Photocrosslinking studies of *S*-acryloyl *O*-ethyl xanthate copolymers

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S-Acryloyl *O*-ethyl xanthate was copolymerized with styrene and methyl methacrylate, giving rise to copolymers containing the photoactive acyl xanthate chromophore. Thin films of these copolymers, on irradiation, undergo phototransformations leading to crosslinked polymers. The photocrosslinking yield of the copolymers depends mainly on their molecular weight and not on the composition of the copolymer. The mechanism of photocrosslinking was investigated through nanosecond laser flash photolysis studies. The 308 nm laser pulse excitation of the copolymers in benzene produces radical intermediates, arising through a C(=O)–S bond fission. The assignment of the photogenerated (ethoxycarbonylthiocarbonyl)thiyl radical is based on its characteristic long wavelength absorption maximum ($\lambda_{max} \sim 660$ nm in benzene), ready quenching by nitroxy radicals and similarity in spectra and kinetics with those of the radical transient, photogenerated from the model substrate, *S*-isobutyryl *O*-ethyl xanthate.

(Keywords: photocrosslinking; copolymer; laser flash photolysis)

INTRODUCTION

Increasing industrial applications of photosensitive polymers in microelectronics, u.v.-curable coatings, etc. have led to the development of a variety of photocrosslinkable polymers[1–7]. Photocrosslinking of such polymers is achieved by light-induced dimerization and radical or ionic processes[8]. Photocrosslinking of polymers having dimerizable chromophores such as cinnamate and chalcone have been well studied[9–11]. Polymers containing other photoactive pendants such as quinonoid[12], thiocyanatoacetyl[13], pyrazine mono- and di-*N*-oxide[14] and diethyldithiocarbamate[15] groups have also been reported. Quite recently Chujo *et al.*[16] have reported the photogelation of a hydrogel based on polyoxazoline having a photoactive coumarin moiety, which is known to undergo [2+2] photocycloaddition.

We report here the synthesis and photocrosslinking behaviour of some copolymers of *S*-acryloyl *O*-ethyl xanthate (AX), a polymerizable monomer containing a xanthate chromophore. Copolymers of AX with styrene (St) and methyl methacrylate (MMA) were prepared through thermal polymerization and the results of their photocrosslinking studies are presented.

EXPERIMENTAL

The i.r. spectra were recorded on a Perkin–Elmer i.r. spectrometer (model 880). The electronic spectra were recorded on Hitachi 220 u.v.-vis. or Cary 219 spectrophotometers. ^{1}H n.m.r. spectra were recorded on a Varian EM-360 n.m.r. spectrometer, using tetramethylsilane as internal standard. Mass spectra were recorded on a Finnigan MAT mass spectrometer (model 8430). G.p.c. analyses were carried out on a Waters ALC/GPC 244 chromatograph, after calibration with standard polystyrene samples. T.g.a. were recorded on a DuPont TA 3000, with 951 thermogravimetric analyser. Glass transition temperatures (T_gs) were recorded on a Mettler TA-3000 thermal system. Photoirradiations were carried out using an Oriel optical illuminator equipped with a 500 W super high pressure mercury lamp (USHIO USH 508 SA) and a 295 long pass filter. Sulfur analyses were carried out by the Midwest Microlaboratory (Indianapolis, USA).

Starting materials

The solvents used were purified and freshly distilled before use. Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol before use. St and MMA, both from Aldrich, were washed with equal volumes of sodium hydroxide (10% in water) to remove the inhibitors and dried over anhydrous sodium sulfate. Potassium *O*-ethyl xanthate was prepared by a reported procedure[17]. Acryloyl chloride, obtained from Aldrich, was used as such. Aldrich Gold-Label solvents were used for laser studies. Benzophenone, thioxanthone, 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxyl (HTEMPO), all from Aldrich, were used as such.

