Acknowledgment. The work described was carried out in ICI's Corporate Laboratory whose enlightened management made it possible for polymer chemists to use microbiological techniques, an unusual combination of skills. The authors listed in the title were the original team responsible but many others participated in examining the value of this approach to polymer synthesis. These included Paul Holmes, Phillip Cheshire, Anthony Pickering, Alan Nevin, David Twose, W. Moran, and D. Platt.

Registry No. DHCD, 17793-95-2; DHCD (homopolymer), 110851-46-2; DHCD-DA, 86504-11-2; DHCD-DA (homopolymer), 86504-12-3; DHCD-DMC, 86504-09-8; DHCD-DEC, 110851-44-0; DHCD-DME, 110851-49-5; DHCD-DP, 86504-08-7; DHCD-DP (homopolymer), 86504-19-0; DHCD-DB, 86504-06-5; DHCD-DB (homopolymer), 86504-13-4; DHCD (bis(*p*-nitrobenzoate) derivative), 110851-42-8; DHCD (bis(*p*-bromobenzoate) derivative), 110851-43-9; $FeCl_3$, 7705-08-0; AsF_5, 7784-36-3; benzene, 71-43-2; acetic anhydride, 108-24-7; neutron, 12586-31-1; sodium naphthalide, 3481-12-7.

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High Molecular Weight Polysilanes with Phenol Moieties

Rumiko Horiguchi, Yasunobu Onishi, and Shuzi Hayase*

Chemical Laboratory, Research and Development Center, Toshiba Corporation, Komukai-Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan. *Received January 13, 1987*

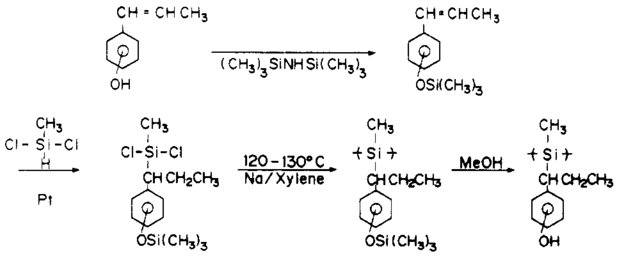
ABSTRACT: High molecular weight polysilanes substituted with pendant phenol moieties were prepared by sodium condensation of dichlorosilanes, whose phenolic OH groups were protected with trimethylsilyl ethers. [2-[[3-[(Trimethylsilyl)oxy]phenyl]methyl]ethyl]methyldichlorosilane (Me-m-1) could homopolymerize to form high molecular weight polysilane (PSi(Me-m-1)). However, monomers substituted with 4-hydroxyphenyl moieties did not give high polymers. The position of the OH in the benzene ring and the number of carbons between Ph and Si seem to determine whether or not the polymer has polysilane structure. The polymer (P(Me-m-1) (M_w 110 000)) with 3-hydroxyphenyl moieties was prepared by gentle hydrolysis of PSi(Me-m-1) in methanol without serious molecular weight decrease. Solubility, photolysis, and thermal stability for the P(Me-m-1) were compared with those for the polysilanes reported previously.

Introduction

Since polysilanes soluble in solvent were synthesized by the reaction of dichlorosilanes with sodium dispersion in *dodecane*, toluene, or xylene,[1,2] many kinds of polysilanes have been reported.[3-7] Recent interest on polysilane syntheses was concentrated on the preparation of high molecular weight polysilanes with functional groups.[8-10] The reason is that high molecular weight polysilanes are potentially useful as UV photoresists,[11] radical photoinitiators,[12] impregnating agents for strengthening ceramics,[13] and precursors for silicon carbide fibers.[14] Synthesizing polysilanes with functional groups would be desirable to make the polysilane application wider.

Recently, polysilanes with halogen moieties in the side chain were synthesized[7] from polysilanes substituted with a double bond, followed by addition of HX to the double bond. However, there have not been any reports published on hydrophilic polysilanes. The authors' goal was to synthesize high molecular weight polysilanes substituted with phenols and to determine the characteristics of these polymers.

