COPOLYMERIZATION OF STYRENE AND ACRYLONITRILE WITH FUNCTIONAL SILANES

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Abstract—Styrene has been copolymerized to high conversions with vinylmethyl diacetoxysilane (VMDAS) and vinylmethyldiethoxysilane (VMDES) in bulk and in toluene at 60 using azobisisobutyronitrile (AIBN) as initiator. Acrylonitrile has also been copolymerized with VMDAS at 50 in bulk using AIBN. The compositions of the copolymers were determined from the silicon contents; reactivity ratios were calculated by the Kelen–Tüdős method. The reactivity ratio r_1 (styrene) is higher for styrene-VMDES than for styrene-VMDAS, indicating higher reactivity of VMDES towards polystyryl radical. VMDAS was found to be more reactive towards the polyacrylonitrile than towards the polystyrene radical. The influences of the silicon comonomer on properties such as intrinsic viscosity, solubility, molecular weight distribution and thermal behaviour were also studied.

INTRODUCTION

Copolymerizations of styrene with vinyltriacetoxy, vinyltriethoxysilane and other vinylsilanes have been reported [1, 2]. The effects of temperature on the monomer reactivity ratios of styrene and vinylmethyldiacetoxysilane have been reported [3]. The aim of this paper is to study the effects of substituents in the silane moiety and those of solvents on the monomer reactivity ratios. For this purpose, copolymerizations of styrene with vinylmethyldiacetoxysilane (VMDAS) and vinylmethyldiethoxysilane (VMDES) in bulk and in toluene were carried out. The reactivities of VMDAS towards styrene and acrylonitrile have also been compared.

EXPERIMENTAL

The purifications of styrene and acrylonitrile and the preparation of VMDAS have been reported previously [2, 3]. Vinylmethyldiethoxysilane (Aldrich Co. U.S.A.) was distilled at 133. AIBN was freshly crystallized from chloroform. Toluene was dried over sodium wire and distilled at 112.

Styrene was copolymerized with VMDES at 60 in bulk using 1% AIBN (by weight on the basis of total monomers)

as initiator [1]. The time required for high conversions was found from time vs. conversion plots. Solution copolymerizations of styrene-VMDAS and styrene-VMDES were performed at 60 in toluene using 1 mol% AIBN as initiator and monomer at 4 mol/l. Monomer feed ratios ranged between 1 to 7.0. Due to the higher reactivity of acrylonitrile compared with styrene, its copolymerization with VMDAS was done at 50 in bulk using 0.5% AIBN (by weight on the basis of total monomers) as initiator. The products were isolated by precipitation in methanol. The purified samples were dried to constant weight at 50 under vacuum. Compositions of copolymers were determined from silicon contents estimated gravimetrically [4].

The infrared spectra of the copolymers were recorded in potassium bromide between 400–4000 cm^{-1} on a Grubb–Parsons spectrophotometer. The intrinsic viscosities of the styrene-VMDAS and styrene-VMDES copolymers were determined at 30 ± 0.2 in toluene using an Ubbelohde suspension level viscometer. Molecular weight distributions (MWD) of polymers were studied from GPC data recorded on a Waters Associates Liquid Chromatograph model LC GPC 244 using μ-styragel columns having porosities 500, 10^3, 10^4 Å. The mobile phase was AR toluene with a flow rate of 2 ml/min, chart speed 0.75 in./min and the usual concentration 0.4 wt %. Five polystyrene standards (Waters Associates) were used to calibrate the columns. The thermogravimetric analyses

Table 1. Copolymerizations of styrene (M_1) with vinylmethyl diacetoxy- and vinylmethyldiethoxysilane (M_2) at 60 in toluene*

M_2	M_2, mol fraction in feed	Conversion (%)	Silicon content in copolymer (%)	m_2, mol fraction in copolymer
VMDAS	0.134	26.7	1.033	0.039
	0.180	31.1	1.505	0.058
	0.273	28.8	2.403	0.096
	0.372	26.4	3.190	0.131
	0.469	14.3	3.795	0.159
VMDES	0.125	20.42	0.718	0.027
	0.15	25.76	0.907	0.034
	0.20	24.95	1.250	0.047
	0.25	24.13	1.654	0.063

* Initiator—AIBN (1 mol%).

Table 2. Copolymerization of styrene (M_1)-vinylmethyldiethoxysilane (M_2) at 60° in bulk*

M_2, mol fraction in feed	Conversion (%)	Silicon content in copolymer (%)	m_2, mol fraction in copolymer
0.137	15.9	0.389	0.015
0.208	13.9	0.619	0.023
0.288	9.4	0.933	0.035
0.386	13.0	1.392	0.053

* Initiator—AIBN (1% by weight on the basis of total monomers).

were carried out with a Stanton Redcroft TG-750 thermo-balance in static air from room temperature to 900° at a heating rate of 10/min. Integral procedural decomposition temperature (IPDT) was also calculated as proposed by Doyle [5]. Activation energy for thermal degradation was calculated as previously [6].

