

# Copolymerization of Acrylonitrile with [(2-Methacryloyloxy)alkoxy]trimethyl Silanes

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Acrylonitrile (AN) was copolymerized with [(2-methacryloyloxy)ethoxy]trimethylsilane (2-MAETMS) and [(2-methacryloyloxy)propoxy]trimethylsilane (2-MAPTMS) in dimethylformamide and dimethylsulfoxide at temperatures between 50° and 70° using azobisisobutyronitrile (AIBN) as initiator. The copolymer composition was determined by silicon estimation and reactivity ratios were calculated by the Kelen-Tudos method. In both the 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 AN-2-MAETMS system. The difference between the activation energies ( $E_{11}-E_{12}$ ) favour self-propagation for the acrylonitrile radical, whereas  $A_{11}/A_{12}$  favours cross-propagation. In case of 2-MAETMS radical,  $E_{22}-E_{21}$  favours cross-propagation but  $A_{22}/A_{21}$  favours self-propagation. The influence of the comonomers on some of the basic properties of copolymers like solubility, intrinsic viscosity, softening and glass transitions have also been studied.

**C**OPOLYMERIZATION of acrylonitrile with various allyl and vinylsilanes e.g., allyltrimethylsilane, dimethylphenyl vinylsilane, methyl vinyl diethoxysilane and vinyltrimethylsilane has been investigated<sup>1-5</sup>. Poor reactivity of vinylsilanes in copolymerization of styrene with vinyltriethoxy, vinyltriacetoxysilane and vinylmethyldiacetoxysilane<sup>6,7</sup> 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 silicon atom is not in the vicinity of vinyl double bond) has been reported previously<sup>8</sup>. The studies have now been extended to the copolymerization of acrylonitrile ( $M_1$ ) with 2-MAETMS and 2-MAPTMS ( $M_2$ ) to determine the effect 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 distilled before use under nitrogen at 77°. DMF was dried over calcium oxide and distilled at 152°. Dimethylsulfoxide (DMSO) was distilled at 95°/20 mm Hg and kept under 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*<sup>9</sup>. 2-MAETMS was distilled at 71-72°/2 mm Hg and 2-MAPTMS at 78-80°/2 mm Hg.

\* The copolymerization of acrylonitrile with 2-MAETMS or 2-MAPTMS was performed in DMF or DMSO in inert atmosphere in the temperature

range 50-70°. AIBN (1 mole % on the basis of total monomers) was used as initiator and the total concentration of monomers amounted to 4 moles/litre. The time necessary for high conversions was found from time vs conversion plots. The products were isolated by precipitation in methanol and purified by repeated dissolution and precipitation. The polymers were then dried at 50° under vacuum to constant weight. The composition of copolymers was determined from silicon contents estimated gravimetrically.

The infrared spectra of the copolymers were recorded in potassium bromide between 700-4000  $\text{cm}^{-1}$  on Grubb Parson spectrophotometer. For determination of copolymer composition, 2.5% of polyacrylonitrile or its copolymers in KBr were prepared and their spectra were recorded. The peak height for the nitrile group at 2260  $\text{cm}^{-1}$  was measured. Considering peak height in case of polyacrylonitrile equivalent to 100 parts of acrylonitrile, corresponding acrylonitrile contents were calculated for AN-2-MAETMS copolymer by the following procedure<sup>11</sup>.

Let A = percent of AN moiety in copolymer and B = 100 - A = percent of comonomer moiety in copolymer. Then number of moles of AN in 100 gm copolymer =  $\frac{A}{53} = X$ , and number of moles of comonomer in 100 g copolymer =  $\frac{B}{M} = Y$ , where M is molecular weight of silylated comonomers used in our studies. Mole fraction of acrylonitrile moiety in the copolymer =  $\frac{X}{X+Y}$

The proton magnetic resonance spectra of the polymers were recorded on a 90 MHz Varian spectrophotometer. 5% (v/v) solution of the

polymer was made in trifluoroacetic acid. Tetramethylsilane was used as internal standard.

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

The softening ranges were measured in capillaries with a temperature rise of about 5°/min.

The solubility of the acrylonitrile copolymers was checked in DMF, DMSO and toluene at 30°.

