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Macrophotoinitiator containing pendent xanthate chromophore: photopolymerization of methyl methacrylate and evaluation of kinetic parameters*

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Copolymer AX-*co*-MMA (**1**) of *S*-acryloyl *O*-ethyl xanthate (AX) and methyl methacrylate (MMA) was prepared and employed as a soluble macrophotoinitiator for the polymerization of MMA. The photoinitiation efficiency of AX-*co*-MMA was compared with that of *S*-acetyl *O*-ethyl xanthate (**2**) which is a low molecular weight photoinitiator. The kinetic parameters of polymerization, initiator efficiency (Φ) and the fraction of primary radicals entering into termination (β) were evaluated. Experimental data and kinetic parameters reveal that the photoinitiation efficiency of AX-*co*-MMA is higher than that of the low molecular weight photoinitiator **2**. The ratio of the rate constants for chain initiation and chain termination by primary radicals were determined to be 3.33×10^6 and 7.64×10^6 for AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate, respectively.

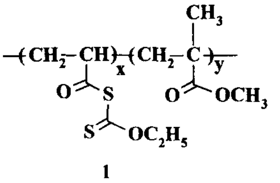
(Keywords: macrophotoinitiator; xanthates; photopolymerization)

INTRODUCTION

Aroyl xanthates and related systems are known to undergo homolytic bond cleavage at the C(=O)-S bond position and are a potential source of free radical intermediates[1,2]. Recently, we have reported the use of *S*-benzoyl *O*-ethyl xanthate as a photoinitiator for the polymerization of methyl methacrylate (MMA)[3]. In addition, the xanthate chromophore has also been used for photografting and photocrosslinking applications[4-6]. Laser flash photolysis studies of several acyl and aroyl xanthates and their polymeric analogues have revealed that the primary photochemical process in all these cases is homolytic bond cleavage at the C(=O)-S bond position giving rise to keto radicals and alkoxy thiocarbonyl thiyl radicals[7].

Our recent studies on the synthesis and photocrosslinking behaviour of some copolymers of *S*-acryloyl *O*-ethyl xanthate (AX) have prompted us to investigate the potential use of the copolymers of AX as polymeric photoinitiators. Polymeric photoinitiators have the advantages of possessing enhanced stability and solubility in addition to their compatibility with the monomers. Moreover, in several cases, polymeric photoinitiators exhibit higher photoinitiation efficiency as compared to the corresponding low molecular weight analogues[8-13]. For these reasons, polymeric photoinitiators are attracting a great deal of interest in u.v. curable coatings and related areas[14-16].

The present study describes the use of the copolymer AX-*co*-MMA (**1**) as a macrophotoinitiator for the polymerization of MMA. Detailed studies on the kinetics of polymerization have been carried out and these data have been compared with the results of an analogous low molecular weight photoinitiator, *S*-acetyl *O*-ethyl xanthate (**2**).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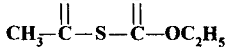
$CH_3-\overset{O}{\overset{\|}{C}}-S-\overset{S}{\overset{\|}{C}}-OC_2H_5$

2

EXPERIMENTAL

Materials and methods

MMA (CDH, India) was washed twice with equal volumes of 5% aqueous sodium hydroxide solution and subsequently with water, followed by distillation under reduced pressure. Potassium *O*-ethyl xanthate[17], acryloyl chloride[18], *S*-acetyl *O*-ethyl xanthate[19] and *S*-acryloyl

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Table 1 Comparison of the rate of polymerization and the molecular weight of the polymers obtained for the photopolymerization of MMA using AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate

	AX-*co*-MMA			*S*-acetyl *O*-ethyl xanthate		
Time (min)	Conversion (%)	R_p (× 10^4) (ms^{-1})	$\bar{M}_n$ (× 10^4)	Conversion (%)	R_p (× 10^4) (ms^{-1})	$\bar{M}_n$(× 10^{-4})
10	4.5	4.5	4.1	2.5	3.8	2.8
15	7.3	4.9	4.0	3.9	4.0	2.8
20	10.2	5.1	4.1	5.7	4.4	2.7
25	12.0	4.8	4.0	7.1	4.4	2.8
30	12.7	4.9	4.2	8.8	4.0	2.9

