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Photocrosslinked polymers based on pendant extended chalcone as photoreactive moieties

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Abstract

The photoreactivity of new homo- and co-photosensitive polymers containing pendant chalcone moieties attached through hexamethylene spacer lengths between the photosensitive group and the backbone were studied. The rates of crosslinking of the prepared polymers were investigated under different conditions in solutions such as: backbone structures, copolymerization, different solvents, different concentrations and different temperatures. The structures of the prepared monomer and polymers were confirmed by different spectroscopic methods and elemental microanalysis. The average molecular weights of the polymers were determined by gel permeation chromatography. The thermal stability of the polymers was measured by thermogravimetric analysis under a nitrogen atmosphere. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photosensitive polymers; Photoresists; Photoreactive methylmethacrylate

1. Introduction

The widespread utilization of functionalized polymers in a variety of fields including chemical [1], biological [2] and technological [3,4] uses is based on the potential advantages of the specific active functional groups and the characteristic properties of the polymeric molecules.

The technological applications of the radiation sensitive polymers have attained considerable interest and have developed to a wide research area in different fields, such as, photolithography [5–8], printing materials [9], liquid crystalline [10–14] and non-linear optical materials [15–17]. The technological applications of many photoresists have been reviewed [6–9,18–20]. Many different photoresist systems are used in the manufacture of various industrial products such as integrated circuits, compact discs, cathode ray tubes and printed circuit boards [20].

The polymers with pendant chalcone groups (α,β-unsaturated carbonyl groups, e.g. cinnamoyl groups) undergo crosslinking upon irradiation with UV light and are regarded as negative-type photoresists. These polymers with the properties of high photosensitivity, the ability to form films, good solubility, resistance towards solvents after crosslinking, thermal stability and resistance towards plasmas and etching agents are very important for practical use as commercial negative photoresist materials. Also, there are photoreactive polymers containing α,β-unsaturated carbonyl group in the backbone [21,22] which have been synthesized and characterized as photoresists.

Polymers with photosensitive groups, such as the cinnamic esters of poly(acrylate and methacrylate) derivatives [23–27], poly(2-hydroxyethyl methacrylate) [28–30], poly(vinylalcohol) [28,31], poly(2-vinyloxyethyl cinnamate) [32], and many other compositions, have been studied as photoresists.

In this connection, the present contribution stems from our continuing interest in the synthesis and characterization of polymeric materials designed from the realization of suitable systems for photosensitive polymers containing pendant chalcone groups as photocrosslinkable units attached directly or through spacer groups. The effects of some factors such as: backbone structures, copolymerization, different solvents, different concentrations, and different temperatures on the rates of crosslinking of the prepared polymers were investigated and evaluated, in order that these materials can be used as negative photoresists.

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2. Experimental

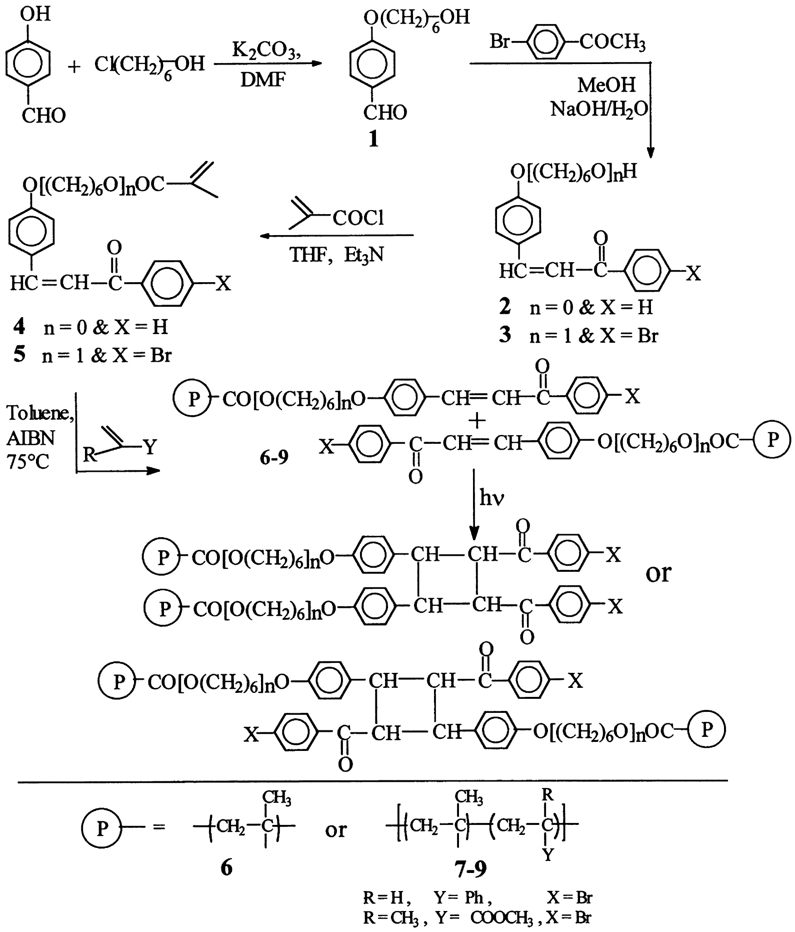
2.1. Materials

Acetophenone, 4-bromoacetophenone, 4-hydroxybenzaldehyde and N,N′-azobisisobutyronitrile (AIBN) were obtained from Fluka (Switzerland) and used without further purification. 6-Chloro-1-hexanol was used as received from Aldrich. Methacryloyl chloride, methylmethacrylate were used after purification by vacuum distillation. Styrene was purified by washing with 1 M NaOH and distillation under vacuum. For thin layer chromatography (TLC) plastic sheets silica gel 60 F_{254} from Merck was used. Silica gel for column chromatography from Fluka was used.

2′-Benzoyl-4-hydroxy styrene (**2**) was synthesized by the reaction of 4-hydroxybenzaldehyde with acetophenone in the presence of NaOH in an ethanol/water mixture [23]. 2′-(Benzoyl)-4-styryl methacrylate (**4**) was prepared [23] from the reaction between (**2**) and methacryloyl chloride in dry THF in the presence of $(Et)_3N$ at 0–4°C. All polymerizations were carried out in toluene and THF purified by distillation over sodium under argon atmosphere.