The glass transition temperatures of polymers were determined with a Perkin-Elmer model DSC-2 differential scanning calorimeter. The polymer samples, weighing 10 mg each, were placed in standard DSC aluminium pans. Empty aluminium pan was used on the reference side of the instrument. Both sample and reference pans were enclosed with aluminium covers and sealed with the special press designed for the purpose. The pans were then placed in the cell compartments of the DSC instrument, where a continuous stream of pure dry helium is made to flow at a rate of 20 cm<sup>3</sup>/min. In order to have a homogeneous polymer sample it was heated for few seconds to a temperature 30° above the  $T_g$  estimated from a preliminary run. After homogenising, the sample was quenched through the glass transition region at a rate of 320°/min as suggested in the literature<sup>12</sup>. After quenching,  $T_g$  values of the polymer sample were determined by heating these at a rate of 20°/min, chart speed 20 mm/min and setting of range control 2 mcal/sec. For quantitative analysis, following settings were used on DSC-2 instrument : rate of heating 20°/min, chart speed : 20 mm/min and sensitivity range 5 mcal/sec. Enthalpy of nitrile group polymerization which occurs in the range 290-340° in copolymers (as an exothermic peak) was calculated from DSC thermograms using the following expression as given in Perkin Elmer handbook<sup>13</sup>.

$$\Delta H = \frac{K.R.A.}{W.C_s}$$

where,  $\Delta H$ =heat of nitrile group polymerization ;  $W$ =weight of sample in mg ;  $C_s$ =chart speed in cm/sec ;  $A$ =area under the curve in cm<sup>2</sup> and  $K$ =instrument constant computed from the following expression and its value found to be 1.46.

$$K = \frac{\Delta H_f \cdot W_{std} \cdot S_{std}}{R.A.}$$

$\Delta H_f$ =heat of fusion of Indium (calibrating standard) in mcal/mg ;  $W_{std}$ =weight of calibrating standard in mg ;  $S_{std}$ =chart speed in cm/sec for the standard run ;  $R$ =setting of range control in mcal/sec (full scale) divided by chart span in cm to yield in mcal/sec cm and  $A$ =area under curve for calibrating standard in cm<sup>2</sup>.  $\Delta H_f$  of Indium was found to be 6.8 cal/g.

## Results and Discussion

Polymerization of acrylonitrile and its copolymerization with 2-MAETMS and 2-MAPTMS was carried out at 60° 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 acrylonitrile may be attributed to side reactions of polyacrylonitrile radical. Patron and others<sup>12,14</sup> suggested that polyacrylonitrile radical undergoes

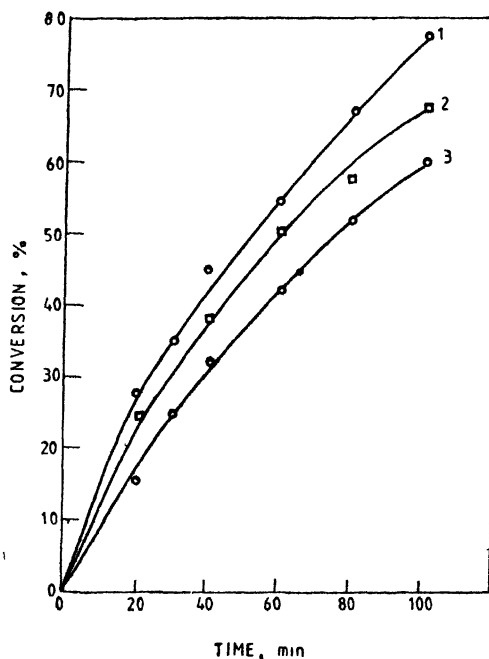
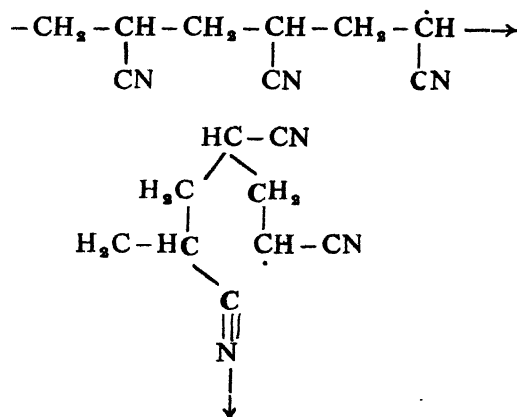
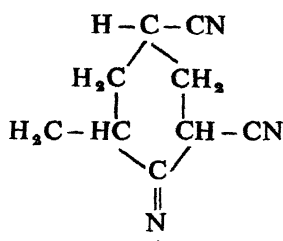


