Synthesis of Polysiloxanes with Pendant Methoxy-Substituted Aromatic Fragments

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ABSTRACT: The synthesis of new polysiloxanes was performed via hydrosilylation reactions of polymethylhydrosiloxane with 4-allyl-1-methoxybenzene and 4-allyl-1,2-dimethoxybenzene in the presence of Karstedt's catalyst $\{Pt_2[(VinSiMe_2)_2O]_3\}$ and platinum hydrochloric acid ($0.1M$ solution in tetrahydrofuran). The hydrosilylation reactions were carried out at 60°C. The molar ratio of $\equiv Si-H$ groups to the allylic compound was 1 : 1.2. The synthesized oligomers were characterized with ^{1}H-NMR, Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetry, and gel permeation chromatography. In the presence of platinum hydrochloric acid, not all active $\equiv Si-H$ bonds took part in hydrosilylation, and because of this, gelation took place and the molecular masses of the extracted parts increased 7–8 times; in contrast to this, in the presence of Karstedt's catalyst, all active $\equiv Si-H$ bonds participated in hydrosilylation, and an increase in the molecular masses did not occurs. The influence of substituted methoxy groups on the glass-transition temperatures was studied. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2567–2571, 2008

Key words: gelation; glass transition; modification; polysiloxanes

INTRODUCTION

Polymer modifications represent a valuable synthetic approach to unique polymer compositions, structures, and properties not readily available by the direct polymerization of monomers. Modified polymeric products already exist in the commercial world, so the approach is not new. However, it is an interesting and challenging opportunity to develop new materials for a variety of specialty applications. In the past years, the catalytic grafting of polymethylhydrosiloxane (PMHS) has emerged as an alternative route for the synthesis of new silicon organic polymers with different properties. Low cost, easy availability, and the presence of catalytically transformable $\equiv Si-H$ bonds in PMHS make it very attractive and interesting for macromolecular grafting.[1,2]

In our previous studies, we investigated hydrosilylation reactions of PMHS with styrene, α-methylstyrene, and phenylacetylene.[3,4] In this work, we continue to present the syntheses and investigations of polysiloxanes with aromatic fragments in the side

chain to determine the correlation between the chemical composition of the polymer and phase-transition temperatures.

Numerous works have been devoted to the modification of PMHS via hydrosilylation in the presence of platinum hydrochloric acid and different platinum complexes.[3–11] Acidic Speier's catalyst cannot be used for all hydrosilylation reactions because it causes isomerization of the allylic bond followed by acidic cleavage of the functional group and, in some cases, gelation of the reaction mixture, even during the process of addition. In such cases, neutral Pt(0) and Pt(II) precursors are used.[5,12,13]

EXPERIMENTAL

Materials and techniques

PMHS was purchased from Acros Organics (Geel, Belgium) and was characterized by Fourier transform infrared (FTIR) and ^{1}H-NMR spectroscopy: $\nu_{Si-H} = 2165$ cm^{-1}, $\nu_{Si-O-Si} = 1048$ cm^{-1}, $\delta_{Si-H} = 4.2$ ppm, and $\delta_{SiMe \ and \ SiMe3} = 0.05$–0.1 ppm. PMHS was also characterized with gel permeation chromatography (GPC): the initial weight-average molecular mass (M_w) of PMHS was equal to 4.29×10^{-3}, and the polydispersity was equal to 1.21. Karstedt's catalyst [platinum(0)–1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex solution in xylene, Pt ∼ 2%), platinum hydrochloric acid, 4-allyl-1-methoxyben-

zene, and 4-allyl-1,2-dimethoxybenzene were obtained from Aldrich (Sigma-Aldrich, Steinheim, Germany) and used as received. Toluene, used in hydrosilylation reactions, was first refluxed over sodium and then distilled under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was dried over and distilled from a K–Na alloy under an atmosphere of dry nitrogen. A $0.1M$ solution of platinum hydrochloric acid in THF was prepared and kept under nitrogen at a low temperature in the dark.

