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ABSTRACT

Acrylonitrile (AN) was copolymerized with [(2-methacryloyloxy)-ethoxy]trimethylsilane (2-MAETMS) and [(2-methacryloyloxy)-propoxy]trimethylsilane (2-MAPTMS) in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) between 50 and 70°C using azobisisobutyronitrile (AIBN) as initiator. The copolymer composition was determined by silicon estimation, and the reactivity ratios were calculated by the Kelen-Tüdös method. In both systems, $r_1(\text{AN})$ and $r_2(2\text{-MAETMS}/2\text{-MAPTMS})$ are higher in DMF compared to the values in DMSO. Arrhenius parameters were derived for the AN-2-MAETMS system. The difference between the activation energies ($E_{11} - E_{12}$) favors self-propagation for the acrylonitrile radical, whereas A_{11}/A_{12} favors cross-propagation. In the case of the 2-MAETMS radical, $E_{22} - E_{21}$ favors cross-propagation but A_{22}/A_{21} favors self-propagation. The influence of the comonomers on some of the basic properties of copolymers (e.g., intrinsic viscosity and glass transition temperature) have also been studied.

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INTRODUCTION

Copolymerization of acrylonitrile with various allyl and vinylsilanes, e.g., allyltrimethylsilane, dimethylphenyl vinylsilane, methyl vinyl diethoxysilane, and vinyltrimethylsilane, has been investigated [1-5]. Poor reactivity of vinylsilanes in the copolymerization of styrene with vinyltriethoxy, vinyltriacetoxysilane, and vinylmethyl diacetoxysilane [6, 7] has been observed by us.

In addition, the effect of silane monomers, e.g., on copolymerization of styrene with [(2-methacryloyloxy)ethoxy]trimethylsilane, 2-MAETMS (in which the silicon atom is not in the vicinity of the vinyl double bond), has been reported previously [8]. The studies have now been extended to the copolymerization of acrylonitrile (M_1) with 2-MAETMS and 2-MAPTMS (M_2) to determine the effects of substituent, solvent medium, and the polymerization temperature on the monomer reactivity ratios.

EXPERIMENTAL

Acrylonitrile (BDH) was dried over fused calcium chloride after making it free from the inhibitor and distilling it before use under nitrogen at 77°C. DMF was dried over calcium oxide and distilled at 152°C. Dimethylsulfoxide (DMSO) was distilled at 95°C/20 mm and kept in a nitrogen atmosphere.

2-MAETMS and 2-MAPTMS were prepared from 2-hydroxyethylmethacrylate (2-HEMA) or 2-hydroxypropylmethacrylate (2-HPMA) and trimethylchlorosilane in the presence of triethylamine following the method of Antiopina et al. [9] 2-MAETMS was distilled at 71-72°C/2 mm and 2-MAPTMS at 78-80°C/2 mm.

The copolymerization of acrylonitrile with 2-MAETMS or 2-MAPTMS was performed in DMF or DMSO in an inert atmosphere in the temperature range 50 to 70°C. AIBN (1 mol% on the basis of total monomers) was used as the initiator, and the total concentration of monomers amounted to 4 mol/L. The time necessary for high conversions was found from time vs conversion plots. Tables 1 and 2 show the actual conversions used for calculating r_1 and r_2 . The products were isolated by precipitation in methanol, and they were purified by repeated dissolution and precipitation. The polymers were then dried at 50°C under vacuum to constant weight. The composition of the copolymers was determined from their silicon content estimated gravimetrically [10].

The infrared spectra of the copolymers were recorded in potassium bromide between 700-4000 cm^{-1} on a Grubb Parson spectrophotometer.

The proton magnetic resonance spectra of the polymers were recorded on a 90 MHz varian spectrophotometer. A 5% (w/v) solution of the polymer was made in trifluoroacetic acid. Tetramethylsilane was used as the internal standard.