Preparation of S-*acryloyl* O-*ethyl xanthate*

A methylene dichloride solution of acryloyl chloride (**1**) (8.9 g, 0.1 mol in 100 ml) solution was gradually added over 1 h to a stirred suspension of potassium *O*-ethyl xanthate (16.0 g, 0.1 mmol) in methylene dichloride (100 ml), maintained at −30°C. The reaction mixture was

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Table 1 Copolymerization[a] of *S*-acryloyl *O*-ethyl xanthate (AX) (**2**) with different monomers (M)

Run	Copolymer	Monomer (mol%) [AX]	[M]	Time (h)	Yield (%)	M_n[b]	AX content of polymer (mol%)[c]
1	AX-*co*-St-I	70	30	24	50	4610	57.9
2	AX-*co*-St-II	50	50	22	53	5452	45.2
3	AX-*co*-St-III	36	64	28	51	6358	34.4
4	AX-*co*-St-IV	16	84	18	61	1550	14.1
5	AX-*co*-MMA-I	80	20	12	36	5190	69.8
6	AX-*co*-MMA-II	50	50	18	48	6540	46.2
7	AX-*co*-MMA-III	30	70	18	53	9180	23.3

[a] Polymerized with AIBN (0.01 M) at 70°C in benzene
[b] Determined by g.p.c. using polystyrene standard
[c] Estimated on the basis of sulfur analysis

stirred for an additional period of 1 h and was allowed to warm up gradually to room temperature. The reaction mixture was treated with water and the methylene dichloride layer was washed several times with water and dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave 15.9 g (90%) of AX (**2**) as a pale yellow liquid. I.r. (neat): 1720 (C=O), 1640 (C=C), 1240 (C=S), 1050 (C–O) cm^{-1}. U.v. λ_{max} (CH_3CN): 220 nm (ε 8170), 278 (9830), 350 (105), 398 (40). ^{1}H n.m.r. ($CDCl_3$): δ 1.45 (3 H, t, CH_3), 4.7 (2 H, q, CH_2), 5.9–6.5 (3 H, m, CH_2=CH). Mass (f.a.b.) *m/e*: 177 (MH^+). Exact mass calculated for $C_6H_8O_2S_2$: 175.99657; found: 175.9963 (high resolution mass spectrometry).

Preparation of copolymers: general procedure

Copolymerizations of **2** with St and MMA were carried out in the dark in presence of AIBN. The required amounts of the monomers, AIBN and solvent, in each case, were taken in Pyrex glass ampoules, which were then degassed by three cycles of the conventional freeze–thaw technique and sealed off under vacuum. The polymerizations were carried out in a constant temperature bath, maintained at 70°C for given lengths of time. Afterwards the contents of the tubes were poured into excess methanol. The precipitated copolymers were purified by three successive reprecipitations from chloroform solutions by methanol. The yields of the copolymers and their compositions are given in *Table 1*. The copolymer compositions were determined through sulfur analysis. Both the i.r. and ^{1}H n.m.r. spectra of the copolymers were in agreement with the structures **3** and **4**, respectively.

Photocrosslinking studies

Photocrosslinking studies were carried out using thin films of the copolymers on glass surfaces. These thin films were prepared by dissolving the copolymer (10 mg) in chloroform (~0.4 ml) and casting them over glass slides at room temperature. Each of these films had an area of ~2.3 × 2.3 cm and were ~10–20 μm thick. The copolymer films were irradiated for 2 h with an Oriel optical illuminator, equipped with a super high pressure Hg lamp and a 295 long pass filter. After irradiation, the polymer films were repeatedly washed with chloroform to remove all of the unchanged copolymer. The photocrosslinking yield was estimated from the weight of the film which remained on the glass slide after irradiation and washing.

The extent of photocrosslinking of the copolymers was followed quantitatively by both i.r. and u.v. spectroscopy. Thin films of the copolymers were made on quartz slides and the u.v. spectral changes were followed as a function of time by recording the u.v. spectra after definite time intervals of irradiation. I.r. spectral studies were carried out by using thin films of the copolymers, cast on NaCl discs.

Laser flash photolysis

For laser flash photolysis, use was made of pulsed outputs at 308 nm (attenuated to ~20 mJ per pulse) from a Lambda Physik EMG 101 MCS excimer laser (50 mJ, 10 ns; XeCl) and at 337.1 nm from a Laser Photonics PRA/model UV-24 nitrogen laser (9 mJ, 10 ns). The details of the kinetic spectrophotometer and data collecting system have been described earlier[18,19]. For transient spectra, a flow cell was used. For kinetics, static cells (path length 2 mm) containing ~1 ml of the solutions for photolysis were used. Unless the effect of oxygen was to be studied, the solutions were deaerated by saturating with high purity argon.