FTIR spectra were obtained on a Nicolet Nexus (Thermo Nicolet Corp., Madison, WI) 470 machine with an mercury-cadmium-telluride detector type B (MCTB) detector. ^{1}H-NMR spectra were recorded on a Bruker (Rheinstetter, Germany) ARX400 NMR spectrometer at a 400-MHz operating frequency with $CDCl_3$ as the solvent and an internal standard.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer (Waltham, MA) TGA-7 machine at a heating rate of 10 K/min. The weight of the sample was in the range of 5–8 mg. The flow rate of nitrogen was 200 mL/min. All TGAs were performed from 20 to 500°C.

Differential scanning calorimetry (DSC) was performed on a PerkinElmer DSC-7 apparatus. Thermal transitions, including glass-transition temperatures (T_g's), were taken as the middle point of the declines. The heating and cooling scanning rates were 10 K/min. The weight of the sample was in the range of 7–9 mg. The temperature range was −90 to 100°C. All DSC analyses were performed under a nitrogen atmosphere.

The molecular weights of the synthesized polymers were determined by GPC on a Waters (Waters Ltd., Watford, UK) 717 apparatus equipped with refractive-index (Waters 410) and UV detectors (Waters 486). The column set comprised 10^2- and 10^5-nm Ultrastyragel (Waters) columns calibrated with narrow molecular weight distribution polystyrene standards. The sample concentration was approximately 1.5 wt % in THF, and the flow rate was 1 mL/min for high performance liquid chromatography (HPLC) grade THF.

Hydrosilylation reaction of α,ω-bis(trimethylsiloxy)methylhydrosiloxane with 4-allyl-1-methoxybenzene

Hydrosilylation was carried out in a three-necked flask equipped with a magnetic stirrer, a tube for a catalyst inlet, a reflux condenser, and a gas inlet.

The initial reaction compounds [1.05 g (0.26 mmol) of α,ω-bis(trimethylsiloxy)methylhydrosiloxane and 2.53 g (16.87 mmol) of 4-allyl-1-methoxybenzene], dissolved in 5 mL of dry toluene, were placed into the flask under an argon atmosphere and then heated until a constant temperature (60°C) was obtained. Then, Karstedt's catalyst (6–8 × 10^{-5} g/

1.0 g of starting substance) was introduced. After the completion of the reaction (8 h), the solvent was partially eliminated, the reaction product was precipitated from the toluene solution by methanol, and 3.4 g (93%) of oligomer I was obtained. Other hydrosilylation reactions were carried out according to the previously discussed method. The amount selected for platinum hydrochloric acid was 5–9 × 10^{-5} g/ 1.0 g of starting substance.[3,4]

The progress of the conversion of active ≡Si—H groups was followed by the disappearance of the ≡Si—H absorption at 2160 cm^{-1}.

RESULTS AND DISCUSSION

Hydrosilylation is an important and easy reaction for the preparation of functionalized polysiloxanes.[14] As we mentioned previously, in our previous studies we investigated hydrosilylation reactions of PMHS with styrene, α-methylstyrene, and phenylacetylene.[3,4] In this work, we present syntheses of organic silicon oligomers with pendant methoxy-substituted aromatic fragments via the hydrosilylation reaction of α,ω-bis(trimethylsiloxy)methylhydrosiloxane with 4-allyl-1-methoxybenzene and 4-allyl-1,2-dimethoxybenzene in the presence of Karstedt's catalyst and platinum hydrochloric acid. The catalysts used in this work were chosen on the basis of their catalytic activity in other hydrosilylation reactions and because of easy accessibility.[15–17]

The molar ratio of PMHS to the allylic compound was 1 : 78 (≡Si—H bonds/allylic compound = 1 : 1.2). Preliminary heating of the initial compounds separately in the presence of catalysts showed that under these conditions, there was no polymerization via unsaturated bonds, cleavage of the siloxane backbone, or gelation. We did not find changes in the NMR and FTIR spectra of the initial compounds. Gas liquid chromatography (GLC) and GPC confirmed that there were no changes under these conditions.

In general, the hydrosilylation of α,ω-bis(trimethylsiloxy)methylhydrosiloxane with 4-allyl-1-methoxy benzene and 4-allyl-1,2-dimethoxybenzene is represented in Scheme 1.

