Vinyl-Substituted Silphenylene Siloxane Copolymers: Novel High-Temperature Elastomers

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ABSTRACT: The synthesis of a series of vinyl-substituted silphenylene siloxane polymers of high molecular weight is described. ^{29}Si NMR spectroscopy indicates that the polymers possess an exactly alternating microstructure of the silphenylene and siloxane moieties. The materials are completely amorphous with glass transition temperatures between −60 and −86 °C. All polymers degrade thermally only above 500 °C under both oxidative or inert atmosphere. The char yields at 900 °C increase with increasing vinyl content from 30% up to almost 70%. Cross-linking of a small fraction of vinyl groups by hydrosilylation gives materials with elastomeric properties. Dynamic mechanical experiments indicate that the bulk of vinyl groups cross-links thermally at temperatures above 230 °C. Therefore, the temperature window for possible applications of these materials as fire-safe elastomers extends from about −86 °C to approximately 230 °C.

Introduction

Polymers with improved fire retardancy are needed for a number of future industrial and commercial applications.[1] In conventional technologies, the admixture of low molecular weight halogenated or phosphorus compounds is widely used in order to improve fire retardancy. The drawback of this technique, however, is the emission of toxic and corrosive gases upon combustion of such materials. Novel concepts for development of flame-retardant polymers focus on a variety of alternatives: high-temperature stable materials that decompose generating flame suppressants[2] or nonflammable polymers,[3] mixtures of plastics with surface-active flame retardants,[4] or materials that slow down radiative or conductive heating of the polymer by formation of porous insulating char or by endothermic phase transitions or decomposition processes. In the area of high-temperature stable elastomers, mainly fluorocarbon elastomers[5] and semifluorinated siloxanes have found commercial applications, both of which are high-cost materials.

The motivation for this work is to develop novel fire-retardant elastomers based on vinyl-substituted silphenylene siloxane copolymers. Silphenylene siloxane polymers are known to be stable at extremely high temperatures. This is due in part to the presence of the rigid silphenylene moiety which interferes with the siloxane redistribution reaction. Silphenylene siloxane polymers have been synthesized and investigated by several research groups over the past 30 years.[6] Flame retardancy of such materials increases as the degradation temperature increases and the emission of combustible gases at higher temperatures decreases. Since no industrially feasible synthetic pathway to the silphenylene diol comonomer has yet been found, these polymers have not been manufactured. Recently, novel concepts to overcome this problem have been investigated.[7]

Substitution of the silphenylene siloxane backbone with vinyl groups has been shown to shift degradation temperatures and char yields to higher values when compared to the corresponding methyl derivatives.[8,9] We have synthesized a series of vinyl-substituted polymers with the highest vinyl content reported to date. The results from synthesis, thermal analysis, and dynamic mechanical analysis are discussed here.

Experimental Section

Materials. 1,4-Bis(hydroxydimethylsilyl)benzene and methylvinyldichlorosilane were donated from General Electric Co. 1,4-Bis(hydroxydimethylsilyl)benzene was recrystallized from toluene, and methylvinyldichlorosilane was distilled prior to use. Bis(dimethylamino)dimethylsilane and divinyldichlorosilane were purchased from Gelest; 1,3-divinyl-1,3-dimethyl-1,3-dichlorodisiloxane was purchased from United Chemical Technologies and distilled before use.

Instrumentation. Gel permeation chromatography was performed on a Waters GPC (mobile phase: THF) using polystyrene standards and a UV detector. ^{1}H and ^{13}C NMR solution spectra were recorded on a Bruker DPX 300 instrument at 300 and 75.47 MHz, respectively. ^{29}Si NMR spectroscopy was carried out on a Varian XL-300 spectrometer. ^{13}C CP/MAS solid-state NMR spectra were recorded on a Bruker DSX-300 spectrometer with magic-angle spinning (MAS) in 7 mm o.d. rotors with 60 kHz ^{1}H decoupling. For the spectrum in Figure 10a, single-pulse excitation with a recycle delay of 2 s was used; the spinning rate was 2.2 kHz, and 64 scans were averaged. For the spectrum in Figure 10b, both single-pulse excitation and cross-polarization yielded similar spectra, with 2 s recycle delays; 3200 scans were averaged. Here, the total suppression of sidebands (TOSS)[10] sequence was applied to remove spinning sidebands, at a spinning rate of 6 kHz. DSC data were obtained using a Perkin-Elmer DSC-7 with a heating rate of 15 °C/min; glass transition temperatures were taken as the inflection points of the Δc_p step. Thermogravimetry was carried out on a Perkin-Elmer TGA-7 with a heating rate of 15 °C/min. Dynamic mechanical measurements were performed on a Rheometric Scientific DMTA-IV in shear sandwich mode (heating rate 2 °C/min, shear frequency 1 Hz). A Hewlett-Packard 5890 series II gas chromatograph connected to a Hewlett-Packard 5972 mass selective detector was used for GC/MS analysis.

