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Studies of Photoreactive Poly(Norbornene Derivatives) Bearing Chalcone Units

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ABSTRACT

New photoreactive poly(norbornene derivatives) containing photocrosslinkable pendant units have been prepared via ring opening metathesis polymerization (ROMP) for the first time. The photochemical behavior of these polymers was investigated in dilute solutions. The rates of photocrosslinking were determined under the influence of different factors such as the backbone structure of the polymer, the substituents on the aromatic ring of the photocrosslinkable units, temperature, concentrations of the photocrosslinkable units in the solution, and the solvent. The studies confirmed that all the prepared polymers have higher UV radiation sensitivity in very dilute solutions in different solvents, and at different temperatures.

Key Words: Photoreactive norbornene polymers; Photosensitive polymers; Photoresist materials; Photocrosslinking polymers.

INTRODUCTION

The photosensitive polymers are mostly used in the field of printing, ink[1−3] and coating.[4,5] The development of photosensitive polymers in electronics makes the technology of integrated circuits (ICs) so important that it causes a revolution of

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calculators and advanced microelectronic devices.[6] Also, photosensitive polymers have been of considerable interest in the technological applications of microlithography,[7,8] liquid crystalline materials,[9–12] and nonlinear optical materials.[13] Many different photoresist systems are used in the manufacture of various industrial products such as holographic recording materials,[14–16] chemically amplified photoresists,[17–19] and integrated circuits,[20] compact discs, cathode ray tubes and printing circuit boards.[21]

It is defined that photosensitive polymers are those with photosensitive groups in the main or pendant chains which crosslink or cleave after irradiation with UV light (or electron beam) depending on whether it is a negative- or positive-type.[4] In general, for a negative-type there are three kinds of photosensitive groups used widely, namely the azide groups,[22] cinnamate groups,[23] and diazo groups.[24]

The polymers with pendent 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 following properties: 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, some photoreactive polymers containing α,β-unsaturated carbonyl groups in the backbone[25,26] have been synthesized and characterized as photoresists.

The present work involves the preparation and characterization of novel photocrosslinkable polymers containing pendent chalcone groups. The photochemical studies of these materials in solution have been investigated under various conditions and evaluated. This work is devoted to syntheses and to characterize new photocrosslinkable polymers polymerized via a ring opening metathesis polymerization technique. These polymers are based on polynorbornene backbone and chalcone groups as photocrosslinkable units. As far as we are aware, materials of this kind have not been reported as yet. The homopolymers, as well as the copolymers of these monomers with norbornene or cyclooctene, were characterized and evaluated as negative resist materials.

