

Table 1: Molecular weight and composition data for the copolymerization of 4-CPMA with BMA.

M_1	conversion (%)	C	m_1	$M_w \times 10^{-4}$	M_w/M_n
0.10	8.04	0.15	0.18	4.05	1.87
0.20	8.25	0.22	0.28	3.98	1.79
0.35	8.60	0.37	0.49	3.82	1.75
0.50	10.04	0.43	0.68	3.15	1.70
0.65	10.82	0.49	0.81	2.12	1.65

M_1 and m_1 are the mole fractions of CPMA in the feed and copolymer, respectively.

protons of the 4-CPMA unit shows a multiplet resonance signal between 8.06–7.23 ppm. Doublet resonance signals at 6.35 and 5.56 ppm are due to olefinic protons of the cinnamoyl group of the 4-CPMA unit. The signal obtained at 3.76 ppm is due to the presence of a $-OCH_2$ proton bonded to ester. The backbone $-CH_2$ proton signal of the two comonomers is observed between 2.76–1.85 ppm. A group of signals between 1.26–0.88 ppm may be due to α-methyl proton of 4-CPMA and BMA; these proton signals indicate the presence of tacticity of the copolymer chain.

^{13}C- Spectra

The ^{13}C-NMR spectra of poly (4-CPMA-co-BMA) shown in Figure 3, with the resonance signal at 174.2 ppm corresponding to esteric carbonyl carbon. The ketone carbon signal is observed at 189.9 ppm. The signals at 118 ppm are due to >CH=CH< (olefinic) carbon connected to the benzene ring. The other aromatic carbons gave signals at 145, 122, 127, 128 and 158.3 ppm. The methyl group of 4-CPMA and BMA showed signals at 18.2 ppm. The signal obtained at 45–43 ppm is assignable to the backbone carbons (—C—) of the

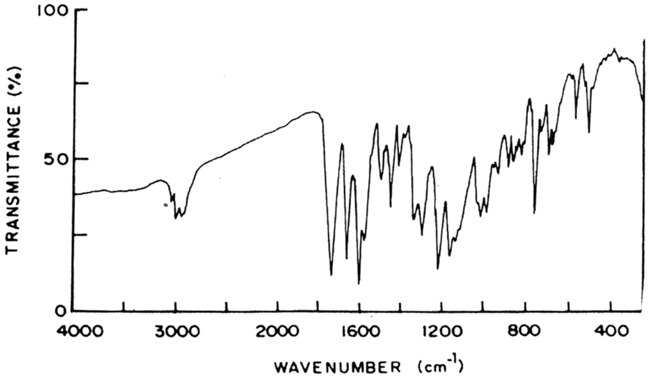


Figure 1: Infrared spectrum of copolymer poly (4-CPMA-co-BMA).

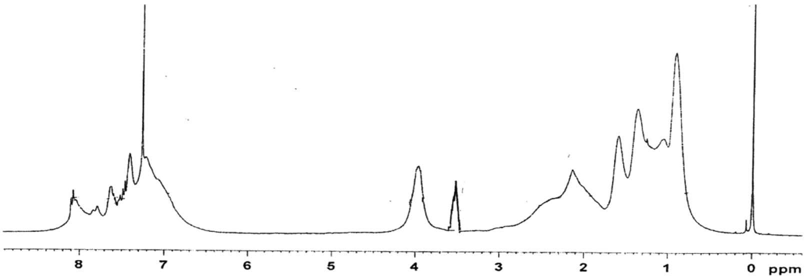


Figure 2: ^{1}H-NMR spectrum of copolymer poly (4-CPMA-co-BMA).

4-CPMA and BMA unit. The methylene carbon of the monomer BMA appears in the region 30.2, 19.33 and 18.3 ppm.

Molecular Weight

Table 1 gives the weight average ($\overline{M_w}$) and number average ($\overline{M_n}$) molecular weight and polydispersity index ($\overline{M_w}/\overline{M_n}$) values for the poly (4-CPMA) and copolymer samples. The ($\overline{M_w}$) values of the copolymer range from 2.12 to 4.05×10^{-4} Da, with polydispersity index values of 1.65–1.87, which seems to be the normal molecular weight distribution expected for the free-radical polymerization of (meth) acrylate monomers [34].

