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# Synthesis, characterization and radical copolymerization behaviour of S-methacryloyl O-ethyl xanthate*

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A new sulfur-containing photosensitive monomer, *S*-methacryloyl *O*-ethyl xanthate (MAX), was synthesized and characterized. Attempts to make the corresponding *S*-acryloyl *O*-ethyl xanthate (AX) under identical experimental conditions resulted in the formation of *S*-(3-hydroxypropionyl) *O*-ethyl xanthate as the major product. The free-radical copolymerization behaviour of MAX with methyl methacrylate (MMA) and styrene (St) has been investigated in detail. The copolymer yield and molecular weight were found to decrease with increasing MAX concentration in the monomer feed, which is attributed to the high chain transfer property of MAX. Copolymer compositions determined independently by sulfur and $^1$H n.m.r. analyses were in good agreement. Reactivity ratios of the monomers were calculated by Finemann-Ross, Kelen-Tüdös and non-linear least-squares methods. Determination of *Q* and *e* values reveals that MAX is an electron-deficient monomer and is more reactive towards electron-rich monomers such as styrene. The MAX-St monomer system has a greater tendency towards alternation during copolymerization than the MAX-MMA monomer system. The thermal stability of the copolymers was found to decrease with increase in MAX mole fraction.

**(Keywords: free-radical copolymerization; *S*-methacryloyl *O*-ethyl xanthate; reactivity ratios)**

## INTRODUCTION

Polymers bearing photosensitive pendent functional groups have great significance in microelectronics, printing and u.v.-curable coating applications[1-3]. Synthesis of new photosensitive monomers and knowledge about their copolymerization behaviour with other monomers are essential for designing copolymers with optimum performance. In this connection we have synthesized a new photosensitive monomer, *S*-methacryloyl *O*-ethyl xanthate (MAX), and studied the copolymerization behaviour of MAX with methyl methacrylate (MMA) and styrene (St).

Recently, we have reported several studies on photopolymerization, photocrosslinking and photografting, using aroyl xanthates and related chromophores[4-7]. We had observed that polymeric photoinitiators bearing xanthate chromophores enhance the rate of polymerization compared with the corresponding low-molecular-weight photoinitiators[7,8]. In addition, such polymers have added significance due to their great affinity for complexation with metal ions having catalytic activities, and offer excellent models for metalloenzymes[9,10].

Because of the possibility of wide-ranging applications of polymers bearing xanthate pendent groups, synthesis of copolymers with appropriate xanthate compositions is important from both practical and theoretical points of view. The present paper describes the synthesis and characterization of *S*-methacryloyl *O*-ethyl xanthate (MAX) and its copolymerization behaviour with methyl methacrylate and styrene. Determination of the copolymer compositions and evaluation of the reactivity ratios are also described.

## EXPERIMENTAL

### *Materials*

All solvents were dried and distilled before use. MMA and St were purified by washing with 10% NaOH solution, followed by distillation under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Potassium *O*-ethyl xanthate[10] and methacryloyl chloride[11] were prepared as per reported procedures.

### *Methods*

Infra-red (i.r.) spectra were recorded on a Perkin-Elmer model 880 spectrometer. The electronic spectra were recorded on a Shimadzu 2100 A spectrophotometer. $^1$H and $^{13}$C nuclear magnetic resonance (n.m.r.) spectra were recorded on a Jeol EX 90 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard. Gel permeation chromatography (g.p.c.) was carried out on a Shimadzu LC-8A GPC system equipped with a refractive index detector. Calibrations were done with standard polystyrene samples. Tetrahydrofuran was used as the eluant at a flow rate of 1 ml min$^{-1}$ at 28°C.

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Thermogravimetry (t.g.) curves were obtained using a Du Pont thermal analyser at a heating rate of 10°C min$^{-1}$ under air. Elemental sulfur analyses were carried out at the Mid West Micro Laboratory, Indianapolis, USA.

