

Influence of the Comonomers (Styrene and Methyl Acrylate) on the Rate of Photocrosslinking of 4-[-3-(4-hydroxybenzylidene)-2-oxocyclohexylidene]methyl]-phenyl Acrylate

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ABSTRACT: [2,6-Bis(4-hydroxybenzylidene)cyclohexanone] (HBC) was prepared by reacting cyclohexanone and *p*-hydroxybenzaldehyde in the presence of acid catalyst. Acrylated derivative of HBC, 4-[-3-(4-hydroxybenzylidene)-2-oxocyclohexylidene]methyl]phenyl acrylate (HBA), was prepared by reacting HBC with acryloyl chloride in the presence of triethylamine. Copolymers of HBA with styrene (S) and methyl acrylate (MA) of different feed compositions were carried out by solution polymerization technique by using benzoyl peroxide (BPO) under nitrogen atmosphere. All monomers and polymers were characterized by using IR and NMR techniques. Reactivity ratios of the monomers present in the polymer chain were evolved by using Finnman-Ross (FR), Kelen-Tudos (KT), and extended Kelen-Tudos (ex-KT) methods. Average values of reactivity were achieved by the following three methods: r_1 (S) = 2.36

± 0.45 and r_2 (HBA) = 0.8 ± 0.31 for poly(S-*co*-HBA); r_1 = 1.62 ± 0.06 (MA); and r_2 = 0.12 ± 0.07 (HBA) for poly(MA-*co*-HBA). The photocrosslinking property of the polymers was done by using UV absorption spectroscopic technique. The rate of photocrosslinking was enhanced compared to that of the homopolymers, when the HBA was copolymerized with S and MA. Thermal stability and molecular weights (M_w and M_n) were determined for the polymer samples. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2494–2503, 2004

Key words: 4-[-3-(4-hydroxybenzylidene)-2-oxocyclohexylidene]methyl]phenyl acrylate; acryloyl chloride; reactivity ratios; Kelen-Tudos; photocrosslinking studies; crosslinking; photoresists; NLO

INTRODUCTION

Polymeric nonlinear optical (NLO) materials has several advantages over the conventional inorganic materials such as high-optical damage threshold, low dielectric constants, large optical nonlinearity, etc. Moreover, these polymer materials can be easily fabricated into a thin film and can be used in wave-guide form as required in several applications. There has been considerable interest in recent years to synthesize a multifunctionable macromolecular material for potential usage in different polymer fields. For NLO applications, the polymers with photocrosslinkable moiety were reported previously.¹ Side-chain polymers are usually prepared in the form of copolymers with NLO active materials attached to the polymer backbone via flexible spacers such as methylene units. Most of the photocrosslinkable polymers were prepared by the reaction of functionally reactive photo-

sensitive moiety with a polymer backbone.^{2,3} The systems, which are used for altering the property of the polymer containing NLO chromophore, were methyl methacrylate (MA),⁴ poly(styrene-*co*-acrylic acid ester),⁵ styrene-maleic anhydride,⁶ etc. Apart from the above examples, photocrosslinkable diblock polymers, such as polystyrene-*block*-poly(2-cinnamoyl ethyl methacrylate),^{7,8} poly(cinnamoyl ethyl methacrylate)-*block*-poly(acrylic acid),⁹ etc., were used to alter the physiochemical, thermal stability, and photocrosslinkable property of the polymer samples bearing the NLO active moiety. To investigate in this area, we chose arylidene polymers as our investigating materials to achieve our objectives. These arylidene compounds had previously been used as anti-inflammatory agents,¹⁰ antimicrobial agents,¹¹ UV absorbing stabilizers,^{12–14} and novel polyester synthesis,^{15,16} etc. Acrylated derivatives of these arylidene compounds were not reported so far in the literature for their potential use in the field of photocurable polymer materials. To investigate the effect of comonomers present in the polymer chain on the rate of photocrosslinking, the photocurable monomer was copolymerized with styrene (S) and MA, and their effect was estimated. Reactivity ratios of the monomers present in

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the polymer samples were evolved by using Finemann-Ross (FR), Kelen-Tudos (KT), and extended Kelen-Tudos (ex-KT)¹⁷⁻²¹ methods.

EXPERIMENTAL

Materials

S and MA (Aldrich, Milwaukee, WI) were distilled under vacuum before being used for copolymerization. Benzoyl peroxide (BPO) was recrystallized by using 1 : 1 (v/v) mixture of methanol and chloroform. All solvents employed for solubility measurements were used as received. Acrylic acid (Fluka, Buchs, Switzerland) and BPO (Fluka) were used for preparing acryloyl chloride. Acryloyl chloride was prepared by adopting the standard procedure given by Stampel.²²

Characterization

FTIR spectrum of the monomers and polymers was recorded on a Nicolet 20DXB spectrophotometer by using the solid KBr pellet method.

FT-NMR spectrum was recorded by using a Bruker 300 MHz instrument for monomer (CDCl₃ as a solvent) and polymers [d₆-dimethyl sulfoxide (d₆-DMSO) as a solvent].

Thermal behavior of the polymers was characterized by using a Mettler 3000 heating analyzer at a rate of 10°C/min in air. Molecular weights of the polymers were obtained by using a Shimadzu instrument, using tetrahydrofuran (THF) as an eluant at a flow rate of 0.3 mL/min.

UV absorption measurements were conducted on a Shimadzu model 160A spectrophotometer by dissolving polymers in THF (HPLC grade) solvent. Elemental analysis was done on Coleman C—H—N analyzer.