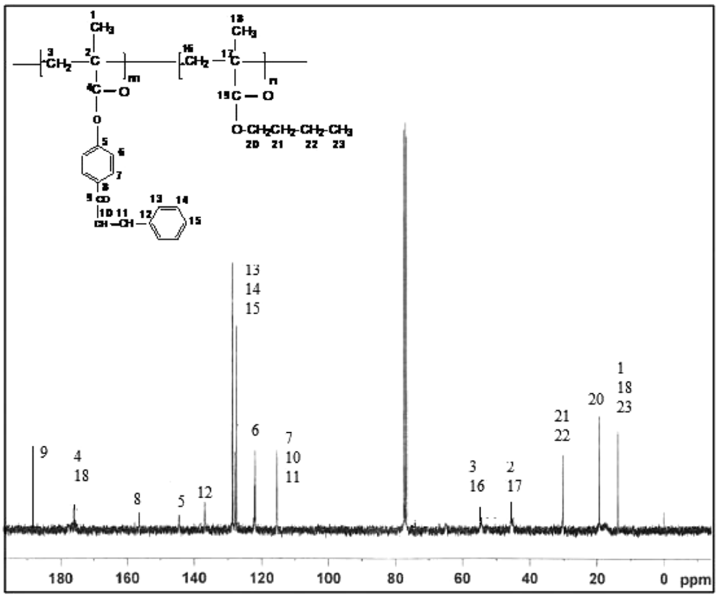


Figure 3: C^{13}-NMR spectrum of copolymer poly (4-CPMA-co-BMA).

Copolymer Composition

Copolymer composition was determined accurately by assigning the resonance peaks in the ^{1}H-NMR spectrum of the copolymer [35–38]. The molar fraction of CPMA in the copolymer was determined by the measurement of the integrated intensities of aromatic protons (9H) at 8.06–7.23 of the cinnamoyl phenyl group in the 4-CPMA and the total protons (3H) from both monomers giving the following expression

$$\text{Molar fraction of 4-CPMA} = 14C/(9\text{-}2C)$$

where C is the ratio of integrated intensity of aromatic protons to that of total protons in the ^{1}H-NMR spectrum.

The values of C and the corresponding molar fraction of CPMA in the copolymer sample are shown in Table 1, which clearly indicates that for all the monomers, the feed composition contains more CPMA.

Monomer Reactivity Ratios

Monomer reactivity ratios are important quantitative values for predicting the copolymer composition and elucidation of copolymerization behavior for any starting feed in batch, semibatch or continous reactors, and for understanding the kinetic and mechanic aspects of the copolymerization. The reactivity ratios of 4-CPMA and BMA were determined by monomer feed and resultant copolymer composition by the applications of the Kelen-Tudos methods, the linear method of r_1 and r_2 determination in which all data are weighed equally and which is insensitive to the transposition of data [39,40]. The reactivity ratio values obtained from the Kelen-Tudos plot are as follows

$$\begin{aligned} r_1(\text{4-CPMA}) &= 2.32 \\ r_2(\text{BMA}) &= 0.56 \\ r_1r_2 &= 1.16 \end{aligned}$$

The products of the reactivity ratio obtained from the above methods are greater than one that indicates random copolymerization of comonomer in the polymer chain. The value of $1/r_1$ (0.42) suggests that the reactivity of growing radical with a 4-CPMA unit seems to be higher towards its own monomer than BMA. Conversely, the reactivity of growing radical with BMA unit as observed by the value of $1/r_2$ (1.85) seems to be higher towards the 4-CPMA monomer than its own monomer. These observations clearly suggest that the copolymer chain contains more of 4-CPMA units than that of BMA.

