Densely Crosslinked Polycarbosiloxanes - Synthesis

ABSTRACT
Novel densely crosslinked polycarbosiloxanes were obtained by using functional branched prepolymers. Soluble prepolymers were prepared from di- and trifunctional alkoxy silane monomers via co-hydrolysis/condensation and final crosslinking occurred via hydrosilylation. The poly(phenylmethylvinylhydro)siloxanes prepolymers have both silicon-vinyl and silicon-hydrogen functionalities and crosslinking took place intermolecularly. For the characterization of the prepolymers $^1$H-NMR, $^{29}$Si-NMR, FT-IR spectroscopy, analytical SEC and VPO were employed. The prepolymers were fractionated with preparative SEC and the fractions analyzed with $^1$H-NMR and analytical SEC. The crosslinking reaction was followed by FT-IR spectroscopy. The polymer networks were fully transparent homogeneous materials and are applicable for optical applications.

This chapter has been appeared as part of a publication in Journal of Polymer Science, Part A: Polymer Chemistry, 35, 41-53 (1997).
Chapter 3

INTRODUCTION

Sol-gel glasses are known for their good transparency and have a structure close to that of SiO$_2$ - quartz glass. Quartz glass is a material with extremely low optical losses and has been used, among other applications, for optical fibers. The disadvantage, however, of sol-gel glasses is that volatile molecules are produced during polymerization, which renders processing difficult and makes it almost impossible to obtain large structures like planar waveguides and optical fibers. It would be very interesting to synthesize materials which have the same kind of structure as the sol-gel glasses but are still processable and offer the possibility to be crosslinked afterwards. During these curing reactions no molecules should be produced, because this can lead to bubble and void formation. Hydrosilylation is an addition reaction, which meets this condition. It is a reaction of a Si-H bond with a carbon-carbon double bond, preferably a Si-CH=CH$_2$ bond, leading to a Si-CH$_2$-CH$_2$-Si structural unit. Hence, a combination of sol-gel and hydrosilylation can offer interesting materials with properties such as low optical losses and high thermal stability. These organic/inorganic hybrid polymer networks are called polycarbosiloxanes, because of the presence of covalent Si-C bonds in their backbone structure.

A substantial amount of research has been done on the synthesis of crosslinked polysiloxanes in which crosslinking takes place via a hydrosilylation reaction.$^{1,2}$ So far these studies have been concerned with using a vinyl-functionalized polyorganosiloxane and a multifunctional Si-H - containing curing agent or a polyorganohydridosiloxane. To our knowledge nothing has been published about crosslinkable polysiloxanes in which both reactive groups (alkenyl and hydrido) are part of the same polymer backbone. These prepolymers, being a one-component system, crosslink intermolecularly, which enhances the processability enormously. The problem of solubility (phase separation) of a second or higher component and the possible evaporation of curing agent is not present here.

The prepolymers described in this chapter have a strongly branched structure. This branching is an important property, because branched prepolymers can offer systems with low shrinkage during curing. For these systems only a minimum number of
Polycarbosiloxanes - synthesis

reactions has to take place to obtain maximum curing without a large influence on the free volume of the polymer system.

EXPERIMENTAL

Materials
Vinylmethyldichlorosilane was obtained from Akros Chimica and used as received for synthesis. Phenyltriethoxysilane and dimethyldiethoxysilane were obtained from Akros Chimica and distilled via spinning band distillation (plate number = 20). The platinum catalyst (Karstedt), methyldichlorosilane, and vinylidimethylchlorosilane were obtained from ABCR and used as received. Toluene was distilled freshly from sodium and benzophenone prior to use. Pentane was distilled from P2O5. Diethyl ether was distilled from P2O5 and just before use from LiAlH4. 1-methyl-2-pyrrolidinone (NMP) and xylene were distilled from CaH2 and stored above 4 Å molecular sieves. Florisil™ magnesium silicate, 30 - 60 mesh and pH = 8.5 was obtained from Fluka AG.

