Syntheses and properties of tetramethyl-*p*-silphenylenesiloxane/alkenylmethylsiloxane copolymers and their derivatives

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Tetramethyl-*p*-silphenylenesiloxane/alkenylmethylsiloxane (TMPS/AMS) copolymers were snyhtesized from *p*-bis-dimethylhydroxysilylbenzene and a series of alkenylmethyldichlorosilanes as the starting materials. The alkenyl groups of the copolymers were vinyl, allyl, 2-(3-cyclohexenyl)ethyl, methacryloxypropyl and 3-bicycloheptenyl groups. The composition ranged from TMPS/AMS mole% ratio of 92/8 to 83/17 and the molecular weights were in the range 10^4 to 10^5. These copolymers were confirmed to have two compositions, one a certain length of TMPS segment and the other an AMS monomer unit, and that they could form films on the basis of the crystallization character of the TMPS segment. The melting temperatures of these copolymers decreased as the TMPS mole content decreased and as the alkenyl group contents were increased. The epoxidation reactions of these copolymers with *m*-chloroperbenzoic acid were carried out and the proportions of conversions of the alkenyl groups into epoxy groups varied depending upon the types of alkenyl groups involved. Cyclic olefin groups such as the 2-(3-cyclohexenyl)ethyl or the 3-bicycloheptenyl group were more easily epoxidized than the vinyl or allyl groups. The TMPS/dimethylsiloxane (DMS) graft copolymer could also be synthesized by the reaction of TMPS/vinylmethylsiloxane copolymer with dimethylhydrosilyl-terminated DMS oligomer in the presence of chloroplatinic acid acting as the catalyst.

Keywords Polysilphenylene; polyalkenylsiloxanes; differential scanning calorimetry; crystallinity; epoxidation; graft copolymer

INTRODUCTION

It is well known that high molecular weight poly(tetramethyl-*p*-silphenylenesiloxane) (polyTMPS) is a crystalline silicon polymer and it tends to have film formation characteristics. Merker and Scott have synthesized polyTMPS[1] and Magill *et al.* have investigated in detail the crystallization kinetics[2-6], thermal properties[7], mechanical properties[8], structural aspects[9] and morphology[10,11]. We have also reported on the thermal degradation of polyTMPS in an earlier paper[12].

Although polyTMPS, having a substituent group, is expected to form a highly functional silicon film, the preparation of polyTMPS containing a functional group in the side-chain has not been carried out. Some studies on silicon polymers having functional groups in their branches have been carried out by some workers. Pittman *et al.* studied the synthesis of poly(arylenesiloxane) by the hetero-functional condensation of bis-silanols with bis-amino silanes[13,14]. The products contained several functional groups in the branches as the bis-amino silanes contain functional groups such as ferocene and others. The poly(arylenesiloxane) thus obtained was an alternate copolymer of silphenylene and siloxane bonds, and they came in the form of viscous oils or stiff gums but not in film form. Mazurek *et al.* synthesized a series of polymers with pendant groups of a complexing ligand capable of interacting wtih *in vivo* chlorophyll[15]. The synthesis was achieved by the hetero-functional condensation of α,ω-difunctional dimethylsiloxane oligomers with a difunctional silane containing the ligand groups attached to a silicon atom by means of an ethylene bridge.

Here, we wish to report the syntheses of tetramethyl-*p*-silphenylenesiloxane/alkenylmethylsiloxane (TMPS/AMS) copolymers by the two step reactions described in equations (1) and (2) by using *p*-bisdimethylhydroxysilylbenzene and a series of alkenylmethyldichlorosilanes as starting materials. These kinds of copolymers are of two compositions, one is a certain length of TMPS segment and the other is an AMS monomer unit. They are expected to be a functional silicon film because of the crystallization character of the long TMPS segment. And it is expected that other kinds of functional groups can be attached to the side-chains of these copolymers by taking advantage of the reactivities of these alkenyl groups. In order to clarify the reactivities of the alkenyl groups on the polymer branches, the epoxidation reactions of the alkenyl groups of the copolymers with *m*-chloroperbenzoic acid were carried out. Furthermore, when tetramethyl-*p*-silphenylenesiloxane/vinylmethylsiloxane copolymer reacted with dimethylhydrosilyl-terminated dimethylsiloxane (DMS) oligomer in the presence of chloroplatinic acid acting as the catalyst, a TMPS/DMS graft copolymer was obtained. Therefore, these derivatives obtained from TMPS/AMS copolymers, that are epoxidized copolymers and TMPS/DMS graft copolymers will also be described.

EXPERIMENTAL

The starting materials for the copolymer synthesis were *p*-bisdimethylhydroxysilylbenzene (TMPS monomer) and five species of alkenylmethyldichlorosilane, which were

