Effect of Silicon Comonomers on Thermal Degradation of Polystyrene

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Synopsis

The thermal degradation of the following organosilicon copolymers: styrene–vinylmethyl-diacetoxysilane, styrene-2-methacryloyloxypropoxytrimethyl silane, styrene–(dimethyl) siloxane–methylvinylsiloxane) diol and hexamethyl cyclotrisiloxane–styrene–hexamethyl cyclotrisiloxane was investigated. The techniques of thermogravimetry, thermomechanical analysis, and differential scanning calorimetry (DSC) were used. The initial decomposition temperature for all the copolymers except styrene–siloxane block copolymers was less than that for polystyrene irrespective of the nature of the silicon comonomer. Integral procedural decomposition temperature of copolymers was higher than that for polystyrene except styrene-2-methacryloyloxy propoxytrimethyl silane copolymers which were showing lower (IPDT) values. Styrene–siloxane copolymers were found to be most thermally stable. Variation in the glass transition temperature and probe displacement under stress is related to the polarity of the silicon moiety in the styrene copolymers.

INTRODUCTION

Polyorganosiloxanes are known for their higher thermal resistance and ability to function over a wide range of temperature. Thermal degradation of poly (phenyl butoxy-silaxanes) occurs at 400°C by a free radical mechanism, the first stage involves cleavage of the butoxy group.[1] For poly(dimethyl silylpropylene siloxane), cleavage of the Si—O bond occurs first at 300–400°C, resulting in the formation of cyclic products which on further heating at 500°C show cleavage of Si—O bonds.[2] The degradation by Si—O bond fracture leads to cyclic product formation while Si—C rupture causes methane formation in hydroxyterminated PDMS. Mechanism of thermal degradation of polydimethylsiloxane (PDMS) was proposed proceeding through terminal end groups (hydroxy groups) and residual acids or alkalies functioning as a catalyst.[3-5] Grassie and MacFarlane[6] has also reported the thermal degradation of PDMS under vacuum.

The volatile products are mixture of cyclic oligomers from trimer upwards. However, in presence of KOH, formation of methane appears to be significant indicating that the action of KOH on thermal degradation of PDMS does not involve chain terminal groups.

Attempts have been made to introduce these unique properties of polysiloxanes in organic polymers by incorporating silicone moiety through copolymerization, e.g., diphenyl–diphenoxysilane–4-4'-dihydroxy diphenylsulfone copolymer showed the highest resistance to thermooxidative deg-

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radation among the various poly(oxyarylene silane) copolymers studied.[7] Nametkin et al.[8] also reported that styrene vinyltrimethylsilane copolymers possess good thermal properties. Synthesis, characterization, and thermal behavior of styrene–vinyl silane and styrene–silaxone copolymers have been reported by us.[9-13]. We now report the relative influence of four structurally different vinyl silicon comonomers, e.g., vinylmethyl–diacetoxysilane (VMDAS), (2-methacryloyloxypropoxytrimethylsilane) (2-MAPTMS), poly(DMS–MVS) diol, and hexamethylcyclotrisiloxane (D_3) on thermal behavior of polystyrene.

EXPERIMENTAL

The purification of styrene, AIBN, toluene, tetrahydrofuran (THF), and preparation of VMDAS and (2-MAPTMS) have been reported previously.[11-14] Hexamethyl cyclotrisiloxane (D_3) and poly(dimethylsiloxane–methyl vinyl siloxane) diol, poly (DMS–MVS) diol were prepared by low temperature hydrolysis of dimethyldichlorosilane and mixture of dimethyldichlorosilane and methylvinyl dichloro silane (1:1 by volume), respectively.[14]

Lithium biphenyl[14] was synthesized by reacting lithium metal with biphenyl in THF at room temperature under anhydrous conditions.

COPOLYMERIZATION

Styrene was copolymerized with each of VMDAS, 2-MAPTMS, and poly(DMS–MVS) diol at 60°C in toluene using 1 mol % AIBN and dilution of 4 mol/L in an inert atmosphere. Styrene was copolymerized anionically with D_3 using lithium biphenyl as intitiator to get poly(dimethylsiloxane–styrene–dimethyl siloxane) P(DMS–St–DMS) block copolymers (Table I). Anionic copolymerization was carried out under high vacuum (10^{-4} mm Hg) with a syringe technique in a specially designed reaction tube. Polymerization was initiated by introduction of lithium biphenyl in THF to which few drops of styrene monomer in toluene were added by syringe through rubber septum at low temperature (0°C).

