Synthesis, Characterization, and Thermal Properties of Poly(methylvinylsilylene-*co*-styrene)

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ABSTRACT: The copolymerization of methylvinyldichlorosilane (MVDCS) and styrene was carried out with various monomer feed ratios under dechlorination conditions with sodium in toluene at 110°C. The copolymers were obtained in 84–95% yields. The copolymerization of MVDCS and styrene with monomer feed ratios of 1 : 0.25 and 1 : 0.5 mainly gave insoluble polymers. The copolymers synthesized with monomer feed ratios of 1 : 1, 1 : 3, and 1 : 7 contained soluble fractions of 3, 26, and 47%, respectively. The copolymers were characterized with infrared, ^{1}H-NMR, gel permeation chromatography, thermogravimetric analysis, pyrolysis/gas chromatography (PGC), X-ray diffraction, and elemental analysis (silicon content). ^{1}H-NMR and PGC studies suggested that the soluble fractions were mainly polystyrene. PGC studies indicated that the copolymers obtained with monomer feed ratios of 1 : 0.25 and 1 : 0.5 did not have any significant amount of polystyryl blocks, whereas the copolymers obtained with higher styrene feed ratios contained appreciable amounts of polystyryl blocks. The composition of the insoluble fractions of the copolymers was obtained from PGC data and was in good agreement with the composition calculated from the silicon content of the copolymers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3774–3784, 2004

Key words: inorganic polymers; polysilanes; thermal properties; chromatography; degradation

INTRODUCTION

Over the last 2 decades, considerable interest has been shown in the synthesis of polycarbosilanes,[1–6] polymers consisting of silicon and carbon in the backbone. These polymers find end uses as precursors for SiC fibers,[1,3,7–10] SiC coatings,[11–13] binders for ceramic components,[14–16] and matrix resins for ceramic–matrix composites.[14,17–19] Yajima and coworkers,[1–4] in their pioneering work, prepared polycarbosilane by the heat treatment of dodecamethylcyclohexane [(Me$_2$Si)$_6$] or poly(dimethylsilane) in an autoclave under an argon atmosphere at temperatures greater than 400°C under pressure or at atmospheric pressure in the presence of a catalyst.

Several synthetic approaches have been reported for the single-step synthesis of polycarbosilanes.[20–28] Schilling and coworkers[29–32] synthesized polycarbosilanes in a single step from vinyl-group-containing chlorosilane monomers. They observed that the vinyl group took part in the polymerization. Thus, methylvinyldichlorosilane (MVDCS) behaves as a tetrafunctional monomer under Wurtz reaction conditions, and this results in the formation of highly crosslinked polycarbosilane.[30–33] Regardless of the alkali metal and solvent used in the dechlorination reaction, MVDCS always gives a highly crosslinked, intractable polycarbosilane.[5] However, the experimental conditions play an important role when MVDCS is copolymerized with other chlorosilanes.[33–35] For example, when MVDCS was copolymerized with dimethyldichlorosilane (DMDCS) and trimethylchlorosilane (TMCS) in the presence of potassium in tetrahydrofuran (THF), a processable branched polycarbosilane was obtained. This polymer did not contain any free vinyl groups, and this indicates their participation in the formation of polycarbosilanes. However, when the copolymerization was carried out with sodium in a toluene/THF or xylene/THF mixture, a vinyl-functionalized polysilane was obtained. Thus, it is evident that the participation of the vinyl group attached to silicon can be controlled by the proper modification of the experimental conditions.

Schilling and a coworker[32,34] observed that vinylic or diene monomers could be used in place of MVDCS for copolymerization with diorganodichlorosilane monomers. They called polycarbosilanes obtained by this method *polysilahydrocarbons*. Following this work, Packirisamy and coworkers[36–40] reported the synthesis and microstructure of polysilahydrocarbons ob-

tained by the copolymerization of styrene with DM-DCS, methylphenyldichlorosilane (MPDCS), and 1,2-bis(chlorodimethylsilyl)ethane (BCDMSE) under dechlorination conditions with sodium in a toluene medium. Sartori and coworkers[41,42] synthesized polysilahydrocarbons through the copolymerization of styrene with DMDCS and diphenyldichlorosilane (DPDCS). There appears to be no report on the copolymerization of MVDCS and styrene under dechlorination conditions. It is believed that during the copolymerization of diorganodichlorosilanes with styrene, disilyl reaction intermediates initiate the polymerization of styrene, and this results in the formation of polydisilahydrocarbons.[36–39] When the copolymerization of styrene is carried out with MVDCS, disilyl reaction intermediates may initiate the polymerization of styrene and vinyl groups attached to silicon. As styrene is expected to be more reactive than a vinyl group attached to silicon, it is likely that the participation of the latter may be suppressed by the former, and this results in the formation of vinyl-functionalized polysilahydrocarbon. On the contrary, if the vinyl group attached to silicon also takes part in the polymerization, a highly crosslinked polysilahydrocarbon is expected to form. In this article, we report the copolymerization of MVDCS and styrene for various monomer feed ratios under dechlorination conditions in toluene with sodium. The obtained copolymers were fractionated into soluble and insoluble fractions. Both the soluble and insoluble fractions were characterized with infrared (IR), thermogravimetric analysis (TGA), and pyrolysis/gas chromatography (PGC). In addition, the soluble polymers were characterized with ^{1}H-NMR and gel permeation chromatography (GPC), whereas the insoluble polymers were characterized with elemental analysis (silicon content) and X-ray diffraction (XRD). In selective cases, polymerization was carried out in xylene/THF mixtures to determine the role played by the reaction medium on the copolymerization. A probable reaction mechanism is proposed for the formation of polysilahydrocarbons.

EXPERIMENTAL

Materials

MVDCS (Petrarch, United States) was freshly distilled before it was used. Styrene (Alfa Biochem, India) was washed with 5% sodium hydroxide (to remove the inhibitors) and then water. It was dried over anhydrous sodium sulfate overnight and then purified by vacuum distillation over calcium hydride.

Toluene and xylene (Qualigens, Mumbai, India) were refluxed and distilled over sodium. THF (Qualigens) was refluxed and distilled over calcium hydride. Sodium metal (Nice Chemicals, Kochi, India) was freshly cut into small pieces after the outer surface was removed, and it was used for the copolymerization of MVDCS and styrene.