$[I] = 5 \times 10^{-3}$ M; [MMA] = 6 M in benzene

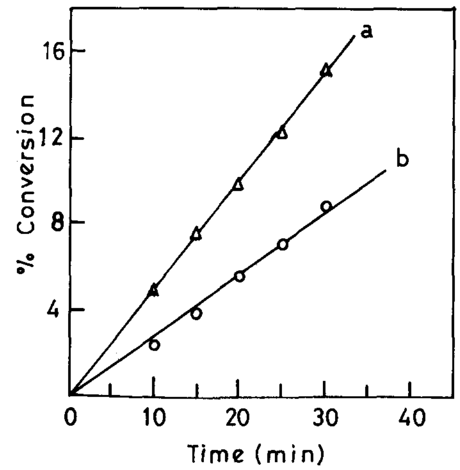

Figure 1 Conversion–time curve for the photopolymerization of MMA (5 M) using a 5×10^{-3} M solution of the initiator in benzene: (a) AX-*co*-MMA; (b) *S*-acetyl *O*-ethyl xanthate

O-ethyl xanthate[6] were prepared by reported procedures. Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol before use. The solvents used were purified and freshly distilled before use.

The i.r. spectra and u.v. spectra were recorded on Perkin–Elmer (model 880) and Shimadzu 2100 A spectrophotometers, respectively. ^{1}H n.m.r. spectra were recorded on a Jeol EX-90 n.m.r. spectrometer, using tetramethylsilane as internal standard. G.p.c. analyses were carried out on a Shimadzu LC-8A equipped with a refractive index detector and Shimpac 802, 804 and 80 M columns connected in series. Calibration was done using standard polystyrene samples. Elemental analyses were carried out by the Midwest Microlaboratory (Indianopolis, USA). Photopolymerization experiments were carried out in a Rayonet (RPR-100) photoreactor equipped with eight 3500 Å fluorescent lamps.

Copolymerization of AX and MMA

AX (4 g, 20 mmol) and MMA (2.05 g, 20 mmol) were dissolved in benzene (5 ml) containing AIBN (100 mg) as the initiator. The polymerization mixture, in a Pyrex glass ampoule, was deoxygenated by three cycles of the conventional freeze–thaw technique and then sealed off under vacuum. Polymerization was carried out at 70°C for 36 h in the dark and the contents were subsequently poured into excess methanol. The precipitated copolymer was filtered and washed with methanol and purified by three successive reprecipitations from chloroform solutions by adding methanol.

The yield of AX-*co*-MMA was 2.9 g (48%). I.r. (neat film) ν_{max}: 1760 (C=O, ester), 1710 (C=O), 1240 (C=S), 1050 (C–O) cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ: 4.65 (q, OCH_2); 3.6 (s, OCH_3); 1.9 (m, CH); 1.4 (t, CH_3); 1.0 (m, CH_2); 0.8 (s, CH_3).

Copolymer composition (AX:MMA): calculated, 50:50; found, 46:54 (by S analysis); $\bar{M}_n = 6540$.

Photopolymerization: general procedure

Polymerization mixtures (10 ml) consisting of known concentrations of MMA and AX-*co*-MMA in Pyrex tubes (1.4 cm diameter, 15 cm long) were stoppered with rubber septums. They were then deoxygenated with argon for 10 min and irradiated (RPR-100, 3500 Å) for known periods of time. The contents of the tubes were poured into excess methanol and the precipitated polymer was washed with methanol. The rates of polymerization were calculated from the slopes of percentage conversion–time curves.

RESULTS AND DISCUSSION

The synthesis of AX and its copolymerization with monomers such as MMA and styrene are reported elsewhere[6]. Our recent studies reveal that photolysis of these polymers either in solution or in the form of films resulted in the formation of crosslinked polymers. The mechanism of photocrosslinking has been examined through nanosecond laser flash photolysis of the copolymers of AX with MMA and styrene.