2.2. Instruments

The molecular weight distribution was determined by gel permeation chromatography (GPC). We used polystyrene gel columns from Polymer Standards Service (10^3, 10^4 and 10^6, particle size 5 μm) and THF as eluent. Polystyrene standards from Polymer Laboratories Inc. were used for calibration. The thermal behaviour of the polymers was investigated by thermogravimetric analysis (TGA) using a Polymer Laboratories STA 625 DSC thermal analyzer. The heating rate was 10°C/min in all cases. Differential scanning calorimetry (DSC) was measured using Shimadzu DSC-50 with a heating rate of 5°C/min in all cases. The UV spectra of the monomers and polymers were recorded with the aid of a Shimadzu UV-2101PC UV–Vis scanning spectrophotometer. The photoreactivity of the polymers was studied by irradiation with UV light at 365 nm using a medium pressure Hg lamp (EMITA VP 60, 180 W) with an interference filter. Infrared (ir) spectra were recorded on a Bomem Michelson M100 FT-ir spectrometer. Specimens were prepared by casting polymer films from chloroform solutions on to NaCl plates. ^{1}H nuclear magnetic resonance



Scheme 1. Preparation of photoreactive monomers and their homo- and copolymerization with different comonomers and formation of cyclobutane ring due to UV irradiation of photosensitive groups.

(n.m.r.) spectroscopic measurements were recorded with a Bruker MSL 300 spectrometer and ^{13}C-n.m.r. were recorded with a Bruker MSL 300 spectrometer.

*2.3. 4-(6-Hydroxy-n-hexyloxy) bezaldehyde (***1***) [Scheme 1]*

6-Chloro-1-hexanol (14.8 g (10 mmol)) was added dropwise with stirring to a solution of 12.2 g (100 mmol) of 4-hydroxybenzaldehyde dissolved in 50 ml dimethylformamide in the presence of 34.5 g (250 mmol) anhydrous potassium carbonate. The reaction mixture was heated to 70°C and stirred overnight. The formation of the product was controlled by thin layer chromatography (t.l.c.) [cyclohexane/ethylacetate (1:1), $R_{f(s)} = 0.71$, $R_{f(p)} = 0.50$]; cooled to room temperature, filtered off, the filtrate diluted with 200 ml diethyl ether and washed with 1 M HCl, 1 M NaOH, H_2O consequently, and dried over anhydrous sodium sulphate. The product was filtered and the solvent evaporated and the highly viscous liquid product was purified by column chromatography (cyclohexane/ethyl acetate (1:1) as eluent) to give 16.94 g (76.3% yield) of pure colorless crystals product (**1**), m.p. = 51.1°C.

Microanalysis ($C_{13}H_{18}O_3$):	C% Calcd = 70.27;	H% Calcd = 8.11
	C% Found = 73.50;	H% Found = 7.69

IR (film on NaCl): ν = 3395, 3072, 2935, 2862, 2740, 1686, 1600, 1570, 1510, 1469, 1428, 1395, 1312, 1259, 1217, 1161, 1105, 1062, 1010, 931, 834, 648 and 516 cm^{-1}.
^{1}H-n.m.r. (CDCl$_3$): δ = 9.86 (*s*, 1H, $-C\underline{H}O$); 7.81 and 6.97 (2d, 4H, Ar–$\underline{H}$; 4.03 (*t*, 2H, Ar–O–$\underline{CH_2}$–); 3.65 (*t*, 2H, $-C\underline{H}_2$–OH); 1.8 (*m*, 1H, –O$\underline{H}$); and 1.64–1.41 ppm [*m*, 8H, $(C\underline{H}_2)_4$].
^{13}C-n.m.r. (CDCl$_3$): δ = 190.97 ($-H\underline{C}=O$); 164.27, 132.07, 129.77, 114.79 (–$\underline{C}$–aromatic); 68.31, 62.80, 32.65, 29.06, 25.85 and 25.56 ppm ($-\underline{C}H_2$).

*2.4. 2′-(4-Bromobenzoyl)-4-(6-hydroxy-n-hexylaxy) styrene (***3***) [Scheme 1]*

A solution of 0.9 g (22.5 mmol) NaOH dissolved in 5 ml distilled water was added dropwise with stirring to a mixture solution of 2.22 g (10 mmol) 4-(6-hydroxy-n-hexyloxy) bezaldehyde (I), 2.0 g (10.05 mmol) 4-bromoacetophenone dissolved in 10 ml methanol at room temperature (14–16°C) and stirred overnight. The formation of the product was controlled by t.l.c. [cyclohexane/ethylacetate (1:1), $R_{f(s)} = 0.319$, $R_{f(p)} = 0.458$]. The reaction mixture was neutralized with 2 M HCl and the formed precipitated product was filtered off and washed with distilled water several times. The crude product was recrystallized from methanol to yield 3.5 g (86.8%) of yellow crystalline product (**3**), m.p. = 121.8°C.

Microanalysis ($C_{21}H_{23}O_3Br$):	C% Calcd = 62.53;	H% Calcd = 5.71;	Br% Calcd = 19.85
	C% Found = 64.00;	H% Found = 6.00;	Br% Found = 16.5

i.r. (film on NaCl): ν = 2922, 2852, 1657, 1601; 1510, 1466, 1393, 1295, 1251, 1214, 1175, 1113, 1067, 1026, 973, 841, 816, 740, 662, 578, 541 and 519 cm^{-1}.
^{1}H-n.m.r. (CDCl$_3$): δ = 7.89–7.27 (*m*, 8H, Ar–$\underline{H}$); 6.94 and 6.91 (2s, 2H, $-C\underline{H}=C\underline{H}-$); 4.01 (*t*, 2H, Ar–O–$\underline{CH_2}$–); 3.67 (*t*, 2H, $-\underline{CH_2}$–OH); 1.82 (*m*, 1H, –O$\underline{H}$); and 1.66–1.45 ppm [*m*, 8H, $-(C\underline{H}_2)_4$].
^{13}C-n.m.r. (CDCl$_3$): δ = 189.46 ($-\underline{C}=O$); 161.50 (–$\underline{C}$H); 145.45 ($\underline{C}$H); 137.29, 131.74, 130.42, 130.01, 127.65, 127.26, 119.00, 115.24 (–$\underline{C}$–aromatic); 68.11, 62.88, 32.70, 29.17, 26.04 and 25.77 ppm ($-\underline{C}H_2$).