RESULTS AND DISCUSSION

*Synthesis of AX (2) and the copolymers with St (AX-*co*-St) (3) and MMA (AX-*co*-MMA) (4)*

AX (**2**) was prepared by the treatment of acryloyl chloride with potassium *O*-ethyl xanthate by a general procedure[20] (*Scheme 1*). The copolymers with St (AX-*co*-St) (**3**) and MMA (AX-*co*-MMA) (**4**) were prepared by thermal polymerization in the presence of AIBN as initiator under different conditions. The details are presented in *Table 1*. The molecular weights of all the copolymers were determined by g.p.c., using polystyrene as standard. G.p.c. analysis of the copolymers has revealed that as the mole fraction of the xanthate chromophore increases, there is a decrease in the molecular weight. The copolymer composition was determined, in each case, through sulfur analysis (see *Table 1*).

The i.r. spectra of the copolymers showed absorption bands at 1740 (C=O), 1240 (C=S) and 1050 cm^{-1} (C–O), due to the acyl xanthate moiety. The u.v. spectra of these

Table 2 Photocrosslinking[a] of AX copolymer films[b]

Run	Copolymer	Initial weight of film (mg)	Final weight of film (mg)	Photocrosslinking yield[c] (%)
1	AX-*co*-St-I	9.4	6.7	71.3
2	AX-*co*-St-II	9.6	7.1	74.0
3	AX-*co*-St-III	8.8	7.2	81.8
4	AX-*co*-St-IV	9.8	3.2	32.6
5	AX-*co*-MMA-I	9.3	7.3	78.5
6	AX-*co*-MMA-II	9.6	8.0	83.3
7	AX-*co*-MMA-III	9.1	8.4	92.3

[a] Irradiation for 2 h with a 500 W high pressure mercury lamp using a 295 long pass filter

[b] Film thickness varies from 10 to 20 μm

[c] Photocrosslinking yield =

$$\frac{\text{weight of copolymer film after irradiation}}{\text{weight of copolymer film before irradiation}} \times 100$$

copolymers showed an absorption maximum around 285 nm due to the xanthate chromophore.

Photocrosslinking studies

Results of the photocrosslinking studies of the different copolymers are presented in *Table 2*. The plots of weight percentage of insoluble fraction of irradiated films of AX-*co*-St and AX-*co*-MMA as a function of irradiation time are presented in *Figure 1*. In the case of AX-*co*-St polymers I, II and III, having 57.9, 45.2 and 34.4% xanthate moiety, respectively, a maximum of 71.3, 74.0 and 81.8% crosslinking yields were obtained after 2 h of irradiation (*Figure 1*). Similarly, the photocrosslinking yields of AX-*co*-MMA-I, II and III were found to be high after the same period of irradiation (2 h) (*Figure 1b*). For AX-*co*-St-IV, having a low percentage of the xanthate group, the photocrosslinking yield was found to be relatively low.

It has been observed that the molecular weights of the copolymers have considerable influence on the photocrosslinking yield. Thus, the photocrosslinking yield percentage of AX-*co*-St-III ($M_n = 6358$) is higher than that of AX-*co*-St-I ($M_n = 4610$), even though the percentage of the photosensitive groups is much lower for AX-*co*-St-III than for AX-*co*-St-I. Similar observations were made in the case of AX-*co*-MMA polymers. In the case of copolymers having low molecular weights and lower xanthate content, the yield of photocrosslinking was found to be low. For copolymers of the same molecular weight, the percentage photoconversion was hardly affected by the copolymer composition. For comparable molecular weight and percentage of the photoreactive groups, the photocrosslinking yields of both AX-*co*-St and AX-*co*-MMA were found to be approximately the same.

Marked spectral changes were observed both in the u.v. and i.r. regions when the copolymers were irradiated. Thus, for thin films of AX-*co*-St and AX-*co*-MMA, on irradiation with a 500 W high pressure mercury lamp, the absorption maximum around 285 nm due to the xanthate chromophore was found to decrease through two isobestic points around 270 and 310 nm during the first 30 min. For longer irradiation times, however, deviations from the isobestic points were observed. Comparison of the i.r. spectral changes of AX-*co*-St, for example, both before and after irradiation revealed that a new absorption band at 1700 cm^{-1} appears after irradiation. This band is attributed to the diketo group, formed between the polymeric chains (**10**, *Scheme 1*). Also, the intensity of absorptions at 1220 and 1040 cm^{-1} were found to decrease due to the photofragmentation of the xanthate chromophore.