Scheme I
Syntheses of Polysilanes with Phenols



Determining how to protect OH moiety was an important point. The protecting group used must have durability to withstand synthesis reagents during monomer and polymer syntheses. In addition, after syntheses, the protecting group must be removed under mild conditions, because the Si–Si bond is easily attacked by base and acid. The trimethylsilyl moiety was selected to achieve these purposes.

Scheme I shows monomer and polymer syntheses. Introduction of the phenol moiety to Si by a Grignard reagent was reported previously;[15] however, the authors' attempts to prepare [[(trimethylsilyl)oxy]phenyl]chloro-

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* To whom all correspondence should be addressed.

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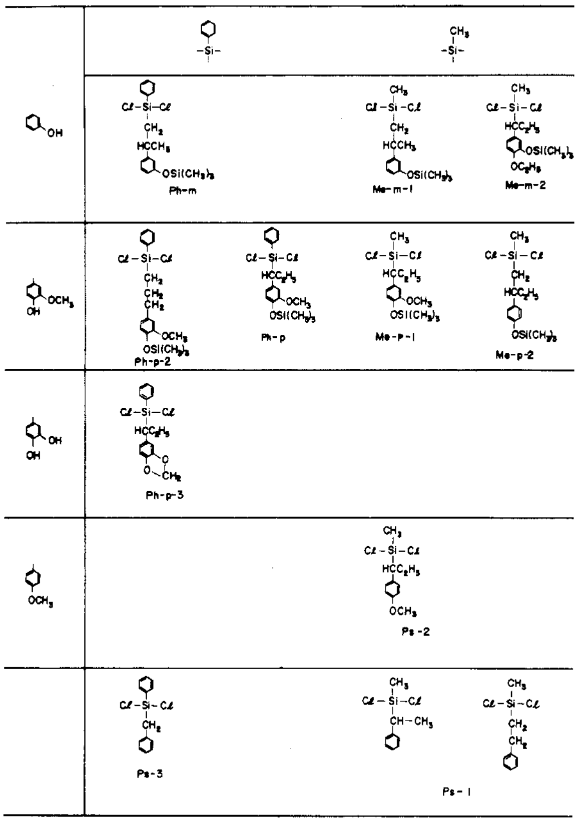
Table I
Monomer Structures



silane by Grignard reagent failed, due to very small yields. Thus, hydrosilylation was employed, because monomers were obtained easily in high yield.

This paper reports the syntheses for monomer and polymer, characterization for polymers, and photolysis behavior and a comparison with polymer characteristics reported before.

Experimental Section

All experiments were conducted under a nitrogen atmosphere. All solvents were dried in CaH_2 and distilled and then stored under N_2 atmosphere.

Monomer structures and abbreviations are summarized in Table I.

Syntheses of Monomers. [1-[4-[(Trimethylsilyl)oxy]-3-methoxyphenyl]propyl]phenyldichlorosilane (Ph-p). Phenyldichlorosilane (200 g) was mixed with 1-[4-[(trimethylsilyl)-oxy]-3-methoxyphenyl]-1-propene (200 g) which was prepared by reaction of isoeugenol with hexamethyldisilazane at room temperature followed by distillation (102–106 °C (5 mmHg), yield 95%). Then, 1 g of Pt complex catalyst, purchased from Toshiba Silicone Co. (not commercially available, under developing catalyst), was added slowly. The reaction mixture turned red immediately, which was accompanied by a slight temperature rise. After it was stirred for 3 h, the reaction mixture was distilled under reduced pressure: yield 54%, bp 190–194 °C (10 mmHg); NMR ($CDCl_3$) δ 7.46–7.22 (m, Ar H), 6.74–6.42 (m, Ar H), 3.58 (s, OCH_3), 2.48 (dd, J = 3.9, 11.5 Hz, CH), 2.15–1.77 (m, CH_2), 0.91 (t, J = 7.2 Hz, CH_3), 0.21 (s, $Si(CH_3)_3$). Further distillation was carried out before polymerization. Si was always added to the double bond carbon adjacent to the phenyl group.