Synthesis of diethoxysilane monomers (vinylmethyldiethoxysilane)
A three-necked round-bottomed flask equipped with a cooler, a teflon-coated magnetic stirring bar and a pressure-equalized dropping funnel, was charged with 200 g (1.4 mol) of vinylmethyldichlorosilane, 150 mL (1.55 mol) of NMP and 300 g of diethyl ether under a dry nitrogen atmosphere. To this solution 130 g (2.8 mol) of ethanol were added dropwise, while stirring at room temperature for 1.5 h. A stream of nitrogen over the reaction mixture was used to remove the larger part of the HCl gas produced. The HCl gas was neutralized in a NaOH (aq)-solution trap. The temperature was raised and maintained at 70°C for about 2 days. The reaction was followed by sequentially taking 1H-NMR spectra of the mixture. After about 95% conversion of the dichloro- to the diethoxysilane the mixture was filtered through a 0.45 µm Teflon filter (Millipore™, Aldrich). The salt residue was washed at least three times with dry ether. The filtrate was cooled down to -20°C to allow the residual NMP.HCl salt to crystallize. After filtering off the residual salt and removal of the ether with a rotary evaporator, the monomer was distilled at reduced pressure via a spinning band distillation yielding 70% of pure vinylmethyldiethoxysilane.
$^1$H-NMR (CDCl$_3$); $\delta$ (ppm): 0.20 (s, Si-CH$_3$, 3 H), 1.23 (t, Si-(OCH$_2$CH$_3$)$_2$, 6 H), 3.78 (q, Si-\((OCH$_2$CH$_3$)$_2$, 4 H), 5.95 (m, Si-CH=CH$_2$, 3 H).

$^{29}$Si-NMR (CDCl$_3$); $\delta$ (ppm): -13.62 (s).

**Synthesis of methyldiethoxysilane**

A three-necked round-bottomed flask under dry nitrogen atmosphere and equipped with a cooler, a Teflon-coated magnetic stirring bar and a pressure-equalized dropping funnel with a tube capable of introducing the alcohol beneath the liquid surface of the charged chlorosilane and solvent, was charged with 30.0 g (0.26 mol) of methyldichlorosilane, 20 g of pentane and 10 g of xylene. To this 24.0 g (0.52 mol) of ethanol diluted with 24 g of pentane were added dropwise in two parts. The first half was added while stirring at room temperature in approximately 25 min, and the second half was added in another approximately 25 min, while stirring at 40°C. A stream of nitrogen was purged through the reaction mixture to remove the larger part of the HCl gas produced. The HCl gas was neutralized in a NaOH (aq)-solution trap. After the total amount of alcohol had been added, the reaction was left to proceed for an additional 30 min. $^1$H-NMR showed a conversion of 85%. Pentane was removed with a rotary evaporator and the residual reaction mixture was distilled twice at atmospheric pressure via a spinning band distillation yielding 60% of pure methyldiethoxysilane.

$^1$H-NMR (CDCl$_3$); $\delta$ (ppm): (d, Si-CH$_3$, 3 H), 1.23 (t, Si-(OCH$_2$CH$_3$)$_2$, 6 H), 3.81 (q, Si-\((OCH$_2$CH$_3$)$_2$, 4 H), 4.57 (m, Si-H, 1 H).

$^{29}$Si-NMR (CDCl$_3$); $\delta$ (ppm): -16.15 (s).

**Synthesis of prepolymer**

A round-bottomed flask was charged with 9.4 g (0.039 mol) of phenyltriethoxysilane, 17.4 g (0.117 mol) of dimethyldiethoxysilane, 8.4 g (0.052 mol) of vinylmethyldiethoxysilane and 7.0 g (0.052 mol) of methyldiethoxysilane. To the mixture 60.5 g (150 wt %) of 20% hydrochloric acid aqueous solution were added dropwise at such a rate that the temperature of the reaction mixture did not exceed 40°C. After the addition was complete, the reaction mixture was stirred for 1 h at room temperature. Then the mixture was combined with 50 mL of toluene and stirred for 3 h at 60 - 70°C. The organic layer was separated and washed with an aqueous sodium bicarbonate solution followed by washing with demineralized water until
the pH was neutral. The remaining water left from the washing procedure was azeotroped off at 130 - 140 °C for 1 - 2 h. After the organic layer was cooled down to room temperature 0.2 g of vinylidimethylchlorosilane (endcapper) was added and the solution stirred for 30 min. Active coal was added and the solution was stirred for half an hour. The reaction solution was filtered over a Florisil™ column and toluene was removed in vacuo by means of a rotary evaporator. The product was combined with 50 mL methanol and filtered through a 0.45 µm Teflon filter (Millipore™). The methanol was removed in vacuo by means of a rotary evaporator and the polymer was filtered through a 0.2 µm Teflon filter. The polymer was kept under reduced pressure and stirred at room temperature for at least 12 h to remove traces of toluene and possibly, low molecular weight volatile oligomeric compounds. The yield was approximately 75% of a very clear and transparent poly(phenylmethylvinylhydro)siloxane of the average compositional formula: \([\text{PhSiO}_{3/2}]_{0.15}[\text{Me}_2\text{SiO}]_{0.45}[\text{ViMeSiO}]_{0.20}[\text{HMeSiO}]_{0.20}\).