The dark red color of living polystyrene was formed, and to this D_3 in THF (solvent for D_3) was added, giving poly(dimethylsiloxane–St–dimethyl siloxane) [P(DMS–St–DMS)] block copolymers. The composition of copolymers was determined from their silicon content estimated gravimetrically.

Polymer Characterization

The intrinsic viscosity was determined in toluene at 30°C using an Ubbelohde suspension level viscometer. Molecular weight distribution (MWD) of polymers were studied from GPC data recorded on Waters Associates Liquid Chromatograph Model LC, GPC-244 using μ-styragel columns and toluene as a mobile phase.[11] DSC (Perkin-Elmer DSC-2 Model) was used for determining the glass transition temperature of styrene copolymers.

Thermomechanical measurements were carried out on compressed polymer sample disks (thickness 0.2 cm) using stanton Redcroft thermomechanical analyzer TMA 691 and a constant load of 5 g was applied to the quartz probe.

The thermogravimetric analysis were carried out with a stanton Redcroft TG-750 thermobalance in static air from room temperature to 900°C at a heating of 10°C/min. Thermal stability of polymers is expressed in terms of IPDT calculated according to Doyle's method.

RESULTS AND DISCUSSION

In Table II is listed a summary of the various styrene copolymers used in conjunction with this study. It is noted that free radical polymerization of styrene with vinyl silane gives polymer of low mol wt, and MWD is also very broad. Silicon content and hence vinyl silane is also less in the copolymer whereas styrene–siloxane block copolymers are of high mol wt, narrow mol wt distribution and higher silicon content. However, styrene–siloxane graft copolymers poly(DMS–MVS-g-St) are intermediate of the two.

Glass Transition Temperature Studies

T_g data of the copolymers from DSC studies show higher T_g in styrene–VMDAS copolymers, while T_g in St–MAPTMS copolymers is low compared to that of polystyrene (Table III). The higher T_g value in this series of copolymers (St–VMDAS) may be related to the steric and polar factors associated with Si(OAC)$_2$ side groups which hinder the chain mobility. The copolymers thus show higher T_g value. On the other hand, the decrease in

TABLE I
Copolymerization of Styrene (A) with Vinyl Silicon Comonomers

S No		Comonomers (B)	Type of copolymer formed
1	VMDAS	$CH_2 = CH$ $\mid$ $H_3C - Si - (OAc)_2$ $\mid$ CH_3	Random, AAABAABAAAA
2	2-MAPTMS	$CH_2 = C$ $\mid$ $COOCH_2CHCH_3$ $\mid$ $OSi(CH_3)_3$	Random, ABAAABBABAAA
3	P(DMS–MVS) diol	$HO \left(\begin{matrix} CH_3 & CH_3 \\ \mid & \mid \\ Si - O - Si \\ \mid & \mid \\ CH_3 & CH_2 = CH \end{matrix} \right)_n OH$	Graft, B-g-A
4	D$_3$	$(H_3C \rightarrow)_2 Si$ ... $Si - (CH_3)_2$ ... $\longrightarrow 3 - \begin{matrix} CH_3 \\ \mid \\ Si - O - \\ \mid \\ CH_3 \end{matrix}$	Block, BAB

TABLE II
Characterization of Polystyrene and Their Copolymers

| Polymer | Composition | | | $[\eta]$ (dL g^{-1}) | $\dfrac{\overline{M}_w}{\overline{M}_n}$ |
	Silicon content (%)	Vinyl silane/ siloxane units (wt %)	Silicon comonomer in copolymer (mol %)		
Polystyrene				0.19	1.6
P(St–VMDAS)	1.51	10.1	5.8	0.17	2.5
P(St–VMDAS)	3.80	25.5	15.9	0.15	2.7
P(St–2MAPTMS)	2.42	18.6	10.0	0.17	1.9
P(St–2MAPTMS)	4.25	32.7	19.0	0.13	2.2
P(DMS–MVS-g-St)	3.60	11.1		0.14	2.2
P(DMS–MVS-g-St)	6.30	17.9		0.16	2.3
P(DMS–St–DMS)	13.5	35.6	5.93	0.23	1.2
P(DMS–St–DMS)	18.6	49.0	8.38	0.26	1.3