*2.5. 2′-(4-Bromobenzoyl)-4-styrylaxyhexyl methacrylate (***5***) [Scheme 1]*

The photoreactive monomer (**5**) was prepared by addition of 2 ml (20 mmol) methacryloyl chloride dropwise to a stirred solution mixture of 3.03 g (7.5 mmol) of chalcone (**3**) and 5 ml (35 mmol) of triethylamine in 75 ml absolute THF

Table 1
Polymerization conditions of homopolymer (**6**) and copolymers (**7**–**9**)

Polymer	Photoreactive monomer				Comonomer[a]			Plym. time (h)	Solvent		Product	
	No.	*n*	wt (g)	mmol	Type	wt (g)	mmol		Type[b]	(ml)	wt (g)	yield (%)
6	5	1	0.2772	0.589	–	–	–	7	Tol/THF(2:1)	6	0.212	76.4
7	4	0	0.211	0.72	MMA	0.6507	6.507	12	Toll	2	0.36	41.8
8	5	1	0.2027	0.431	MMA	0.391	3.911	7	Tol/THF(3:2)	5	0.348	58.5
9	5	1	0.2075	0.441	St	0.412	3.961	7	Tol/THF(3:2)	5	0.41	65.1

[a] MMA = methylmethacrylate; St = styrene
[b] Tol = toluene; THF = tetrahydrofurane

at 0–4°C. After complete addition, the reaction mixture was stirred at room temperature for 3 h. The formation of the product was controlled by t.l.c. [cyclohexane/ethylacetate (1:1), $R_{f(s)} = 0.458$, $R_{f(p)} = 0.91$]. The precipitated quaternary ammonium salt was filtered off and the THF was evaporated under reduced pressure. The resultant solid was dissolved in 100 ml CH_2Cl_2 and washed successively twice with 1 M HCl, 1 M NaOH, distilled water, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the product was purified by column chromatography (cyclohexane/ethylacetate 2:1) to give 2.6 g (73.5% yield) of yellowish crystals of (**5**), m.p. = 95.4°C.

Microanalysis ($C_{25}H_{27}O_4Br$):	C% Calcd = 63.69;	H% Calcd = 5.73;	Br% Calcd = 16.99
	C% Found = 65.50;	H% Found = 4.70;	Br% Found = 16.50

i.r. (film on NaCl): $\nu = 2943$, 2866, 1709, 1657, 1595, 1571, 1513, 1472, 1423, 1395, 1342, 1322, 1295, 1265, 1216, 1173, 1113, 1071, 1024, 1004, 988, 935, 824, 798, 726 and 653 cm^{-1}

^{1}H-n.m.r. ($CDCl_3$): $\delta = 7.82-7.19$ (*m*, 8H, Ar–$\underline{H}$); 6.86 and 6.82 (2s, 2H, –C$\underline{H}$=C$\underline{H}$–); 6.02 and 5.47 (2s, 2H, –C$\underline{H}_2$=C–); 4.09 (*t*, 2H, Ar–O–C$\underline{H}_2$–); 3.93 (*t*, 2H, –C$\underline{H}_2$–OOC–); 1.87 (s, 3H, –C$\underline{H}_3$); and 1.78–1.40 ppm [*m*, 8H, –(C$\underline{H}_2$)$_4$].

^{13}C-n.m.r. ($CDCl_3$): $\delta = 189.40$ (–$\underline{C}$ = O); 167.15 (–$\underline{C}$OO); 161.46 and 145.39 (–$\underline{C}$H=CH–); 137.30, 136.53, 131.89, 130.41, 130.00, 127.63, 127.29, 125.31, 119.01 and 114.99 (–$\underline{C}$–Aromatic); 68.03, 64.65, 29.09, 28.60, 25.83 and 25.77 (–$\underline{C}H_2$); and 18.40 ppm (–$\underline{C}$H3)

2.6. Synthesis of photoreactive polymers

The homopolymer and copolymers were prepared via a solution-free radical technique using N,N′-azobis-isobutyronitrile (AIBN). As a typical example, run (**6**) is described in details as follows.

A mixture solution of 0.277 g monomer (**5**) dissolved in 5 ml of freshly distilled anhydrous toluene/THF (2:1) and 0.003 g of AIBN as initiator was flushed with oxygen-free nitrogen for 40 min, and heated with stirring overnight at 80°C. The polymerization solution was cooled and poured on to 100 ml of stirred methanol. The precipitated polymer was filtered off, washed with ethanol, and dried in vacuo, to give 0.212 g (yield 76.5%) of homopolymer (**6**). All data for synthesis of homo- and co-polymers with methylmethacrylate and styrene are summarized in Table 1.

2.7. Photoreactivity measurements

The photoreactivity of the prepared monomers, homo- and copolymers was studied by dissolving the sample in an organic solvent and irradiated with UV light at 365 nm using a medium-pressure mercury lamp (EMITA VP 60, 180 W) at a distance of 17.5 cm from the surface of the light source for different intervals of time. After each irradiation period, the UV spectra were recorded on a Shimadzu 2101PC scanning spectrophotometer. The rate of disappearance of the double bond in the photosensitive groups was followed by using the expression

$$\text{Percent of decay} = \frac{A_0 - A_T}{A_0} \times 100$$

where A_0 and A_T are absorption intensities at $\lambda_{max} = 348$ or 313 nm (see also Table 2), due to double bond of the photosensitive groups after irradiation times $t = 0$ and $t = T$, respectively.

3. Results and discussion

3.1. Synthesis

The methacrylate photoreactive polymers containing

Table 2
Average number molecular weights, average weight molecular weights, polydispersity index, thermal properties and ultraviolet data of homopolymer (**6**) and copolymers (**7**–**9**)

Polymer	Molecular weight			T_g^b	Thermal properties			UV data^f		
	$M_n \times 10^4$	$M_n \times 10^4$	PDI^a (M_w/M_n)	(°C)	TDG^c (°C)	Wt. loss (%)	Residue^d (%)	Decreased ($\lambda_{C=C}$)	Increased (λ_{C-C})	Isobestic point (λ)
6	0.3395	0.46643	1.3738	73	345-460	85.8^e	14.2	348	238	261
7	1.4632	2.6899	1.8383	156	245-410	95.4	4.6	313	239	269
8	0.37933	0.8892	2.3441	72	240-455	85.2	14.8	347	239	268
9	0.87993	3.5101	3.9891	88	360-435	85.4	14.6	348	239	268

[a] PDI: Polydispersity

[b] T_g: Glass transition temperature determined from the DSC measurements

[c] TDG: temperature decomposition range

[d] Residue at 530°C under nitrogen atmosphere

[e] At 780°C.