Using a and b for the percentages of fragments, we have the following: $(a + b)(x) = n = 65$ and $m = 1.2n$ (≡Si—H bonds/allylic compound = 1 : 1.2)
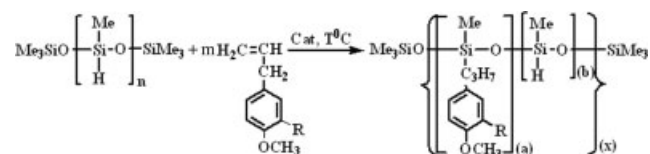
Scheme 1 General scheme of the hydrosilylation reaction of PMHS with 4-allyl-1-methoxybenzene and 4-allyl-1,2-dimethoxybenzene (T = temperature).

TABLE I
Some Physicochemical Properties of the Synthesized Oligomers

Symbol	Catalyst	Yield (%)	T_g (°C)	Temperature of 5% mass loss (°C)	$M_w \times 10^{-3}$/ $M_n \times 10^{-3}$ (D)	Elemental composition (calcd/found)		
						C (%)	H (%)	Si (%)
I	Karstedt's catalyst	93	−35	270–300	15.1/7.70 (1.96)	68.06/68.29	8.37/8.49	14.84/14.88
II	H$_2$PtCl$_6$	31	−39	260–290	77.9/20.3 (3.84)	—	—	—
III	Karstedt's catalyst	92	−41	270–300	16.9/8.16 (2.07)	64.31/64.48	8.14/8.29	12.86/12.79
IV	H$_2$PtCl$_6$	29	−44	250–280	—	—	—	—

M_n, number-average molecular weight; D, polydispersity.

when R = H (oligomer I, Karstedt's catalyst; oligomer II, platinum hydrochloric acid) and R = OCH$_3$ (oligomer III, Karstedt's catalyst; oligomer IV, platinum hydrochloric acid).

The synthesized oligomers (I–IV) were vitreous liquids that were quite soluble in ordinary aromatic-type organic solvents. During the syntheses of oligomers II and IV, partial gelation took place, causing the decrease in the yield (see Table I). For further investigations, soluble parts were extracted from the crosslinked systems. Structures and compositions of the oligomers were established on the basis of elemental analysis, FTIR and NMR spectral data, and molecular masses from GPC. Some resulting physicochemical properties of the synthesized oligomers are presented in Table I.

In the FTIR spectra of oligomer I, we observed absorption bands characteristic for asymmetric valence oscillation of linear ≡Si—O—Si≡ bonds at 1030 cm^{-1} and absorption bands characteristic for ≡Si—C and ≡Si—CH$_3$ at 767 and 1261 cm^{-1}. Also, we observed a band at 835 cm^{-1} characteristic for a 1,4-disubstituted benzene ring.

In the FTIR spectra of oligomer III, we observed absorption bands characteristic for asymmetric valence oscillation of linear ≡Si—O—Si≡ bonds at 1028 cm^{-1} and absorption bands characteristic for ≡Si—C and ≡Si—CH$_3$ at 767 and 1261 cm^{-1}. Also, we observed absorption bands at 728, 841, 1505–1600, and 3020–3060 cm^{-1} characteristic for a 1,2,4-trisubstituted benzene ring.

In the FTIR spectra of oligomers II and IV, we additionally observed an absorption band around 2165 cm^{-1} corresponding to unreacted ≡Si—H bonds. This indicates that during the hydrosilylation reaction, the conversion of all active ≡Si—H groups did not take place. Also, we found a signal around 1185 cm^{-1} characteristic for silsesquioxane bonds (SiO$_{3/2}$), which indicates the proceeding of the branching process through the formation of silsesquioxane bonds and explains the increase in the molecular weights (see Table I).