### *Synthesis of* S-*methacryloyl* O-*ethyl xanthate* (*MAX*)

To a stirred suspension of potassium *O*-ethyl xanthate (16.0 g, 0.1 mol) in methylene dichloride (100 ml), maintained at 0°C, was gradually added a solution of methacryloyl chloride (10.4 g, 0.1 mol) in methylene dichloride (100 ml). The reaction mixture was stirred for an additional period of 1 h and allowed to warm up gradually to room temperature. The reaction mixture was washed several times with water and the organic layer was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave 17.0 g (90%) of MAX as a yellow liquid. I.r. (neat) $\nu_{max}$ (cm$^{-1}$): 1720 (C=O), 1640 (C=C), 1240 (C=S), 1050 (C–O). U.v. ($CHCl_3$) $\lambda_{max}$ (nm): 280 ($\varepsilon$, 10 380), 395 (90). $^1$H n.m.r. ($CDCl_3$) $\delta$ (ppm): 1.45 (t, 3H, $CH_3$), 2.0 (s, 3H, $CH_3$), 4.7 (q, 2H, $CH_2$), 5.9–6.5 (m, 2H, $CH_2$). $^{13}$C n.m.r. ($CDCl_3$) $\delta$ (ppm): 204, 186, 144, 126, 71, 18, 14. Mass spectrum (*m/e*): 191 (*M*+1), 147, 122, 115, 103, 87, 73, 69.

### *Copolymerization of MAX: general procedure*

The required amount of monomers, solvent and initiator (AIBN) were taken in glass ampoules stoppered with a rubber septum. The polymerization mixture was de-aerated with dry oxygen-free nitrogen for 15 min and heated at 60°C for known periods of time. The copolymers were precipitated by pouring the reaction mixture into an excess of petroleum ether. After two reprecipitations by pouring a chloroform solution into petroleum ether, the copolymers were dried in a vacuum oven at 30°C for 24 h. All the new copolymers were characterized through spectral data; the data for a representative MAX–MMA copolymer are given as follows. I.r. (neat film) $\nu_{max}$ (cm$^{-1}$): 1740 (C=O, ester), 1710 [(C=O)–S], 1256 (C=S), 1041 (C–O). $^1$H n.m.r. ($CDCl_3$) $\delta$ (ppm): 4.6 (q, $OCH_2$), 3.6 (s, $OCH_3$), 1.9–0.84 (broad multiplet of alkyl and methylene protons in the polymer backbone). $^{13}$C n.m.r. ($CDCl_3$) $\delta$ (ppm): 202.7, 199.1, 177.7, 124.7, 70.4, 54.2, 51.9, 45.1, 30.2, 17.8, 13.4.