[f] In chloroform.

α,β-unsaturated carbonyl moieties as photosensitive groups attached directly [23] or through hexamethylene spacer groups between the photoreceptive groups and the polymer backbone, were synthesized as outlined in Scheme 1. The chalcone (**2**) was prepared by reacting 4-hydroxybenzaldehyde with acetophenone in ethanol/water mixture in the presence of sodium hydroxide as base [24]. The chain extended chalcone derivatives (**3**) which contained oxy(hexamethylene) spacer groups between the functional hydroxyl group and the photoreactive chalcone groups was prepared in two steps. The first step is the nucleophilic displacement of potassium salt of 4-hydroxy-benzaldehyde with 6-chloro-1-hexanol in DMF to give (**1**) in a good product yield (76.3%). The second step is the reaction of extended benzaldehyde (**1**) with 4-bromoacetophenone in aqueous/methanolic sodium hydroxide solution using the same conditions for preparation of (**2**) to give a high yield (87%) of product (**3**). The formed chalcones (**3**) reacted with methacryloyl chloride in THF in the presence of $(Et)_3N$ at 0–4°C to obtain the monomers (**5**) in the same manner [23]. The melting points were determined from DSC measurements in the temperature range 20–200°C with a heating rate of 10°C/min. The structure of the monomers was confirmed by the elemental microanalysis, FT-i.r., ^{1}H-NMR and ^{13}C-NMR spectra which corresponds to the structure (see Section 2).

The homopolymers (**6**) and copolymers, containing a dilute concentration of the photoreceptor part, with different comonomers such as methylmethacrylate and styrene (**7**–**9**), with pendant photosensitive chalcone groups, were prepared via the solution-free radical polymerization technique using the AIBN initiator. The polymerization time was 7–12 h. This procedure was followed by GPC in order to determine the degree of polymerization, and the results are listed in Table 2. The polymerization solution was poured on to methanol and the dry-produced polymers were obtained in a good yield (42–76%).

3.2. Polymer solubility

The solubilities of the prepared polymers in various solvents were tested. They were easily soluble in polar aprotic solvents such as DMF, DMSO, N-methyl-2-pyrrolidone, dioxane, THF and in chlorinated solvents such as $CHCl_3$, CH_2Cl_2, chlorobenzene. They were insoluble in alcohols such as methanol, ethanol and 2-propanol, and in hydrocarbons such as benzene, toluene and xylenes. The solubility of the photoreactive polymers is one of the important requirements for practical uses of such polymers, and the solubility test shows that there is a high chance for using many solvents required for practical uses.

3.3. Structure

The chemical structures of the polymers were confirmed with FT-i.r., ^{1}H-n.m.r. spectroscopic methods and showed that the appearing peaks corresponded to the structure. The i.r. spectra of the polymers showed absorption bands at about 2945, 1440 cm^{-1} due to ($-CH_2-$); 1725, 1330 cm^{-1} which confirm ester group; at 1660, 1292 cm^{-1} due to the Ar–C=O and at 1590 cm^{-1} due to C=C conjugated of the chalcone moiety, whereas the absorption bands at 1750 cm^{-1} of polymerizable ethylenic groups had disappeared. Absorption bands at 1510 cm^{-1} are assignable to aromatic C=C stretching, and those at 1448 cm^{-1} due to CH_3 bending vibrations. The FT-i.r. spectra of the prepared polymers were comparable with those of extended chalcone monomer as presented in Fig. 1. The complete ^{1}H-n.m.r. spectra of polymers (**6**–**9**) are shown in Fig. 2. They exhibit a multiplet at 7.85–7.15 ppm due to aromatic protons. Olefinic protons of pendant chalcone are observed as a broad singlet at about 6.9 and 6.8 ppm. (N.B. the intensity of the peaks was observed at a higher intensity in the case of homopolymer (**6**), but in the case of copolymer (**7**, **8**) the peak intensity was lower, due to the dilution resulting from the methylmethacrylate comonomer, while in the case of copolymer (**9**) we observed that the peak overlapped with the aromatic protons region.) A broad signal was observed at about 4.0 ppm, which corresponds to ($-CH_2-$). A singlet at 3.5 ppm corresponds to methoxy protons of MMA unit. The signals of backbone methylene protons appear as broad at about 2.05–1.8 ppm. A broad signal at 1.2–0.85 ppm due to the $\alpha-CH_3$ protons is presented.

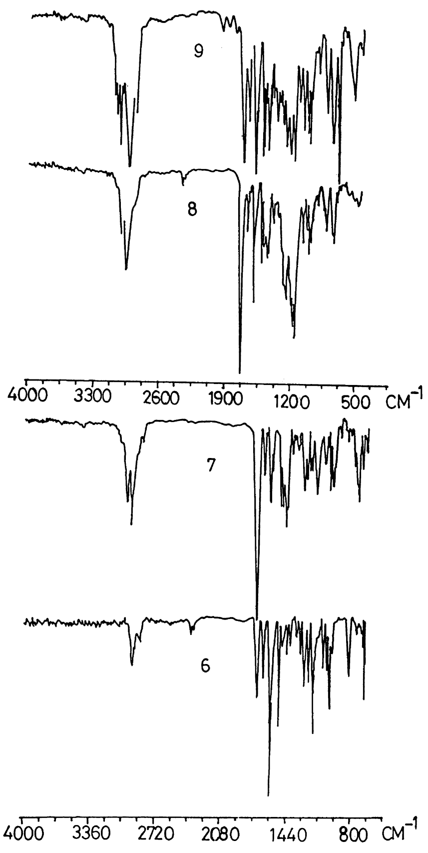


Fig. 1. i.r. spectra of polymers (**6**–**9**).