In the ^{1}H-NMR spectra of oligomer I (Fig. 1), we observed two singlet signals for methyl protons in the ≡Si—Me and ≡SiMe$_3$ fragments with chemical shifts of 0.06 and 0.1 ppm. Also, we observed a triplet signal of methylene protons in the ≡Si—CH$_2$— fragment with a chemical shift of δ ≈ 0.53 ppm, which indicated that the hydride addition proceeded according to the anti-Markovnikov rule. A signal with a chemical shift of δ ≈ 1.89 ppm, characteristic for methine protons in a =CH—CH$_3$ fragment, showed that the reaction also proceeded according to the Markovnikov rule. In ^{1}H-NMR spectra, we observed signals with a chemical shift of δ ≈ 1.45 ppm characteristic for methyl protons in a =CH—CH$_3$ fragment, with a chemical shift of δ ≈ 1.61 ppm characteristic for methylene protons in —CH$_2$CH$_2$CH$_2$—, with a chemical shift of δ ≈ 2.5 ppm characteristic for methylene protons in a Ph—CH$_2$— fragment, and with a chemical shift of δ ≈ 3.81 ppm characteristic for methyl protons in a —OCH$_3$ group. Also, in the spectra we observed multiple signal characteristic for protons of the phenyl group in the range of δ ≈ 6.78–7.29 ppm. We calculated the ratio of the fragments from a comparison of ≡Si—CH$_2$—, ≡Si—CH=, =CH—CH$_3$, and ≡Si—CH$_3$ intensities. The ratio of the fragments obtained from the anti-Markovnikov and Markovnikov rules was equal to 8 : 1.

In the ^{1}H-NMR spectra of oligomer III (Fig. 2), we additionally observed a signal with a chemical shift of δ ≈ 3.69 ppm characteristic for methyl protons of 2-methoxy group. The ratio of the fragments obtained from the anti-Markovnikov and Markovnikov rules was calculated by the same method used for oligomer I, and it was equal to 6 : 1.
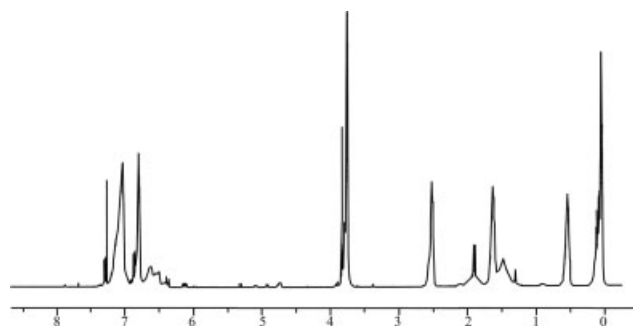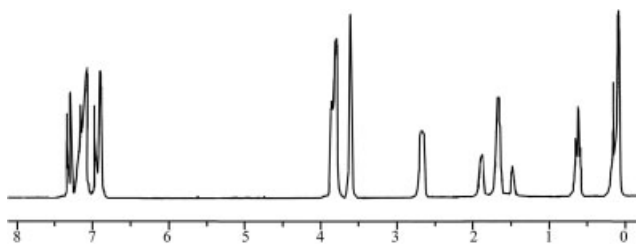

Figure 1 ^{1}H-NMR spectrum of oligomer I.

Figure 2 ^{1}H-NMR spectrum of oligomer III.

In the ^{1}H-NMR spectra of oligomers II and IV, we observed signals with a chemical shift of $\delta \approx 4.1$ ppm characteristic for active $\equiv$Si—H groups, which showed, together with the results of FTIR spectra, that not all active $\equiv$Si—H groups participated in the hydrosilylation reaction in the presence of platinum hydrochloric acid.

The synthesized oligomers were studied with GPC, and the average molecular masses were determined (see Table I). Figure 3 shows the molecular weight distribution curves for oligomers I, II, and III. For oligomers I and III, monomodal curves can be seen. The determined average molecular weights of synthesized oligomers I and III insignificantly exceeded the theoretical values calculated for the full hydrosilylation.

In Figure 3, we can observe a bimodal curve for oligomer II. As shown in Table I, the determined average molecular weight of synthesized oligomer II exceeded the theoretical value of the calculated molecular weight by 5–6 times in the case of full hydrosilylation. This indicated, together with FTIR spectral data, which showed absorption bands characteristic for silsesquioxane bonds ($SiO_{3/2}$), that during hydrosilylation reactions in the presence of platinum hydrochloric acid, the branching process also took place through the formation of $\equiv$Si—O—Si$\equiv$ and $\equiv$Si—Si$\equiv$ bonds, as discussed earlier.[18–24] The branching process indicated that traces of platinum hydrochloric acid were still active in the separated product.

