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THERMAL AND DIELECTRIC PROPERTIES OF STYRENE AND ACRYLONITRILE COPOLYMERS WITH VINYL SILANES

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Abstract—Thermal behaviour of copolymers of styrene with 2,6-dimethyl-2,7-octadiene-6-trimethylsilyl ether (linalloxytrimethylsilane, LTMS) and [(2-methacryloyloxy) ethoxy]-trimethylsilane (2-MAETMS) and acrylonitrile-LTMS copolymers has been studied by TGA and DTA. The initial decomposition temperature (IDT) for all the copolymers is less than for polystyrene and polyacrylonitrile irrespective of the nature of the silicon comonomer. However, integral procedural decomposition temperatures (IPDT) and the activation energies for thermal degradation are higher for copolymers. Dielectric measurements have been made at temperatures between 30 and 140° in the frequency range 2.5×10^5–10^7 Hz. The higher activation energies of dipolar losses in copolymers are related to the polarity of the silicon moiety in the styrene copolymers.

INTRODUCTION

Polyorganosiloxanes are known for their ability to function over a wide range of temperatures and they exhibit good dielectric properties [1–7]. Thermal degradation of poly(phenylbutoxysiloxanes) occurs at >400° by a free radical mechanism; the first stage involves cleavage of the butoxy group [8]. For poly(dimethylsilyl propylene siloxane), cleavage of the Si-O bond occurs first at 300–400° resulting in the formation of cyclic products which, on further heating at >500°, show cleavage of Si—C bonds [3]. Attempts have also been made to introduce these unique properties of polysiloxanes in organic polymers by the introduction of a silicon moiety through copolymerization, e.g. diphenyldiphenoxysilane-4,4′-dihydroxy diphenyl sulphone copolymer showed the highest resistance to oxidative thermal degradation amongst the various poly(oxyarylenesilane) copolymers studied [9]. Nametkin *et al.* [10] also reported that styrene–vinyltrimethylsilane copolymers possess good thermal properties and the dielectric constant does not vary over the range 20–170°. Thermal behaviour of a few styrene–vinylsilane copolymers has been studied previously [11, 12].

We now report the thermal and dielectric properties of other styrene-, acrylonitrile–vinylsilane copolymers.

EXPERIMENTAL

The preparations of monomers and St-2MAETMS copolymers have been described previously [12, 13].

Copolymerizations of St–LTMS were carried out in bulk by mixing styrene and LTMS with benzoyl peroxide (0.2% by weight). The reaction was carried out at 60° for about 6 hr in nitrogen. The products were isolated by precipitation in methanol. The purified samples were dried to constant weight at 50° under vacuum. The compositions of copolymers were determined from silicon contents estimated gravimetrically. AN–LTMS copolymers were prepared similarly.

Thermogravimetric Analysis (TGA) was done on a Stanton HT-D Thermobalance in static air from room temperature to 600° at a heating rate of 6°/min. Primary thermograms were obtained from TGA traces by plotting the percentage residual weight against temperature. The activation energy of thermal degradation has been calculated by using the Dharwadkar and Karkhanawala [14] equation:

$$\ln\ln(1-\alpha)^{-1} = \frac{E^*}{RT_i^2}\cdot\frac{100}{T_f - T_i}\,\theta + C$$

where

α = weight loss at a particular temperature,
E^* = activation energy,
T_i = initial decomposition temperature,
T_f = final decomposition temperature,
$\theta = T - T_s$ where T is the temperature under consideration,
T_s = maximum decomposition temperature,
C = constant, and
R = gas constant

values of $\ln\ln(1-\alpha)^{-1}$ were plotted against the corresponding θ values. The slope of the straightline gives

$$\frac{E^*}{RT_i^2} \times \frac{100}{(T_f - T_i)}$$

from which E^* was calculated.

Differential Thermal Analysis (DTA) was done on a Stanton Redcroft differential thermal analyser, with calcined alumina as reference, at a heating rate of 6°/min. Chromel alumel was used as thermocouple.

Dielectric measurements were performed with a 'Q' meter (circuit magnification meter model DF-1245, Marconi Instruments) having a frequency range 1 KHz–300 MHz with the use of an oscillator in the temperature range 30–140°. The samples were powdered and compressed into discs 1.6 cm in dia and 0.05–0.15 cm thickness. Silver paste was applied on both surfaces of the pellet to ensure good electrical contact with the brass electrodes. The samples were inserted between the electrodes and placed in a temperature test chamber.