TABLE 1. Copolymerization of Acrylonitrile (M_1) with 2-MAETMS (M_2)

Temperature (°C)	Medium	M_1 mole fraction in feed	Conver- sion (%)	Copolymer composition		
				Silicon content (%)	m_1 mole fraction	$[\eta]^a$ (dL/g)
50	DMF	0.92	25.3	5.73	0.845	0.39
		0.90	25.2	6.42	0.816	0.43
		0.875	21.3	7.44	0.768	0.49
		0.80	19.9	8.85	0.685	0.55
60	DMF	0.92	31.6	6.55	0.810	0.41
		0.90	30.4	7.36	0.772	0.44
		0.875	28.1	8.23	0.724	0.51
		0.80	30.1	9.58	0.632	0.56
70	DMF	0.92	32.9	7.59	0.760	0.49
		0.90	32.5	8.51	0.707	0.53
		0.875	30.3	9.39	0.648	0.56
		0.90	27.7	10.39	0.563	0.59
60	DMSO	0.92	28.7	6.90	0.795	0.42
		0.90	25.1	7.71	0.754	0.48
		0.875	26.3	8.48	0.709	0.51
		0.80	27.1	9.55	0.623	0.56

^aIntrinsic viscosity at 30°C in DMF.

The intrinsic viscosity was determined in DMF at 30°C using an Ubbelohde suspension level viscometer.

Differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2 model) was used for determining the glass transition temperatures and the enthalpy of nitrile group oligomerization. In order to have a homogeneous polymer sample, it was heated for a few seconds to a temperature of 30°C above the second-order transition estimated from a preliminary run. After homogenizing, the sample was quenched and T_g was determined at a heating rate of 20°C/min.

TABLE 2. Copolymerization of Acrylonitrile (M_1) with 2-MAPTMS (M_2) at 60°C

Medium	M_1 mole fraction in feed	Conver- sion (%)	Copolymer composition		
			Silicon content (%)	m_1 mole fraction	$[\eta]^a$ (dL/g)
DMF	0.92	29.5	4.98	0.868	0.33
	0.90	26.5	6.07	0.823	0.36
	0.875	25.1	6.76	0.790	0.40
	0.80	24.3	8.20	0.705	0.42
DMSO	0.92	29.9	6.54	0.801	0.37
	0.90	26.4	7.62	0.742	0.41
	0.875	28.4	7.91	0.724	0.43
	0.80	24.5	9.23	0.625	0.49

^aIntrinsic viscosity at 30°C in DMF.

For quantitative analysis, the following settings were used on the instrument: rate of heating 20°C/min, chart speed 20 mm/min, and sensitivity range 5 mcal/s.

The enthalpy of nitrile group polymerization was determined by comparing the peak area of the sample to that of a known weight of the indium reference material using Eq. (1) as given in the Perkin-Elmer handbook [11]:

$$\Delta H = \frac{K.R.A.}{W.Cs} \quad (1)$$

K is the instrument constant, determined using a known weight (W) of indium, which was found to be 1.46:

$$K = \frac{\Delta H_f W.Cs}{R.A.} \quad (2)$$

where W = weight of sample/standard in mg; Cs = chart speed (cm/s),

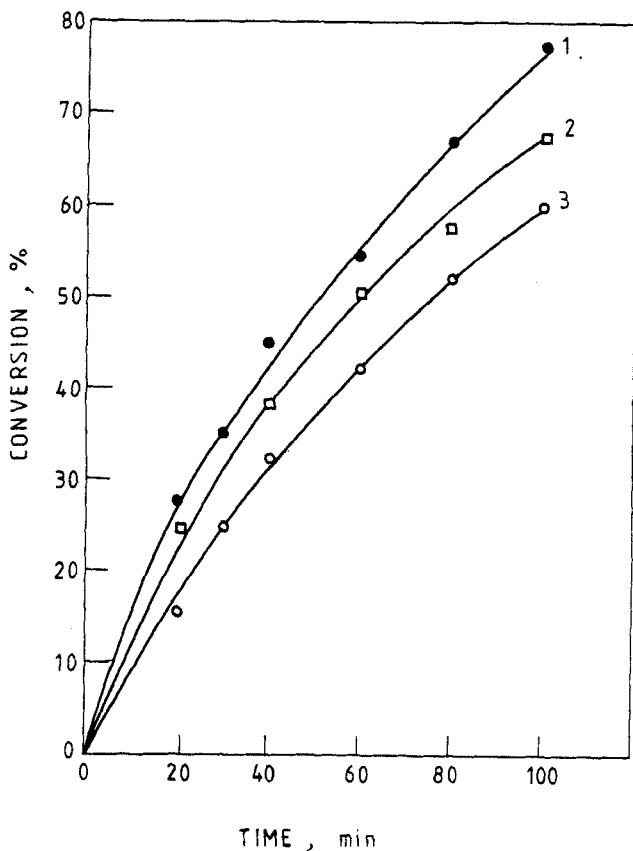


FIG. 1. Time vs conversion plot for polymerization of (1) AN-2-MAETMS, (2) AN-2-MAPTMS, and (3) AN at 60°C in DMF.