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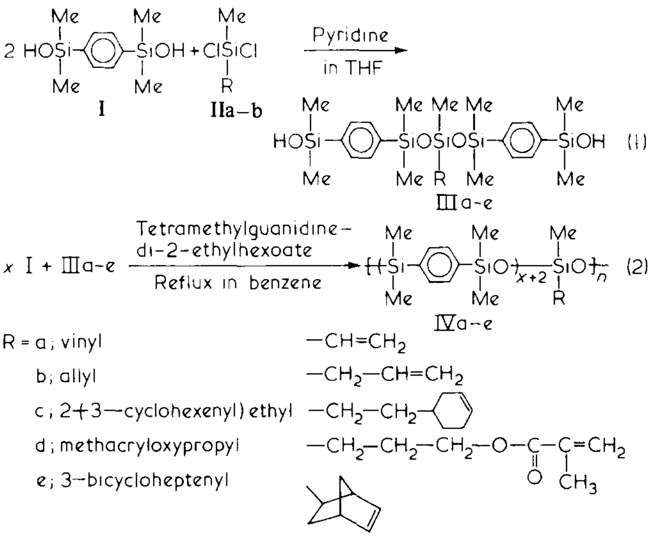
vinylmethyldichlorosilane (IIa), allylmethyldichlorosilane (IIb), 2(3-cyclohexenyl)ethylmethyldichlorosilane (IIc), methacryloxypropylmethyldichlorosilane (IId) and 3-bicycloheptenylmethyldichlorosilane (IIe). The copolymers were prepared by the reactions as shown in equations (1) and (2);



Syntheses

*Preparation of 1,3-bis-(*p*-dimethylhydroxysilylphenyl)-2-vinyl-1,1,2,3,3-pentamethyltrisiloxane (IIIa).* To a mixture of 15.29 g (0.0676 mol) TMPS monomer (I) and 5.5 ml (0.068 mol) pyridine in tetrahydrofuran (100 ml), a solution of 4.76 g (0.0338 mol) freshly distilled vinylmethyldichlorosilane (IIa) in benzene (60 ml) was added dropwise over a period of 3 h at room temperature under a nitrogen atmosphere. After 12 h stirring, the reaction mixture was filtered under reduced pressure to remove precipitated pyridine hydrochloride, and the solvent and any unreacted methylvinyldichlorosilane evaporated off. The product was then dried *in vacuo* at 60°C for 24 h. The weight of the product, which was a white highly viscous oil, was 14.1 g (80.2% yield). The structure of the product (IIIa) was confirmed by ^{1}H n.m.r.; shifts relative to TMS were: *d* (ppm) = 0.11 (3H, s), 0.30 (24H, s), 4.84 (2H, s), 5.94 (3H, m), 7.40 8H, s).

Compounds IIIb, IIIc, IIId and IIIe were prepared by the same procedure as for IIIa using the other alkenylmethyldichlorosilanes instead of vinylmethyldichlorosilane. ^{1}H n.m.r. shifts relative to TMS for compounds IIIb–e were:

IIIb; *d* (ppm) = 0.50 (3H, s), 0.30 (24H, s), 1.49 (2H, d), 4.70 (2H, m), 4.84 (2H, s), 5.20 (1H, m), 7.40 (8H, s).
IIIc; *d* (ppm) = 0.04 (3H, s), 0.30 (24H, s), 1.22 (4H, m), 1.91 (6H, m), 4.84 (2H, s), 5.52 (2H, m), 7.40 (8H, s).
IIId; *d* (ppm) = 0.02 (3H, s), 0.30 (24H, s), 1.72 (2H, m), 1.90 (3H, s), 4.12 (4H, m), 4.84 (2H, s), 5.68 (1H, d), 6.22 (1H, d), 7.40 (8H, s).
IIIe; *d* (ppm) = 0.08 (3H, s), 0.30 (24H, s), 1.05 (4H, m), 1.80 (1H, m), 2.83 (2H, m), 4.84 (2H, s), 5.85 (2H, m), 7.40 (8H, s).

*Polymerization of I and IIIa to prepare tetramethyl-*p*-silphenylenesiloxane/vinylmethylsiloxane (IVa).* A mixture of TMPS monomer (*x* mol) and compound IIIa (1 mol) was refluxed in benzene for 16 h adding 0.1 g tetramethylguanidine di-2-ethylhexoate as the catalyst with an azeotrope trap. This polymerization procedure is same as the method Merker and Scott used to polymerize bis-silanols[1]. The copolymer IVa obtained was reprecipitated in ethanol to remove the catalyst and any low-molecular weight materials. The composition of the TMPS unit and the vinylmethylsiloxane unit and the TMPS segment length of the copolymer could be varied with changes in the ratio of the TMPS monomer and compound IIIa. The structure and TMPS segment length were confirmed by ^{1}H n.m.r. ^{1}H n.m.r. shifts relative to TMS were: *d* (ppm) = 0.11 (s), 0.30 (s), 5.94 (m), 7.40 (s).

Copolymers IVb, IVc, IVd and IVe were prepared by the same procedure as IVa, using compounds IIIb, IIIc, IIId and IIIe respectively, instead of IIIa. ^{1}H m.m.r. shifts relative to TMS were: IVb; *d* (ppm) = 0.05 (s), 0.30 (s), 1.49 (d), 4.70 (m), 5.20 (m), 7.40 (s). IVc; *d* (ppm) = 0.04 (s), 0.30 (s), 1.22 (m), 1.91 (m), 5.52 (m), 7.40 (s). IVd; *d* (ppm) = 0.02 (s), 0.30 (s), 1.72 (m), 1.90 (s), 4.12 (m), 5.68 (d), 6.22 (d), 7.40 (s). IVe; *d* (ppm) = 0.08 (s), 0.30 (s), 1.05 (m), 1.80 (m), 2.83 (m), 5.85 (m), 7.40 (s).

Characterizations

^{1}H n.m.r. spectra were measured on solutions of samples in carbon tetrachloride and recorded on a JEOL JNM-PS-100 n.m.r. spectrometer.

