Polymer Bulletin 20, 455-461 (1988)

Polymer Bulletin

Comb polysiloxanes with ω-hydroxyoligo(oxyethylene) side chains

E. Wu, Ishrat M. Khan, and Johannes Smid

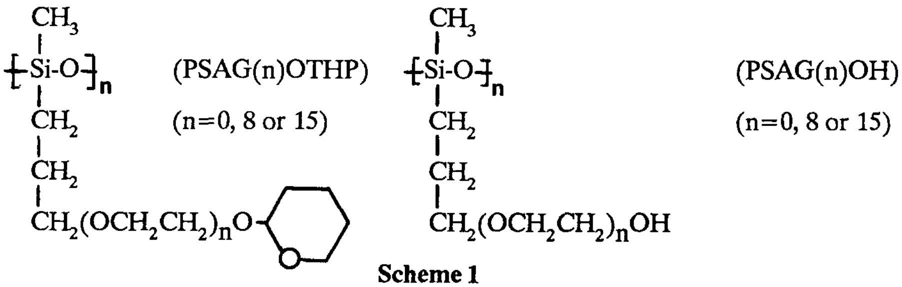
Polymer Research Institute, Chemistry Department, College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13210, USA

Summary. Comb-like polysiloxanes with pendant chains of the type $(CH_2)_3(OCH_2CH_2)_nOH$ (n= 0, 8 or 15) were synthesized by hydrosilylation of poly(methylsiloxane) with the corresponding monoallyl glycols in which the hydroxyl group was protected with tetrahydropyran. The polymers were characterized by ^1H and ^{29}Si NMR, and by GPC and DSC. A considerable fraction of small cycles is formed for the n=o compound during the deprotection reaction. Side chain crystallization occurs but is slower than for polymers containing side chains with terminal methoxy groups.

Introduction

We recently reported on the synthesis and applications of comb-like polysiloxanes with oligo(oxyethylene) side chains (1-3). These comb polymers can solubilize alkali perchlorates and triflates yielding solvent-free polymer electrolytes with room temperature conductivities in the order of 10^{-4}S cm^{-1} (1,2,4,5), a value that makes them of potential interest for use in solid state alkali batteries. Since a considerable fraction of the current is carried by the anion, attempts have been made to immobilize the anion covalently on the polymer (6-9). An alternative approach would be to use a slow moving bulky or long chain anion, or to impede anion transport by chelating them to polymer-bound moieties. A hydroxyl function on the polymer could accomplish this, and may at the same time break up ionic clusters or enlarge, through hydrogen bonding with the anion, the interionic ion pair distance, resulting in improved conductivity behavior. Hydroxyl functionality in polysiloxanes will also modify the chemical and physical properties of the polymer, for example, their water solubility or adhesion characteristics (10).

This paper describes the synthesis and characterization of comb polysiloxanes with ω-hydroxyoligo(oxyethylene) side chains (Scheme 1). The polymers, abbreviated as PSAG(n)OH (n = 0, 8 or 15) were synthesized



Scheme 1

by hydrosilylation of poly(methylsiloxane) (PHMS) with the monoallyl ether of a glycol in which the terminal hydroxy group was protected by a tetrahydropyran group (Scheme 1). The protecting group was subsequently removed with pyridinium tosylate as catalyst yielding polysiloxanes with a terminal hydroxyl group on each side chain.

Experimental

ω-Hydroxyoligo(oxyethylene)-3-prop-1-enes of the general formula $CH_2=CHCH_2(OCH_2CH_2)_nOH$ (abbreviated as AG(n)OH, n being 8 or 15) were made by addition of ethylene oxide to the potassium salt of allyl alcohol. The latter was obtained by adding under vacuum carefully dried allyl alcohol to the potassium salt of the dicarbanion dimer of α-methylstyrene (11) in tetrahydrofuran until the red carbanion color had disappeared. Enough ethylene oxide (dried on a potassium mirror) was then added to obtain the desired length of the oligo(oxyethylene) chain, and the reaction continued for 48 hrs at ambient temperature. After protonation with water the AG(n)OH compound was precipitated in hexane to remove the α-methylstyrene dimer, and subsequently purified on an alumina column with methanol as eluant. Two products in about 70% yield were made for which ^1H NMR yielded average n values of 8 and 15, respectively. ^1H NMR, ($CDCl_3$) δ ppm, 2.90 (t, 1, OH); 3.30-3.90 (m, 4n, $-OCH_2CH_2O$); 3.95-4.05 (dd, 2, $CH_2C=C$); 5.20-5.80 (m, 2, $H_2C=C$); 5.90 (m, 1, C=CH).

