

Structure and Properties of Acrylonitrile-[(2-Methacryloyloxy)alkoxy]trimethyl Silane Copolymers

P. BAJAJ, D. C. GUPTA, and A. K. GUPTA, *Department of Textile Technology, Indian Institute of Technology, Delhi, New Delhi 110 029, India*

Synopsis

Dielectric, x-ray diffraction, density, thermomechanical, and thermogravimetric studies on polyacrylonitrile (PAN), poly[acrylonitrile-(2 methacryloyloxy)ethoxytrimethylsilane] [poly(AN-2MAETMS)], and poly[acrylonitrile-(2 methacryloyloxy)propoxytrimethylsilane] [poly(AN-2MAPTMS)] copolymers have been carried out for investigating their structure. The glass transition temperature as indicated from the dielectric and thermomechanical analysis data are lower for the copolymers as compared to PAN. Crystallinity is influenced by the introduction of the silylated acrylic comonomer units but the crystalline lattice remains similar to that of PAN. The changes observed in the various properties of these copolymers clearly suggest a more closely packed structure of poly(AN-2MAETMS) than poly(AN-2MAPTMS), and the uninterrupted PAN sequences are longer in the former. Thermal stability of copolymers has also been investigated.

INTRODUCTION

The structure of polyacrylonitrile in the solid state has been studied by a number of authors.¹⁻¹⁴ In earlier publications, polyacrylonitrile has been considered as a single-phase paracrystalline solid.³⁻⁶ Later, Hinrichsen⁷ and Minami et al.⁸ have proposed a two-phase structure to explain the two transitions.

Infrared⁹⁻¹² and dielectric^{10,13,14} measurements have suggested a second-order transition in the region of 100°C. Viscoelastic properties of polyacrylonitrile have also been studied by many workers,^{10,15,16} but the relaxation mechanism does not seem to be well ascertained for the two absorptions at 105°C (4.5 Hz) and 140°C (5.5 Hz) in the temperature dependence of dynamic loss modulus (E'') and dynamic loss tangent ($\tan \delta$). Similar observations have been made for acrylonitrile copolymers,^{17,18} e.g., acrylonitrile (AN)-vinyl acetate (VAc), AN-methacrylic acid, and AN-sodium 4-vinyl benzene sulfonic acid, but two absorptions of $\tan \delta$ at 110 and 160°C (denoted, respectively, as α_{II} and α_I relaxation by some authors) have been attributed to the molecular motions in the crystalline and amorphous region, respectively.

Recently, dielectric studies on polyacrylonitrile (PAN) and poly(acrylonitrile-2 hydroxyethyl methacrylate) copolymers in the frequency region 0.1–100 kHz showed a $\tan \delta$ peak between 110 and 140°C for PAN, while in copolymers, the peak temperature and peak heights depend sensitively on the composition of copolymers.¹⁹

The introduction of silicon comonomer in organic copolymers modifies the dielectric properties, as shown by Nametkin et al.²⁰ for poly(styrene-vinyl trimethyl silane) and Bajaj and Babu²¹ for poly[styrene(2-methacryloyloxy-ethoxy)trimethylsilane] copolymers.

We now report the structural investigations of poly[acrylonitrile-(2 methacryloyloxy)ethoxytrimethylsilane] [poly(AN-2MAETMS)] and poly[acrylonitrile-(2 methacryloyloxy)propoxytrimethylsilane] [poly(AN-2 MAPTMS)] by dielectric, density, x-ray diffraction, thermogravimetry and thermomechanical measurements.

EXPERIMENTAL

PAN, poly(AN-2-MAETMS), and poly(AN-2-MAPTMS) were synthesized by free radical polymerization in dimethyl formamide at 60°C according to the method described previously.²² The composition of copolymers was determined by silicon and nitrogen contents.

The density measurements were carried out using a density gradient column (Devenport, London) comprising a mixture of *n*-heptane and carbon tetrachloride. Polymer disks were prepared under constant pressure and time, and then kept in a vacuum oven at 70°C for 10–12 hr prior to density measurements. The stable position of the specimens in the density gradient column was checked over a long duration of time (up to 48 hr) to confirm the absence of swelling effects on these copolymers in a heptane/carbontetrachloride containing column.