Synthesis of 2,6-bis(4-hydroxybenzylidene)cyclohexanone (HBC)

In a 500-mL round-bottom flask containing 160 mL methanol, 24.4 g (0.2 mol) of *p*-hydroxybenzaldehyde and 11.4 mL (0.1 mol) of cyclohexanone were added and fitted with a condenser and a mechanical stirrer. HCl gas was passed into the reaction mixture and stirring was continued at room temperature until the contents of the flask became dark pink in color. Then, the contents of the flask were poured into a large quantity of distilled water, and the precipitate was filtered and dried in a vacuum at 30°C. Recrystallization of the product was done by using methanol.

Yield = 28.3 g (92.5%). ¹H-NMR (CDCl₃, δ): 10.2 (2H, b), 7.2 (1H, s), 7.4 (1H, s), 7.5–7.8 (8H, m), and 2.2 (6H, m). IR (cm⁻¹): 3250 (—OH), 3032 (aromatic CH), 2942 (aliphatic CH), 1658 (C=O), and 1598 (vinylic). Elemental analysis

calculated for C₂₀H₁₈O₃ (306.4): C, 76.41%; H, 5.92%. Found: C, 76.36%; H, 5.91%.

Synthesis of 4-(e)-[(3Z)-3-(4-hydroxybenzylidene)-2-oxocyclohexylidene]methyl]phenyl acrylate (HBA)

HBA was prepared by taking 10.1 g (0.03 mol) of HBC and 4.9 mL (0.035 mol) of triethylamine in a 500-mL round-bottom flask containing 200 mL of ethyl methyl ketone (EMK), fitted with a mechanical stirrer and a pressure equalizer. Acryloyl chloride [2.7 mL (0.03 mol)] diluted with 25 mL EMK was taken in a pressure equalizer and was slowly added dropwise to the reaction mixture at 0–5°C. After the addition was completed, the reaction mixture was filtered and the filtrate was taken in a 250-mL separating funnel. The contents of the separating funnel were washed with distilled water and dried in anhydrous sodium sulfate. HBA was obtained by evaporating the solvent.

Yield = 10.9 g (92%). ¹H-NMR (CDCl₃, δ): 10.0 (1H, b), 7.0–7.8 (10H, m), 6.2 (2H, d), 6.4 (1H, t), and 2.1 (6H, s). ¹³C-NMR (CDCl₃, δ): 20, 24, 120.5, 122.7, 125.3, 127.4, 128.0, 128.9, 129.4, 129.8, 130.3, 130.1, 132.5, 133.7, 150.8, 163.2, and 188.0. IR (cm⁻¹): 3346 (—OH), 3040 (aromatic CH), 2936 (aliphatic CH), 1739 (ester C=O), 1657 (C=O), 1600 (vinylic), and 1254–1162 (O=C—O). Elemental analysis calculated for C₂₃H₂₀O₄ (360.4): C, 76.65%; H, 5.59%. Found: C, 76.61%; H, 5.60%.

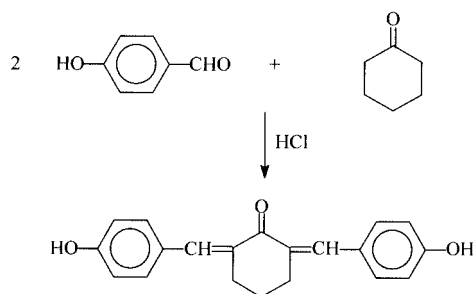
Synthesis of poly(HBA)

Poly(HBA) was prepared by the free-radical solution polymerization technique. HBA (1.0 g) dissolved in EMK and BPO (2 mg) was taken in a polymerization tube and degassed with oxygen-free nitrogen gas. The polymerization tube was kept in a constant temperature water bath at 70 ± 1°C for 24 h. After 24 h, the contents were poured into excess methanol, and the resultant precipitate was filtered and dried in vacuum at 40°C.

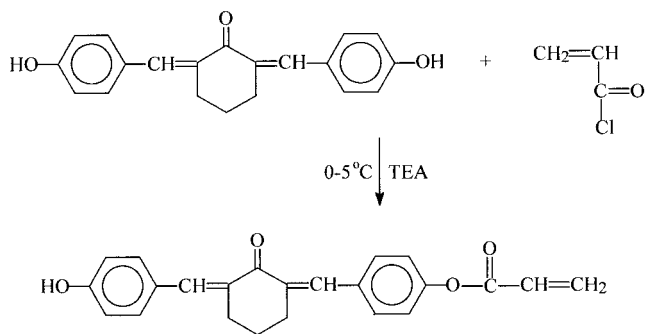
¹H-NMR (d₆-DMSO, δ): ¹H-NMR (d₆-DMSO, δ): 9.9 (1H, b), 7.2–7.8 (10H, m), and 2.2 (6H, m), 2.0 (1H, s) and 1.4 (2H, s). IR (cm⁻¹): 3407 (—OH), 3065 (aromatic CH), 2926 (aliphatic CH), 1733 (ester C=O), 1652 (C=O), 1602 (vinylic), and 1240–1132 (O=C—O).

Synthesis of poly(s-co-HBA)

Copolymers were prepared by taking different mole ratios of S and HBA monomers in feed composition. Appropriate quantities of S and HBA dissolved in EMK and BPO (1% w/w based on total weight of solvent and monomers 1 and 2) were taken in a polymerization tube and degassed with oxygen-free nitrogen gas. The tube was kept in a constant temperature water bath for a definite period of time so as to obtain the conversion under 15%. The contents were poured



Scheme 1 Synthesis of HBC.