Copolymerization of MVDCS and styrene under dechlorination conditions

In toluene

In a typical experiment, the copolymer PMVSS-I was synthesized by the reaction of a mixture of MVDCS (7.053 g, 0.049 mol) and styrene (1.3 g, 0.0125 mol) with sodium (2.5 g, 0.108 mol) in 35 mL of toluene under a nitrogen atmosphere. Sodium was made into a fine dispersion in refluxing toluene with a mechanical stirrer. The reaction was continued for 2 h. At the end of the reaction, the unreacted sodium was neutralized with a methanol/toluene mixture, and the polymer was precipitated in excess methanol. The methanol-insoluble fraction was isolated by filtration and washed several times with distilled water and then with methanol. The polymer, obtained as a pale yellow solid, was dried *in vacuo* at 80°C for 10 h. With this procedure, copolymers were synthesized with MVDCS/styrene molar ratios of 1 : 0.5, 1 : 1, 1 : 3, and 1 : 7, and the copolymers were obtained in 80–90% yields. All the copolymers, after drying in a vacuum oven at 80°C for 10 h, were washed with toluene for the extraction of the soluble fraction. In a typical example, 1 g of the copolymer synthesized with a 1 : 3 molar ratio of MVDCS and styrene was soaked in toluene, and the mixture was stirred for 2 h. After the insoluble polymer was allowed to settle, the soluble fraction was isolated by filtration with a sintered funnel. This process was repeated three times to ensure the complete removal of the soluble fraction. The filtrate was concentrated by the distillation of toluene. The soluble polymer was precipitated in excess methanol. Both the soluble and insoluble polymers were dried at 80°C for 10 h. The copolymers synthesized from MVDCS and styrene in 1 : 0.25, 1 : 0.5, and 1 : 1 ratios were found to contain no soluble fraction, and they are designated PMVSS-I, PMVSS-II, and PMVSS-III, respectively. Copolymers synthesized with 1 : 3 and 1 : 7 ratios contained both insoluble and soluble fractions. The insoluble fractions obtained from the copolymers synthesized with the ratios of 1 : 3 and 1 : 7 are designated PMVSS-IV and PMVSS-V, and the corresponding soluble fractions are designated PMVSS-IV$_S$ and PMVSS-V$_S$, respectively.

For comparison with the aforementioned copolymers, the homopolymer poly(methylvinylsilylene) was synthesized through the dechlorination of MVDCS with sodium with an experimental procedure similar to that described for the synthesis of the copolymers.

In a xylene/THF mixture

With the aforementioned experimental procedure, a copolymer was synthesized by the reaction of a mixture of 7.05 g (0.049 mol) of MVDCS and 2.6 g (0.025 mol) of styrene in 42.5 mL of a xylene/THF mixture (7 : 1 v/v) at 105°C.

Characterization

FTIR spectra of the polymers were recorded with a PerkinElmer Spectrum GXA spectrometer and Spectrum V3.02 software. The background in IR was recorded and subtracted from the spectra of the samples with the software. The background-corrected spectra were used for absorbance measurements. ^{1}H-NMR spectra were recorded on a JEOL FX 90Q 90-MHz spectrometer and at 400 MHz on a Bruker 400 AMX spectrometer. The molecular weights were determined by GPC with a Waters ALC GPC 244 instrument with 10^4, 10^3, 500, and 100 microstyragel columns and with THF as the eluent. The molecular weights are reported with respect to polystyrene (PS) standards. TGA was performed on a thermal analysis system in conjunction with a 951 TGA unit at a heating rate of 10°C/min under a nitrogen atmosphere. XRD patterns of the polymers and the ceramic residue at 900 and 1400°C were recorded on a Philips 1729 instrument equipped with a PW 1710 diffractometer control unit and a nickel filter with Cu Kα radiation.

Estimation of silicon[43]

The silicon-containing polymer sample was converted into its sodium salt by sodium carbonate fusion. The extract was dehydrated with perchloric acid, ignited, and volatilized with hydrofluoric acid. The obtained residue was ignited and weighed. The weight loss represents the silica formed. From the amount of silica formed, the percentage of silicon was calculated as follows:

Percentage of silicon

$$= \frac{\text{Weight of silica formed} \times 28.08 \times 100}{60.08}$$

PGC studies

Pyrolysis experiments of the copolymers synthesized from MVDCS and styrene and the homopolymers synthesized from MVDCS and from styrene were carried out with a CDS 100 pyroprobe interfaced with a Fisons HRGC Mega 2 gas chromatograph equipped with a digital temperature programmer and a flame ionization detector. About 0.5–1 mg of each sample was placed in a quartz sample boat, which was kept in

TABLE I
Comparison of the Yields and Soluble Fractions of PMVSS Synthesized from Different Molar Ratios of Styrene and MVDCS

Molar ratio of styrene to MVDCS in the feed	Polymer yield (%)	Soluble fraction (%)
0.25	94	—
0.5	95	—
1.0	92	3
3.0	84	26
7.0	94	47

the coil probe of the pyrolyzer. The probe was placed in the heated interface, and the sample was pyrolyzed in helium (carrier gas) at 700°C for 20 s. The volatile degradation products were analyzed by gas chromatography (GC). The injector and detector were kept at 250°C. The carrier gas (helium) flow rate was 40 mL/min.

The GC analyses were carried out with an OV-17 stainless steel column (3-mm i.d. × 2 m). The column temperature was programmed from 90 to 220°C at a heating rate of 20°C/min. The chromatogram was processed by Fisons Chromcard GC software with a personal computer, and quantitative data were obtained by the area summation method.

RESULTS AND DISCUSSION

Synthesis and characterization of polysilahydrocarbons from MVDCS and styrene

Poly(methylvinylsilylene-*co*-styrene) was synthesized by the Wurtz-type reaction of MVDCS and styrene in different molar ratios in toluene at 110°C. The copolymers were obtained in high yields of 84–95%. They were separated into soluble and insoluble fractions with toluene. The insoluble fractions obtained from the copolymers synthesized with MVDCS/styrene monomer feed ratios of 1 : 0.25, 1 : 0.5, 1 : 1, 1 : 3, and 1 : 7 are designated PMVSS-I, PMVSS-II, PMVSS-III, PMVSS-IV, and PMVSS-V, respectively. The polymer yields and the percentage of soluble fractions obtained for the different copolymers are compared in Table I. The copolymers obtained with MVDCS/styrene feed ratios of 1 : 0.25 and 1 : 0.5 were found to contain no soluble fraction, whereas the copolymers synthesized with monomer feed ratios of 1 : 1, 1 : 3, and 1 : 7 gave soluble fractions of 3, 26, and 47%, and they are designated PMVSS-III$_S$, PMVSS-IV$_S$, and PMVSS-V$_S$, respectively.