X-ray diffraction patterns (intensity versus diffraction angle plots) were obtained on a Phillips x-ray diffractometer equipped with a scintillation counter and a chart recorder. Cu K α radiation was used. The x-ray scan was divided into crystalline and noncrystalline regions according to the method suggested by Bell and Dumbleton.²³ The ratio of the crystalline area to the total area (A_C/A_T) was taken as the index of crystallinity.

Dielectric measurements were performed in the range 1–10 kHz in temperature ranging from room temperature to 150°C on Systronics LCR Bridge 921. The sample disks (0.4 cm thick and 1.25 cm diameter) were made by compressing the powdered sample. Disk surfaces were silver coated to ensure good electrical contact with the electrodes and placed in a thermostatted sample cell.

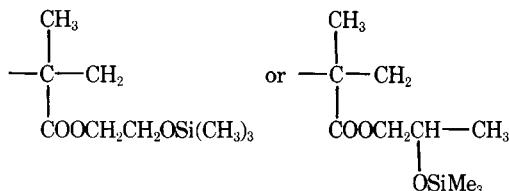
Thermomechanical measurements were carried out on compressed sample disks using Stanton Redcroft thermomechanical analyzer, TMA 691. The sample disks (0.2 cm thick) were prepared under load of 10 tons and then kept in a vacuum oven at 50°C for 10 hr before being subjected to this analysis. The probe used for the TMA was a quartz rod, radius 0.0564 cm, with a pointed end. The sample disk was placed under the end of the probe, and after cooling at the starting temperature (–100°C) with liquid air, the probe was adjusted to just touch the surface of the sample using the probe position controller. A load of constant weight (5 g) was applied to the probe in one experiment and the displacement of the probe was recorded as a function of temperature. The temperature was increased from –100 to 220°C at a heating rate of 10°C/min. In another experiment, the effect of probe load (2, 5, and 10 g) on the probe displacement was studied.

Thermogravimetric analysis was done on a Stanton Redcroft TG750 thermobalance in nitrogen atmosphere at temperature ranging from room temperature to 950°C at a heating rate of 10°C/min. Thermal stability of polymers is expressed in terms of integral procedural decomposition temperature (IPDT) calculated according to Doyle's method.²⁴ The activation energy of thermal degradation was also calculated as described previously.²¹

RESULTS AND DISCUSSION

Dielectric Measurements

Dielectric data for PAN, poly(AN-2 MAETMS), and poly(AN-2 MAPTMS) in the temperature range 30–150°C at various frequencies of measurement are shown in Figures 1–3, respectively. At room temperature, ϵ' (dielectric constant) for copolymers is higher than PAN, thereby indicating higher polarization in the copolymers. Higher ϵ' value in copolymers may be attributed to higher dipole moment of silylated comonomers, i.e.,



and the increased polarization may be due to these bulky silicon side substituents which may hinder the nitrile dipole-dipole interaction, thus rendering more nitrile group dipoles free for orientation.

Further, the dielectric constant of PAN and its copolymers remains almost unchanged with increase in temperature up to a certain temperature, which is consistent with the glass transition temperature T_g of these polymers, as described in the following discussion. However, above T_g it increases with increase in temperature at all frequencies because of the thermal expansion and consequently high mobility of chain segments of the polymers.

The effect of silylation on dielectric properties of poly(AN-2 MAETMS) and

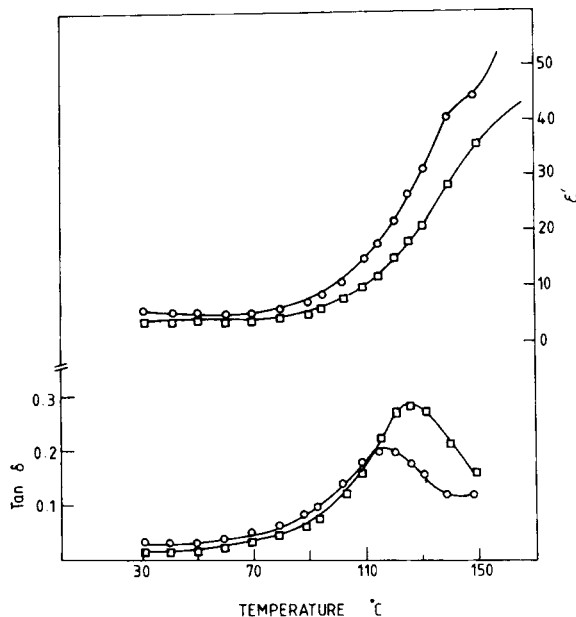


Fig. 1. Dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) as function of temperature for polyacrylonitrile at (□) 10^4 Hz and (○) 10^3 Hz.