Laser flash photolysis studies

In order to shed light on the transients involved in the phototransformations of the copolymers under investigation, both AX-*co*-St-II (**3**) and AX-*co*-MMA-I (**4**) and a model substrate containing the acyl xanthate chromophore, namely *S*-isobutyryl *O*-ethyl xanthate (**11**) were subjected to laser flash photolysis studies. Attempts were made to observe transients in terms of their absorption at 315–750 nm over 100 ns–100 μs following nanosecond laser pulse excitation. Upon 308 nm laser excitation, a benzene solution of **3** gave rise to absorbance changes with two distinct maxima at 330 and 660 nm. Similarly, 308 nm laser excitation of **4** and the model compound **11** gave two transient species with absorption maxima at 350 and 660 nm, in each case. The absorption spectra and decay traces of the transients observed with **3**, **4** and **11** are presented in *Figures 2*, *3* and *4*, respectively. With all three substrates under study, the longer wavelength absorption has a broad maximum at ~660 nm and second-order decay rates ($2k/\varepsilon$) of 4.6×10^6–9.5×10^6 cm s^{-1} (at 660 nm) (where k is the second-order rate constant and ε is the extinction coefficient). This transient is not quenched by oxygen or ferrocene, but is quenched by free radical quenchers such as TEMPO (the quenching rate constant, $k_q = 1.3 \times 10^9$–1.5×10^9 M^{-1} s^{-1}) and HTEMPO ($k_q = 1.2 \times 10^9$–1.3×10^9 M^{-1} s^{-1}). On the basis of the quenching studies

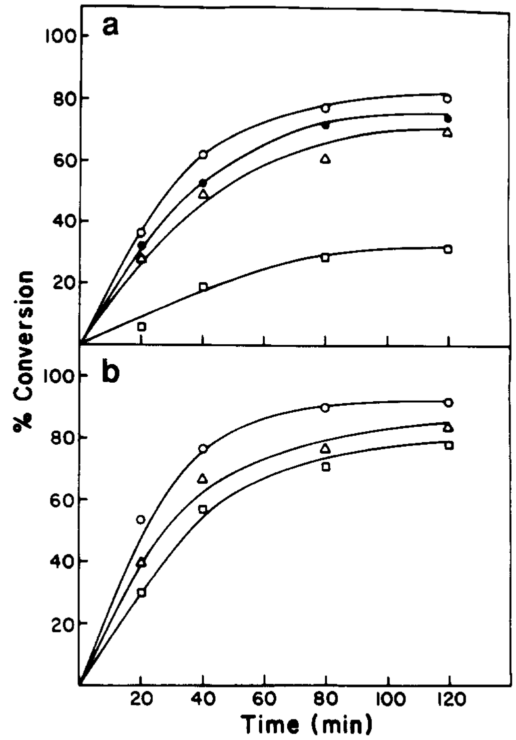
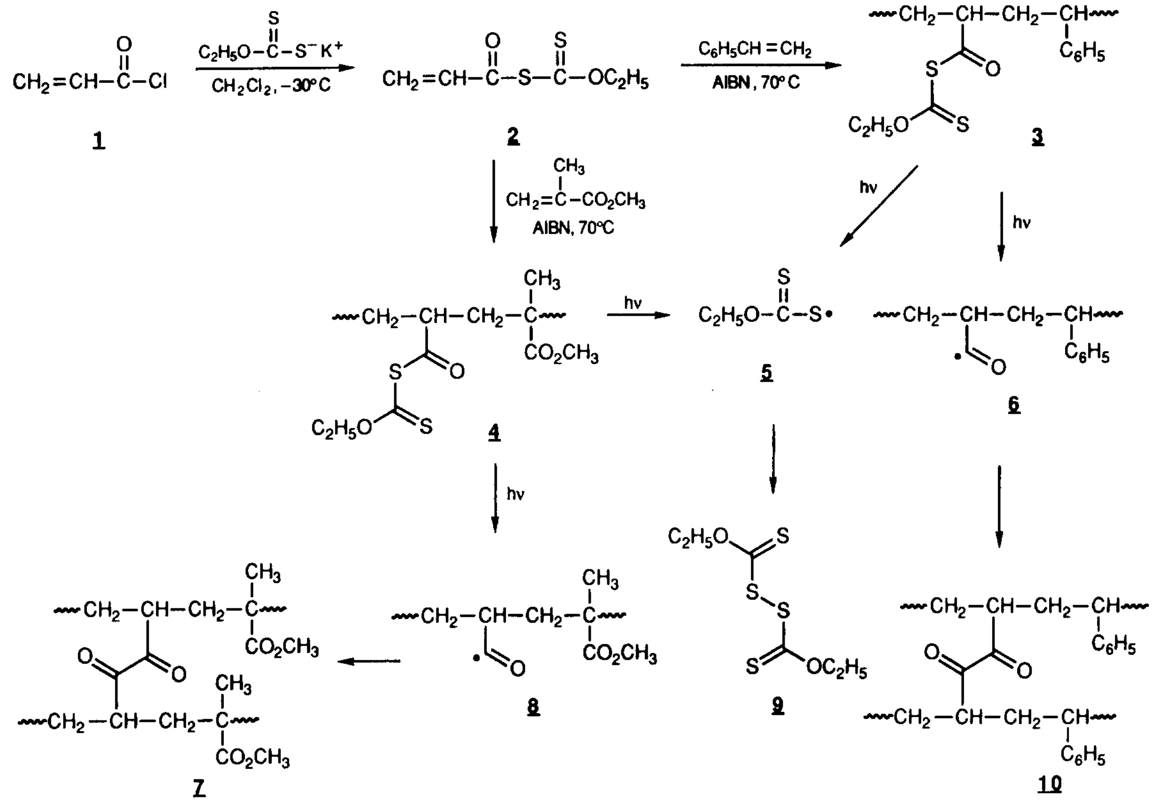