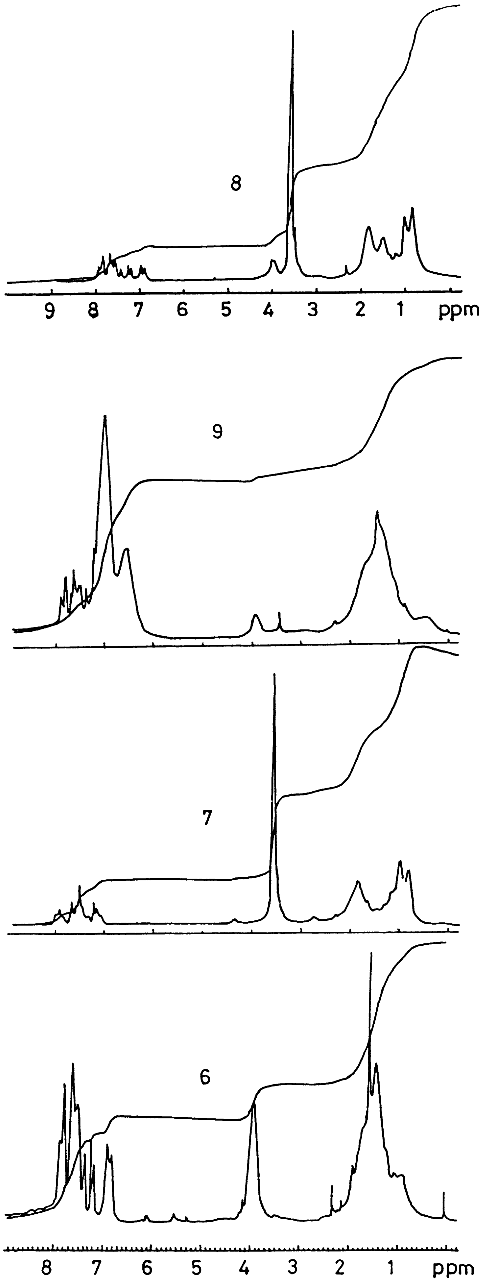


Fig. 2. ^{1}H-n.m.r. spectra of homopolymer (**6**) and copolymer (**7**–**9**).

The values of number average molecular weight (M_n), mass average molecular weight (M_w) and polydispersity index (PDI) of polymers (**6**–**9**) are determined by gel permeation chromatography and listed in Table 2. The data indicated that M_n was found to range from 0.339×10^4 to 1.46×10^4 g/mol; $M_w = 0.466 \times 10^4$ to 3.51×10^4 g/mol. The molar mass distribution of polymer (**9**) is broad (PDI = 3.98) compared with polymers (**6**–**8**) (PDI = 1.37–2.34). This must be due to a high difference in the reactivity of the monomers. The PDI of polymers are close to the theoretical values of PDI for polymers produced via radical recombination and disproportionation [33,34]. Hence, the PDI values of these polymers suggest a tendency for chain termination by recombination for polymer (**6**), and by disproportination for copolymers (**7**) and (**8**). Also, from the molecular weight data, we observed that the homopolymers have lower molecular weights and lower PDI than the copolymers. This may be attributed to the difference in the reactivity of vinyl groups between the photoreactive monomers and the comonomers.

3.4. Thermal properties

The glass transition temperatures (T_g) of the polymers were determined by d.s.c. and the data are presented in Table 2. They show a single T_g, thus indicating the formation of random copolymers. The copolymer (**7**) has the highest T_g and polymers (**6**) and (**8**) have nearly the same T_g. The results indicate that the T_g depends on the comonomer type and the spacer length between the photoreactive groups and the backbone of the polymer, since T_g decrease with increasing spacer.

The thermogravimetric analyses (t.g.a.) of the prepared polymers were measured under a nitrogen atmosphere in the temperature ranges 20–700°C, in order to investigate the thermal stability. The t.g.a. data are illustrated in Table 2 for all the polymers, and Fig. 3 shows the t.g.a. traces for the homopolymers (**6**) and copolymers (**7**–**9**). The t.g.a. data in Table 2 and Fig. 3 indicate that the homopolymers decompose at higher temperatures and decompose in a single stage and have good thermal and thermal oxidative stability required for a negative photoresist, in comparison with the homopolymers which contain no spacer length between the backbone of the polymer and the photoreactive groups [24]. Thermogravimetric data for copolymers indicate that the copolymers (**7**, **8**) undergo decomposition at relatively lower temperatures than polymer (**6**) and take a broad range of decomposition in two stages, while copolymer (**9**) undergoes decomposition at higher temperatures and the polymer decompose rapidly in one stage in a narrow temperature range. These results indicate that comonomer types play an important role in the thermal stability of the produced polymers, since the phenyl group in the case of polymer (**9**) gives better thermal and thermal oxidative stability required for a negative photoresists than MMA in the case of polymer (**7**, **8**), which contains the same ratios of the photoreactive groups, and the spacer lengths have no significant effect on the thermal stability of copolymers containing a lower ratio of photoreactive groups.

3.5. Photochemical properties

The photocrosslinking reactions of the prepared photosensitive chalcone, monomer and polymers were studied in polymer solutions, with concentration ranges of 10.8–138 mg/l, by irradiation with UV light (365 nm, 180 W) at $\lambda = 365$ nm and the effect of light was followed by measuring the rate of disappearance of the C=C bond of the photosensitive groups in their UV spectra. The changes

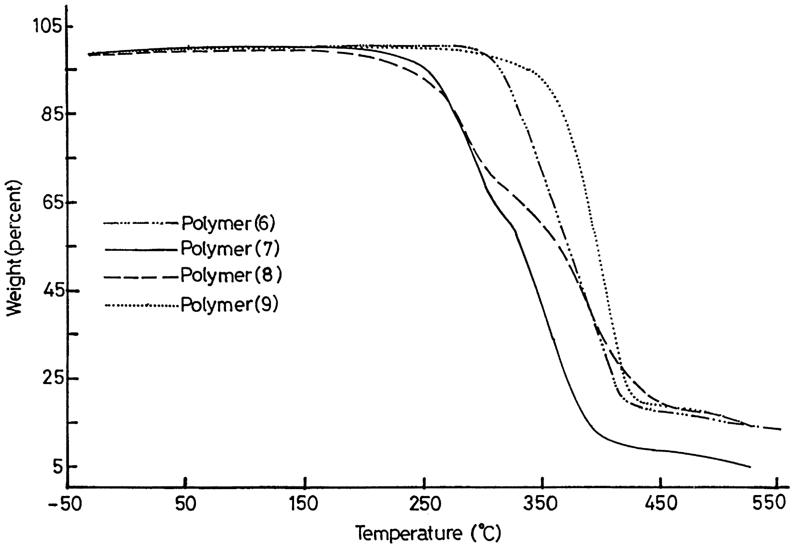


Fig. 3. Thermogravimetric (t.g.a.) measurements in nitrogen atmosphere for homopolymer (**6**) and copolymers (**7**–**9**).

in the absorption peaks of the photoreactive polymers are illustrated in Figs. 4 and 5, and the results in the forms of disappearance rates are illustrated in Figs. 6–10, under different conditions, such as concentration, solvents, temperatures, length of spacer between the photosensitive groups and the polymer backbone, and copolymerization. It is seen that the polymer containing chalcone moieties directly attached to the backbone (**7**) was characterized by maximum absorption at shorter wavelength ($\lambda_{max} = 312$ nm) than the polymer containing extended chalcone moieties (**6**) ($\lambda_{max} = 345$ nm) as illustrated in Fig. 4. The copolymers (**8**, **9**) showed maximum absorption at the same λ_{max} as in homopolymer (**6**) as shown in Fig. 4 and Table 2.