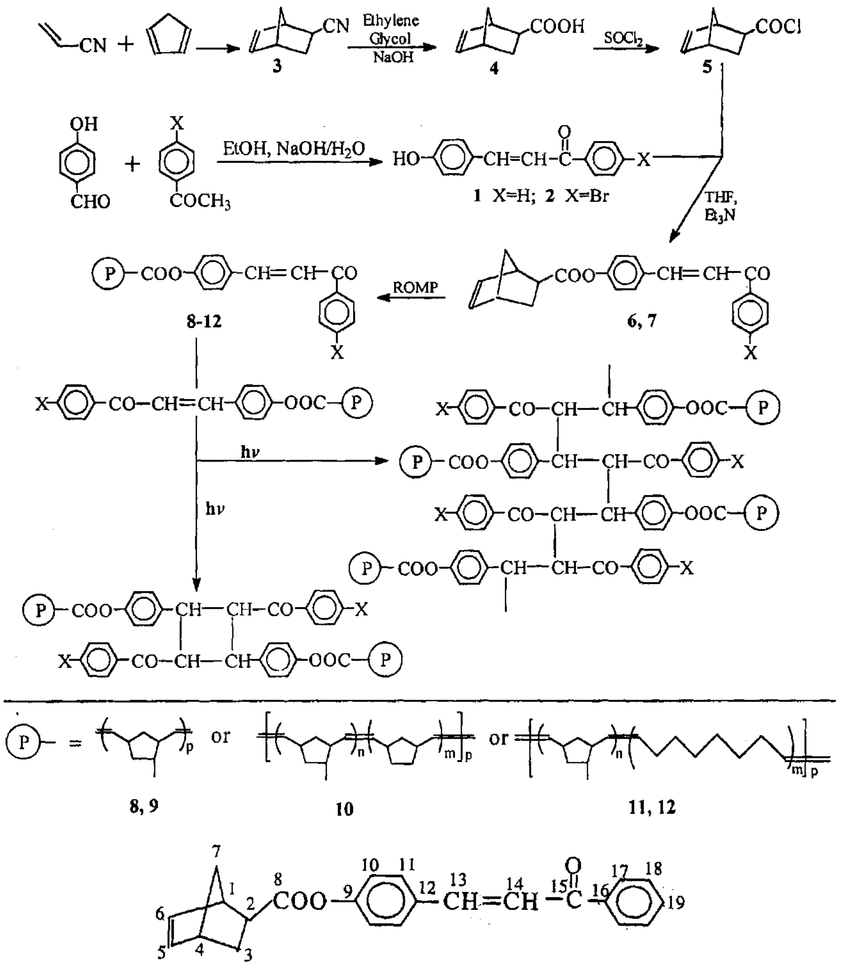
EXPERIMENTAL

Materials

Cyclopentadiene was obtained by thermal degradation of commercially available dicyclopentadiene and purified by distillation. Acetophenone, 4-bromoacetophenone, 4-hydroxybenzaldehyde, and acrylonitrile that were applied during the synthesis were obtained from Fluka (Switzerland) and used without further purification. All polymerization was carried out in dichloromethane purified by distillation over phosphorus pentaoxide under argon atmosphere.

Synthesis of Chalcones 1, 2 [Sch. 1]

The synthesis of chalcones was carried out as described before.[27,28] This was achieved by dissolving acetophenone and 4-hydroxybenzaldehyde (1:1 mole ratio) in



Scheme 1. Preparation of monosubstituted photoreactive norbornene monomers and polymers and photoreactions of the polymers.

ethanol, then an aqueous NaOH solution was added dropwise under stirring at 14–16°C overnight. The precipitate formed on neutralization with 2N HCl was filtered off, thoroughly washed with water and recrystallized from ethanol to give 4-hydroxystyryl phenyl ketone **1** as yellow crystals in 57% yield. The product had m.p. 182–184°C (in Ref.[29], the m.p. is 181–182°C).

4-Hydroxystyryl-4′-bromophenyl ketone **2** was prepared by added an aqueous NaOH solution to a solution of 4-bromoacetophenone and 4-hydroxybenzaldehyde. The product was recrystallized from ethanol to give a bright yellow crystalline product **2** in 66% yield. m.p. 175–176°C (in Ref.[29]: m.p. is 177–178°C).

Norborn-5-ene-2-carboxylic Chloride 5 [Sch. 1]

This compound was prepared following the procedure described in Ref.[30] through several steps.

Norborn-5-ene-2-carbonitrile **3** was prepared by refluxing a mixture of freshly distilled cyclopentadiene (1.5 mole) and acrylonitrile (1.0 mole) in diethyl ether for 5 h. Product **3** was obtained with 98% yield after evaporation of the solvent and excess cyclopentadiene, then distillation.

A solution mixture of KOH (2.3 mole) and norborn-5-ene-2-carbonitrile **3** (0.76 mole) in dry ethylene glycol was heated at 110°C for 12 h with stirring. After cooling, the reaction solution was acidified with concentrated HCl and extracted in diethyl ether to give 2-norbornene-5-carboxylic acid **4** (0.66 mole) in 87% yield.

A mixture of norborn-5-ene-2-carboxylic acid **4** (0.217 mole) and thionyl chloride (0.67 mole) in dry toluene was refluxed for 2 h followed by distillation of toluene and excess thionyl chloride. The residue was distilled under vacuum (15 mm Hg) and gave (0.20 mole) with 92% yield of norborn-5-ene-2-carboxylic chloride **5**.

The conformation of the structures of these compounds was investigated by spectroscopic methods. The data of which were corresponding to the structures.

Preparation of Monomers 6, 7 [Sch. 1]

A solution of norborn-5-ene-2-carboxylic chloride **5** (32.6 mmol) in THF was added dropwise to a stirred mixture of 4-hydroxystyryl phenyl ketone **1** (32 mmol) and triethylamine (50 mmol) in absolute tetrahydrofuran (THF). After stirring for 3 h at room temperature, the quaternary ammonium salt precipitated was filtered off and the THF was evaporated under reduced pressure. The solid residue was dissolved in dichloromethane and washed successively with HCl, NaOH, distilled water then dried over anhydrous Na_2SO_4 followed by evaporation of the solvent under reduced pressure. The product was crystallized from cyclohexane/ethyl acetate to give (28 mmol) in 85% yield as faint yellow crystals; norborn-5-ene-2-carboxyloyloxy(4-styryl phenyl ketone) **6**; with m. p. 141°C.

Elementary analysis: Calculated C-% = 80.23; H-% = 5.81; Found C-% = 79.96; H-% = 5.89.

IR (film on NaCl): $\nu = 3067$ (C—H aromatic); 2947 (C—H aliphatic); 1747 (C═O ester); 1658 (C═O keto); 1592, 1413 cm^{-1} (CH═CH).