1H-NMR (CDCl3): \(\delta\) (ppm): 0.10 (s, Si-Me), 4.75 (s, Si-H), 5.59 (m, Si-Vi), 7.35 - 7.65 (d, Si-Ph).

29Si-NMR (CDCl3): \(\delta\) (ppm): 16.3 - 22.3 (m, Me₂SiO), 31.2 - 34.8 (m, ViMeSiO), 34.8 - 36.7 (m, HMeSiO), 78.0 - 81.2 (m, PhSiO₃/₂).

Preparation of the curing catalyst (Karstedt)
Platinum-divinyltetramethyldisiloxane complex with 3 - 3.5 wt % of platinum in vinyl-terminated polydimethylsiloxane was dissolved in 1,3-divinyltetramethyldisiloxane to give a 0.1 wt % platinum concentration. For the use of 1 ppm, based on weight, elemental Pt, 1 µL of the Pt-solution should be taken per gram prepolymer. The Pt-solution is stored at 4°C.

Curing of the poly(phenylmethylvinylhydro)siloxane prepolymer
To 2.0 g of poly(phenylmethylvinylhydro)siloxane 1 ppm platinum catalyst (Kartstedt) was added. After stirring for 10 min, the mixture was filtered through a 0.2 µm Teflon filter and cured by heating for 24 h at 150°C.

Analysis
1H-NMR spectra were obtained on a Varian Gemini-200 spectrometer (199.97 MHz) or on a Varian VXRB300 spectrometer (299.9 MHz) in CDCl₃ and using CHCl₃ as an internal standard. Tetramethysilane (TMS) was used as the external standard (0 ppm). 29Si-NMR
Chapter 3

spectra were recorded on the Varian VXR300 with TMS as the external standard (0 ppm). For measuring the prepolymer, chromium-III-acetylacetonate was added to the CDCl₃-polymer solutions to reduce the T₁-relaxation time. The delay time was 6 s, the line broadening was 2 Hz and the spectral width was 16,000 Hz. IR-spectra were recorded on a Mattson Instruments FT-IR spectrometer. The measurements were performed using a thin film on KBr-pellets. The polymers were cured on the same KBr-pellets. SEC measurements were made on a Spectra Physics P 1000 coupled with a Shodex RI-71 refractive index tester and a Viskotek H502 viscometer and the molecular weights were measured relative to polystyrene standards. THF (spectroscopical grade) was used as the solvent and eluent. Preparative SEC was conducted with a PL-gel (Polymer Laboratories) 600 * 25 mm column with polystyrene particles of 10 µm size with a pore size of 10³ Å. The system was coupled to a Waters R401 differential refractometer and THF (distilled from CaH₂) was used as the solvent and eluent. VPO measurements were performed in toluene at 45°C on a Knauer Vapour Pressure Osmometer.

RESULTS AND DISCUSSION

Monomer preparation

Alkoxy silanes

During the reaction forming alkoxy silanes from chlorosilanes a large amount of hydrogen chloride is produced (Figure 1). In the first method a strong base, such as an amine (e.g. triethylamine, pyridine or NMP), was used to neutralize the hydrogen chloride by forming a complex. In the second method two inert solvents were used, one having a boiling point lower than the alkoxy silane and the other having a higher boiling point. A stream of dry nitrogen gas was purged through the reaction solution to remove the hydrogen chloride gas produced. The second method turned out to be favorable for the production of Si-H functionalized alkoxy silanes. In the first and most used method Si-H alcoholysis takes place under the influence of the hydrogen chloride or the amine-hydrogen chloride complex present.
Polycarbosiloxanes - synthesis

Figure 1. Synthesis of dialkoxy silanes via two different procedures.