IR spectral studies

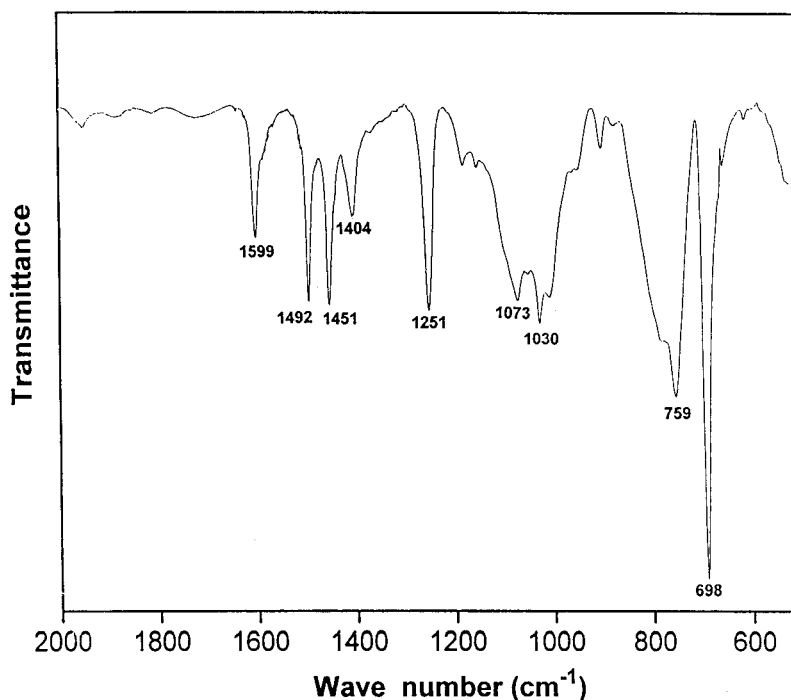The IR spectrum of PMVSS-IV is shown in Figure 1. All the copolymers exhibit broad absorption peaks at

Figure 1 IR spectra of PMVSS-IV.

1073 and 1030 cm^{-1} due to silahydrocarbon[44] and carbosilane linkages,[45] respectively. The characteristic strong band of Si—Me due to symmetric deformation[46] appears at 1251 cm^{-1}. The shoulder peak at 785 cm^{-1} is due to Si—Me (rocking). Peaks corresponding to the aromatic moiety[47] of styrene can be found at 1599, 1492, and 1451 cm^{-1}. The strong peaks at 759 and 698 cm^{-1} are due to a monosubstituted aromatic moiety.[47] The sharp absorption peaks at 1251 cm^{-1} due to Si—Me and at 1599 and 1492 cm^{-1} due to the phenyl group of styrene were used to calculate the ratio of absorbance (A) values. The ratios of A_{1599} to A_{1251} and A_{1493} to A_{1251} for the insoluble fractions of the copolymers are given in Table II. With an increase in the styrene concentration in the feed, both A_{1599}/A_{1251} and A_{1492}/A_{1251} increase, and this suggests that the concentration of the styryl units in the copolymers increases with the increase in the styrene concentration in the monomer feed.

TABLE II
Comparison of the Ratio of the Absorbance of Aromatic Units to Si—Me Units of PMVSS Synthesized with Different Molar Ratios of Styrene and MVDCS

Copolymer	$A_{1492\ (Ar)}/A_{1251\ (Si—Me)}$	$A_{1599\ (Ar)}/A_{1251\ (Si—Me)}$
PMVSS-I	0.40	0.24
PMVSS-II	0.55	0.32
PMVSS-III	0.86	0.54
PMVSS-IV	1.14	0.72
PMVSS-V	1.74	1.04

The IR spectra of PMVSS-IV$_S$ and PMVSS-V$_S$ closely resemble that of PS, and a feeble peak can be observed at 1251 cm^{-1}, indicating the presence of a small number of CH$_3$Si—CH—CH$_2$— groups.

XRD studies

The wide-angle X-ray diffraction (WAXD) pattern of the homopolymer poly(methylvinylsilane) (PVMS) exhibits a broad peak in the region of 16–28° (2θ value), and it is attributed to the semicrystalline nature of the polymer. However, WAXD patterns of the insoluble fractions of the copolymers exhibit no characteristic peak, and this suggests that the copolymers are amorphous.

^{1}H-NMR spectral studies of the soluble polymers

In the ^{1}H-NMR spectrum of PMVSS-IV$_S$, broad signals can be observed in the region of 1.5–2 ppm, and they are assigned to the methylene and methine protons of styryl units. The peak at 6.7 ppm is attributed to the meta and para protons, whereas the peak at 7.2 ppm is due to the ortho protons of phenyl groups present in the polymer. A weak signal observed at 0.6 ppm is attributed to Si—Me groups of the methylvinylsilylene unit. The absence of a signal in the region of 5–6 ppm indicates the absence of free vinyl groups in PMVSS-IV$_S$. A similar observation can be made for PMVSS-V$_S$. Thus, ^{1}H-NMR spectral studies of the soluble fractions reveal that they are mainly PS. The

soluble fractions are probably formed by the silyl-initiated homopolymerization of styrene.

Molecular weight analysis

The GPC curves of PMVSS-IV$_S$ and PMVSS-V$_S$ are shown in Figure 2. PMVSS-IV$_S$ has a weight-average molecular weight (M_w) of 25,000 and a polydispersity of 6.2, whereas PMVSS-V$_S$ has an M_w value of 38,000 and a polydispersity of 2.8. The molecular weight data suggest that the molecular weight increases with an increase in the styrene concentration in the monomer feed. This increase in the molecular weight may be attributed to the reduction in the number of initiating species (silyl intermediates) formed as the styrene concentration is increased in the monomer feed.

Our recent studies on the copolymerization of DMDCS, MPDCS, and BCDMSE with styrene have revealed that under dechlorination conditions, polar reaction intermediates formed from styrene can also mediate the polymerization.[39,40,48,49] Such intermediates may initiate the homopolymerization of styrene and result in the formation of PS. To determine if PMVSS-IV$_S$ and PMVSS-V$_S$ were formed in a similar way, we performed the polymerization of styrene (without MVDCS) with sodium (by using a sodium-to-styrene molar ratio equivalent to that used for the copolymer synthesis). PS obtained in this reaction had an M_w value of 6600, whereas M_w was 25,000 for PMVSS-IV$_S$ and 38,000 for PMVSS-V$_S$. Thus, the molecular weight data suggest that PMVSS-IV$_S$ and PMVSS-V$_S$ are not formed because of polymerization initiated by polar styryl intermediates but are probably formed by the silyl-initiated polymerization of styrene.

Thermal properties

The thermogravimetry (TG) curves of PMVSS-I to PMVSS-V and the homopolymer PMVS are compared in
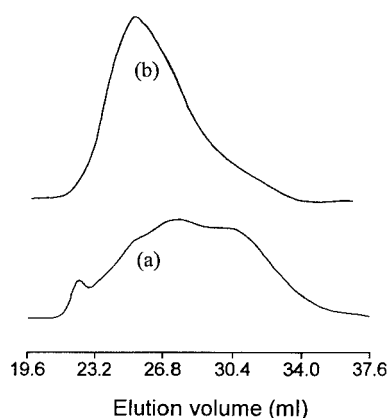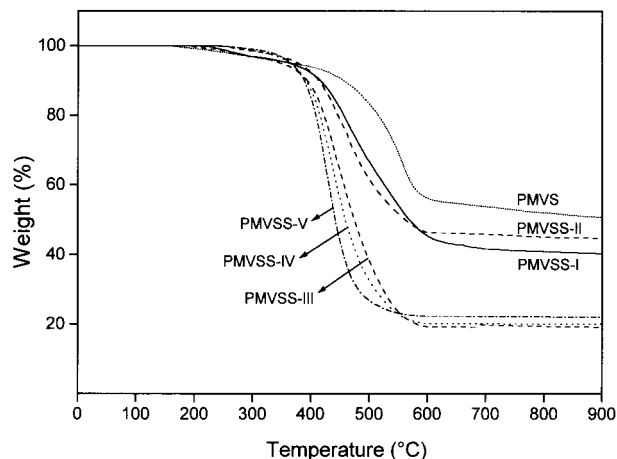
Figure 3 TG curves of PMVS and PMVSS-I to PMVSS-V.