[1-[4-[(Trimethylsilyl)oxy]-3-methoxyphenyl]propyl]-methyldichlorosilane (Me-p-1) was prepared by reaction of 1-[4-[(trimethylsilyl)oxy]-3-methoxyphenyl]-1-propene with methyldichlorosilane in the same way as Ph-p: yield, 75%, 155–160 °C (5 mmHg); NMR ($CDCl_3$) δ 0.23 (s, $Si(CH_3)_3$), 0.55 (s, $SiCH_3$), 0.92 (t, J = 7.1 Hz, CH_3), 1.80–2.38 (m, $CHCH_2$), 3.79 (s, OCH_3), 6.55–6.28 (m, Ar H).

[2-[3-[(Trimethylsilyl)oxy]phenyl]propyl]phenyldichlorosilane (Ph-m) was prepared by the reaction of trimethylsilyloxylated *m*-isopropenylphenol with phenyldichlorosilane in the presence of Pt catalyst described in the section on (Ph-p) synthesis. *m*-Isopropenylphenol was purchased from Mitsui Petroleum Chemical Co.: yield 70%, bp 174–176 °C (3 mmHg); NMR ($CDCl_3$) δ 0.24 (s, $Si(CH_3)_3$), 1.31 (d, J = 6.8 Hz, CH_3), 1.72 (d, J = 6.8 Hz, CH_2), 3.10 (m, CH), 6.66–7.63 (m, Ar H).

[2-[3-[(Trimethylsilyl)oxy]phenyl]propyl]methyldichlorosilane (Me-m-1) was prepared in the same way as (Ph-m): yield 49%, bp 130–135 °C (14 mmHg); NMR ($CDCl_3$) δ 0.23 (s, $Si(CH_3)_3$), 0.55 (s, $SiCH_3$), 1.34 (d, J = 3.5 Hz, CH_3), 1.52 (d, J = 7.4 Hz, CH_2), 3.06 (m, J = 7.0 Hz, CH), 6.67–7.15 (m, Ar H).

The product (Me-p-2) from trimethylsilylated *p*-isopropenylphenol and methyldichlorosilane was **[2-[4-[(trimethylsilyl)oxy]phenyl]propyl]methyldichlorosilane**: yield 10%, 135–140 °C (10 mmHg). The yield of the Me-p-3 was rather low, because of oligomerization of isopropenylphenol by the acidic Pt complex. Phenyldichlorosilane did not add the trimethylsilylated isopropenylphenol, because the vinyl polymerization greatly surpassed the hydrosilylation due to steric hindrance of phenyl moiety.

[3-[4-[(Trimethylsilyl)oxy]-3-methoxyphenyl]propyl]-phenyldichlorosilane (Ph-p-2) was prepared from trimethylsilylated eugenol and phenyldichlorosilane: yield 45%, 207–210 °C (9 mmHg); NMR ($CDCl_3$) δ 0.23 (s, $SiCH_3$), 1.31 (t, J = 6.4 Hz, $SiCH_2$), 2.12–1.70 (m, $CH_2CH_2{}^oCH_2$), 2.62 (t, J = 7.2 Hz, $PhCH_2{}^o$), 3.67 (s, OCH_3), 7.74–7.34, 6.79–6.54 (m, Ar H).

[1-(3,4-Methylenedioxyphenyl)propyl]phenyldichlorosilane (Ph-p-3) was synthesized by the reaction of trimethylsilylated isosafrole with phenyldichlorosilane: yield 40%, bp 183–185 °C (9 mmHg); NMR ($CDCl_3$) δ 0.85 (t, J = 7.2 Hz, CH_3), 1.8–2.1 (m, CH_2), 2.48 (dd, J = 3.9, 11.5 Hz, CH), 5.84 (s, CH_2), 6.4–6.7, 7.2–7.6 (m, Ar H).

[1-[4-(Ethyloxy)-3-[(trimethylsilyl)oxy]phenyl]propyl]-methyldichlorosilane (Me-m-2) was also prepared by the reaction of trimethylsilylated isosafroeugenol with methyldichlorosilane: yield 67%, 160–163 °C (24 mmHg); NMR ($CDCl_3$) δ 0.23 (s, $Si(CH_3)_3$), 0.55 (s, $SiCH_3$), 0.89 (t, J = 7.08 Hz, $OCH_2CH_3{}^o$, 1.40 (t, J = 7.09 Hz, CH_3), 1.80–2.38 (m, $CHCH_2$), 3.98 (q, J = 6.84 Hz, $OCH_2{}^oCH_3$), 6.69–6.73 (m, Ar H)).