T_g in St–2-MAPTMS copolymer series may be explained on the basis attributed to the chemical nature and size of side groups. As the bulkiness of the side substituent increases, total cohesive energy density of the polymer system decreases, leading to low T_g values. In fact, by introducing bulky side group, the chain mobility is hindered, sterically. However, in the present work the bulky side substituents (2-MAPTMS) reduce the intermolecular interactions considerably, thus leading to low T_g values. Similarly low T_g values were observed for (siloxane–St–siloxane) block and styrene–siloxane graft copolymers. Silicones as such show T_g below room temperature (−123°C), thus thereby lowering the T_g of polystyrene, when DSC studies of styrene–siloxane copolymers were carried out above room temperature.

Thermomechanical Analysis

A study of the thermomechanical behavior of polystyrene and P(St–2-MAPTMS), P(St–siloxane) block, and graft copolymers under similar experimental conditions reveal the effect of 2-MAPTMS and siloxane comonomers on the thermal behavior of polystyrene under deformation

TABLE III
Thermal Behavior of Polystyrene and Its Copolymers

Polymer	Comonomer in copolymer (wt %)	T_g (°C)	IDT (°C)	D_{max} (°C)	IPDT (°C)
Polystryene	—	98	275	365	368
P(St–VMDAS)	10.1	101	255	396	386
P(St–VMDAS)	25.5	105	235	420	410
P(St–2MAPTMS)	18.6	78	265	351	346
P(St–2MAPTMS)	32.7	74	245	333	319
P(DMS–MVS-g-St)	11.1	96	265	399	395
P(DMS–MVS-g-St)	17.9	94	260	420	428
P(DMS–St–DMS)	35.6	89	295	425	467
P(DMS–St–DMS)	49.0	85	325	457	518

condition (Fig. 1). Transitions associated with polystyrene and copolymers, particularly T_g as observed by DSC studies, were absent in the TMA curves. But significant change in probe displacement is observed, and thermal expansion of copolymers can be seen in the vicinity of the second order transition. In polystyrene, the displacement begins at 60°C detected by the shift in base line of the displacement vs. temperature curve, but the penetration of the probe is poor due to the rigid chain structure of polystyrene. Therefore, polystyrene (PS) does not show substantial degree of change in displacement. In (St–2-MAPTMS) copolymers displacements starts between
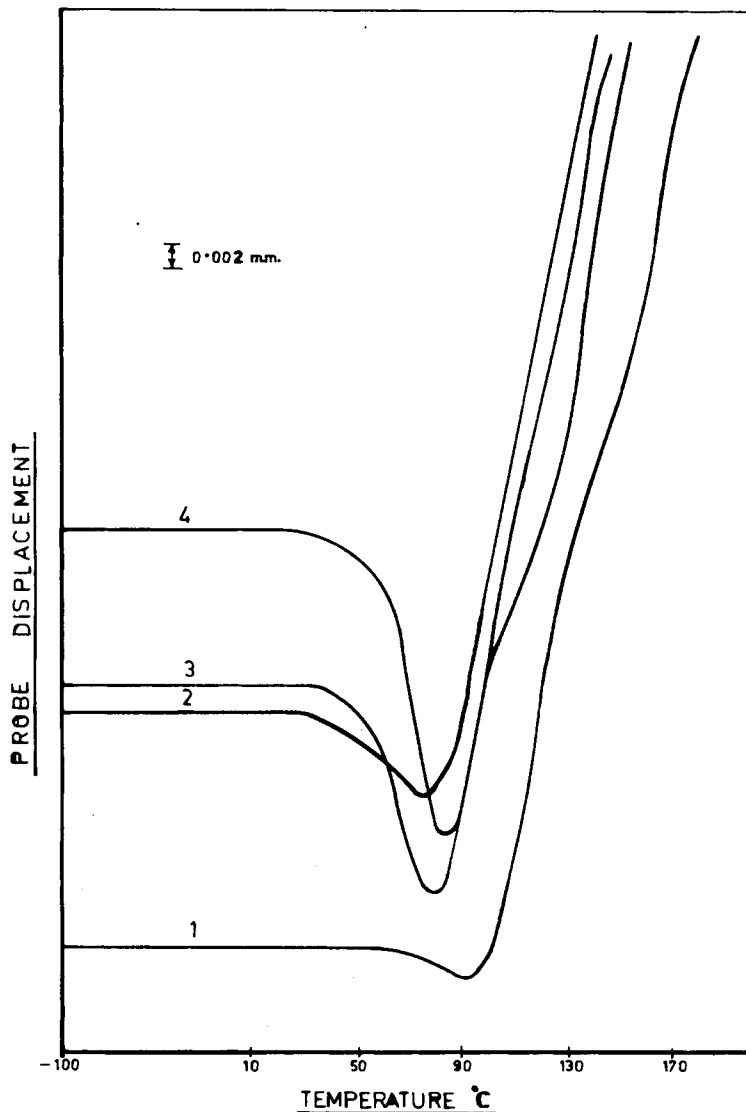