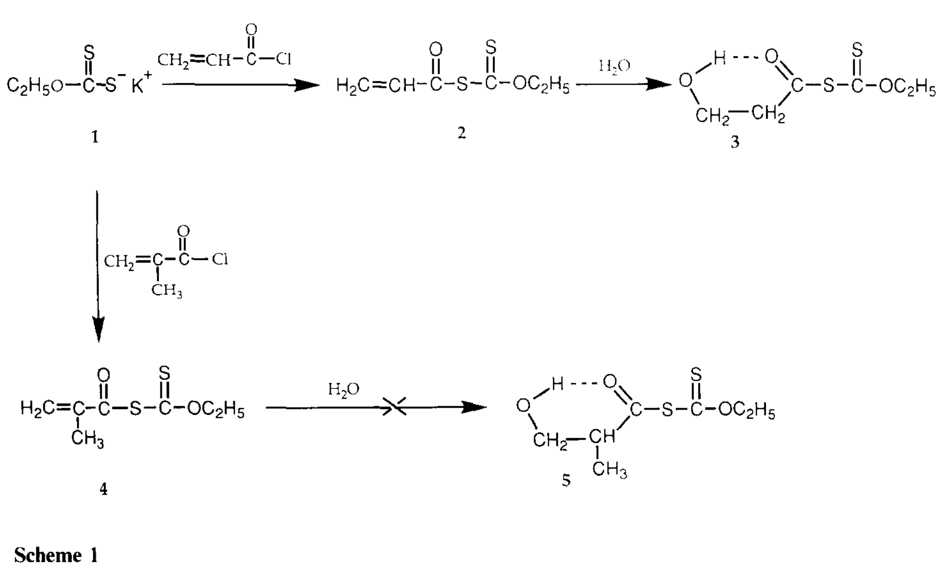
## RESULTS AND DISCUSSION

### *Preparation of monomers*

The sulfur-containing monomer, MAX (**4**), was prepared in high yield by the reaction of methacryloyl chloride with potassium *O*-ethyl xanthate (*Scheme 1*), whereas the attempted preparation of *S*-acryloyl *O*-ethyl xanthate (AX, **2**), under identical conditions, gave a low yield of **2**. The major product formed in this reaction was a solid, melting at 69–70°C and identified as *S*-(3-hydroxy propionyl) *O*-ethyl xanthate (**3**). The i.r. spectrum of **3** showed a characteristic absorption due to a strongly hydrogen-bonded OH group at 3400–2800 cm$^{-1}$. The $^1$H n.m.r. spectrum showed the presence of a highly deshielded proton at $\delta$ 11.3, which could be assigned to an intramolecularly hydrogen-bonded proton. The mass spectrum of **3** showed the molecular ion peak at 194, in agreement with the assigned structure. It is inferred that **3** is formed from **2** and can be understood in terms of the Michael addition of water to **2**, under the conditions of work-up (room temperature) (*Scheme 1*). However, under identical work-up conditions we could not obtain the water-added product from **4**, probably because MAX is a weak Michael acceptor.

### *Copolymerization of MAX with MMA and St*

Copolymers of MAX with MMA and St were prepared according to *Scheme 2*. All copolymerizations of MAX were carried out in benzene using AIBN as initiator, which resulted in the formation of pale yellow polymers. All copolymers were characterized by their spectral data. The $^1$H n.m.r. spectra of two representative copolymers, MAX–MMA and MAX–St, are shown in *Figure 1*. The results of copolymerization for the monomer systems MAX–MMA and MAX–St using 0.16 mol l$^{-1}$ of AIBN at 60°C in benzene are shown in *Tables 1* and *2*. When the copolymerizations were carried out using different mole fractions of MAX for a definite period, the rate of copolymerization ($R_p$) was found to decrease with increasing mole fraction of MAX in the comonomer (*Figure 2*). This observation indicates that MAX has a retardation tendency during copolymerization which could be due to the high chain transfer property of MAX.

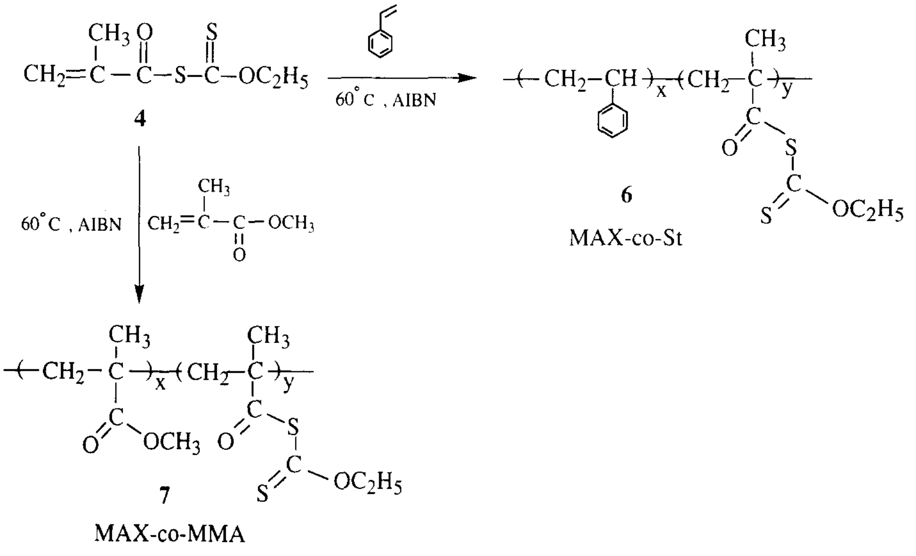


**Scheme 1**

However, the copolymerization rate was found to increase with increasing AIBN concentration. Detailed studies have shown that, to obtain maximum copolymer yield for each comonomer composition, there is an optimum value for the ratio of the mole fraction of MAX to that of AIBN.

### *Copolymer composition*

Copolymerizations were carried out under low conversions for determining the copolymer compositions. Each copolymer composition was calculated independently through n.m.r. and elemental sulfur analyses. The n.m.r. analyses were carried out by comparing the integrated intensity of the resonance signal at $\delta$ 4.6 (assigned to the O–$CH_2$ protons of the xanthate group) with that at $\delta$ 3.6 (assigned to the O–$CH_3$ protons of the methacrylate group, *Figure 1a*) or with that at $\delta$ 7.1 (assigned to the protons in the aromatic ring, *Figure 1b*) for the MAX–MMA and MAX–St systems, respectively. Information on copolymer compositions based on n.m.r.