The intrinsic viscosities $[\eta]$ of the copolymers were measured with an Ubbelohde viscometer in toluene at 25°C, and the viscosity-average molecular weights were calculated using the Staudinger equation for TMPS homopolymer, i.e. $[\eta] = 1.12 \times 10^{-4}\ \bar{M}_v^{\,0.75}$.[1]

Melting points and heat of fusion measurements were carried out by using a Shimadzu SC-20 differential scanning calorimeter at a heating rate of 5°C/min in a He stream. Potassium nitrate and indium of high purity were used as calibration standards for the heat of fusion determinations. Before the heat of fusion measurements, all samples were melted at 160°C for 10 min and isothermally crystallized at a temperature 10 degrees below their own melting temperature over a period of 48 h.

The crystallinity percentages of all the samples were calculated according to equation (3):

$$\text{Per cent crystallinity} = (\Delta H_f/\Delta H_f^*) \times 100 \qquad (3)$$

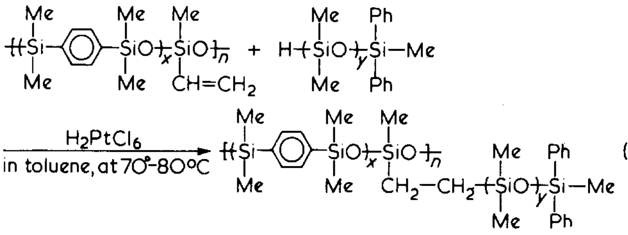
where ΔH_f denotes the samples' heat of fusion and ΔH_f^* is the heat of fusion for perfectly crystalline polyTMPS where the value is 13.0 cal/g.[6]

Epoxidation reaction of the copolymers

In order to clarify the reactivities of the carbon–carbon double bonds of these polymers, the epoxidation reactions of copolymers IVa–e using *m*-chloroperbenxoic acid (MCPBA) as reagent were performed. 0.70 g of copolymers IVa-1, IVb-1, IVc-1, IVd-1 and IVe-1 were dissolved in 20 ml of dichloromethane respectively, and to these solutions 10 ml dichloromethane solutions containing 0.15 g MCPBA were added slowly dropwise. After the additions were completed, the reaction mixtures were stirred for 24 h at 0°C or 40°C, the reflux temperature of dichloromethane. The solutions were then poured into excess ethanol and the precipitates were separated by filtration and dried *in vacuo* over a period of 24 h. The structure of the products and the proportions of the convertions of alkenyl groups into epoxy groups were confirmed by ^{1}H n.m.r.

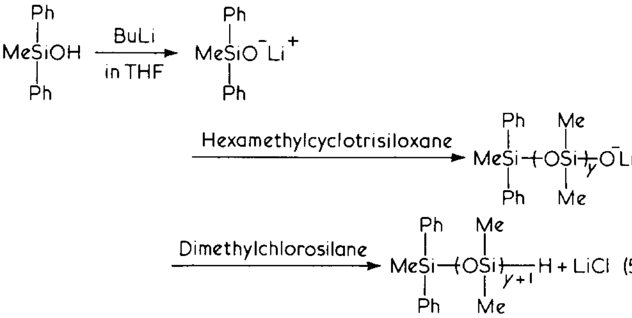
Synthesis of TMPS/DMS graft copolymer

The synthesis of the TMPS/DMS graft copolymer was achieved by the addition reaction of the terminal hydrosilyl group to the vinyl group of copolymer IVa as shown in equation (4):



(4)

The preparation method of the dimethylhydrosilyl-terminated DMS oligomer is by anionic polymerization preparing the diphenylsiloxane/dimethylsiloxane block copolymers as described by E. E. Bostick[16] as shown in equation (5):



$$\mathrm{MeSi(Ph)_2OH} \xrightarrow[\text{in THF}]{\text{BuLi}} \mathrm{MeSi(Ph)_2O^-Li^+} \xrightarrow{\text{Hexamethylcyclotrisiloxane}} \mathrm{MeSi(Ph)_2{-}\!(OSiMe_2)_y{-}O^-Li^+} \xrightarrow{\text{Dimethylchlorosilane}} \mathrm{MeSi(Ph)_2{-}\!(OSiMe_2)_{y+1}{-}H + LiCl} \quad (5)$$

All the procedures were carried out in a dry box under a nitrogen atmosphere. Methyldiphenylsilanol (3.490 g (1.631×10^{-2} mol)) was dissolved in tetrahydrofuran (30 ml), and to this solution 10 ml of a n-hexane solution of butyllithium (1.631 mol l^{-1}) and hexamethylcyclotrisiloxane (8.00 g (3.548×10^{-2} mol)) were added dropwise. The reaction mixture was stirred for 24 h at room temperature, and then to this mixture dimethylchlorosilane (2.55 g (2.70×10^{-2} mol)) was added dropwise to halt the polymerization reaction and to end-block with a hydrosilyl group. The mixture was then poured into excess methanol and the methanol was decanted off. The product was dried *in vacuo* at 90°C over a period of 24 h and a transparent viscous oil was obtained. The structure and the number-average molecular weight were determined by ^{1}H n.m.r. spectrum; shifts relative to TMS were: d (ppm) = 0.11 (39H, s), 0.61 (3H, s), 4.68 (1H, m), 7.28 (6H, m), 7.44 (4H, m); $\bar{M}_n = 672$ (= about 6 DMS units).