^{1}H-NMR ($CDCl_3$): $\delta = 8.04-7.05$ (m, 10 H, H^{13}, H^{14}, $H_{aromatic}$); 6.30 (m, 1 H, H^6); 6.06 (m, 2H, H^5); 3.4 (s, 1H, H^1); 3.24 (s, 1H, H^2); 3.05 (s, 1H, H^4); 2.50 (m, 2H, H^3, exo); 2.05 (m, 2H, H^3, endo); 1.70–1.30 ppm (m, 2H, H^7).

Norborn-5-ene-2-carboxyloyloxy(4-styryl-4′-bromophenyl ketone) **7** was prepared as described for compound **6** by addition of compound **5** (12 mmol) to a stirred mixture of 4-Hydroxystyryl-4′-bromophenyl ketone **2** (10 mmol) and triethylamine (20 mmol) in dry THF. The product was crystallized from cyclohexane/ethyl acetate to give (6.7 mmol, yield 67%) as faint crystals of the product **7** with m.p. of 144°C.

Elementary analysis: Calculated C-% = 65.25; H-% = 4.49; Br-% = 18.91; Found: C-% = 64.98; H-% = 4.56; Br-% = 18.54.

IR (film on NaCl): $\nu = 3063$ (C—H aromatic); 2971 (C—H aliphatic); 1750 (C=O ester); 1658 (C=O keto); 1600, 1415 cm^{-1} (CH=CH).

^{1}H-NMR ($CDCl_3$): $\delta = 7.94-7.05$ (m, 10 H, H^{13}, H^{14}, $H_{aromatic}$); 6.30–6.05 (m, 2H, H^5, H^6); 3.40 (s, 1H, H^1); 3.24 (s, 1H, H^2); 3.05 (s, 1H, H^4); 2.50 (m, 2H, H, exo); 2.05 (m, 2H, H endo), 1.70–1.30 ppm (m, 2H, H^7).

Preparation of Polymers

The polymers were prepared via ring opening metathesis polymerization (ROMP) technique[31] using a molybdenum carbene complex {[Mo(CH-*t*-Bu) (NAr) (O-*t*-(CH_3)(CF_3)$_2$)] (NAr = 2,6-diisopropylaniline)} as initiator under nitrogen as outlined in Sch. 1. As a typical example, preparation of polymer **8** is described in detail. All data relevant to the individual experiments are summarized in Table 1 for the preparation of all polymers.

The monomer **6** (0.50 g) was dissolved in freshly distilled and dried methylene chloride (5 ml) then a solution of the initiator (0.0045 g) in methylene chloride was added. The reaction solution was stirred for 1 h at room temperature. The polymerization reaction was quenched by the addition of ~150 mg of benzaldehyde. The solution was poured into 100 ml methanol. The polymer precipitated was filtered off, washed, and dried to constant weight in vacuum. The yield was 0.44 g of polymer **8**, this corresponds to 88% conversion of monomer to polymer.

Photochemical Studies

The photoreactivity of the prepared polymers was studied on a polymer solution under different factors. The polymer solution was irradiated at 16.5 cm distance from the light source at $\lambda = 365$ nm using EMITA VP 60, 180 W medium-pressure mercury lamp for different intervals. The full UV spectra of the samples before and after irradiation, in the wavelength range 450–200 nm, were recorded on a Shimadzu 2101 PC Scanning Spectrophotometer (Fig. 2). The disappearance rate of the double bond in the reactive groups was followed by using the first order expression:

$$kt = Ln(A_o/A_o - A_t)$$

where A_o and A_t are absorbances due to double bond after irradiation times t = 0 and t, respectively and k is the rate constant. Figures 3–6 show the relation between $Ln(A_o/A_o - A_t)$ and t (min.).

Instruments

Infrared spectra were recorded with a Bomem Michelson M100 FTIR spectrometer. Specimens were prepared by casting polymer films from chloroform solutions onto NaCl plates. ^{1}H-NMR spectroscopic measurements were recorded in $CDCl_3$ with a Bruker MSL 300 spectrometer. Average molecular weights were determined by gel permeation chromatography (GPC). The polystyrene gel columns from Polymer Standards Service

Table 1. Polymerization conditions and characteristic properties of photoreactive poly(norbornene) derivatives **8–12**.

					Products						
	Reactive[a] monomer		Comonomer[b]			Average molecular weights[c]			Thermal properties[d]		
										TDG	
Polymer	No.	n	Type	m	Yield (%)	$M_n \times 10^4$	$M_w \times 10^4$	PDI (M_w/M_n)	T_g	1st stage	2nd stage
8	**6**	1.000	—	—	86	5.3064	7.0476	1.3748	105.6	320–525	525–625
9	**7**	1.000	—	—	94	6.6696	8.5277	1.2785	108.5	285–480	480–620
10	**6**	0.248	Nb	0.752	95	14.173	31.398	2.2152	92.2	250–490	490–620
11	**6**	0.090	Cy8	0.910	82	10.338	27.040	2.6155	42.0	250–525	525–650
12	**6**	0.211	Cy8	0.789	71	8.5691	19.696	2.2985	67.4	230–500	500–630

[a] n: is the mole ratio.

