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Styrene/Methyl Methacrylate-Vinyltris-(methoxyethoxy)silane Copolymers: Synthesis, Characterization, and Thermal Degradation

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ABSTRACT

Vinyltris(methoxyethoxy)silane (VTMES) was copolymerized with methyl methacrylate (MMA) and styrene (St) in bulk at 60°C using benzoyl peroxide as free radical initiator. The copolymer compositions were determined from elemental analysis, and reactivity ratios were calculated by the Kelen-Tüdös graphical method. For MMA-VTMES, $r_1 = 11.2 \pm 0.88$ and $r_2 = 0 \pm 0.16$, and for St-VTMES, $r_1 = 11.2 \pm 2.0$ and $r_2 = 0 \pm 0.34$. In both systems r_2 is near zero, indicating that VTMES undergoes little or no polymerization under the experimental conditions. The influence of the silicon comonomer on some of the basic properties of the copolymers (e.g., intrinsic viscosity, solubility, and thermal behavior) was studied.

INTRODUCTION

Vinylsilanes have been copolymerized with various organic monomers, including styrene (St) and acrylonitrile (AN), and the reactivity ratios were determined [1-10]. Radical copolymerizations of MMA

with vinyltriacetoxysilane [11] and vinyltriethoxysilane [12] (VTES) as well as styrene with VTES [13], 2,6-dimethyl-2,7-octadiene-6-trimethylsilyl ether [14], [(2-methacryloyloxy)ethoxy]trimethylsilane [15], and vinylmethyldiacetoxysilane [16] were reported by us earlier.

The objective of the present investigation was to study the free-radical copolymerization of styrene (St) and methyl methacrylate (MMA) with vinyltris(methoxyethoxy)silane (VTMES) and to study the effect of the silicon moiety on viscosity, solubility, and thermal properties of the copolymers.

EXPERIMENTAL

Materials

Styrene was purified by drying over activated MgSO_4 followed by distillation at $34^\circ\text{C}/7$ torr. Methyl methacrylate (Aldrich) was distilled under reduced pressure for over 4 A Molecular Sieves prior to use. Vinyltris(methoxyethoxy)silane (VTMES) (Fluka) was distilled under reduced pressure prior to use. Benzoyl peroxide (BDH) was purified by recrystallization from methanol.

Copolymerization

Copolymerization was carried out by adding predetermined amounts of MMA/VTMES or St/VTMES in stoichiometric ratio to Pyrex sample tubes. Benzoyl peroxide (Bz_2O_2) (0.2 wt%) was added to initiate polymerization. The tubes were degassed under high vacuum by four freeze-thaw cycles. The sealed tubes were placed in a thermostat maintained at $60 \pm 0.1^\circ\text{C}$. The reactions were restricted to low conversions in order to use the differential form of the copolymerization equation. After the desired time the reaction mixture was poured into methanol. The product was washed with methanol and purified by repeated precipitation by methanol from a solution in chloroform. The purified copolymers were dried at 50°C under vacuum.

The compositions of the copolymers were calculated from elemental analysis.

Polymer Characterization

The infrared spectra of the polymers were recorded in Nujol mull between 400 and $4\,000\text{ cm}^{-1}$ on a Unicam SP-1200 spectrophotometer.

The intrinsic viscosity of the MMA-VTMES and St-VTMES copolymers were determined at 30°C in toluene by means of a Ubbelohde suspension level viscometer.

The glass transition temperatures (T_g) were determined on a Stanton-Redcroft differential thermal analyzer with calcined alumina as a reference at a heating rate of 6°C/min in static air.

Thermogravimetric analysis (TGA) was carried out with a Stanton-Redcroft TG-750 thermobalance in static air. The thermograms were run from room temperature to 500°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The reaction conditions and results of copolymerizations of MMA and St with VTMES are summarized in Tables 1 and 2. The monomer

TABLE 1. Copolymerization of MMA (M_1) and VTMES (M_2)^a

Mole fraction M_1 in feed	Conversion, wt%	Mole fraction m_1 in copolymer
0.9	9.8	0.989
0.8	8.6	0.978
0.7	6.5	0.963
0.6	7.4	0.946
0.4	4.8	0.905

^a Polymerization conditions: Catalyst, Bz_2O_2 (0.1 wt%); temperature, 60 ± 0.1°C.

TABLE 2. Copolymerization of Styrene (M_1) and VTMES (M_2)^a

Mole fraction M_1 in feed	Conversion, wt%	Mole fraction m_1 in copolymer
0.9	10.2	0.990
0.8	9.7	0.976
0.7	8.4	0.964
0.5	7.5	0.924
0.3	6.2	0.865

^a Polymerization conditions: Catalyst, Bz_2O_2 (0.1 wt%); temperature, 60 ± 0.1°C.

reactivity ratios were obtained from the copolymer composition by using the Kelen-Tüdös [17] graphical method. The reactivity ratios for MMA-VTMES were $r_1 = 11.1 \pm 0.88$ and $r_2 = 0 \pm 0.16$, and for St-VTMES, $r_1 = 11.2 \pm 2.0$ and $r_2 = 0 \pm 0.34$.