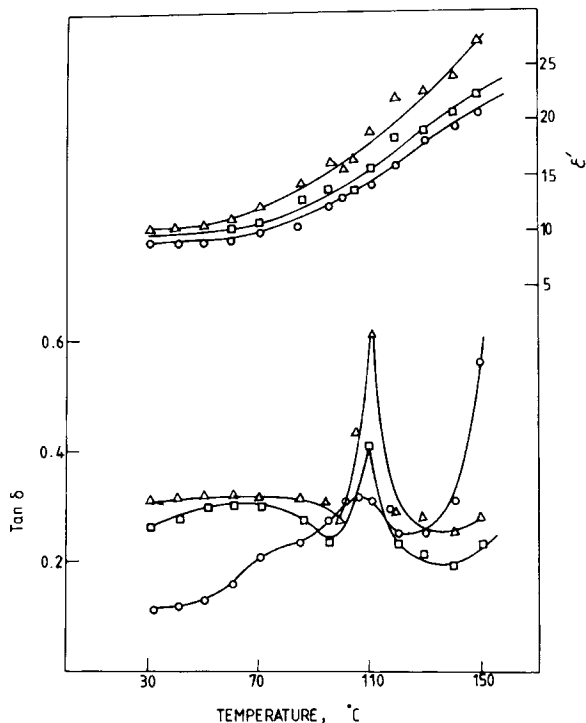


Fig. 2. Dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) as function of temperature for AN-2MAETMS copolymer ($m_2 = 8.2$ mole %) at (Δ) 10^4 Hz, (\square) 5×10^3 Hz, and (\circ) 10^3 Hz.

poly(AN-2 MAPTMS) can be studied by comparing the relative magnitudes of ϵ' of these copolymers with poly(AN-2 hydroxyethyl methacrylate) (AN-HEMA) copolymers.¹⁹ A comparison of the dielectric constants as functions of temperature shows some difference in these silylated copolymers, with respect to those involving purely organic comonomers. In PAN and poly(AN-HEMA) the dielectric constant rises considerably with increasing temperature above T_g , while in poly(AN-2 MAETMS) and poly(AN-2 MAPTMS) the rise in ϵ' is smaller than that of the organic copolymers (Table I). At 10^3 Hz, the ϵ' value reaches 60 at about 150°C in PAN, whereas in the poly(AN-HEMA)-I copolymer it rises to 70.¹⁹ On the contrary, in silylated copolymers, the dielectric constant increases to 20–25 in spite of the higher ϵ' value at room temperature. In other words, silylated copolymers do not show abrupt rise in ϵ' with increase in temperature.

Polydimethyl siloxane oils and resins are known for their good dielectric properties, since ϵ' and $\tan \delta$ values vary only slightly with temperature and frequency. The electrical indices of cocondensation silicone resins, however, depend on the nature and the amount of organic component.

In the present study, though the silicon moiety is present only as a side substituent instead of Si–O–Si bonds in the main backbone of the polymer as in silicones, it still influences the ϵ' value at higher temperature.

The $\tan \delta$ variations with temperature clearly show one rather prominent peak at around 110°C for poly(AN-2 MAETMS) and at about 95 – 100°C for poly(AN-2 MAPTMS), and one smaller peak at 130°C for 10^4 Hz and 115°C for 5×10^3 Hz

