

THERMAL BEHAVIOUR OF TRIMETHOXY SILANE MODIFIED ALKYL METHACRYLATES

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The paper deals with the thermal behaviour of trimethoxy silane (MTS) modified ethyl methacrylate (EMA) and butyl methacrylate (BMA). Several copolymer samples were prepared by varying the molar ratio of MTS with respect to EMA or BMA. The copolymerisation was carried out at 78 °C for 120 min using benzoyl peroxide as an initiator. Incorporation of MTS in alkyl methacrylates resulted in an increase in thermal stability. Hydrolytic cross-linking of copolymer having higher mole fraction of MTS gave a cross-linked product with better thermal stability.

Trimethoxy silane modified polymers can be obtained by copolymerisation of unsaturated silanes and vinyl monomers or graft copolymerisation reactions. The copolymers thus obtained can be hydrolyzed to give triols which may be further condensed to give disiloxanols, tri-siloxanols and higher oligomers, thereby leading to the formation of cross-linked copolymers. These modified copolymers can be used as adhesion promotor for thermoplastics.

Methacrylate functional silanes copolymerise with styrene and acrylic monomers [1]. The copolymers can be crosslinked in presence of moisture to give flexible cured elastomers. In our earlier paper we have reported copolymerisation of γ -methacryloxypropyl trimethoxy silane (MTS) and methyl methacrylate (MMA) [2]. Several copolymer samples were prepared by changing the molar ratios of two monomers in the initial monomer feed and the effect of structure on the thermal behaviour was investigated by using TG technique. It would be of interest to investigate the effect of alkyl group in alkyl methacrylate on the thermal behaviour and hydrolytic stability of copolymers. Therefore, the present studies, which deal with the copolymerisation of MTS with ethyl methacrylate (EMA) and butyl methacrylate (BMA) were undertaken. The structure of such copolymers and their hydrolytic condensation products is depicted in Fig. 1.

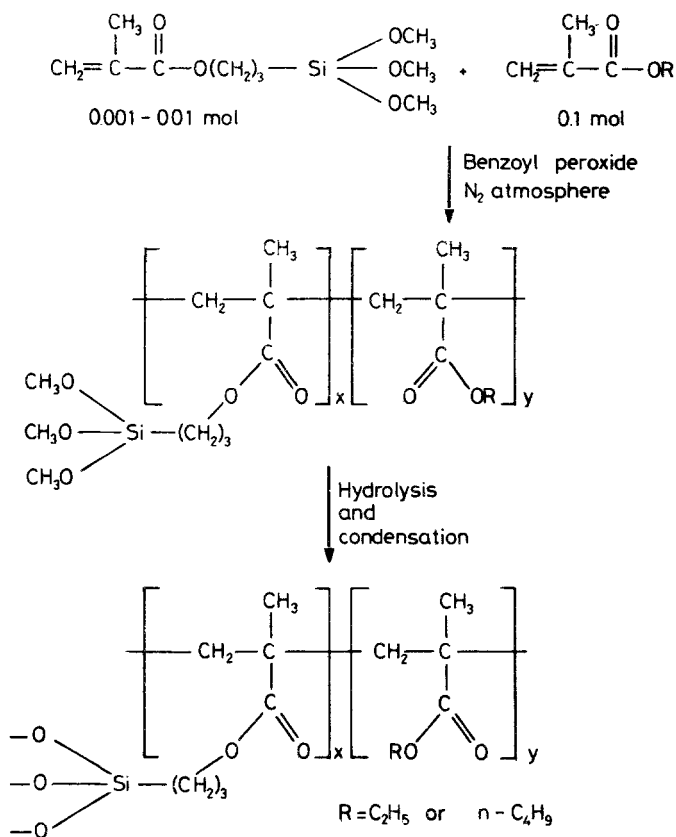


Fig. 1 Reaction scheme showing co-polymerization of γ -methacryloxypropyl trimethoxy silane with alkylmethacrylates

Experimental

The details of synthesis of MTS have been described elsewhere [2]. Copolymerization of EMA (E. Merck) and BMA (Riedel) with MTS was carried out in nitrogen atmosphere at 78° for 120 min using benzoyl peroxide as an initiator (1%) and benzene as a solvent (20% w/w). The copolymers of EMA : MTS and BMA : MTS have been designated as ES and BS, respectively. The mole fraction of MTS with respect of EMA/BMA was varied as follows: 0.0099 (1), 0.0196 (2), 0.0291 (3), 0.0476 (5), 0.0654 (6) and 0.099 (7) and this has been indicated by writing the number shown in the parentheses above as a subscript to the copolymer designation. Thus the copolymer obtained by copolymerisation of EMA with a mole fraction of 0.0099 of MTS at 78° for 120 min has been designated as ES₁.

