

Copolymerization of γ -Methacryloxy Propyl Trimethoxy Silane and Methyl Methacrylate

INDRA K. VARMA, ANIL K. TOMAR and R. C. ANAND, *Centre for Materials Science & Technology and Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016 India*

Synopsis

Copolymerization of methyl methacrylate (MMA) with low mole fractions of γ -methacryloxypropyl trimethoxy silane (MTS) was investigated with an aim to synthesize copolymers which can be cross-linked by hydrolytic cleavage of methoxy groups. Several copolymer samples were prepared by changing the molar ratios of two monomers in the initial monomer feed. Rate of copolymerization depended on the concentration of monomers and increased with an increase in MTS concentration. The copolymers were characterized by infrared (IR) and ^1H nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and intrinsic viscosity determination. The effect of structure on thermal behavior was investigated by using dynamic thermogravimetry in nitrogen atmosphere. An attempt was made to identify products of degradation using mass spectrometry. Copolymers were also hydrolyzed in water and cross-linked. The effect of MTS in copolymers on percentage gel formation was determined.

INTRODUCTION

Trimethoxy silane-modified polymers are good adhesion promoters for bonding thermoplastics with glass or hydrophilic minerals. Water-resistant adhesion may be obtained by modifying the interface through surface reaction of a silane-modified polymer. For example, trimethoxy silane-modified polystyrene is a good adhesion promoter for polystyrene and a vinyl trimethoxy silane-grafted polystyrene is a good primer for polyethylene. A minimum of 5–10 trimethoxysilyl groups are necessary in a copolymer (MW 10,000) for optimal performance.¹

Dow Corning Co.^{2–5} earlier reported melt grafting of hydrolyzable silanes onto polyolefins. Such graft copolymers after shaping can be cross-linked in the presence of moisture. Developments in the field of moisture cross-linkable silane-grafted polyolefins have been reviewed by Dan Munteanu.⁶

Information regarding copolymerization of unsaturated hydrolyzable silanes with vinyl monomers is available mostly in patent literature. The products thus obtained have been used in electric insulation, as laminated paper, adhesion (metal to plastic), and cross-linked mouldings. Only a few reports are available in the literature where details of these copolymerization and characterization of copolymers are described.

Silane modification of some acrylic copolymers has also been reported in the literature.⁷ Vinyl silanes (e.g., vinyl trimethoxy silane) copolymerize readily with vinyl esters, vinyl chloride, allyl esters, maleates, and vinyl pyrrolidone,

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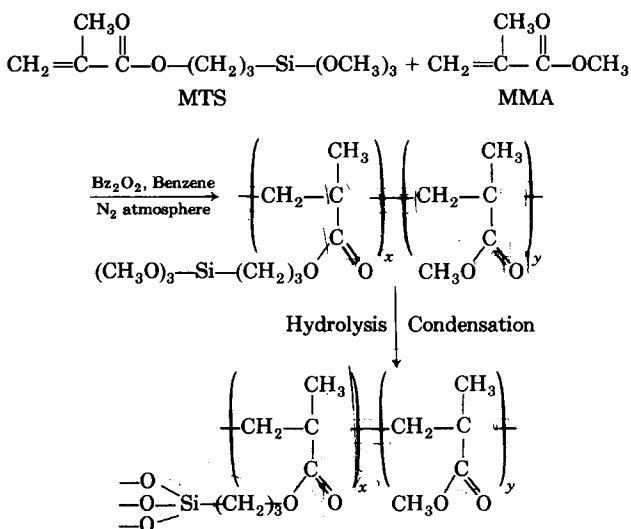


Fig. 1. Reaction scheme for cross-linking.

but poorly with methyl methacrylate and styrene. However, methacrylate-functional silane copolymerizes with styrene and acrylic monomers which may be cross-linked in the presence of atmospheric moisture to give flexible cured elastomers.⁸

It would be of interest to study the copolymerization of methyl methacrylate (MMA) with γ -methacryloxy propyl trimethoxy silane (MTS). The linear copolymers thus obtained can be used as adhesion promoters for thermoplastics. The hydrolysis of trimethoxy group of such silane-modified MMA would give triols which may condense to give disiloxanols, trisiloxanols, and higher oligomers, thus leading to the formation of cross-linked polymers as depicted in Figure 1.