Fig. 1. Time vs conversion plot for polymerization of (1) AN-2-MAETMS (2) AN-2-MAPTMS (3) AN at 60° in DMF

cyclization or oligomerization in DMF forming cyclic imine radical leading to low reactivity in propagation reactions which results into both, decrease of reaction rate and molecular weight. Due to bulky side substituents in silylated comonomers, 2-MAETMS and 2-MAPTMS, cyclization will be to a lesser degree thereby leading to higher copolymerization rate. Further, the copolymerization





rate for P(AN-2-MAPTMS) is lower than P(AN-2-MAETMS) due to increased size of side substituents in 2-MAPTMS,



It is also interesting to note that no autoacceleration occurs in solution copolymerization of acrylonitrile as observed in bulk polymerization of acrylonitrile by Bamford and Jenkins<sup>16</sup>.

Results of copolymerization of acrylonitrile with 2-MAETMS and 2-MAPTMS are shown in Tables 1 and 2. Copolymer composition vs composition of monomer feed plot (Fig. 2) indicates that copolymers have low acrylonitrile content than the monomer feed. At the same feed ratio however, the copolymers have higher acrylonitrile ( $m_1$ ) content in DMF solution as compared to polymers prepared in DMSO. This may be due to the higher reactivity of 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 compositions data, reactivity ratios

TABLE 1—COPOLYMERIZATION OF ACRYLONITRILE ( $M_1$ ) WITH 2-MAETMS ( $M_2$ )

Medium	$M_1$ mole fraction in feed	Conver- sion %	Copolymer composition silicon content %	$M_1$ mole fraction	$[\eta]$ dl g <sup>-1</sup>
50°					
DMF	0.92	23.8	5.79	0.845	0.39
	0.90	25.2	6.42	0.816	0.48
	0.875	21.3	7.44	0.768	0.49
	0.80	19.9	8.85	0.685	0.55
60°					
	0.92	31.6	6.55	0.810	0.41
	0.90	30.4	7.96	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°					
	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
	0.80	27.7	10.39	0.568	0.59
80°					
DMSO	0.92	28.7	6.30	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

$[\eta]$  Intrinsic viscosity at 30° in DMF.

TABLE 2—COPOLYMERIZATION OF ACRYLONITRILE ( $M_1$ ) WITH 2-MAPTMS ( $M_2$ ) AT 60°

Medium	$M_1$ mole fraction in feed	Conver- sion %	Copolymer composition silicon content %	$M_1$ mole fraction	$[\eta]$ dl g <sup>-1</sup>
DMF	0.92	29.5	4.98	0.868	0.38
	0.90	26.5	6.07	0.828	0.36
	0.875	25.1	6.76	0.790	0.40
	0.80	25.3	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	0.48
	0.80	24.5	9.23	0.625	0.49

$[\eta]$  Intrinsic viscosity at 30° in DMF.

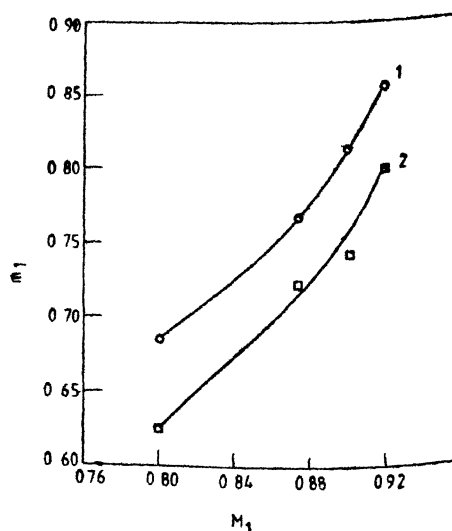


Fig. 2. Initial copolymer composition vs composition of monomer feed

- (1) AN-2-MAPTMS in DMF  
(2) AN-2-MAPTMS in DMSO

were calculated according to Kelen-Tudos method<sup>16</sup> represented by equation (ii).