Fig. 5 and Table 2 show the changes in UV absorption spectra of polymers (**6**, **7**) before and after irradiation at the interval period of time, in which the maximum absorption at $\lambda = 313$ or 348 nm of the C=C bond decreases drastically upon irradiation, whereas at about $\lambda = 239$ nm the –C–C– group increases gradually. Isobestic points appear at about $\lambda = 261$ or 268 nm which can be attributed to the decrease in the conjugated system upon irradiation with a concomitant in the absorbance at a shorter wavelength due to single bond formation in the cyclobutane ring. Thus, these polymers react photochemically according to a mechanism similar to that found for cinnamic acid and its derivatives, in which cyclobutane structures [35] were formed (Scheme 1).

The decay rates of photoreactive groups in polymers (**6**–**9**) were studied in chloroform solutions and the data are presented in Fig. 6. The figure shows that polymer (**8**), which contains extended pendant photosensitive moieties, is

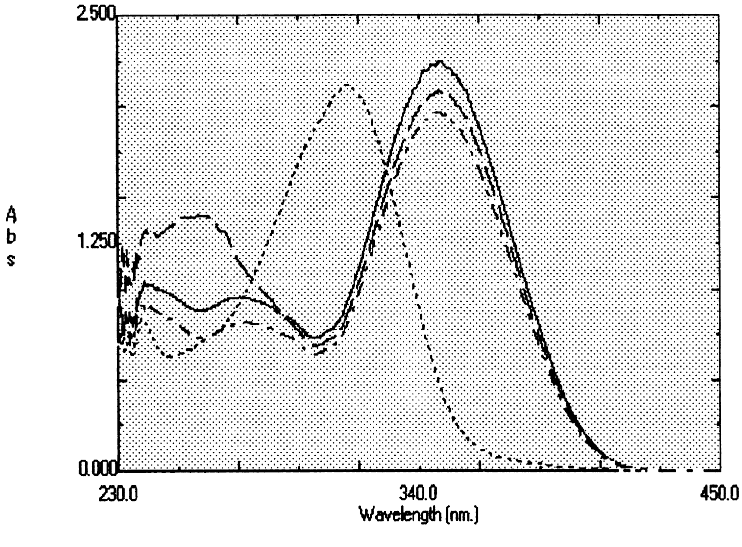


Fig. 4. Full-scan UV spectra of polymers (**6**–**9**) at room temperature in chloroform solution: polymer **6** (–·–·–); polymer **7** (- - - -); polymer **8** (——); and polymer **9** (– – –).

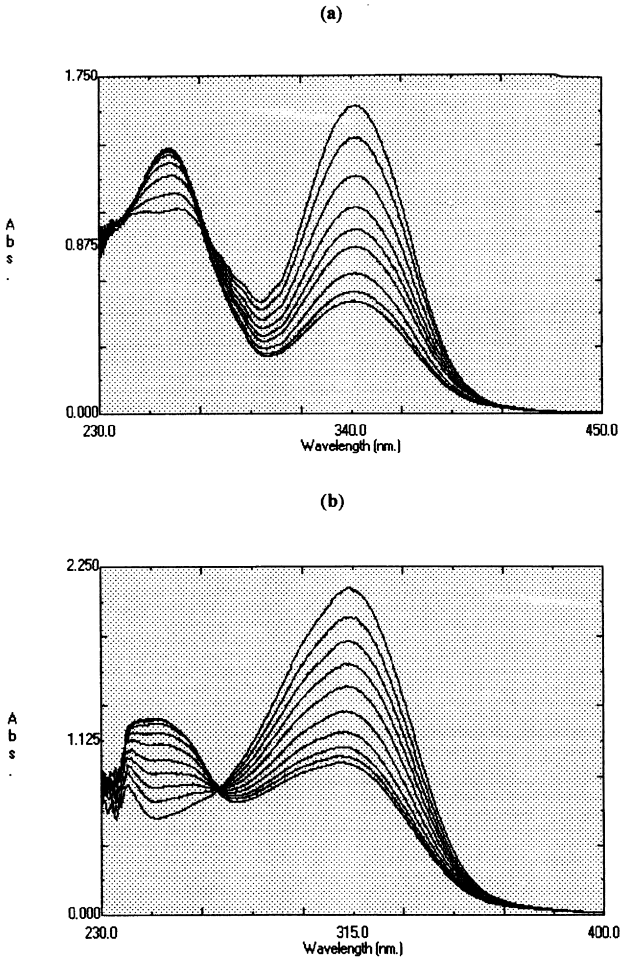


Fig. 5. Decrease changes in the UV absorption spectra upon irradiation of polymers (**6**) and (**7**): (a) Polymer (**6**) in dioxane solution, top to bottom, after irradiation time $t = 0$, 0.5, 1.0, 2.0, 3.75, 6.5, 10, 21.18, 45 and 80.34 min; (b) Polymer (**7**) in chloroform solution, top to bottom, after irradiation time $t = 0$, 1.0, 2.5, 4.0, 6.5, 10, 15, 25, 45 and 75.23 min.