EXPERIMENTAL

γ -Methacryloxypropyl trimethoxy silane (MTS) used in copolymerization was synthesized in the laboratory using trichlorosilane and allyl methacrylate. Trichlorosilane was obtained from National Physical Laboratory, Delhi and purified by fractional distillation. Allyl methacrylate was synthesized by refluxing methacrylic acid (Fluka) with thionyl chloride (Merck) for 2 h at 80°C and then adding allyl alcohol (IDPL) to the reaction mixture and refluxing it for 2 h at 55°C. It was cooled and poured into cold water. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic portion was washed with water, sodium bicarbonate (15%), and water. It was dried over anhydrous sodium sulfate and distilled under reduced pressure to give pure allyl methacrylate at 60–65°/45 mm.

Trichlorosilane was added to allyl methacrylate in the presence of mesityl oxide-platinum dichloride complex catalyst (in acetone) in N₂ atmosphere to give γ -methacryloxypropyl trichlorosilane, which on methanolysis gives MTS (b.p. 98°/5 mm). The purity of monomer was checked by ¹H NMR and IR spectroscopy. Methyl methacrylate (BDH) was purified by washing with 5%

NaOH to remove inhibitor, then washed with distilled water and finally dried over anhydrous CaCl_2 . It was distilled under reduced pressure before use. Benzoyl peroxide (BDH) was recrystallized from methanol. Benzene was dried over sodium and distilled and stored in a colored bottle having sodium wire.

Copolymerization of MMA and MTS in N_2 atmosphere was carried out in benzene solution (20% w/w) using 1% benzoyl peroxide as an initiator. Several copolymers were prepared by taking different molar ratios of γ -methacryloxypropyl trimethoxy silane (MTS) and methyl methacrylate (MMA) in the initial feed. The time of copolymerization was varied so as to carry out the conversion from 10 to 40%. The copolymer solution in benzene was poured in dry petroleum ether. The precipitated copolymers were filtered and dried at 60°C for 12 h. Effect of temperature on copolymer composition was studied by carrying the polymerization at 70° and 78°C .

The composition of copolymers was determined by carbon and hydrogen analysis using Perkin Elmer 240 C elemental analyzer. For silicon estimation, the polymer sample was charred at 200°C by adding few drops of 1:1 HNO_3 : H_2SO_4 solution. It was then heated in a furnace at 800°C for 2 h and silicon oxide thus obtained was weighed on cooling. The copolymer composition was then calculated.

Intrinsic viscosity of copolymers in chloroform was measured at $30 \pm 1^\circ\text{C}$ using a Ubbelohde viscometer. Copolymers were also characterized by recording IR spectra in KBr pellets using Nicolet DX FTIR spectrometer. The ^1H NMR spectra of copolymers were recorded in CDCl_3 using Jeol JNM FX-100 FT-NMR spectrophotometer using tetramethyl silane as an internal reference.

Thermal behavior of copolymers was investigated by using DuPont 1090 thermogravimetric analyzer having a 951 TG module, at heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere. A 10 ± 2 mg sample was used.

The hydrolysis of copolymers in the presence of water at 85°C was carried out for different time intervals. The extent of crosslinking was evaluated by treating the hydrolyzed copolymer with dimethyl formamide (DMF) at 100°C for 1 h. The insoluble portion after this treatment was separated, washed with acetone, and weighed, and represented the cross-linked material.

RESULTS AND DISCUSSION

Several copolymers were obtained by copolymerization of MMA with low mole fractions of MTS in the initial feed. These copolymers were characterized by IR and ^1H NMR spectroscopy. The characteristic peaks of MMA and MTS were observed in IR spectra of copolymers (Fig. 2) at 1740 cm^{-1} ($\nu\text{C} = \text{O}$), $1458 - 1450\text{ cm}^{-1}$ (CH_2 -bending), 1088 cm^{-1} (Si—O—C bending), 486 cm^{-1} (Si—O—C antisymmetric band). The peak at 1088 cm^{-1} increased in intensity as the MTS content was increased in the feed.