Prepolymer preparation

The polymerization reaction of poly(phenylmethylvinylhydro)siloxanes is sketched in Figure 2. Throughout this paper the names in parentheses always indicate the substituents of the Si-atoms. This becomes clearer with the help of Figure 2. The phenyl groups originate from phenyltriethoxysilane (PTES), the methyl groups from dimethyldiethoxysilane, the vinyl groups from vinylmethyldiethoxysilane, and the hydro groups from methyldiethoxysilane.

Figure 2. Reaction scheme of the polymerization of poly(phenylmethylvinylhydro)-siloxanes.
Chapter 3

The monomers are polymerized via co-hydrolysis followed by a condensation process (similar to the sol-gel method). The mechanism which is proposed for the sol-gel process, is briefly sketched here.

\[
\begin{align*}
\text{Si—OR} + \text{H}_2\text{O} & \rightarrow \text{Si—OH} + \text{ROH} \\
\text{Si—OH} + \text{HO—Si} & \rightarrow \text{Si—O—Si} + \text{H}_2\text{O} \\
\text{Si—OR} + \text{HO—Si} & \rightarrow \text{Si—O—Si} + \text{ROH}
\end{align*}
\]

These reactions are catalyzed by acids and bases. The way the sol-gel process evolves depends on the reaction conditions, such as pH, composition, reactivity, solvent and catalyst. The nature of the catalyst and in particular the pH of the reaction medium has a very pronounced effect on the hydrolysis and the condensation reactions and therefore on the structure of the resulting polymer (network). Under acidic conditions (pH < 5) the hydrolysis rate of alkoxysilanes is high relative to the rate of condensation. In the case of tetraethoxysilane (TEOS) for instance, the acid-catalyzed hydrolysis tends to produce weakly branched "polymeric-like" structures. In contrast, a basic environment tends to promote more of a dense-cluster growth, due to a higher condensation rate with respect to hydrolysis (hydrolysis is the rate-limiting step) and colloidal particles are produced.\(^5\,6\) Phase separation may play here a role as well. The use of phenyltriethoxysilane in the system results in a branched polymeric structure. The dialkoxysilanes are responsible for an extension of the polymeric chains. With the mole fractions of PTES used, no pregelation occurred during the synthesis of the polymers, which was proved by the complete solubility of the prepolymers in common organic solvents (chloroform, THF and toluene). During the hydrolysis/condensation step, besides a branched polymeric structure also ring structures are being formed. However, since the polymerization proceeds at rather high concentrations in the first step, the formation of ring structures will be somewhat suppressed.\(^5\,7\,9\) Furthermore, the use of an acidic catalyst and low pH (< 1) tends to produce more linear-like branched polymeric structures as is described above.\(^5\,6\)
Nevertheless, in the toluene step of the polymerization, cyclization is likely to occur, because in (strongly) diluted systems ring formation may be favored over linear polycondensation. The presence of ring-like structures is demonstrated with SEC-measurements (see Molecular weights of the prepolymer section).

After the hydrolysis/condensation process, the use of a base, such as KOH, is known to promote further condensation reactions and the opening of any rings produced, resulting in linear polysiloxanes with high molecular weights. However, the Si-H bonds of the poly(phenylmethylvinylhydro)siloxanes were not stable against such bases. The Si-H bonds react with the base so as to form a siloxane bond and hydrogen gas. This is depicted in the reaction scheme below.

\[
\text{Si-H} + \text{KOH} \rightarrow \text{Si-OK} + \text{H}_2
\]

\[
\text{Si-OK} + \text{HO-Si} \rightarrow \text{Si-O-Si} + \text{KOH}
\]

The disappearance of Si-H bonds is demonstrated with FT-IR spectroscopy (Figure 3). The Si-H vibration is located at 2168 cm\(^{-1}\) and disappears during treatment with KOH. Still, a catalyst will be necessary in these systems, because the chain Si-OH end groups are not as reactive as the Si-OH groups of the monomers.\(^6\) The Si-OH end-groups all have the same reactivity according to Flory's principle of equal reactivity of reactive end-groups irrespective of the length of the chains connected to these end groups. Of course, electronegativity or inductive effects of substituents will influence the reactivity to a certain extent (e.g. dialkyldiols have higher condensation rates than diphenyldiols). The change in reactivity has been demonstrated in a study of Lasocki and Chrzczonowicz.\(^{10}\) The polycondensation kinetics of dimethylsilanediol were compared to those of tetramethyldisiloxanediol. Due to the lower acidity of the OH-groups of tetramethyldisiloxanediol compared to dimethylsilanediol, the disiloxanediol monomer condenses at a lower rate. The effect of a lower reactivity for Si-OH end-groups, explains the low molecular weight of the prepolymer and further condensation should be promoted by a proper catalyst. Such a catalytic system is described in Appendix C of this thesis.
Figure 3. The IR-spectrum of a poly(phenylmethylvinylhydro)siloxane prepolymer based on 25 mol % phenyltriethoxysilane (PTES) before and after treatment with KOH. The prepolymer was treated with 0.2 wt % KOH for 1.5 h in boiling toluene while distilling off toluene and water (reaction product).