The reaction mixture of 2.00 g (vinyl group 9.22×10^{-4} mol) of copolymer IVa-3 and 1.70 g (11.7×10^{-4} mol) of dimethylhydrosilyl-terminated DMS oligomer thus obtained and 8 μl ethanol solution of chloroplatinic acid (0.218 mol l^{-1}) in 20 ml of toluene was stirred at 70°–80°C under a nitrogen atmosphere. The mixture was poured into ethanol (400 ml) and the product was reprecipitated several times with benzene–ethanol and dried *in vacuo* for 24 h. The structure and the composition of this graft copolymer were confirmed by ^{1}H n.m.r.

Dynamic mechanical measurements of copolymer IVa-3 and the graft copolymer were made using Iwamoto Instruments' dynamic viscoelastometer with a low temperature chamber for a temperature range from −150°C to the melting temperature. The frequency was fixed at 11 Hz. For this study the samples were carefully melt-moulded at 200°C for 5 min in a hot press to a thickness of 0.03 cm and were quenched to room temperature. The samples were then cut into rectangular strips of length 5.0 cm and width 0.5 cm.

RESULTS AND DISCUSSION

Characterizations

Table 1 summarizes the results of the characterizations of TMPS homopolymer and the copolymers containing alkenyl groups in their side-chains. It was shown by ^{1}H n.m.r. measurements that the ratio of TMPS monomer and the compounds IIIa–e was compatible with that of the TMPS segment and the alkenylmethylsiloxane (AMS) unit in each case. The compositions ranged from TMPS/AMS mole% ratio of 92/8 to 83/17. The viscosity-average molecular weights of all the copolymers were in the range of 10^4 to 10^5, therefore high molecular weight copolymers could be obtained by this method. In this range of compositions and molecular weights, the products were white fibre-forming elastomers like the

Table 1 Characterizations of TMPS homopolymer and TMPS/AMS copolymers

Sample No.	Alkenyl group	Mole ratio R/TMPS	TMPS content (mol %)	TMPS content (wt %)	[η]	$\bar{M}_v$ (x10^{-4})	T_m (°C)	ΔH_f (cal/g)	Crystallinity (%)
polyTMPS*		–	100	100	3.343	92.6	140	13.0	100
IVa–1	Vinyl	1/5	83	92	1.404	29.1	121	4.3	33
IVa–2	Vinyl	1/7	87	93	1.258	25.2	128	9.7	75
IVa–3	Vinyl	1/9	90	96	2.108	50.1	130	10.9	84
IVa–4	Vinyl	1/11	92	97	2.425	60.3	134	11.6	89
IVb–1	Allyl	1/5	83	91	2.277	55.5	118	4.0	30
IVb–2	Allyl	1/7	87	94	2.224	53.8	123	7.4	57
IVb–3	Allyl	1/11	92	96	1.715	38.0	131	10.0	77
IVc–1	2–(3-Cyclohexenyl)ethyl	1/5	83	86	1.457	30.6	117	3.2	25
IVc–2	2–(3-Cyclohexenyl)ethyl	1/7	87	90	1.868	42.6	121	7.5	58
IVc–3	2–(3-Cyclohexenyl)ethyl	1/9	90	92	1.244	24.8	127	9.0	69
IVd–1	Methacryloxypropyl	1/5	83	85	0.500	7.35	113	1.4	11
IVd–2	Methacryloxypropyl	1/7	87	89	0.648	10.4	120	5.0	38
IVd–3	Methacryloxypropyl	1/9	90	91	1.937	44.7	127	9.1	70
IVe–1	3-Bicycloheptenyl	1/5	83	87	0.417	5.77	108	0.90	6.9
IVe–2	3-Bicycloheptenyl	1/7	87	91	0.518	7.71	119	4.5	35
IVe–3	3-Bicycloheptenyl	1/9	90	92	0.434	6.09	124	6.7	52

* Synthesized by the same procedure as the method of Merker and Scott[1]

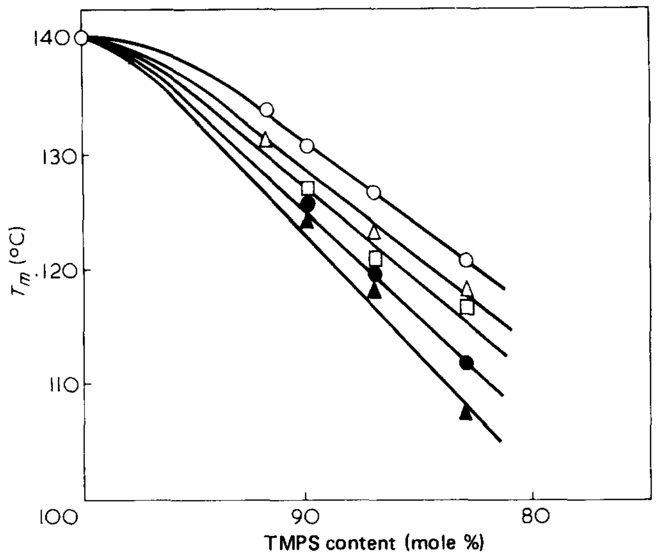


Figure 1 Plots of melting temperatures against TMPS mole contents of tetramethyl-*p*-silphenylenesiloxane/alkenylmethylsiloxane copolymers, (○), R = vinyl; (△), R = allyl; (□), R = 2–(3-cyclohexenyl)-ethyl; (●), R = methacryloxypropyl; (▲), R = 3-bicycloheptenyl

TMPS homopolymer. Casting of solutions of each of the copolymers in benzene resulted in very tough, white elastomeric films. It is thought that a certain length of TMPS segment in the main chain causes the film formation characteristics in this type of copolymer.