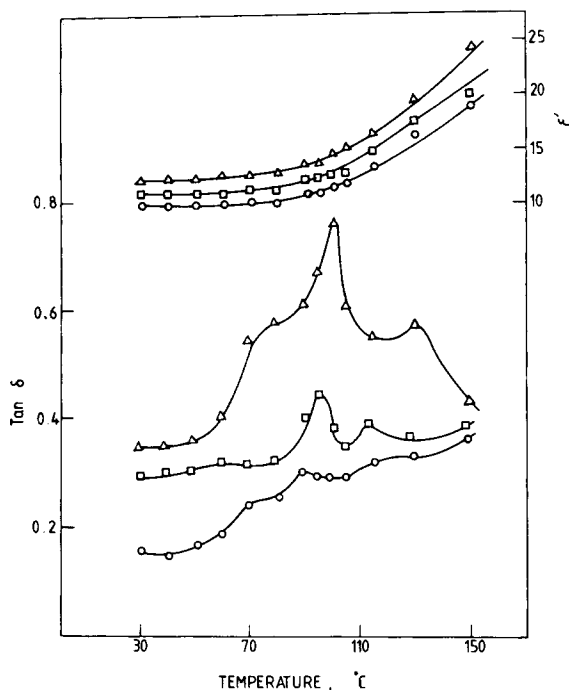


Fig. 3. Dielectric constant (ϵ') and dielectric loss tangent ($\tan \delta$) as function of temperature for AN-2MAPTMS copolymer ($m_2 = 7.8$ mole %) (symbols as in Fig. 2).

only in the case of poly(AN-2 MAPTMS) (Fig. 3). Apart from these two peaks, a broad shoulder is also apparent at the lower-temperature side of the main peak which is not well resolvable. Moreover, some interference owing to the reported β relaxation of poly(2-MAETMS)²¹ may also be expected in this region.

In these data the dielectric constant ϵ' does not seem to show a corresponding variation at these peak positions. However, the scatter of the data points may be indicative of the overlapping effects of these relaxations.

As stated in the following discussion on x-ray diffraction results of these copolymers, the introduction of silylated comonomers reduces the crystallinity, but the crystalline lattice is not affected. This indicates the presence of silylated comonomers in the amorphous part of the copolymer. The relaxations re-

TABLE I
Physical Properties of Polyacrylonitrile and Its Copolymers

Sample	m_2 (mole%) in copolymer	Density (g cm^{-3})	Crystal- linity (%)	ϵ' (30°C) at frequency 10^4 Hz	$\tan \delta_{\max}$ at frequency 10^4 Hz
PAN	—	1.1685	38.0	5.0	0.27
poly(AN-2MAETMS)	8.2	1.1663	29.9	10.5	0.62
poly(AN-2MAETMS)	15.5	1.1635	21.0	—	—
poly(AN-2MAPTMS)	7.8	1.1655	25.0	12.0	0.77
poly(AN-2MAPTMS)	13.2	1.1620	19.1	—	—
poly(AN-HEMA)-I	4.2	—	18.9	5.0	0.18
poly(AN-HEMA)-II	11.9	—	17.2	5.0	0.12

sponsible for the main peak thus seem attributable to the motion of molecular chains in the amorphous region of these copolymers. Occurrence of the peak at higher temperature for poly(AN-2-MAETMS) relative to that for poly(AN-2MAPTMS) suggests stronger intermolecular interactions of the silylated units in the former copolymer. A higher density value for poly(AN-2 MAETMS) than for poly(AN-2 MAPTMS) also suggests tighter packing in the former copolymer (Table I).

The Arrhenius plots corresponding to the main peaks for both copolymers are shown in Figure 4. Similarity in the nonlinear shapes of these curves for the copolymers with that for PAN and the fact that the relaxation of polyacrylonitrile has been shown to be the Williams-Landel-Ferry (WLF) type involving the motion of main chain in the amorphous phase¹⁹ support our above-mentioned explanation for the relaxation mechanism of main peak. The activation energies obtained through the linear extrapolations of these Arrhenius plots for both these copolymers are 40–50 kcal/mole, which is slightly lower than that for PAN.

As regards the high-temperature peak in poly(AN-2,MAPTMS) at 130°C for 10⁴ Hz, one interesting point is that its position on the temperature scale is coincident with the peaks observed for PAN. At the lowest frequency, however, the peak position could not be ascertained, probably because of the proximity of another relaxation peak. The resemblance to the PAN peak may imply the existence of longer sequences of PAN in the copolymer chain, which might account for the observed relaxation of the PAN type. Owing to the low content of the comonomer (7.8 mole %), this possibility cannot be denied. Moreover, the x-ray diffraction results also indicate the presence of uninterrupted PAN sequences in the copolymer. On this basis, the absence of this high-temperature relaxation peak in poly(AN-MAETMS) would mean either absence of such long uninterrupted PAN sequences in the copolymer chain or the presence of a very small amount of such sequences which are unable to display this high-temperature relaxation.

