

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Negative Photoresist Materials Based on Poly(Norbornene Derivatives-co-styrene-co-maleic Anhydride)

Ahmed Rehab^a

^a Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt

To cite this Article Rehab, Ahmed(2005) 'Negative Photoresist Materials Based on Poly(Norbornene Derivatives-co-styrene-co-maleic Anhydride)', *Journal of Macromolecular Science, Part A*, 42: 3, 327 – 339

To link to this Article: DOI: 10.1081/MA-200050465

URL: <http://dx.doi.org/10.1081/MA-200050465>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Negative Photoresist Materials Based on Poly(Norbornene Derivatives-co-styrene-co-maleic Anhydride)

AHMED REHAB

Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt

Photosensitive polymers of norbornene-co-styrene-co-maleic anhydride with different mole ratios were synthesized as a polymer matrix for UV photoresist. These polymers were prepared by radical polymerization under controlled conditions. These polymers have a higher glass transition temperature than polystyrene and are chemically reactive with certain functional groups. The photochemical behaviors of these polymers were investigated in solutions. The rates of photocrosslinking were studied under the influence of different factors such as the backbone structure of the polymer, the substituents on the aromatic ring of the photocrosslinkable units, the temperature, the 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.

Keywords photosensitive polymers, photoreactive norbornene polymers, styrene-maleic anhydride photopolymers, photoresist materials, photocrosslinking polymers

Introduction

The photoreactive polymers have been of considerable interest in the technological applications of microlithography (1, 2), liquid crystalline materials (3–5), and nonlinear optical materials (6). Many different photoresist systems are used in the manufacture of various industrial products such as holographic recording materials (7–9), chemically amplified photoresists (10, 11), formation of images and surface relief gratings, (12) compact discs, cathode ray tubes and printing circuit boards (13). Also, the photosensitive polymers are mostly used in the field of printing, ink (14, 15) and coating (16, 17). The development of photosensitive polymers in electronics makes the technology of integrated circuits (ICs) so important that it causes a revolution of calculators and advanced micro-electronic devices (18).

Generally, the photosensitive polymers are those with photosensitive groups in the main or pendant chains, which crosslink (negative-type) or cleave (positive-type) after irradiation with UV light (or electron beam) depending on whether it is a negative- or

Received April 2004; Accepted August 2004

Address correspondence to Ahmed Rehab, Department of Chemistry, Faculty of Science, Tanta University, 31527 Tanta, Egypt. E-mail: rahmed@dec1.tanta.edu.eg or rehab220956@yahoo.com

positive-type. For a negative-type, there are three kinds of photosensitive groups widely used, namely, the azide groups (19), cinnamate groups, and diazo groups (20).

The growth in the microelectronic device industry has been supported by microlithography and photoresist technologies. Methacrylate copolymers with pendant alicyclic groups (21) and cycloolefin-maleic anhydride copolymers (22) have been proposed for their high transparency and good dry-etching resistance.

Copolymerization of styrene with maleic anhydride is created with a copolymer (SMA), which has a higher glass transition temperature than polystyrene and is chemically reactive with certain functional groups. Thus, SMA polymers are often used in blends or composites where interaction or reaction of the maleic anhydride provides for desirable interfacial effects. Also, these polymers are soluble in alkaline aqueous systems and selected organic solvents. They are an excellent film former, and provide a high degree of water resistance in aqueous formulations. Typical applications are as a surface size treatment for paper, adhesive modifier, emulsifier, binder, pigment dispersant, viscosity modifier, and as an ingredient in coatings for printed circuit board manufacture.

In continuation of our work (23–25) to synthesis and study the photochemical behavior of a new negative-type photosensitive polymers, the present work involves the preparation and characterization of new photocrosslinkable polymers which are based on polynorbornene backbone and cinnamate groups as photocrosslinkable units copolymerized with styrene and maleic anhydride. The photochemical studies of these materials in solution have been investigated under various conditions and evaluated as negative resist materials. The different properties of the solid films of these polymers will be studied in work to follow.

Experimental

Materials and Measurements

Styrene supplied from Aldrich was used after washing with 2 N NaOH solution and dried over sodium sulphate anhydrous. Maleic anhydride was used as supplied from Merck-Schuchardt. Benzoyl peroxide was used as supplied from BDH laboratory reagents, Chemical Ltd. (England). Cyclopentadiene was obtained by thermal degradation of commercially available dicyclopentadiene and purified by distillation. Acetophenone, 4-bromoacetophenone, 4-hydroxybenzaldehyde, and acrylic acid were bought from Fluka (Switzerland) and used without further purification. All polymerization were carried out in tetrahydrofuran (THF), supplied from Fluka and dried over NaOH, then refluxed with sodium metal followed by distillation. 1,4-Dioxane was supplied from Aldrich. Dimethylformamide (DMF), chloroform and dichloromethane (CH_2Cl_2) were used as supplied from Prolabo.

Infrared spectra were carried out on a Perkin-Elmer 1430 Ratio-recording infrared spectrophotometer using the potassium bromide disc technique in the wavenumber range of 4000 to 400 cm^{-1} . The thermal behaviors of the polymers were investigated by thermogravimetric analysis (TGA) Shimadzu TGA-50 in the temperature range from $\approx 30^\circ\text{C}$ to 800°C in all cases and differential scanning calorimetry (DSC) using a Shimadzu DSC-50 in the temperature range from $\approx 30^\circ\text{C}$ to 480°C in all cases. ^1H -NMR spectroscopic measurements were recorded in DMSO with a Bruker MSL 300 spectrometer.

