

COPOLYMERIZATION OF STYRENE, ACRYLONITRILE AND METHYL METHACRYLATE WITH γ -METHACRYLOXYPROPYL TRIMETHOXY SILANE

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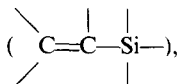
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(Received 11 May 1988; in revised form 27 July 1988)

Abstract— γ -Methacryloxypropyl trimethoxy silane (MPTMS) was copolymerized with methyl methacrylate (MMA) and with styrene (STY) in toluene and with acrylonitrile (AN) in bulk at $65 \pm 0.1^\circ\text{C}$ using benzoyl peroxide as initiator. The compositions of the copolymers were determined from silicon contents estimated gravimetrically; the reactivity ratios were determined by the Kelen–Tüdös graphical method. For copolymerization of STY(M_1) with MPTMS(M_2), the reactivity ratios are $r_1 = 0.45 \pm 0.04$ and $r_2 = 0.9 \pm 0.01$; for AN(M_1) with MPTMS(M_2) they are $r_1 = 0.11 \pm 0.03$ and $r_2 = 3.7 \pm 0.02$; for MMA(M_1) with MPTMS(M_2) they are $r_1 = 0.74 \pm 0.06$ and $r_2 = 1.33 \pm 0.02$. In all cases, r_2 is greater than r_1 indicating that copolymers have blocks of MPTMS units interrupted by one or more organic comonomer units such as AN, STY or MMA. A comparison of relative reactivities of MPTMS, [(2-methacryloyloxy)propoxy] trimethyl silane, [(2-methacryloyloxy)propoxy] dimethylphenyl silane, [(2-methacryloyloxy)propoxy] diphenylmethyl silane and [(2-methacryloyloxy)ethoxy] trimethyl silane has been made. The influence of silicon comonomer on the properties of copolymers, such as solubility and thermal behaviour, was also studied.

INTRODUCTION

In free radical copolymerization of vinyl silane monomers with monomers such as acrylonitrile (AN), styrene (STY), methyl methacrylate (MMA), the position of the Si atom with respect to the vinyl group greatly influences the reactivity of the vinyl silane monomer. If the Si atom is close to the vinyl group



the reactivity ratio for the silane monomer was found to be zero or close to zero [1–9] because of $d\pi$ – $p\pi$ interactions between the Si atom and the vinyl group. The poor polymerizability of vinyl silanes with free radical initiators is demonstrated from the polymerization of *p*-styryl silane containing vinyl groups in which polymerization proceeds through styryl groups but not through vinyl groups attached to silicon [10]. The poor reactivity of vinyl silane monomers with organic monomers such as AN, STY, MMA and haloacrylates was confirmed by our earlier studies [11–13].

If the Si atom is away from the vinyl group, the reactivity of the silane monomer is enhanced due to the absence of $d\pi$ – $p\pi$ interactions and the copolymer is enriched in silane units. Bajaj *et al.* have reported copolymerization of AN with [(2-methacryloyloxy)alkoxy] trimethyl silanes [17] and STY with [(2-methacryloyloxy)propoxy] trialkyl(aryl) silanes [14] and with [(2-methacryloyloxy)ethoxy] trimethyl silane [15].

It appears that copolymerization of organic monomers with functional silane monomers (having the Si atom away from the vinyl group) containing functional groups like acetoxy, ethoxy or methoxy attached to silicon has not been studied in detail. These copolymers have potential in the area of moisture curable flexible elastomers [23] and in room temperature vulcanization of silicone rubbers [16, 24]. To optimize the physical properties, it was desirable to control the content of functional silane in the copolymers. With this objective, the copolymerizations of AN, MMA and STY with γ -methacryloxypropyl trimethoxy silane MPTMS were studied to determine the monomer reactivity ratios.

EXPERIMENTAL

Materials

STY, MMA, AN and benzoyl peroxide were purified as reported earlier [11, 13]. MPTMS (Fluka AG) was distilled under vacuum before use. Toluene was dried over Na wire and distilled over 4Å molecular sieves.