Higher reactivity of 2-MAETMS in comparison to 2-MAPTMS²² toward polyacrylonitrile growing radical further supports the above statement. The lower crystallinity values for poly(AN-2 MAETMS) obtained by x-ray diffraction (described below) also suggest the smaller size of such uninterrupted polyacrylonitrile sequences in this case.

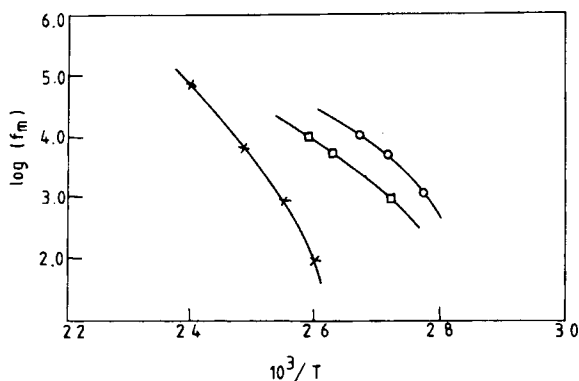


Fig. 4. Arrhenius plot— $\log f_m$ vs. $1/T$ for (X) PAN, (□) poly(AN-2MAETMS) copolymer ($m_2 = 8.2$ mole %), and (O) poly(AN-2MAPTMS) copolymer ($m_2 = 7.8$ mole %).

X-Ray Diffraction

X-ray diffraction pattern of polyacrylonitrile, poly(AN-2 MAETMS), and poly(AN-2 MAPTMS) is shown in terms of intensity I vs. 2θ (θ being the angle of diffraction), Figure 5. Since all these curves were taken under similar experimental conditions, a quantitative analysis of these results is justified.

For polyacrylonitrile, we observe three peaks: a sharp peak at $2\theta = 16.5^\circ$ (peak 1), a diffuse peak at $2\theta = 27^\circ$ (peak 2), and another small but sharp peak at 29.5° (peak 3). In the copolymers, the sharp peaks are reduced considerably, and with the increase in comonomer content (2 MAETMS or 2MAPTMS) peak 3 disappears. Peak 3 seems well consistent with the second-order Bragg reflection corresponding to peak 1. Its absence at higher comonomer content may be attributed to the lower intensity of the first-order reflections (peak 1). Peak 2 may be considered as the amorphous reflection, which is also consistent with the data reported for completely amorphous polyacrylonitrile.⁵

Crystallinity index estimated from these diffractograms according to the method suggested by Bell and Dumbleton²³ is given in Table I. The sharp peak at 16.5° corresponding to Bragg spacings about 5.4 \AA present in PAN and its copolymers is in agreement with the previous reports on polyacrylonitrile.²³ Because of the low precision in locating the diffuse reflection (peak 2), any comment about the changes produced by copolymerization would be quite unreliable.

Presence of sharp crystalline peaks 1 and 3 and diffuse amorphous reflection peak 2 clearly indicates the presence of a two-phase structure in PAN and these copolymers. Although the introduction of silylated comonomers reduces the crystallinity, the unchanged crystalline structure (on the basis of Bragg spacing)