Photolysis of AX-*co*-MMA in the presence of MMA initiated polymerization instead of the crosslinking of AX-*co*-MMA. However, on prolonged irradiation or with a higher concentration of MMA small amounts of crosslinked polymers were also obtained. In order to have a better insight into the efficiency of photoinitiation by AX-*co*-MMA, detailed studies on the kinetics of polymerization of MMA have been carried out. The percentage conversion of MMA under different irradiation times using AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate and their respective rates of polymerization are shown in *Table 1*. A plot of the percentage conversion against irradiation time gave a linear relationship (*Figure 1*). The rate of polymerization (R_p) in each case was determined from the slope of the plot. From *Figure 1* it was found

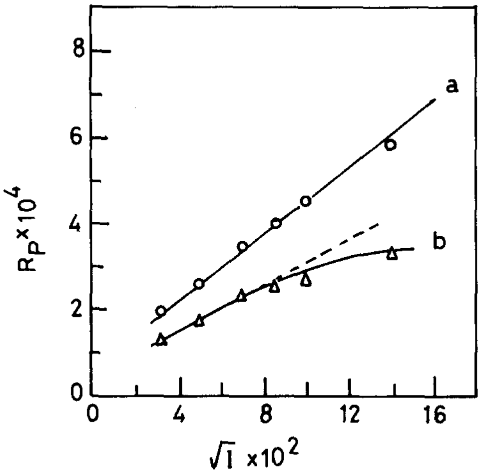

Figure 2 Relationship between the rate of polymerization and initiator concentration for the photopolymerization of MMA (5 M in benzene): (a) AX-*co*-MMA; (b) *S*-acetyl *O*-ethyl xanthate

that the R_p of MMA in AX-*co*-MMA is higher than that of *S*-acetyl *O*-ethyl xanthate.

Effect of initiator and monomer concentrations on the rate of polymerization

The influence of the initiator concentration on R_p was studied over a concentration range of 1×10^{-3}–1×10^{-2} M in benzene at fixed monomer concentration, light intensity and path length. It has been found that R_p increases with increase in the initiator concentration (*Figure 2*). A linear relationship was noticed for lower conversion of MMA when R_p was plotted against $\sqrt{I}$ (*Figure 2a*). However, deviation of the plot from the origin reveals a linear decrease in the rate of polymerization. In the case of *S*-acetyl *O*-ethyl xanthate, deviation from linearity was more predominant especially at higher initiator concentrations (*Figure 2b*). Similarly, the effect of MMA concentration on R_p was studied at constant initiator concentration. A plot of monomer concentration against R_p gave a linear relationship for both AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate (*Figure 3*). At very low monomer concentrations, polymerization could not be observed. The reason for this could be that, at very low monomer concentrations, radical initiation results in the oligomerization or even simple radical addition of the initiator fragments to the double bond of the monomer. The influence of initiator and monomer concentrations on R_p reveals that the kinetic parameters of polymerization deviate from the simple kinetic equation:

$$R_p = k\sqrt{I}\,[M] \tag{1}$$

particularly at higher initiator concentrations. This deviation could be the result of the change in the kinetic parameters, primarily due to the mode of termination as well as the enhanced chain transfer property which are found to be more predominant in the case of *S*-acetyl *O*-ethyl xanthate. The possibility of such terminations could be envisaged by considering the following kinetic schemes.

$$I \xrightarrow{k_d} I^{\bullet} + I'^{\bullet} \tag{2}$$

$$I^{\bullet} + M \xrightarrow{k_i} M_n^{\bullet} \tag{3}$$

$$M_n^{\bullet} + I \xrightarrow{k_{CT}} P + I^{\bullet} \tag{4}$$

$$M_{n+1}^{\bullet} + M_n^{\bullet} \xrightarrow{k_t} P \tag{5}$$

$$M_{n+1}^{\bullet} + I'^{\bullet} \xrightarrow{\sigma\, k_t} P \tag{6}$$

where $I^{\bullet}$ and $I'^{\bullet}$ are the initiating and terminating radicals, respectively, and M_n is the growing polymer radical.