**Scheme 2**

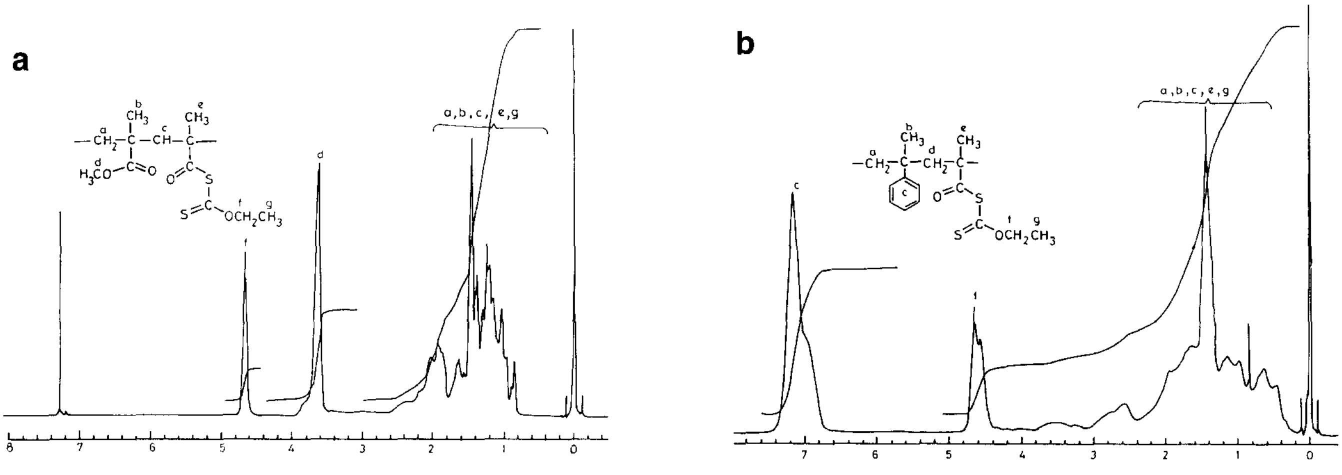


**Figure 1** $^1H$ n.m.r. spectra of (a) MAX–MMA and (b) MAX–St

**Table 1** Radical copolymerization of MAX ($M_1$) with MMA ($M_2$) at 60°C[a]

| $M_1$ in monomer (mol%) | Polymerization time (h) | Conversion (%) | Rate of polymerization ($R_p \times 10^6$) | $M_1$ in copolymer (mol%) | | $\bar{M}_n \times 10^{-3}$ |
|---|---|---|---|---|---|---|
| | | | | $^1H$ n.m.r. | S analysis | |
| 10 | 1.5 | 13 | 27.0 | 12 | 14 | 10.5 |
| 20 | 2.0 | 7 | 8.6 | 21 | 20 | 4.4 |
| 30 | 12.0 | 13 | 3.9 | 31 | 31 | 1.9 |
| 40 | 24.0 | 17 | 2.7 | 39 | 37 | 1.4 |
| 50 | 24.0 | 10 | 1.6 | 46 | 45 | – |
| 60 | 33.0 | 8 | 1.01 | 58 | 59 | – |

[a] [AIBN] = 0.16 mol $l^{-1}$; $M_1 + M_2 = 4.5$ mol $l^{-1}$ in benzene

**Table 2** Radical copolymerization of MAX ($M_1$) with St ($M_2$) at 60°C[a]

| $M_1$ in monomer (mol%) | Polymerization time (h) | Conversion (%) | Rate of polymerization ($R_p \times 10^5$) | $M_1$ in copolymer (mol%) |  | $\bar{M}_n \times 10^{-3}$ |
|---|---|---|---|---|---|---|
|  |  |  |  | $^1$H n.m.r. | S analysis |  |
| 10 | 1.5 | 19 | 4.2 | 21 | 21 | 6.7 |
| 20 | 1.5 | 16 | 3.6 | 28 | 30 | 5.6 |
| 30 | 4.0 | 20 | 2.8 | 33 | 33 | 5.1 |
| 40 | 5.0 | 18 | 1.8 | 43 | 44 | 4.6 |
| 50 | 5.0 | 13 | 1.1 | 48 | 48 | 4.0 |
| 60 | 8.0 | 15 | 0.84 | 57 | 56 | – |