Glass Transition Temperature (Tg)

The glass transition temperature (Tg) of poly (4-CPMA), poly (butyl methacrylate) and their copolymer is presented in Table 2. The copolymers exhibit a

Table 2: Tg and TGA data for copolymers of CPMA with BMA system.

m_1	m_2	Tg (°C)	DTR (°C) Stage 1	DTR (°C) Stage 2	IDT (°C)
0.00	1.00	20	200–350 (98)	–	205
0.18	0.82	105	–	–	–
0.28	0.72	114	254–461 (64)	505–650 (36)	240
0.49	0.51	118	274–485 (72)	512–665 (28)	260
0.68	0.32	124	284–393 (77)	410–600 (23)	274
0.81	0.19	–	–	–	–
1.00	0.00	147	220–452 (81)	450–600 (15)	242

m_1 and m_2 are molar fractions of CPMA with BMA, respectively, in the copolymer.
DTR = Decomposition Temperature Range, IDT = Temperature at which 10% weight loss of polymer occurred.

single glass transition temperature (Tg), thereby indicating the formation of a random copolymer for the monomer feed compositions. The Tg values for PCPMA and PBMA are 147 and 20°C. The Tg value of the copolymers depends on the copolymer composition and increases with an increase in the 4-CPMA content in the copolymer chain, which may be due to aromatic pendant groups (chalcone moieties) and the butyl group introduced into the polymer system.

Thermogravimetric Analysis

The rapid evaluation of the thermal stability of the polymer was done by TGA technique. Table 2 shows the differential TGA data for the two homopolymers and copolymer samples. The initial decomposition temperature (IDTs) of PCPMA and PBMA are 242 and 205°C, respectively. The IDT of the copolymers depends on the composition of the constituent monomer and increases with an increase of CPMA content in the copolymer. PBMA decomposes in a single stage in the temperature range of 200–350°C, with the weight loss about 98%. PCPMA undergoes thermo-oxidative decomposition in two stages, the first stage at 220–452°C with the weight loss about 81%, and the second stage at 450–600°C with the weight loss about 15%. All the copolymers undergo two stages similar to PCPMA. As the CPMA content in the copolymer increases, the weight loss increases in the first stage (254–381°C) and decreases in the second stage (400–650°C). The total weight loss of copolymers in both decomposition stages is about 97%.

Photocrosslinking Properties

The photocrosslinking reactions of polymers were carried out on thin polymer films which were cast from a chloroform solution of polymer on a quartz slide and by irradiation with a high-pressure mercury lamp in the absence of

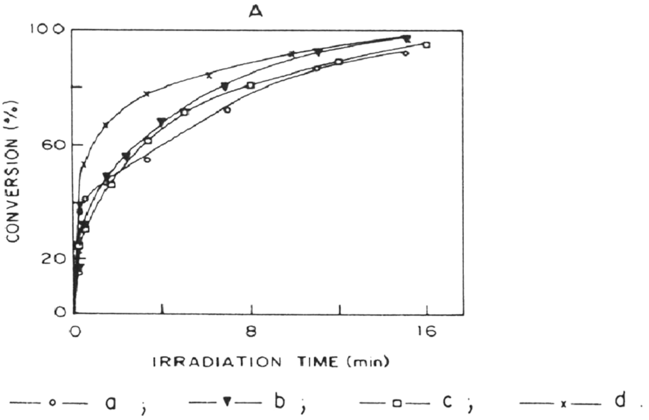
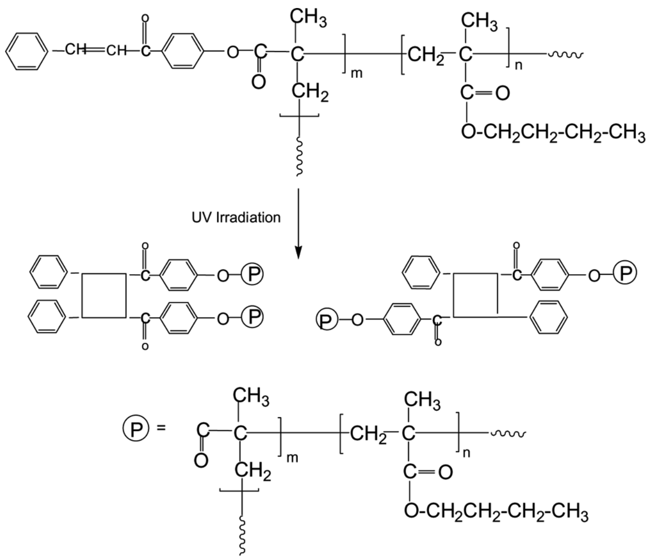