Polymerization

Predetermined amounts of organic monomer (STY, MMA or AN), silane monomer (MPTMS), with or without solvent (toluene) and benzoyl peroxide were charged in pyrex glass ampoules which were degassed under high vacuum by freeze–thaw cycles. The sealed ampoules were placed in a thermostat maintained at $65 \pm 0.1^\circ\text{C}$. After a given time, the contents of the tubes were poured into a large amount of dry methanol. Copolymerizations were restricted to low conversions in order to use the differential form of the copolymerization equation. The copolymers STY/MPTMS and MMA/MPTMS were purified by repeated precipitations in methanol from toluene solution. The purified copolymers were dried at 50°C under vacuum

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to constant weight. The compositions of copolymers were determined from silicon contents, estimated gravimetrically [18].

Characterization

The i.r. spectra of the polymers were recorded in nujol mull between 400 and 4000 cm^{-1} on a Unicam SP-1200 spectrophotometer. The glass transition temperatures (T_g) were determined on a Stanton Redcraft differential thermal analyser with calcined alumina as reference and at a heating rate of 6°C/min in static air. Thermogravimetric analysis (TGA) was carried out using Dupont 900 thermo-balance in N_2 atmosphere from ambient temperature to 500°C for STY/MPTMS and MMA/MPTMS systems and for AN/MPTMS system from ambient temperature to 900°C, at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The compositions of initial monomer mixtures, copolymers and conversions are summarized in Tables 1–3. The reactivity ratios were determined by the Kelen–Tüdös graphical method [19]. A typical Kelen–Tüdös plot for STY/MPTMS copolymer is shown in Fig. 1. The dependence of the composition of the copolymers on the composition of the feed is shown in Fig. 2(a–c). The values of r_1 and r_2 are presented in Table 4.

Figure 2(a, b) for MMA/MPTMS and AN/MPTMS copolymers show that the copolymers contain larger amount of silane units (M_2) than the feed indicating that the reactivity of MPTMS towards the poly MPTMS radical exceeds that of AN

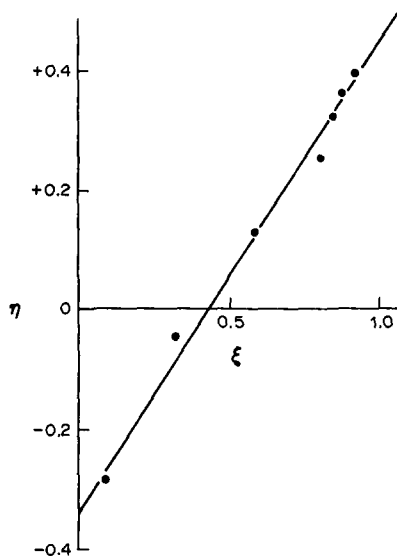


Fig. 1. Typical Kelen–Tüdös plot for STY/MPTMS system.

or MMA towards the radical ($k_{22} > k_{21}$). The greater polymerizability of MPTMS seems to be consistent with similar systems reported by other workers [14, 15, 17].

Since $r_1 < 1$ and $r_2 > 1$ in MMA/MPTMS and AN/MPTMS, the copolymer consists of blocks of MPTMS units interrupted with one or more MMA or AN units. The relative reactivities of the silane monomer towards the macro radicals was as follows:



On the basis of reactivity ratios, the relative reactivities of γ -methacryloxypropyl trimethoxy silane (MPTMS), [(2-methacryloyloxy)propoxy]-trimethyl silane (2-MAPTMS), [(2-methacryloyloxy)propoxy]-dimethylphenyl silane (2-MAPDMPs), and [(2-methacryloyloxy)propoxy]-diphenylmethyl silane (2-

Table 1. Copolymerization of STY(M_1) and MPTMS(M_2)^a

Mole fraction of M_1 in feed	Conversion (%)	Silicon content (%)	Mole fraction of M_1 in copolymer
0.93	10.1	3.07	0.872
0.90	11.6	3.96	0.826
0.88	9.8	4.57	0.792
0.85	8.7	5.52	0.733
0.70	9.5	7.25	0.602
0.50	7.5	8.77	0.456
0.20	9.6	10.81	0.187

^aPolymerization conditions: initiator, benzoyl peroxide (0.4% by weight); temperature, $65 \pm 0.1^\circ\text{C}$; solvent, toluene; monomer concentration, 4 mol/l.