[a] [AIBN] = 0.16 mol l$^{-1}$; $M_1 + M_2 = 4.5$ mol l$^{-1}$ in benzene

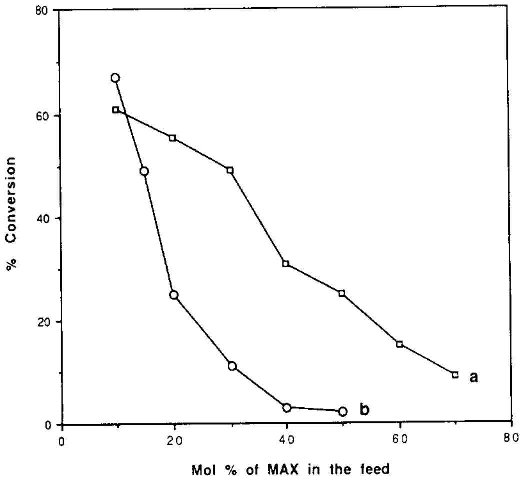


**Figure 2** Effect of MAX concentration on copolymerization of (a) MAX–St and (b) MAX–MMA

analysis was in good agreement with that obtained from the elemental sulfur analyses using the equation

$$W(\mathrm{S}) = \frac{64.14 m_1}{M_1 m_1 + M_2(1 - m_1)} \times 100 \quad (1)$$

where $W(\mathrm{S})$ and $m_1$ represent the weight percentage of sulfur and the mole fraction of MAX in the copolymer, and $M_1$ and $M_2$ are the molecular weights of the comonomers.

To study the copolymerization behaviour, the mole fraction of MAX in the copolymers obtained by $^1$H n.m.r. analysis was plotted against the mole fraction of MAX in the monomer feed (see *Figures 3* and *4* for the MAX–MMA and MAX–St monomer systems, respectively).

### *Reactivity ratio*

On the basis of the Mayo and Lewis terminal copolymerization model[12], the reactivity ratios for MAX ($r_1$) and its comonomer ($r_2$) can be determined by considering the following propagation reactions:

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1\cdot$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2\cdot$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_1\cdot$$

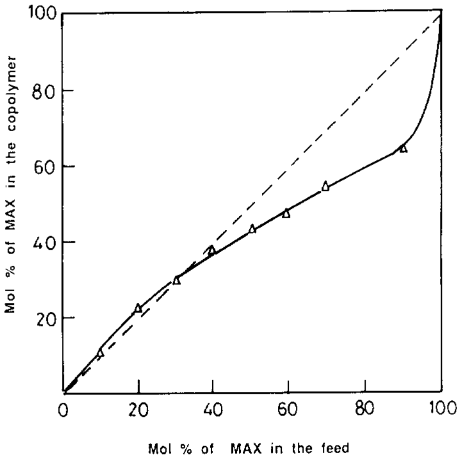


**Figure 3** Copolymer composition curve for MAX–MMA monomer system by $^1$H n.m.r. spectral analysis

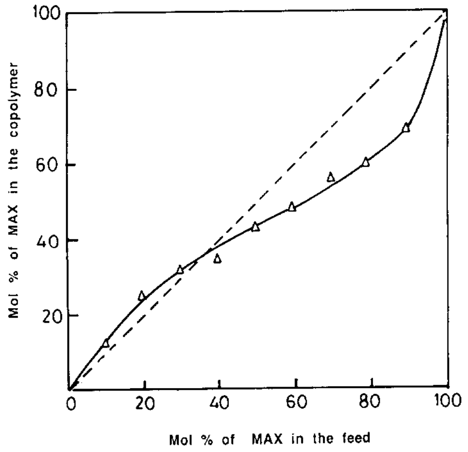


**Figure 4** Copolymer composition curve for MAX–St monomer system by $^1$H n.m.r. spectral analysis

The reactivity ratios of MAX ($r_1 = k_{11}/k_{12}$) and its comonomer ($r_2 = k_{22}/k_{21}$) were calculated from the copolymer compositions by using the graphical methods of Finemann–Ross (FR)[13] and Kelen–Tüdös (KT)[14] and by a non-linear least-squares (NLLS)[15] method. The Finemann and Ross equation relating the feed and copolymer compositions can be written as

$$\frac{F_1(f_1 - f_2)}{F_2 f_1} = \frac{f_2 F_1^2 r_1}{f_1 F_2^2} - r_2 \quad (2)$$

