Synthesis and Characterization of Photochromic Homopolymer/Copolymer

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ABSTRACT: Photochromic spiropyran homopolymer/copolymers have been prepared by radical polymerization of 5-acrylamino-1,3,3-trimethylindolino-6'-nitro-8'-methoxy spiropyran using different vinyl monomers such as methyl methacrylate, methyl acrylate, and styrene. The polymerization was carried out at 80°C in dimethylformamide using α,α'-azobisisobutyronitrile as initiator. The polymers have been characterized by viscometry, gel permeation chromatography, thermogravimetric analysis, and infrared spectroscopy. The kinetics of photochromic behavior have been investigated by preparing a film of one copolymer blended with poly(methyl methacrylate). This film, on exposure to sunlight or suitable wavelength, showed a very strong photochromic effect. The decoloration reaction kinetics follow a first-order relationship. The duration for return of the color depends upon the intensity of incident light, ambient temperature, moisture content, and thermal treatment of the film. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 841–848, 1997

Key words: photochromic homopolymer/copolymer; methyl methacrylate; methyl acrylate; styrene, PMMA

INTRODUCTION

Of all the photochromic systems studied up to now, the spiropyrans have received the most attention.[1–6] In particular, spiropyrans, being among the most typical organic photochromic compounds, have been currently attracted as photoreceptors in photochromic polymers.[7] Their photochromism involves a scission reaction of the bond between the spirocarbon and the pyran oxygen atoms followed by a change of molecular configuration. The solution behavior of photochromic polymers containing a heterocyclic benzopyrylospiran group, incorporated either as side group or as constituents of the polymer backbone, has been reported.[8–11] Vandewijer and Smets[12] reported the results of examinations of the photochromic behavior of spiropyran copolymers prepared by radical copolymerization of 5-methacrylamino-3,3'-dimethyl-6'-nitrobenzthiazolino spiropyran with different vinyl monomers.

In this paper we report the synthesis and photochromic behavior of spiropyran copolymers prepared by radical copolymerization of 5-acrylamino-1,3,3-trimethylindolino-6'-nitro-8'-methoxy spiropyran and different vinyl monomers.

EXPERIMENTAL

Materials

All the chemicals were of AR grade, *N,N*-dimethylacetamide was distilled under reduced pressure over P_2O_5. Dimethylformamide (DMF) was freed from formic acid by refluxing with methanol and then fractionally distilled, α,α'-azobisisobutyronitrile was purified three times by recrystallization from ethanol and dried at room temperature, decomp. 103–104°C. Methyl methacrylate (MMA),

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Reaction Scheme

Scheme 1
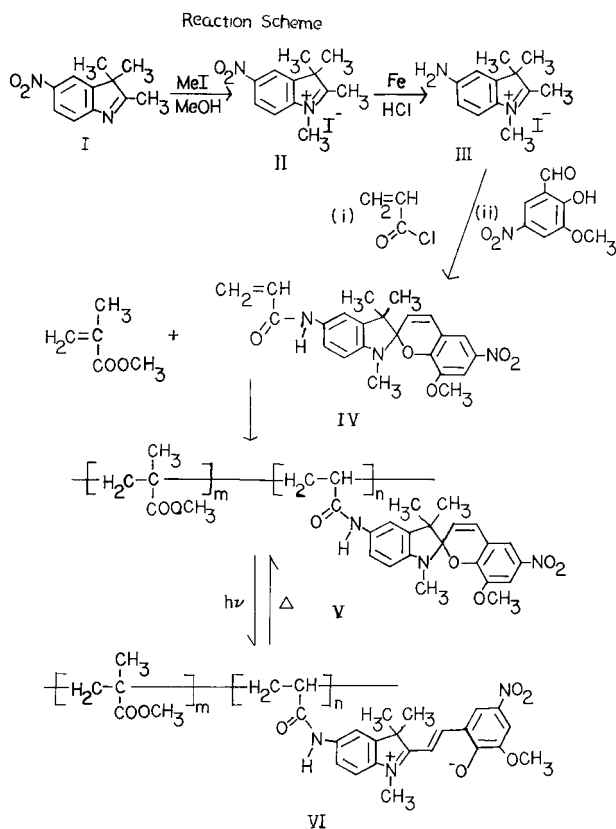
methyl acrylate (MA), and styrene (S) were freed from inhibitor by washing with 4% aqueous sodium hydroxide solution, washing with distilled water, drying over fused calcium chloride, and finally distilling under reduced pressure.