[b] m: is the mole ratio; Nb: norbornene; Cy8: cyclooctene.

[c] PDI: polydispersity index (M_w/M_n).

[d] Tg: glass transition temperature; TDG: temperature decomposition range.

(10^3, 10^4 and 10^6, 5 particle size, 5 μm) and THF as eluent was used. Polystyrene standards from Polymer Laboratories Inc. were used for calibration. The thermal behavior of the polymers was investigated in the temperature range from ≈25°C to 800°C by thermogravimetric analysis (TGA) Shimadzu TGA-50 with heating rate l0°C/minute in all cases (Fig. 1).

RESULTS AND DISCUSSION

Synthesis and Characterization

The norbornene monomers containing photoreactive chalcone moieties as pendent groups were prepared through two steps as illustrated in Sch. 1. The first step involved the reaction of 4-hydroxybenzaldehyde with acetophenone or 4-bromoacetophenone in the presence of sodium hydroxide in ethanol/water mixture to prepare the chalcones **1**, **2**. The second step included the reaction of the chalcones **1**, **2** with norborn-5-ene-2-carboxyloyl chloride **5** in the presence of triethylamine in tetrahydrofuran at room temperature (12–15°C) to obtain the monomers **6**, **7**. TLC showed that there are two products with very close R_f values on the chromatoplate after multiple development using cyclohexane/ethyl acetate 9:1 as eluent. The structure of the monomers was confirmed by FT-IR and NMR spectra, which revealed that the monomers were exo and endo isomers. The melting temperature of the monomers was determined from DSC measurements, which showed that the monomers have a relatively low melting temperature and a relatively high decomposition temperature in comparison with the acrylate and methacrylate monomers containing the same photosensitive groups.[32]

The homopolymers **8**, **9** and copolymers **10**–**12**, were prepared by the ROMP technique using highly active fluoro-substituted Molybdenum–carbene initiator (Mo(CH-*t*-Bu)(NAr)-($OCCH_3(CF_3)_2$) with NAr = 2,6-diisopropylaniline) in dichloromethane under inert conditions at room temperature (Table 1, Sch. 1). The polymerization time was a few minutes for the polymers **8**–**10** and about 1 h for the copolymers **11**, **12**. Relatively high concentrations of the monomers were used to shift the polymerization equilibrium to the polymer especially in the case of copolymerization with cyclooctene. After quenching with benzaldehyde the solution was dropped slowly into methanol to precipitate the polymer in good yields of 71–94%. The prepared polymers were easily soluble in polar aprotic solvents like dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone or tetrahydrofuran and in chlorinated solvents like chloroform, chlorobenzene and dichloromethane. They were insoluble in alcohols like ethanol, methanol, 2-propanol and in hydrocarbons like benzene, toluene, and xylene.

The synthesis procedure was followed by GPC (Table 1). The average number molecular weight M_n and average mass molecular weight M_w of the white solid polymers ($M_n = 5.3 \times 10^4$ and 6.7×10^4 g/mol; $M_w = 7.0 \times 10^4$, 5.3×10^4 g/mol with polydispersity index PDI = 1.4, 1.3 for homopolymers **8**, **9**, respectively. Also, $M_n = 8.6 \times 10^4 - 14.2 \times 10^4$ g/mol; $M_w = 19.7 \times 10^4 - 31.4 \times 10^4$ g/mol with polydispersity index PDI = 2.2–2.3 for copolymers **10**–**12**. From the molecular weight determination, we can state that the homopolymers have lower molecular weights and PDI than the co-polymers. This was attributed to the difference in the polymerization reactivity