R = setting range (mcal/s) full scale divided by chart span in cm to give the yield in mcals/cm, A = area (cm²), ΔH = heat of nitrile group polymerization, and ΔH_f = heat of fusion of indium (6.8 cal/g).

RESULTS AND DISCUSSION

Polymerization of acrylonitrile and its copolymerization with 2-MAETMS and 2-MAPTMS was carried out at 60°C in DMF for different intervals of time. It has been observed that the rate of copolymerization is higher than that of homopolymerization of acrylonitrile (Fig. 1), which may be related to the higher reactivity of silane comonomers. In addition, the slow rate of homopolymerization of

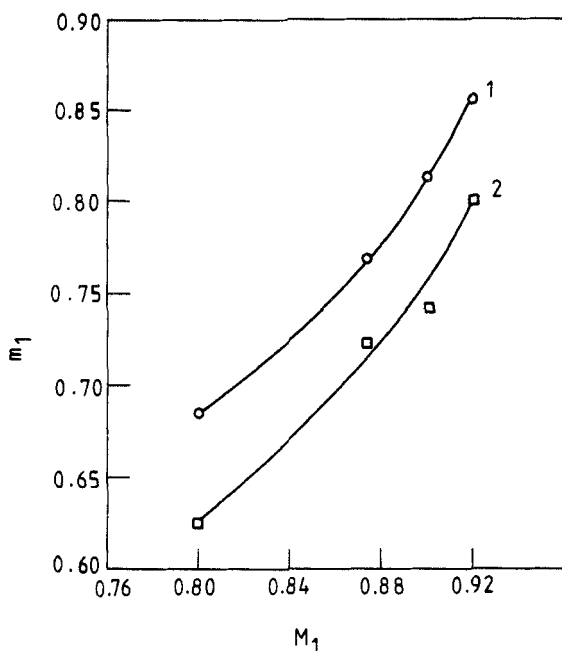


FIG. 2. Initial copolymer composition vs composition of monomer feed: (1) AN-2-MAPTMS in DMF and (2) AN-2-MAPTMS in DMSO.

acrylonitrile (m_1) content in DMF solutions compared to polymers prepared in DMSO. This may be due to the higher reactivity of the polyacrylonitrile radical in DMF which is a solvent with about the same polarity and dielectric constant (AN, $\epsilon = 38$; DMF, $\epsilon = 35$). From these copolymer composition data, reactivity ratios were calculated according to the Kelen-Tüdös method [15] represented by

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (3)$$

By plotting the η value 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 the corresponding $-r_2/\alpha$ and r_1 , respectively, both as intercepts. The 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 [16]. Kelen-Tüdös plots for AN-2-MAETMS and AN-2-MAPTMS systems in DMF and DMSO are given in Figs. 3 and 4.