The product (Ps-1) from styrene and methyldichlorosilane was a mixture of **(1-phenylpropyl)methyldichlorosilane and (2-phenylpropyl)methyldichlorosilane.** The two were not separated by distillation under reduced pressure: yield 34%, bp 93–102 °C (10 mmHg); ^1H NMR ($CDCl_3$) δ 0.67, 0.60, 1.57, 1.49, 1.37, 2.92–2.50, 7.36–7.22 (mixture of the two monomers).

[1-(4-Methoxyphenyl)propyl]methyldichlorosilane (Ps-2) was prepared by hydrosilylation of methyldichlorosilane with 1-(4-methoxyphenyl)propene: yield 55%, bp 115–117 °C (5 mmHg); NMR ($CDCl_3$) δ 0.58 (s, $SiCH_3$), 0.89 (t, J = 7.08 Hz, CH_3), 1.73–2.36 (m, $CHCH_2$), 3.75 (s, OCH_3), 6.78–7.12 (m, Ar H).

Benzylphenyldichlorosilane (Ps-3) was prepared by reacting phenyltrichlorosilane with benzyl magnesium chloride.

Polymer Preparation. All solvents used were dried over CaH_2, followed by Na, and were distilled before polymerization. The polymerization was carried out in the same way as that reported previously.[1,2] The typical course was as follows. Sodium 1 mol, was dispersed in 150 mL of toluene at 110 °C. Dichlorosilanes, 0.33 mol, were added dropwise to the dispersed sodium. Then the mixture was stirred at 110 °C. The reaction mixture was filtered and toluene-soluble matter was collected. After the toluene was removed, methanol was added to the residue and the mixture was stirred until the residue was dissolved, after which the trimethylsilyl moiety was removed by hydrolysis. After removal of methanol under reduced pressure, the residue was dissolved in 5% aqueous NaOH solution and the insoluble matter was filtered off. The aqueous solution was slightly acidified with HCl, precipitating the polymer. The polymer was extracted with diethyl ether and the ether layer was dried over $MgSO_4$. Ether was removed and the polymer *was purified by precipitation in toluene* in order to obtain high molecular weight polymer. Before hydrolysis of the trimethylsilyl moiety, the polymer was soluble in nonpolar solvents, like xylene and toluene. However, after hydrolysis, the polymer became soluble in a polar solvents like alcohol. Table II summarizes the polymerization conditions and the results.

Table II
Polymer Syntheses and Characterizations

run	polymer	monomer	polym syntheses T, °C	polym syntheses t, h	polym yield,[b] %	polysilane yield, %
1	P(Ph-p)	Ph-p	130	8	10	0
2[a]	P(Ph-p)(SiMe) 2:1	Ph-p (1) SiMe (1)	130	8	60	0
3[a]	P(Ph-p)(SiMe) 1.3:1	Ph-p (1) SiMe (1)	110	3	65	9
4	P(Me-p-1)	Me-p-1	110	1	47	0
5	P(Ph-m)	Ph-m	110	1	43	0
6[a]	P(Ph-m)(SiMe) 1.6:1	Ph-m (1) SiMe (1)	110	8	60	15
7	P(Me-m-1)	Me-m-1	110	2	65	9
8	P(Me-p-2)	Me-p-2	110	2	50	0
9[a]	P(Ph-p-2)(SiMe) 1:1	Ph-p-2 (1) SiMe (1)	110	2	51	0
10[a]	P(Ph-p-3)(SiMe) 1:1	Ph-p-3 (1) SiMe (1)	110	2	50	0
11	P(Me-m-2)	Me-m-2	110	2	73	0
12	P(Ps-1)	Ps-1	110	65	66	46
13	P(Ps-2)	Ps-2	110	5	45	0
14	P(Ps-3)	Ps-3	110	5	35	30