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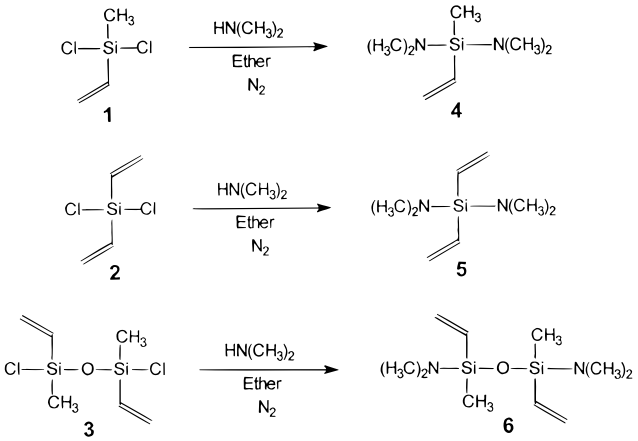

Figure 1. Synthesis of vinyl-substituted bis(dimethylamino)silanes.

Preparation of Vinyl-Substituted Bis(dimethylamino)silanes (4−6). Freshly distilled dichlorosilane **1**, **2**, or **3** (160 mmol) and anhydrous ether (25 mL) were placed in the dropping funnel of a dry, nitrogen-purged apparatus equipped with dry ice condenser, mechanical stirrer, gas inlet valve, and dropping funnel. Anhydrous ether (25 mL) was added to the flask and cooled with a dry ice/acetone mixture. An excess of anhydrous dimethylamine (about 35 g, 770 mmol) was condensed into the ether phase. The dichlorosilane solution was then added dropwise over a period of 1 h. After removal of the cooling bath, the reaction mixture was allowed to warm to room temperature. After stirring for an additional hour, the precipitated dimethylammonium chloride was quickly filtered in order to minimize exposure of the reaction mixture to moisture. The salt was quickly washed with ether. After drying of the combined filtrates over Na$_2$SO$_4$, the solvent was removed and the residue was fractionated using a Vigreux column. Depending upon the boiling point of the product, fractionation was either carried out under nitrogen (compound **4**) or under reduced pressure (compounds **5** and **6**).

*Bis(dimethylamino)methylvinylsilane (**4**):* Yield: 68%. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.10$ (s, 3H, SiC*H*$_3$), 2.48 (s, 12H, SiN(C*H*$_3$)$_2$), 5.71 (dd, 1H, SiC*H*=CH$_2$), 5.91−6.16 (m, 2H, SiCH=C*H*$_2$) ppm. ^{13}C NMR (CDCl$_3$): $\delta = -5.09$ (Si*C*H$_3$), 38.04 (SiN(*C*H$_3$)$_2$), 132.93 (SiCH=*C*H$_2$), 136.76 (Si*C*H=CH$_2$) ppm. Anal. Calcd for C$_7$H$_{18}$N$_2$Si: C, 53.11%; H, 11.46%; N, 17.69%. Found: C, 52.13%; H, 11.96%; N, 18.06%.

*Bis(dimethylamino)divinylsilane (**5**):* Yield: 64%. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 2.51$ (s, 12H, SiN(C*H*$_3$)$_2$), 5.73 (dd, 2H, SiC*H*=CH$_2$), 5.93−6.20 (m, 4H, SiCH=C*H*$_2$) ppm. ^{13}C NMR (CDCl$_3$): $\delta = 38.11$ (SiN(*C*H$_3$)$_2$), 134.25 (SiCH=*C*H$_2$), 135.14 (Si*C*H=CH$_2$) ppm. Anal. Calcd for C$_8$H$_{18}$N$_2$Si: C, 56.41%; H, 10.65%; N, 16.45%. Found: C, 56.57%; H, 10.91%; N, 16.24%.

*1,3-Bis(dimethylamino)-1,3-dimethyl-1,3-divinyldisiloxane (**6**):* Yield: 61%. ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.12$ (s, 6H, SiC*H*$_3$), 2.49 (s, 12H, SiN(C*H*$_3$)$_2$), 5.75 (dd, 2H, SiC*H*=CH$_2$), 5.72−6.10 (m, 4H, SiCH=C*H*$_2$) ppm. ^{13}C NMR (CDCl$_3$): $\delta = -2.42$ (Si*C*H$_3$), 37.64 (SiN(*C*H$_3$)$_2$), 133.30 (SiCH=*C*H$_2$), 137.07 (Si*C*H=CH$_2$) ppm. Anal. Calcd for C$_{10}$H$_{24}$N$_2$OSi$_2$: C, 49.13%; H, 9.89%; N, 11.46%. Found: C, 48.78%; H, 9.90%; N, 11.50%.

Polymer Synthesis. In a flask equipped with mechanical stirrer and reflux condenser, 1,4-bis(hydroxydimethylsilyl)benzene (7.998 g, 35.32 mmol) was added under argon atmosphere. Dry toluene (14 mL) and an aliquot of 34.61 mmol of freshly distilled bis(dimethylamino)silane compound (see Figure 1) was added by syringe. After refluxing the reaction mixture for 1 h, an additional amount of the corresponding bis(dimethylamino)silane (20 μL portions each time) was added at time intervals of 15 min, until there was no further significant dimethylamine evolution and the viscosity increased strongly. Upon precipitation of the reaction mixture into methanol (80 mL), a transparent gumlike material was obtained in over 90% yield. The product was dried at 60 °C in a vacuum oven.