RESULTS AND DISCUSSION

Thermal properties of polystyrene (PS), styrene–linalloxytrimethylsilane (St–LTMS), styrene-[(2-meth-

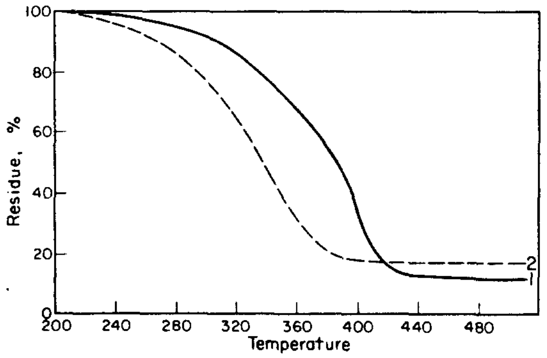


Fig. 1. Thermogravimetric Analysis: (1) Styrene (83.8)-2-MAETMS (16.2 mole %); (2) styrene (81.6)-2-HEMA (18.4 mole %) copolymer.

acryloyloxy)-ethoxy]trimethylsilane, (St-2MAETMS) copolymers and polyacrylonitrile (PAN) and acrylonitrile-linalloxytrimethylsilane (AN-LTMS) copolymers have been examined by studying their primary thermograms (Fig. 1-3). It is evident that the initial decomposition temperature (IDT) in all the copolymers is less than for polystyrene and polyacrylonitrile irrespective of the nature of the silicon comonomer. The IDT further decreases with increase of silicon content in the styrene copolymers.

The thermal stability of the copolymers has also been evaluated by finding the decomposition temperatures, T_D, at different weight losses. For St-LTMS copolymers, the rate of decomposition increases up to 320° but then the trend reverses. At 80% weight loss, the decomposition temperature of polystyrene and St-LTMS copolymers containing 3.6 and 5.4 mole % of the silicon monomer are 368, 377 and 382° respectively indicating that polystyrene decomposes at a greater rate than the copolymers. The maximum decomposition temperature in polystyrene is observed at 338° but the introduction of LTMS monomer raises the maximum decomposition temperature to 346° for 3.6 mole % and 350° for 5.4 mole % of the silicon monomer. A similar trend has also been observed in AN-LTMS copolymer having 3.6 mole % of the silane monomer as compared to that of polyacrylonitrile (Table 1).

Thermal analysis of copolymers St-2MAETMS St-2HEMA having 16.2 and 18.4 mole % acrylate units respectively have been carried out in order to

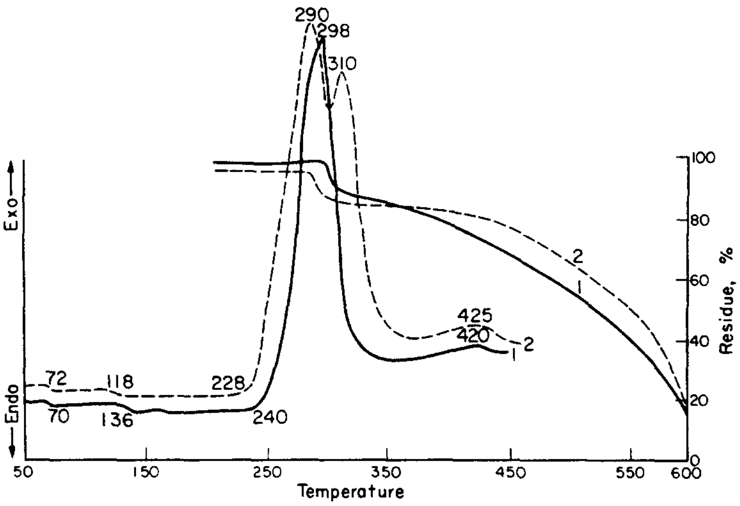


Fig. 2. TGA and DTA traces of (1) Polyacrylonitrile; (2) acrylonitrile (96.4)-LTMS (3.6 mole %) copolymer.