characterized by faster decay rates and undergoes higher photocrosslinking rates (about 70%) than polymer (**7**), which contains photosensitive groups directly attached to the polymer backbone, and undergoes lower photocrosslinking rates (about 50%). These results may be attributed to two factors. The first is the formation of cyclobutane rings as a result of photocrosslinking and leads to a bulk structure neighboring the backbone of the polymer chains and leads to a decrease in both the decay rates and photocrosslinking, in comparison with polymer (**6**), which has an extended photosensitive group. The second is the shift of maximum absorbance wavelength toward longer wavelength ($\lambda_{max} =$ 348 nm) in the case of polymer (**6**) and leads to an increase in the effect of light on the rates of crosslinking, due to the nearest used light wavelength ($\lambda = 365$ nm) compared with the case of polymer (**7**) with a maximum absorbance wavelength ($\lambda_{max} = 312$). Fig. 6 also shows that the copolymerization has an effect on the photocrosslinking rates in comparison with the homopolymers. The results illustrate that the photocrosslinking rates of copolymers (**8**, **9**) are faster than polymer (**7**) and slower than homopolymer (**6**) in the first part of the figure. Moreover, we find that copolymers (**8**, **9**) have nearly the same rates and the crosslinking ratios go up more than in the case of homopolymer (**6**). Also polymer (**9**), which contains a styrene comonomer, still goes up compared with polymer (**8**), which contains a methyl methacrylate comonomer. The values of disappearance rate observed in the case of samples (**8**, **9**) was attributed to the distance separating the photoreactive parts in the backbone of these polymers due to the copolymerization.

The photocrosslinking rates of polymer (**6**) were studied in different solution concentrations (10.8, 18, 28.8 and 36 mg/l) in dimethylformamide (DMF) and the results are presented in Fig. 7. The figure illustrates that the increase in concentration of the photoreactive groups is accompanied by a decrease in the photocrosslinking rates during the first period of irradiation but after a long time (about 10 min), there is no significant change in the disappearance rates of the photoreactive groups.

The effects of solvents on the photocrosslinking rates of the prepared polymers were studied on polymer (**6**) and the results are shown in Fig. 8. These results indicate that the rate of disappearance of the $C=C$ of photoreactive groups are very fast in the first 3–5 min followed by slower rates and some difference in the amount of maximum decay rates in the range 60–75%. Also, the results indicate that there is no clear regular difference in the rate of photocrosslinking which can be determined in chlorinated solvents such as chloroform, dichloromethane and carbon tetrachloride, and aprotic polar solvents (such as dioxane and dimethylformamide).

The effects of temperature on photocrosslinking of the polymers were studied at a constant concentration (36 mg/l) of polymer sample (**6**) in DMF at different temperatures (30, 50, 80°C). The results are shown in Fig. 9. The results indicate that the rate of disappearance of the $C=C$ of photoreactive groups are very fast in the first 5 min followed by slower rates and maximum decay rates in the range 60–65%. Also, the results show that the rate of crosslinking slightly increased with decreasing temperatures. However, lower temperature (30°C) leads to higher decay rates for the photoreactive groups compared with the decay rates at a higher temperature (50°C), and this gives a lower crosslinking rate than at 80°C. These results may be attributed to the temperature increase leading to the increases in the termination process via reaction of the free radicals, produced from double bond cleavage of the photosensitive groups by light, with the medium and gases presented in the photoreaction process.

In general, the rates of decay in the $C=C$ bond of chalcones on exposure to UV radiation with time indicated that: (i) the rate is fast in the first few minutes followed by a slow rate; (ii) there is no clear kinetic order which can be determined; (iii) the rate of disappearance of the $C=C$ bond depends on several factors, such as spacer units between the sensitive moieties and the backbone of polymer chains, copolymerization, concentration and temperature; (iv) the

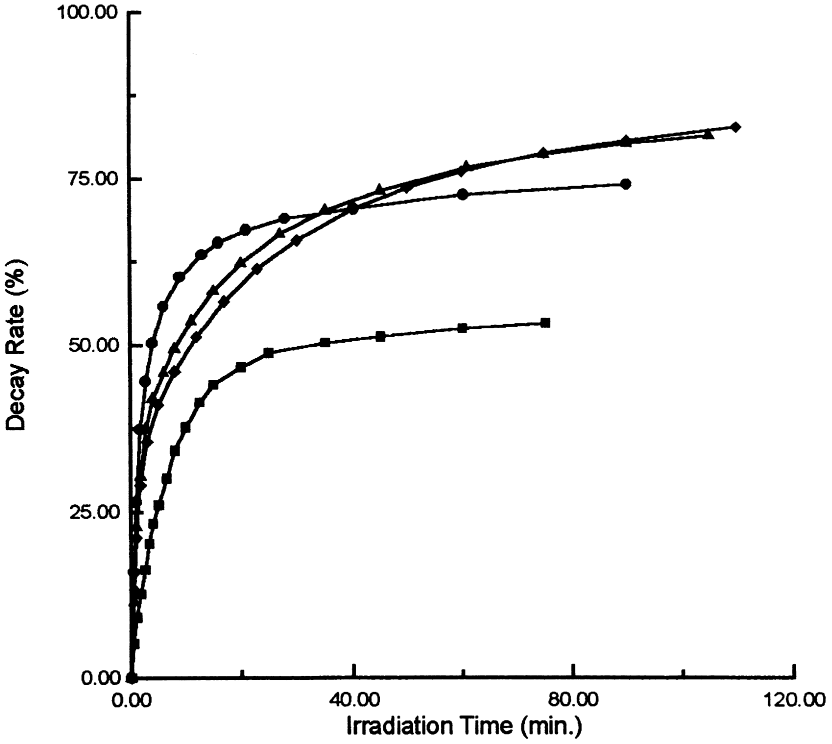


Fig. 6. Disappearance rates of C=C of photoreactive groups of homopolymers (**6**) [– • –], and copolymers (**7**) [–■–], (**8**) [– ▲ –], and (**9**) [– ◆ –] in chloroform solutions at 30°C.