ω-Tetrahydropyranyloligo(oxyethylene) allyl ether, abbreviated as AG(n)OTHP, was prepared by stirring at room temperature for 6 hrs a 20% methylene chloride solution of AG(n)OH, dihydropyran and pyridinium tosylate (molar ratio 1:2.5:0.1) (12). After removal of CH_2Cl_2 the residue was dissolved in ethyl ether, the insoluble tosylate removed by filtration, and the crude product flash chromatographed. The pure product (yield 90%) was a transparent, slightly yellowish oil which showed no hydroxyl band in the IR. ^1H NMR, ($CDCl_3$) δ ppm, 1.4-2.0 (m, 6, CH_2 in THP ring); 3.3-3.9 (m, 4n, OCH_2CH_2O); 4.02 (dd, 2, $CH_2C=C$); 4.63 (t, 1, -OCHO-); 5.25 (m, 2, $H_2C=C$); 5.9 (m, 1, C=CH).

The tetrahydropyranyl ether of allyl alcohol (AOTHP) was synthesized in a similar manner as AG(n)OTHP. The ether solution of the product, after filtration of the insoluble tosylate, was rota-evaporated and then vacuum distilled yielding 80% of pure product (66-67°C /18 mm Hg) with no OH showing in the IR. ^1H NMR, ($CDCl_3$) δ ppm, 1.50-1.90 (m, 6, CH_2 in THP ring); 3.40-4.45 (m, 4, $-CH_2O-$); 4.66 (t, 1, -OCHO-); 5.25 (m, 2, $CH_2=C$; 5.96 (m, 1, C=CH).

Poly{[ω-tetrahydropyranyloxyoligo(oxyethylene)propyl]methylsiloxane}s with eight or fifteen ethylene oxide units in the side chains (abbreviated as PSAG(n)OTHP, n = 8 or 15) were synthesized by adding two drops of the catalyst platinum tetramethyldivinyldisiloxane (Petrarch) to a 20% THF solution of poly(methylsiloxane) (PHMS, Petrarch, MW 2150) and AG(n)OTHP (10% excess over PHMS). After keeping the mixture at 40°C for 2-3 days, the polymer was precipitated as a very viscous oil from a 9/1 (v/v) mixture of hexane/THF. No absorbance from OH (3400 cm^{-1}) or unreacted Si-H (2160 cm^{-1}) could be detected in the IR. Yield 90%. ^1H NMR ($CDCl_3$), δ ppm, 0.07 (s, 3, $Si-CH_3$); 0.33-0.75 (dd, 2, $Si-CH_2$); 1.40-1.90 (m, 8, $SiC-CH_2$ and CH_2 in THP ring); 3.30-3.90 (m, 4n, OCH_2CH_2O); 4.63 ppm (t, 1, OCHO).

Poly{[ω-hydroxyoligo(oxyethylene)propyl]methylsiloxane}s, abbreviated as PSAG(n)OH were obtained by heating a 20% ethanolic solution of PSAG(n)OTHP at 55°C for 6 hrs in the presence of pyridinium tosylate (molar ratio 10:1) (12). After passing over a short active Al_2O_3 column to remove the tosylate, the solution was concentrated, and the product precipitated from 4/1 (v/v) hexane/THF mixture to yield a slightly brownish viscous oil. A strong OH band at 3450 cm^{-1} was indicated in the IR. ^1H NMR ($CDCl_3$), δ ppm, 0.07 (s, 3, $SiCH_3$); 0.33-0.75 (dd, 2, $SiCH_2$); 1.40-2.00 (m, 2, Si-C-CH_2); 2.70 (S, 1 OH); 3.23-3.90 (m, 4n, OCH_2CH_2O).