The prepolymer was endcapped with vinyldimethylchlorosilane to ensure reactive end groups towards hydrosilylation. The number of dangling ends will be reduced by this procedure, which will have a positive effect on the mechanical and thermal properties of the polymers. Since not all of the reactive end groups are replaced by vinyldimethylsilane, most of the residual Si-OH end groups react with methanol in the fractionation step forming Si-OMe groups, as can be observed in the $^1$H-NMR spectra (Figure 4). These Si-OMe as well as residual Si-OEt groups may enhance the stability of polysiloxanes against humidity.

The fractionation step was performed by using methanol to remove higher molecular weight fractions, which do not dissolve in the polar solvent. The fractionation was carried out in order to improve the uniformity in molecular weight of the prepolymer.
Polycarbosiloxanes - synthesis

The transparency of the final polymer is greatly enhanced after fractionation, because higher molecular weight fractions tend to phase separate, in this system. The prepolymers showed a sharp increase in viscosity depending on the PTES mole fraction and, therefore, on the amount of branching. The prepolymers with 15 mol % of PTES showed a rather low viscosity. The prepolymers with 25, 30 and 35 mol % PTES incorporated showed a moderate viscosity, which increased to a high viscosity for the 45 mol % PTES prepolymers. A PTES content of more than 45 mol % led to intractable, highly viscous polymers.

The 1H-NMR-spectra show the incorporation of the various siloxy units (Figure 4). Residual phenyl-Si-OEt and Si-OMe end groups can be observed as well. The third Si-OEt group of phenyltriethoxysilane is less reactive towards hydrolysis than the first two Si-OEt groups; hence a part of the Si-OEt groups will not hydrolyze and do not participate in the condensation reactions. The peaks in the spectra are broad, which is a common feature for polymers. Condensation reactions are sensitive to differences in reactivity. This leads to variations in composition along the polymer chain, which is responsible for a broad distribution in electronic environments.

The same feature, even more pronounced, can be observed in the 29Si-NMR spectra (Figure 5). A broad distribution of peaks is seen. For less complex oligomeric systems, triads and pentads can be detected.\textsuperscript{12} The peaks are assigned according to ref. 12c. The dimethylsiloxyl (D) units are clearly seen in the spectra around -19.3 ppm. Due to the electronegativity the vinylmethylsiloxyl and hydridomethylsiloxyl (D) units are shifted upfield to -33.0 ppm and -35.75 ppm, respectively. The phenyltrisiloxyl (T) units are observed at a much higher field due to the three oxygen atoms surrounding the Si-atom, at -79.6 ppm. Residual, only double condensed phenylethoxy groups can be observed, at -72.2 ppm at which position also some uncondensed phenylhydroxy groups may be located. The upturn starting at -74 ppm is due to absorptions from SiO\textsubscript{2} units of the quartz NMR-tube.
Figure 4. $^1$H-NMR spectrum of a poly(phenylmethylvinylhydro)siloxane prepolymer with 15 mol % phenyltriethoxysilane incorporated.

Figure 5. $^{29}$Si-NMR spectrum of a poly(phenylmethylvinylhydro)siloxane prepolymer with 15 mol % phenyltriethoxysilane incorporated.
Polycarbosiloxanes - synthesis

Molecular weights of the prepolymer

Polymers prepared by a condensation mechanism are known for their low molecular weight and broad distribution in molecular weight. An absolute way to measure the number-average molecular weight ($M_n$) is by vapor pressure osmometry (VPO). The results, after fractionation of the prepolymer, are given in Table 1. A trend can be noticed, in which the molecular weight increases for higher percentages of PTES. For higher degrees of branching more end-groups are available for a reaction with other oligomeric species or monomers leading to higher molecular weights.