D.s.c. measurements could elucidate the dependence of TMPS segment length on the thermal properties and the limiting TMPS segment length in forming films. *Figure 1* shows the effects of TMPS segment length on the melting points of the copolymers. The melting point of the TMPS homopolymer was 140°C and those of the copolymers were lowered remarkably as TMPS mole contents were decreased. This phenomenon suggests that the copolymerization reaction, indicated in equation (2), gives the copolymers which consist of the expected TMPS segment and AMS monomer unit. However, the larger the functional groups of the copolymers were, the lower the melting points of the copolymers were. According to Magill *et al.* polyTMPS can crystallize in the form of a chain-folded lamellae[9], and the copolymer melting temperature depends upon the size of the chain-folded lamellae of the TMPS segment[6,7]. It appears that the copolymer, having large substituent groups, finds it hard to form folded crystals of the TMPS segment. In all cases, where the TMPS mole content was less than 80%, the melting points decreased considerably and the film formation characters were lost.

Figure 2 shows the effects of TMPS mole content on the crystallinities. It is also recognized that the large substituent groups lower the crystallinities and disturb the formations of the folded crystals of the TMPS segment. These curves are extrapolated to find the point of intersection at 80% TMPS mole content. Therefore, it is presumed that this kind of copolymer, whose TMPS mole content is less than 80%, cannor form TMPS fold crystals and is a completely amorphous copolymer. It was found that those copolymers having less than 80% TMPS mole content could not form films by the casting from the benzene solutions as described above, and the melting points peaks on the d.s.c. curves could not be observed.

The effect of limiting TMPS segment length on crystal formation was clarified by the plots of crystallinities against TMPS average segment length (*Figure 3*), giving a result of 4–5 TMPS monomer units for these types of copolymers. Magill *et al.* stated that at least 8 TMPS units were necessary for crystal formation of TMPS/DMS block copolymers on the basis of selective chemical degradations and small angle X-ray scattering results[17].

Epoxidation reaction

Table 2 shows the results of the epoxidation reactions of these copolymers using MCPBA as the reagent. These results indicated that the proportion of conversion of carbon–carbon double bonds to epoxy groups varied

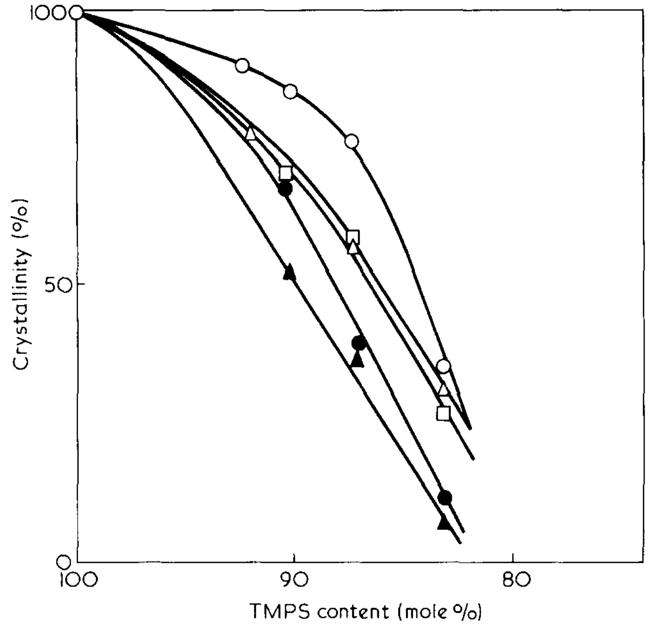


Figure 2 Plots of crystallinities against TMPS mole contents of tetramethyl-*p*-silphenylenesiloxane/alkenylmethylsiloxane copolymers, (○), R = vinyl; (△), R = allyl; (□), R = 2–(3-cyclohexenyl)ethyl; (●), R = methacryloxypropyl; (▲), R = 3-bicycloheptenyl

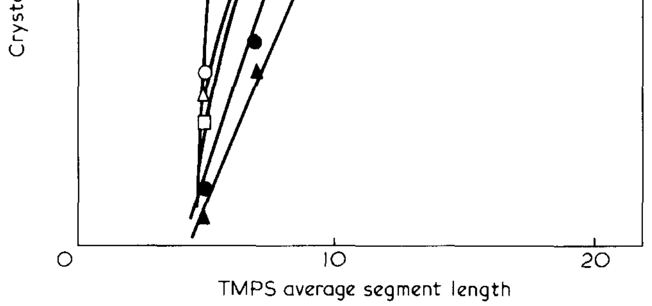


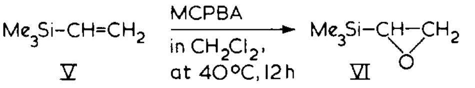
Figure 3 Plots of crystallinities against TMPS average segment length of tetramethyl-*p*-silphenylenesiloxane/alkenylmethylsiloxane copolymers, (○), R = vinyl; (△), R = allyl; (□), R = 2–(3-cyclohexenyl)-ethyl; (●), R = methacryloxypropyl; (▲), R = 3-bicycloheptenyl