Fig. 1.   Thermomechanical analysis of: (1) polystyrene; (2) P(St–2MAPTMS), $m_2 = 18.6$ wt %; (3) P(DMS–MVS-g-St), siloxane content $=$ 17.9 wt %; (4) P(DMS-b-St-b-DMS), siloxane content $=$ 35.6 wt %.

35 and 45°C, depending on the size and the amount of 2-MAPTMS present in the copolymers. In these copolymers due to the bulky side substituent, molecular packing is reduced and probe displacement starts at lower temperature. P(St–siloxane) block and graft copolymers also give probe displacement at lower temperature (25–35°C) due to the presence of rubbery siloxane units. The probe displacement was higher in case of siloxane–St–siloxane block copolymers compared with P(PDMS–MVS-g-St) graft copolymers and styrene–2-MAPTMS copolymers. The displacement is maximum in P(DMS–St–DMS) block copolymers (m_2 = 40 wt % siloxane) having the highest amount of silicon comonomer. The temperature for maximum displacement may correspond to the glass transition temperature of polymers under a given load. Nametkin et al.[15] have also correlated the glass transition temperature of styrene–vinyl trimethyl (phenyl) silane copolymers with the deformation in TMA curves, while LeBlanc[16] has observed the absence of a clear and well-defined transition point in the vicinity of polystyrene ($T_g \approx$ 100°C) in styrene–butadiene block copolymers.