Phase behaviors of the obtained oligomers were characterized with DSC. We display in Figure 4 only
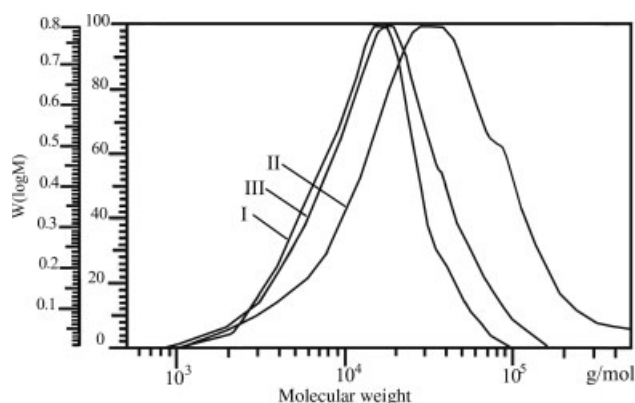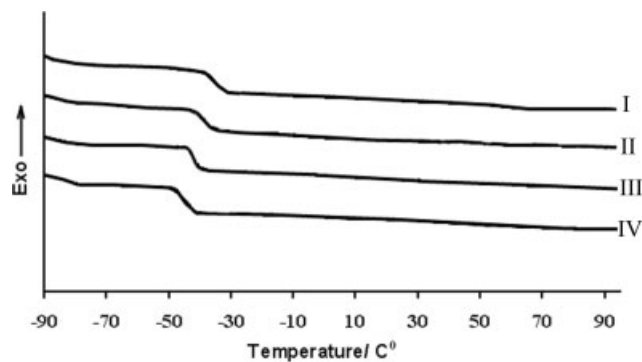

Figure 4 DSC curves of oligomers I, II, III, and IV.

the second DSC heating thermograms because there were no significant differences between the first and second heating runs. There were only single endothermic peaks that corresponded to the T_g's (see Table I). All transitions were reversible, and they did not change with repeated heating and cooling cycles. T_g is an important parameter with respect to the structure and property of a polymer. In general, the T_g value is strongly influenced by the chain flexibility and molecular weight of the polymer and the length of the spacer group.[9,25] By comparing the DSC results of this work with the results of our previous work [T_g of polymethyl(phenethenyl)siloxane was −45°C, and T_g of polymethyl(phenethyl)siloxane was −50°C],[3,4] we found that T_g increased. By comparing the values of T_g's, we determined that T_g of oligomer I was higher than T_g of branched oligomer II; the same phenomenon occurred for oligomers III and IV (see Table I). We suppose that in branched oligomers II and IV, the intermolecular interaction was lower than that in unbranched oligomers I and III.

We performed TGA investigations in a nitrogen atmosphere. Table I shows the temperatures at which 5% mass losses occurred. We observed that 5% mass losses for branched oligomers II and IV occurred at lower temperatures (260–290 and 250–280°C) than those for unbranched oligomers I and III

Figure 3 GPC curves of synthesized oligomers I, II, and III.
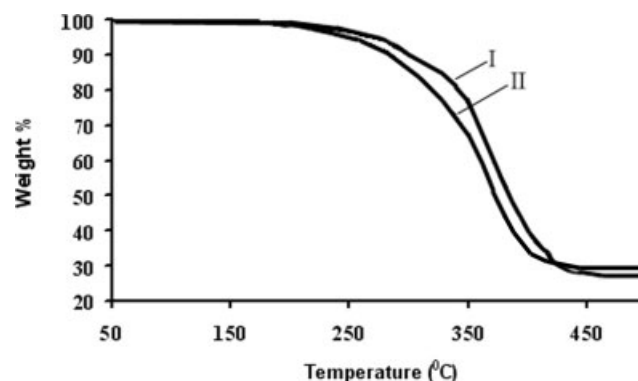

Figure 5 TGA curves of oligomers I and II.

(270–300 and 270–300°C). We display in Figure 5 TGA curves for oligomers I and II. Also, we concluded that the synthesized oligomers had high thermal stability.