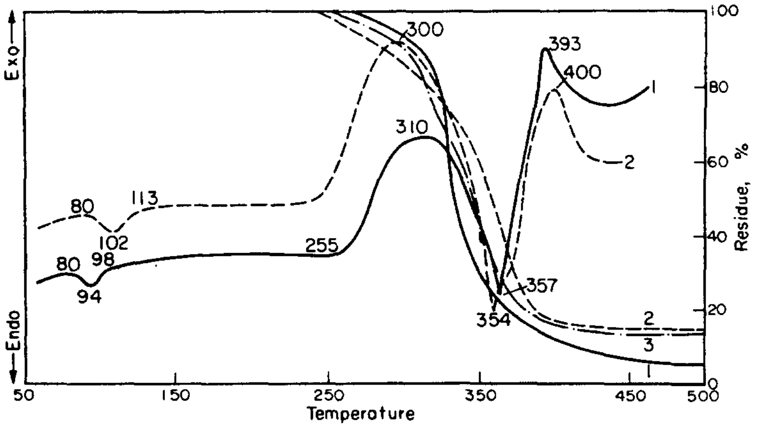


Fig. 3. TGA and DTA traces of (1) Polystyrene; (2) styrene (94.6)-LTMS (5.4 mole %); (3) styrene (96.4)-LTMS (3.6 mole %) copolymer.

Table 1. Thermogravimetric and glass transition temperature. Data of styrene, acrylonitrile and vinylsilicon polymers and copolymers

Sl. No.	Polymer*	m_2, mole % of silicon comonomer in copolymer	D_{max}	IPDT	E^* kJ/mole	T_g
1.	Polystyrene	0	338	357	67 ± 15	94
2.	Poly (St-LTMS)	3.6	346	365	105 ± 13	97
3.	Poly(St-LTMS)	5.4	350	370	105 ± 8	102
4.	Polyacrylonitrile	0	478	501	113 ± 18	70
5.	Poly (AN-LTMS)	3.6	485	511	122 ± 16	72
6.	Poly (St-2 MAETMS)	16.2	354	359	109 ± 15	—
7.	Poly (St-2 HEMA)	18.4	324	347	97 ± 9	—
8.	Poly(St-2 MAETMS)	18.9	—	—	—	99
9.	Poly (St-2MAETMS)	34.6	—	—	—	103
10.	Poly (2 MAETMS)	100	—	—	—	112

* St—Styrene; LTMS—Linalloxytrimethylsilane; 2 MAETMS—[(2 methacryloyloxy)ethoxy]-trimethylsilane; AN—acrylonitrile.

evaluate the effect of the silicon moiety in styrene copolymers. It has been found from the thermograms (Fig. 1) that the initial decomposition temperature of St-2HEMA is less than that of St-2MAETMS copolymer and also the decomposition of the former is greater than that of the latter up to 420°, thereafter the trend reverses. This effect could be perhaps due to the formation of crosslinks in the St-2HEMA as a result of loss of water.

The thermal stability of silicon copolymers, as deduced from the integral procedural decomposition temperatures and energies of activation (Table 1), are higher than for polystyrene and polyacrylonitrile. This reveals that introduction of silane moiety enhances the thermal stability.

Differential thermal analysis

The glass transition temperatures of the copolymers irrespective of the nature of the substituent are higher than for polystyrene (Table 1). The higher T_g of the copolymers may be due to the presence of bulky side groups which hinder the rotation of the units. The higher T_g has also been observed in St-2MAETMS and St-vinyltriacetoxysilane copolymers [11, 12].

The DTA trace of PAN exhibits a major exotherm starting at 240° with a maximum at 298° (Fig. 2), followed by an endothermic dip at 350° with a small exothermic peak near 420°. Besides affecting the intermolecular forces and the backbone rigidity, the presence of foreign units in copolymers often interferes with the cleavage of the molecule during thermal degradation. In AN-LTMS polymer with 3.6 mole per cent silicon monomer, the first major exotherm occurs at 290° with a shoulder peak at 310°. Hence the threshold degradation temperature is lowered by the introduction of LTMS units into PAN.

A broad exotherm in polystyrene begins at about 255°, has a peak at 310° and another exotherm at 393°; whereas in the copolymer, the first exotherm begins at 240° with a peak at 300°. However, the second exotherm is shifted upwards, i.e. 400° (Fig. 3). From DTA data, it may be concluded that, in both the AN-LTMS and St-LTMS copolymers, the first major exotherm is shifted to a lower temperature due to the introduction of silicon comonomer. These results are in agreement with the initial decomposition values obtained by TGA.