RESULTS AND DISCUSSION

The copolymer compositions (in mole fraction m_2) are shown in Tables 1 to 3 with corresponding weight % conversions. From these data, reactivity ratios were calculated by the Kelen–Tüdös method applied for high conversions [7]. Advantages of this method over the conventional intersection and Fineman–Ross methods have already been emphasized and its applicability for high conversion data has been reported [8, 9]. The Kelen–Tüdös method takes the conversion into account, eliminating error due to changes in monomer ratio and copolymer composition. The method developed is as follows:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha}$$

where

$$\eta = \frac{G}{\alpha + F}, \quad \xi = \frac{F}{\alpha + F}$$

$$G = \frac{y - 1}{Z}, \quad F = \frac{y}{Z^2}$$

$$y = \frac{m_1}{m_2} \quad \text{and} \quad Z = \frac{\log(1 - \xi_1)}{\log(1 - \xi_2)}$$

$$\xi_2 = W \cdot \frac{\mu + x_0}{\mu + y}, \quad \xi_1 = \xi_2 \cdot \frac{y}{x_0}$$

$$x_0 = \frac{M_1}{M^2} \quad \text{and} \quad \mu = \frac{\mu_2}{\mu_1}$$

where M_1, M_2 are the molar concentrations in the monomer feed and m_1, m_2 are the molar concentrations in the copolymer. W is the weight conversion and μ_1, μ_2 are the molecular weights of the monomer M_1 and M_2 respectively. Similarly, ξ_1, ξ_2 are the partial molar conversions. α is expressed as:

$$\alpha = \sqrt{F_M \cdot F_m}$$

where

F_m = minimum mole ratio of the monomer feed;
F_M = maximum mole ratio of the monomer feed.
By plotting η values calculated from the experimental data as a function of ξ, a straight line is obtained which on extrapolation to $\xi = 0$ and $\xi = 1$ gives $-(r_2)/\alpha$ and r_1 respectively both as intercepts. Kelen–Tüdös plots are illustrated in Figs 2 and 3. From the time vs conversion plot for styrene and styrene-VMDES, it is clear that copolymerization is slower than homopolymerization of styrene under identical conditions. The slower copolymerization can be explained as reported for styrene-VMDAS [3].

From Table 4, it is clear that r_1 (styrene) is smaller in solution than in bulk [3]. The lower value in solution may be due to the greater diffusion of the bulky silane monomer in solution. Nametkin et al. [10] have also reported higher r_1(AN) value in bulk than in solution for acrylonitrile-vinyltrimethyl(phenyl)silane copolymerization. On the basis of reactivity ratios, VMDAS appears to be more reactive than VMDES towards the polystyryl radical. On comparing the relative reactivities of styrene and acrylonitrile

Table 3. Copolymerization of acrylonitrile (M_1)-vinylmethyldiacetoxysilane (M_2) at 50° in bulk*

M_2, mol fraction in feed	Conversion (%)	Silicon content in copolymer (%)	m_2, mol fraction in copolymer
0.10	24.8	2.305	0.049
0.122	22.0	2.699	0.059
0.15	21.3	3.103	0.069
0.20	19.2	4.104	0.097
0.25	11.2	4.752	0.116

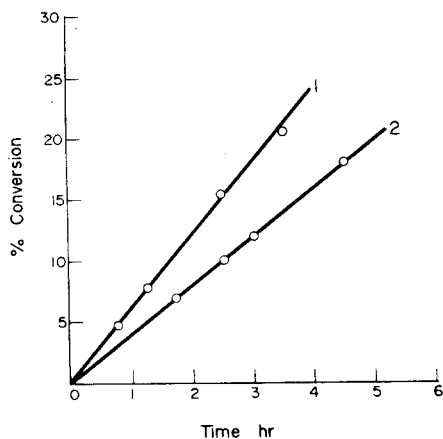* Initiator—AIBN (0.5% by weight on the basis of total monomers).

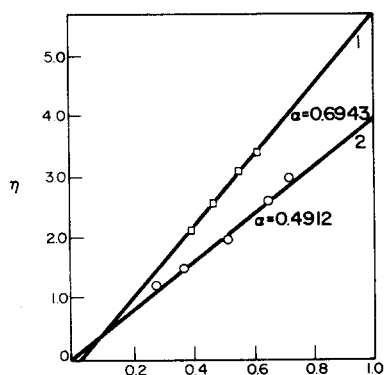Fig. 1. Time vs. Conversion plots for polymerization of (1) styrene and (2) styrene-VMDES at 60°.