The following are examples of analytical data.

*Polymer **ViMe***: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.12$ (s, 3H, H$_2$C=HCSiC*H*$_3$), 0.31 (s, 12H, Si(C*H*$_3$)$_2$), 5.64−6.14 (m, 3H, *H*$_2$C=*H*CSiCH$_3$), 7.53 (s, 4H, Aryl-*H*) ppm. ^{13}C NMR (CDCl$_3$): $\delta = -0.20$ (H$_2$C=HCSi*C*H$_3$), 0.99 (Si(*C*H$_3$)$_2$), 132.46 (Aryl-*C*H), 133.24 (H$_2$C=H*C*SiCH$_3$), 137.38 (H$_2$*C*=HCSiCH$_3$), 140.86 (Aryl-*C*Si) ppm. ^{29}Si NMR (CDCl$_3$): $\delta = -0.42$ (*Si*(CH$_3$)$_2$), −32.24 (H$_2$C=HC*Si*CH$_3$) ppm. Anal. Calcd for C$_{12}$H$_{22}$O$_2$Si$_3$: C, 51.01%; H, 7.85%. Found: C, 49.71%; H, 7.74%.

*Polymer **ViVi***: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.33$ (s, 12H, Si(C*H*$_3$)$_2$), 5.73−6.08 (m, 6H, Si(C*H*=C*H*$_2$)$_2$), 7.54 (s, 4H, Aryl-*H*) ppm. ^{13}C NMR (CDCl$_3$): $\delta = 1.02$ (Si(*C*H$_3$)$_2$), 132.48 (Aryl-*C*H), 134.70 (Si(*C*H=CH$_2$)$_2$), 135.51 (Si(CH=*C*H$_2$)$_2$), 140.73 (Aryl-*C*Si) ppm. ^{29}Si NMR (CDCl$_3$): $\delta = 0.41$ (*Si*(CH$_3$)$_2$), −46.63 (*Si*(CH=CH$_2$)$_2$) ppm. Anal. Calcd for C$_{13}$H$_{22}$O$_2$Si$_3$: C, 53.01%; H, 7.53%. Found: C, 54.31%; H, 7.33%.

*Polymer **ViMeViMe***: ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 0.14$ (s, 6H, H$_2$C=HCSiC*H*$_3$), 0.33 (s, 12H, Si(C*H*$_3$)$_2$), 5.70−6.09 (m, 6H, *H*$_2$C=*H*CSiCH$_3$), 7.57 (s, 4H, Aryl-*H*) ppm. ^{13}C NMR (CDCl$_3$): $\delta = -0.34$ (H$_2$C=HCSi*C*H$_3$), 1.01 (Si(*C*H$_3$)$_2$), 132.43 (Aryl-*C*H), 133.27 (H$_2$C=H*C*SiCH$_3$), 137.15 (H$_2$*C*=HCSiCH$_3$), 140.80 (Aryl-*C*Si) ppm. ^{29}Si NMR (CDCl$_3$): $\delta = -0.34$ (*Si*(CH$_3$)$_2$), −33.00 (H$_2$C=HC*Si*CH$_3$) ppm. Anal. Calcd for C$_{16}$H$_{28}$O$_3$Si$_4$: C, 50.47%; H, 7.41%. Found: C, 49.99%; H, 7.35%.

Results and Discussion

The motivation to investigate flame-retardant elastomers by substituting a silphenylene siloxane polymer backbone with a high number of vinyl groups is the following:

Vinyl-substituted siloxanes can be cured by addition of a multifunctional Si−H compound under catalysis with a variety of platinum complexes.[11] The hydrosilylation reaction of the double bonds with the Si−H cross-linker will then generate a network structure. Depending upon the ratio of cross-linker to vinyl groups, the cross-link density of such a system can be controlled over a broad range. Materials can thus be obtained with properties ranging from a slightly cross-linked elastomer to a highly cross-linked resin type structure. For elastomers, our concept is to transform a polymer with high vinyl content by hydrosilylation of a small amount of all vinyl groups present. The bulk of the unsaturated functionalities will then remain and be available to thermally cross-link at temperatures higher than the application temperature of the elastomer, i.e., in case of a fire. The resulting resin structure will then guarantee high char yields and, hence, good flame retardancy.

The synthesis of silphenylene siloxane copolymers was carried out by the disilanol−diaminosilane deficiency polycondensation route. After its original development by Burks and co-workers,[12] this synthetic procedure has successfully been adapted by a number of investigators in order to prepare high molecular weight polymers with exactly alternating chemical structures.[8,12−15] Table 1 shows the polymers synthesized in this investigation. We have used this technique for preparation of novel silphenylene siloxane derivatives with a high degree of vinyl functionalization (see Figure 2).