The composition of the copolymers was determined by carbon and hydrogen analysis using a Perkin-Elmer 240 elemental analyser and silicon estimation. Copolymers were also characterized by recording IR spectra in KBr pellets using a Nicolet DX FTIR spectrophotometer. The ^1H and ^{13}C NMR spectra of copolymers were recorded in chloroform and trifluoroacetic acid as solvent, respectively on a Jeol JNM FX-100 FT-NMR spectrophotometer using tetramethyl silane as an internal reference.

The thermal behaviour of copolymers was investigated by using DuPont 1090 thermogravimetric analyzer having a 951 TG module, at a heating rate of 10 deg/min in nitrogen atmosphere. The thermal behaviour of water cross-linked copolymers of EMA:MTS and BMA:MTS was also studied in nitrogen atmosphere.

Results and discussion

The results of elemental analysis of various copolymer samples are given in Table 1. Copolymers having low silicon content corresponding to 1 MTS unit per 138 EMA units and 60 BMA units or high silicon content corresponding to 1 MTS unit per 10 EMA or 10 BMA units could be obtained by changing the MTS concentration in the initial monomer feed.

The intrinsic viscosity of the copolymers was also determined and the results are given in Table 2. The structure of copolymers was studied by IR spectroscopy. The characteristic peaks due to carbonyl groups of alkyl methacrylates and Si-O-C

Table 1 Elemental composition of copolymers of MTS with alkyl methacrylates

Sample designation	Composition, %			Empirical formula
	carbon	hydrogen	silicon	
ES ₁	61.86	8.46	0.173	C ₈₃₆ H ₁₃₇₃ O ₃₀₀ Si
ES ₂	62.72	8.69	0.124	C ₁₁₇₈ H ₁₉₆₃ O ₄₀₂ Si
ES ₃	63.13	8.83	0.428	C ₃₄₄ H ₅₇₈ O ₁₁₃ Si
ES ₅	58.48	8.08	1.13	C ₁₂₁ H ₂₀₀ O ₅₀ Si
ES ₆	60.60	8.35	1.48	C ₉₆ H ₁₅₈ O ₃₅ Si
ES ₇	52.90	8.19	1.98	C ₆₉ H ₁₁₆ O ₂₇ Si
BS ₁	64.03	9.42	0.307	C ₄₈₇ H ₈₅₉ O ₁₅₀ Si
BS ₂	63.53	9.52	0.550	C ₂₆₉ H ₄₈₅ O ₈₄ Si
BS ₃	65.54	9.67	1.09	C ₁₄₀ H ₂₄₈ O ₃₈ Si
BS ₅	64.13	9.38	1.04	C ₁₄₄ H ₂₅₃ O ₄₁ Si
BS ₆	64.36	9.43	1.29	C ₁₁₆ H ₂₀₅ O ₃₄ Si
BS ₇	63.03	9.30	1.73	C ₈₅ H ₁₅₀ O ₂₆ Si

Table 2 Intrinsic viscosity of various copolymers

Sample designation	Mole fraction of MTS in copolymers	Intrinsic viscosity, dL/g
ES ₁	0.0070	0.8081
ES ₂	0.0046	1.5023
ES ₃	0.0178	0.7511
ES ₅	0.0488	1.6619
ES ₆	0.0651	0.8065
ES ₇	0.0823	4.803
BS ₁	0.0158	0.590
BS ₇	0.0939	1.055

group of MTS were observed at 1740 cm^{-1} and 1080 cm^{-1} , respectively. An increase in intensity of the 1080 cm^{-1} band was observed on increasing the MTS concentration in the copolymers. In the pmr spectra of copolymers the proton signal due to methoxy proton of MTS was observed at 3.6 ppm. The composition of copolymers could also be determined by integration of this signal. The other proton resonance signals observed in NMR are given in Table 3.