Poly{(ω-tetrahydropyranyloxypropyl)methylsiloxane (PSAOTHP) with n=0 was prepared by hydrosilylation of PHMS as described for n=8 or 15. After removal of THF the residual oil was flash-chromatographed using Al_2O_3 with hexane/ethyl acetate (3/1) as eluant. A transparent, viscous oil was obtained after removing solvent and excess allyl tetrahydropyranyl ether under vacuum. IR gave no SiH stretch at 2160 cm^{-1}. The product was then dissolved in ethanol and the protecting group removed with pyridinium tosylate as described for n=8 or 15. The final product, poly{(3-hydroxypropyl)methylsiloxane} (PSAOH) showed a strong OH band in the IR at 3400 cm^{-1}.

Measurements

^1H NMR spectra were run on a Varian EM360 or XL-100, and ^{29}Si NMR on a Mohawk NMC-250. A Waters GPC-1A was used for gel permeation chromatograms while glass transition temperatures were obtained on a Perkin Elmer DSC-4 (20°C/min) and taken at the inflection point.

Results and Discussion

Direct hydrosilylation of PHMS with monoallyl ether glycols of the type $CH_2{=}CHCH_2(OCH_2CH_2)_nOH$ and platinum tetramethyldivinyldisiloxane as catalyst led to cross-linked materials. For this reason the hydroxyl group was protected by reaction with dihydropyran and pyridinium tosylate (PT) as catalyst. After purification by distillation and chromatography no OH absorption band can be detected in the IR. The subsequent hydrosilylation reaction with PHMS yields soluble polymers for both AOTHP and AG(n)OTHP. No SiH absorption can be detected in the IR or ^1H NMR, although reaction times are longer for larger oligo-oxyethylene chains (1). We also explored the use of trimethylsilyl as protecting group, but the hydrosilylation reaction with the trimethylsilyl allyl ethers also produced cross-linked materials. The $Si(CH_3)_3$ group is probably cleaved off during the reaction, and the hydroxyl can then react with SiH.

The deprotection reaction with PT as catalyst left less than 10% THP groups on the polymer (^1H NMR). After precipitation of the PSAG(n)OH polymer in 9/1 (v/v) hexane-THF (or 8/2 for PSAOH) no THP groups could be detected by ^1H NMR.

In earlier studies no significant degradation of the comb polysiloxane was found in the reaction of PHMS with ω-methoxyoligo(oxyethylene) allyl ethers (1). On the other hand, reacting PHMS with methoxypolyethylene glycol and zinc octanoate yielded redistribution products including small cycles caused by backbiting reactions (2). This is common when acidic or basic catalysts or intermediates are present in a polysiloxane system (13). GPC and ^{29}Si NMR showed that in the hydrosilylation of PHMS with the THP-protected allyl ether the fraction of small cycles was less than 0.05. However, one may anticipate that the deprotection reaction in the presence of pyridinium tosylate may be accompanied by redistribution. The GPC scan of PSAOH, the comb polysiloxane with hydroxypropyl side chains, displays three bands, the dominant ones appearing at high retention volume (fig. 1a). That