The characteristic proton resonance signals of copolymer are given in (Fig. 3). The peaks were at $\delta = 3.6$ (due to $-\text{COOCH}_3$ and OCH_3), $\delta = 1.89$ (due to $-\text{CH}_3$ protons), $\delta = 1.0$ (due to $-\text{CH}_3$ of MMA & MTS), and $\delta = 0.8$ (due to CH_2 proton of $-\text{CH}_2-\text{Si}\langle$).

The effect of mole fraction of MTS on percentage conversion was determined by taking different molar ratios of MMA and MTS in initial feed

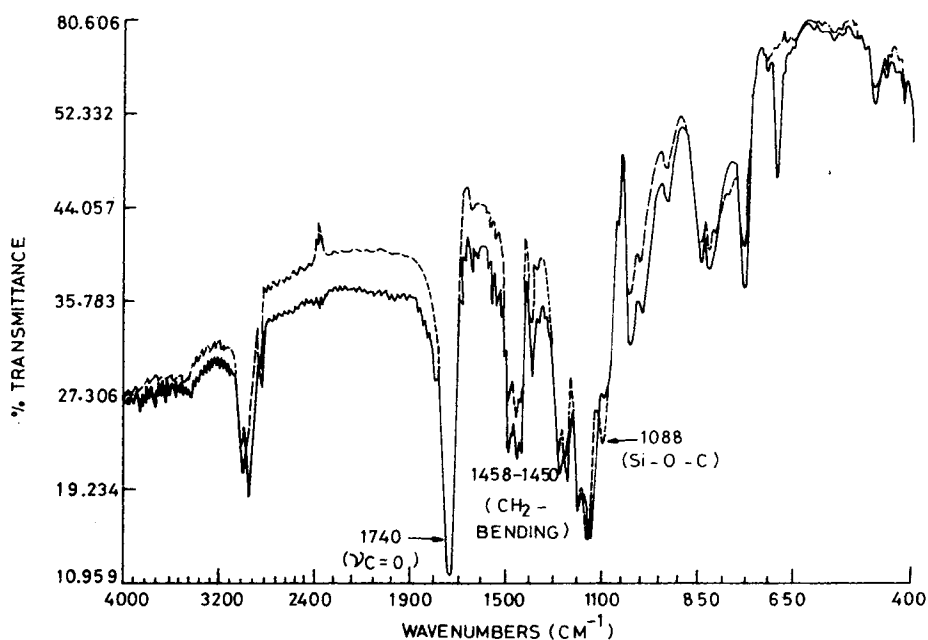


Fig. 2. IR spectra of copolymers of MMA and MTS containing 0.0301 mole fraction (—) and 0.123 mole fraction (---) of MTS in copolymer.