Figure 4: Rate of disappearance of double bond (C=C) of poly (4-CPMA-co-BMA) m_1:m_2 0.28:0.72 (b) 0.49:0.51 (c) 0.68:0.32 and (d) 0.81:0.19 up on irradiation at 340 nm.

photo sensitizer. The photocrosslinking properties of copolymers have been studied by irradiation of the polymer film, and by measuring the changes in the UV absorption intensity at 310–333 nm due to >C=C< of the pendant cinnamoyl group of the CPMA unit. Typical changes in the UV spectral pattern of the copolymer film for different time intervals of irradiation are presented in Figure 4. The copolymer shows an absorption peak at 350 nm due to π-π^* transition of pendant 4-cinnamoyl phenyl unit of 4-CPMA. An isobestic point occurs at 280 nm due to cis-trans isomerization during initial irradiation.



Scheme 2: Photo crosslinking of copolymer poly (4-CPMA-co-BMA).

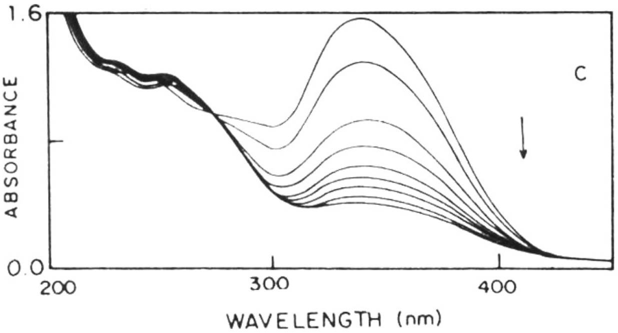


Figure 5: Change in the ultraviolet spectra upon irradiation of copolymer poly (4-CPMA-co-BMA) m_1:m_2, 0.81:0.19 after 0, 0.25, 0.5, 1.5, 3.5, 6, 10, 15, 20 min.

The absorption intensity at 350 nm decreases immediately with irradiation time and disappears almost completely with in 20 min of irradiation time. After irradiation of UV light, the copolymer became insoluble in polar aprotic and chlorinated solvents in which it was soluble before irradiation. The decrease in UV absorption intensity and the insoluble nature of the copolymer are due to the crosslinking of copolymer through $2\pi + 2\pi$ cyclodimerization of the C=C group of the pendant 4-CPMA unit. Scheme 2 shows $2\pi + 2\pi$ cycloaddition in the presence of UV light. The π electron system of the copolymer was destroyed by $2\pi + 2\pi$ cycloaddition and results in a decrease in the UV absorption intensity with irradiation time [41–42]. The rate of disappearance of the double bonds of the pendant cinnamoyl group in CPMA and for the copolymer sample with the irradiation time is shown in Figure 5. It is seen that the photoconversion rate for the copolymer is faster than that of CPMA content in the copolymer chain. The presence of butyl groups enhances the higher rate of photoconversion in the copolymer. Thus, the copolymer can be used as a negative photoresist in photolithographic applications.

CONCLUSIONS

The copolymer of CPMA with BMA was synthesized and characterized with UV, IR, ^{1}H-NMR, C^{13}-NMR and gel permeation chromatography. The TGA in air shows good thermal stabilities of the copolymers with the initial decomposition temperature starting at 220°C. The polydispersity index value showed that termination of copolymerization can be carried out via the free radical recombination method. The reactivity ratio values strongly suggest that the copolymer chain contains more 4-CPMA units than BMA monomer units. The rate of photocrosslinking of the copolymer films increases with an increase in the 4-CPMA content in the copolymer chain. The rate of curing of the copolymers occurs within 60s of irradiation in the absence of a sensitizer.

The photocrosslinking properties in the absence of photosensitizer reveals that the copolymer possesses higher rates of photoconversion, and they can find applications as photoresists and coating materials.

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