Synthesis of Norborn-5-ene-2-carboxyloyl Chloride I

This compound was prepared following a procedure described in Reference 25 through several steps as illustrated in the following procedure: A mixture of freshly distilled cyclopentadiene (62.5 g, 940 mmol) and acrylonitrile (32.5 g, 615 mmol) were dissolved in 100 mL of diethyl ether and refluxed for 5 h. After evaporation of the solvent and excess cyclopentadiene, the product was purified by distillation to give 71 g (96% yield) of norborn-5-ene-2-carbonitrile. The product (47.5 g, 400 mmol) was added to a solution of KOH (75 g, 2.5 mol) in 250 mL of dry ethylene glycol, then heated at a temperature $\approx 110^\circ\text{C}$ for 12 h with stirring. After cooling, the reaction solution was acidified with concentrated HCl, and extracted with diethyl ether (3 times with 150 mL each). The obtained product was 118 g (89% yield) of norborn-5-ene-2-carboxylic acid. The norborn-5-ene-2-carboxylic acid (20.5 g, 150 mmol) was converted to norborn-5-ene-2-carboxyloyl chloride **I** by reflux with thionyl chloride (90 g) in 100 mL of dry toluene for 2 h, followed by distillation of toluene and excess thionyl chloride. The residue was distilled in vacuum to give 22 g (93% yield). The structure of these compounds was investigated by spectroscopic methods and corresponded to the structures.

Preparation of Photoreactive Units II_{a,b}

The photoreactive units were prepared by the same conditions as described in references (23) and (24). This was achieved by adding an aqueous NaOH solution dropwise, under stirring at room temperature, to a mixture of acetophenone and 4-hydroxybenzaldehyde in ethanol. The precipitate formed on neutralization with 2N HCl was filtered off, washed with water, and recrystallized from ethanol to give **II_a** [4-hydroxystyryl phenyl ketone] as yellow crystals with 59% yield. The product had a m.p. of 180–182°C (in reference (26), the m.p. is 181 ~ 182°C). The photoreactive unit **II_b** [4-Hydroxystyryl-4'-bromophenyl ketone] was prepared under the same conditions by adding NaOH to a solution mixture of 4-bromoacetophenone and 4-hydroxybenzaldehyde to give a bright yellow crystalline product with 76% yields. m.p. 176–178°C (in reference (26), the m.p. is 177–178°C). The structure of these compounds was investigated by spectroscopic methods and corresponded to the structures.

Preparation of Monomers III_{a,b}

A solution of **I** [norborn-5-ene-2-carboxyloyl chloride] (10.2 g, 65 mmol) in 25 mL fresh distilled THF was added dropwise to a stirred mixture of **II_a** [4-hydroxystyryl phenyl ketone] (15.5 g, 64 mmol) and triethylamine (10.08 g, 100 mmol) in 150 mL of fresh distilled THF. After complete addition, the stirring was continued for 3 h at room temperature. The precipitated quaternary ammonium salt was filtered off and the THF was evaporated under reduced pressure. The solid residue was dissolved in dichloromethane and washed successively with 1N HCl (twice), 1N NaOH (once) and finally with distilled water. After drying over anhydrous Na₂SO₄, the solvent was removed under reduced pressure. The crude product was recrystallized from cyclohexane/ethyl acetate (volume ratio 10:1) to give 19.5 g (87% yield) of faint yellow crystals monomer [norborn-5-ene-2-carboxyloxy (4-styryl phenyl ketone)] **III_a** with a m.p. of 140–141°C.

The monomer **III_b** was prepared by the addition of a solution of **I** (4.75 g, 30 mmol) dropwise to a stirred mixture of 7.58 g (25 mmol) of **II_b** and 10.8 g of triethylamine in 100 mL of dry THF. The product was recrystallized from cyclohexane/ethyl acetate

(vol. ratio 10 : 1) to give 7.45 g (6.7 mmol) of faint crystals with a 70% yield. The product **III_b** [norborn-5-ene-2-carboxyloxy(4-styryl-4'-bromophenyl ketone)] had a m. p. of 143–144°C. The structure of these compounds was investigated by spectroscopic methods and corresponded to the structures as seen in the references.

Preparation of Polymers **IV_{a-d}**

A series of copolymers were synthesized by a solution-free radical technique (27). The polymerization was achieved in a dry system using benzoyl peroxide as an initiator. As a typical example, run **IV_a** was described in detail.

A mixture of the monomer **III_a** (0.636 g, 1.85 mmol), maleic anhydride (0.221 g, 2.25 mmol) and styrene (1.18 g, 11.25 mmol) were dissolved in 5 mL of freshly distilled and dried THF, then added benzoyl peroxide (0.043 g) as initiator. The reaction solution was stirred for a few minutes at room temperature, then 1 h at reflux. The solution was poured dropwise into 200 mL of methanol. The precipitated powder was filtered off, washed, and dried to a constant weight *in vacuo*. The yield was 1.06 g (52% yield) of polymer **IV_a**. All data relevant to the individual experiments are summarized in Table 1.