Table 2. Copolymerization of MMA(M_1) and MPTMS(M_2)^a

Mole fraction of M_1 in feed	Conversion (%)	Silicon content (%)	Mole fraction of M_1 in copolymer
0.95	8.9	1.76	0.934
0.90	7.8	3.15	0.872
0.85	5.5	4.28	0.814
0.83	6.2	5.03	0.771
0.50	8.7	9.62	0.365

^aPolymerization conditions: as for Table 1.

Table 3. Copolymerization of AN(M_1) and MPTMS(M_2) in bulk^a

Mole fraction of M_1 in feed	Conversion (%)	Silicon content (%)	Mole fraction of M_1 in copolymer
0.95	6.3	7.76	0.711
0.90	5.8	8.81	0.617
0.85	4.2	9.83	0.490
0.80	3.1	10.31	0.412
0.50	5.3	11.29	0.188

^aOther polymerization conditions: as for Table 1.

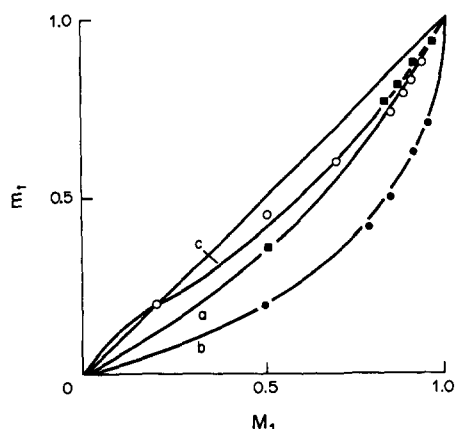
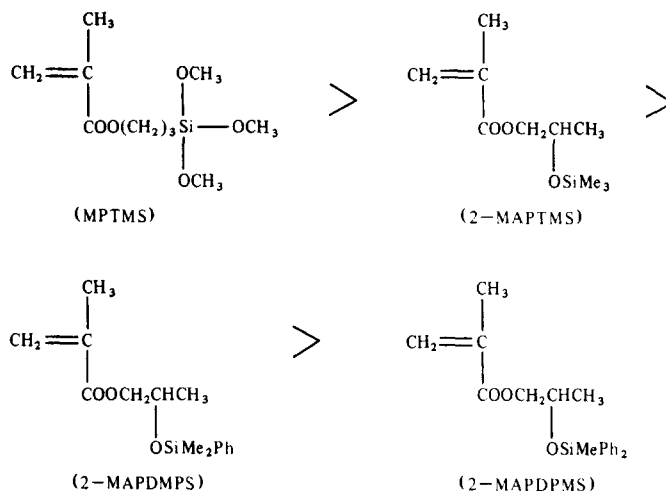


Fig. 2. (a) (■) Monomer feed-composition curve for MMA/MPTMS copolymer. (b) (●) Monomer feed-composition curve for AN/MPTMS copolymer. (c) (○) Monomer feed-composition curve for STY/MPTMS copolymer.

Table 4. Monomer reactivity ratios (MRR) for copolymerization of STY, MMA or AN with MPTMS

System	r_1	r_2
STY(M_1)-MPTMS(M_2)	0.45 ± 0.04	0.9 ± 0.01
MMA(M_1)-MPTMS(M_2)	0.74 ± 0.06	1.33 ± 0.02
AN(M_1)-MPTMS(M_2)	0.11 ± 0.03	3.7 ± 0.02

MAPDPMS) towards polystyryl radicals is as follows:



Monomer (M_2)	r_1
2-MAPDPMS [14]	1.05 ± 0.02
2-MAPDPMS [14]	0.96 ± 0.05
2-MAPTMS [14]	0.95 ± 0.03
MPTMS	0.45 ± 0.04

Similarly, the relative reactivities of (MPTMS), (2-MAPTMS) and [(2-methacryloyloxy)ethoxy] trimethyl silane (2-MAETMS) towards poly AN radicals are as follows:



Monomer (M_2)	r_1
2-MAPTMS [17]	0.48 ± 0.03
2-MAETMS [17]	0.22 ± 0.08
MPTMS	0.11 ± 0.03

In both cases, MPTMS monomer seems to be more reactive than the other silane monomers towards poly AN or poly STY radicals because of its high polarity.

Characterization and properties

i.r. Spectra. The presence of an absorption band at $1080\text{--}1115\text{ cm}^{-1}$ due to $\nu_{\text{as}}(\text{Si}-\text{O}-\text{C})$ confirms the incorporation of MPTMS in the copolymer.