Figure 3. PMVS has the highest overall thermal stability and gives a ceramic residue of 50.7% at 900°C under an inert atmosphere. The overall thermal stability and the ceramic residue decrease with the incorporation of styryl moieties by way of copolymerization. This is understood as follows: the incorporation of styryl units results in a reduction of the concentration of methylvinylsilyl units, which results in a reduction of crosslinking. Although it is expected that the overall thermal stability and ceramic residue should gradually decrease from PMVSS-I to PMVSS-V (i.e., as the styrene concentration increases in the monomer feed), the thermograms of PMVSS-I and PMVSS-II are significantly different from those of PMVSS-III to PMVSS-V. PMVSS-I and PMVSS-II have similar thermal properties. They are stable up to 410°C and undergo degradation above this temperature, leaving behind a ceramic residue of 43–46%. PMVSS-III to PMVSS-V, however, differ in their composition and exhibit similar thermal properties. They are stable up to 370°C and undergo degradation above this temperature, leaving behind a ceramic residue of 19–23%. The marked difference in the ceramic yield at 900°C and the lower thermal stability for PMVSS-III to PMVSS-V in comparison with those of PMVSS-I and PMVSS-II suggest that the copolymer structure undergoes a drastic change when the styrene-to-MVDCS ratio in the monomer feed is increased from 0.5 to 1.0 or higher. The ceramic yields of PMVSS-I and PMVSS-II are comparable to that of polycarbosilane through the heat treatment of poly(dimethylsilane), as reported by Yajima and coworkers.[1–4]

The TG curves of PMVSS-IV$_S$ and PMVSS-V$_S$ resemble that of the PS homopolymer, and no ceramic residue was observed at 900°C.

Ceramic residue

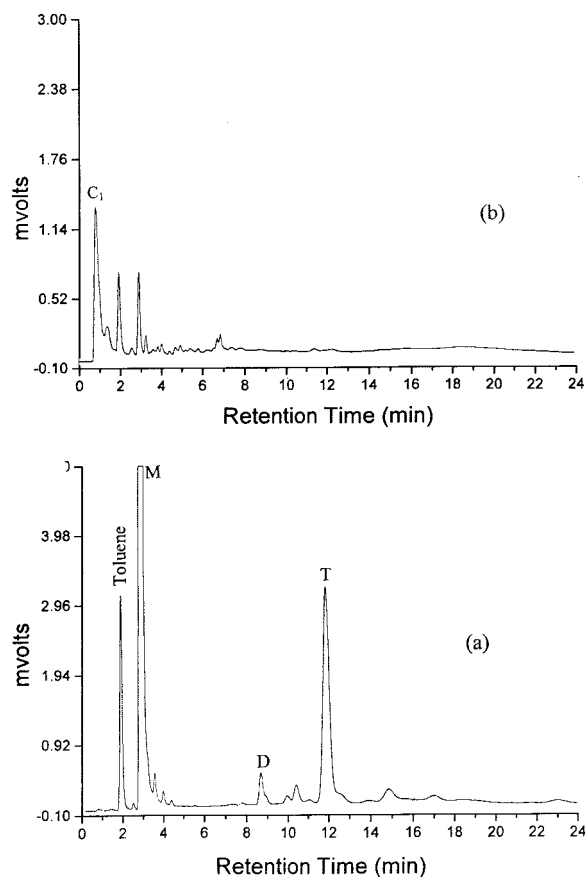The ceramic residues obtained by the heat treatment of PMVSS and PMVSS at 900°C are amorphous in

Figure 2 GPC curves of (a) PMVSS-IV$_S$ and (b) PMVSS-V$_S$.

Figure 4 Pyrograms of (a) PS and (b) PMVS.

nature, as evidenced by XRD. When the residues were heat-treated at 1400°C for 5 h 8 under an inert atmosphere, peaks corresponding to the β-SiC phase were observed by XRD. A detailed study on the conversion of these polymers into SiC ceramics and a compositional analysis of the ceramics that form are in progress and will form part of a future publication.

PGC studies

PMVSS-I to PMVSS-V are completely insoluble, and so their characterization by spectroscopic methods is rather difficult. PGC is a valuable tool for the characterization of intractable and crosslinked polymers.[50–52] The observed thermal behavior of poly(methylvinylsilylene-*co*-styrene) can be better explained by a detailed understanding of the copolymer composition and structure. For this purpose, PGC studies of both the insoluble and soluble fractions were carried out. Before the pyrolysis of the copolymers, the pyrolysis of PS and PMVS homopolymers was carried out independently at 700°C for a better understanding of the various products formed during the pyrolysis of the copolymers. The pyrograms (pyrolysis chromatograms) of PS and PMVS are shown in Figure 4. PS is known to yield styrene monomer and the dimer and

trimer of styrene as characteristic products. Under the experimental conditions used for the pyrolysis, PS gave the monomer (M) and trimer (T) of styrene as major products and the dimer (D) of styrene as a minor product. Toluene was also detected as one of the major products formed. The identification of the peaks of these products was confirmed with standard samples. The pyrogram of PMVS shows three major peaks, and the first peak has been identified as methane (C_1), possibly formed by the cleavage of Si—CH_3 groups. It has been identified by a comparison of the methane peak in the pyrogram of poly(dimethylsiloxane) carried out under identical conditions.[53] Hurwitz et al.[54] reported from TG-IR studies that methane was the primary volatile species formed from poly(methylsilane) at 525°C. Methane evolution was also reported by Hasegawa and Okamura[7] during the pyrolytic conversion of polycarbosilane to SiC fibers. The insoluble polymers, PMVSS-I to PMVSS-V, were pyrolyzed under conditions identical to those of PMVS and PS, and a typical pyrogram of PMVSS-III is shown in Figure 5. A number of additional peaks can be seen as a result of the distribution of the monomers in the polymers, indicating them to be copolymers and not mere physical mixtures of homopolymers. The concentrations of the major representative products resulting from styryl and methylvinylsilane (MVS) units in the polymers are given in Table III. The concentration of C_1 produced varies systematically with the MVDCS/styrene ratio in the feed. As the C_1 peak is not hindered by any other peak and is formed from an MVS unit, the C_1 concentration may be taken as an index of the MVS content in the polymer. In the case of PMVSS-I and PMVSS-II, the yield of the polymers is greater than 95%, and there is no soluble polymer fraction formed. Therefore, the ratio of the monomeric units in these polymers can be taken as the same as that in the monomer feed. Hence, taking PMVSS-I and PMVSS-II as standards and assuming the amount of C_1 produced is linear with respect to the concentration
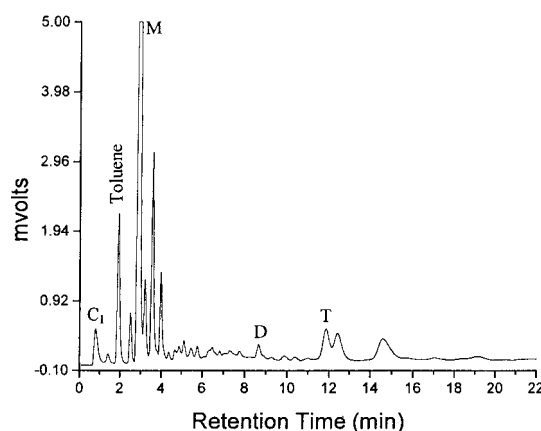