Photochemical Studies of Polymers

The photoreactivity of the prepared polymers was studied on dilute solutions of polymer in different solvents and different concentration and irradiated with medium-pressure mercury lamp (EMITA VP60, 180 W) at a distance of 18.5 cm from the light source for different intervals of time. After each irradiation, the UV spectra were recorded on a Shimadzu 2101PC Scanning Spectrophotometer. The rate of disappearance of the double bond in the reactive chalcone groups was followed by the expression:

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

where A_0 and A_T are absorption intensities due to double bond after irradiation times $t = 0$ and $t = T$, respectively.

Table 1
Polymerization conditions of polymers **IV_{a-d}**

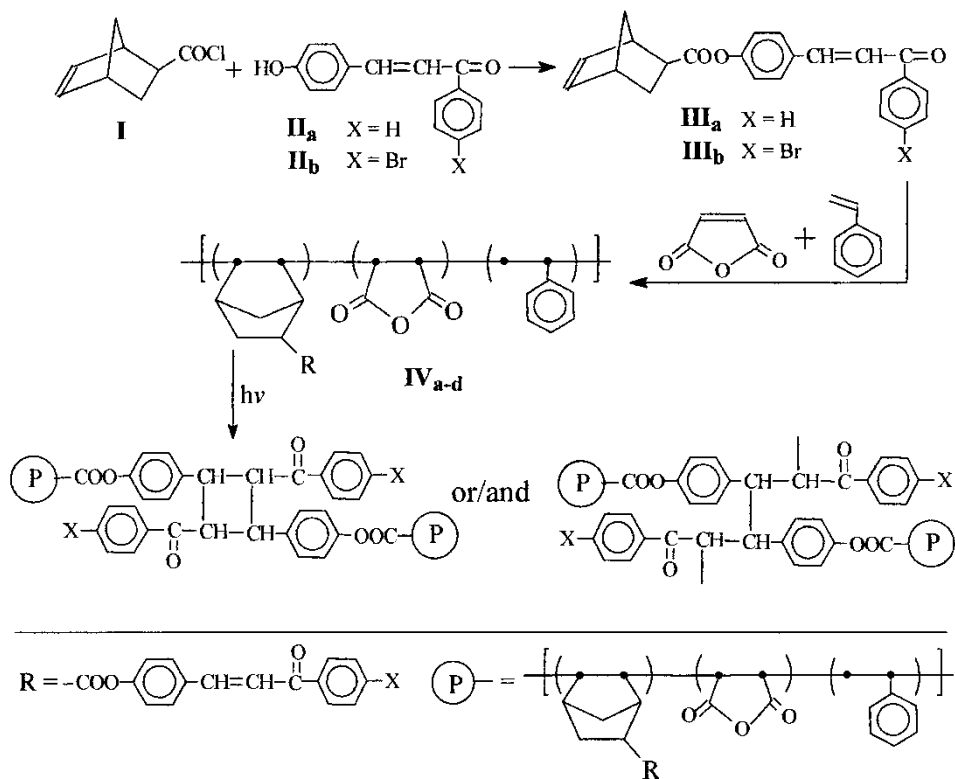
Run	Type	Nb-Chalc		Maleic anhydride		Styrene		Product	
		Wt (g)	mmol	Wt (g)	mmol	Wt (g)	mmol	Wt (g)	Yield (%)
IV_a	III_a	0.636	1.85	0.221	2.25	1.18	11.25	1.06	52.0
IV_b	III_a	0.516	1.5	0.662	6.75	0.702	6.75	1.57	84.5
IV_c	III_a	0.520	1.5	1.103	11.25	0.235	2.25	1.49	80.4
IV_d	III_b	0.639	1.5	0.668	6.75	0.716	6.75	1.94	95.8

Results and Discussion

Synthesis and Characterization

The norbornene monomers containing chalcone moieties as pendent photoreactive groups were prepared through two steps as illustrated in Sch. 1. The first step is the preparation of the acid chloride of 2-norbornene-5-carboxylic acid **I** and the photosensitive groups **II_{a,b}** as in the Experimental section. The second step is reacting the acid chloride of 2-norbornene-5-carboxylic acid **I** with photosensitive groups **II_{a,b}** in tetrahydrofuran in the presence of triethylamine at room temperature to give the monomers **III_{a,b}**. The structure of the monomers was confirmed by IR and NMR spectra and corresponded to the structure as in reference (25).

The polymers **IV_{a-d}**, containing the photosensitive units as pendant groups, were prepared by a solution free radical polymerization technique using benzoyl peroxide as initiator under dry and controlled conditions at reflux in THF (Table 1, Sch.1). The polymerization time was about 1 h. The solution was dropped slowly after cooling into methanol to precipitate the polymer in a good yields 52–95%. The prepared polymers were easily soluble in 1,4-dioxane and in polar aprotic solvents like dimethylformamide, dimethylsulfoxide, and tetrahydrofuran and fairly soluble in chlorinated solvents such as chloroform. They were insoluble in alcohols like ethanol, methanol, 2-propanol and in hydrocarbons like benzene, toluene, and xylene.



Scheme 1. Preparation and photoreactions of the polymers **IV_{a-d}**.