Fig. 2. Kelen–Tüdős plots. (1) styrene (M$_1$)-VMDES (M$_2$) copolymerization $r_1 = 5.7 \pm 0.02$, $r_2 = 0.13 \pm 0.06$ (2) styrene-VMDAS copolymerization at 60 in toluene $r_1 = 4.01 \pm 0.03$, $r_2 \cong 0$.

monomers towards VMDAS, the polyacrylonitrile radical is found to be more reactive towards the silane than the polystryl radical. Nametkin et al. [10] and Scott and Price [11] also reported higher reactivity of polyacrylonitrile radical towards vinyltrimethylsilane.

Infrared spectra

Characteristic absorption bands of styrene, acrylonitrile and VMDAS have been observed in the i.r. spectra of copolymers. Strong absorption at 700 cm^{-1} due to the phenyl ring and at 3030 cm^{-1} due to aromatic C—H stretching and strong absorption at 1724 cm^{-1} for C=O acetoxy group are observed in
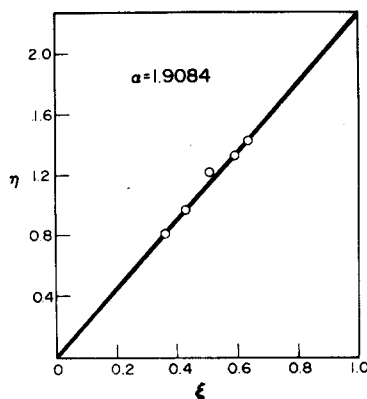

Fig. 3. Kelen–Tüdős plot for acrylonitrile (M$_1$)-VMDAS (M$_2$) copolymerization at 50° in bulk. $r_1 = 2.26 \pm 0.25$, $r_2 \cong 0$.

the IR spectra of styrene-VMDAS copolymers. Bands at 1026 and 1260 cm^{-1} for v_{a_s} Si—O—C vibrations are shown in copolymers. AN-VMDAS copolymers showed strong bands at 2252 and 1493 cm^{-1} due to nitrile groups, together with characteristic bands for acetoxysilane as in styrene-VMDAS. Styrene-VMDES copolymers like styrene-VMDAS copolymers show the same characteristic bands at 960 cm^{-1}, 1155 cm^{-1} and 1180 cm^{-1} due to the ethoxy group and absorption at 1025 and 1070 cm^{-1} for v_{a_s} (Si—O—C) bands. Smith [12] has also reported 1700-1770 cm^{-1} bands for >C=O of acetoxysilane and 1160–75 and 940–970 cm^{-1} bands for ethoxysilanes.

Solubility

The solubilities of styrene-VMDAS and styrene-VMDES copolymers in various solvents are as for polystyrene. However, AN-VMDAS copolymer having 5 mol% VMDAS does not dissolve in a wide range of polar solvents e.g. dioxane, dimethylformamide, tetrahydrofuran and hexamethylphosphoramide, although polyacrylonitrile is soluble in hot DMF and other polar solvents. Insolubility of the AN-VMDAS copolymer may be due to crosslinks arising from hydrolysis of some acetoxy groups.

Viscosity

The intrinsic viscosities of the styrene-VMDAS and styrene-VMDES copolymers drops with increase in the silicon content as compared to polystyrene (Tables 5 and 6). This effect may be attributed to the low reactivity of the polymeric radical having a vinyl-silane terminal unit ($\sim\!M_1M_2'$) as compared with a polystyryl radical ($\sim\!M_1M_1'$).

Table 4. Evaluation of reactivity ratios for styrene and acrylonitrile-vinylsilane systems

S. No.	Monomer pair	Medium	Temp. (°C)	r_1	r_2
1	Styrene-VMDAS	Bulk [3]	60	10.4 ± 0.3	0
2	Styrene-VMDAS	Toluene	60	4.01 ± 0.03	0
3	Styrene-VMDES	Bulk	60	11.7 ± 0.01	0
4	Styrene-VMDES	Toluene	60	5.7 ± 0.02	0.13 ± 0.06
5	Acrylonitrile-VMDAS	Bulk	50	2.26 ± 0.25	0

Table 5. Molecular weight distribution of (St-VMDAS) and (St-VMDES) copolymers

Polymer	m_2, mol % in copolymer	$[\eta]$ dl/g	$\overline{M}_n$ $\times 10^3$	$\overline{M}_w$ $\times 10^3$	$\overline{M}_w/\overline{M}_n$
Polystyrene	—	0.176	20	32	1.60
P(St-VMDAS)	3.9	0.170	16	29	1.81
P(St-VMDAS)	5.8	0.165	14	35	2.50
P(St-VMDAS)	13.1	0.158	13	35	2.69
P(St-VMDAS)	15.9	0.150	10	30	3.0
Polytyrene	—	0.250	62	94	1.52
P(St-VMDES)	2.3	0.225	43	71	1.65
P(St-VMDES)	5.3	0.190	27	50	1.85

* $[\eta]$—intrinsic viscosity in toluene at 30°.

