

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. ²⁹Si 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°C 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 percent up to almost 70 percent. 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.

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1. 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 which decompose generating flame suppressants [2] or non-flammable polymers [3], mixtures of plastics with surface active flame retardants [4] or materials which 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.

2. Experimental Section

Materials. 1,4-Bis(hydroxydimethylsilyl) benzene and methylvinyl dichlorosilane were donated from General Electric Company. 1,4-Bis(hydroxydimethylsilyl) benzene was recrystallized from toluene, methylvinyl dichlorosilane was distilled prior to use. Bis(dimethylamino) dimethylsilane and divinyl dichlorosilane were purchased from Gelest, 1,3-divinyl-1,3-dimethyl-1,3-dichloro disiloxane 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. ^1H and ^{13}C NMR solution spectra were recorded on a Bruker DPX 300 instrument at 300MHz 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 ^1H decoupling. For the spectrum in Figure 10a, single-pulse excitation with a recycle delay of 2 seconds was used; the spinning rate was 2.2 kHz, 64 scans were averaged. For the spectrum in Figure 10b, both single-pulse excitation and cross-polarization yielded similar spectra, with 2-second recycle delays; 3200 scans were averaged. Here, the total-suppression of sidebands (TOSS) [Dixon, JCP 77, 1800 (1982)] 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.

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 1h. After removal of the cooling bath, the reaction mixture was allowed to warm up 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 Na₂SO₄, 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 %

¹H NMR (CDCl₃, 300 MHz): δ = 0.10 (s, 3H, SiCH₃), 2.48 (s, 12H, SiN(CH₃)₂), 5.71 (dd, 1H, SiCH=CH₂), 5.91-6.16 (m, 2H, SiCH=CH₂) ppm.

¹³C NMR (CDCl₃): δ = -5.09 (SiCH₃), 38.04 (SiN(CH₃)₂), 132.93 (SiCH=CH₂), 136.76 (SiCH=CH₂) ppm.

Anal. Calcd. for C₇H₁₈N₂Si: 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 %

¹H NMR (CDCl₃, 300 MHz): δ = 2.51 (s, 12H, SiN(CH₃)₂), 5.73 (dd, 2H, SiCH=CH₂), 5.93-6.20 (m, 4H, SiCH=CH₂) ppm.

¹³C NMR (CDCl₃): δ = 38.11 (SiN(CH₃)₂), 134.25 (SiCH=CH₂), 135.14 (SiCH=CH₂) ppm.

Anal. Calcd. for C₈H₁₈N₂Si: 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-divinyl disiloxane (**6**): Yield: 61 %

¹H NMR (CDCl₃, 300 MHz): δ = 0.12 (s, 6H, SiCH₃), 2.49 (s, 12H, SiN(CH₃)₂), 5.75 (dd, 2H, SiCH=CH₂), 5.72-6.10 (m, 4H, SiCH=CH₂) ppm.

¹³C NMR (CDCl₃): δ = -2.42 (SiCH₃), 37.64 (SiN(CH₃)₂), 133.30 (SiCH=CH₂), 137.07 (SiCH=CH₂) ppm.

Anal. Calcd. for C₁₀H₂₄N₂OSi₂: 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 freshly distilled bis(dimethylamino) silane compound (see Figure 1) was added by syringe. After refluxing the reaction mixture for 1h, an additional amount of the corresponding bis(dimethylamino) silane (20 μL portions each time) was added at time intervals of 15 minutes, 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 gum like material was obtained in over 90 percent yield. The product was dried at 60°C in a vacuum oven.

Examples of analytical data:

Polymer **ViMe**:

¹H NMR (CDCl₃, 300 MHz): δ = 0.12 (s, 3H, H₂C=HCSiCH₃), 0.31 (s, 12H, Si(CH₃)₂), 5.64-6.14 (m, 3H, H₂C=HCSiCH₃), 7.53 (s, 4H, Aryl-H) ppm.

¹³C NMR (CDCl₃): δ = -0.20 (H₂C=HCSiCH₃), 0.99 (Si(CH₃)₂), 132.46 (Aryl-CH), 133.24 (H₂C=HCSiCH₃), 137.38 (H₂C=HCSiCH₃), 140.86 (Aryl-CSi) ppm.

²⁹Si NMR (CDCl₃): δ = -0.42 (Si(CH₃)₂), -32.24 (H₂C=HCSiCH₃) ppm.

Anal. Calcd. for C₁₂H₂₂O₂Si₃: C, 51.01%; H, 7.85%. Found: C, 49.71%; H, 7.74%.

Polymer ViVi:

^1H NMR (CDCl_3 , 300 MHz): $\delta = 0.33$ (s, 12H, $\text{Si}(\underline{\text{C}}\text{H}_3)_2$), 5.73-6.08 (m, 6H, $\text{Si}(\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}_2)_2$), 7.54 (s, 4H, Aryl- $\underline{\text{H}}$) ppm.

^{13}C NMR (CDCl_3): $\delta = 1.02$ ($\text{Si}(\underline{\text{C}}\text{H}_3)_2$), 132.48 (Aryl- $\underline{\text{C}}\text{H}$), 134.70 ($\text{Si}(\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}_2)_2$), 135.51 ($\text{Si}(\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}_2)_2$), 140.73 (Aryl- $\underline{\text{C}}\text{Si}$) ppm.

^{29}Si NMR (CDCl_3): $\delta = 0.41$ ($\underline{\text{S}}\text{i}(\text{CH}_3)_2$), -46.63 ($\underline{\text{S}}\text{i}(\text{CH}=\text{CH}_2)_2$) ppm.

Anal. Calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si}_3$: C, 53.01%; H, 7.53%. Found: C, 54.31%; H, 7.33%.