Figure 1 (a) Photocrosslinking of AX-*co*-St polymer films: (△) AX-*co*-St-I; (●) AX-*co*-St-II; (○) AX-*co*-St-III; (□) AX-*co*-St-IV. (b) Photocrosslinking of AX-*co*-MMA polymer films: (□) AX-*co*-MMA-I; (△) AX-*co*-MMA-II; (○) AX-*co*-MMA-III



Scheme 1

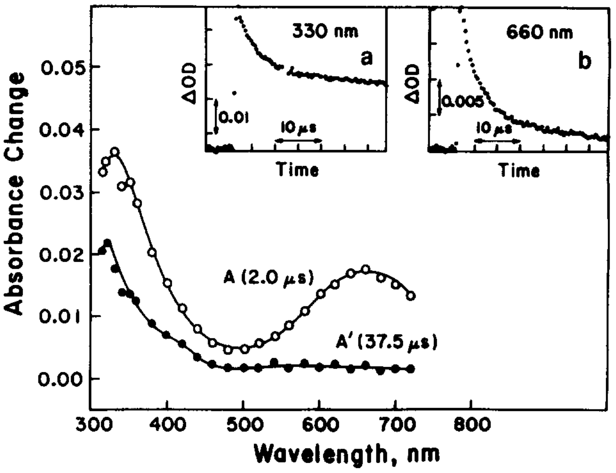


Figure 2 Transient absorption spectra (A, A') of 3, following 308 nm (10 ns) laser pulse excitation in benzene at 295 K. The insets show the kinetic decay traces at (a) 330 nm and (b) 660 nm. The times (after laser flash) at which the spectra were recorded are given in the figure

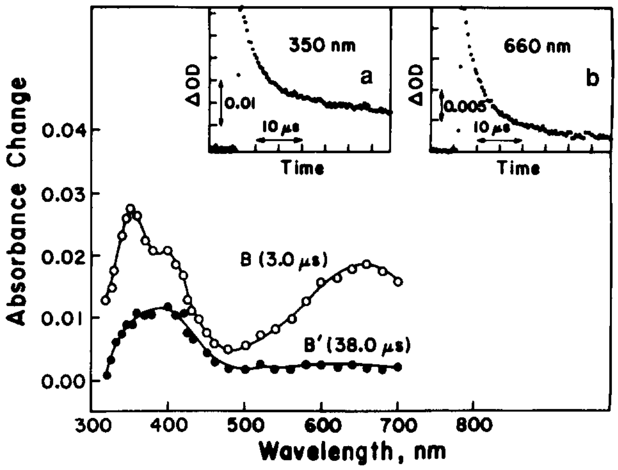


Figure 3 Transient absorption spectra (B, B') of 4, following 308 nm (10 ns) laser pulse excitation in benzene at 295 K. The insets show the kinetic decay traces at (a) 350 nm and (b) 660 nm. The times (after laser flash) at which the spectra were recorded are given in the figure