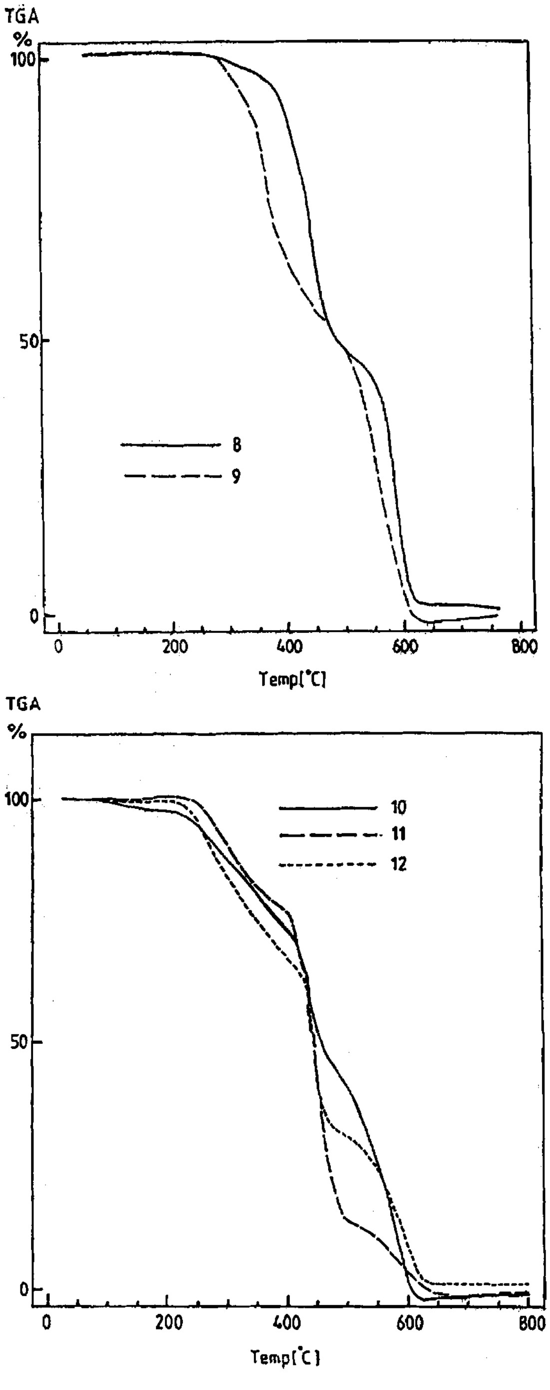


Figure 1. Thermogravimetric analysis diagram for polymers **8–12**.

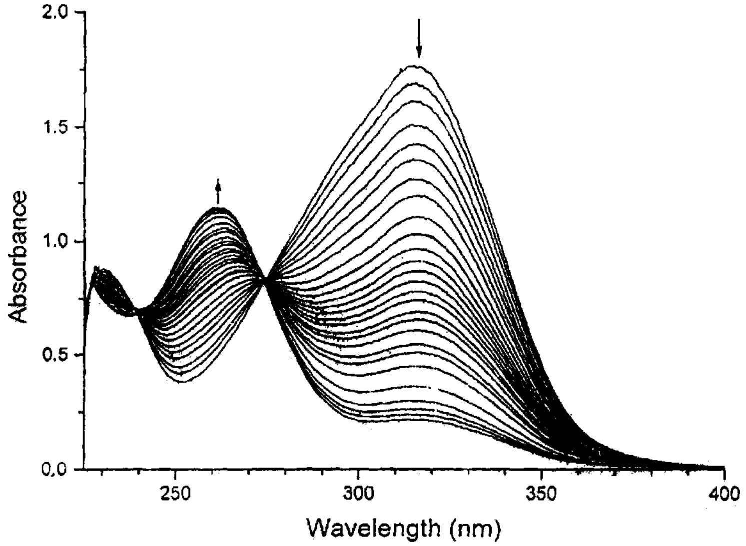


Figure 2. Full spectra of polymer **9** in dichloromethane before irradiation and after different irradiation periods; from up to down at ≈315 nm [time = 0, 0.25, 0.5, 0.75, 1, 1.33, 1.67, 2.17, 2.75, 3.25, 3.75, 4.25, 5.25, 6, 6.75, 7.5, 8.75, 10, 12, 15, 18, 24, 30, 40, 50, 60, and 75 min.].