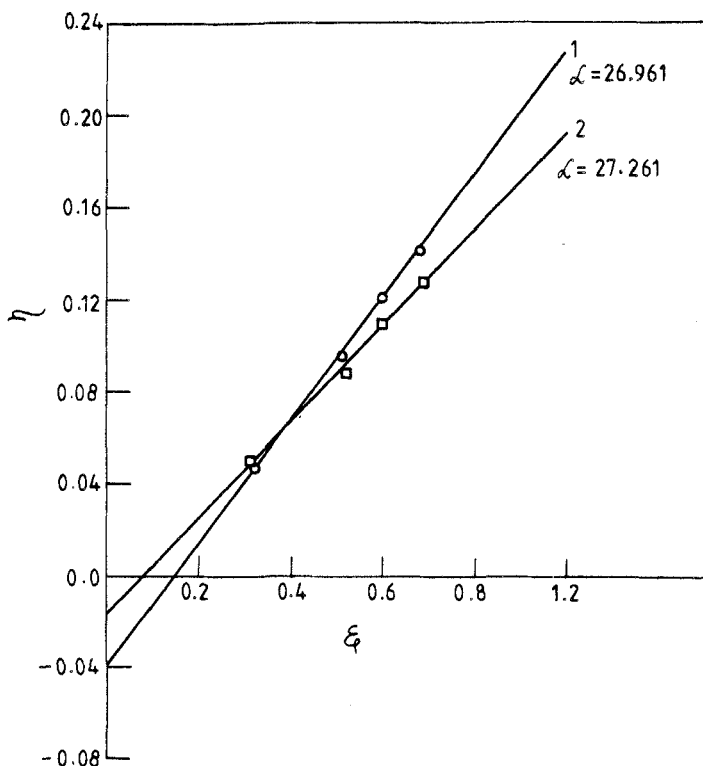


FIG. 3. Kelen-Tüdös plot for copolymerization of AN-2-MAETMS at 60°C in (1) DMF, $r_1 = 0.229$ and $r_2 = 1.018$; and (2) DMSO, $r_1 = 0.193$ and $r_2 = 0.463$.

Values of r_1 and r_2 (Tables 3 and 4) were calculated from the data by the linear least square method. The reactivity ratios in DMF at 60°C are:

AN-2-MAETMS copolymer system: $r_1 = 0.229$, $r_2 = 1.018$

AN-2-MAPTMS copolymer system: $r_1 = 0.485$, $r_2 = 1.157$

The reciprocal of $r_1(\text{AN})$ in both the systems, viz., AN-2-MAETMS ($1/r_1 = 4.37$) and AN-2-MAPTMS ($1/r_1 = 2.06$) in DMF, indicates the higher reactivity of 2-MAETMS compared with 2-MAPTMS toward the polyacrylonitrile radical. Moreover, $1/r_1(\text{AN})$ values of AN-HEMA and AN-HPMA systems [17] are 37.04 and 27.78, respectively, implying higher reactivity of the hydroxyalkylacrylates in comparison to their silylated derivatives, i.e., 2-MAETMS and 2-MAPTMS.

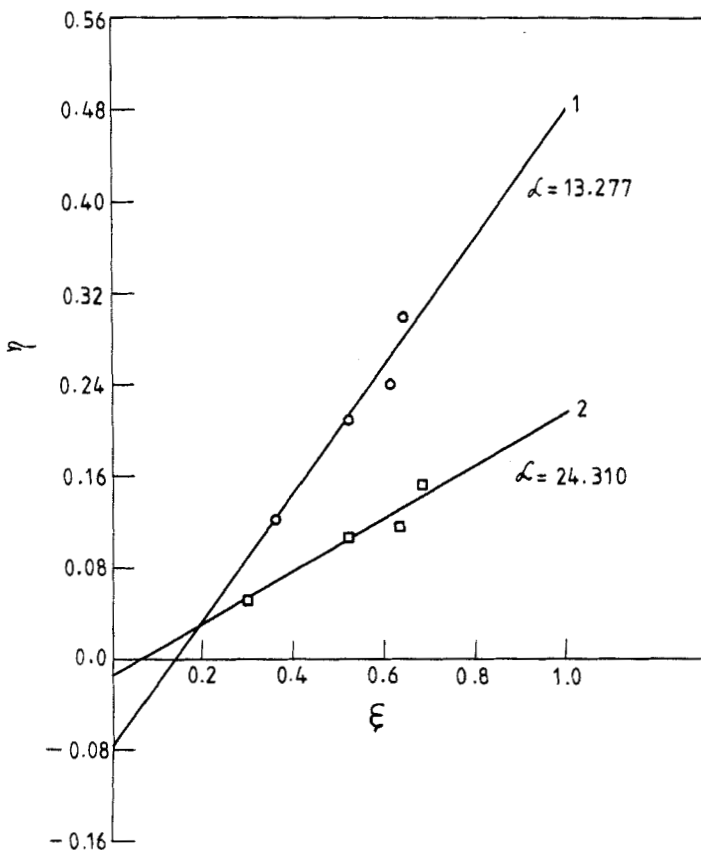


FIG. 4. Kelen-Tüdös plot for AN-2-MAPTMS copolymerization at 60°C in (1) DMF, $r_1 = 0.485$ and $r_2 = 1.157$; and (2) DMSO, $r_1 = 0.216$ and $r_2 = 0.394$.