and also based on earlier reports[21], on the flash photolysis studies of analogous substrates, the 660 nm transient is assigned to the (ethoxycarbonylthiocarbonyl)thiyl radical 5 (*Scheme 1*). The differences in the $2k/\varepsilon$ value of this radical, as obtained from the three different substrates, reflect the sensitivity of measured second-order rate constants to the contribution of competing first-order processes (not taken into account).

The short wavelength maxima at 330–350 nm (*Figures 2–4*) were primarily due to long-lived (or permanent) photoproducts, which were not amenable to kinetic analysis using our nanosecond laser set-up. The short-lived components in this u.v. spectral region gave the hint of quenching by both oxygen and nitroxy radicals; however, reliable quenching data could not be obtained because of the weak nature of these transient components. Aliphatic acyl radicals absorb at <300 nm ($\lambda_{max} = 260$ nm for pivaloyl radical in dichloromethane)[22] and have insignificant absorption at $\leqslant 350$ nm. While the acyl-type radicals probably contribute to the observed transient absorptions at 330–350 nm, we could not identify them definitely under our experimental conditions.

Compound **11** quenched benzophenone and thioxanthone triplets with diffusion-controlled rate constants of 6.3×10^9 and 9.4×10^9 M^{-1} s^{-1} (in benzene), respectively. These experiments were done under the laser excitation of the ketones at 337.1 nm; at this wavelength, the ground-state absorption due to **11** was negligible ($\leqslant 20\,M^{-1}\,cm^{-1}$). Although there was evidence in the transient spectra for the formation of (ethoxycarbonylthiocarbonyl)thiyl radical at 600–700 nm as a result of the carbonyl triplet quenching by **11**, the yield of the radical appeared to be very low. For example, with benzophenone triplet sensitizer in benzene, the yield was estimated to be $190/\varepsilon$, where ε was the extinction coefficient of the radical at 660 nm. Inefficient radical formation via xanthone triplet quenching has been previously noted for various xanthate substrates[21].

Mechanism of photocrosslinking

Acyl xanthates [R–(C=O)–S–C(=S)–OR′] are known to undergo phototransformations leading to a variety of products. It has been suggested that the photolysis of acyl xanthates proceeds through a free radical pathway, involving the initial fragmentation of a C(=O) bond[20,23,24]. An alternative mode of fragmentation, involving C(=S)–S bond cleavage has also been observed in the case of some *S*-benzoyl *O*-alkyl xanthates[25]. Recent laser flash photolysis studies of some aroyl xanthates and carboxylic dithiocarbamic anhydrides have shown that the primary photoreactions in aroyl xanthates for example, involves a C(=O)–S fission and that these photofragmentations are triplet state mediated processes[21].

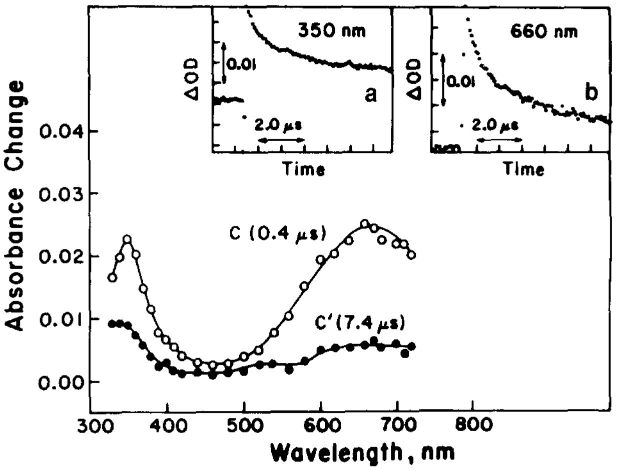
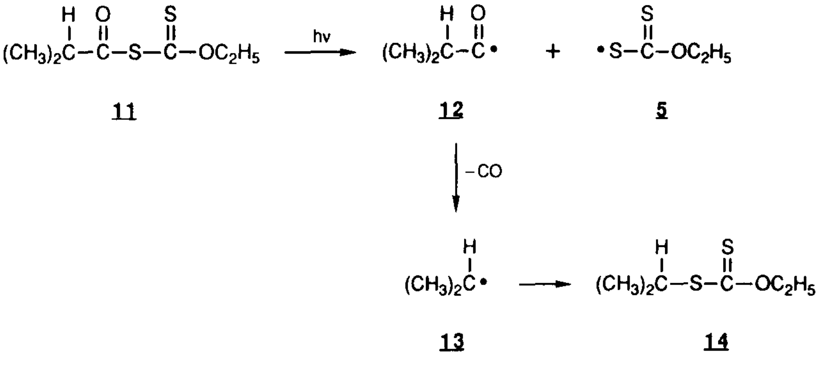