**Table 3** Reactivity ratios by terminal model

| | MAX–MMA | | | MAX–St | | |
|---|---|---|---|---|---|---|
| Method | $r_1$ | $r_2$ | $r_1r_2$ | $r_1$ | $r_2$ | $r_1r_2$ |
| FR | $0.65 \pm 0.05$ | $0.81 \pm 0.08$ | 0.53 | $0.37 \pm 0.03$ | $0.47 \pm 0.02$ | 0.17 |
| KT | $0.62 \pm 0.06$ | $0.80 \pm 0.04$ | 0.50 | $0.37 \pm 0.05$ | $0.46 \pm 0.06$ | 0.17 |
| NLLS | $0.60 \pm 0.08$ | $0.76 \pm 0.04$ | 0.46 | $0.36 \pm 0.08$ | $0.44 \pm 0.06$ | 0.17 |

where $f_1$, $F_1$ and $f_2$, $F_2$ are the mole fractions of monomers 1 and 2 in the polymer and the feed, respectively, and $r_1$ and $r_2$ are the respective reactivity ratios. A plot of the left-hand side of equation (2) *versus* $f_2F_1^2/f_1F_2^2$ gives $r_1$ and $r_2$ as the slope and the intercept, respectively. The KT method uses a modified form of the Mayo–Lewis equation

$$\eta = r_1\xi - r_2/\alpha \tag{3}$$

where $\eta$ and $\xi$ are functions of $f$ and $F$, and $\alpha$ is an arbitrary parameter. All calculations were based on the validity of the terminal model of copolymerization, which was evident from the linearity of the KT plots for both systems under study.

A comparison of the reactivity ratios obtained by these three different methods is given in *Table 3*. The data reveal that MAX–St has a greater tendency towards alternation as indicated by the $r_1r_2$ values. The alternation tendency of monomers during copolymerization suggests that there could be the possibility of some weak donor–acceptor interactions between the electron-rich styrene and electron-deficient MAX, although this has not been proved experimentally.

### Q *and* e *values of MAX*

Even though the $Q$–$e$ scheme is an empirical one, information on these values is useful for a new monomer. The $Q$ and $e$ values of MAX were determined by the Alfrey–Price $Q$–$e$ scheme[16] using the reactivity ratios obtained experimentally by the KT method. The equation relating the $Q$–$e$ parameters with the reactivity ratios is given as[17]

$$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)] \tag{4}$$

Known values of $e_2 = -0.8$ and $Q_2 = 1.0$ for styrene and $e_2 = 0.38$ and $Q_2 = 0.75$ for MMA were used for the MAX–St and MAX–MMA copolymer systems, respectively. From equation (4), the values of $Q$ and $e$ for MAX are found to be 0.91 and 0.29, respectively. The positive $e$ value indicates that MAX has an electron-deficient double bond. This is reasonable since the copolymerization of MAX with St, which has an electron-rich double bond, showed strong tendency for alternation compared with the copolymerization of MAX with MMA, which has an electron-deficient double bond.

### *Molecular weights of the copolymers*

The number-average molecular weights ($\bar{M}_n$) of the copolymers, MAX–MMA and MAX–St systems are shown in *Tables 1* and *2*, respectively. These data reveal that there is considerable decrease in the molecular weight with increase in MAX mole fraction. Further, it is also obvious that the effect of MAX concentration on the molecular weight of the copolymers is more significant in the case of the MAX–MMA system, as shown in *Figure 5* (curve a). This is probably due to the enhanced chain transfer property of MAX in the MAX–MMA monomer system. This was further confirmed by using small amounts of MAX as a chain transfer agent for the free-radical polymerizations of MMA and St using AIBN as the initiator. Determination of $\bar{M}_n$ in both cases clearly indicates the role of MAX in controlling the molecular weight of the polymers by a chain transfer process (*Table 4*).