Effect of Solvents on Reactivity Ratios

A perusal of the reactivity ratios in DMF and DMSO (Table 3) reveals that both $r_1(\text{AN})$ and $r_2(2\text{-MAETMS or } 2\text{-MAPTMS})$ are higher in DMF compared to the values in DMSO. A change in $r_1(\text{AN})$ value due to solvents means a change in the ratio k_{11}/k_{12} , where k_{11} and k_{12} are the rate constants for the addition of acrylonitrile and silylated methacrylate monomers 2-MAETMS and 2-MAPTMS, respectively, to the polyacrylonitrile radical. Low $r_1(\text{AN})$ in DMSO may therefore be attributed to the greater diffusion of bulky silylated comonomers, leading to greater cross-propagation as suggested by Nametkin et al.

TABLE 3. Reactivity Ratio Values for Acrylonitrile-[2-methacryloyloxy]-alokoxy] trimethylsilane Systems at 60°C

Monomer pair	Medium	r_1	r_2
AN-2-MAETMS	DMF	0.229 ± 0.02	1.018 ± 0.10
AN-2-MAETMS	DMSO	0.193 ± 0.01	0.463 ± 0.01
AN-2-MAPTMS	DMF	0.485 ± 0.02	1.157 ± 0.03
AN-2-MAPTMS	DMSO	0.216 ± 0.01	0.394 ± 0.01

[3] for acrylonitrile-vinyltrimethylsilane and acrylonitrile-vinyl-dimethylphenylsilane systems in DMF. It has also been shown that acrylonitrile may be associated with DMF [18], being similar in polarity and dielectric constant. So a third kind of acrylonitrile monomer species may be expected in this series of experiments for polymerization. The change in $r_1(\text{AN})$ with changing solvent may reflect the competition between the different species in propagation rates. The drop in $r_2(2\text{-MAETMS})$ or 2-MAPTMS in DMSO also confirms the greater diffusion of these bulky monomers in a more polar medium and an enhanced cross-propagation rate. However, higher r_1 and r_2 values have been observed in DMSO for AN-HEMA and AN-HPMA systems in comparison to the values obtained in DMF [17]. The change in reactivity ratio values after silylation of HEMA and HPMA may be due to the change in polarity of these silylated monomers.

Temperature Dependence of Reactivity Ratios

A study of the temperature dependence of the reactivity ratios for the AN-2-MAETMS system in DMF reveals that r_1 decreases and r_2 increases with an increase in the copolymerization temperature (Table 4). A similar trend has been observed in styrene-2-MAETMS [8] and styrene-vinylmethyldiacetoxysilane [7] systems. However, $r_2(2\text{-MAETMS})$ increases with an increase in the polymerization temperature. At higher temperatures, greater solvation and diffusion of the bulky silylated monomer would enhance both the rates of cross-propagation and self-propagation, i.e., $K_{12} \gg K_{11}$ and $K_{22} > K_{21}$, which explains the decrease in r_1 and the increase in r_2 values with an increase in the polymerization temperature. Arrhenius parameters are given in Table 4. The activation energies ($E_{11} - E_{12}$) favor self-propagation of the polyacrylonitrile radical while the ratio of preexponential factors favors cross-propagation. For the 2-MAETMS radical, the difference $E_{22} - E_{21}$ is 51.46 kJ/mol, favoring cross-propagation, but A_{22}/A_{21} favors self-addition.