Dielectric measurements

Dielectric data for polystyrene, poly[(2 methacryloyloxy)ethoxy]trimethylsilane and styrene–vinylsilicon copolymers in the range 30–140° at 2.5 × 10^5 to 10^7 Hz are shown in Figs. 4–6. The dielectric constants, ϵ', of polystyrene and its copolymer (styrene–linalloxytrimethylsilane) are 2.54 and 2.56 respectively, indicating that the introduction of silane monomer (5.4 mole %) does not affect the ϵ' value. The dielectric constant of polystyrene and its copolymer gradually decrease with the increase of temperature at all frequencies because of the thermal expansion of the polymers. However, the dielectric constant decreases abruptly above T_g.

The dielectric losses are very low with tan $\delta \simeq 3 \times 10^{-4}$ over the frequency range 2.5 × 10^5–10^7 Hz at 30° in polystyrene and styrene–linal-

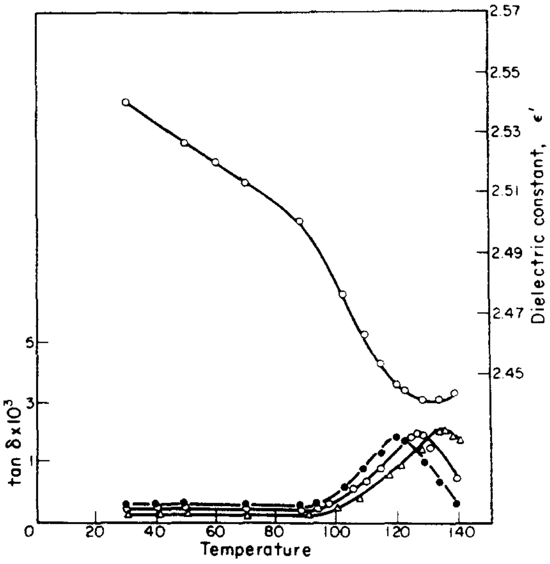


Fig. 4. Dielectric constant and dielectric loss tangent as a function of temperature for polystyrene. ●, 2.5 × 10^5 Hz; ○, 1 × 10^6 Hz; △, 1 × 10^7 Hz.

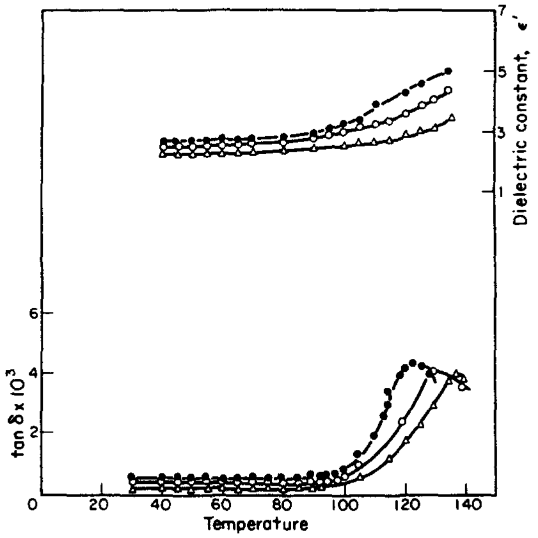


Fig. 5. Dielectric constant and dielectric loss tangent as a function of temperature for styrene (92.3)-2-MAETMS (7.7 mole %). ●, 2.5 × 10^5 Hz; ○, 1 × 10^6 Hz; △, 1 × 10^7 Hz.

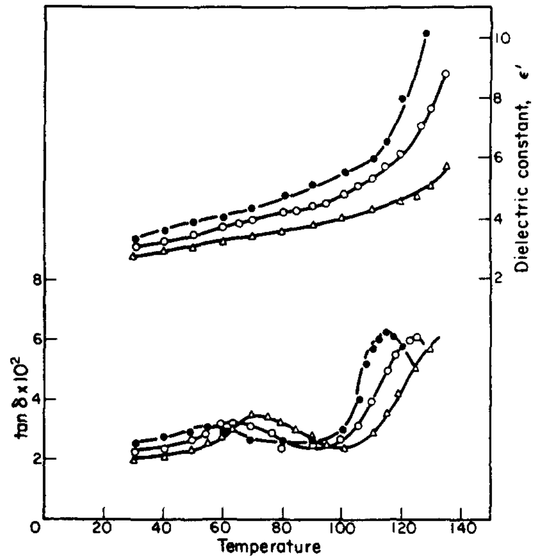
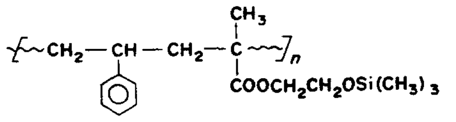