Thermogravimetric Analysis

Effect of silicon comonomers on thermal stability of polystyrene was studied by thermogravimetric analysis. Thermograms obtained by plotting percentage residual weight against temperature for polystyrene, P(St–VMDAS), P(St–2-MAPTMS), and styrene–siloxane block and graft copolymers are given in Figures 2–4. A perusal of thermal analysis data (Table III) reveals that initial decomposition temperature (IDT) is lowered by the introduction of silicon comonomer in polystyrene except in styrene–siloxane block copolymers. The IDT of St–VMDAS (m_2 = 15.9 mol %) is 235°C, in St–2-MAPTMS copolymer (m_2 = 19.0 mol %) the IDT is 245°C, and the
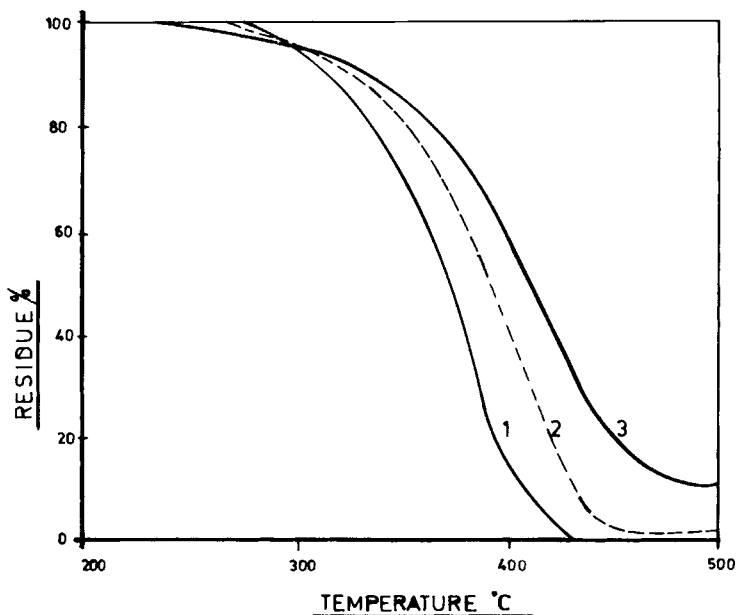
Fig. 2. TGA thermograms for: (1) polystyrene; (2) P(St–VMDAS), m_2 = 5.8 mol %, 10.1 wt %; (3) P(St–VMDAS), m_2 = 15.9 mol %, 25.5 wt %.
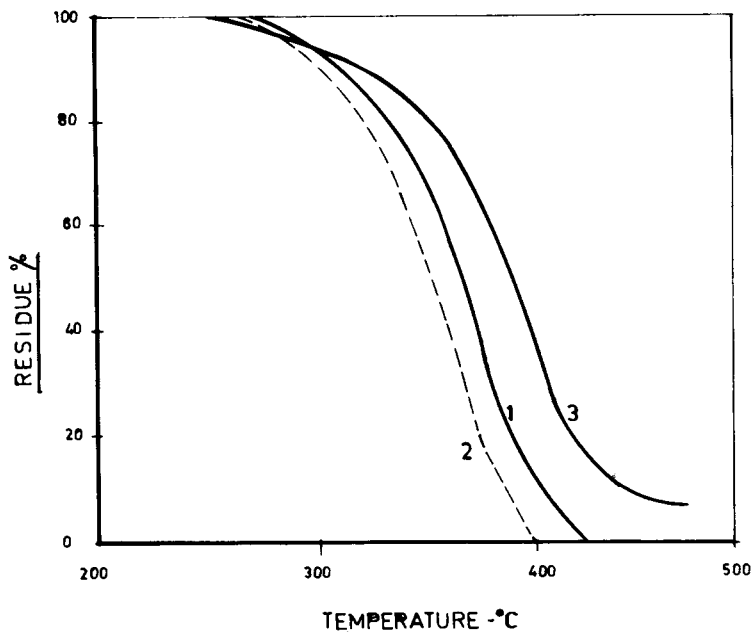
Fig. 3.   TGA thermograms for: (1) polystyrene; (2) P(St–2MAPTMS), m_2 = 10.0 mol %, 18.6 wt %; (3) P(DMS–MVS-g-St), siloxane content = 17.9 wt %.

IDT of styrene–siloxane graft copolymer (17.9 wt % siloxane) P(DMS–MVS-g-St) is 260°C in comparison to the IDT of polystyrene (275°C). However, IDT of styrene–siloxane block copolymers P(DMS–St–DMS) was higher than that of polystyrene. The threshold temperature for weight loss further increases in styrene–siloxane block copolymers with an increase in the siloxane content.
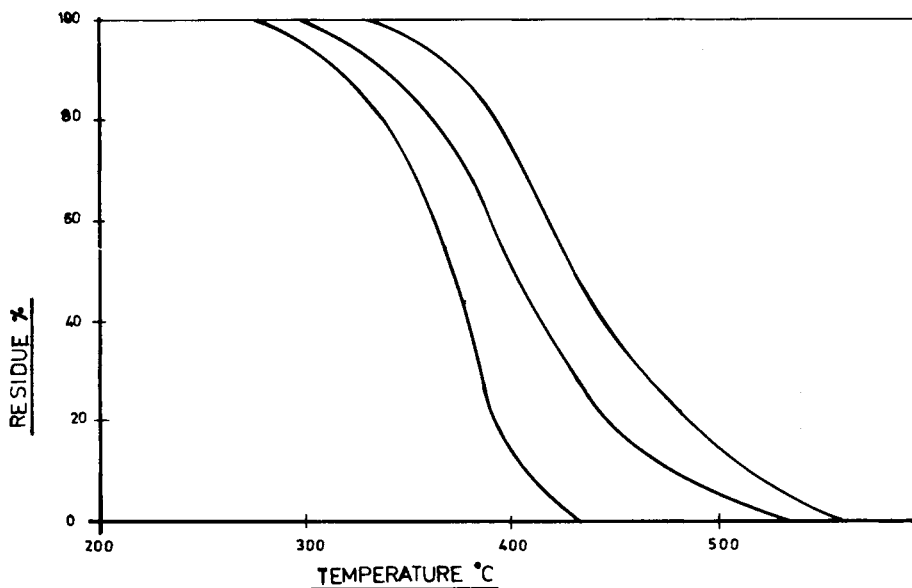