TABLE 4. Reactivity Ratios and Arrhenius Parameters for the AN-2-MAETMS System in DMF

Monomer reactivity ratio	Polymerization temperature (°C)		Difference in energies of activation (kJ/mol)	Ratios of frequency factors	Difference in entropies of activation (J/k·mol)
	50	70			
$r_1(\text{AN})$	0.361 ± 0.04	0.229 ± 0.02	0.124 ± 0.01	0.06 ± 0.01	-23.16 ± 0.3
$r_2(2\text{-MAETMS})$	0.810 ± 0.09	1.018 ± 0.10	1.332 ± 0.12	1.82 ± 0.01	4.92 ± 0.1

Polymer Characterization

Intrinsic Viscosity

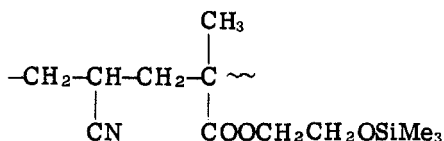
The intrinsic viscosity of acrylonitrile copolymers increases with an increase in the 2-MAETMS or 2-MAPTMS comonomer content (Tables 1 and 2). This may be due to the higher reactivity of the growing silane radical ($\sim M_2'$) present at the growing chain end which will enhance the rate of propagation (Fig. 1), leading to high molecular weight copolymers. Further, the change in intrinsic viscosity due to the introduction of silylated comonomers may be related with the change in hydrodynamic volume in such copolymer systems.

Infrared Spectra

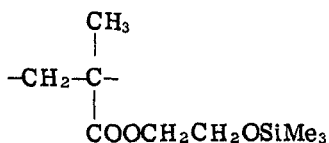
IR spectra of AN-2-MAETMS and AN-2-MAPTMS copolymers show characteristic absorption bands of acrylonitrile and silylated methacrylate comonomers. A strong band at 1240 and 1250 cm^{-1} in AN-2-MAPTMS and AN-2-MAETMS copolymers, respectively, due to $(\text{CH}_3)_3\text{Si}$ confirms the formation of copolymers. Other bands observed are at 763-769 and 840 cm^{-1} due to the trimethylsilyl group. A strong band at 1110 cm^{-1} due to $\nu_{\text{as}} \text{Si-O-C}$ has also been observed. The aliphatic C-H bands at 2959 and absorption at 2260 cm^{-1} due to the nitrile group have also been observed. However, the absorption bands at 1695 and 1754 cm^{-1} may be due to the presence of cyclic structures. Grassie and associates [19] have also assigned these bands to cyclic structures in their study of heat-treated polyacrylonitrile.

Proton Magnetic Resonance Spectra

PMR spectra of radically initiated PAN is identical with those reported by Murano and Yamadera [20]. In the copolymer there is a multiplet in the region, 7.62-8.5 τ , due to methylene protons of the polymer backbone, and a quintet due to methine proton in the range 6.4-7.6 τ . A sharp singlet at 9.8 τ is associated with Me_3Si protons:

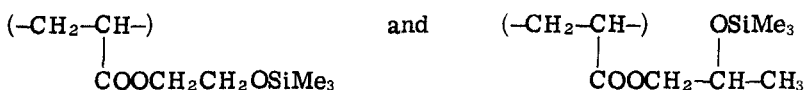


A triplet at 8.8 τ confirms the presence of C- CH_3 protons. Two broad peaks at 6.25 and 5.9 τ may be related to CH_2O protons present in silylated methacrylate. The presence of two signals clearly indicates the nonequivalence of the two CH_2O groups due to different neighboring groups:



Differential Scanning Calorimetry (DSC)

DSC data for PAN and its copolymers are given in Table 5. A decrease in T_g may be due to the introduction of bulky silicon side substituents



which reduce the intermolecular interactions between the molecular chains. Kimmel and Andrews [21] have also suggested that the decrease in the transition at the lower temperature is due to the chain mobility caused by weakening of the van der Waals forces.

The sharp exotherm for PAN becomes broader and also shifts to higher temperatures with the introduction of silylated comonomers (Fig. 5). It is interesting to note that in P(AN-2-MAPTMS) with a higher content of silylated comonomer (13.2 mol%), a small shoulder at 352°C along with the main exothermic peak at 337°C also appears. Quantitative measurements show that the total amount of heat evolved between 270 and 400°C, associated with the nitrile group oligomerization, is also dependent on the composition of the polymer. Typical results are reported in Table 5. The occurrence of the broad exotherm in copolymers at higher temperatures than that for polyacrylonitrile indicates delayed initiation and slows propagation of nitrile