The relative low molecular weights and the presence of ring structures explain why no pregelation has been observed. For instance, for the case of 45 mol % PTES in the poly(phenylmethylvinylhydro)siloxanes the gel-point would be expected at $p = 0.65$ in conversion of functional groups. The value of $P_n$ was found to be 27 which corresponds to $p = 0.79$ and gelation should have started to take place. However, gelation is strongly postponed due to the formation of ring structures during the polymerization. The calculated value for $p_{gel}$ does not have any physical meaning for these systems, because theory assumes that no intramolecular reactions do take place. The molecular weights were also determined with SEC and according to these measurements the prepolymer had a typical $M_n$ of 1600 g/mol and a weight-average molecular weight ($M_w$) of 4000 g/mol. The degree of dispersion ($M_w / M_n$) was 2.5, which is remarkably low. From the SEC measurements, no significant tendency in molecular weight could be observed for different degrees of branching. This is due to the fact that for SEC the molecular weights of the prepolymer are apparently too low to be measured accurately on an absolute scale. Additionally, for the higher amounts of PTES, lower molecular weights are determined compared to the VPO-measurements. This can be explained by the branched nature of the polymeric chains, resulting in a smaller hydrodynamic volume compared to their linear counterparts. It will result in extended elution times in SEC and the absolute values for the molecular weights determined according to the polystyrene standards, are therefore too low.
Table 1. The number-average molecular weight ($M_n$) and the number-average degree of polymerization ($P_n$) of the prepolymers determined with VPO.

<table>
<thead>
<tr>
<th>mol fraction PTES</th>
<th>$M_n$</th>
<th>$\bar M_{\text{monomer}}$</th>
<th>$P_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>1000</td>
<td>82.0</td>
<td>12</td>
</tr>
<tr>
<td>0.25</td>
<td>1200</td>
<td>87.5</td>
<td>14</td>
</tr>
<tr>
<td>0.30</td>
<td>1500</td>
<td>90.2</td>
<td>17</td>
</tr>
<tr>
<td>0.35</td>
<td>1700</td>
<td>93.0</td>
<td>18</td>
</tr>
<tr>
<td>0.45</td>
<td>2700</td>
<td>98.5</td>
<td>27</td>
</tr>
</tbody>
</table>

From the SEC measurements a bimodal distribution in molecular weight was obtained, indicating that ring-like structures were formed during the polycondensation process. By forming a ring via an intramolecular reaction two reactive groups disappear. This results in less reactive groups being available for further condensation reactions compared to chains growing without the ring forming side-reaction, resulting in a lower molecular weight. This process might explain the development of the bimodal distribution in molecular weight. A second and probably additional explanation can be that the smaller hydrodynamic volume of the rings results in longer elution times in SEC, corresponding to a lower molecular weight. This in analogy to branched macromolecules.

**Distribution in composition**

The prepolymers were fractionated by preparative SEC in order to study the composition in relation to the molecular weight. Important is whether the polymeric molecules containing ring structures have the same composition in functional groups as the molecules without ring structures. The results are given in Table 2. The poly(phenylmethylvinylhydro)siloxanes were divided into three fractions (Figure 6). Fraction 3 contained the ring-like structures, fraction 2 a mixture of ring containing structures and the branched structure without rings and fraction 1 contained only the branched part. As can be seen from Table 2, the distribution of functional groups is
Polycarbosiloxanes - synthesis

fairly homogeneous as a function of molecular weight. The rather homogeneous content of functional groups implies that the ring structures are also incorporated into the network, during the curing process.

Table 2. The ratio of Si-phenyl units over the Si-vinyl and Si-H units for different molecular weight fractions of the prepolymers.

<table>
<thead>
<tr>
<th></th>
<th>ratio Si-ph/Si-vi</th>
<th>ratio Si-ph/Si-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepolymer</td>
<td>1.48</td>
<td>2.43</td>
</tr>
<tr>
<td>fraction 1</td>
<td>1.68</td>
<td>2.51</td>
</tr>
<tr>
<td>fraction 2</td>
<td>1.49</td>
<td>2.81</td>
</tr>
<tr>
<td>fraction 3</td>
<td>1.78</td>
<td>2.37</td>
</tr>
</tbody>
</table>

For the poly(phenylmethylvinylhydro)siloxane prepolymers fraction 1 is the higher molecular weight branched part, fraction 2 is the middle fraction containing some ring structures and fraction 3 is the lower molecular weight part consisting mainly of ring structures.