Preparation of 2,3,3-Trimethyl-5-nitroindolenine (I)

This compound was prepared by the method described in the literature.[13] This compound was recrystallized from ligroin, mp 124–125°C.

Preparation of 1,2,3,3-Tetramethyl-5-nitroindolinium Iodide (II)

A mixture of 2,3,3-trimethyl-5-nitroindoline (0.02 mol, 4.08 g), methyl iodide (0.03 mol, 2.82 g), and methanol (10 parts) was reacted under autoclave for 4 to 6 h at 110°C. The quaternary salt was dissolved in water and filtered to yield the title compound, mp 200–203°C.

Preparation of 5-Amino-1,2,3,3-tetramethylindolinium Iodide (III)

A mixture of 1,2,3,3-tetramethyl-5-nitroindolinium iodide (0.1 mol 34.6 g), hydrochloric acid (0.2 mol, 17.3 mL), iron powder (30 g), and water (100 mL) was refluxed in a waterbath for 1 h. The resulting solution was filtered and concentrated to produce crystals, mp 190–191°C.

Preparation of 5-Acrylamino-1,3,3-trimethylindolino-6′-nitro-8′-methoxy spiropyran (IV)

A mixture of 5-amino-1,2,3,3-tetramethylindolinium iodide (0.01 mol, 3.16 g), hydroquinone (0.3 g), and triethylamine (1.5 mL) was dissolved in anhydrous N,N-dimethylacetamide (20 mL) and the mixture was cooled to 0–5°C. To this cold solution acryloylchloride[14] (1.35 mL) was added dropwise followed by stirring for 2 h. The resulting solution was kept overnight. The brown precipitates of triethylamine chlorohydrate were filtered off and the filtrate was added to a solution of 5-nitro-o-vanillin (0.01 mol, 1.97 g) in dimethylacetamide (15 mL) containing one drop of piperidine. The mixture was boiled for a few seconds and poured into ice-cold water. Precipitated spiropyran monomer was filtered off, washed with water, and recrystallized in dimethylformamide, decomposition 220–228°C.

IR (KBr): 1690 cm^{-1} (CONH), 990 cm^{-1} (H$_2$C=C—), 1250 cm^{-1}, and 1050 cm^{-1} are due to asymmetric stretching of =C—O—C and symmetric stretching of C=O—C; 2860 cm^{-1} C—H bending of —O—CH$_3$, 1530 cm^{-1}, and 1350 cm^{-1} are due to asymmetric and symmetric stretching of (—NO$_2$).

ANAL. Calcd for C$_{23}$H$_{23}$N$_3$O$_5$: C, 65.55%; H, 5.46%; N, 9.97%; O, 19.0%. Found: C, 65.01%; H, 5.32%; N, 9.68%; O, 19.67%.

Preparation of Homopolymer (HP)

The vinylspiropyran monomer (**IV**) (1 g) was homopolymerized in dimethylformamide (5 mL) for 8 h using α,α'-azobisisobutyronitrile (0.01 g) as initiator at 80°C. The resulting mixture was poured into methanol. The HP was redissolved in chloroform and reprecipitated in methanol.

The same experimental conditions were used for the homopolymerization of MMA, MA, and S.