Table 2 Results of epoxidation reactions of tetramethyl-*p*-silphenylenesiloxane/alkenylmethylsiloxane copolymers with *m*-chloroperbenzoic acid at (1) 0°C or (2) 40°C for 12 h

Sample No.	Alkenyl group	Yield (%) (1)	Yield (%) (2)
IVa–1	Vinyl	14–27	58–67
IVb–1	Allyl	Crosslinked	Crosslinked
IVc–1	2–(3-Cyclohexenyl)ethyl	100	100
IVd–1	Methacryloxypropyl	0	0
IVe–1	3-Bicycloheptenyl	100	100

depending upon the kinds of alkenyl groups appearing in the side-chain. As the values of intrinsic viscosity of all the epoxidized products did not change, it was found that the molecular weights of the copolymers were not influenced by the epoxidation reaction. The vinyl group of copolymer IVa-1 was epoxidized to a 14–27% yield at 0°C and a 58–67% yield at 40°C. The 2-(3-cyclohexenyl)ethyl group of copolymer IVc-1 and the 3-bicycloheptenyl group of copolymer IVe-1 were epoxidized to a 100% yield in both cases. However, it was noticed that copolymer IVb-1 was crosslinked and insoluble in all solvents when the allyl group reacted with *m*-chloroperbenzoic acid. However, the structure of the product could not be confirmed as it was insoluble in all solvents. The methacryloxypropyl group of copolymer IVd-1 did not react with *m*-chloroperbenzoic acid and this may be due to the carbon–carbon double bond being stabilized by the resonance effect between the π-electrons of the carbon–carbon double bond and the carbon–oxygen double bond of the ketone group, which is located at the α-position of the carbon–carbon double bond.

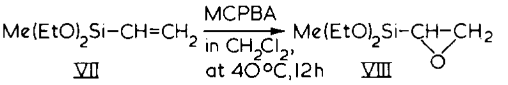
In order to confirm that the proportions of the conversion of the alkenyl groups into epoxy groups depends upon the structures of the alkenyl groups, low molecular weight silicon compounds having the same structures as these copolymers were reacted with *m*-chloroperbenzoic acid under similar conditions. The silicon compounds used were trimethylvinylsilane, diethoxymethylvinylsilane, allyltrimethylsilane, methacryloxypropyltrimethoxysilane and 2-(3-cyclohexenyl)ethylmethylsilane. The products of these low molecular weight silicon compounds were easily separated from the starting materials by distillation after the epoxidation reaction. In all cases, the reaction mixtures of these silicon compounds and *m*-chloroperbenzoic acid in dichloromethane, were refluxed for 12 h and the structures of the products, which were purified by the distillation, were determined by ^{1}H n.m.r., i.r. and mass spectrometry. The results are summarized in equations (6)–(10):



$$Me_3Si{-}CH{=}CH_2 \xrightarrow[\text{in } CH_2Cl_2,\ \text{at } 40°C,\ 12h]{MCPBA} Me_3Si{-}\underset{\diagdown O \diagup}{CH{-}CH_2} \qquad (6)$$

V b.p. = 55°C, m/e; M^+ = 100

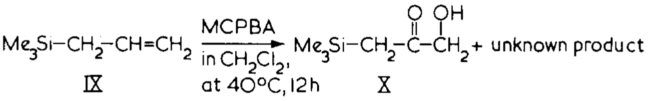
VI b.p. = 109°C, m/e; M^+ = 116 (93% yield)



$$Me(EtO)_2Si{-}CH{=}CH_2 \xrightarrow[\text{in } CH_2Cl_2,\ \text{at } 40°C,\ 12h]{MCPBA} Me(EtO)_2Si{-}\underset{\diagdown O \diagup}{CH{-}CH_2} \qquad (7)$$

VII b.p. = 133~134°C, m/e; M^+ = 160

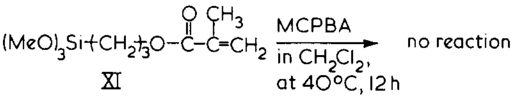
VIII b.p. = 77~78°C/25 mmHg, m/e; M^+ = 176 (30~40% yield)



$$Me_3Si{-}CH_2{-}CH{=}CH_2 \xrightarrow[\text{in } CH_2Cl_2,\ \text{at } 40°C,\ 12h]{MCPBA} Me_3Si{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}\overset{OH}{\overset{|}{C}}H_2 + \text{unknown product} \qquad (8)$$

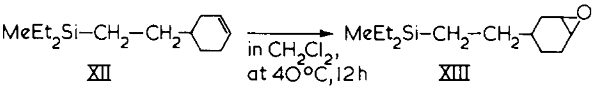
IX b.p. = 85~86°C, m/e; M^+ = 114

X b.p. = 150°C/23 mmHg, m/e; M^+ = 147 (60% yield)



$$(MeO)_3Si{+}CH_2{+}_3O{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow[\text{in } CH_2Cl_2,\ \text{at } 40°C,\ 12h]{MCPBA} \text{no reaction} \qquad (9)$$

XI b.p. = 78~81°C/20 mmHg



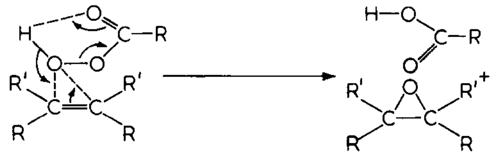
(10)

XII b.p. = 148°C/20 mmHg, m/e; M^+ = 210

XIII b.p. = 95~99°C/1 mmHg, m/e; M^+ = 226, (95% yield)

These results are compatible with those of the epoxidation reactions of copolymers IVa–d.