Figure 5 Pyrogram of PMVSS-III.

TABLE III
Concentration of the Characteristic Products at a
Pyrolysis Temperature of 700°C from the Copolymers

| | | Concentration of the product (wt %) | | |
| | | | Styrene | | |
Copolymer	CH_4 (C_1)	Monomer (M)	Trimer (T)	M/T ratio
PMVSS-I	10.7	47.5	0.8	59.4
PMVSS-II	8.2	48	0.8	60.0
PMVSS-III	4.5	58.3	1.9	30.7
PMVSS-IV	2.3	60.8	3.3	18.4
PMVSS-V	0.7	76.2	4.2	18.1
PS	<0.05	87.5	7.6	11.5

Figure 6 Plot of $A_{\mathrm{Ar}}/A_{\mathrm{Si-Me}}$ versus the ratio of styryl to PMVS units obtained from PGC: (■) A_{1492}/A_{1251} and (●) A_{1599}/A_{1251}.

of the MVS unit, we can calculate the concentration of the MVS unit (x) in copolymers PMVSS-III to PMVSS-V from the amount of C_1 (y) formed from them, using the following linear relationship, $y = mx + c$. As two sets of x and y values are available from PMVSS-I and PMVSS-II, the values of m and c can be obtained. The compositions of the copolymers are listed in Table IV.

As discussed earlier, the FTIR spectra of the copolymers show a characteristic Si—CH_3 peak from MVS units at 1251 cm^{-1} and aromatic peaks from styryl units at 1492 and 1599 cm^{-1}. Hence, a plot of the ratio of absorbance (A) values of the aromatic peak and Si—CH_3 peak versus the ratio of the monomeric units in the copolymers, as obtained from the PGC data, should be linear if the calculated values of the compositions are correct. A_{1492}/A_{1251} and A_{1599}/A_{1251} (Table II), versus the calculated ratios of the monomeric units in the copolymer (Table IV), are plotted in Figure 6, and the linear relationship in both the cases validates the methodology adopted to arrive at the composition.
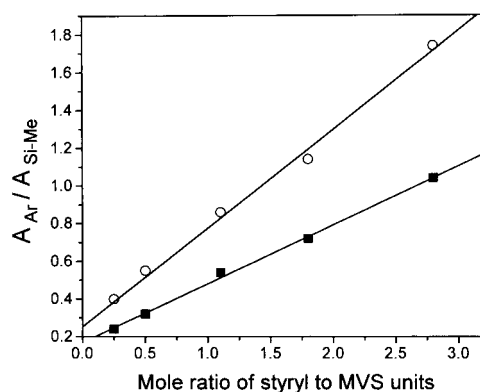
To confirm the compositions of copolymers PMVSS-III to PMVSS-V determined from PGC data, we estimated the silicon content of the copolymers by a wet analysis method, and the values are given in Table IV. The close agreement of the calculated silicon content and the experimentally observed values further vali-

dates the PGC method used for the compositional analysis.

PS can be considered to be blocks of styrene and produces mainly the monomer (87.5%) and the trimer (7.6%) under the pyrolysis conditions used. As isolated styrene contributes little to the production of the trimer, the concentration of the trimer in the products is a measure of the number of styrene blocks present in the copolymers. The concentration of the styrene trimer in the pyrolyzates of PMVSS-I and PMVSS-II is very small, and this indicates the presence of very few styrene blocks. This is also evident from the very high monomer-to-trimer ratio in the products (Table III). In the case of PMVSS-III, the concentration of the trimer in the products is significant, showing the presence of an appreciable number of styrene blocks. This is consistent with the much lower monomer-to-trimer ratio. In the case of PMVSS-IV and PMVSS-V, the concentration of the trimer in the products is very high, and the monomer-to-trimer ratio is very low; this shows the presence of a number of styrene blocks in them, as expected because of the very high styrene content in the monomer feed. Thus, the concentration of the trimer and the ratio of the monomer to the trimer indicate that PMVSS-I and PMVSS-II are different from PMVSS-III, PMVSS-IV, and PMVSS-V with respect to their structure, the former set of polymers having very few styrene blocks and the latter set of polymers having a high concentration of styrene blocks.

Soluble polymer fractions

The feed ratios of styrene to MVDCS for PMVSS-IV and PMVSS-V are much higher than their styryl content. Hence, excess styrene may formed PS with the incorporation of a small number of MVS units (initiating species) and is recovered as a soluble polymer; the yield is expected to be in good agreement with the high yields of the soluble fraction (Table I). The solu-
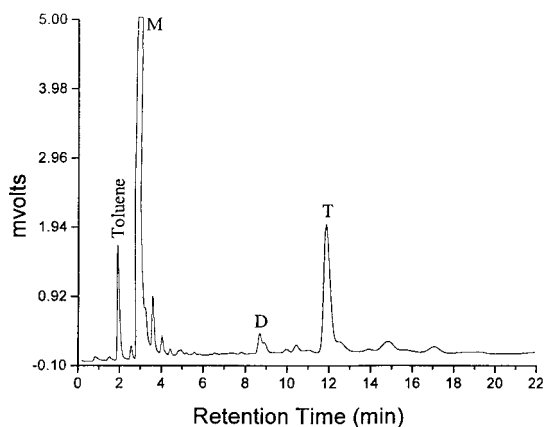
TABLE IV
Composition of the PMVSS Copolymers
Obtained from PGC

| Copolymer[a] | Molar ratio of styryl to to MVS units (a) | Silicon content (%) | |
		Calcd from a	Found[b]
PMVSS-III	1.1	14.9	15.6
PMVSS-IV	1.8	10.9	11.2
PMVSS-V	2.8	7.8	7.1

[a] Insoluble fractions.
[b] By the wet analysis method.