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

By plotting  $\eta$  value calculated from the experimental data as a function of  $\xi$ , a straight line is obtained, which on extrapolation to  $\xi=0$ , and  $\xi=1$  gives corresponding  $-\frac{r_2}{\alpha}$  and  $r_1$  respectively both as intercepts. Advantages of this method over the conventional intersection and Fineman-Ross method have already been emphasized and its applicability for high conversion data has been reported<sup>17</sup>. Kelen-Tudos plots for AN-2-MAETMS and AN-2-MAPTMS systems in DMF and DMSO are given in Figs. 3 and 4 and values of  $r_1$  and  $r_2$  (Tables 3,4) were calculated from the data by linear least square

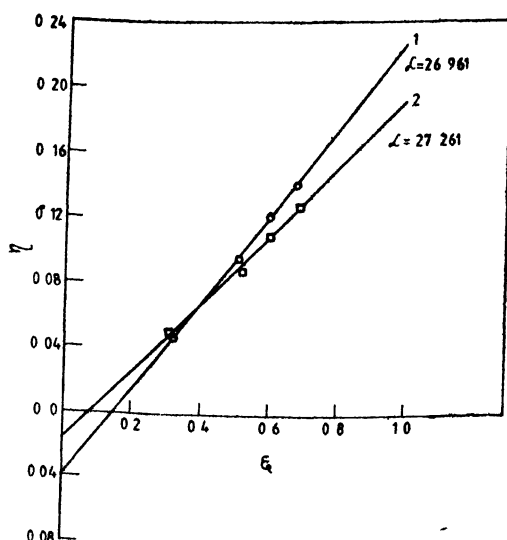


Fig. 3. Kelen-Tudos plot for copolymerization of AN-2-MAETMS at 60° in  
(1) DMF,  $r_1=0.229$  and  $r_2=1.018$   
(2) DMSO,  $r_1=0.198$  and  $r_2=0.468$

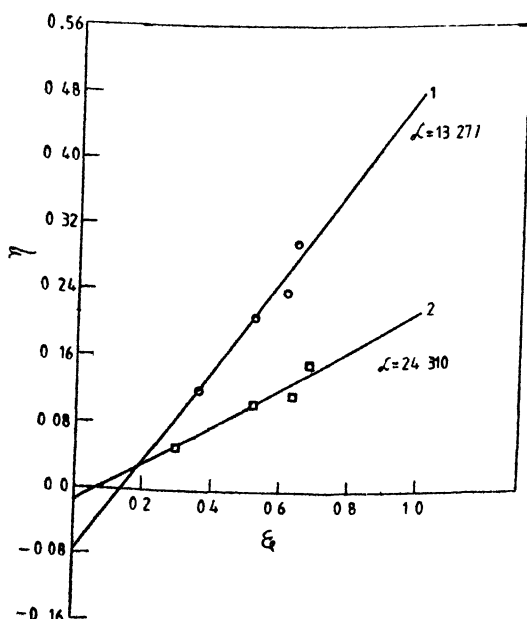


Fig. 4. Kelen-Tudos plot for AN-2-MAPTMS copolymerization at 60° in  
(1) DMF,  $r_1=0.485$  and  $r_2=1.157$   
(2) DMSO,  $r_1=0.216$  and  $r_2=0.394$

method. The reactivity ratios in DMF at 60° are given below :

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  $r_1$  (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 towards polyacrylonitrile radical. Moreover,  $1/r_1$  (AN) values of AN-HEMA and AN-HPMA systems<sup>18</sup> are 37.04 and 27.78 respectively implying higher reactivity of hydroxyalkylacrylates in comparison to their silylated derivatives i.e., 2-MAETMS and 2-MAPTMS.