The vinyl-substituted bis(dimethylamino)silanes needed as starting materials were synthesized according to Figure 1 in a variation of a procedure by Pittman et al.[14]

Bis(dimethylamino)silanes are much less sensitive to hydrolysis than the corresponding dichlorosilane derivatives, which facilitates the handling of these monomers. Furthermore, their lower reactivity is one factor respon-

Table 1. Structure, Molecular Weight, and Glass Transition Temperatures of Silphneylene Siloxane Copolymers with Varying Vinyl Content

name	R_1	R_2	$M_w \times 10^3$ [g/mol]^b	$M_n \times 10^3$ [g/mol]^b	T_g [°C]^d
MeMe	CH_3	CH_3	455	266	−59
Vi30Me	30% $CH{=}CH_2$ 70% CH_3	CH_3	300	124	−61
Vi50Me	50% $CH{=}CH_2$ 50% CH_3	CH_3	*c*	*c*	−61
Vi70Me	70% $CH{=}CH_2$ 30% CH_3	CH_3	*c*	*c*	−63
ViMe	$CH{=}CH_2$	CH_3	*c*	*c*	−63
ViVi	$CH{=}CH_2$	$CH = CH_2$	*c*	*c*	−71
ViMeViMe	*a*	*a*	*c*	*c*	−86

[a] See Figure 2 for structural details. [b] Determined by gel permeation chromatography in THF. [c] Not completely soluble in THF. [d] Determined by differential scanning calorimetry.

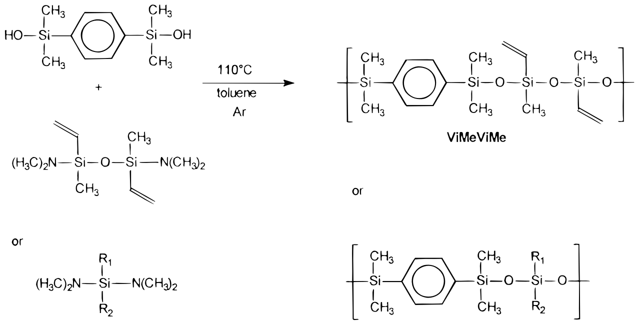

Figure 2. Synthesis of vinyl-substituted silphenylene siloxane copolymers.

sible for formation of an exactly alternating polymer microstructure without homopolymer sequences when used in an AB type polycondensation with a disilanol comonomer such as 1,4-bis(hydroxydimethylsilyl)benzene. At room temperature, bis(dimethylamino)silanes can easily be handled with exposure to air. At higher temperatures, they will eventually react in the presence of moisture, forming cyclic tri- and tetrasiloxanes as well as linear oligosiloxanes as the main hydrolysis products. This reaction can be monitored in situ by evaporating a (moist) solution of a bis(dimethylamino)silane such as **4** into a gas chromatography column and analyzing the separated fractions by mass spectroscopy (Figure 3). The peaks in the GC trace can then be assigned to the species listed in Table 2. Figure 3b shows the mass spectrum of fraction 1 of the GC trace as an example.

To avoid any hydrolytic side reactions, the polycondensation of 1,4-bis(hydroxydimethylsilyl)benzene and bis(dimethylamino)silane was performed under strict exclusion of water in the reaction mixture as described in the Experimental Section. All polymers were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. Parts a and b of Figure 4 show the ^1H and ^{29}Si NMR spectra of polymer **ViVi**, respectively. Both spectra indicate the high purity of the sample. The ^{29}Si NMR spectrum shows two singlets, which correspond to the two types of silicon atoms present, confirming that the polymer has indeed an exactly alternating microstructure. However, a side reaction seems to take place during the polycondensation of materials with high vinyl content. Although it occurs to an extent of less than 1%, this side reaction gives rise to a very small amount of cross-linking. Since the effect is so small, analysis of the nature and reason for the cross-linking reaction has been very difficult. It seems, however, that some vinyl groups start to cross-link during polymerization, making molecular weight data difficult to obtain. Therefore, Table 1 only gives GPC data for the absolutely un-cross-linked silphenylene siloxane polymers. The degree of polymerization before the onset of cross-linking of the slightly cross-linked samples is assumed to be in the

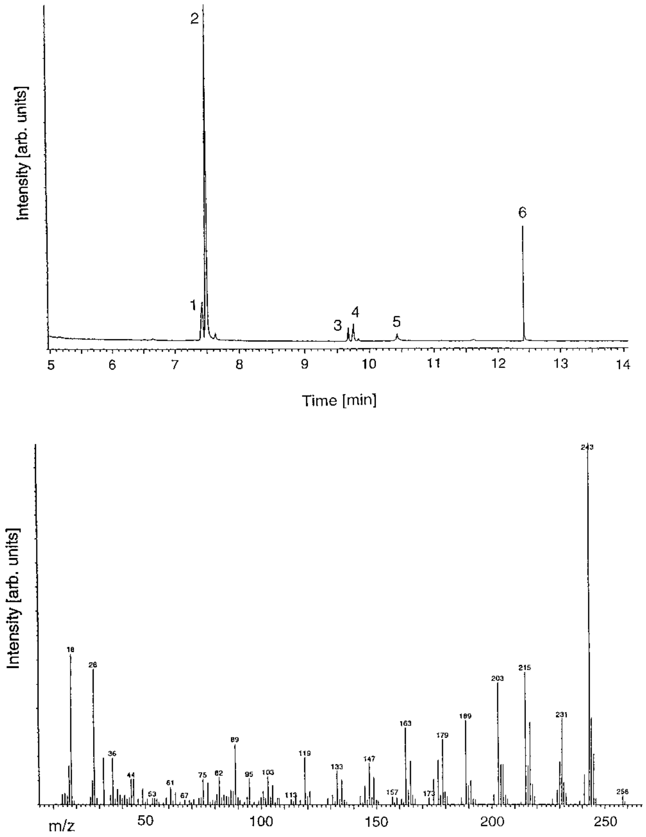

Figure 3. (a, top) Gas chromatography trace of a bis(dimethylamino)methylvinylsilane solution in (moist) dichloromethane. (b, bottom) Mass spectrum of fraction 1 of this particular GC trace.