Scheme 2 Synthesis of HBA.

into an excess amount of methanol and the resultant polymer was filtered and dried in a vacuum at 40°C. $^1\text{H-NMR}$ (d_6 -DMSO, δ): 9.8 (1H, b), 7.9–7.0 (15H, m), 2.2 (6H, m), 1.9 (2H, s), and 1.0–1.5 (4H, m). IR (cm^{-1}): 3259 (—OH), 3053 (aromatic CH), 2939 (aliphatic CH), 1739 (ester C=O), 1649 (C=O), 1596 (vinylic), and 1243–1163 (O=C—O).

Synthesis of poly(MA-co-HBA)

All the experimental conditions given in the above section was followed for the preparation of poly(MA-co-HBA).

$^1\text{H-NMR}$ (d_6 -DMSO, δ): 9.8 (1H, b), 7.0–8.0 (10H, m), 3.6 (3H, s), 2.2 (6H, s), 2.0 (2H, s) and 1.0–1.6 (4H, m). IR (cm^{-1}): 3422 (—OH), 3038 (aromatic CH), 2918 (aliphatic CH), 1734 (ester C=O), 1653 (C=O), 1609 (vinylic), and 1230–1166 (O=C—O).

Photoreactivity of the polymers

Photoreactivity of the polymers was studied by dissolving in THF and the resulting polymer solution was irradiated at selected time intervals by using a high-pressure mercury lamp at a distance of 15 cm. The rate of disappearance of >C=C< of the pendent α,β -unsaturated ketone unit of the polymer was followed by measuring the UV absorption intensity of the solution (around 350 nm) after each exposure interval by using the expression

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

where A_0 and A_t are the absorption intensities due to >C=C< chromophore after irradiation of times $t = 0$ and $t = t$, respectively.

RESULTS AND DISCUSSION

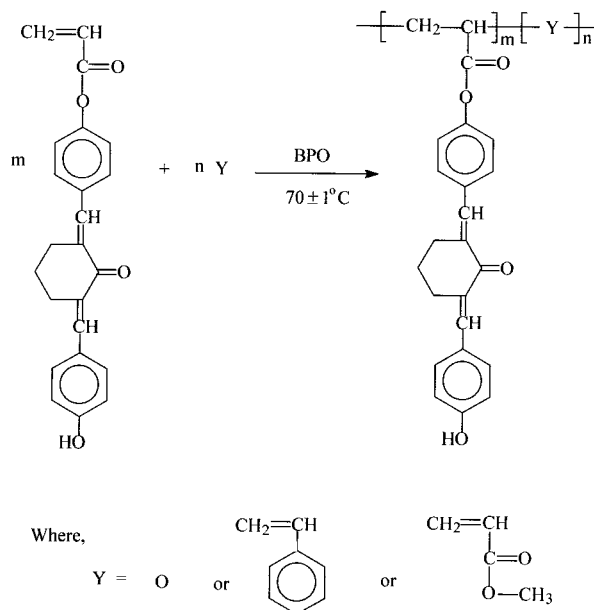
Synthesis of HBC was carried out by using the modified method of Claisen–Schmidt reaction (Scheme 1). HBA monomer was synthesized by using an acrylation process (Scheme 2). Homo- and copolymers of HBA were prepared by using a free-radical solution polymerization technique (Scheme 3). The feed com-

position experimental data for poly(S-co-HBA) and poly(MA-co-HBA) were presented in the Tables I and II, respectively.

Determination of copolymer composition

Copolymer composition was determined from the $^1\text{H-NMR}$ data of the polymer.^{23,24} From the chemical shift values of the $^1\text{H-NMR}$, it was evident that the copolymer chain contains both monomeric units.

$^1\text{H-NMR}$ spectrum of poly(S-co-HBA) clearly indicates that the methine (2H) protons of S and HBA units in the chain and the aromatic —OH (1H) protons of HBA units were well separated from each other. Because these two sets of chemical shifts were distinctly separated, their integral values were taken conveniently for the accurate determination of mole fraction of monomeric units present in the copolymer chain. The following equation was derived by using



Scheme 3 Copolymer constituent units of S, MA, and HBA.

TABLE I
Composition Data for Poly(S-co-HBA)

Feed composition (M ₁)	Conversion (%)	Integral value		C = I _m /I _{ar}	Copolymer composition (m ₁)
		I _m	I _{ar}		
0.15	12.3	0.51	2.038	0.2502	0.2502
0.30	4.9	0.672	1.734	0.3875	0.3875
0.50	10.5	3.279	5.161	0.6353	0.6353
0.70	5.6	1.825	2.296	0.7949	0.7949
0.85	3.5	6.438	6.859	0.9386	0.9386

[Monomer 1 + Monomer 2] = 0.5 mol/L. Solvent: EMK. Temperature: 70 ± 1°C. Initiator: BPO [1% (w/w) of monomers 1 and 2].

the ¹H-NMR values. Assume m₁ is the mole fraction of S present in the copolymer chain and m₂ (1 - m₁) is that of HBA. To derive the equation, we took two protons representing both S and HBA, and one aromatic —OH proton representing the HBA unit

$$C = \frac{\text{Integral value of methine proton (I}_m)}{\text{Integral values aromatic —OH proton (I}_{ar})}$$

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

On simplification,

$$m_1 = C$$

Integral values of I_m and I_{ar} were given in Table I.