The very low values of r_2 indicate that VTMES does not homopolymerize detectably under the experimental conditions. The low reactivity of VTMES may be due to $d\pi$ - $p\pi$ bonding between silicon and the double bond. The low polymerizability of silane monomer seems to be consistent with our earlier studies [18, 19], and similar observations have been made by other workers [4, 20]. Since $r_1 \gg 1$ in all cases, the copolymers will contain larger random blocks of poly-MMA or poly-St interrupted with silyl units.

Price et al. [4] reported reactivity ratios for styrene-vinyltriethoxysilane (VTES) copolymerization at 60°C ($r_1 = 22 \pm 5$, $r_2 = 0$). These show that VTMES is nearly twice as reactive as VTES toward polystyryl radical, which is due to the greater polarity of the former.

The intrinsic viscosities of copolymers (Table 3) progressively decreased with an increase in VTMES content. This may be attributed to poor reactivity of silane monomer at the propagating chain end of the polymer.

Polymer Characterization and Properties

Solubility

The solubilities of St-VTMES and MMA-VTMES copolymers in various solvents are the same as those of the corresponding homopolymers,

TABLE 3. Composition and Intrinsic Viscosity of Silane Copolymers

Polymer	m_2 , mol%	$[\eta]$, dL/g
P(MMA)	-	1.145
P(MMA-VTMES)	2.2	1.122
P(MMA-VTMES)	5.4	0.730
P(MMA-VTMES)	9.5	0.525
P(St)	-	0.834
P(St-VTMES)	2.4	0.607
P(St-VTMES)	7.6	0.334
P(St-VTMES)	13.5	0.212

TABLE 4. Thermogravimetric Analysis of MMA-VTMES and Styrene-VTMES Copolymers

No.	Polymer ^a	m ₂ , mol%	IDT, °C	DT at various weight losses, °C			D _{max} , ^c °C	IPDT, ^d °C
				10%	30%	70%		
1	MMA	-	200	235	265	310	265	293
2	MMA-VTMES	2.2	225	313	331	375	411	358
3	MMA-VTMES	3.7	252	328	343	385	423	372
4	St	-	260	312	350	365	360	358
5	St-VTMES	2.4	271	390	418	445	434	430
6	St-VTMES	3.6	290	399	425	450	451	440

^aPolymers: MMA, methyl methacrylate; St, styrene; VTMES, vinyltris(methoxyethoxy)silane.

^bInitial decomposition temperature.

^cMaximum decomposition temperature.

^dIntegral procedural decomposition temperature.

poly-St and poly-MMA, which are fairly soluble in a wide range of solvents like chloroform, carbon tetrachloride, benzene, and toluene.

Infrared Spectra

Absorption bands at 1 026-1 115 cm⁻¹ due to ν_{as} (Si-O-C) are observed in the spectra of St-VTMES and MMA-VTMES copolymers, which confirms the introduction of the silicon moiety in the polymers. St-VTMES copolymers showed bands at 700 and 3 030 cm⁻¹ due to the phenyl ring of styrene. MMA-VTMES copolymers showed a band at 1 730 cm⁻¹ due to ν (C=O) of MMA.

Thermal Behavior

Thermograms for poly-MMA, poly-St, and the copolymers indicate a one-stage weight loss. Table 4 reveals that the initial decomposition temperature (IDT) of copolymers are above those for the corresponding homopolymers and increase with increasing proportion of silane in the copolymers. As shown in Table 4, the stabilities of St-VTMES copolymers exceed those of MMA-VTMES copolymers. The integral procedural decomposition temperature (IPDT) [14] indicates greater thermal stability for the copolymers than for PMMA and PSt. This behavior

TABLE 5. Glass Transition Temperature of MMA-VTMES and St-VTMES Copolymers

No.	Polymer	m_2 , mol%	T_g , °C
1	Poly(MMA)	-	105
2	Poly(MMA-VTMES)	2.2	71
3	Poly(MMA-VTMES)	5.4	63
4	Poly(St)	-	97
5	Poly(St-VTMES)	2.4	88
6	Poly(St-VTMES)	7.6	72
7	Poly(St-VTMES)	13.5	60

is attributed to the presence of silane units close to the chain ends, which may alter the mode of degradation.

The glass transition temperatures of copolymers containing VTMES were lower than those of the homopolymers (Table 5), more so with increasing silane content. This may be due to the free rotation of methoxyethoxy groups around the silicon atom.

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