Kinetic parameters and efficiency of initiation

The kinetic parameters can be evaluated from the relationship between the rate of polymerization (R_p), monomer concentration [M] and the initiator concentration [I], according to the following equation as shown by Niwa *et al.*[20]:

$$[M]/R_p = \lambda/[I]^{1/2} + \mu/[M] \tag{7}$$

where $\lambda = (k_t/k_d)/k_p$ and $\mu = \sigma k_t/k_i k_p$.

Equation (7) predicts a linear relationship between $[M]/R_p$ and the reciprocal of the square root of the initiator concentration. Accordingly, a plot of $[M]/R_p$ *versus* $1/[I]^{1/2}$ at a constant monomer concentration gave a straight line for both AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate as shown in *Figure 4*. The value of λ and μ were obtained from the slope and the intercept, respectively, and are shown in *Table 2*. It is found that the values of λ for both AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate are nearly the same. However, the value of μ for *S*-acetyl *O*-ethyl xanthate is found to be higher than that of AX-*co*-MMA which could be due to the high efficiency of primary radical termination of the former.

In order to evaluate the degree of primary radical termination during polymerization, the initiator efficiency (Φ) and the fraction of primary radicals entering into termination (β) have been calculated using:

$$\beta = \sigma\, R_t/R_d = \Phi^{1/2}/1 + (\lambda[M]/\mu[I]^{1/2}) \tag{8}$$

where $\sigma\, R_t$ and R_d are the rate of termination by primary radicals and the rate of initiator decomposition, respectively. The value of Φ can be obtained from the

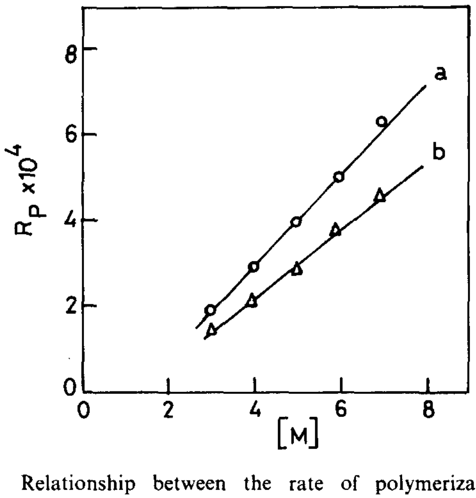

Figure 3 Relationship between the rate of polymerization and monomer concentration for the photopolymerization of MMA using a 5×10^{-3} M solution of the initiator in benzene: (a) AX-*co*-MMA; (b) *S*-acetyl *O*-ethyl xanthate

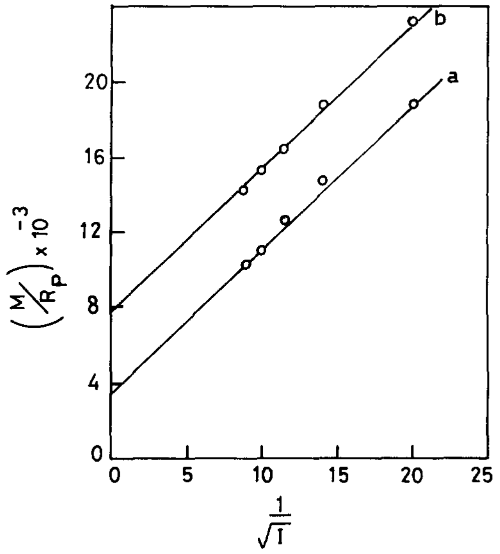

Figure 4 Plot of equation (7) showing the dependence of the rate of polymerization on initiator concentration: (a) AX-*co*-MMA; (b) *S*-acetyl *O*-ethyl xanthate

Table 2 Kinetic parameters for the photopolymerization of MMA

Initiator	λ ($\times 10^{-2}$) ($mol^{1/2} l^{-1/2}$)	μ ($\times 10^{-4}$) ($mol\, s\, l^{-1}$)	$\sigma k_t/k_i$ ($\times 10^{-6}$)
AX-*co*-MMA	7.8	1.7	3.33
S-acetyl *O*-ethyl xanthate	7.7	3.9	7.64

known values of λ, R_p, $[I]^{1/2}$ and [M] according to the following equation:

$$\Phi^{1/2} = \lambda R_p / [I]^{1/2}[M] \qquad (9)$$

The values of $\Phi^{1/2}$ and β of different initiator and monomer concentrations for the polymerization of MMA using AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate are presented in *Tables 3* and *4*, respectively. It is found that under identical conditions of polymerization, $\Phi^{1/2}$ decreases with an increase in initiator concentration whereas β increases. In contrast, with an increase in monomer concentration, $\Phi^{1/2}$ increases while β decreases. This is because, at high monomer concentration, there is maximum utilization of the initiator radicals for polymerization due to the increased availability of the monomer molecules. In such cases, secondary reactions such as initiator radical recombination and other radical deactivation processes will be inefficient. It is also found that the rate of primary radical termination decreases under higher monomer concentration and hence the mode of termination in such cases could be either by disproportionation or by polymer chain recombination. This may be the reason for the formation of a small amount of crosslinked polymer under high monomer concentration. The ratio of the rate constants of termination and initiation by the primary radicals (σ k_t/k_i) can be obtained from the known values of μ and k_p. Using the mean value of k_p for MMA at 30°C as $195.8\, l\, mol^{-1}\, s^{-1}$, the ratio σ k_t/k_i is 3.33×10^6 and 7.64×10^6 for AX-*co*-MMA and *S*-acetyl *O*-ethyl xanthate, respectively. These values indicate that the rate of primary radical termination is higher in the case of *S*-acetyl *O*-ethyl xanthate compared to AX-*co*-MMA. This could be the reason for the enhanced efficiency of AX-*co*-MMA for the photopolymerization of MMA. In addition to this, photolysis of AX-*co*-MMA results in high local concentration of the initiating radicals which enhances the rate of initiation and thereby the overall efficiency of polymerization. The number-average molecular weight ($\bar{M}_n$) values of the polymers prepared using AX-*co*-MMA are found to be higher than those of the polymers obtained from *S*-acetyl *O*-ethyl xanthate. This observation further substantiates the enhanced primary radical termination property of *S*-acetyl *O*-ethyl xanthate.

Table 3 Initiator efficiency (Φ) and the fraction of primary radicals terminating the chain (β) for the photopolymerization of MMA using AX-*co*-MMA under various monomer and initiator concentrations

[I] ($\times 10^3$) ($mol\, l^{-1}$)	$\Phi^{1/2}$	β	[M] ($mol\, l^{-1}$)	$\Phi^{1/2}$	β
1.0	0.91	0.11	3.0	0.67	0.23
2.5	0.83	0.15	4.0	0.78	0.22
5.0	0.75	0.18	5.0	0.75	0.18
7.5	0.70	0.19	6.0	0.93	0.19
10.0	0.72	0.22	7.0	1.02	0.19
12.5	0.67	0.22	–	–	–

Table 4 Initiator efficiency (Φ) and the fraction of primary radicals terminating the chain (β) for the photopolymerization of MMA using *S*-acetyl *O*-ethyl xanthate under various monomer and initiator concentrations

[I] ($\times 10^3$) ($mol\, l^{-1}$)	$\Phi^{1/2}$	β	[M] ($mol\, l^{-1}$)	$\Phi^{1/2}$	β
1.0	0.55	0.14	3.0	0.51	0.28
2.5	0.51	0.17	4.0	0.59	0.28
5.0	0.50	0.21	5.0	0.61	0.26
7.5	0.45	0.21	6.0	0.67	0.25
10.0	0.44	0.22	7.0	0.69	0.24
20.0	0.37	0.22	–	–	–

CONCLUSIONS

A copolymer AX-*co*-MMA of *S*-acryloyl *O*-ethyl xanthate with MMA was prepared and used as a soluble macrophotoinitiator for the polymerization of MMA. Detailed evaluation of the kinetic parameters reveals that AX-*co*-MMA (**1**) has higher photoinitiation efficiency than *S*-acetyl *O*-ethyl xanthate (**2**). The low molecular weight initiator **2** shows more deviation from the simple kinetic equation probably due to high chain transfer and primary radical termination. Polymeric photoinitiators having photosensitive pendent xanthate chromophores have potential use as high conversion photoinitiator systems for u.v. curable coating formulations.

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