Figure 7 Pyrogram of PMVSS-IV$_S$.

ble polymers thus obtained, PMVSS-IV$_S$ and PMVSS-V$_S$, should behave more or less like PS. A close resemblance of their pyrograms with that of PS suggests that they are mostly PS. A typical pyrogram of a soluble polymer, PMVSS-IV$_S$, is shown in Figure 7. This is further supported by the observation that the thermograms of the soluble fractions (PMVSS-IV$_S$ and PMVSS-V$_S$) resemble that of PS. ^{1}H-NMR spectra of the soluble fractions also indicate that they are PS with the incorporation of a negligible quantity of MVS units.

Thermal degradation

Styrene blocks form linear chain segments between the crosslinks and reduce the crosslink density of the polymers. PMVSS-I and PMVSS-II have highly crosslinked structures because the amount of styrene present in them is lower and the styryl blocks are negligible, as inferred from pyrolysis studies. Hence, they are expected to be thermally more stable. The production of methane upon decomposition indicates the cleavage of Si—CH$_3$ bonds, which results in further crosslinking, as shown in Scheme 1, similar to the crosslinking reaction upon the decomposition of poly-(dimethylsiloxane)s[52] and the methylene insertion reaction during the heat treatment of poly(dimethylsilane).[7]

The decomposition of these highly crosslinked polymers, resulting in volatile fragments, is rather difficult, and so they are expected to yield a high amount of char residue. This is actually found to be so from their TGA curves (Fig. 3). The char residue is 44% for both PMVSS-I and PMVSS-II. PMVSS-III to PMVSS-V have greater linear segments because of the presence of increasing styrene blocks in them. This reduces their thermal stability and facilitates the formation of volatile fragments by the cleavage of the chain backbone involving styryl linkages. Hence, they are expected to be less stable and leave much less ceramic residue.

This behavior of these polymers is evident from their thermograms (Fig. 3).

The incorporation of styrene into the polymers is expected to reduce their thermal stability in a progressive manner. However, the thermograms in Figure 3 show a sudden change in the thermal degradation behavior of PMVSS-III, PMVSS-IV, and PMVSS-V in comparison with that of PMVSS-I and PMVSS-II. The marked difference between the thermograms of the former set of polymers and those of the latter set of polymers is consistent with the gross difference in the structures of the two sets of polymers with respect to the concentration of styrene blocks in them, as discussed earlier.

Copolymerization of MVDCS and styrene in a xylene/THF mixture

Schilling and a coworker[33,35] reported that MVDCS possessed uniquely high reactivity toward sodium and that the use of a polar-solvent/nonpolar-solvent blend moderated the reactivity. They reported that vinyl-functionalized polysilanes were obtained by the reaction of MVDCS with DMDCS or methyldichlorosilane and TMCS in refluxing toluene/THF or xylene/THF mixtures. In an attempt to synthesize vinyl-functionalized processable polysilahydrocarbon, the polymerization of MVDCS and styrene (1 : 0.5) was carried out in a xylene/THF mixture (7 : 1 v/v). The polymer (PMVSS-VI) was obtained in an 86% yield. The fractionation of this polymer with toluene did not yield any soluble fraction. The insolubility of this polymer indicated that —SiCH=CH$_2$ took part in the polymerization, and this resulted in the formation of a highly crosslinked polymer. This observation suggests that the use of a polar-solvent/nonpolar-solvent mixture could not suppress the participation of —SiCH=CH$_2$ during the copolymerization of MVDCS with styrene.

Probable reaction mechanism

As previously discussed, poly(methylvinylsilylene-*co*-styrene), obtained by the reaction of MVDCS and sty-
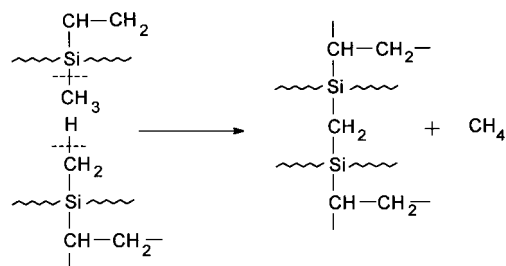
Scheme 1 Formation of additional crosslinks through the elimination of methane.

rene, mostly gave crosslinked insoluble polymers, and this made it difficult to elucidate the microstructures of these polymers. In the absence of microstructural analysis, it is rather difficult to propose a definite reaction mechanism. However, through a comparison with similar systems in which the microstructures of the polymers are understood, we may be able to propose a mechanism for the formation of crosslinked polysilahydrocarbons from MVDCS and styrene. Microstructural analyses of poly(tetramethyldisilylene-co-styrene)[36] and poly(methylphenylsilylene-co-styrene)[38,39] by ^{29}Si- and ^{13}C-NMR spectra suggested that disilyl and styryl moieties alternated with each other. PGC studies of poly(tetramethyldisilylene-co-styrene) synthesized from DMDCS and styrene in a 1 : 0.5 molar ratio[36] indicated that no polystyryl block was present, and this supported the microstructure derived from NMR spectral studies.

PGC studies of poly(methylvinylsilylene-co-styrene) obtained with monomer feed ratios of 1 : 0.25 and 1 : 0.5 (MVDCS/styrene) indicated that a very small number of polystyryl blocks was present. Thus, it is reasonable to believe that the styryl unit alternates with silyl units in these polymers. In the case of poly-(tetramethyldisilylene-co-styrene)[36] and poly(methylphenylsilylene-co-styrene)[38,39] obtained from styrene-to-diorganodichlorosilane feed ratios of 1.5 or less, mainly alternating units of disilyl and styryl are present in the polymer backbone, and it is believed that the copolymer formation proceeds through mediation by disilyl polar reaction intermediates. In line with the mechanism proposed for the formation of the aforementioned copolymers,[39] the copolymerization of MVDCS and styrene involving disilyl reaction intermediates can be given, as shown in Scheme 2.

The insoluble nature of the polymers suggests the involvement of vinyl groups in the polymerization, although residual vinyl groups may be present in insignificant concentrations. There are two possible ways by which the —SiCH=CH$_2$ group can undergo polymerization. The polymerization of the vinyl group can be initiated either by silyl anions or by styryl anions, as shown in Scheme 3. It is difficult to determine which one of these steps is taking place. When the styrene concentration is very high (i.e., for MVDCS/styrene ratios of 1 : 3 and 1 : 7), the addition of styrene to the growing chain is more probable, resulting in the formation of polystyryl blocks.