Table I   Reaction Composition and Properties of Homopolymer/Copolymer

Polymer No.	Monomer Composition	Absorption Maxima,[a] λ_{max}	$\bar{M}_w$[b] by GPC $\times 10^3$	Viscosity,[c] η (dL/g)
	IV : MMA			
A	0 : 10	—	20.34	0.250
A1	0.1 : 9.9	565	13.43	0.174
A2	0.3 : 9.7	570	12.08	0.101
A3	0.5 : 9.5	570	10.92	0.082
A4	1.0 : 9.0	570	7.99	0.063
	IV : MA			
B	0 : 10	—	22.42	0.281
B1	0.1 : 9.9	595	15.70	0.210
B2	0.3 : 9.7	600	13.04	0.208
B3	0.5 : 9.5	600	12.56	0.181
B4	1.0 : 9.0	601	10.87	0.167
	IV : S			
C	0 : 10	—	25.64	0.375
C1	0.1 : 9.9	580	12.78	0.205
C2	0.3 : 9.7	585	11.89	0.181
C3	0.5 : 9.5	585	9.62	0.167
C4	1.0 : 9.0	590	8.71	0.139
HP	Homopolymer of vinylspiropyran	603	0.911	0.020

[a] Absorption spectra in chloroform.
[b] Gel permeation chromatography in THF based on polystyrene standards.
[c] Intrinsic viscosity in chloroform at 30°C.

Preparation of Copolymer

The vinylspiropyran monomer (**IV**) and the comonomers MMA, MA, and S with four different weight ratios of 0.1 : 9.9, 0.3 : 9.7, 0.5 : 9.5, and 1 : 9 were polymerized using α,α'-azobisisobutyronitrile as initiator. The synthesis of the copolymer for MMA monomer is presented in Scheme 1.

A mixture of vinylspiropyran monomer (1 g), MMA (9 g), DMF (2 mL) and α,α'-azobisisobutyronitrile (0.1 g) were heated at 80°C for 8 h. The viscous solution was poured into methanol. The polymer was redissolved in chloroform and reprecipitated three times in methanol.

Measurements

Intrinsic viscosities of poly(methyl methacrylate) (PMMA) (**A**), poly(methyl acrylate) (**B**), polystyrene (**C**), and their corresponding copolymers were measured in chloroform at 30 ± 0.05°C with a Ubbelohde viscometer. Visible spectra were recorded on a Carlzeiss UV/VIS Specord Spectrophotometer. A Perkin–Elmer model 983 recording infrared (IR) spectrophotometer was used for IR spectra of the samples in KBr pellets. The gel permeation chromatograms were generated using a Waters gel permeation chromatography (GPC) system. The HPLC-grade tetrahydrofuran (THF) was used as a mobile phase at a flow rate of 1.0 mL/min. The GPC system was equipped with two ultrastyragel columns packed with styrene–DVB copolymers of 10^3 and 10^6 Å porosity, connected in series to cover an exclusion limit of 200 to 10×10^6. A Waters 410-RI detector was used with internal temperature of 35°C for peak detection. The GPC system was calibrated with eight different polystyrene standards having molecular weights ranging from 2000 to 2.5×10^6. The thermal stability of the polymers was determined with a DuPont 951 thermogravimetric analyzer connected with a DuPont 990 thermal analyzer in static air at a heating rate of 10°C/min. The kinetic measurements of photochromic behavior were carried out using a Beckman DK-2A Ratio Recording Spectrophotometer and sunlight as an irradiation source.