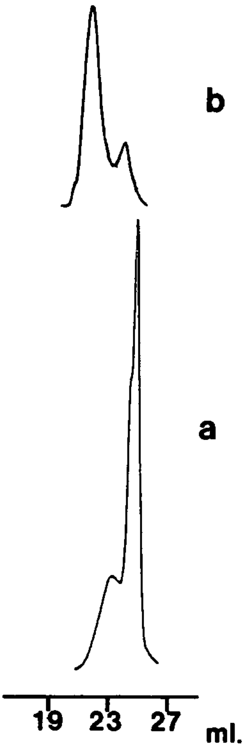


Figure 1. GPC tracings (retention volume) for (a) PSAOH and (b) PSAG(8)OH

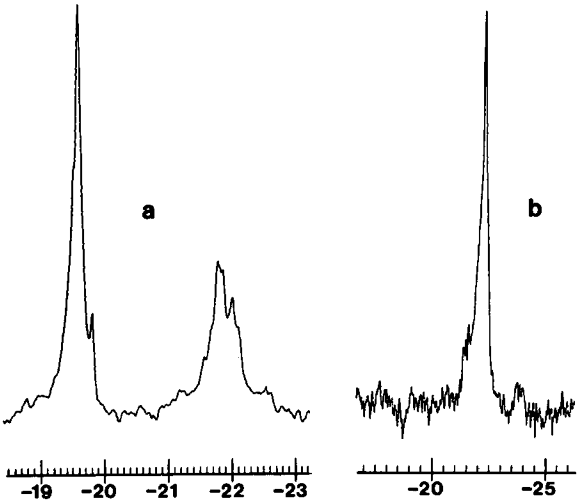


Figure 2. ^{29}Si NMR (50 MHz) spectrum of (a) PSAOH and (b) PSAG(8)OH.

these are likely to be the cyclic tetramer and pentamer appears to be confirmed from the ^{29}Si NMR spectrum of this polymer (fig. 2a). The peak at -19.8 ppm (displaying stereochemical resolution) has been identified as that of a cyclic tetrasiloxane, while the -21.9 ppm peak belongs to a cyclic pentasiloxane (1,2,14), the rest being higher cyclics and linear polymer (1). Apparently, the deprotection reaction of PSAOTHP with pyridinium tosylate as catalyst is accompanied by extensive redistribution which results in formation of cycles. This appears not to occur to any great extent when a comb polysiloxane with the longer AG(n)OTHP side chain is deprotected. Although the GPC scan of PSAG(8)OH is bimodal (fig. 1b), the main peak appears at low retention volume. The small band at high retention volume is not that of a cyclic tetrasiloxane since in the ^{29}Si NMR spectrum of this comb polysiloxane no peak at -19.8 ppm is found (fig. 2b). It could be a higher cycle, since its hydrodynamic volume is expected to be less than that of a linear polymer. The main ^{29}Si NMR band is above -22.0 ppm (fig. 2b), which is where linear polysiloxane (or higher cycles) absorb (2,3). Apparently, backbiting reactions leading to small cycles are hindered by long side chains on the comb polysiloxane. This conclusion also emerges from studies on the ring opening polymerization of cyclic tetrasiloxanes with long oligo(oxyethylene) substituents (15).

The glass transition and melt temperatures of the THP-protected and deprotected polymers are listed in Table 1. Included are data for two

Table 1. Glass Transition and Melt Temperatures of Comb Polysiloxanes

Polymer	T_g°C	T_m°C
PSAOTHP	-49	
PSAOH	-47	
PSAG(8)OTHP	-64	-22
PSAG(8)OH	-68	-12
PSAG(15)OH	-66	17.5
PAGS8*	-73	-1
PAGS12*	-60	24

*Taken from reference 1.

polymers with $(CH_2)_3(OCH_2CH_2)_nOCH_3$ (n=8, 12) side chains reported earlier (2). The DSC scans of two of the polymers PSAG(8)OH and PSAG(15)OH are shown in fig. 3. Both polymers exhibit side chain crystallization yielding melt endotherms typical for comb polysiloxanes and poly(methacrylate)s with oligo(oxyethylene) side chains (2,16). Crystallization exotherms are found on rapid cooling and reheating the polymers (fig. 3). These exotherms do not show up in the comb polysiloxanes whose side chains have terminal methoxy groups, except for lightly cross-linked materials or on adding small quantities of soluble alkali salts (2). The terminal hydroxyl groups in the PSAG(n)OH polymers most likely form hydrogen bonds with either their own oxyethylene chains or a neighboring one. The increased coiling or physical crosslinking of side chains hinders the crystallization process and also lowers the T_m values relative to the PAGS polymers. THP-substituents also hinder crystallization resulting in low T_m values and smaller endo and exotherms.