Fig. 4.   TGA thermograms for: (1) polystyrene; (2) P(DMS-b-St-b-DMS), siloxane content = 35.6 wt %; (3) P(DMS-b-St-b-DMS), siloxane content = 49.0 wt %.

The relative thermal stability of various copolymers was also evaluated from these thermograms from the decomposition temperature at different weight losses.

The decomposition rate is higher for St–VMDAS copolymers in the initial stage but trend reverses after 300°C (Fig. 2). In other words, the rate of decomposition is reduced after 300–325°C in copolymers with respect to polystyrene. Higher rate of decomposition in the initial stage may be due to the presence of strong electron withdrawing side substituent, $Si(OAC)_2$. This will induce the cleavage of Si—C and Si—O bonds, thereby liberating acetic acid along with other volatile products. The maximum decomposition temperature (D_{max}) in polystyrene occurs at 365°C, but the introduction of VMDAS monomer in the styrene copolymer raises the D_{max} to 396°C for 5.8 mol % and 426°C for 15.9 mol % of VMDAS. So the effect appears to be more pronounced with the increase of silicon content.

To make a comparative study, thermal degradation of St–2-MAPTMS copolymers was studied. As the copolymers with exact mol % of various silane comonomers were not obtained, it is, therefore, not possible to make direct correlation between the nature of the silicon side substituents and thermal behavior of the copolymers. Initial decomposition temperature IDT of St–VMDAS is higher than for St–2-MAPTMS copolymers (Table III). Further the rate of decomposition in styrene-silylated methacrylate copolymers is faster than polystyrene and St–VMDAS copolymers (Fig. 3). The D_{max} is also lowered by the introduction of 2-MAPTMS comonomer into polystyrene. Introduction of bulky electron withdrawing side substituent therefore may be responsible for the lower IDT of these copolymers. This suggests that nature of the substituent influences the nature of decomposition.

Thermogravimetric curves of styrene–siloxane graft and block copolymers were also compared with that of polystyrene (Fig. 4). IDT of styrene–siloxane diol copolymers P(DMS–MVS-g-St) (17.9% siloxane) is 260°C lower that of polystyrene (275°C). In case of block copolymers P(DMS–St–DMS), IDT is 295 and 320°C, respectively, for 35.6 and 49.0 wt % siloxane comonomer, higher than polystyrene. D_{max} of styrene–siloxane block copolymers is also higher compared to polystyrene and other copolymers. The higher D_{max} and IDT data of styrene–siloxane block copolymers compared to that of styrene–siloxane graft copolymers (where siloxane units are attached to polystyrene in the side chain) and polystyrene may be due to the presence of Si–O–Si units in the polystyrene backbone.