Films of 0.05 mm thickness were prepared by spreading the 1% PMMA solution in chloroform
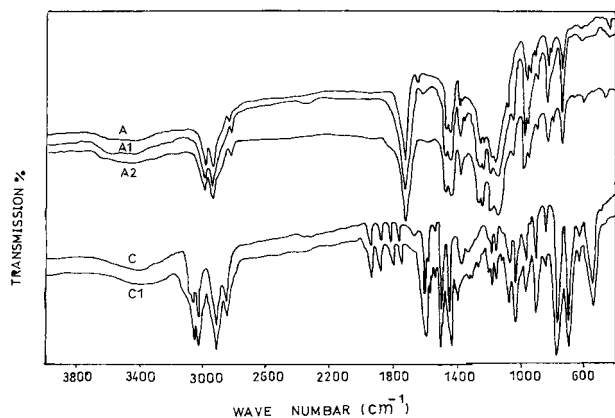
(a)
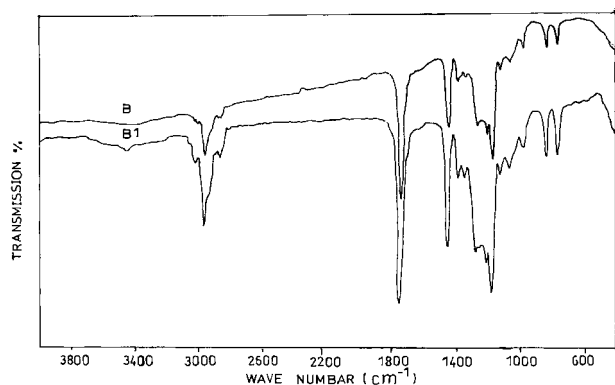
(b)

Figure 1 (a) Infrared spectra of poly(methyl methacrylate) (**A**); copolymer (**A1**); copolymer (**A2**); polystyrene (**C**); and copolymer (**C1**). (b) Infrared spectra of poly(methyl acrylate) (**B**), and copolymer (**B1**).

containing 0.50 g copolymer (**A1**) over a glass plate followed by evaporation of the solvent at room temperature. The film was left at least overnight (24 h) before measurement of photochromism.

The film was exposed to natural bright sunlight in the summer season for 30 to 180 s and immediately placed in a Beckman DK-2A Ratio Recording Spectrophotometer. The change in absorbance was recorded by scanning a spectrum at various time intervals at 35°C.

RESULTS AND DISCUSSION

All the copolymers were soluble in common organic solvents, i.e., chloroform, THF, toluene, acetone, DMF, etc. All the copolymers as well as the homopolymers were characterized by intrinsic viscosity, visible spectra, GPC, and thermogravimetric analysis (TGA).

The intrinsic viscosities and weight average molecular weights ($\bar{M}_w$) of all the copolymers and homopolymers are listed in Table I. The $\bar{M}_w$ data obtained from GPC measurements reveal that the photochromic copolymers are of low molecular weight, ranging from 7.9 to 22.42×10^3. Increasing the concentration of vinylspiropyran monomer decreases the copolymer's molecular weight to some extent. It was also found that radical homopolymerization of the vinylspiropyran monomer (**IV**) yields only a trimer.

Table II Thermal Characteristics of Photochromic Homopolymer/Copolymer

Polymer No.	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	IPDT (°C)	Activation Energy, E (kJ/mol)
A	282.5	324.0	362.5	378.75	20.06
A1	300.0	337.5	382.5	329.06	17.50
A2	300.0	337.5	385.0	395.26	20.94
A3	312.5	337.5	389.0	396.56	21.01
A4	300.0	330.0	380.5	392.81	20.82
B	250.0	287.5	333.5	412.62	21.86
B1	312.5	337.5	381.0	375.82	19.91
B2	325.0	350.5	405.5	387.00	20.51
B3	337.5	380.0	420.0	372.50	19.79
B4	325.0	337.5	401.0	392.62	20.81
C	250.0	330.0	335.0	426.00	22.33
C1	337.5	362.5	415.5	419.20	22.20
C2	350.0	370.0	435.5	428.00	22.67
C3	350.0	380.0	437.0	434.25	23.00
C4	325.0	370.0	400.0	412.50	21.85
HP	225.0	305.0	312.5	333.37	17.67

(a)