The chemical structures of the polymers were confirmed with a IR spectroscopic method and appearing peaks correspond with the structure (Fig. 1). Thermal properties were characterized by measuring thermogravimetric (Tg) and differential scanning calorimetry (DSC). The DSC of the polymers shows that the polymers have a higher glass transition temperature (Table 2) than polystyrene, due to the cyclic structure of the polymer backbone resulting from the six-member ring of norbornene derivatives and anhydride five-member ring. The thermal stability of the polymers was studied by thermogravimetric analysis in a nitrogen atmosphere in the temperature range $\approx 30^\circ\text{C}$ to 800°C with a heating rate of 10°C per min. The decomposition temperature range of the polymers are illustrated in Fig. 2 and Table 2, which shows that these polymers have two stages of weight loss. The first stage of weight loss ranged from $\approx 230^\circ\text{C}$ to $\approx 400^\circ\text{C}$ due to thermal decomposition of the pendant groups and the anhydride groups. The second stage of weight loss ranged from $\approx 490^\circ\text{C}$ to $\approx 590^\circ\text{C}$ due to further thermal decomposition of the polymer backbone.

Photochemical Properties

The photocrosslinking properties of the prepared polymers have been investigated by study the effect of UV light (366 nm, 180 W at a distance of 18.5 cm from the light

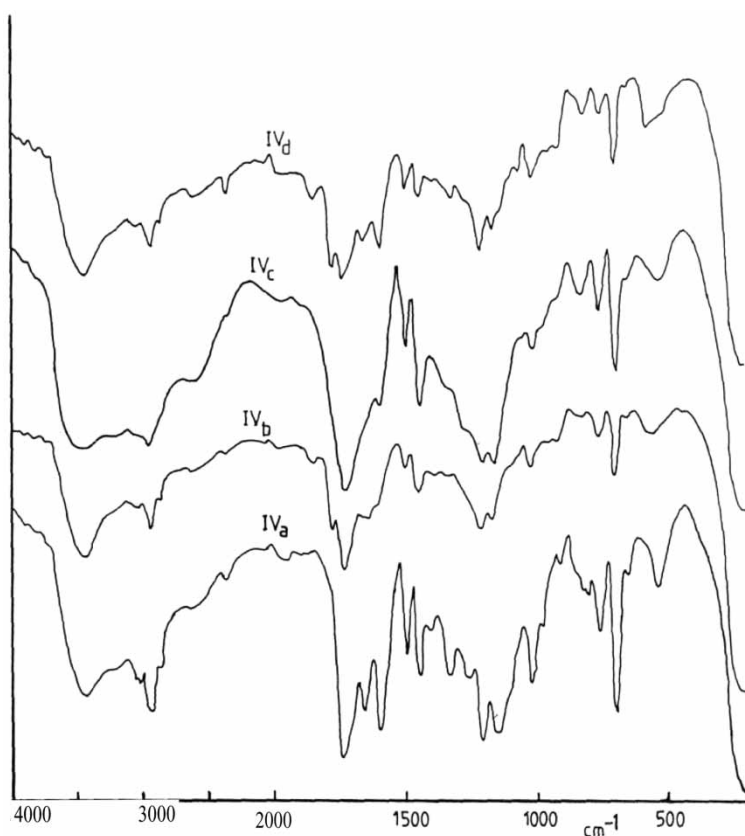


Figure 1. IR spectra for polymers IV_{a-d}.

Table 2
Thermal properties of the polymers **IV_{a-d}**

Polymer	TGA Data (DTR) ^a				DSC (T _g)
	First stage		Second stage		
	Temp. range	Wt loss%	Temp. range	Wt loss%	
IV_a	260–400	67	500–530	29	163
IV_b	230–390	60	490–540	37	167
IV_c	250–400	56	500–560	40	165
IV_d	230–395	66	490–590	31	164

^aDecomposition temperature range.

source) using a medium-pressure Hg lamp on the polymers solution. The irradiation effect was followed by measuring the UV absorption changes of the polymer solution due to photoreactive nature of the chalcone unit on the polymer.

The changes in the UV absorption before and after irradiation at an interval period of time, in which the maximum absorption at the longest wavelength (at about $\lambda = 310\text{--}317\text{ nm}$) of the C=C bond, decreases drastically upon irradiation, whereas that of the -C-C- group increases gradually (at about $\lambda = 240\text{--}265\text{ nm}$). Isobestic point was noticed (at about $\lambda = 263\text{--}267\text{ nm}$) which may be attributed to the formation of a *trans-cis* isomerization of the double bond. The further irradiation results in a fast

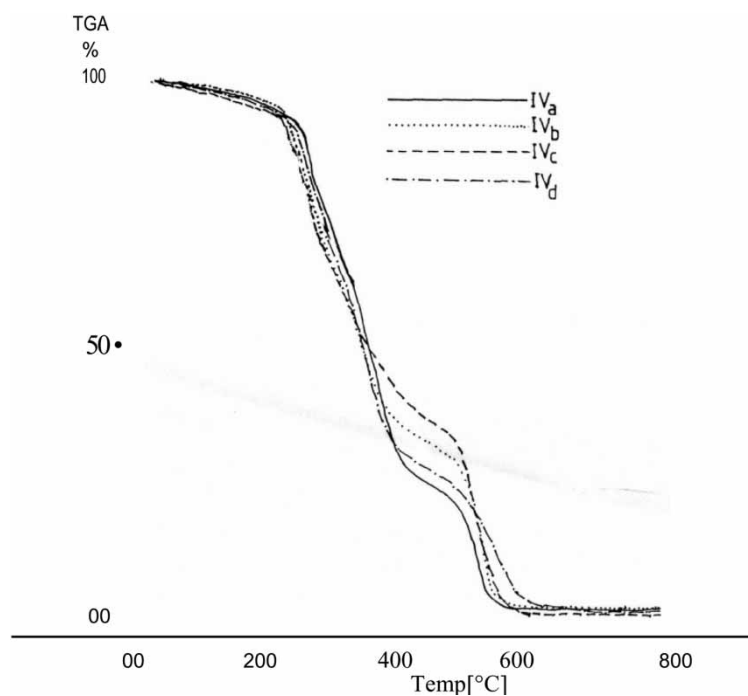


Figure 2. Thermogravimetric analysis diagram for polymers.

decrease in absorption intensity spectrum (see Fig. 3 for polymer **IV_a** as example). This clearly indicates the single bond formation in the cyclobutane ring by the π - π cycloaddition of pendant photoreactive moiety of the polymer which destroys conjugation in the entire π -electron system, hence results in a decrease in UV absorption intensity due to a photoreactive unit (28, 29).