In the case of poly(MA-co-HBA), the ¹H-NMR spectrum clearly indicates that the methoxy proton of the MA unit and the hydroxy proton (aromatic) of the HBA units present in the polymer chain were well separated and these two sets of integral values were taken for calculating the mole fraction of MA (m₁) and the mole fraction of HBA (m₂) present in the polymer chain. The equation used for calculation is

$$C = \frac{\text{Integral value of —OCH}_3 \text{ proton in MA unit (I}_m)}{\text{Integral value of aromatic —OH proton in HBA unit (I}_{hy})}$$

$$C = \frac{3m_1}{(1 - m_1)}$$

On simplification,

$$m_1 = \frac{C}{3 + C}$$

The integral values of I_m and I_{hy} were presented in Table II.

Reactivity ratios

Mole fraction curves representing feed versus mole fraction (S or MA) present in the copolymer chain were shown in Figures 1(a) and 2(a) for copoly(S-HBA) and copoly(MA-HBA), respectively. These curves clearly indicate that the polymerization proceeded in the random pathway. The reactivity of the monomers S(r₁) [or MA (r₁)] and HBA(r₂) were evolved by using the following graphical methods: (a) Finemann–Ross, (b) Kelen–Tudos, and (c) extended Kelen–Tudos.

Fineman–Ross method

A plot of G versus H was a straight line shown in Figures 1(b) and 2(b) for poly(S-co-HBA) and poly(MA-co-HBA), respectively. The reactivity ratio r₁ (S) and r₂ (HBA) for poly(S-co-HBA) were found to be

TABLE II
Composition Data for the Poly(MA-co-HBA)

Feed composition (M ₁)	Conversion (%)	Integral value		C = I _m /I _h	Copolymer composition (m ₁)
		I _m	I _h		
0.15	7.2	5.749	2.681	2.1443	0.4168
0.30	12.9	0.326	0.079	4.1266	0.579
0.50	3.5	1.813	0.256	7.082	0.7024
0.70	8.9	2.925	0.247	11.8421	0.7979
0.85	14.1	0.886	0.032	27.6875	0.9022

[Monomer 1 + Monomer 2] = 0.5 mol/L. Solvent: EMK. Temperature: 70 ± 1°C. Initiator: BPO [1% (w/w) of monomers 1 and 2].