CONCLUSIONS

Comb-type polymethylorganosiloxanes with methoxy-substituted aromatic fragments in the side chain were synthesized via hydrosilylation reactions in the presence of Karstedt's catalyst {Pt$_2$[(VinSiMe$_2$)$_2$O]$_3$} and platinum hydrochloric acid. Karstedt's catalyst was found to be a successful catalyst for full hydrosilylation of all active ≡Si—H bonds, whereas in the presence of platinum hydrochloric acid, not all silane bonds participated in hydrosilylation, and partial gelation took place. Synthesized polymers were investigated with ^{1}H-NMR and FTIR spectroscopy and with DSC, TGA, and GPC. DSC investigations showed that the insertion of polar methoxy groups into aromatic side fragments reduced T_g in comparison with polymethyl(phenethenyl)siloxane and polymethyl(phenethyl)siloxane.

References

1. Chauhan, B. P. S.; Rathore, J. S.; Glloxhani, N. Appl Organomet Chem 2005, 19, 542.
2. Chauhan, B. P. S.; Boudjouk, P. Tetrahedron Lett 2000, 41, 1127.
3. Mukbaniani, O.; Tatrishvili, T.; Titvinidze, G.; Mukbaniani, N. J Appl Polym Sci 2006, 101, 388.
4. Mukbaniani, O.; Tatrishvili, T.; Titvinidze, G.; Mukbaniani, N.; Lezhava, L.; Gogesashvili, N. J Appl Polym Sci 2006, 100, 2511.
5. Iwahara, T.; Kusakabe, M.; Chiba, M.; Yonezawa, K. J Polym Sci Part A: Polym Chem 1993, 31, 2617.
6. Chien, L. C.; Cada, L. G. Macromolecules 1994, 27, 3721.
7. Matisons, J. G.; Provatas, A. Macromolecules 1994, 27, 3397.
8. He, X. Z.; Zhang, B. Y.; Xiao, L. J.; Wang, Y.; Wu, H. Q. J Appl Polym Sci 2005, 97, 498.
9. Sun, Q. J.; Zhang, B. Y.; Jia, Y. G.; Yang, L. J Appl Polym Sci 2005, 97, 1196.
10. Mukbaniani, O.; Zaikov, G.; Tatrishvili, T.; Titvinidze, G.; Mukbaniani, N. Macromol Symp 2007, 247, 364.
11. Mukbaniani, O.; Zaikov, G. E.; Tatrishvili, T.; Titvinidze, G.; Phatsatsia, S. Macromol Symp 2007, 247, 393.
12. Jonas, G.; Stadler, R. Acta Polym 1994, 45, 14.
13. Marciniec, B.; Gulinski, J.; Kopylova, L.; Maciejewski, H.; Grundwald-Wyspianska, M.; Lewandowski, M. Appl Organomet Chem 1997, 11, 843.
14. Brook, M. A. Silicon in Organic, Organometallic and Polymer Chemistry; Wiley: New York, 1999.
15. Yuriev, V. P.; Salimgareva, I. M. Hydrosilylation Reactions of Olefins; Nauka: Moscow, 1982 (in Russian).
16. Silicon in Polymer Synthesis; Kricheldorf, H. R., Ed.; Springer: Berlin, 1996.
17. Marciniec, B. Comprehensive Handbook on Hydrosilylation; Pergamon: Oxford, 1994.
18. Gray, G. W.; Lacey, D.; Nestor, G.; White, M. S. Makromol Chem Rapid Commun 1986, 7, 71.
19. Lipowitz, J.; Bowman, S. A. J Org Chem 1973, 38, 162.
20. Corey, J. Y. Adv Silicon Chem 1991, 1, 327.
21. Tilley, T. D. Comments Inorg Chem 1990, 10, 37.
22. Harrod, J. J.; Mu, Y.; Samuel, E. Polyhedron 1991, 10, 1239.
23. Pukhnarevich, V. B.; Voronkov, M. G.; Kopylova, L. I. Usp Khim 2000, 69, 150.
24. Mukbaniani, O.; Titvinidze, G.; Tatrishvili, T.; Mukbaniani, N.; Brostow, W.; Pietkiewicz, D. J Appl Polym Sci 2007, 104, 1176.
25. Hu, J. S.; Zhang, B. Y.; Liu, Z. J.; Zhang, B. L. J Appl Polym Sci 2002, 86, 2670.