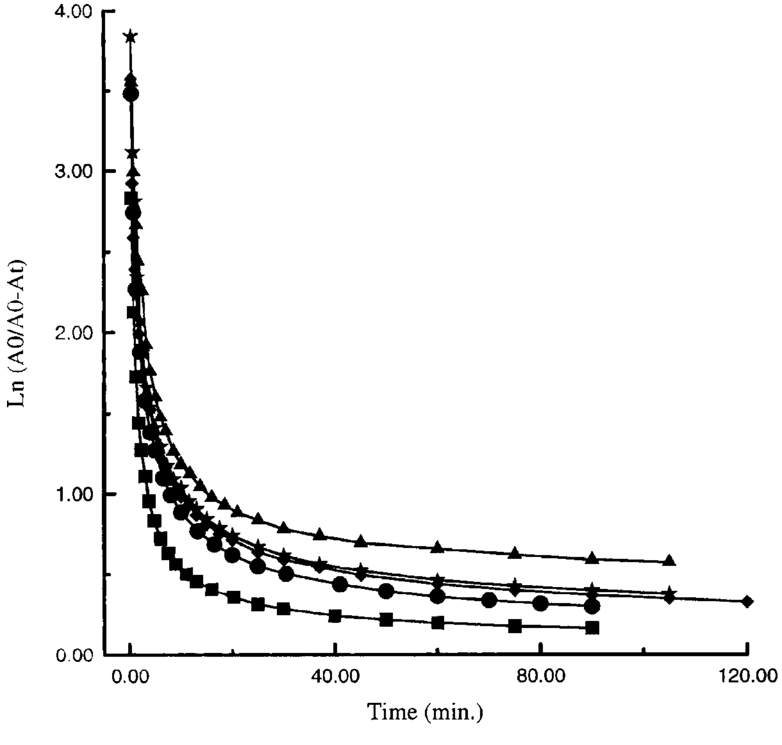


Figure 3. Rate of disappears of different polymeric samples 8 (●); 9 (■); 10 (▲); 11 (▲) and 12 (★) in dioxan.

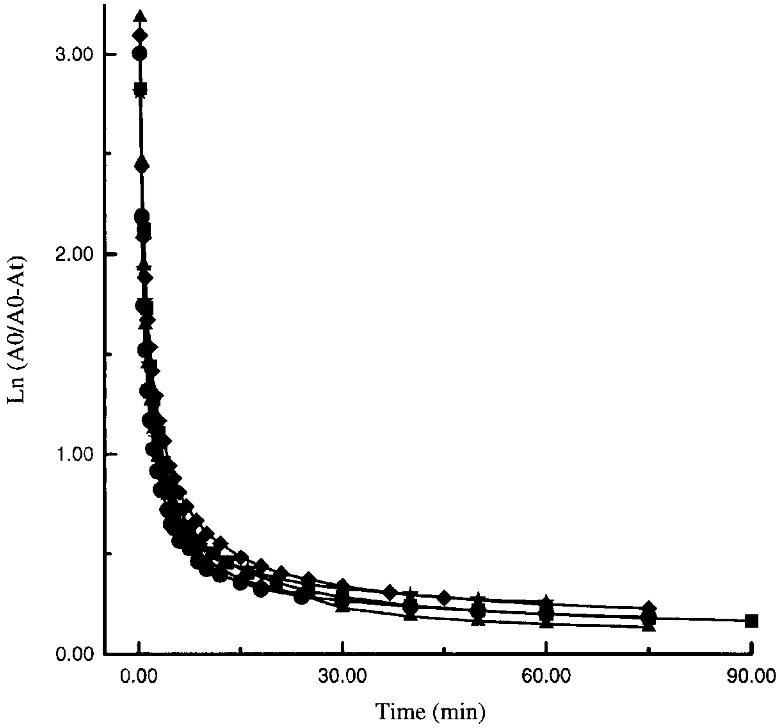


Figure 4. Rate of disappears of polymeric sample **9** in different solvents; chloroform (●); dichloromethane (▲); dimethylformamide (★); dioxan (■) and tetrahydrofuran (◆).

of the monomers. The higher molecular weights and PDI of the copolymers coming from the low reactivity of the comonomers, which leads to increase the polymerization time as compared with the photoreactive monomer, and late the chain termination and give high molecular weight polymers. The polymers containing cyclooctene as co-monomer have lower than average molecular weights than the polymer containing norbornene co-monomer and higher PDI. The molecular weight decreases with increasing the content of cyclooctene ratio. This is attributed to low reactivity of cyclooctene and a small conversion to polymer as compared with norbornene.[30] Also, the GPC diagrams showed that the copolymers had broader curves than the homopolymers. This illustrates the higher polydispersity of these polymers. The chemical structures of these polymers were confirmed with FT-IR and NMR spectroscopic methods. The peaks and signals that appeared correspond to the structure as shown in the Experimental part.

The thermal properties of the polymers were characterized by measuring the differential scanning colorimeter (DSC) and thermogravimetric analysis (TGA). The glass transition temperatures of the polymers were determined from DSC measurements and showed that the polymers have a lower glass transition temperature (Table 1) than the monomers. This gives these polymers an interest in the application at lower temperatures. The copolymers were found to have lower Tg than the homopolymers. Also, the copolymers containing cyclooctene comonomer **11** and **12** have lower T_g than the