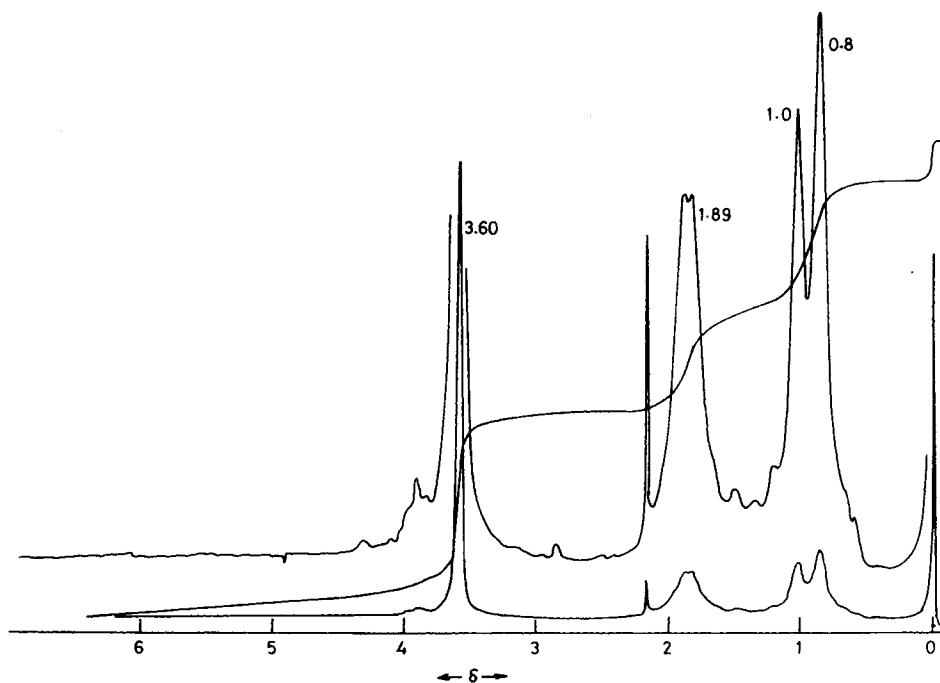


Fig. 3. $^1\text{H-NMR}$ spectrum of copolymer of MMA containing 0.097 mole fraction of MTS.

and keeping the time and temperature of polymerization constant (60 min at 78°C). Only a marginal increase in percentage conversion was observed by increasing the mole fraction of MTS from 0.0099 to 0.074. However, at higher mole fraction of MTS a slight increase in % conversion was observed (Table I).

The results of element analysis of these copolymers are given in Table II. Copolymers having low silicon content corresponding to 1 MTS unit per 63 MMA units or high silicon content corresponding to 1 MTS unit per 5 MMA units (Sample No. 8) could be obtained by changing the mole fraction of MTS from 0.0099 to 0.0909 in initial feed.

The rate of copolymerization as determined from % yield as a function of time, was found to depend on monomer feed ratio. An increase in MTS concentration leads to an increase in the rate of copolymerization (Fig. 4). The percentage yield of copolymers depended on the temperature of polymerization and an increase from 70° to 78°C resulted in 1.8–2.4 times increase (Table III).

Increase in mole fraction of MTS in monomer feed resulted in a corresponding increase in mole fraction of MTS in copolymer indicating thereby the formation of random copolymers (Table IV). This behavior was observed even when % conversion was as high as 40%. MTS concentration in copolymers was found to be slightly higher than that taken in the initial feed, indicating a slight preference of growing polymer radical for MTS. The intrinsic viscosity

TABLE I
Effect of Mole Fraction of MTS on % Conversion

Sample no.	Mole fraction of MTS in feed M_1	% Conversion (after 60 min)
1	0.0099	24.8
2	0.0196	27.6
3	0.0291	24.3
4	0.0348	23.0
5	0.0476	22.8
6	0.0678	29.0
7	0.0740	27.2
8	0.0909	35.8

TABLE II
Elemental Composition of Copolymers

Sample no.	% Composition			Empirical formula
	Carbon	Hydrogen	Silicon	
1	59.81	7.95	0.426	$C_{327.6}H_{523}O_{130.2}Si$
2	59.90	7.97	0.655	$C_{213.4}H_{346.5}O_{85.2}Si$
3	60.98	8.30	1.03	$C_{138.4}H_{226.1}O_{50.4}Si$
4	57.70	7.90	1.49	$C_{90.5}H_{149}O_{38.6}Si$
5	59.9	8.20	2.38	$C_{58.7}H_{96.4}O_{21.7}Si$
6	56.7	7.82	2.80	$C_{47.2}H_{78.2}O_{20.6}Si$
7	56.5	7.92	3.10	$C_{43.1}H_{71.5}O_{18.3}Si$
8	58.8	7.80	3.45	$C_{38.4}H_{63.4}O_{16.2}Si$