Figure 6. The SEC chromatogram for a 25 mol % phenyltriethoxysilane (PTES) poly(phenylmethylvinylhydro)siloxane prepolymer, before and after fractionation into three fractions. Fraction 1 corresponds to the higher molecular weight part and fraction 2 and 3 to the lower and lowest molecular weight part, respectively. Fraction 3 is assumed to consist mainly of branched ring-like structures.
Preparation of the polymer networks

The curing reaction is a hydrosilylation reaction, which is an addition reaction that proceeds, almost entirely (> 95%), in an anti-Markovnikov way (see cartoon below). The best catalysis has been obtained with the Karstedt platinum catalyst, which is a complex of platinum with 1,3-divinyltetramethyldisiloxane that is highly soluble in the prepolymer.

Other researchers have often used the Speiers catalyst (PtH₂Cl₆) to catalyze the hydrosilylation. The problem is, however, that the Speiers catalyst is not stable in the presence of alcohols. PtH₂Cl₆ reacts with a hydroxyl group (e.g., Si-OH) to produce HCl, which causes a lowering of the concentration of active catalyst. This would make the curing reaction uncontrollable and unpredictable.

The poly(phenylmethylvinylhydro)siloxane prepolymer is a self-crosslinking system in which crosslinking takes place intermolecularly (Figure 7). Besides these intermolecular reactions also a number of intramolecular reactions may take place, which only lead to a densification of the network and are not favorable because they give rise to (inelastic) loops in the polymer network structure.
Polycarbosiloxanes - synthesis

\[ \text{Pt-catalyst \ heat} \]

\[ \text{Pt-catalyst \ heat} \]

Figure 7. Intermolecular crosslinking of the poly(phenylmethylyvinylhydro)siloxanes.

The stability of the poly(phenylmethylyvinylhydro)siloxanes is remarkable. In fact these prepolymers do not show any signs of gelation for at least 3 years when stored at 4°C. Even after addition of the catalyst (1 ppm) the polymers do not gel at room temperature for at least 3 months. Gelation only takes place at elevated temperatures. At 70°C the polymers start to gel after 4 days. At 100°C gelation proceeds in 3 h and at 150°C within 1 h. Clearly, the curing reaction is very sensitive to temperature. This allows one to choose the right processing conditions. The curing time and temperature have a large influence on the ultimate properties of the polymer (e.g. the mechanical properties). The best properties, with the use of 1 ppm Pt-catalyst, were obtained by curing for 24 h at 150°C. The thermal properties (glass transition temperatures) and the mechanical properties of these densely crosslinked polymers are described in an
Chapter 3

appeared article and also in chapter 4 of this thesis.\textsuperscript{14,15} The thermal stability of these systems is given in chapter 7.\textsuperscript{16}

Conversion of the crosslinking reaction

The conversion of Si-H and Si-C=C bonds can be followed by infrared spectroscopy. The absorbances of the two individual groups were related to the Si-CH\textsubscript{3} absorbances. The Si-CH\textsubscript{3} absorbance (1261 cm\textsuperscript{-1}) will remain the same throughout the reaction and can act as an internal standard. The IR-spectra of an uncured poly(phenylmethylvinylhydro)siloxane prepolymer and the corresponding cured polymer are shown in Figure 8. The individual absorbances of the Si-H and Si-C=C bonds (2168 and 1596 cm\textsuperscript{-1}, respectively) are nicely isolated peaks and allow a convenient determination of the conversion. The results are listed in Table 3.

![Graph showing IR-spectra](image)

**Figure 8.** IR-spectra of a 35 mol % phenyltriethoxysilane (PTES) poly(phenylmethylvinylhydro)siloxane prepolymer and the corresponding cured polymer (24 h / 150°C).
Polycarbosiloxanes - synthesis