Table 2. GC/MS Peak Assignment of a Bis(dimethylamino)methylvinylsilane Solution in (Moist) Dichloromethane (See Figure 3)

C fraction no.	elution time [min]	identification of major fragments [*m/z*]	assignment to chemical species
1	7.42	258 (M^+); 243 ($M^+ - CH_3$); 231 ($M^+ - CH{=}CH_2$); 215 ($M^+ - CH_3{-}CH{=}CH_2$); 203 ($M^+ - 2(CH{=}CH_2)$)	trimethyltrivinylcyclotrisiloxane, $C_9H_{18}O_3Si_3$ (258.5)
2	7.49	175 ($M^+ + OH$); 157 (M^+)	bis(dimethylamino)methylvinylsilane, $C_7H_{18}N_2Si$ (158.32)
3	9.67	344 (M^+); 329 ($M^+ - CH_3$); 317 ($M^+ - CH{=}CH_2$); 301 ($M^+ - CH_3{-}CH{=}CH_2$); 290 ($M^+ - 2(CH{=}CH_2)$)	tetramethyltetravinylcyclotetratrasiloxane, $C_{12}H_{24}O_4Si_4$ (344.66)
4	9.75	243 (M^+); 231 ($M^+ - CH_3$); 217 ($M^+ - CH{=}CH_2$)	1,3-bis(dimethylamino)-1,3-dimethyl-1,3-divinyldisiloxane, $C_{10}H_{24}N_2OSi_2$ (244.49)
5	10.42	126; 113; 99; 85.	not assignable
6	12.42	44 (M^+); 28 ($M^+ - H{-}CH_3$)	dimethylamine, C_2H_7N (45.09)

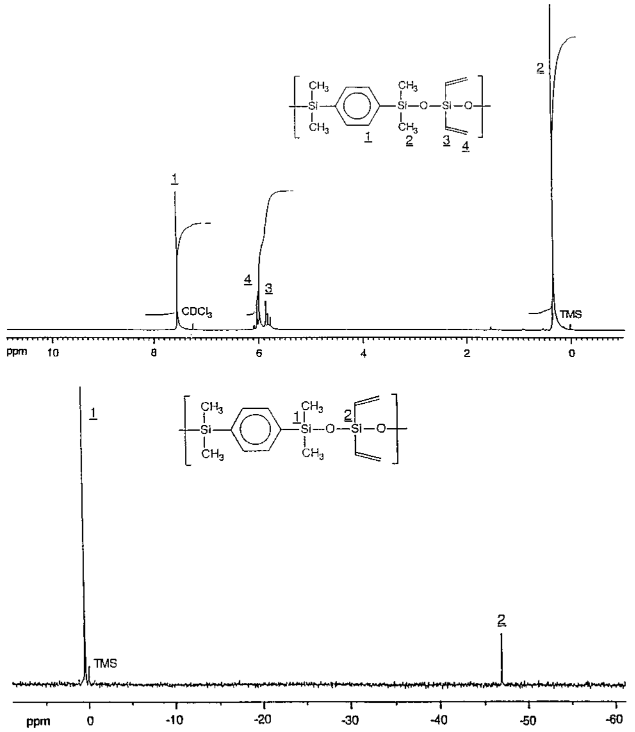

Figure 4. Spectroscopic clarification of polymer microstructure. (a, top) ^{1}H and (b, bottom) ^{29}Si NMR spectrum of a **ViVi** solution in CDCl$_3$.

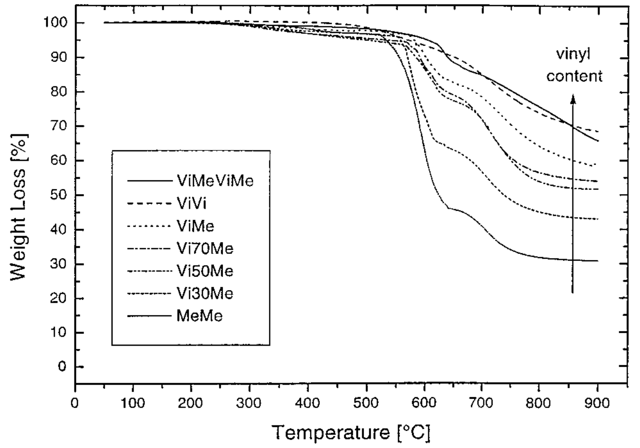

Figure 5. Thermogravimetric scans under oxidative atmosphere (dry air, heating rate 15 °C/min).

same range. It is possible that the small proton resonances seen in Figure 4a between 0.5 and 2.0 ppm may be assigned to cross-linked structures.

Thermal and Mechanical Properties. The influence of the vinyl content on thermal stability and char yield was systematically studied by thermogravimetry (TGA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMTA).