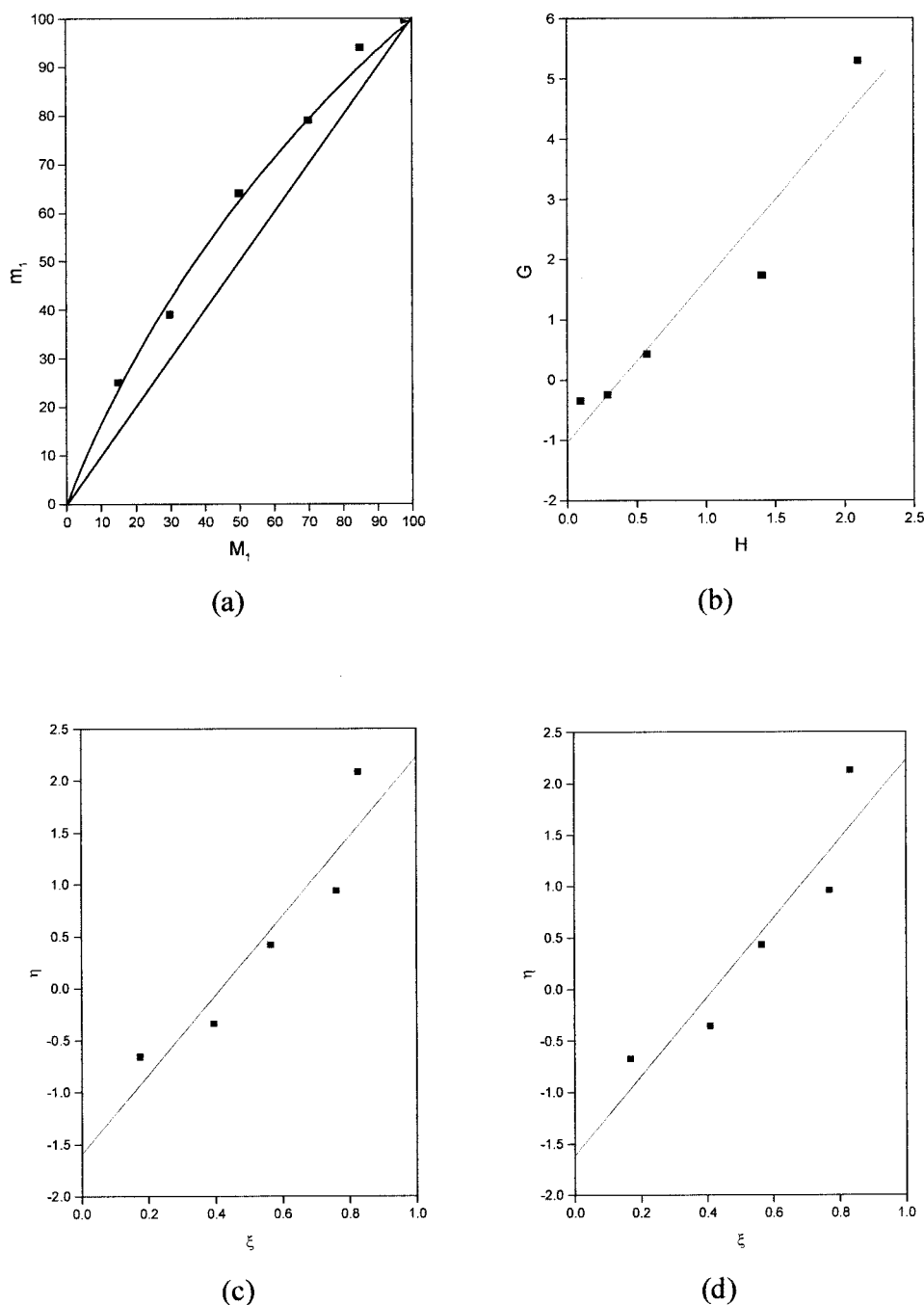


Figure 1 (a) Copolymer composition against the initial monomer concentration curve; (b) Finemann–Ross plot; (c) Kelen–Tudos and (d) extended Kelen–Tudos plots for poly(S-*co*-HBA).

2.68 ± 0.45 and 1.03 ± 0.51 , respectively. In the case of poly(MA-*co*-HBA), the r_1 (MA) and r_2 (HBA) of the monomers were found to be 1.47 ± 0.04 and 0.12 ± 0.07 , respectively. In both copolymers, the value of $r_1 r_2$ was found to be less than 1, showing that the polymerization proceeded via random copolymerization.

Kelen–Tudos method

To overcome some of the drawbacks present in the Finemann–Ross method, Kelen–Tudos introduced an-

other linear equation for calculating the reactivity ratios.

A plot of η versus ξ gives the straight line shown in Figures 1(c) and 2(c) for S-HBA copolymer and MA-HBA copolymer systems, respectively. From the intercept values, r_1 and r_2 were calculated. The reactivity ratio r_1 (S) and r_2 (HBA) for poly(S-*co*-HBA) were found to be 2.21 ± 0.44 and 0.71 ± 0.22 , respectively; but in the case of poly(MA-*co*-HBA), the r_1 (MA) and r_2 (HBA) of the monomers were found to be 1.45 ± 0.09 and 0.11 ± 0.03 , respectively.

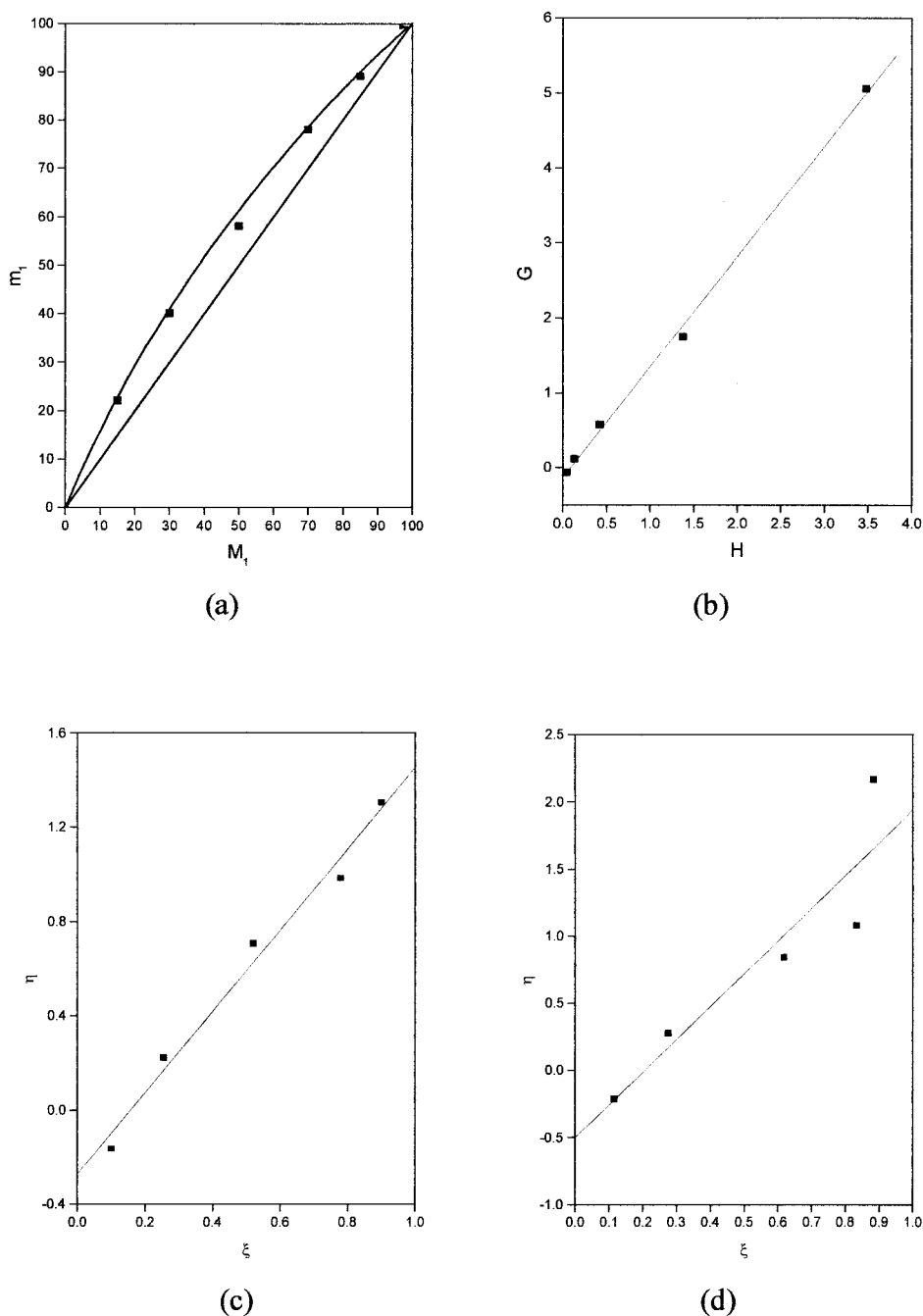


Figure 2 (a) Copolymer composition against the initial monomer concentration curve; (b) Finemann–Ross plot; (c) Kelen–Tudos and (d) extended Kelen–Tudos plots for poly(MA-co-HBA).