Trimethylvinylsilane (V) was epoxidized to form VI with a 93% yield as shown in equation (6). However, diethoxymethylvinylsilane (VII) was epoxidized to form VIII to only a 30–40% yield and the remainder was the starting material (VII). The most satisfactory representation of the transition state for the epoxidation reaction of olefins and peroxidic reagents is illustrated below[18]:



(11)

In general, this representation is supported by the fact that the peroxy acid acts as an electrophilic species in the oxidation and that the olefin reactivity is increased by electron-donating alkyl substituents. Consequently, the reason why the proportion of conversion to epoxy-compound of trimethylvinylsilane (V) is greater than that of diethoxymethylvinylsilane (VII) is thought to be that the trimethylsilyl group on V is a stronger electron-donating substituent than the diethoxymethylsilyl group on VII because the ethoxy groups on the silicon atom of VII result in an electron-attracting substituent. In the case of the epoxidation of copolymer IVa-1, as the electronic structure around the vinyl group of copolymer IVa-1 was similar to that of diethoxymethylvinylsilane and not trimethylvinylsilane, the proportion of the conversion of vinyl group into epoxy group was only 58–67% at 40°C.

The reaction of allyltrimethylsilane with MCPBA gave compound X (60% yield) and another unknown product. The boiling point of the unknown product was found to be higher than that of X. The structure of the unknown product could not be confirmed, but it was considered that it might have the structure of a dimer of X where X was dimerized by the condensation reaction of the hydroxy group on X. Therefore, the reason why copolymer IVb-1 was crosslinked by the reaction with MCPBA might be explained on the basis of the dimerization reaction.

Methacryloxypropyltrimethoxysilane (XI) did not react with MCPBA in this way (equation (9)) in agreement

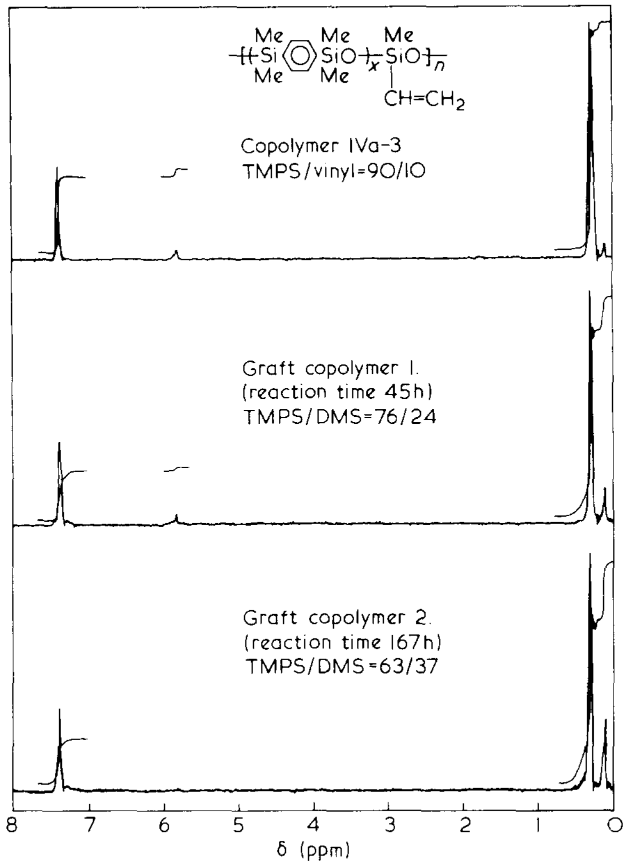


Figure 4 ^{1}H n.m.r. spectra of copolymer IVa-3 and TMPS/DMS graft copolymers

with the results for copolymer IVd-1 which could not be epoxidized by MCPBA. Very low reactivity is generally believed to be encountered with olefins conjugated with carbonyl or other strongly electron-attracting substituents[19].

2-(3-Cyclohexenyl)ethyldiethylmethylsilane (XII) was epoxidized to form XIII with a 95% yield, which agrees well with the finding that copolymer IVc-1 was epoxidized to a 100% yield by MCPBA. Hence, it is clear that cyclo-olefin groups such as the 3-cyclohexenyl group on copolymer IVc-1 or the 3-bicycloheptenyl group on copolymer IVe-1 are easily epoxidized by MCPBA in comparison with the vinyl or allyl groups.

TMPS/DMS graft copolymer

Figure 4 shows the ^{1}H n.m.r. spectra of copolymer IVa-3 and the TMPS/DMS graft copolymers which are synthesized using copolymer IVa-3 and the dimethylhydrosilyl-terminated DMS oligomer. In the ^{1}H n.m.r. spectrum of copolymer IVa-3 the signals for the methyl and phenylene protons of the TMPS unit were 0.30 and 7.40 ppm respectively, and those for the methyl and vinyl protons of the methylvinylsiloxane unit were 0.11 and 5.84 ppm respectively. The ratio of the integrated peaks of the proton signals emanating from the vinyl and phenylene groups equalled 1/9 and for this value it is noticed that the TMPS average segment length of copolymer IVa-3 was about 9. In the spectrum for graft copolymer 1, which was isolated from the reaction mixture after being reacted for 45 h, the area of the signals for vinyl protons decreased by half and the signal for methyl protons of the DMS unit in the branch appeared at 0.11 ppm. From the ratio of the two signals for methyl protons at 0.11 and 0.30 ppm the composition of TMPS/DMS is calculated to be 76/24. In the case of graft copolymer 2, which was isolated after a reaction time of 167 h, the proton signal for the vinyl group disappeared and that for the methyl group of the DMS increased at 0.11 ppm. The composition of graft copolymer 2 is determined to be 63/37, which is reasonable where the TMPS and DMS average segment lengths were about 9 and 6 respectively. A long reaction time is required for the synthesis of the TMPS/DMS graft copolymer by this method, but we think that it can be shortened through concentration of the reaction mixture.