Thermal stability of copolymers has also been determined by calculating IPDT values. The IPDT values of St–VMDAS, poly(DMS–MVS–O–St), and poly(DMS–St–DMS) are higher than that for polystyrene (Table III). The higher thermal stability of VMDAS may be due to the presence of polar bulky side substituents $Si(OAC)_2$ in the polystyrene chain. Introduction of siloxane units both as side substituent and in the backbone improves the thermal stability of polystyrene. The higher IPDT values for styrene–siloxane block copolymer compared with styrene–siloxane diol graft copolymer accounted for higher thermal stability of these polymers. The higher stability[5] of styrene–siloxane block copolymers may be explained due to the presence of Si—O—Si bonds which have higher bond energy and low

reactivity of depolymerizing radicals due to the neighboring methyl groups $(CH_3)_2Si$ groups. Moreover, at higher temperatures, some cyclic siloxane structures may also be formed or some intermolecular cross linking will enhance the thermal stability of the block copolymers. In styrene–siloxane graft copolymers, Si—O—Si units present in the side chain increasing thermal stability to lesser extent in comparison to poly(DMS–St–DMS). However, the introduction of 2-MAPTMS in polystyrene backbone, thermal stability decreases as evidenced from their lower IPDT values. These copolymers may be arranged in the order of decreasing thermal stability as follows:

P(DMS–St–DMS) > P(DMS–MVS-g-St)

> P(St–VMDMS) polystyrene > P(St–2-MAPTMS)
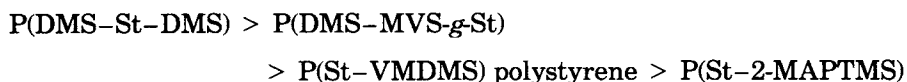
The above thermal stability data led us to the conclusion that nature of silicon moiety plays an important role in changing the thermal stability of polystyrene. Thermal stability was greatly enhanced by introduction of siloxane units (Si—O—Si) in the backbone of polystyrene as indicated by higher D_{max} and IPDT values.

References

1. A. I. Sidnev, Yu. L. Khavashehevskaya, A. F. Moiseev, I. A. Zubkov, and A.-N. Pravednikov, *Vysokomol. Soedin,* **A12**, 2656 (1970); *Chem. Abstr.,* **74**, 100436t (1971).

2. K. A. Andrianov, G. Garzo, T. Szekely, M. Blazso, L. M. Volkova, N. V. Delazari, and J. Tamas, *Vysokomol. Soedin.,* **B13**, 593 (1971); *Chem. Abstr.,* **76**, 47087 (1972).

3. V. V. Rode, M. A. Verkhotin, and S. R. Rafikov, *Vysokomol. Soyed* **A11**, 1529 (1969).

4. K. A. Andrianov, V. S. Papkov, G. L. Slonimskii, A. A. Zhdanov and S. Ye. Yakushkina, *Vysokomol. Soyed* **A11**, 2030 (1969).

5. Yu. A. Aleksandrova, J. S. Nikitina, and A. N. Pravednikov, *Vysokomol. Soyed,* **A10**, 1078 (1968).

6. N. Grassie and I. G. MacFarlane, *Eur. Polym. J.,* **14**, 875 (1978).

7. E. D. Arsen'eva, N. V. Aulova, M. B. Fromberg, N. P. Gashmikova, and A. G. Grozdov, *Vysokomol. Soedin* **14**, 212 (1972); *Chem. Abstr.,* **76**, 127589 y (1972).

8. N. S. Nametkin, I. N. Kozhukhova, S. G. Durga'yan, and V. G. Filippova, *Vysokomol. Soedin.* **A11**, 2869 (1969).

9. P. Bajaj, Y. P. Khanna, and G. N. Babu, *J. Polym. Sci.* **14**, 465 (1976).

10. P. Bajaj and G. N. Babu, *Eur. Polym. J.,* **13**, 305 (1977).

11. P. Bajaj and D. C. Gupta, *Eur. Polym. J.,* **15**, 271 (1979).

12. P. Bajaj and D. C. Gupta, *J. Polym. Sci.,* **21**, 1347 (1983).

13. P. Bajaj, S. K. Varshney, and A. Mishra, *J. Polym. Sci.,* **18**, 295 (1980).

14. P. Bajaj, D. C. Gupta, and S. K. Varshney, *Polym. Eng. Sci.,* **23**, 820 (1983).

15. N. S. Nametkin, V. G. Filippova, and S. G. Durgar'yan, *Vysokomol. Soedin.* **A10**, 2216 (1968).

16. J. L. LeBlanc, *J. Appl. Polym. Sci.,* **21**, 2419 (1977).

17. M. Blazso and T. Szekely, *Eur. Polym. J.,* **10**, 733 (1974).