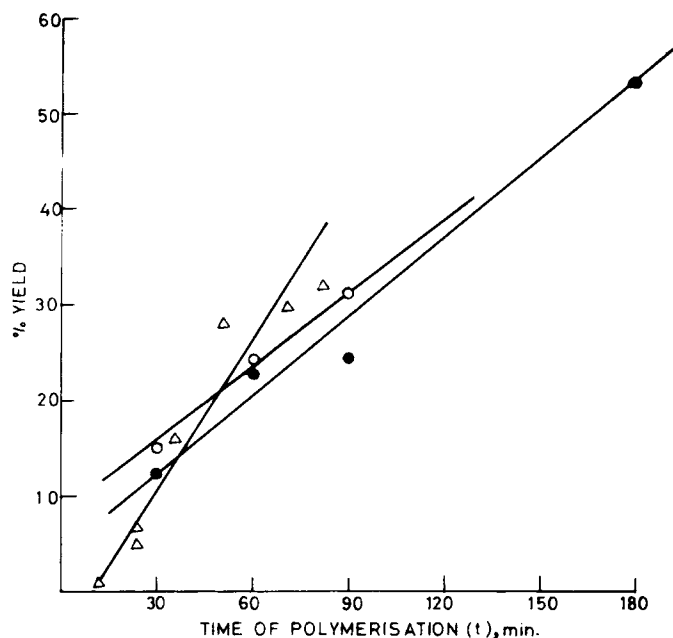


Fig. 4. Effect of time of copolymerization on percentage yield. (○) 1 : 0.03 mole ratio of MMA and MTS in feed. (●) 1 : 0.05 mole ratio of MMA and MTS in feed. (△) 1 : 0.1 mole ratio of MMA and MTS in feed.

TABLE III
Effect of Temperature on Percentage Conversion (Reaction time 90 min)

Sample no.	MTS in initial feed (mole fraction)	Yield (%)	
		70° C	78° C
1	0.0099	17.40	41.10
2	0.0196	20.16	40.35
3	0.0291	19.17	37.20
4	0.0348	21.00	37.80

of most of the copolymers was around 0.42 ± 0.05 dL/g. Copolymers containing more than 12% of MTS were partially insoluble in chloroform, hence their intrinsic viscosity could not be determined.

Thermal behavior of these copolymers was investigated in nitrogen atmosphere by using a DuPont thermal analyzer. A typical thermogravimetric (TG) trace is shown in Figure 5. Copolymers were stable up to 160°C and started losing weight above this temperature. The DTG curve showed three to four maxima, indicating thereby that decomposition takes place in distinct steps. Almost complete loss in weight occurred above 410°C in most of the copolymers. The residual weight above this temperature depended on the initial silicon content of copolymers. The maximum weight loss in copolymers was around $298 \pm 3^\circ\text{C}$ and $380 \pm 3^\circ\text{C}$ for MMA and MTS, respectively. No significant change in thermal behavior of polymethylmethacrylate was ob-

TABLE IV
Effect of Mole Fraction of MTS in Feed on Mole Fraction of MTS in Copolymer

Sample No.	MTS in feed M_1 (mole fraction)	% Conv.	MTS in Copolymer m_1 (mole fraction)	$[\eta]^{dl}/g$
A	0.0099	11.3	0.0181	0.55
A ₁	"	24.8	0.0117	0.345
A ₂	"	41.1	0.0131	0.42
B	0.0196	27.6	0.0308	0.43
B ₁	"	40.3	0.0198	0.435
C	0.0291	15.2	0.0430	0.43
C ₁	"	24.3	0.0225	0.465
C ₂	"	37.2	0.0292	—
D	0.0348	23.0	0.0424	0.274
E	0.0476	12.24	0.0301	0.57
E ₁	"	22.8	0.028	—
F	0.0678	29.0	0.1146	—
G	0.074	27.2	0.0888	0.508
H	0.0909	8.42	0.124	0.755
H ₁	"	6.0	0.131	—
H ₂	"	37.5	0.123	—

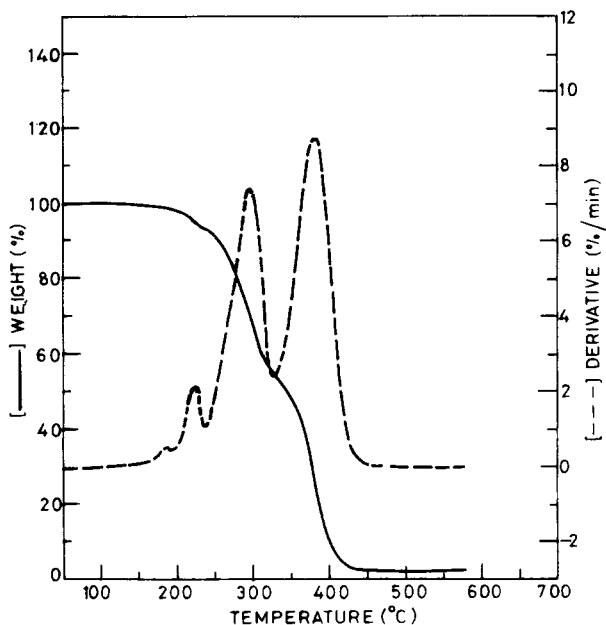


Fig. 5. TGA trace of copolymer of MMA containing 0.0117 mole fraction of MTS.