(b)
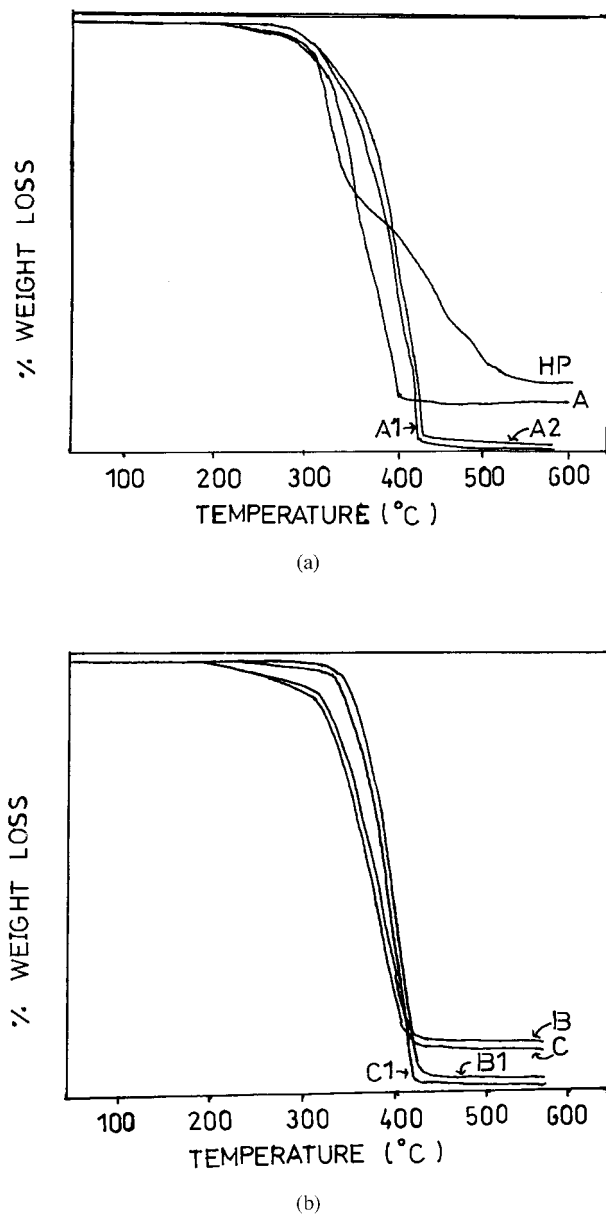
Figure 2 (a) Thermograms of polymers: poly(methyl methacrylate) (**A**); copolymer (**A1**); copolymer (**A2**); and homopolymer (**HP**). (b) Thermograms of polymers: polystyrene (**C**); copolymer (**C1**); polymethylacrylate (**B**); and copolymer (**B1**).

The absorption spectra were recorded using chloroform as solvent. The influence of the solvent is also very pronounced in the coloration and decoloration kinetics.[15,16] The merocyanine (**VI**), formed by ultraviolet irradiation of (**V**), are zwitterionic species and display a strong solvatochromism.[17,18]

IR spectra of some of the selected homopolymer/copolymers are depicted in Figure 1. All the spectra show common characteristic bands as follows: 3000 cm^{-1} ($\nu_s CH_3 O + \nu_a CH_2$), 2970 cm^{-1} ($\nu_a CH_3$); 2860 cm^{-1} ($\nu_s CH_3 + \nu_a CH_2$), 1730 cm^{-1} ($\nu C{=}O$), 1460 cm^{-1} ($\nu_a CH_2$), 1440 cm^{-1} ($\nu_a CH_3 O$), and 730 cm^{-1} ($\nu_a CH_2$). The band at 1380 cm^{-1} indicates the presence of amide linkage in copolymer. 1250 cm^{-1} are due to asymmetric stretching of $={=}C{-}O{-}C$ and symmetric stretching of $C{=}O{-}C$; 1530 cm^{-1} and 1350 cm^{-1} are due to asymmetric stretching and symmetric stretching of $-NO_2$.