The rate of disappearance of the $\text{C}=\text{C}$ of the cinnamoyl groups on exposure to UV radiation was represented in Figs. 4–7. Generally, the rates of dimerization or crosslinking were found to rise quickly in the first period of time followed by a gradual decrease in rates. It was found that the maximum conversion percentage ranged 42–52% after irradiation time = 90 min. Also, the study indicates that the rates of disappearance of the $\text{C}=\text{C}$ bond appear to depend significantly on the structure of the polymers, including the effect of the phenyl substituent, and the temperature. The effect of solvents appeared to have a small effect on the rates of conversion of the cinnamoyl groups to the dimerized or crosslinked form. The concentration showed no significant effect on the rates of disappearance of the $\text{C}=\text{C}$ bond.

The effect of polymer structure was investigated by measuring the decay rates of the photosensitive group of the polymers **IV_{a-d}** in 1,4-dioxane at constant temperature (30°C) and constant concentration (36 mg/L) and are illustrated in Fig. 4. The figure shows that the ratio of maleic anhydride plays an important factor on affecting the decay rates of the polymers **IV_{a-d}**. The conversion of the cinnamoyl groups to the dimerized or crosslinked form in the polymers **IV_b** and **IV_d** were found to be nearly the same and higher than in the polymers **IV_a** and **IV_c**. These results indicate that the substitution in the phenyl group of the photosensitive group doesn't appear to have a clear difference affecting the decay rates in the samples **IV_{b,d}**. Also, these results can be attributed to the difference ratios in the polymer composition and the low ratio of maleic anhydride in the samples **IV_{a,c}**. The maximum conversion percentage of the cinnamoyl groups to the

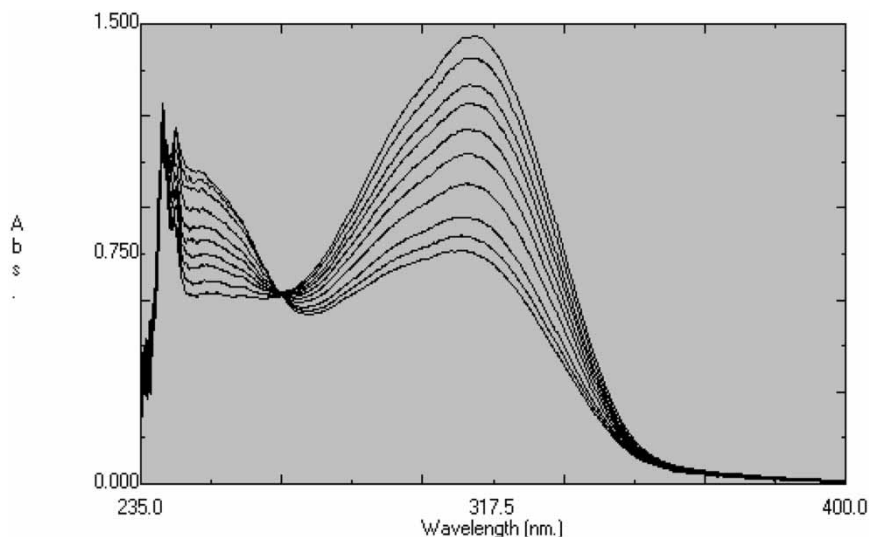


Figure 3. Full UV spectra for polymer **IV_a** with 65 mg/L in 1,4-dioxane at 30°C before irradiation and after different irradiation periods; from up to down at 312 nm [time = 0, 1, 3.5, 5.5, 8.5, 12, 18, 30, 45, and 90 min].