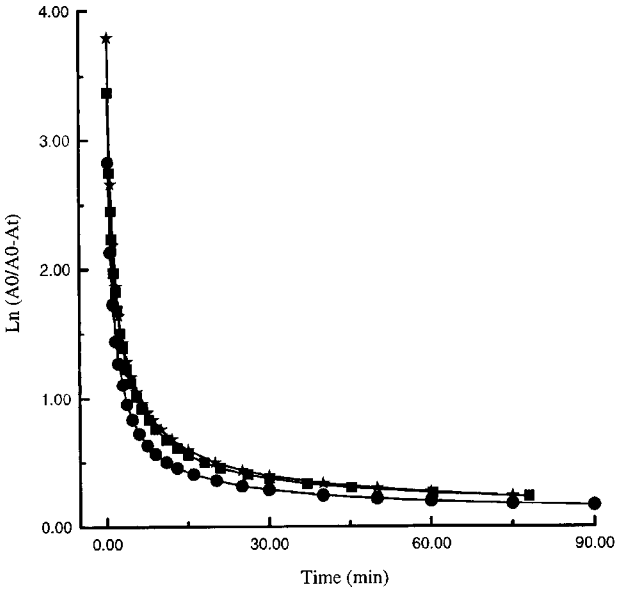


Figure 5. Rate of disappears of polymeric sample **9** at different temperatures; at 25°C (●); at 50°C (■) and at 80°C (★) in dioxan.

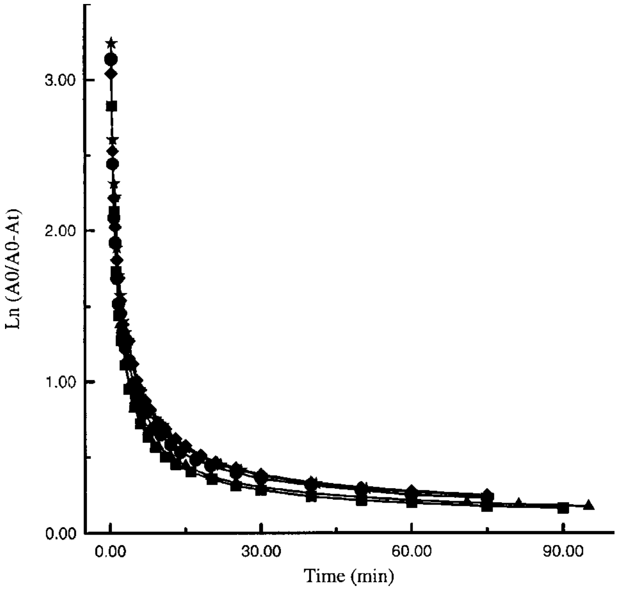


Figure 6. Rate of disappears of polymeric sample **9** in dioxan at different concentrations; 10 mg/l (●); 28.4 mg/l (■); 36 mg/l (▲); 40 mg/l (★) and 50 mg/l (◆).

copolymer containing norbornene comonomer **10** due to the flexible rubber-like backbone structure. The decomposition temperature range of the polymers (Table 1) shows that these polymers are thermally stable below approximately 280°C. Also, the thermograms (Fig. 1) show that the decomposition of the polymers takes place in two steps. The first occurs between ≈250°C and ≈500°C, and may be due to the decomposition of the pendent groups. The second occurs between ≈500°C and ≈630°C and may be due to the decomposition of the polymer backbone.

Photochemical Properties

The UV spectra of the polymers were determined under different variables such as polymer structure, solvents, temperature and concentrations. The spectral data, illustrated in Table 2 , show that there are differences in the absorption values at $\lambda_{max} \approx 310-312$ nm (1.628 for polymer **8** and 1.811 for polymer **9**) using the same concentration in mg/l. This difference was attributed to the presence of bromide substitution in the aromatic ring of the photosensitive group in polymer **9**. Also, there are differences in the absorption values at λ_{max} in the case of the copolymers **10**–**12**, using the same concentration (28.4 mg/l) in the same solvent (1,4-dioxane). This may be due to the difference in the polymer backbone and change in the intensity of the photosensitive part responsible for the absorption at these wavelengths. In the case of using different solvents for the same polymer with

Table 2. Some UV data for the polymers before and after irradiation under different variables.

Sample	Solv[a]	Abs.	λ_{max} (nm)	Temp. (°C)	Conc. (mg/l)	ε	Decay (%)[b]
8	Diox	1.628	310	25	28.4	0.0573	72.3
9	Diox	1.811	313	25	28.4	0.0638	83.8
10	Diox	1.192	312	25	28.4	0.0420	53.8
11	Diox	0.882	311	25	28.4	0.0311	65.4
12	Diox	0.928	311	25	28.4	0.0328	67.1
9	DMF	1.831	317	25	28.4	0.0645	77.4
9	THF	1.768	315	25	28.4	0.0623	79.8
9	CH_2Cl_2	1.758	315	25	28.4	0.0619	87.7
9	$CHCl_3$	1.854	316	25	28.4	0.0653	83.3
9	Diox	1.709	313	50	28.4	0.0602	79.5
9	Diox	1.650	313	80	28.4	0.0581	79.2
9	Diox	0.620	313	25	10	0.0620	79.4
9	Diox	2.394	313	25	36	0.0665	82.3
9	Diox	2.583	313	25	40	0.0646	78.2
9	Diox	3.246	314	25	50	0.0649	78.0
9	Diox	2.641	310	25	36	0.0734	71.4

[a] Diox = 1,4-dioxane; DMF = dimethylformamide; THF = tetrahydrofuran.
[b] Percent of decay after 75 min of irradiation with UV light.

a constant concentration, there is no clear difference in the absorption values at λ_{max}, which indicates that we can use many solvents without affecting the reactivity of the polymer and that the molar absorptivity is nearly the same in most the solvents. The increase of temperature leads to a small decrease in the absorption values at λ_{max}, in the same solvent with a constant concentration, which may be attributed to an increase of the kinetic energy of molecules and leads to thermal crosslinking.