Figure 4 Transient absorption spectra (C, C′) of **11**, following 308 nm (10 ns) laser pulse excitation in benzene at 295 K. The insets show the kinetic decay traces at (a) 350 nm and (b) 660 nm. The times (after laser flash) at which the spectra were recorded are given in the figure

On the basis of the present studies and also based on analogy to earlier reports[20,21,23,24], it is plausible that the xanthate moieties in the copolymers AX-*co*-St (**3**) and AX-*co*-MMA (**4**), on irradiation, undergo homolytic cleavage to give the acyl radicals **6** and **8**, respectively. These radicals subsequently recombine to form crosslinking points between the polymeric chains. It may be mentioned in this connection that the steady-state irradiation of the model compound **11** is known to give the decarbonylated product, *S*-isopropyl *O*-ethyl xanthate **14** (*Scheme 2*)[20]. It has been suggested that the initial photofragmentation of **11** leads to the isobutyryl radical **12** and the thiyl radical **5** and that **12** undergoes decarbonylation, under the steady-state reaction conditions, to give the isopropyl radical **13**. Subsequent recombination of **13** and **5** results in the formation of the decarbonylated product **14**. Similar decarbonylation[26] is also possible with the acyl-type macroradicals from **3** and **4**; however, the fact that the diketo moiety is shown by i.r. to be present in the photocrosslinked materials from **3** and **4** suggests that the coupling of the acyl radicals competes favourably against decarbonylation.

Photocrosslinking of the copolymers **3** and **4**, on irradiation, was evident through the analysis of the sulfur contents in both the irradiated and unirradiated samples of these polymers. The sulfur contents of the irradiated copolymers were found to be lower than in the corresponding unirradiated samples. Thus, the sulfur content of an irradiated sample of AX-*co*-St-III was found to be 12.3%, whereas in the unirradiated sample it was 16.9%. This decrease in the sulfur content of the irradiated copolymer is attributed to the photocleavage of the xanthate radical giving rise to the (ethoxythiocarbonyl)thiyl radical **5**, which can dimerize to give **9**. Subsequent extrusion of **9**, on chloroform washing of the irradiated polymeric film, will indicate a lower sulfur content, as observed.

The t.g.a. of the copolymer AX-*co*-St-III before and after photolysis indicated a higher thermal stability for the irradiated sample. The percentage weight loss of the copolymer before irradiation was higher than that of the irradiated copolymer in the same temperature range. Measurements of the T_g of the photocrosslinked copolymers have indicated an increase in the T_g, compared to that of the uncrosslinked one. Thus, the T_g of AX-*co*-St-III before and after irradiation was found to be 55 and 74°C, respectively. This increase in T_g was taken as a measure of the change in the physical properties of the copolymer by crosslinking. It is known that the



Scheme 2

crosslinking reaction of a polymer can decrease its free volume which in turn can raise its T_g value[15].

CONCLUSIONS

Photosensitive copolymers of AX with monomers such as St and MMA were prepared. These copolymers undergo photocrosslinking on irradiation and the photocrosslinking yields are influenced by the molecular weight of the polymer rather than the percentage of the photosensitive group. Laser flash photolysis studies of the copolymers **3** and **4** and a model substrate **11** reveal that the primary photoprocess in these systems involves a C(=O)–S bond fission to generate the corresponding acyl radicals. The photocrosslinking of the copolymers **3** and **4** is believed to be due to the coupling of these acyl radicals, across polymeric chains.

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