The TGA scans of all polymers under oxidative atmosphere show that the onset of major thermal degradation evidenced by an abrupt change of slope shifts from about 520 °C (reference sample **MeMe** without vinyl groups) to higher temperatures as the vinyl content increases (Figure 5). Similar behavior has been observed previously.[8,9] Polymers **ViVi** and **ViMeViMe**, which have never been synthesized before, have degradation temperatures of over 600 °C, corresponding to the highest temperature stability of a poly(silphenylene siloxane) reported so far.

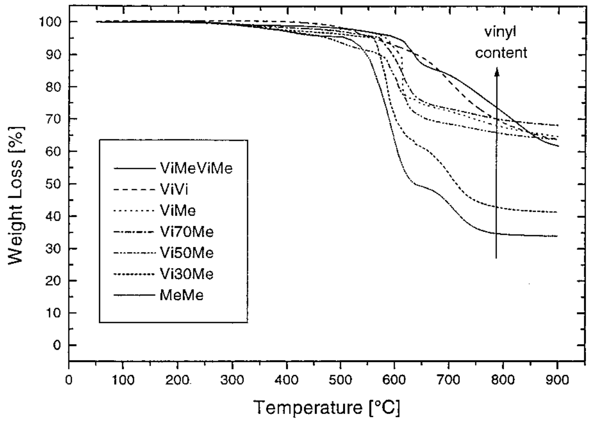

Figure 6. Thermogravimetric scans under inert atmosphere (nitrogen, heating rate 15 °C/min).

Since all TGA scans exhibit essentially the same two-step weight loss profile, the samples seem to degrade via a common mechanism. The slight weight loss of less than 3% between 280 and 450 °C may be due to splitting off of side chains and some subsequent cross-linking through oxygen bridges as suggested by Dvornic and co-workers.[15] The cleavage of N(CH$_3$)$_2$ end groups may also contribute to this initial weight loss. More details of the degradation mechanism are currently under investigation using TGA connected to a GC/MS analytical unit.

Owing to an increasing vinyl volume fraction, the char yields at 900 °C increase from 30% (**MeMe**) to almost 70% (**ViMeViMe**). Similar results with respect to degradation temperatures and char yields are obtained in TGA experiments under inert atmosphere (Figure 6). A char yield of 70% in air or nitrogen is a remarkable result for a siloxane elastomer.

DSC studies to reveal the phase behavior of the polymers expectedly show the complete absence of crystallinity in all samples. The glass transition temperatures decrease from −59 to −71 °C as the vinyl content increases (Table 1). The glass transition of polymer **ViMeViMe** occurs at even lower temperature (−86 °C) due to the larger volume fraction of flexible siloxane units in the backbone.

Between T_g and about 250 °C, we observe no thermal transitions in any of the samples. At temperatures between 250 and 300 °C and about 450 °C, broad exothermic signals with transition enthalpies between roughly −20 and −210 J/g (as a function of vinyl content) are detected in all vinyl-containing polymers.[16] Figure 7 shows the DSC scan of **ViMeViMe** as an example. Because there is no heat flow in the DSC experiment of the reference polymer **MeMe** in this temperature range, these exothermic signals are assigned to a thermally induced cross-linking process of vinyl side groups. Depending upon the vinyl content, the resulting materials range between flexible elastomeric networks with a moderate degree of cross-linking to highly cross-linked, brittle resins at higher vinyl contents; after heating the resinous samples to 450 °C, the glass transition is no longer seen due to the strongly restricted molecular motions in the highly cross-linked materials. The glass transition temperature of **MeMe**, on the other hand, remains essentially unchanged, even after a thermal excursion to 450 °C.

Dynamic mechanical thermal experiments support the interpretation of the DSC results. As a consequence

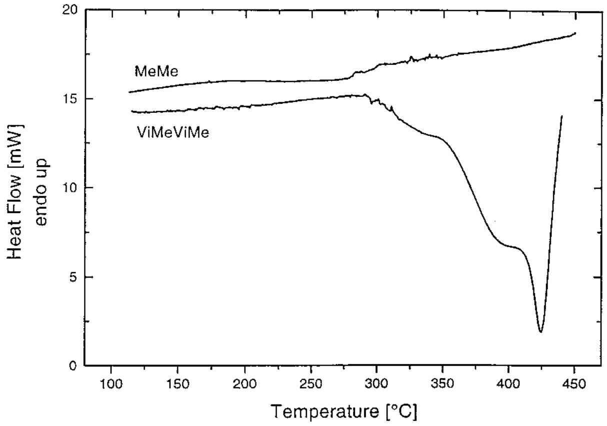

Figure 7. High-temperature DSC scans of vinyl-substituted polymer **ViMeViMe** and polymer **MeMe** without vinyl groups (15 °C/min).