The photochemical behavior of the prepared polymers in solutions is illustrated in Figs. 2–6. On irradiation with UV light (366 nm, 180 W), the change of optical absorbance is rather similar for all the polymers. The absorption maximum at $\lambda_{max} \approx 310$ nm decreased and an isobestic point at 280 nm is established.

The effect of irradiation on the polymers was studied in polymer solutions with UV light at $\lambda = 365$ nm and the light effect was followed by measuring the rate of decay of the —C═C— of the cinnamoyl groups (Fig. 2). The figure shows the full UV spectra (example polymer **9**) before and after irradiation at interval periods of time. Initial irradiation has shown a *trans–cis* isomerization of the double bond, as was evident by the appearance of the isobestic point at ≈280 nm. Further irradiation results in a fast decrease in absorption at $\lambda_{max} \approx 310–315$ nm. This behavior clearly indicates the cyclobutane ring by the $2 + 2$ addition of pendant chalcone units of polymer, which can be attributed to the decrease in the conjugated system upon irradiation with a concomitant in the absorbance at a shorter wavelength. Thus, these polymers react photochemically according to a mechanism similar to that found for cinnamic acid and its derivatives in which a cyclobutane structure or crosslinking were formed,[33] Sch. 1. Generally, the rates of dimerization or crosslinking were found to very fast in the first few minutes followed by a gradual decrease in rates.

The decay rates of photosensitive group in the polymers (Fig. 3) show that the homopolymers **8** and **9** have higher decay rates than the copolymers **10**–**12**. Also, the conversion of the cinnamoyl groups to the dimerized or crosslinked form in the polymers **8** and **9** was found to be higher than in the polymers **10**–**12**. This result may be attributed to the difference in the polymer structure and decrease in the intensity of the photoreactive groups, due to copolymerization.

The effect of solvents on the rates of dimerization or crosslinking were studied on a polymer sample **9** and the results are shown in Fig. 4, in which, there is no clear difference in the rate of conversion in different solvents such as, chloroform, dichloromethane, dioxane, tetrahydrofuran, and dimethylformamide. These results indicate that the reactivity of these polymers doesn't change with changing the solvent, especially in the first few minutes of irradiation. Therefore, a variety of solvents can be recommended for use with these materials.

The temperature effect on the decay rate of the photosensitive groups in the polymer solutions was investigated with a constant concentration of polymer **9** in dioxane at different temperatures (25, 50, and 80°C) as in Fig. 5. The results indicate that the decay rates are high and nearly similar during the first few minutes (3–4 min) followed by low rates with maximum conversion percentage of 80% after irradiation time = 75 min.

The effect of concentration of the photosensitive polymers on the rates of photocrosslinking was studied on polymer **9** in dioxane as shown in Fig. 6. The results indicate that the increase in the concentration of the polymer is accompanied with a small decrease in the conversion rates. This may be due to the decrease in the movement of the unirradiated molecules in concentrated solutions than in dilute ones.

Generally, the conversion rates were characterized (in all cases) by no clear order, which may be first order in different cases. The first stage is very fast decay rates, which occurs in the first few minutes. The final stage is very slow with a gradual decrease in the decay rates. The values of conversion rates ranged between 0.65 and 0.85 after long irradiation time (75–120 min). This indicates that complete conversion cannot be achieved, which may be due to chain fragmentation reactions that 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.

CONCLUSION

Preparation of new photosensitive polymers via ring opening metathesis polymerization techniques for the first time was achieved. These polymers are based on monosubstituted norbornene derivatives containing chalcone moieties as photocrosslinkable pendant units. The photochemical reactivity of these polymers was investigated in dilute solutions. The decay rates of photosensitive groups of the polymers were determined under different variables such as the backbone structure of the polymer, substituents on the aromatic ring of the photocrosslinkable units, temperature, concentrations of the photocrosslinkable polymer in the solution, and the nature of solvent. The studies confirmed that all the polymers are characterized by higher sensitivity to UV radiation even in very dilute solutions. The sensitivity to UV radiation was still higher with changing the backbone of the polymers, changing the temperature and solvents.

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