Table 3 Determination of copolymer composition by using pmr technique

Position of pmr signal, ppm	ES ₁	ES ₇	BS ₁	BS ₇
0.9–1.19	222–223 (H)	53 (H)	729 (H)	70 (H)
1.2–2.2	78 (H)	20 (H)	666 (H)	74 (H)
3.6	9 (H)	9 (H)	9 (H)	9 (H)
3.97–4.07	74 (H)	18 (H)	207 (H)	22 (H)
Copolymer	EMA 36–37	EMA 8–9	BMA 102–103	BMA 10–11
Composition	MTS 1	MTS 1	MTS 1	MTS 1

Thermogravimetric traces of various polymeric samples were characterized by noting the initial decomposition temperature (T_i), the temperature of maximum rate of weight loss (T_{max}) and final decomposition temperature T_f . In some copolymers the decomposition proceeded in more than one step. T_{max} associated with each step was noted. These results are summarised in Tables 4 and 5.

In BS copolymers no weight loss was observed before 200° . Above this temperature the copolymers started decomposing and almost total loss in weight was observed around 400° . As the MTS mole fraction increased in copolymers, the single step decomposition changed into two step decomposition (Table 2).

The thermal behaviour of water cross-linked copolymers of EMA:MTS was studied. Only marginal effect on the thermal behaviour was observed after cross-

Table 4 Effect of mole fraction of MTS on the thermal behaviour of ES copolymers

Characteristic properties	ES ₁	ES ₂	ES ₅	ES ₇	*ES ₇
$T_{i(1)}$, °C	140	170	140	135	240
T_{max-1} , °C	180	190	185	185	250
% weight loss	13	7	10	9	20
$T_{i(2)}$, °C	210	210	210	210	270
T_{max-2} , °C	250	270	245	265	299
% weight loss	10	18	12	12	25
$T_{i(3)}$, °C	270	270	270	—	325
T_{max-3} , °C	300	306	305	—	370
% weight loss	22	30	28	—	50
$T_{i(4)}$, °C	325	325	330	330	—
T_{max-4} , °C	371	350	375	375	—
% weight loss	53	43	48	52	—

* Sample cross-linked by hydrolysis.

Table 5 Thermal behaviour of BS copolymers

Thermal properties	BS ₁	BS ₃	BS ₅	BS ₆	BS ₇
$T_{i(1)}$, °C	246	243	259	260	245
T_{max-1} , °C	303	299	303	304	302
% weight loss	98	99	62	64	72
$T_{i(2)}$, °C	—	—	325	325	325
T_{max-2} , °C	—	—	350	350	—
% weight loss	—	—	37	35	25

linking of copolymers having low mole fraction of MTS. On increasing the mole fraction of MTS the stability of copolymers increased and only a single step degradation was observed.

These results thus indicate that incorporation of MTS in alkyl methacrylates results in an increase in thermal stability. Hydrolytic cross-linking of the copolymer having higher mole fraction of MTS leads to cross-linked products with better thermal stability.

References

- 1 E. P. Plueddemann (to Dow Corning), U.S. Patent, 3 (1969) 453, 230.
- 2 I. K. Varma, A. K. Tomar and R. C. Anand, J. Appl. Polym. Sci., 33 (1987) 1377.

Zusammenfassung — Vorliegende Arbeit beschäftigt sich mit dem thermischen Verhalten von Äthylmethakrylat (EMA) und Butylmethakrylat (BMA), das mit Trimethoxysilan (MTS) modifiziert wurde. Unter Anwendung verschiedener Molverhältnisse von MTS und EMA bzw. BMA wurden einige Kopolymerproben hergestellt. Die Kopolymerisation wurde 120 Minuten lang bei 78 °C und mit Benzoylperoxid als Initiator durchgeführt. Der Einbau von MTS in Alkylmethakrylate führt zu einer Steigerung der thermischen Stabilität. Eine hydrolytische Vernetzung der Kopolymere mit größeren Molanteilen an MTS ergeben vernetzte Produkte mit verbesserter thermischer Stabilität.

Резюме — Изучено термическое поведение этилметакрилата (ЭМА) и бутилметакрилата (БМА), модифицированных триметоксисилоном (МТС). Путем изменения молярного соотношения МТС в ЭМА и БМА получено несколько сополимеров. Сополимеризация была проведена при 78 °C в течении 120 мин, используя в качестве инициатора реакции перекись бензоила. Введение МТС в алкилметакрилаты приводит к увеличению их термоустойчивости. Гидролитическое сшивание сополимера, содержащего более высокую мольную фракцию МТС, дает продукт с лучшей термической устойчивостью.