**Effect of solvents on reactivity ratios :** A perusal of the reactivity ratios in DMF and DMSO (Table 3) reveals that both  $r_1$ (AN) and  $r_2$ (2-MAETMS or 2-MAPTMS) are higher in DMF compared to the values in DMSO. A change in  $r_1$ (AN)

TABLE 3—REACTIVITY RATIO VALUES FOR ACRYLONITRILE-[2-METHACRYLOYLOXY]-ALKOXY TRIMETHYLSILANE SYSTEMS AT 60°

Monomer pair	Medium	$r_1$	$r_2$
AN-2-MAETMS	DMF	$0.229 \pm 0.02$	$1.018 \pm 0.10$
AN-2-MAETMS	DMSO	$0.198 \pm 0.01$	$0.468 \pm 0.01$
AN-2-MAPTMS	DMF	$0.485 \pm 0.02$	$1.157 \pm 0.03$
AN-2-MAPTMS	DMSO	$0.216 \pm 0.01$	$0.394 \pm 0.01$

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 i.e. 2-MAETMS and 2-MAPTMS respectively, to the polyacrylonitrile radical. Low  $r_1$ (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*<sup>8</sup> for acrylonitrile-vinyl-trimethylsilane and acrylonitrile-vinyl-dimethylphenylsilane systems in DMF. It has also been shown that acrylonitrile may be associated with DMF<sup>19</sup> 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  $r_1$ (AN) with changing solvent may reflect the competition between the different species in propagation rates. The drop in  $r_2$ (2-MAETMS or 2-MAPTMS) in DMSO also confirms the greater diffusion of these bulky monomers in a more polar medium and enhanced cross-propagation rate. However, higher  $r_1$  and  $r_2$  values

TABLE 4—REACTIVITY RATIOS AND ARRHENIUS PARAMETERS FOR AN-2-MAETMS SYSTEM IN DMF

Monomer reactivity ratio	Polymerization Temperature, °C			Difference in energies of activation kJ mole <sup>-1</sup>	Ratio of frequency factors	Difference in entropies of activation Jk <sup>-1</sup> mole <sup>-1</sup>
	50	60	70			
$r_1$ (AN)	$0.361 \pm 0.04$	$0.229 \pm 0.02$	$0.124 \pm 0.01$	$51.46 \pm 0.4$	$0.06 \pm 0.01$	$-28.16 \pm 0.8$
$r_2$ (2-MAETMS)	$0.810 \pm 0.09$	$1.018 \pm 0.10$	$1.332 \pm 0.12$	$-22.53 \pm 0.3$	$1.82 \pm 0.01$	$4.92 \pm 0.1$

have been observed in DMSO for AN-HEMA and AN-HPMA systems in comparison to the values obtained in DMF<sup>18</sup>. 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 AN-2-MAETMS system in DMF reveals that  $r_1$  decreases and  $r_2$  increases with increase in the copolymerization temperature (Table 4). A similar trend has been observed in styrene-2-MAETMS<sup>8</sup> and styrene-vinylmethyl diacetoxysilane<sup>7</sup> systems. However,  $r_2$ (2-MAETMS) increases with increase in the polymerization temperature. At higher temperatures, greater solvation and diffusion of the bulky silylated monomer would enhance both the rate of cross-propagation and self propagation i.e.  $K_{12} > K_{11}$  and  $K_{22} > K_{21}$ , which explains the decrease in  $r_1$  and increase in  $r_2$  values with increase in the polymerization temperature. Arrhenius parameters are given in Table 4. The activation energies ( $E_{12} - E_{11}$ ) favour self propagation of the polyacrylonitrile radical whilst the ratio of pre-exponential factors favours cross-propagation. For the 2-MAETMS radical, the difference  $E_{22} - E_{21}$  is 51.46 kJmole<sup>-1</sup> favouring cross-propagation but  $A_{22}/A_{21}$  favours self-addition.