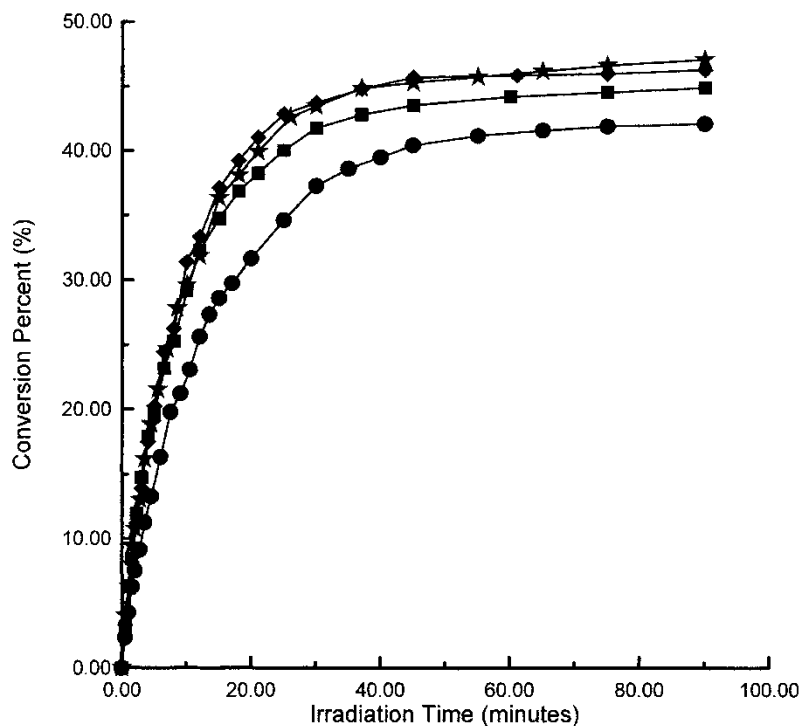


Figure 4. Rate of disappearance of the $-C=C-$ of the cinnamoyl groups on the different polymeric samples IV_a (●); IV_b (★); IV_c (■) and IV_d (◆) with 36 mg/L in 1,4-dioxane at 30°C.

dimerized or crosslinked form after irradiation time = 90 min were found in the 42–47% range.

The effect of solvents (such as, 1,4-dioxane, THF, DMF and chloroform) on the rates of dimerization or crosslinking was studied on a polymer sample IV_d at a constant temperature (30°C) and constant concentration (36 mg/L), and the results are shown in Fig. 5. The maximum conversion percentage of the cinnamoyl groups to the dimerized or crosslinked form after irradiation time = 90 min were found in the range 44–52%. From Fig. 5, it was found that there is no clear difference in the first few minutes (about 10 min) of irradiation. However, a small difference in the rate of conversion in the different solvents appeared, after a small period of irradiation. The rates of disappearance of the $-C=C-$ bond followed the order of $DMF \geq CHCl_3 > 1,4\text{-dioxane} > THF$. This difference can be attributed to a difference in solubility of these polymers and depends on the nature of the solvents.

Figure 6 illustrates the effect of the temperature on the decay rate of the photosensitive groups in the polymer solutions and was investigated with a constant concentration (65 mg/L) of the polymer IV_a in 1,4-dioxane at different temperatures (30, 50, and 80°C). The results indicate that the decay rates are fast in the first period of irradiation and there is no difference at all in temperature. However, the rates depend on the temperature after a small period of irradiation that follows the order $30^\circ C < 50^\circ C < 80^\circ C$. The maximum conversion percentage was found to be 42%, 47%, and 52%, respectively after irradiation time = 90 min. The results showed that the temperature play an effective factor on the photocrosslinking or dimerization of the photosensitive groups,

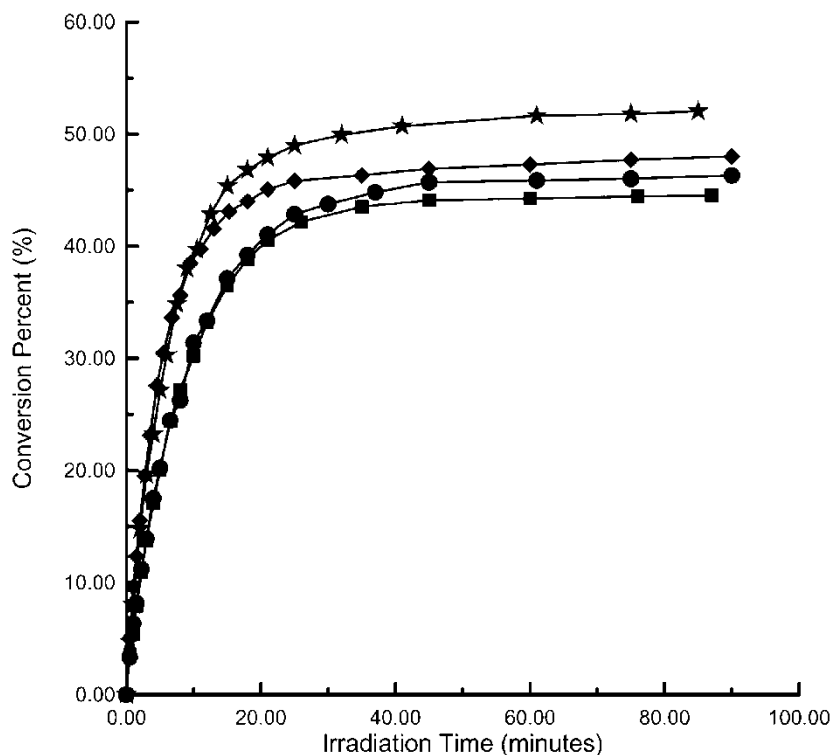


Figure 5. Decay rates of photosensitive groups of polymer IV_a in different solvents; 1,4-dioxane (●); DMF (★); THF (■) and $CHCl_3$ (◆) with 36 mg/L at 30°C.

since the increase in temperature increases the activation energy and hence, increases the rate of conversion.

The effect of concentration of the photosensitive polymers on the rates of conversion was studied on a polymer IV_a in 1,4-dioxane at 30°C with 10, 36, and 65 mg/L as shown in Fig. 7. The results indicate that there is no clear effect on the conversion rates with increasing or decreasing the concentration of the polymer. It was seen that the maximum conversion percentage ranged 42–47% after irradiation time = 90 min. Also, these results indicate that the photoreactivity of these polymers doesn't change with changing the concentration especially in the first few minutes of irradiation. Therefore, a variety of concentrations can be used with these materials depends on the application used.