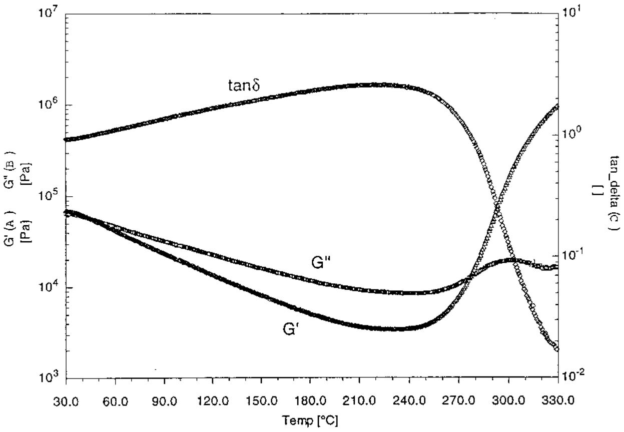

Figure 8. Temperature dependence of shear storage (G') and loss (G'') moduli as well as tan δ of polymer **Vi30Me** (heating rate: 2 °C/min), measured under nitrogen.

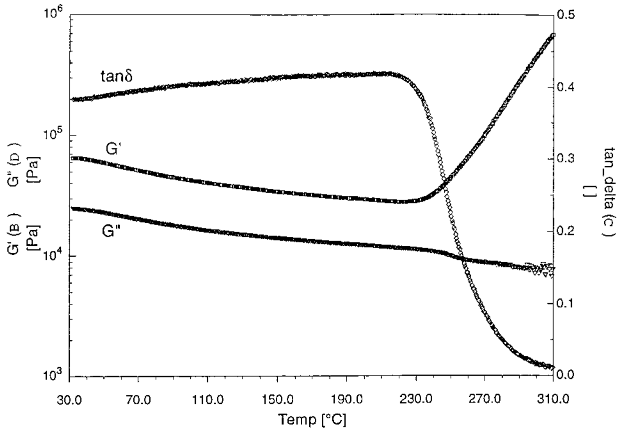

Figure 9. Temperature dependence of shear storage (G') and loss (G'') moduli as well as tan δ of polymer **ViMe** (heating rate: 2 °C/min), measured under nitrogen.

of thermally induced cross-linking of vinyl groups, the shear storage moduli G' of all vinyl-containing polymers increase at temperatures above 230 °C. (Figures 8 and 9 show polymers **Vi30Me** and **ViMe** as examples.). These somewhat lower onset temperatures as compared to those from DSC experiments are due to both the higher sensitivity of DMTA for this process and the smaller heating rate of the DMTA experiment (2 vs 15 °C/min in DSC), which causes less thermal lag. As expected, the loss modulus tan δ decreases upon cross-linking.

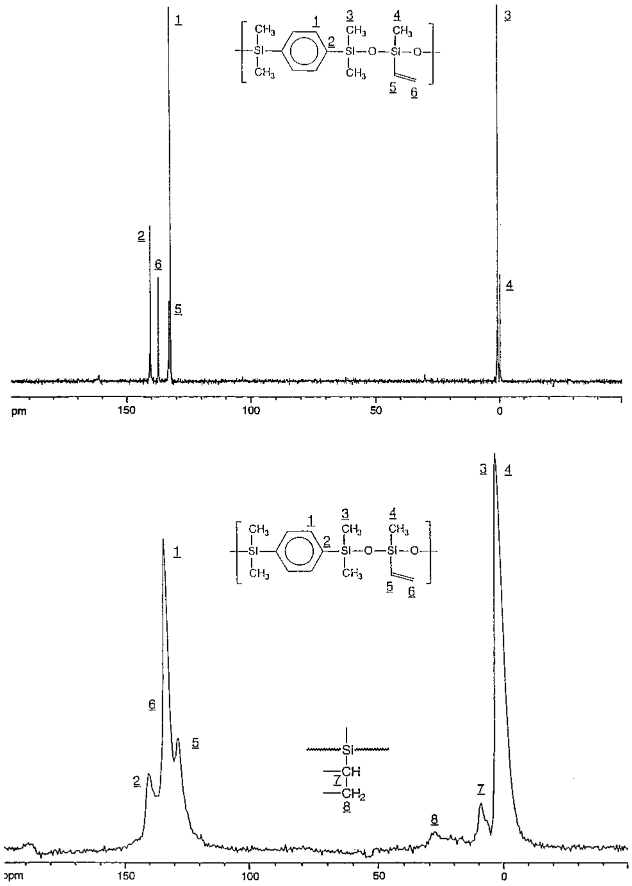

Figure 10. ^{13}C MAS solid-state NMR spectra of a neat **ViMe** sample. (a, top) As prepared; spectrum acquired after direct (single-pulse) excitation. (b, bottom) After thermal treatment at 450 °C for 1 h in air; spectrum acquired after cross-polarization and total suppression of sidebands.

Spectroscopic evidence for the cross-linking of vinyl groups comes from ^{13}C CP/MAS solid-state NMR spectroscopy. Figure 10a shows the spectrum of a neat **ViMe** sample. The extremely narrow line widths are similar to the ones of the corresponding solution NMR spectrum. This is a direct indication of the high mobility of all molecular moieties in this fully amorphous sample. The exact assignment of the carbon signals is based on a $^{1}H-^{13}C$ shift correlation (HETCOR) NMR spectrum, which is not shown here. After heating the sample to 450 °C for 1 h prior to the measurement, the line widths of the ^{13}C CP/MAS NMR spectrum broaden considerably (Figure 10b) as a consequence of the decreased mobility in the now cross-linked, brittle resinlike sample. The resonances at 9 and 29 ppm are assigned to $-Si-CH_2-$ and $-Si-CH_2CH_2-$ units, respectively; these signals correspond to the cross-linking sites of the network. Since the molecular mobility is restricted more and more as the cross-linking reaction of neighboring vinyl moieties proceeds, not all of the vinyl groups initially present can adopt the conformational and topological environment necessary for further cross-linking to occur. Therefore, the signal corresponding to those unreacted vinyl functionalities can still be observed after the thermal treatment (Figure 10b).