Extended Kelen–Tudos method

A plot of η versus ξ gives the straight line shown in Figures 1(d) and 2(d) for poly(S-co-HBA) and poly(MA-co-HBA), respectively. From the intercept values at $\xi = 0$ and $\xi = 1$, r_1 and r_2 were calculated. The reactivity ratio r_1 (S) and r_2 (HBA) for poly(S-co-HBA) was found to be 2.21 ± 0.46 and 0.66 ± 0.21 , respectively. However, in the case of poly(MA-co-HBA), the r_1 (MA) and r_2 (HBA) values of the monomers were found to be 1.93 ± 0.04 and 0.13 ± 0.1 , respectively (Table III).

Molecular weights

Molecular weight of the S-HBA copolymer and MA-HBA copolymer was done by using gel permeation chromatographic method. The number-average, weight-average molecular weights and the polydispersity values for poly(S-co-HBA) were found to be $M_n = 1.64 \times 10^4$, $M_w = 2.78 \times 10^4$, and 1.70, respectively. The number-average, weight-average molecular weight and the polydispersity values for poly(MA-co-HBA) were found to be $M_n = 1.58 \times 10^4$, $M_w = 3.06 \times 10^4$, and 1.94, respectively. In both the cases, the

TABLE III
 r_1 and r_2 Values of the Copolymers

Polymer	Method	r_1	r_2
Poly(S-co-HBA)	FR	2.68 ± 0.45	1.03 ± 0.51
	KT	2.21 ± 0.44	0.71 ± 0.22
	ex-KT	2.21 ± 0.46	0.66 ± 0.21
Poly(MA-co-HBA)	FR	1.47 ± 0.04	0.12 ± 0.07
	KT	1.45 ± 0.09	0.11 ± 0.03
	ex-KT	1.93 ± 0.04	0.13 ± 0.1

polydispersity value was less than 2, qualitatively suggesting that the polymer was terminated by disproportionation method typically similar to acrylates ($\cong 2$).

Thermal stability

Thermogravimetric analysis was used to study the thermal stability of poly(HBA), poly(S-co-HBA), and poly(MA-co-HBA). All the polymer samples showed two-stage distinct weight loss. The TGA and DTG curves for the four polymer samples were shown in Figure 3. For poly(S-co-HBA) (50 : 50), the first-stage decomposition was observed around 375°C and the second decomposition was revolved around 560°C. These two-stage decomposition mechanisms clearly indicate that the poly(S-co-HBA) has higher thermal stability than poly(HBA). Similarly, the poly(MA-co-HBA) (50 : 50) shows two-stage decomposition centered around 365 and 470°C. The percentage decomposition at various temperatures was shown in the Table IV.

Photocrosslinking properties of the polymers

The change in the UV absorption pattern of the polymers containing HBA as a constituent of the polymer chain was present in the Figures 4-6. The polymer containing HBA unit in the (co)polymer chain shows the absorption maximum around 350 nm because of the $\pi-\pi^*$ transition of >C=C< of the pendant cinnamoyl group present in the polymer side chain. When these polymer samples in solution were irradiated by using a UV lamp, there is a decrease in the intensity of absorption maximum around 350 nm (Table V). This is due to the formation of the cyclobutane ring by $2\pi-2\pi$ cycloaddition of the olefinic double bond present in the polymer chain. This is the reason we observe the decrease in the intensity of absorption maximum upon irradiation with UV light. This type of decrease in the intensity of the absorption maximum in the presence of UV light was previously reported.²⁵ When we observe the UV spectral pattern of the polymer sample in solution form, there is an existence of

isobestic point in the range between 315 and 320 nm. These isobestic points may be due to the *cis-trans* isomerization of the chalcone double bond. Because we carried out our photocrosslinking studies in the solution phase, the photoisomerization of the polymer chain cannot be ruled out. The question of disruption of the chromophore aggregates does not arise here, as there is no ordered arrangement in the solution, and hence, cyclization takes precedence over *cis-trans* isomerization. This in turns decreases the intensity of the absorption maximum of the chalcone unit. This type of cyclization precedence over *cis-trans* isomerization was also reported in the earlier references.²⁶⁻²⁹ The rate of photocrosslinking of the >C=C< present in the copolymer sample was present in Figure 7. This clearly indicates that the rate of photocrosslinking of >C=C< was enhanced when the photocrosslinkable monomer was copolymerized with S and MA. The most probable reason for the low rate of photocrosslinking of poly(HBA) upon irradiation with UV light is (1) due to the bulky nature of the photocrosslinkable moiety and (2) due to the presence of a large number of HBA units (100%) present in the polymer chain. These two factors effectively reduce the favorable position