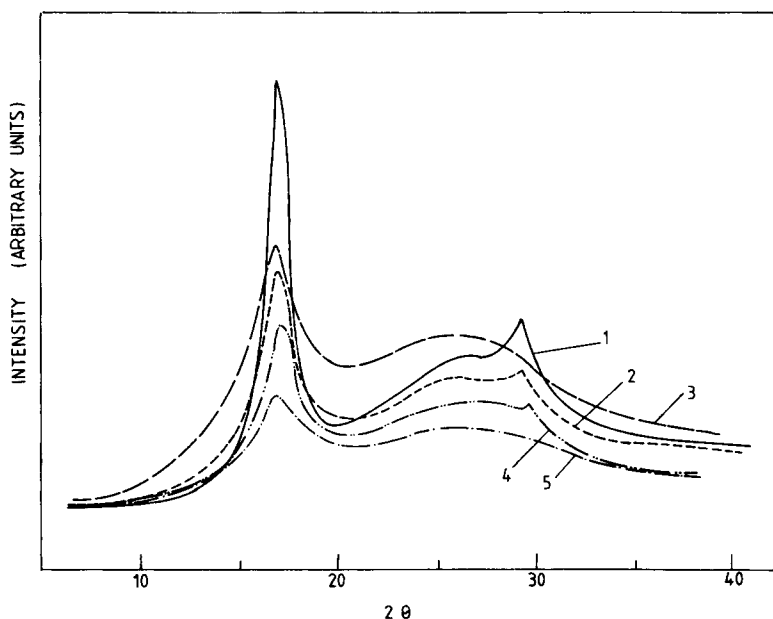


Fig. 5. X-ray diffractograms of (1) PAN; (2) AN-2MAETMS copolymer ($m_2 = 8.2$ mole %); (3) AN-2MAETMS copolymer ($m_2 = 15.5$ mole %); (4) AN-2MAPTMS copolymer ($m_2 = 7.8$ mole %); (5) AN-2MAPTMS copolymer ($m_2 = 13.2$ mole %). Same range of counts for full-scale deflection was used in all cases except curve (3), which was obtained at a lower range.

would imply that the molecular chains of these copolymers retain uninterrupted polyacrylonitrile sequences of sufficient length to form the crystalline lattice. The crystallinity index decreases with the increase in silylated comonomer content; in other words, introduction of bulky silylated side substituents hinders the crystallization of copolymers.

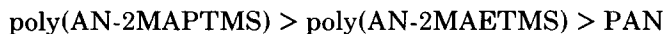
Thus, these data clearly indicate the presence of silylated comonomer units in the amorphous region, because their presence in the crystalline region should either modify the lattice (thus the Bragg spacing) or make it completely impossible to form. The formation of a completely amorphous structure may be feasible at higher comonomer content in the copolymer.

Density

The density of polyacrylonitrile samples as measured by the flotation method was found to be 1.1685, which is lower than the density data reported¹⁰ for polyacrylonitrile films prepared either in dimethylformamide (1.1776 g cm^{-3}) or from an NaCNS solution (1.1863 g cm^{-3}). This difference in density values may be related with the low-molecular packing in polyacrylonitrile disks (as compared to films) used for density measurement. The introduction of silylated acrylic comonomers reduces the density of the copolymers with respect to polyacrylonitrile. However, at equimolar concentration of 2MAETMS and 2MAPTMS, the density of poly(AN-2MAETMS) is higher than the corresponding poly(AN-2MAPTMS) copolymers. Molecular packing in polyacrylonitrile is mostly due to the strong dipole-dipole interactions between the nitrile groups of the adjacent chains. The introduction of bulky silylated acrylic monomers hinders the dipolar interactions between the nitrile groups, thereby reducing the molecular packing of polymer chains and hence the density of the copolymers. The higher crystallinity of PAN also supports their higher density because of the more compact structure of polyacrylonitrile.

Thermomechanical Behavior

The effect of silylated comonomers in poly(AN-2 MAETMS) and poly(AN-2MAPTMS) is revealed by the change in probe displacement in thermomechanical curves. As thermomechanical analysis (TMA) has been carried out on polymer pellets, true transitions may not be observed, but significant differences in the thermal expansion of samples can be seen around the second-order transition (Fig. 6). In polyacrylonitrile the probe displacement is quite low as compared to its copolymers. Moreover, the displacement in PAN begins at 42°C , whereas in copolymers it starts between 3 and 15°C , depending on the size and the amount of comonomer present in the copolymers. The order of maximum displacement has been found to be as under



In polyacrylonitrile, the chains are closely packed because of nitrile dipole-dipole attractions, but incorporation of bulky silicon side substituents in copolymers hinders the dipolar interaction; this brings some flexibility in molecular chains. This explains the lower threshold temperature and maximum probe displacement in copolymers. Rigidity of polyacrylonitrile chains is further ex-