#### Polymer characterization :

**Solubility :** The introduction of silylated methacrylates comonomer influences the solubility of polyacrylonitrile in polar and nonpolar solvents. The solubility of PAN in DMF is 12.9 g/100 ml at 30°. By introducing 15.5 mole % of 2-MAETMS and 13.2 mole % 2-MAPTMS in PAN backbone, the solubility of copolymers decreases from 12.9 g/100 ml to 10.7 g and 9.9 g/100 ml respectively at 30° in DMF. In a similar manner, the solubility of PAN and its copolymers viz. AN-2-MAETMS ( $m_2 = 15.5$  mole %) and AN-2-MAPTMS ( $m_2 = 13.2$  mole %) in DMSO are 13.2, 10.4 and 10.1 g/100ml at 30°. However, PAN was found to be insoluble in toluene, whereas AN-2-MAPTMS ( $m_2 = 13.2$  mole %) copolymers show 0.8 g and 0.5 g/100 ml solubilities in toluene at 30°.

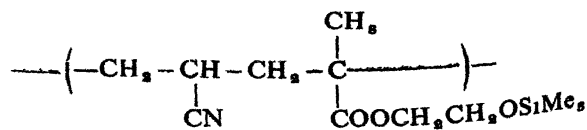
**Softening range :** Polyacrylonitrile shows colour change from yellow to brownish between 220-240° and then turns black above 260°. Poly(AN-2-MAETMS) and poly(AN-2-MAPTMS) copolymers show colour change from yellow to red between 180-200° along with softening and above 240-250°, they attain deep red colour.

**Intrinsic viscosity :** The intrinsic viscosity of acrylonitrile copolymers increases with increase in 2-MAETMS or 2-MAPTMS comonomer content (Tables 1 and 2). This may be due to the higher reactivity of the growing silane radical ( $\sim \dot{M}_2$ ) present at the growing chain end which will enhance the rate of propagation, as shown in Fig. 1. Further the change in intrinsic viscosity due to the introduction of silylated comonomers may be related with

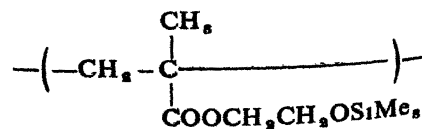
the change in hydrodynamic volume in such copolymer systems.

**Infrared spectra :** IR spectra of AN-2-MAETMS and AN-2-MAPTMS copolymers show characteristic absorption bands of acrylonitrile and silylated methacrylate comonomer. A strong band at 1240 and 1250 cm<sup>-1</sup> in AN-2-MAPTMS and AN-2-MAETMS copolymers respectively confirms the formation of copolymer. Other bands observed are at 763-769 and 840 cm<sup>-1</sup> due to trimethylsilyl group. A strong band at 1111 cm<sup>-1</sup> due to Si-O-C has also been observed. The aliphatic C-H bands at 2959 and absorption at 2260 cm<sup>-1</sup> due to nitrile group have also been observed. However, the absorption bands at 1695 and 1754 cm<sup>-1</sup> may be due to the presence of cyclic structures. Grassie and associates<sup>20</sup> have also assigned these bands to cyclic structures in their study of heat treated polyacrylonitrile. Quantitative analysis of AN-2-MAETMS copolymers by IR spectra permit us to estimate the copolymer composition. The amount of AN in one of the copolymer was found to be 75 mole % AN against 72.6 mole % AN obtained by elemental analysis. However, for calculating reactivity ratios, compositions based on silicon contents were used.

**Proton magnetic resonance spectra :** PMR spectra of radically initiated PAN is identical with those reported by Murano and Yamadera<sup>21</sup>. In the copolymer there is a multiplet in the region 7.62-8.5  $\tau$  due to methylene protons of the polymer backbone and to quintet due to methine proton in the range of 6.4-7.6  $\tau$ . A sharp singlet at 9.8  $\tau$  is associated with  $\text{Me}_3\text{Si}$  protons. Presence of a triplet



at 8.8  $\tau$  confirms the presence of C-CH<sub>3</sub> protons. Two broad peaks at 6.25  $\tau$  and 5.9  $\tau$  may be related to CH<sub>2</sub>O protons present in silylated methacrylate. Presence of two signals clearly indicates the nonequivalence of the two CH<sub>2</sub>O groups due to different neighbouring groups :