Thermogravimetric studies have been carried out for all the homopolymers as well as copolymers at the heating rate of 10°C/min. In order to determine the thermal stability trend, TG parameters such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{max} (temperature of maximum rate of degradation), IPDT (integral procedure decomposition temperature), and the activation energy E of the degradation process were calculated and are presented in Table II. Some selected TG curves are presented in Figure 2. It is observed that, thermally, photochromic copolymers are fairly stable compounds; with increased concentrations of vinylspiropyran monomer, the thermal stability has been increased to some extent.

The photochromic behavior appeared to be highly dependent upon the chemical structure of the polymer molecular chains, including the kind and ratio of comonomers as well as the chemical structure of the functional portion.[19]

The monomer ratio in the copolymer formation also plays an important role in the film formation; with increased concentration of vinylspiropyran monomer in the copolymer, the resultant film becomes brittle.

Spectral Changes During Irradiation

Figure 3(a) shows spectral changes of copolymer (A1) film during irradiation. On exposure to bright sunlight or a light source of suitable wavelength—a 500-W tungsten lamp or 150-W xenon lamp,[20] the film showed very good photochromic effect, i.e., colorless to blue. The absorption spectra reveal that no peak is observed before irradiation but a peak is obtained at 585 nm when exposed to sunlight, because of photoinduced isomerization. The absorption peak intensity increases with irradiation time. Table III summarizes the results of the change in rate at different time intervals of copolymer (A1) film during irradiation.
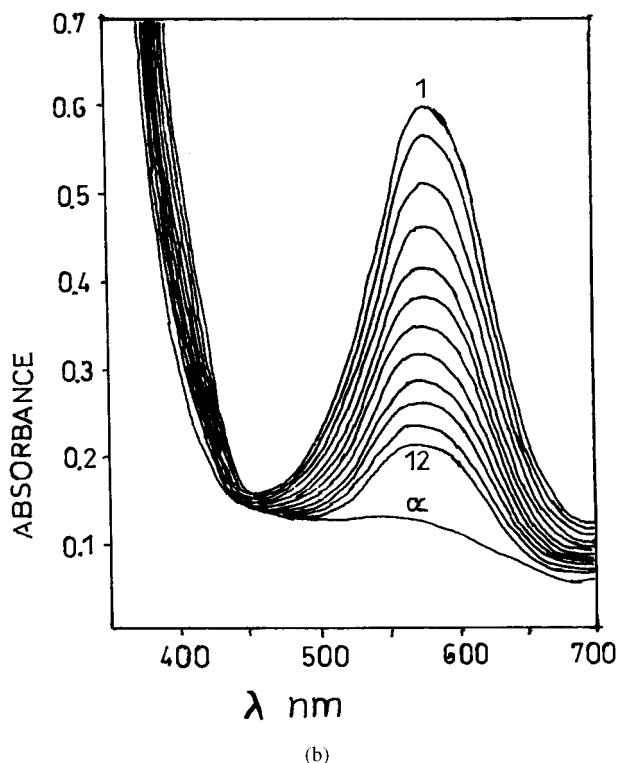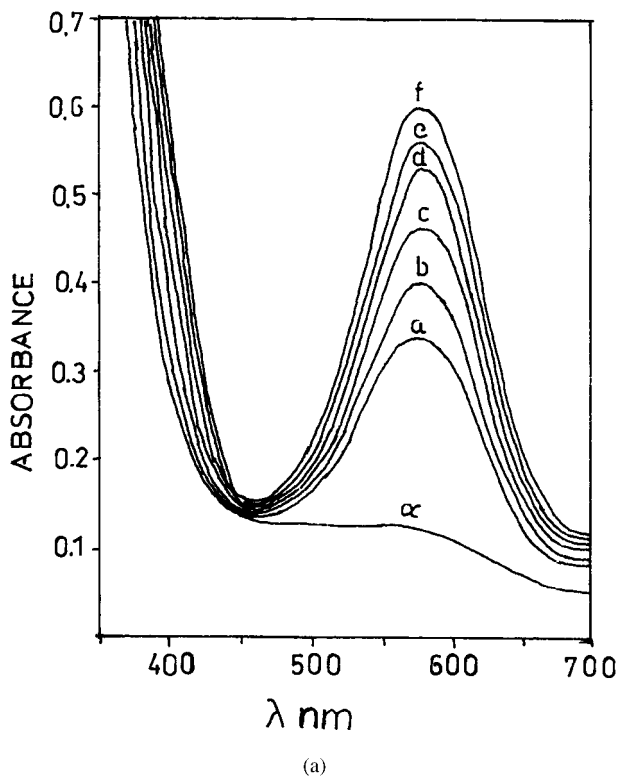
Figure 3 (a) Spectral changes in copolymer A1 film during irradiation at 35°C: (a) 30 s; (b) 60 s; (c) 90 s; (d) 120 s; (e) 150 s; and (f) 180 s. (b) Rate of return to the original spectrum in the dark for 2.5-min expo-