Generally, the conversion rates were characterized (in all cases), but no clear order can be calculated, since many attempts were made to introduce the results of irradiation kinetically. The attempts suggested that the rates might be going in the first order with different stages. The first stage has 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 percentage ranged between 42% and 52% after a long irradiation time (75–90 min). This indicates that complete conversion cannot be achieved, which may be due to high molecular weight and chain fragmentation reactions that accompany the photocrosslinking process, which leads to a reduction in 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.

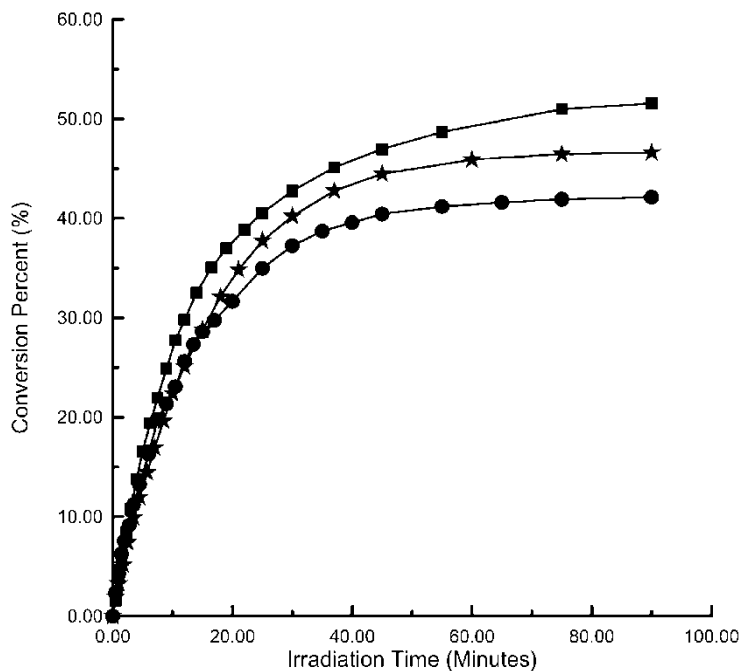


Figure 6. Rate of conversion to dimerize or crosslinking of polymeric sample IV_a at different temperatures; at 30°C (●); at 50°C (★) and at 80°C (■) with 65 mg/L in 1,4-dioxane.

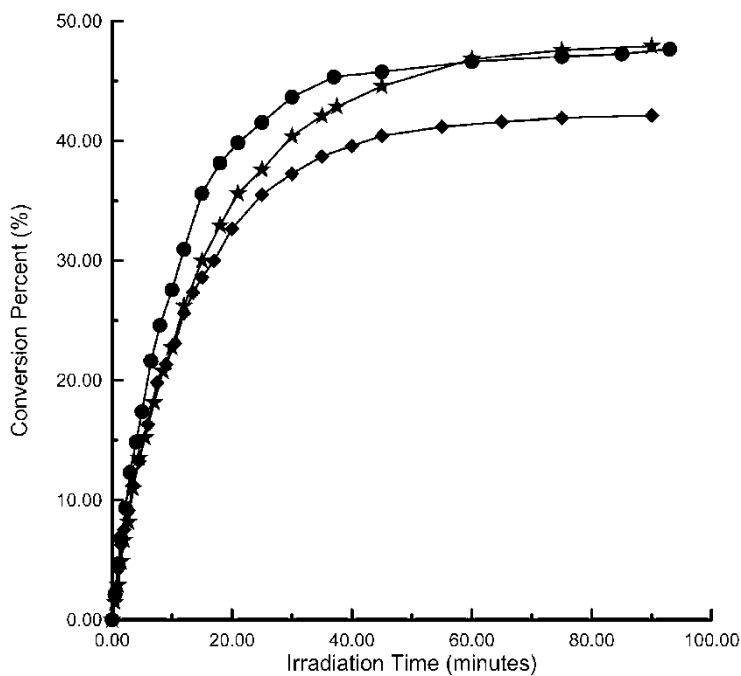


Figure 7. Disappearance rates of the $-C=C-$ of the cinnamoyl groups on the polymer IV_a at different concentrations [10 mg/L (●); 36 mg/L (◆) and 65 mg/L (★)] in 1,4-dioxane at 30°C.

Conclusion

New photosensitive polymers were prepared by radical polymerization techniques. These polymers are based on photoreactive norbornene derivatives copolymerized with styrene and maleic anhydride. The photochemical reactivity of these polymers was investigated in solutions. The disappearing 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 a 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, the temperature, the concentrations and finally, changing the solvents.