To understand at what stage of the polymerization the vinyl groups participated, we quenched the polymerization of MVDCS and styrene with monomer feed ratios of 0.5 : 1 and 1 : 1 after 15 min of reaction. Insoluble polymers were obtained in high yields (>90%), and this indicated that the vinyl groups took part in the polymerization even during the early stages of the reaction.
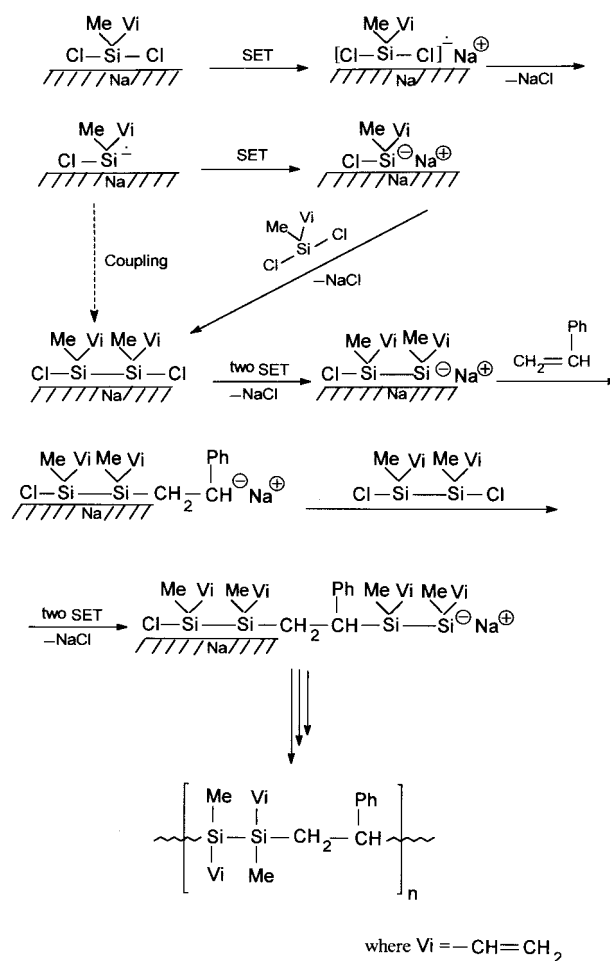
Scheme 2 Reaction scheme for the formation of poly-(methylvinylsilylene-co-styrene).

When the styrene/MVDCS ratio is further increased to 3 or 7, it is likely that distyryl/oligostyryl reaction intermediates, as proposed for the copolymerizations of styrene with MPDCS,[39] DMDCS,[48] and BCDMSE,[40] also operate (Scheme 4). The vinyl group present in the copolymer probably undergoes polymerization, as shown in Scheme 3, and this results in the formation of a crosslinked polymer.

CONCLUSIONS

The copolymers synthesized from MVDCS and styrene under dechlorination conditions with the monomer feed ratios of 1 : 0.25 and 1 : 0.5 did not contain any soluble fractions, whereas those synthesized with the monomer feed ratios of 1 : 1, 1 : 3, and 1 : 7 contained soluble fractions of 3, 26, and 47%. The insoluble fraction of the copolymers was formed because of the participation of vinyl groups in the copolymerization with styrene, and this resulted in the formation of crosslinked polymers. IR, ^{1}H-NMR, PGC, and TGA studies of the soluble fractions of the copol-
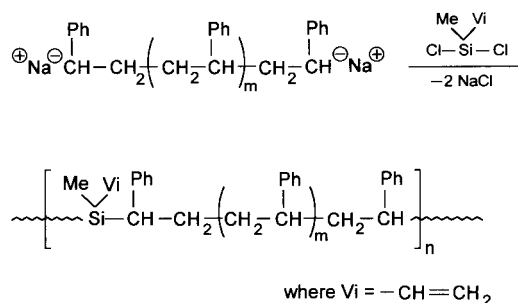
ymers suggested that they were mostly PS. The soluble fractions of the copolymers obtained for the monomer feed ratios of 1 : 3 and 1 : 7 had M_w's of 25,000 and 38,000, respectively, which were much larger than that of PS formed by sodium initiation under identical conditions; this suggested that the soluble fractions were not formed by sodium-initiated polymerization but were probably formed by initiation by silyl reaction intermediates.

PGC studies suggested that the copolymers obtained with the monomer feed ratios (MVDCS/styrene) of 1 : 0.25 and 1 : 0.5 did not contain any polystyryl blocks, whereas the copolymers (insoluble fractions) obtained with the monomer feed ratios of 1 : 1, 1 : 3, and 1 : 7 contained an appreciable number of polystyryl blocks. The PGC data were used to calculate the compositions of the insoluble fractions of the copolymers. The ratio of styryl units to methylvinylsilyl (MVS) units in the insoluble fractions of the copolymers was the same as that in the monomer feed for the monomer feed ratios (MVDCS/styrene) of 1 : 0.25 and 1 : 0.5. However, when the styrene concentration in the feed was increased, the concentration of styryl units present in the insoluble fractions of the copolymers was found to be less than that in the monomer feed, and the difference was more pronounced for the monomer feed ratios of 1 : 3 and 1 : 7.

A probable reaction mechanism involving disilyl reaction intermediates has been proposed. The polymerization of vinyl groups attached to silicon may be initiated by either silyl or styryl reaction intermedi-
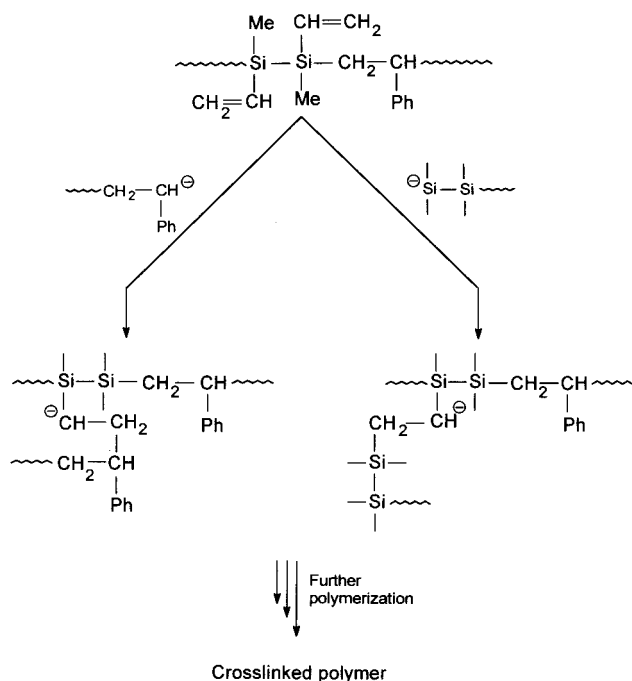
Scheme 4 Reaction scheme for the formation of poly-(methylvinylsilylene-*co*-styrene) through the involvement of distyryl/oligostyryl reaction intermediates.

ates, and this results in the formation of insoluble polymers as the major reaction products. At very high concentrations of styrene, distyryl or oligostyryl reaction intermediates may mediate the polymerization.