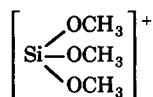
served by incorporation of low mole fraction of MTS in the backbone. From the TG trace, initial decomposition temperature (IDT), final decomposition temperature (FDT), and % char yield at 450°C were determined. From DTG trace, the onset of degradation at various stages (T_1), the temperature of maximum rate of weight loss (T_{max}) were noted and these results are summarized in Table V.

TABLE V
Results of Thermogravimetric Analysis of Copolymers

Characteristic properties	MTS in copolymer (mole fraction)					
	0.013	0.0117	0.0226	0.0301	0.0424	0.121
<i>First step</i>						
T_1 (°C)	132	128	115	100	122	100
T_{max} (°C)	180	174	157	180	182	152
Weight loss (%)	15	14	12	12	12	12
<i>Second step</i>						
T_1 (°C)	236	240	225	235	240	240
T_{max} (°C)	298	297	300	298	298	295
Weight loss (%)	28	27	29	24	29	38
<i>Third step</i>						
T_1 (°C)	328	326	325	325	328	325
T_{max} (°C)	382	383	380	382	383	380
Weight loss (%)	55	57	56	59	56	45
FDT (°C)	407	410	405	411	407	410
Char yield (%)	2	2	3	5	3	5

In order to understand the decomposition mechanism of these copolymers the volatile degradation products were subjected to electron impact-induced fragmentation in a GC-MS instrument. The polymer sample was introduced on the ion probe and temperature was increased to 160, 250, 300, and 350 °C. The copolymer samples containing MTS mole fraction 0.013 (A) and 0.120 (B) were selected for this study.

At 160 °C in sample A, base peak was at m/e 41 and the highest fragment ion was observed at m/e 121. Other prominent fragment ions were at m/e 100, 69, 39, 28, and 18. The presence of m/e 100 is understandable in terms of depolymerization of polymethylmethacrylate leading to MMA formation. The fragment ion at 121 may be due to



Increasing temperature of ion probe to 250, 300, and 350 °C did not affect the fragmentation pattern significantly and base peak was at m/e 41, 28, and 41, respectively. Very low intensity fragment ions were observed at m/e 281, 216, and 175 in the mass spectrum at a temperature of 350 °C of ion probe.

Similar fragmentation pattern was observed in Sample B at temperatures of 160, 250, 300, and 350 °C with base peaks at m/e 41, 69, 41, and 100, respectively. Additional fragment ions at m/e 281 and 216 were observed at all these temperatures. The major difference was in the intensity of the various fragment ions.

At higher temperatures the intensity of m/e 281 and 216 ions increased (Fig. 6). The decomposition of copolymers perhaps proceeds mainly by depolymerization reaction leading to the formation of MMA and MTS which undergo electron impact-induced fragmentation leading to the formation of