The intrinsic viscosities [η] of copolymer IVa-3 and graft copolymer 2, measured in toluene at 25°C, were 2.108 and 2.641 respectively, i.e., value for the graft copolymer was higher than that for copolymer IVa-3.

The results of the dynamic mechanical measurements of copolymer IVa-3 and graft copolymer 2 showed the remarkable differences between the two copolymers (*Figures 5* and *6*). The curves of E', E'' and $\tan\delta$ of copolymer IVa-3 (*Figure 5*) were very similar to those of the TMPS homopolymer[8], whose major transition was observed at around 0°C for this frequency. This major transition peak of E'' and $\tan\delta$ is the primary amorphous relaxation of the TMPS segment which comprised 90 mol% in copolymer IVa-3. The E'' peak occurred at around −70°C for the TMPS/DMS graft copolymer (*Figure 6*) in accord with a shift of the relaxation behaviour to a lower temperature due to the presence of a more flexible DMS component in the branch.

This kind of graft copolymer has interesting solid and solution properties compared with TMPS/DMS block copolymers which have been synthesized by some workers[20,21]. Details of this investigation will be forthcoming in future publications.

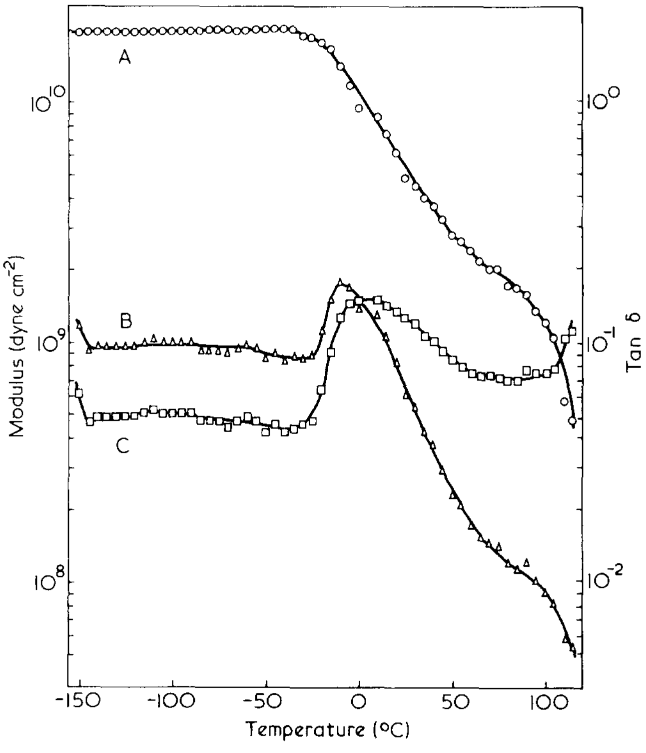


Figure 5 A, E'; B, E''; C, tan δ of copolymer IVa-3 plotted against temperature at 11 Hz

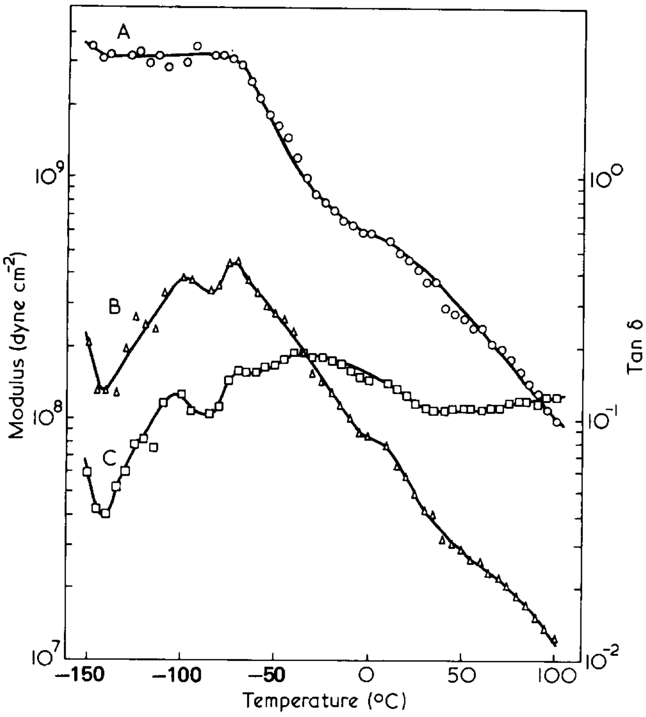


Figure 6 A, *E'*; B, *E''*; C, tan δ of TMPS/DMS graft copolymer plotted against temperature at 11 Hz

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