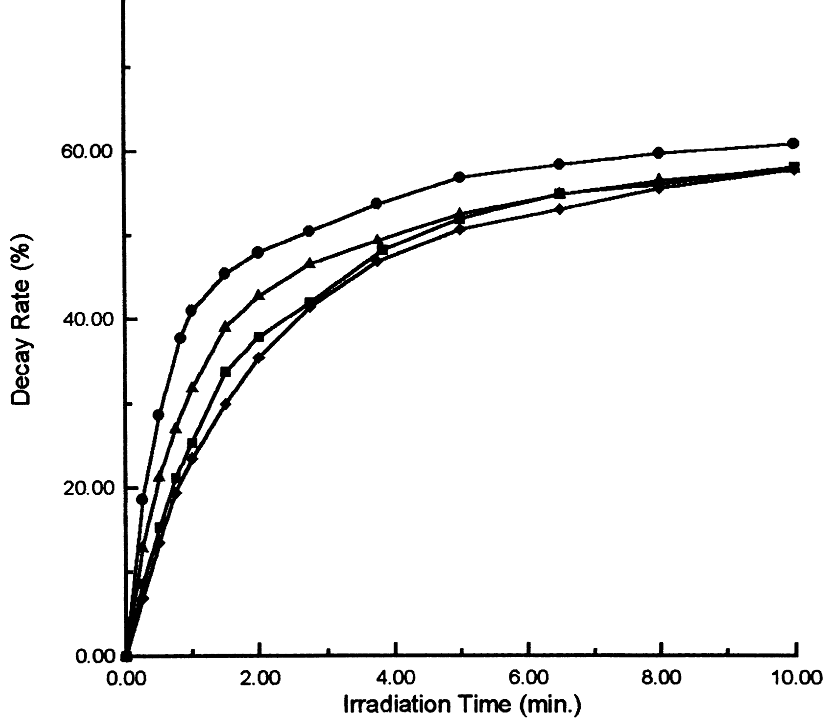


Fig. 7. Disappearance rates of C=C of photoreactive groups of homopolymer (**6**) in DMF solution at different concentrations [– • –] at 10.8 mg/l; [– ▲ –] at 18.0 mg/l; [– ■ –] at 28.8 mg/l; and [– ◆ –] at 36 mg/l at 30°C.

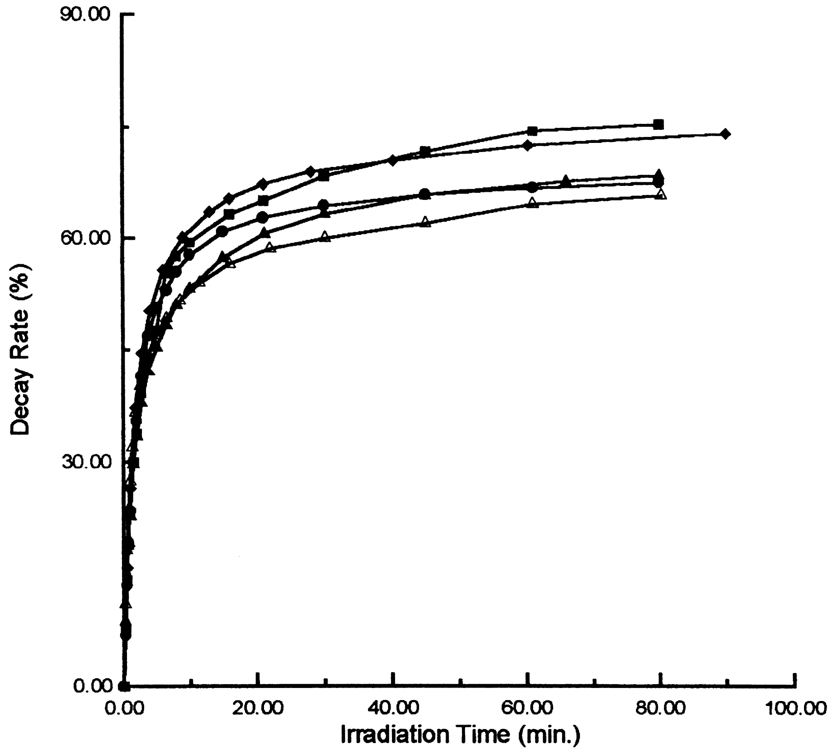


Fig. 8. Effect of solvents on the disappearance rates of C=C of photoreactive groups of homopolymer (**6**) at 30°C; in carbon tetrachloride [– △ –], in dichloromethane [– ■ –], in dioxane [– ▲ –], in DMF [– • –], and in chloroform [– ◆ –].

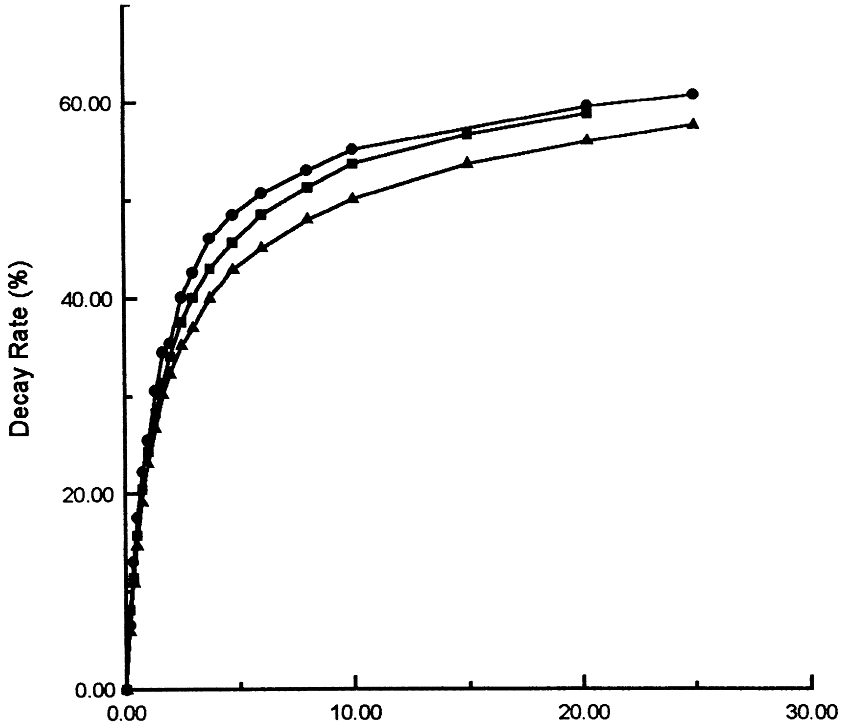


Fig. 9. Effect of temperature on the disappearance rates of C=C of photoreactive groups of polymer (**6**) in DMF: [– • –] at 30°C; [– ■ –] at 50°C; and [– ▲ –] at 80°C.

copolymer types and the solvent used in the photocrosslinking process have no significant effect on the rate of dimerization of the C=C bond; (iv) the final values of the disappearance rates ranged between 60% and 87%. This indicates that complete crosslinking cannot be achieved even after a long irradiation time (150 min). This may be due to chain fragmentation reactions which accompany the photocrosslinking process and reduce the yield of crosslinking. Moreover, intramolecular crosslinks can be formed by the dimerization of adjacent chalcone groups. Intramolecular links do not contribute to network formation and will also lower the yield of crosslinking.

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