References

1. Yajima, S.; Hayashi, J.; Omori, M. Chem Lett 1975, 931.
2. Yajima, S.; Omori, M.; Hayashi, J.; Okamura, K.; Matsuzawa, T.; Liaw, C. F. Chem Lett 1976, 551.
3. Yajima, S.; Hasegawa, Y.; Hayashi, J.; Imura, M. J Mater Sci 1978, 13, 2569.
4. Yajima, S. Ceram Bull 1983, 62, 993.
5. Laine, R. M.; Babonneau, F. Chem Mater 1993, 5, 260.
6. Birot, M.; Pillot, J. P.; Dunogues, J. Chem Rev 1995, 95, 1443.
7. Hasegawa, Y.; Okumura, K. J Mater Sci 1983, 18, 3633.
8. Funayama, O.; Kato, T.; Tahiro, Y.; Isoda, T. J Am Ceram Soc 1993, 76, 717.
9. Yajima, S.; Okumara, K.; Hayashi, J. Chem Lett 1975, 1209.
10. Yajima, S.; Hasegawa, Y.; Imura, M. J Mater Sci 1978, 13, 3567.
11. Yajima, S.; Okumara, K.; Shishido, T.; Hasegawa, Y. Ger. Pat. 2,945,650 (1980).
12. Mucalo, M. R.; Milestone, N. B. J Mater Sci 1994, 29, 5934.
13. Mucalo, M. R.; Milestone, N. B.; Vickridge, I. C.; Swain, M. V. J Mater Sci 1994, 29, 4487.
14. Zeigler. Macromol Chem Macromol Symp 1991, 50, 107.
15. Schwab, S. T.; Blanchard, C. R.; Graef, R. C. J Mater Sci 1994, 29, 6320.
16. Su, S. R. In Synthesis and Processing of Ceramics; Scientific Issues 249; Rhine, W. E.; Shaw, T. M.; Gottschall, R. J.; Chen, Y., Eds.; Materials Research Society: Pittsburgh, PA, 1992; p 383.
17. Krukonis, V.; Michael, M. P.; Anderson, S. D. Report AD-A277349 (AFSOR-94-0081TR); 1994; p 37.
18. Zheng, G. B.; Santo, H.; Uchiyama, Y.; Kobayashi, K.; Cheng, H. M. J Mater Sci 1999, 34, 827.
19. Zheng, G. B.; Santo, H.; Uchiyama, Y.; Kobayashi, K.; Cheng, H. M. J Mater Sci Lett 1998, 17, 2047.
20. Smith, T. L., Jr. U.S. Pat. 4,631,179 (1986).

Scheme 3 Reaction scheme for the participation of silicon vinyl groups in the polymerization.

21. Bacque, E.; Pillot, J. P.; Birot, M.; Dunogues, J. Macromolecules 1988, 21, 30.
22. Wu, H. J.; Interrante, L. V. Chem Mater 1989, 1, 564.
23. Seyferth, D.; Lang, H. Organometallics 1991, 10, 551.
24. Pillot, J. P.; Bacque, E.; Dunogues, J.; Orly, P. Ger. Pat. 3,717,450 (1987).
25. van Aefferdan, B.; Habel, W.; Sartori, P. Chem Ztg 1991, 115, 1336.
26. Whitmarsh, C. K.; Interrante, L. V. Organometallics 1991, 10, 1336.
27. Habel, W.; Harnek, B.; Nover, C.; Sartori, P. J Organomet Chem 1994, 464, 13.
28. Habel, W.; Mayer, L.; Sartori, P. J Organomet Chem 1994, 474, 63.
29. Schilling, C. L., Jr.; Wesson, J. P.; Williams, T. C. Org Coat Appl Polym Sci Proc 1981, 46, 137.
30. Schilling, C. L., Jr.; Williams, T. C.; Wesson, J. P. Am Ceram Soc Bull 1983, 62, 912.
31. Schilling, C. L., Jr.; Wesson, J. P.; Williams, T. C. J Polym Sci Polym Symp 1983, 70, 121.
32. Schilling, C. L., Jr.; Williams, T. C. ONR Technical Report TR 83-2; 1983.
33. Schilling, C. L., Jr. ONR Technical Report TR 83-3; 1983.
34. Schilling, C. L., Jr. Brit Polym J 1986, 8, 355.
35. Schilling, C. L., Jr.; Williams, T. C. ONR Technical Report TR 83-1; 1983.
36. Rama Rao, M.; Packirisamy, S.; Ravindran, P. V.; Narendranath, P. K. Macromolecules 1992, 25, 565.
37. Packirisamy, S.; Rama Rao, M.; Narendranath, P. K.; Ravindran, P. V. In Macromolecules: Current Trends; Venkatachalam, S.; Joseph, V. C.; Ramaswamy, R.; Krishnamurthy, V. N., Eds.; Allied: New Delhi, 1995; p 92.
38. Packirisamy, S.; Ambadas, G.; Rama Rao, M.; Ninan, K. N. In Macromolecules: New Frontiers; Srinivasan, K. S. V., Ed.; Allied: New Delhi, 1998; p 1003.
39. Packirisamy, S.; Ambadas, G.; Rama Rao, M.; Balagangadharan, V. P.; Ninan, K. N. Macromolecules, submitted.
40. Ambadas, G.; Packirisamy, S.; Rama Rao, M.; Ninan, K. N. To be submitted.
41. van Aefferden, V. B.; Habel, W.; Sartori, P. Chem Ker Ztg 1990, 14, 259.
42. Adrain, T.; Habel, W.; Sartori, P. J Prakt Chem 1993, 335, 288.
43. Annual Reports of ASTM Standards; American Society of Testing and Materials: West Conshohocken, PA, 1982; Part 17, Chapter 169, p 137.
44. Dvornic, P. R.; Gerov, V. V. Macromolecules 1994, 27, 1068.
45. Bacque, E.; Pilot, J. P.; Birot, M.; Dunogues, J. Macromolecules 1988, 21, 30.
46. Analysis of Silicones; Smith, A. L., Ed.; Wiley: New York, 1974.
47. Pretsch, E.; Buhlmann, P.; Affolter, C. Structural Determination of Organic Compounds: Tables of Spectral Data, 3rd ed.; Springer-Verlag: New York, 2000.
48. Ambadas, G.; Packirisamy, S.; Ninan, K. N. To be submitted.
49. Ambadas, G. Ph.D. Thesis, University of Kerala, 2001.
50. Radhakrishnan, T. S.; Rama Rao, M. J Appl Polym Sci 1987, 34, 1985.
51. Rama Rao, M.; Radhakrishnan, T. S. J Appl Polym Sci 1990, 41, 2251.
52. Rama Rao, M.; Sebastian, T. V.; Radhakrishnan, T. S.; Ravindran, P. V. J Appl Polym Sci 1991, 42, 753.
53. Radhakrishnan, T. S. J Appl Polym Sci 1999, 73, 441.
54. Hurwitz, F. I.; Kacik, T. A.; Bu, X.-Y.; Masnovi, J.; Heimann, P. J.; Beyene, K. J Mater Sci 1995, 30, 3130.