Polymer ViMeViMe:

^1H NMR (CDCl_3 , 300 MHz): $\delta = 0.14$ (s, 6H, $\text{H}_2\text{C}=\text{HCSi}\underline{\text{C}}\text{H}_3$), 0.33 (s, 12H, $\text{Si}(\underline{\text{C}}\text{H}_3)_2$), 5.70-6.09 (m, 6H, $\underline{\text{H}}_2\text{C}=\underline{\text{H}}\text{CSiCH}_3$), 7.57 (s, 4H, Aryl- $\underline{\text{H}}$) ppm.

^{13}C NMR (CDCl_3): $\delta = -0.34$ ($\text{H}_2\text{C}=\text{HCSi}\underline{\text{C}}\text{H}_3$), 1.01 ($\text{Si}(\underline{\text{C}}\text{H}_3)_2$), 132.43 (Aryl- $\underline{\text{C}}\text{H}$), 133.27 ($\text{H}_2\text{C}=\text{H}\underline{\text{C}}\text{SiCH}_3$), 137.15 ($\text{H}_2\underline{\text{C}}=\text{HCSiCH}_3$), 140.80 (Aryl- $\underline{\text{C}}\text{Si}$) ppm.

^{29}Si NMR (CDCl_3): $\delta = -0.34$ ($\underline{\text{S}}\text{i}(\text{CH}_3)_2$), -33.00 ($\text{H}_2\text{C}=\text{HCSi}\underline{\text{C}}\text{H}_3$) ppm.

Anal. Calcd. for $\text{C}_{16}\text{H}_{28}\text{O}_3\text{Si}_4$: C, 50.47%; H, 7.41%. Found: C, 49.99%; H, 7.35%.

3. 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 [10]. 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 coworkers [11], 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 [8,11-14]. 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. [13]. 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 responsible 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.

In order 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.

Table 1 shows the polymers synthesized in this investigation. All polymers were characterized by ^1H , ^{13}C and ^{29}Si NMR spectroscopy. Figures 4a and 4b 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 one percent, 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 uncross-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 same range.

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 shifts from about 520°C (reference sample **MeMe** without vinyl groups) to higher temperatures as the vinyl content increases (Figure 5). Similar behaviour 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.

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 three percent between 280°C 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

coworkers [14]. 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 percent (**MeMe**) to almost 70 percent (**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 percent in air or nitrogen is a remarkable result for a siloxane elastomer.

DSC studies to reveal the phase behaviour of the polymers expectedly show the complete absence of crystallinity in all samples. The glass transition temperatures decrease from -59°C 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 $250\text{-}300^\circ\text{C}$ and about 450°C , broad exothermic signals with transition enthalpies between roughly -20 J/g and -210 J/g (as a function of vinyl content) are detected in all vinyl containing polymers [15]. 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 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 the DSC experiments are due to both the higher sensitivity of DMTA for this process and the smaller heating rate of the DMTA experiment (2°C/min vs. 15°C/min in DSC), which causes less thermal lag. As expected, the loss modulus $\tan\delta$ decreases upon cross-linking.

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 linewidths 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 ^1H - ^{13}C shift correlation (HETCOR) NMR spectrum, which is not shown here. After heating the sample to 450°C for one hour prior to the measurement, the linewidths 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 resin-like sample. The resonances at 9 ppm and 29 ppm are assigned to $-\text{Si}-\underline{\text{C}}\text{H}_2-$ and $-\text{Si}-\text{CH}_2\underline{\text{C}}\text{H}_2-$ 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 neighbouring 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 behaviour can not be given at this time. It is known that silphenylene siloxane polymers undergo siloxane redistribution reactions (see Figure 12) below the apparent degradation temperature [16]. This process may change the sample viscosity and, thus, the shear moduli. Because the siloxane redistribution reaction is known to scan

with little enthalpy change, this process is consistent with the lack of detectable heat flow in the DSC experiment of **MeMe**. Based on the observations of Dvornic and coworkers [14], 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 has been synthesized. The polymers are completely amorphous gums with glass transition temperatures ranging from -86°C 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 percent 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 upon 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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Captions

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

Figure 2: Synthesis of vinyl substituted silphenylene siloxane copolymers.

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

Figure 4: Spectroscopic clarification of polymer microstructure.

a) ^1H and b) ^{29}Si NMR spectrum of a **ViVi** solution in CDCl_3 .

Figure 5: Thermogravimetric scans under oxidative atmosphere (dry air, heating rate $15^\circ\text{C}/\text{min}$).

Figure 6: Thermogravimetric scans under inert atmosphere (nitrogen, heating rate $15^\circ\text{C}/\text{min}$).

Figure 7: High temperature DSC scans of vinyl substituted polymer **ViMeViMe** and polymer **MeMe** without vinyl groups ($15^\circ\text{C}/\text{min}$).

Figure 8: Temperature dependence of shear storage (G') and loss (G'') moduli as well as $\tan\delta$ of polymer **Vi30Me** (heating rate: $2^\circ\text{C}/\text{min}$), measured under nitrogen.

Figure 9: Temperature dependence of shear storage (G') and loss (G'') moduli as well as $\tan\delta$ of polymer **ViMe** (heating rate: $2^\circ\text{C}/\text{min}$), measured under nitrogen.

Figure 10: ^{13}C MAS Solid State NMR spectra of a neat **ViMe** sample.

a) as prepared; spectrum acquired after direct (single-pulse) excitation.

b) after thermal treatment at 450°C for 1 hour in air; spectrum acquired after cross polarization and total suppression of sidebands.

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

Figure 12: Proposed mechanism of redistribution reactions in silphenylene siloxane polymers according to [16a].