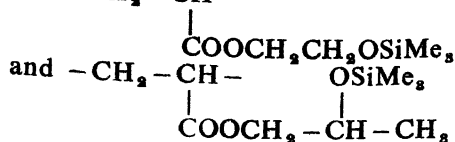


**Differential scanning calorimetry (DSC) :** DSC data for PAN and its copolymers are given in Table 5. Two distinct endothermic transitions have been observed, one occurring at about 71 to 87° and the other at 129 to 131°. Kimmel and Andrews<sup>22</sup> have proposed the concept of a heterobonded solid-state structure to explain these glass transitions. They have suggested that transition at the lower

TABLE 5—DSC ANALYSIS OF PAN COPOLYMERS

Polymer	m <sub>2</sub> in copolymer	Endotherms I	Endotherms II	Exotherm peak maxima	ΔH calg <sup>-1</sup>
PAN	—	87	181	293	111
P(AN-2-MAETMS)	8.2	83	181	324	127
P(AN-2-MAETMS)	15.5	77	129	333	144
P(AN-2-MAPTMS)	7.8	81	129	328	137
P(AN-2-MAPTMS)	13.2	71	129	337	150

temperature was the result of chain mobility caused by weakening of the Vander Waals forces, while the transition at the higher temperature resulted from intermolecular dipole-dipole dissociation of the nitrile groups in more localized sections of the chain. The  $T_g$  values of AN copolymers are lower in comparison to the PAN. A decrease in  $T_g$  may be due to the introduction of bulky silicon side substituents  $-\text{CH}_2-\text{CH}-$



which reduces the intermolecular interactions between the molecular chains. The results of DSC

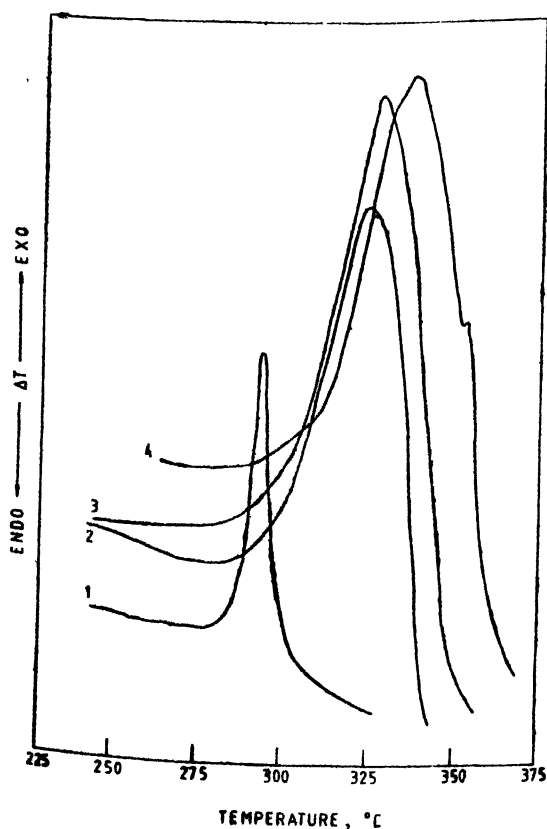


Fig. 5. DSC thermograms of  
(1) PAN  
(2) AN-2-MAETMS copolymer, ( $m_2=8.2$  mole%)  
(3) AN-2-MAPTMS copolymer, ( $m_2=7.8$  mole%)  
(4) AN-2-MAPTMS copolymer, ( $m_2=13.2$  mole%)  
at heating rate of  $20^\circ/\text{min}$ .

are illustrated in Fig. 5. The sharp exotherm for PAN becomes broader and also shifts to higher temperatures with the introduction of silylated comonomers. It is interesting to note that in P(AN-2-MAPTMS) with higher content of silylated comonomer (13.2 mole %), a small shoulder at  $352^\circ$  along with the main exothermic peak at  $337^\circ$  also appears. The quantitative measurements show that the total amount of heat evolved between  $270-400^\circ$ , to be 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 the delayed initiation and show propagation of nitrile oligomerization due to the introduction of bulky silylated side substituents. Shifting of the exotherm to higher temperature with increase in the size of side substituents in case of AN-2-MAPTMS copolymers further substantiates the role of steric factors in cyclization.

Grassie *et al.*<sup>16</sup> have already shown that the 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 observed changes in  $\Delta H$  values.

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