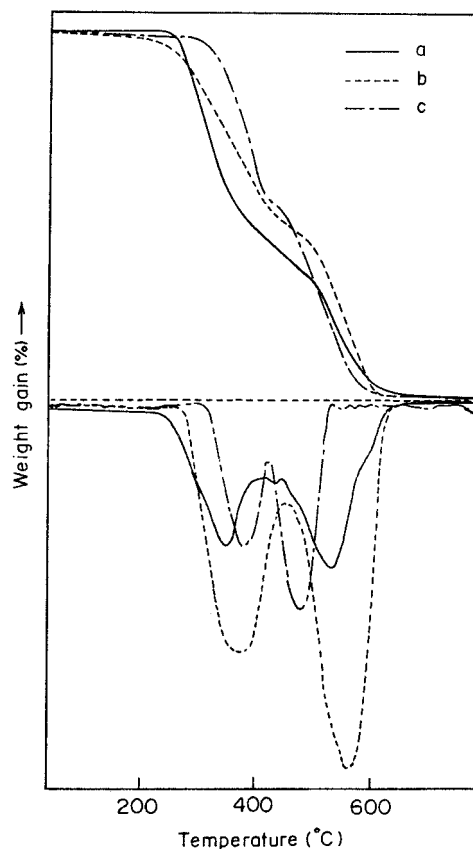


Figure 3 TGA and DTG curves of poly(HBA) (—), poly(S-co-HBA) (50 : 50) (---), and poly(MA-co-HBA) (50 : 50) (- - -).

TABLE IV
Molecular Weights and Percentage Decomposition of the Polymers

Sample	Composition	% Decomposition at various temperatures				$M_n \times 10^4$	$M_n \times 10^4$	M_w/M_n
		20	40	60	80			
Poly(HBA)	100	343	408	492	564	2.53	1.38	1.83
Poly(S-co-HBA)	50 : 50	350	426	500	568	2.78	1.64	1.70
Poly(MA-co-HBA)	50 : 50	379	427	464	493	3.06	1.58	1.94

for the formation of cyclobutane ring upon irradiation with UV light. Among the two probable reasons cited for a low-rate photocrosslinking, the first reason (i.e., bulky nature of the photocrosslinkable moiety) cannot be eliminated or minimized. However, the second reason, cited above, can be minimized through the copolymerization technique. Even though the photocrosslinking property was carried out in the solution phase, the bulky nature of the chromophore has some impact on the rate of photocrosslinking of the polymer sample. Therefore, to eliminate the drawback of our system, we copolymerized the photocrosslinkable monomer with S and MA. As we expected, the rate of photocrosslinking was enhanced and is shown in Figure 7. The rate of photocrosslinking follows the order poly(HBA) < poly(S-co-HBA) < poly(MA-co-HBA). These comonomers present in the polymer chain provide the flexibility to the polymer backbone, thereby providing proper orientation for the cyclobutane ring formation. This sort of assistance provided by the comonomer on the rate of photocrosslinking property was increased in the order

of MA > S. To find out the number of monomeric units present in the polymeric chain, the copolymer systems were subjected to the available graphical methods such as FR, KT, and ex-KT. The monomer reactivity ratios were presented in the Table III. In both the copolymer systems, the number of commercial monomers (S or MA) present in the polymer chain will be more than that of the HBA. Apart from the assistance provided by the MA units on the rate of photocrosslinking through increasing the flexibility of polymer chain in poly(MA-co-HBA), these MA units due to their high reactivity in polymerization process are involved in preventing the entry of more numbers of HBA units into the polymer chain, thereby reducing the crowding and increasing the proper orientation for the formation of cyclobutane ring structure. This sort of two-way assistance given by the comonomers on increasing the rate of photocrosslinking is more pronounced in the case of MA than S. Although we may not be able to quantify the assistance of the comonomers on the rate of photocrosslinking, we are pretty confident that the

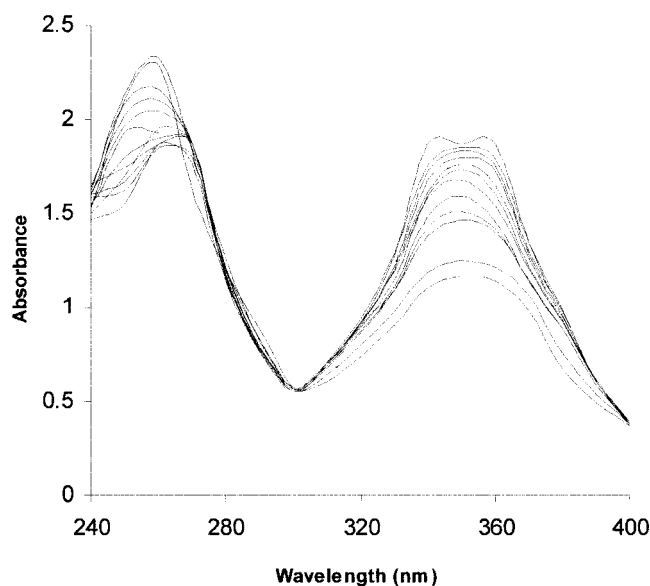


Figure 4 Effect of UV irradiation (0 to 1500 s) on poly(HBA).