An average conversion of 50%, based on the Si-C=C bonds, was measured for the polymers with up to 35 mol % PTES incorporated. A small decrease in conversion can be observed upon going to higher mol fractions PTES and eventually a drop in the conversion for the 45 mol % PTES polymer. This can be explained as follows. Owing to the bulkiness of the phenyl group and the increase in the number of branching (crosslink) points, the vinyl and hydrido groups become more spatially hindered and have fewer possibilities to react with each other. The higher conversions of the Si-H groups are a consequence of side reactions for which the following possibilities are suggested:\(^\text{17}\)

\[
\begin{align*}
\text{Si}-\text{H} \quad \text{H}_2\text{O} \quad &\quad \text{Si}-\text{OH} \quad + \quad \text{H}_2 \\
\text{Si}-\text{H} \quad \text{CH}_3\text{O} \quad &\quad \text{Si}-\text{O} \quad + \quad \text{CH}_4 \\
\text{Si}-\text{H} \quad \text{H}_2\text{O} \quad &\quad \text{Si}-\text{OH} \quad + \quad \text{H}_2
\end{align*}
\]

More Si-H side reactions will take place with an increasing amount of branching, because more end groups are present and capable of reacting with the Si-H groups (Table 3). The sensitivity for these Si-H side reactions is increased by the presence of the platinum catalyst.\(^\text{18}\)

<table>
<thead>
<tr>
<th>Mol fraction PTES</th>
<th>Conversion Si-H (%)</th>
<th>conversion Si-C=C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>61</td>
<td>53</td>
</tr>
<tr>
<td>0.25</td>
<td>66</td>
<td>49</td>
</tr>
<tr>
<td>0.30</td>
<td>67</td>
<td>48</td>
</tr>
<tr>
<td>0.35</td>
<td>67</td>
<td>47</td>
</tr>
<tr>
<td>0.45</td>
<td>72</td>
<td>30</td>
</tr>
</tbody>
</table>
In the IR-spectra (Figure 8) a change in the broad Si-O-Si peak can be observed. The peak at 1135 cm\(^{-1}\) is attributed to the phenyl-Si-O\(_{3/2}\) units and the peak at 1086 cm\(^{-1}\) to the vinyl-Si-O, hydrido-Si-O and dimethyl-Si-O units. The shoulder at 1029 cm\(^{-1}\) is ascribed to the dimethyl-Si-O units. Remarkably, the shoulder turns into a peak during curing at 150°C. Our explanation is that due to end-group reactions new Si-O-Si bonds are formed which give additional absorption (higher peak area). For the lower PTES mol fraction and therefore higher dimethyldiethoxysilane mol fractions, more additional dimethyl-Si-O units are formed in the cured polymer. This explains the decrease of the peak (shoulder) for the polymer networks with higher mol fractions of PTES (Figure 9). The peak is a strong indication that intermolecular end-group reactions do take place, which give an increase in molecular weight, because the peak appears only for long chain polymers.\(^{19}\)

The Si-CH\(_2\)-CH\(_2\)-Si structural units are invisible in the infrared spectra, because the corresponding absorption peaks (1180 - 1120 cm\(^{-1}\)) are overlapped with the Si-O-Si peaks.

The conversion of Si-C=Si bonds and by that the crosslink density, can be increased by using an excess of Si-H bonds. Also, a higher concentration of Pt-catalyst will increase the conversion; the presence of platinum will inversely affect the optical properties of these polymer systems, however.\(^{20}\)
Figure 9. The peaks of the Si-O-Si units in the infrared spectra of the poly(phenyl-methylvinylhydro)siloxane polymer networks with an increasing phenyl-Si-O_{3/2} content. The curves are offset for clarity.

CONCLUSIONS

Highly dense, crosslinked polymer networks were prepared from alkenyl- and hydrido-functionalized, branched polysiloxane prepolymers. The prepolymers were prepared from alkoxy silanes via a co-hydrolysis/condensation mechanism (sol process). Crosslinking of the prepolymers proceeded via intermolecular hydrosilylation.

The prepolymers had a rather low molecular weight ($\bar{M}_n$) of about 1000 g/mol for prepolymers based on 15 mol % PTES increasing to about 2700 g/mol for prepolymers based on 45 mol % PTES. The prepolymers had a bimodal distribution in molecular weight, due to cyclization reactions in the polycondensation process. The prepolymers were a mixture of branched ring-like and branched linear-like structures.

The poly(phenylmethylvinylhydro)siloxanes are self-crosslinking, one-component systems, which advances processing and no additional components have to be added, which may be volatile or lead to phase separation.
REFERENCES AND NOTES

15) Chapter 4 of this thesis.
16) Chapter 7 of this thesis.
Polycarbosiloxanes - synthesis