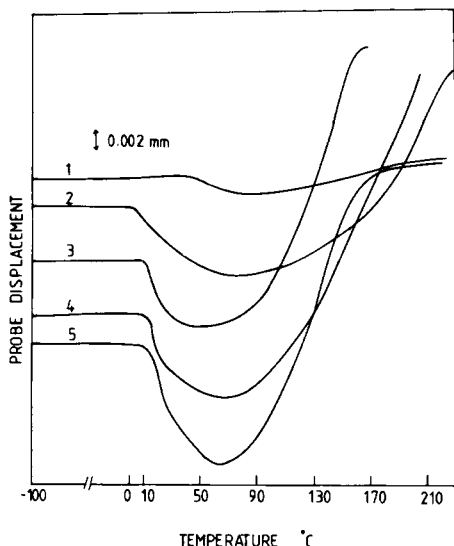


Fig. 6. Thermomechanical analysis curves of (1) PAN; (2) AN-2MAETMS copolymer ($m_2 = 8.2$ mole %); (3) AN-2MAETMS copolymer ($m_2 = 15.5$ mole %); (4) AN-2MAPTMS copolymer ($m_2 = 7.8$ mole %); (5) AN-2MAPTMS copolymer ($m_2 = 13.2$ mole %) at heating rate of $10^\circ\text{C}/\text{min}$ and load 5 g.

pressed from the temperature corresponding to maximum displacement, e.g., in PAN it is around 90°C , while in copolymers it shifts to lower temperatures (62 – 50°C) as a result of the reduction in intermolecular interactions. Under the given set of conditions, the temperature for maximum displacement may be related with the second-order transition (T_g) of the polymers.

It is interesting to mention that Nametkin et al.²⁰ have also correlated the glass transition temperature of styrene–vinyltrimethyl (phenyl)silane copolymers with the deformation in TMA curves. On the contrary, LeBlanc²⁵ has observed the absence of a clear, well-defined transition point in the vicinity of polystyrene ($T_g \approx 100^\circ\text{C}$) in styrene–butadiene block copolymers.

The probe displacement as a function of load has also been studied. In PAN, varying the load between 2 and 10 g showed no significant changes in the probe displacement, while poly(AN-2 MAPTMS) (Fig. 7) clearly brings out the effect of load on the probe. At 2-g load the probe penetration started at 28°C , which decreased to 10 – 15°C by increasing the load.

James et al.²⁶ have determined the softness of silicone rubbers by thermomechanical analysis. By varying the load, elastic modulus E was calculated with the following equation:

$$F = 16 E r^{1/2} p^{3/2}/9$$

where F is the force, r is the probe radius, and p is the penetration. The load in grams was plotted versus the TMA penetration to the $\frac{3}{2}$ power. A straight line is obtained and slope of this line will give elastic modulus values. Thus, we find that at equimolar concentration of comonomers, the elastic modulus of poly-(AN-2 MAETMS) ($m_2 = 8.2$ mole %) is $9.048 \times 10^6 \text{ dyn}/\text{cm}^2$, and in poly(AN-2MAPTMS) ($m_2 = 7.8$ mole %) the value is $6.496 \times 10^6 \text{ dyn}/\text{cm}^2$. These elastic moduli data are quite consistent with the density values also.

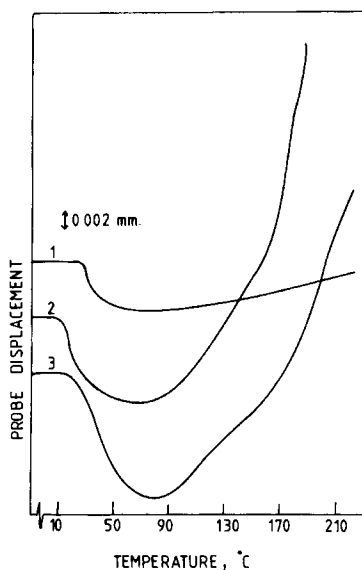


Fig. 7. Effect of load on thermomechanical analysis curves of AN-2MAPTMS copolymer (7.8 mole %) at load of (1) 2 g, (2) 5 g, (3) 10 g, and heating rate $10^{\circ}\text{C}/\text{min}$.