References

1. Reiser, A., Ed. (1989) *Photoreactive Polymers—The Science and Technology of Resists*. John Wiley & Sons, Inc.: New York.
2. Thompson, L.F., Wilson, C.G., and Bowden, M.J., Eds. (1994) *Introduction to Microlithography*. Am. Chem. Soc.: Washington, DC.
3. Kawatsuki, N., Uchida, E., and Yamamoto, T. (2003) Photocontrol of birefringence and in-plane molecular orientation in copolymer liquid crystal films with 4-methoxyazobenzene and photocross-linkable side groups. *Macromol. Chem. Phys.*, 204 (4): 584–490.
4. Nwabunma, D. and Kyu, T. (2001) Phase behavior, photopolymerization, and morphology development in mixtures of eutectic nematic liquid crystal and photocurable monomer. *Polymer*, 42: 801–806.
5. Kawatsuki, N. and Yamamoto, T. (1999) Photoinduced alignment control of photoreactive side-chain polymer liquid crystal by linearly polarized ultraviolet light. *App. Phys. Lett.*, 74 (7): 935–937.
6. Hanemann, T., Noel, C., and Haase, W. (1995) Novel photocrosslinkable systems for nonlinear optics. *Adv. Mater.*, 7 (5): 465–468.
7. Lessard, R.A. and Manivannan, G. (1995) Holographic recording materials: an overview. *Proc. SPIE-Int. Soc. Opt. Eng.*, 2405: 2–23.
8. Theissen, U., Zilker, S.J., Pfeuffer, T., and Stroehriegel, P. (2000) Photopolymerizable cholesteric liquid crystals-new materials for holographic applications. *Adv. Mater.*, 12 (22): 1698–1700.
9. Kozlovsky, M.V., Podgornov, F.V., Wang, G., and Haase, W. (2003) Photoselection-governed holographic grating recording in a chiral side chain azo dye liquid crystalline polymers. *Phys. Status Solidi (a)*, 198 (1): 242–247.
10. Kim, J.-B. and Lee, J.-J. (2002) Synthesis and characterization of norbornene-based polymers with 7,7-dimethyloxepan-2-one acid labile groups for chemically amplified photoresists. *Polymer*, 43 (6): 1963–1967.
11. Kim, J.-B., Kim, H., and Choi, J.-H. (1999) Synthesis of poly(2-trimethylsilyl-2-propyl methacrylate) and their application as a dry-developable chemically amplified photoresist. *Polymer*, 40: 1617–1621.
12. Kimura, T., Kim, J.-Y., Fukuda, T., and Matsuda, H. (2002) UV-curable azobenzene polymer bearing photo-crosslinkable moiety for stabilization of photo-fabricated surface relief structure. *Macromol. Chem. Phys.*, 203 (16): 2344–2350.
13. Nishikubo, T., Iizawa, T., Yamada, M., and Tsuchiya, K. (1983) Study of photopolymer. XVII. Synthesis of novel photosensitive polymers with pendant photosensitive group and photosensitizer groups. *J. Polym. Sci.: Polym. Chem. Edn.*, 21: 2025–2045.
14. Pappas, S.P. (1985) *UV Curing Science and Technology*. In: Pappas, S.P., Ed.; Marketing Corp.: Norwalk, CT; Vol. 2.

15. Whitcombe, M.J., Gilbert, A., and Mitchell, G.R. (1992) Syntheses and photochemistry of side-chain liquid crystal polymers based on cinnamate ester. *J. Polym. Sci. Polym. Chem. Edn.*, 30: 1681–1691.
16. Roffey, C.G., Ed. (1982) *Photopolymerization of Surface Coating*. Wiley-Interscience: New York.
17. Angiolini, L., Caretti, D., Carlini, C., Corelli, E., and Salatelli, E. (1999) Polymeric photoinitiators having benzoin methylether moieties connected to the main chain through the benzyl aromatic ring and their activity for ultraviolet-curable coatings. *Polymer*, 40: 7197–7207.
18. Mizoguchi, K. and Hasegawa, E. (1996) Photoactive polymers applied to advanced microelectronic devices. *Polym. Adv. Technol.*, 7: 471–477.
19. Kodak Co. Polymeric Azides Azidophthalic Anhydrides. U. S. Pat. 30963111, July 2, 1963.
20. Lee, W.E., Calvert, J.G., and Malmberg, E.W. (1961) Photodecomposition of diazonium salt solutions. *J. Am. Chem. Soc.*, 83: 1928–1934.
21. Kim, J.B., Kim, J.Y., and Jung, M.H. (1999) Synthesis of copolymers containing 3-hydroxycyclohexyl hethacrylate and their application as ArF excimer laser resists. *Polymer*, 40 (1): 273–276.
22. Lee, K.K., Jung, J.C., and Jhon, M.S. (1998) Maleic anhydride type ArF photoresist. *Polymer*, 39: 4457–4458.
23. Rehab, A. (1998) New photosensitive polymers as negative photoresist materials. *Eur. Polym. J.*, 34 (12): 1845–1855.
24. Rehab, A. and Salahuddine, N. (1999) Photocrosslinked polymers based on pendant extended chalcone as photoreactive moieties. *Polymer*, 40 (9): 2197–2207.
25. Rehab, A. (2003) Studies on photoreactive poly(norbornene derivatives) bearing chalcone units. *J. Macromol. Sci. A: Pure Appl. Chem.*, A40 (7): 689–703.
26. Unruh, C.C. (1959) Poly(vinyl-trans-benzalacetophenone). *J. Appl. Polym. Sci.*, 2: 358–362.
27. Kim, J.-B., Lee, J.-J., and Kang, J.-S. (2000) Poly(5-((2-trimethylsilyl-2-propyl) oxycarbonyl)-norbornene-co-maleic anhydride) for 193-nm lithography. *Polymer*, 41: 6939–6942.
28. Watanabe, S. and Kato, M. (1984) Preparation and properties of photocrosslinkable poly(2-vinylxyethyl cinnamate). *J. Polym. Sci. Polym. Chem. Ed.*, 22 (11): 2801–2808.
29. Curme, H.G., Natale, C.C., and Kelley, D.T. (1976) Photosensitized reactions of cinnamate esters. *J. Phys. Chem.*, 71: 767–770.