Table III   Photochromic Behavior of Copolymer (A1) Film

Irradiation Time (s)	Absorbance Ratio	$k_1 \times 10^{-2}$ (s^{-1})
30	0.327	3.718
60	0.178	2.876
90	0.133	2.234
120	0.120	1.766
150	0.086	1.632
180	0.058	1.574

The first-order rate constant k_1 was determined by using the equation

$$k_1 = (2.303/t)\log(D_0/D)$$

where D_0 and D denote absorbances before and during irradiation, respectively, and t is irradiation time. The rate-constant data clearly indicate that the rate constant k_1 decreases with increase of irradiation time.

Spectral Recovery in the Dark

The spectral recovery in the dark is of a thermal nature; the reverse process takes place rather slowly in the solid state, such as film at ordinary temperatures. The rate of return to the original spectrum in the dark was recorded for various exposure time of copolymer film at different time intervals. Figure 3(b) shows such spectra for 2.5-min exposure time, and Figure 4 shows the plot of absorbance versus recovery time of different exposure times. The return rate is rapid in the begining and slows after 10 min.

The first-order rate constant for the recovery of the film was obtained from the expression[21]

$$k_{\text{obs}} = (2.303/t)\log(D_0/D_t - D_\alpha)$$

in which D_0, D_t, and D_α refer to the absorbance at the beginning of the run, at time t, and after complete return, respectively. Figure 5 shows a plot of $\ln(D_0/D_t - D_\alpha)$ versus t for various exposure times. The rate constant k is calculated from

sure time at different time intervals in minutes. Curves 1–12 and α show 0, 1, 3, 6, 10, 15, 21, 28, 36, 45, 55, 67, and infinite time, respectively.
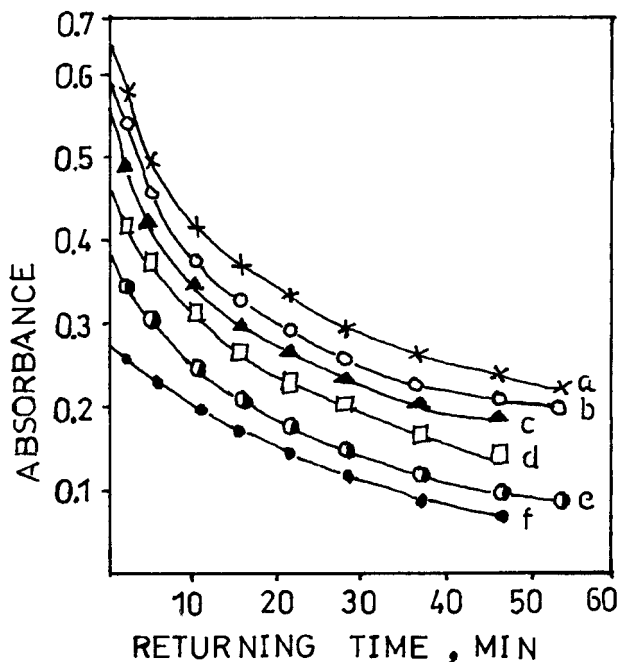
Figure 4 The plot of absorbance versus recovery time of different exposure times: (a) 30 s; (b) 60 s; (c) 90 s; (d) 120 s; (e) 150 s; and (f) 180 s.