Despite the absence of vinyl groups, the shear storage modulus G' of polymer **MeMe** increases upon heating (Figure 11). The corresponding onset temperature of 300 °C, however, is considerably higher than found for all vinyl-substituted derivatives. An explanation for this behavior cannot be given at this time. It is known that

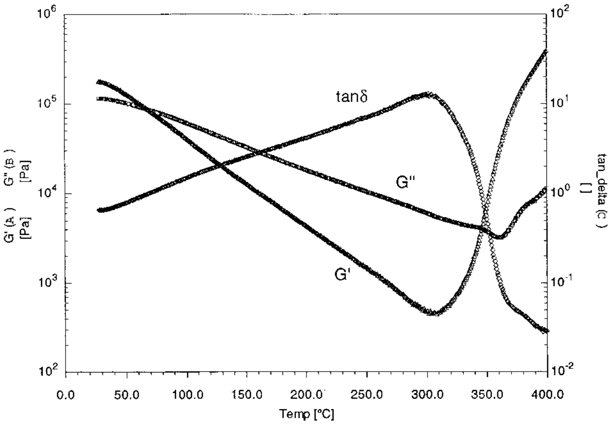

Figure 11. Temperature dependence of shear storage (G') and loss (G'') moduli as well as tan δ of polymer **MeMe** (heating rate: 2 °C/min), measured under nitrogen.

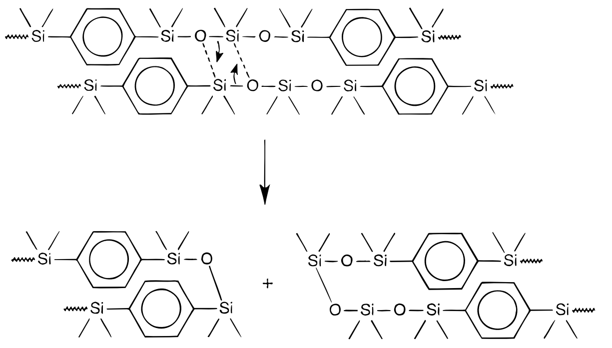

Figure 12. Proposed mechanism of redistribution reactions in silphenylene siloxane polymers according to ref 17a.

silphenylene siloxane polymers undergo siloxane redistribution reactions (see Figure 12) below the apparent degradation temperature.[17] This process may change the sample viscosity and, thus, the shear moduli. Because the siloxane redistribution reaction is knowm to scan with little enthalpy change, this process is consistent with the lack of detectable heat flow in the DSC experiment of **MeMe**. On the basis of the observations of Dvornic and co-workers,[15] the increase of G' above 300 °C may be induced by side-chain cleavage and subsequent cross-linking via oxygen bridges.

The siloxane redistribution reaction with subsequent formation of small volatile molecular species has been shown to be an important factor in the degradation mechanism of silphenylene siloxane polymers. The following influence of the vinyl groups accounts for the results with our samples: At temperatures below the onset of siloxane redistribution reactions, the vinyl functionalities in vinyl-substituted silphenylene siloxane polymers cross-link. The restricted mobility within the resulting network presumably prevents redistribution reactions from happening on a larger scale. This will lower the formation of volatile siloxane species and increase the char yield with increasing vinyl content as observed in the TGA experiments.

Conclusions

A series of strictly alternating vinyl-substituted (i.e., cross-linkable) silphenylene siloxane copolymers with systematically varying vinyl content have been synthesized. The polymers are completely amorphous gums with glass transition temperatures ranging from −86 to −59 °C as a function of vinyl content and volume fraction of highly mobile siloxane units. The materials degrade thermally above 500 °C. As the vinyl content increases, both the onset temperature of major degradation and the char yield at 900 °C shift to higher values. Polymer **ViMeViMe** has an extremely high degradation temperature of over 600 °C and a char yield of almost 70% in air, which makes it a promising candidate for potential applications as a flame-retardant elastomer. The reason for the remarkable thermal stability is ascribed to a cross-linking reaction of the vinyl functionalities, which occurs slightly below the onset of siloxane redistribution reactions around 300 °C. The redistribution reaction is the principal mechanism of thermal degradation of initially alternating poly(silphenylene siloxane)s. Because the thermal stability depends on the vinyl content, i.e., the cross-link density above 230 °C, we conclude that network formation hampers siloxane redistribution reactions in a significant way. Since the polymers form highly cross-linked network structures upon heating, the phase range for use as elastomeric materials is limited to from −86 °C until about 230 °C. DSC, DMTA, and solid-state NMR spectroscopy have been demonstrated to be versatile tools in studying vinyl cross-linking in these systems.

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References and Notes

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