Solubility. The silane homo and copolymers were sparingly soluble in dimethyl sulphoxide, dimethylformamide and *N*-methyl pyrrolidone. Polymers exposed to air for a week became insoluble in all solvents. The insolubility of the copolymers suggests an increase in inter-chain interactions or partial cross-linking.

Glass transition temperature. The copolymers of all systems showed decrease in T_g with increase of MPTMS (Table 5). This may be due to the presence of long silyl pendant group in MPTMS which shields the intermolecular interactions arising from either carbonyl groups or from nitrile dipole-dipole interactions. The lowering of T_g is also due to the free rotation of methoxy groups bonded to silyl groups,

consistent with our earlier reports [11, 13, 20]. Similar results were obtained by other workers for AN/[[(2-methacryloyloxy)alkoxy] trimethyl silane [17] and for STY/[[(2-methacryloyloxy)propoxy] trialkyl (aryl) silane [14] copolymers.

Thermogravimetric analysis

Thermal degradations of poly STY, poly(STY/MPTMS), poly MMA, poly(MMA/MPTMS), poly AN, poly(AN/MPTMS) and poly(MPTMS) were studied by TGA in N_2 (see Table 6 and Figs 3-5).

Thermograms for poly STY, poly MMA and their copolymers with MPTMS exhibit single stage weight loss. Initial decomposition temperature (IDT) of copolymers are above those for the corresponding homopolymers. The relative thermal stabilities of polymers can be assessed by their integral procedural decomposition temperature (IPDT) proposed by Doyle [21]. IPDT values indicate that the copolymers

Table 5. Glass transition temperature of STY/MPTMS, MMA/MPTMS and AN/MPTMS copolymers

No.	Polymer	M_2 (mol%)	T_g ($^\circ\text{C}$)
1	Poly(STY)	—	97
2	Poly(STY/MPTMS)	8.0	80
3	Poly(STY/MPTMS)	18.0	75
4	Poly(STY/MPTMS)	54.0	56
5	Poly(MMA)	—	105
6	Poly(MMA/MPTMS)	13.0	75
7	Poly(MMA/MPTMS)	23.0	66
8	Poly(AN)	—	93
9	Poly(AN/MPTMS)	15.0	84
10	Poly(AN/MPTMS)	63.0	56
11	Poly(MPTMS)	100.0	48

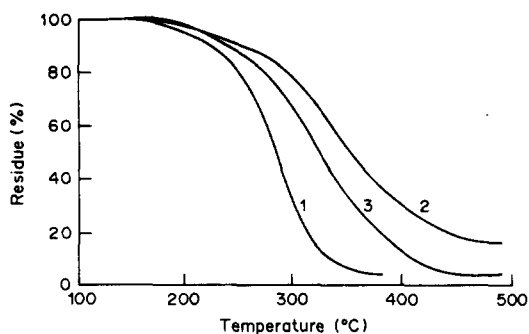


Fig. 4. Thermogravimetric analyses of (1) poly MMA, (2) poly(87MMA/13MPTMS) and (3) poly(77MMA/23MPTMS).

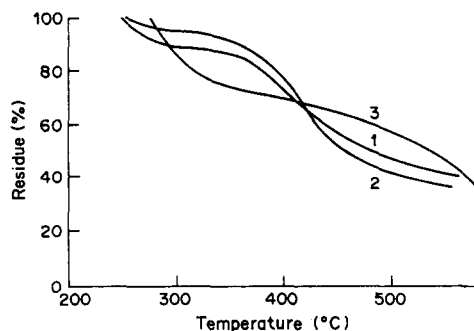
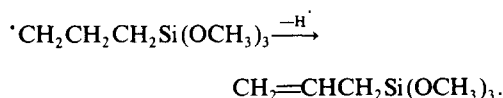


Fig. 5. Thermogravimetric analyses of (1) poly(MPTMS), (2) poly(59AN/41MPTMS) and (3) poly AN.

The isoimide polymer radical may then proceed with the cyclization while the displaced trimethoxysilylpropyl radical may decompose to give allyltrimethoxysilane.



Product analysis studies are in progress.

Acknowledgements—The authors are grateful to CSIR for awarding a Senior Research Fellowship to V.L.R. The

authors thank Dr S. Pakirisamy and Mr S. Venkatachalam for help in preparing the manuscript.

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