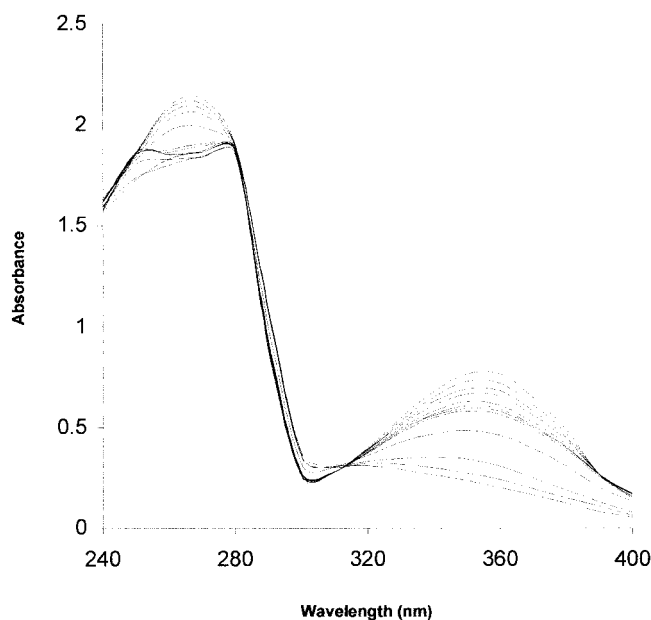


Figure 5 Effect of UV irradiation (0 to 1500 s) on poly(S-co-HBA).

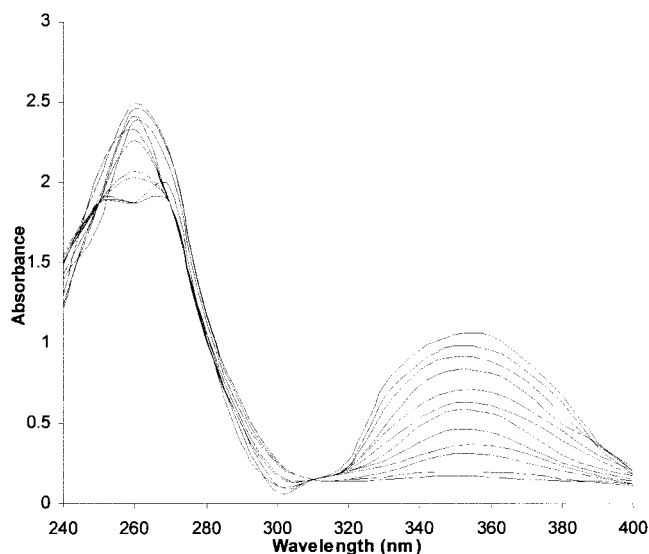


Figure 6 Effect of UV irradiation (0 to 1500 s) on poly(MA-co-HBA).

smaller molecular size comonomer with high reactivity can give good assistance on the rate of photocrosslinking. In our investigation, we successfully increased the rate of photocrosslinking from 37.7% [for poly(HBA)] to 89% [for poly(MA-co-HBA)]. This shows that in bulky systems such as HBA, the introduction of flexible (or small) molecules into the polymer backbone will increase the rate of photocrosslinking of the polymer sample.

CONCLUSION

Novel arylidene monomer (HBA) was synthesized by acrylation process. HBA monomer was subjected to homo- and copolymer (with S and MA) process. The

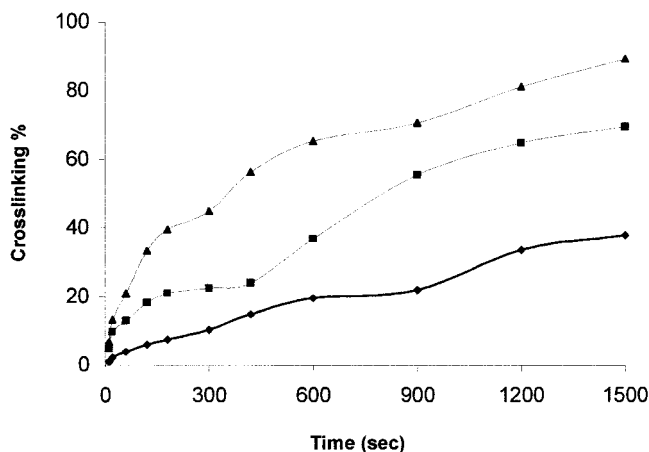


Figure 7 Rate of disappearance of $>C=C<$ chromophore in (a) poly(HBA) (-◆-); (b) poly(S-co-HBA) (-■-); and (c) poly(MA-co-HBA) (-▲-).

TABLE V
Rate of Disappearance of the Olefinic Bond Present in the Polymer Chain

IT	Poly(HBA)		Poly(S-co-HBA)		Poly(MA-co-HBA)	
	A (353 nm)	C (%)	A (353 nm)	C (%)	A (357 nm)	C (%)
0	1.873	0	0.765	0	1.050	0
10	1.854	1	0.728	4.8	0.980	6.7
20	1.831	2.2	0.691	9.7	0.910	13.3
60	1.800	3.9	0.666	12.9	0.830	21.0
120	1.762	5.9	0.626	18.2	0.700	33.3
180	1.734	7.4	0.605	20.9	0.635	39.5
300	1.679	10.4	0.594	22.4	0.580	44.8
420	1.594	14.9	0.582	23.9	0.460	56.2
600	1.508	19.5	0.484	36.7	0.365	65.2
900	1.464	21.8	0.342	55.3	0.310	70.5
1200	1.246	33.5	0.271	64.6	0.201	80.9
1500	1.167	37.7	0.235	69.3	0.167	89.1

IT = irradiation time in seconds; A = absorbance value; C = crosslinking percentage.

reactivity ratios of the monomers present in the copolymer chain was estimated by using FR, KT, and ex-KT methods. The average value of three methods shows that the synthesized monomer was less reactive than the commercial monomers S and MA. All the polymer samples were subjected to photocrosslinking studies. The rate of photocrosslinking was enhanced when the photocrosslinkable monomer was copolymerized with S and MA.

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