Table 6. Thermal behaviour of styrene (M_1)-VMDAS (M_2) copolymers

S. No.	Polymer	m_2, mol% in copolymer	IDT*	DT at different wt losses					D_{max}†	IPDT‡	E*§ Kcal/mol
				10%	20%	40%	60%	80%			
1	Polystyrene	—	275	318	340	363	378	390	365	368	24
2	P(St-VMDAS)	3.9	260	318	340	365	385	408	380	375	24
3	P(St-VMDAS)	5.8	255	325	355	380	400	420	396	386	27
4	P(St-VMDAS)	13.1	238	330	360	393	415	440	415	406	30
5	P(St-VMDAS)	15.9	235	363	363	395	420	445	425	410	35

* IDT—Initial decomposition temperature; † D_{max}—Maximum decomposition temperature; ‡ IPDT—Integral procedural decomposition temperature; § E*—Activation energy for thermal decomposition.

Molecular weight Distribution (MWD)

Molecular weight dispersity ($\overline{M}_w/\overline{M}_n$) has been evaluated from the GPC curves (see Table 5). The data show that MWD of styrene-VMDAS and styrene-VMDES copolymers is broader than that of polystyrene. Further, polydispersity increases with increase in the silicon content. $\overline{M}_n$ also decreases with increase in silicon content in the copolymer. This result can be related with the drop in intrinsic viscosity.

Thermal Analysis

The thermal analysis data in Figs 4 and 5 show that initial decomposition temperature (IDT) is lowered by the introduction of silicon comonomer. How-

ever, in St-VMDAS copolymers, the trend reverses after 300° and in AN-VMDAS after 325°. In other words, the rate of decomposition is reduced above 300° or 325° in copolymers with respect to corresponding homopolymers i.e. polystyrene and polyacrylonitrile. Higher rate of decomposition in the initial stage may be due to the presence of the strong electron withdrawing substituent, Si(OAc)$_2$. This will induce the cleavage of the Si-O bond, liberating acetic acid. Above 325° in AN-VMDAS, the chain terminal radicals or hydrogen atoms from the tertiary carbon hydrogen bond or acetoxy radicals in the system may react with nitrile groups to initiate the polymerization of nitrile groups. Thus the higher rate of oligomerization of nitrile groups in copolymers may lead to more
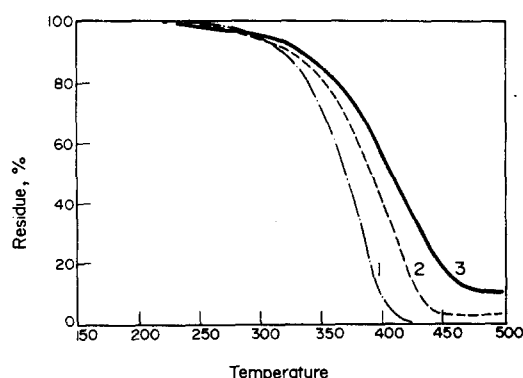

Fig. 4. Thermogravimetric analysis of (1) polystyrene. (2) styrene-VMDAS copolymer, (m_2 = 5.8 mol%), (3) styrene-VMDAS copolymer (m_2 = 15.9 mol%).
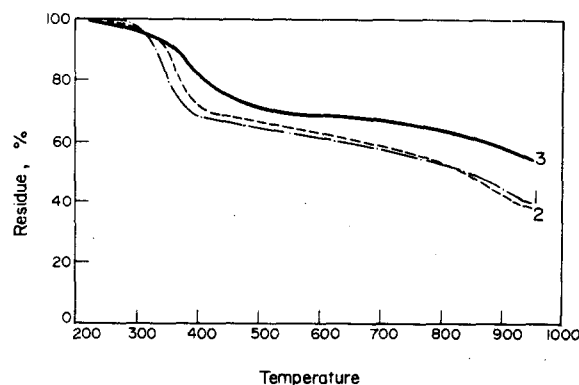

Fig. 5. Thermogravimetric analysis of (1) polyacrylonitrile (2) acrylonitrile-VMDAS copolymer (m_2 = 4.9 mol%), (3) acrylonitrile-VMDAS copolymer (m_2 = 11.6 mol%).

cyclized structure, and so to higher thermal stability of copolymers.

The relative thermal stability has also been evaluated from IPDT and the activation energies, further indicating the higher thermal stability of copolymers (Table 6).

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