the above plot. It seemed that the rate constant k decreases with increasing irradiation time. Fifty-percent recovery of the return absorbances in the dark were calculated from the terms (D_t/D_α) $\times 100$ versus t (Fig. 6). Table IV shows the results of recovery in the dark. It was found that the time
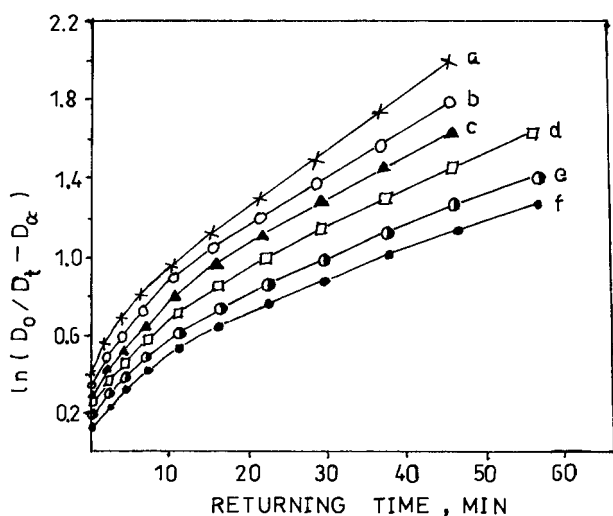
Figure 5 Relationship between $(D_0/D_t - D_a)$ versus t, time of returning in the dark for copolymer A1 film at different irradiation times: (a) 30 s; (b) 60 s; (c) 90 s; (d) 120 s; (e) 150 s; and (f) 180 s.
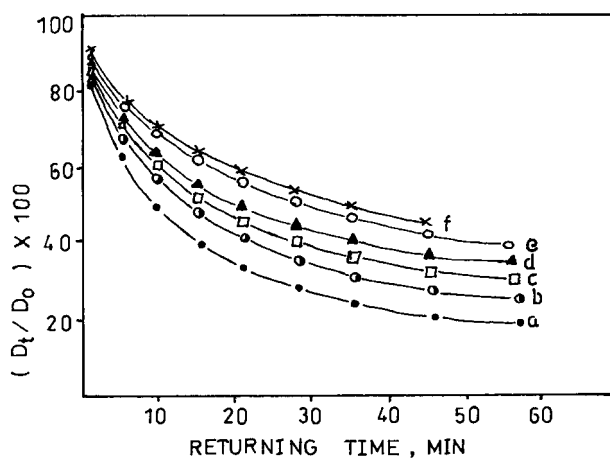
Figure 6 A plot of $(D_t/D_0) \times 100$ versus t, where D_0 and D_t denote the absorbance immediately after exposure time and the returning time in the dark, respectively. t is returning time in minutes: (a) 30 s; (b) 60 s; (c) 90 s; (d) 120 s; (e) 150 s; and (f) 180 s.

for 50% recovery increased with increasing irradiation time.

CONCLUSIONS

A new monomer, 5-acrylamino-1,3,3-trimethylindolino-6′-nitro-8′-methoxy spiropyran (**IV**), was synthesized and copolymerized with MMA, MA, and S. Polymers were obtained in good yield; these polymers exhibit photochromic effects. It was found that first-order rate constants decrease with increasing irradiation time. The thermogram of copolymers reveals that when the vinyl spiropyran monomer concentration is increased,

Table IV   Recovery in the Dark Rate Constant k for Different Irradiation Times

Irradiation Time (s)	50% Recovery (min)	$k_{obs} \times 10^{-2}$ (s^{-1})
30	14	3.2
60	15	2.66
90	30	2.28
120	36	1.8
150	40	1.5
180	45	1.5

thermal stability of the copolymer increases to some extent.

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