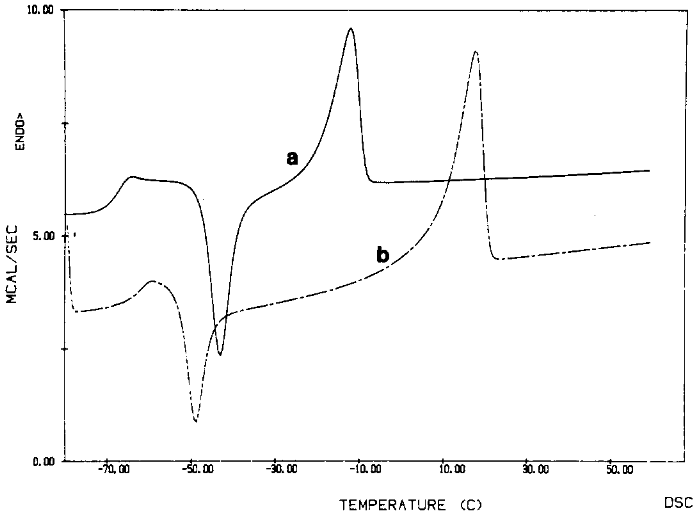


Figure 3. DSC scans of (a) PSAG(8)OH and (b) PSAG(15)OH.

Differences in the T_g values are rather small and more difficult to rationalize because of the chain length distribution of the oligo(oxyethylene) side chains and the presence of small cycles, especially in the PSAOH polymer.

The PSAG(n)OH polymers and their THP derivatives are soluble in most common organic solvents, e.g., THF, toluene, methanol and ethanol, ethyl acetate and halogenated hydrocarbons. They are insoluble in hydrocarbons. PSAG(8)OH is slightly water soluble (1% by weight) but not PSAG(15)OH, an observation consistent with the solubility behavior of comb polysiloxanes with $O(CH_2CH_2O)_nCH_3$ side chains (2,3). The cloudpoint of PSAG(8)OH in water is 92°C, higher than for the comb polysiloxanes or poly(methacrylate)s with pendant $O(CH_2CH_2O)_8CH_3$ chains. Hydroxyl interaction with the aqueous environment probably increases the cloudpoint while solubility is limited because of the tendency of side chains to crystallize (3).

In conclusion, we have successfully synthesized and characterized comb polysiloxanes with ω-hydroxyloligo(oxyethylene) side chains. Protection of the hydroxyl functionality prior to hydrosilylation and subsequent deprotection results in well defined comb polymers. Their salt complexes are currently being explored.

Acknowledgement. The financial support of this project by the National Science Foundation Polymers Program, grant DMR 8722245 and by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

References

1. D. Fish, I.M. Khan and J. Smid, Makromol. Chem. Rapid Commun. 7, 115 (1986).
2. D. Fish, I.M. Khan, E Wu and J. Smid, Brit. Polym. J. 20, 281 (1988).
3. I.M. Khan, Y. Yuan, D. Fish, E Wu and J. Smid, Macromolecules, in press.
4. R. Spindler and D.F. Shriver, J. Amer. Chem. Soc. 110, 3036 (1988).
5. P.G. Hall, G.R. Davies, J.E. McIntyre, I.M. Ward, D.J. Bannister and K.M.F. LeBrocas, Polym. Commun. 27, 98 (1986).
6. G.B. Zhou, I.M. Khan and J. Smid, Polym. Commun., in press.
7. L.C. Hardy and D.F. Shriver, J. Amer. Chem. Soc. 107, 3823 (1985).
8. D.J. Bannister, G.R. Davies, I.M. Ward and J.F. McIntire, Polymer, 25, 1291 (1984).
9. J.F. LeNest, A. Gandini, H. Cheradame and J.P. Cohen Addad, Polymer Commun. 28, 302 (1987).
10. Y. Kawakamie, T. Aoki and Y. Yamashita, Polym. Bull. 18, 473 (1987).
11. C.L. Lee, J. Smid and M. Szwarc, J. Phys. Chem. 66, 904 (1962).
12. M. Miyashita, A. Yoshikoshi and P.A. Grieco, J. Org. Chem. 42, 3772 (1977).
13. P.V. Wright in "Ring Opening Polymerization", ed. by K.J. Ivin and T. Saegusa, Elsevier, New York (1984), Vol. 2, p. 1058.
14. E.A. Williams in "Annual Reports on NMR Spectroscopy", G.A. Webb, Ed. (1979), Vol. 9, p. 221.
15. D. Fish, I.M. Khan and J. Smid, Polym. Prepr. 29, (2), 1988, (in press).
16. I. Nwankwo, D.W. Xia and J. Smid, J. Polym. Sci., Polym. Phys. Ed. 26, 581 (1988).

Accepted September 14, 1988 K