Fig. 6. Dielectric constant and dielectric loss tangent as a function of temperature for poly [(2 methacryloyloxy)-ethoxy]trimethylsilane. ●, 2.5 × 10^5 Hz; ○, 1 × 10^6 Hz; △, 1 × 10^7 Hz.

loxytrimethylsilane copolymer (Table 2). This result is in agreement with the losses obtained for polystyrene by Von Hippel [15] over the range 10^2–10^{10} Hz at 25°. The dielectric loss appears to be independent of temperature up to the glass transition region, above which there is the α-relaxation peak in polystyrene in the range 120–135° over the frequency range 2.5 × 10^5–10^7 Hz with tan $\delta_{max} \simeq 3 \times 10^{-3}$ (Fig. 4) as observed by Saito and Nakajima [16]. The α-relaxation peak appears to be due to deformations accompanied by changes in the directions of dipoles. With increase of frequency, tan δ_{max} shifts towards higher temperatures.

Introduction of the polar silicon side substituent in polystyrene (the group being bulkier than the phenyl group) further shifts tan δ_{max} towards higher temperatures, i.e. 124–136° in the same frequency range; this effect may be related to the hindrance of main chain motions (dipole segmental motion).

The higher ε' value in St-2MAETMS copolymer as compared to St-LTMS copolymer may be related to the higher polarity of the silicon side substituent



Unlike polystyrene and St-LTMS copolymer, the dielectric constant of St-2MAETMS copolymer is almost independent of temperature below T_g; however, it increases with increase in temperature beyond the glass transition region. This observation has also been made for polymethyl methacrylate and poly α-chloromethacrylate [17].

The dielectric loss peak in St-2MAETMS is also higher than for polystyrene and St-LTMS copolymer. This effect may also be due to the restricted rotation of the main chain segments because of the methyl and $-COOCH_2-CH_2OSi(CH_3)_3$ substituents in the copolymer (Fig. 5). By comparing tan δ_{max} of polystyrene, St-LTMS and St-2MAETMS, one may say that higher the polarity of the polymer the greater will be the magnitude of relaxation.

In the case of poly[(2 methacryloyloxy)ethoxy]-trimethylsilane (Fig. 6), the dielectric constant is 3.3–2.7 over the frequency range 2.5 × 10^5–10^7 Hz, i.e. higher than styrene copolymers. It is interesting to note that a small β peak at 55° along with a large α peak at 115° was also observed in the case of 2-MAETMS polymer. The β process in 2-MAETMS polymer may be attributed to the dipole group losses perhaps associated with the rotation of $-COOCH_2CH_2O Si(CH_3)_3$ side groups. This process may be identical

Table 2. Dielectric properties of styrene-vinylsilicon copolymers

Sl. No.	Polymer*	m_2, mole % of silane comonomer in copolymer	T_g	ε' Frequency 2.5 × 10^3 Hz at 30°	tan δ × 10^3 frequency range 2.5 × 10^5–10^7 Hz at 30°
1.	Polystyrene	0	94	2.54	0.3–0.4
2.	Poly (St-LTMS)	5.4	102	2.56	0.3–0.6
3.	Poly (St-2MAETMS)	7.7	97	2.7	0.3–0.7
4.	Poly (2-MAETMS)	100	112	3.7	20–26

* St—styrene; LTMS—linalloxytrimethylsilane; 2 MAETMS—[(2 methacryloyloxy)ethoxy]-trimethylsilane.

with those in polyalkyl α-chloro-acrylates [17]. Absence of the β peak in the copolymer however may be due to the low content of silicon comonomer in St-2 MAETMS copolymer. Mikhailov and Krasner [18] also did not obtain a peak for styrene–methyl methacrylate copolymer having even 24 mole % of methyl methacrylate.

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