**Table 4** Effect of a catalytic amount of MAX on $\bar{M}_n$ for the polymerization of MMA and St[a]

| MMA (g) | MAX (mg) | $\bar{M}_n$ | St (g) | MAX (mg) | $\bar{M}_n$ |
|---|---|---|---|---|---|
| 3 | 0 | 167156 | 3.12 | 0 | 34069 |
| 3 | 6 | 64518 | 3.12 | 6 | 32902 |

[a] AIBN, 50 mg; temperature, 60°C

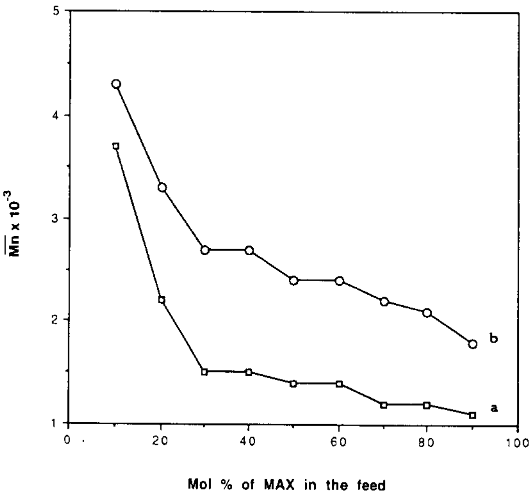


**Figure 5** Effect of MAX concentration on molecular weight of the copolymers: (a) MAX–MMA and (b) MAX–St

### *Thermal characteristics of MAX copolymers*

Since thermal analysis is a powerful tool to analyse the thermal stability of polymeric materials, the copolymers of MAX were subjected to thermogravimetric analysis to evaluate the effect of incorporation of MAX units into the copolymer chain. Typical thermograms of MAX–St copolymers having different copolymer compositions are shown in *Figure 6*, which clearly indicate that the overall stability of the copolymers decreases with increasing mole percentage of MAX in the copolymer. It is observed that the incorporation of MAX units decreases the initial decomposition temperature by 10–20°C. All

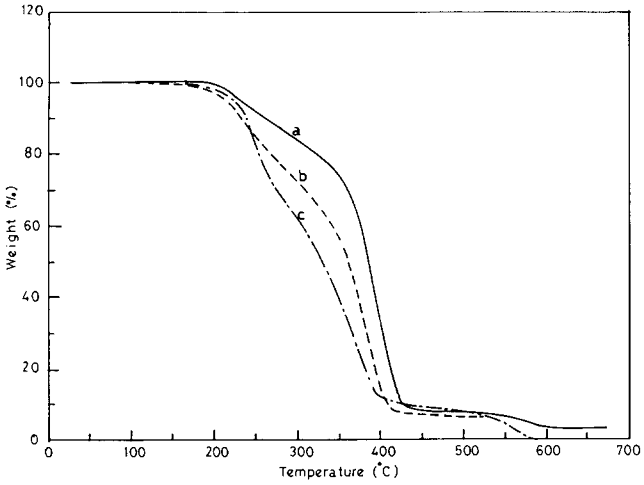


**Figure 6** T.g.a. curves of MAX–St copolymers with MAX contents of (mol%): (a) 10, (b) 30 and (c) 70

decompositions are mainly by a two-stage process. The initial weight loss between 200 and 250°C could be due to the elimination of $CS_2$, which is enhanced with increasing amount of MAX units in the copolymer. The second weight loss between 320 and 430°C is found to decrease with increasing MAX mole fraction in the copolymer. The overall decrease in thermal stability of MAX copolymers with increase in MAX mole fraction could be attributed to the reduction in their molecular weights with increase in MAX mole fraction.

## CONCLUSIONS

Reaction of potassium *O*-ethyl xanthate with methacryloyl chloride gave *S*-methacryloyl *O*-ethyl xanthate (MAX), whereas the reaction of acryloyl chloride with potassium *O*-ethyl xanthate resulted in the formation of *S*-(3-hydroxypropionyl) *O*-ethyl xanthate. Copolymerization of MAX with MMA and St was performed in benzene using AIBN as initiator. The copolymer compositions determined by $^1H$ n.m.r. and sulfur analysis were in good agreement and the monomer reactivity ratios were determined from the copolymer compositions. Determination of *Q* and *e* parameters revealed that MAX is an electron-deficient monomer and hence prefers electron-rich monomers such as St for copolymerization. Copolymer compositions and *Q*–*e* values indicate that MAX shows an alternation tendency during copolymerization. The low molecular weight of the copolymers indicates the involvement of chain transfer reactions of MAX during copolymerization. Molecular weights and thermal stability of the copolymers were found to decrease with increase in MAX mole fraction.

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