TABLE 5. DSC Data of PAN Copolymers

Polymer	m_2 in copolymer (mol%)	Endotherm peak ($^{\circ}\text{C}$)	Exotherm peak maxima ($^{\circ}\text{C}$)	ΔH (cal/g)
PAN	-	87	293	111
P(AN-2-MAETMS)	8.2	83	324	127
P(AN-2-MAETMS)	15.5	77	333	144
P(AN-2-MAPTMS)	7.8	81	328	137
P(AN-2-MAPTMS)	13.2	71	337	150

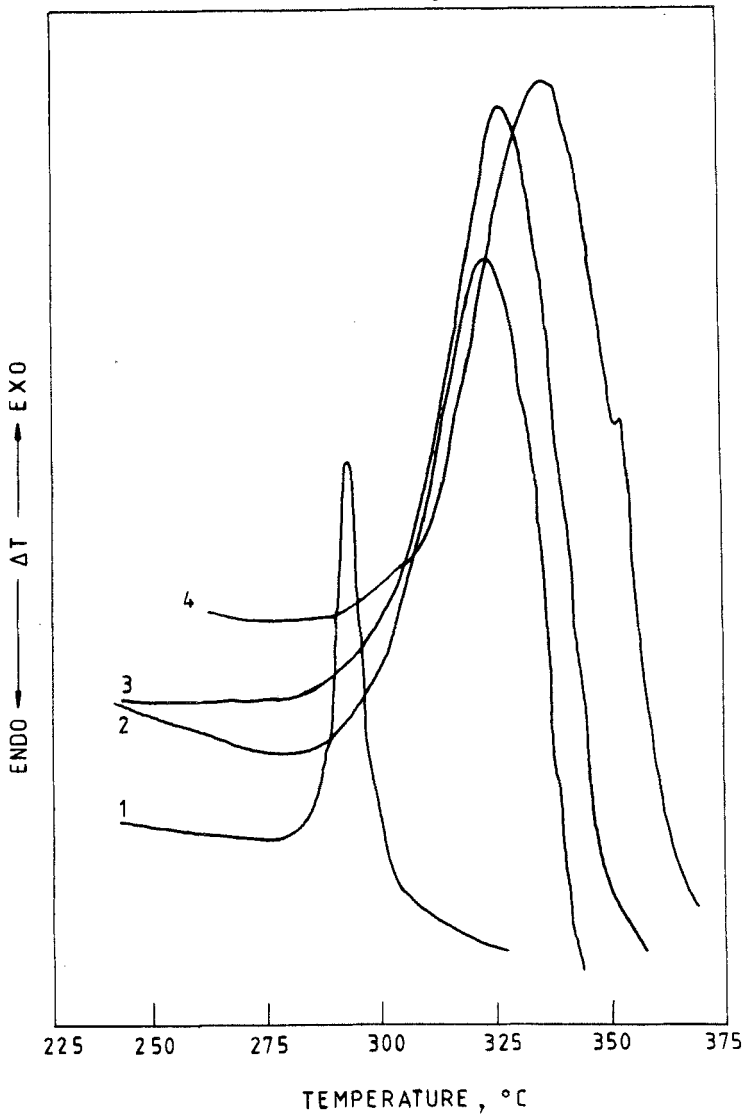


FIG. 5. DSC thermograms of (1) PAN, (2) AN-2-MAETMS copolymer ($m_2 = 8.2$ mol%), (3) AN-2-MAPTMS copolymer ($m_2 = 7.8$ mol%), and (4) AN-2-MAPTMS copolymer ($m_2 = 13.2$ mol%) at a heating rate of $20^\circ/\text{min}$.

oligomerization due to the introduction of bulky silylated side substituents. Shifting of the exotherm to higher temperatures with an increase in the size of side substituent in the case of AN-2-MAPTMS copolymers further substantiates the role of steric factors in cyclization.

Guyot et al. [22] have shown that nitrile oligomerization can be initiated through a molecular mechanism by the carboxylic group of the acid unit. After the first step, an amide structure is formed by isomerization following molecular propagation, while radical propagation is assumed in pure polyacrylonitrile. Similarly, in the present study the presence of silylated side substituents will change the mode of initiation and propagation of nitrile oligomerization, thereby leading to broader exotherms at higher temperatures. This also accounts for the observed changes in ΔH values.

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