Thermogravimetric Analysis

Typical thermal degradation curves obtained with polyacrylonitrile and poly(AN-2MAETMS) under nitrogen atmosphere are shown in Figure 8. The thermal analysis data in Table II show that the threshold degradation temperature is lowered by the introduction of silylated acrylic monomer units into

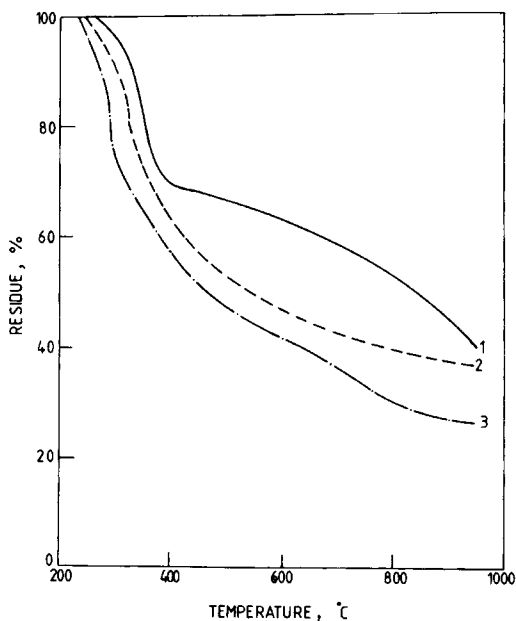


Fig. 8. Thermogravimetric analysis curves of (1) polyacrylonitrile; (2) AN-2MAETMS copolymer ($m_2 = 8.2$ mole %); (3) AN-2MAETMS copolymer ($m_2 = 15.5$ mole %).

TABLE II
Thermal Analysis of Acrylonitrile-[(2-Methacryloyloxy)Alkoxy]Trimethylsilane

Sample No.	Polymer	m_2 (mole %) in copolymer	IDT ^a	D_{\max} ^b	IPDT ^c	E^d (kcal/mole)
1	PAN	—	260	345	680	30
2	poly(AN-2MAETMS)	8.2	245	335	654	27
3	poly(AN-2MAETMS)	15.5	235	315	610	23
4	poly(AN-MAPTMS)	7.8	240	327	647	25
5	poly(AN-2MAPTMS)	13.2	225	310	632	20

^a Initial decomposition temperature.

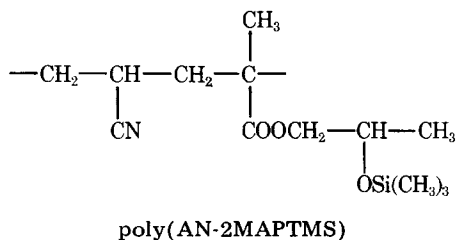
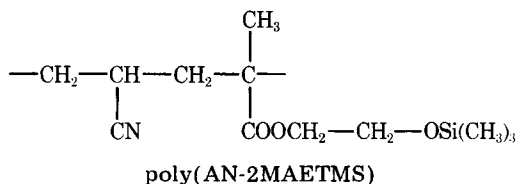
^b Maximum decomposition temperature.

^c Integral procedural decomposition temperature.

^d Activation energy for thermal degradation.

polyacrylonitrile. The mechanisms of degradation of polyacrylonitrile and its copolymer have been proposed by Grassie et al.,^{27,28} who have illustrated the effects of several comonomers on the rapid exothermic oligomerization of nitrile groups. According to them, acrylate and methacrylate copolymers give a diluent effect, there is no marked initiation or retardation of the exotherm, and the reaction is not efficiently blocked. However, in our present study, the introduction of silylated acrylic comonomer enhances the rate of degradation. The higher rate of degradation observed in the copolymers may be due to the higher amount of chain scission instead of nitrile oligomerization. This may be related to the bulky side substituents; 2MAPTMS being bulkier than 2MAETMS, the steric requirements for cyclization being less easily satisfied in poly(AN-2 MAPTMS) than poly(AN-2MAETMS). Thus, hydrogen abstraction and the chain scission become more predominant, which may be responsible for poor thermal stability of copolymers.

Further, poly(AN-2MAETMS) copolymers are more thermally stable than poly(AN-2MAPTMS), as shown from their higher D'_{\max} and IPDT values (Table II) because of their more compact structure:



Finally, activation energy of thermal degradation also confirms the above statement. The thermal stability of acrylonitrile polymers shows the following order:



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