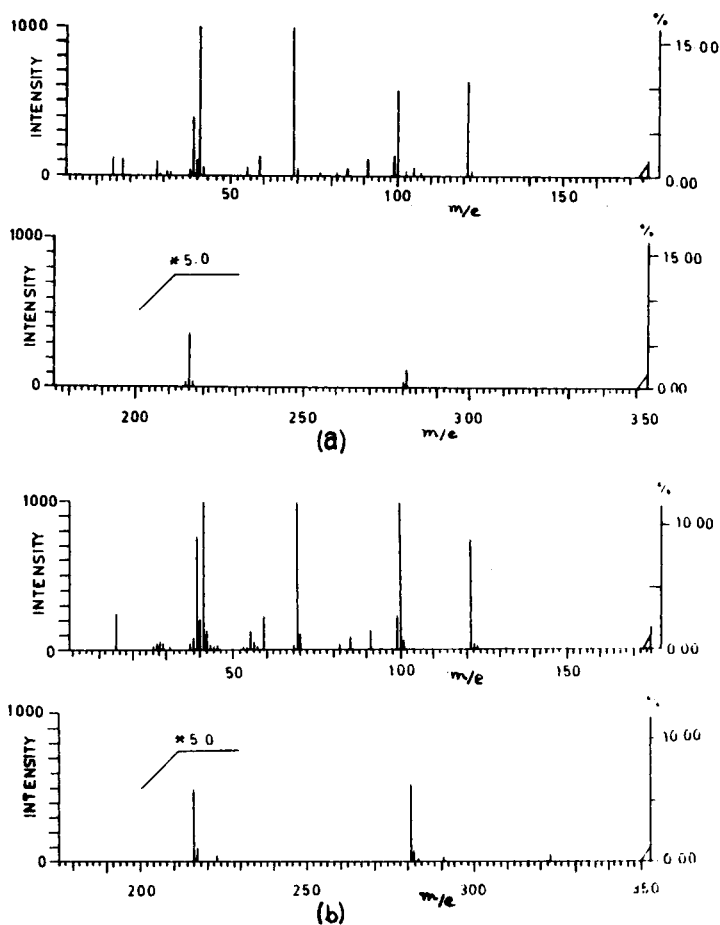
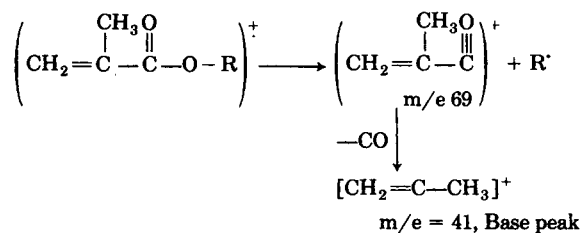


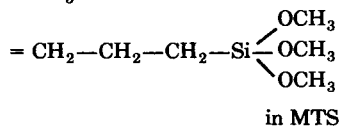
Fig. 6. Mass spectrum of copolymer of MMA containing 0.121 mole fraction of MTS at temperature of ion probe (a) 160°C; (b) 350°C.

various fragment ions observed in mass spectrum, as shown in the following scheme.



where

R = CH₃ in MMA



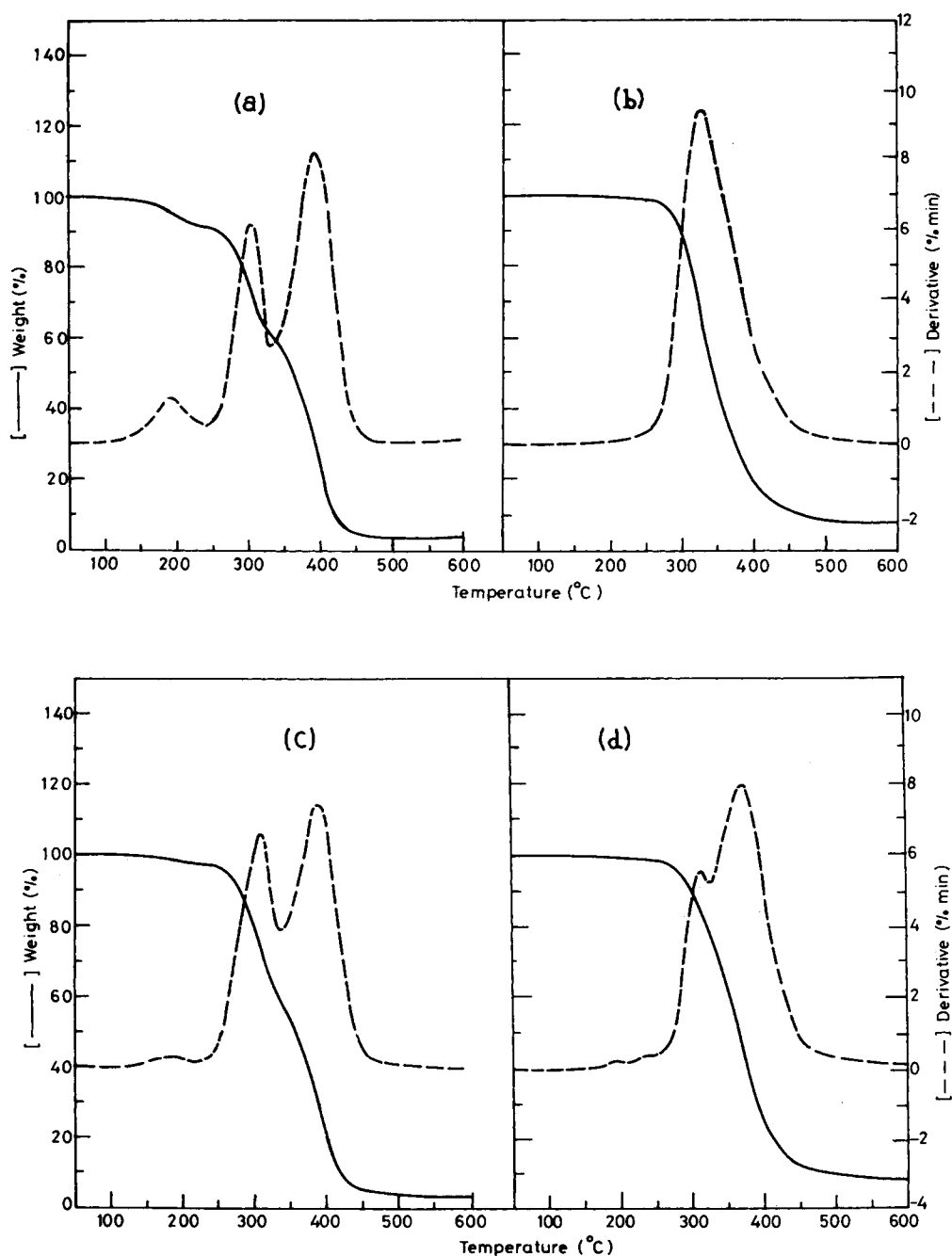


Fig. 7. TG traces of cross-linked copolymer of MMA containing (a) 0.013, (b) 0.1508 (time of hydrolysis 1 h), (c) and (d) 0.0539 (time of hydrolysis 1 h and 24 h, respectively) mole fraction of MTS in backbone.

The DMF-insoluble cross-linked gel was weighed and extent of crosslinking was determined. The extent of crosslinking was found to depend on the concentration of MTS in the copolymer and the duration of hydrolysis reaction (Table VI). At higher MTS concentration, time of hydrolysis had insignificant effect on cross-linking reaction. More than 96% gel formation was observed after 30 min of hydrolysis. However, at low MTS concentration in copolymer, increase in time of hydrolysis from 30 min to 24 h increased the gel formation. These results thus indicate that polymethylmethacrylate can be cross-linked to give a polymer network completely/partially insoluble in DMF by incorporating 3.22–30.6% MTS in the backbone.

The thermal stability of these cross-linked copolymers was also investigated by thermogravimetric analysis (TGA). Hydrolysis of copolymers containing low mole fraction of MTS only marginally affected the thermal behavior and multiple peaks in DTG trace were observed [Fig. 7(a)] at positions similar to the uncross-linked polymer. However, a single peak in DTG trace was observed in the samples containing high % of MTS in the backbone (30.6%). The polymer was stable up to 250 °C and started losing weight above this temperature [Fig. 7(b)]. These results thus indicate an improvement in thermal stability of cross-linked methylmethacrylate copolymers containing higher MTS in the backbone.

Effect of time of hydrolysis of the copolymers on the stability of the cross-linked product was evaluated by hydrolyzing the copolymers containing 0.054 mole fraction of MTS for 1 h and 24 h [Fig. 7(c, d)]. A slight improvement in thermal stability of the copolymers hydrolyzed for 24 h was observed. A multiple step decomposition in the DTG trace was observed when hydrolysis was carried out for shorter durations.

CONCLUSION

These results thus indicate that the copolymers of MMA with MTS can be easily crosslinked by heating in water at 85 °C. The extent of crosslinking is increased by increasing the duration of hydrolysis reaction. The cross-linked polymers are thermally more stable than the uncross-linked copolymers.

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