[a] Copolymer with SiMe (dimethyldichlorosilane). Values are the mean ratio of monomer units before and after polymerization. [b] Structures for polymeric products besides polysilanes are not identified. Polymer yields include that of polysilane. Run 3, P(Ph-p)(SiMe): M_w, 650,1600: NMR (acetone-d_6) δ 0.22 ($SiCH_3$), 0.90 (CH_3), 2.03 ($CHCH_2$), 3.81 (OCH_3), 6.5–8.0 (Ar H); IR (cm^{-1}) 3450, 2975, 2100, 1610, 1520, 1458, 1375, 1250, 1155, 1130, 1145, 768; UV (THF, nm) 285. Run 6, P(Ph-m)(SiMe): M_w 7500; NMR (acetone-d_6) δ 0.22 ($SiCH_3$), 0.94 ($CH_2{}^oPh$), 1.76 (CH_2), 2.57 (CH_2Si), 3.86 (OCH_3), 6.5–8.0 (Ar H); UV (THF, nm) 320, 272. Run 7, P(Me-m-1): M_w 110 000; NMR (acetone-d) 0.40 ($SiCH_3$), 1.22 (CH_2CH_3), 2.9 (CH), 6.65–7.18 (Ar H); IR (cm^{-1}) 3300, 2950, 1590, 1450, 1250, 1150, 1090, 1010, 940, 880, 785, 750, 705; UV (THF, nm) 297, 335. Run 12, P(Ps-1): ^1H NMR (acetone-d_6) δ 0.54, 1.60, 2.84, 7.18 (mixture of two polymers): IR (cm^{-1}) 3025, 2950, 1610, 1500, 1455, 1415, 1250, 1085, 760, 700; UV (THF, nm) 335, 290.

Photolyses. Photolyses were carried out by using a high-pressure mercury lamp.

Quantum Yield. A sample in methanol was coated to a thickness of around 0.5 μm on the quartz plate, using a spinner. The sample was treated at 90 °C for 10 min to evaporate methanol. The irradiation was conducted by using a CA 800 apparatus (COBILT) which was equipped with a high-pressure mercury lamp. *No filter was used. However, since polysilanes with phenol moiety have UV absorption below 350 nm and 254-nm light was not detected in the light emitted from the high-pressure mercury lamp because of UV absorption by the lens system, 313 nm would be almost the only light which is effective for the polymer photodecomposition.* The photodegradation was followed with UV spectrometry and gel permeation chromatography.

Bleaching of the Polymer. Bleaching of polysilanes was carried out in THF or methanol.

The molecular weight distribution of the polymers was determined with a Toyo Soda Model 801 gel permeation chromatograph at 40 °C. Four columns were connected in series, each packed with G-2000H_8×3 and G 4000H_8 (Toyo Soda Polystylene Gel). Tetrahydrofuran was used as a solvent, and the instrument was calibrated to a first approximation with polystyrene standard of known molecular weight.

^1H NMR spectra were measured by a JEOL FX 90Q spectrometer.

Results and Discussion

Polymerization. Table II summarizes the polymerization conditions and results. All monomers gave polymeric products. In order to identify the polymeric products as being polysilane, the UV spectrum before and after UV irradiation was observed. Polysilanes are known to absorb in the UV between 280 and 350 nm,[1,2] and this UV absorption was destroyed by UV irradiation in solution. Polymers from the phenylsilyl compounds, Ph-p and Ph-m, did not have a polysilane structure (runs 1 and 5). The copolymer which was prepared from Ph-p and dimethyldichlorosilane by reacting for 8 h at 130 °C (run 2) was also not polysilane. The authors do not have sufficient knowledge about the structure of these polymers.

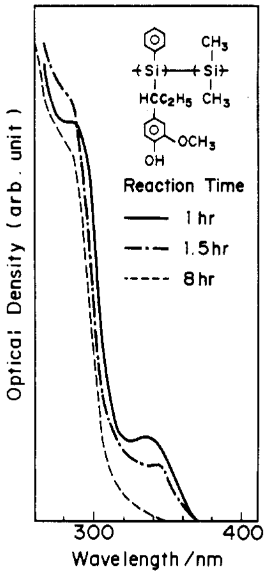


Figure 1. UV spectrum change for polysilanes during syntheses.

In run 2, a vigorous viscosity rise was observed about 1 h after the temperature was raised. However, the viscosity gradually decreased during further reaction. In order to examine the reason for the viscosity change, the molecular weight distribution was determined in the course of the polymerization. Polysilane was obtained at 9% yield, when the polymerization was stopped at 3 h (run 3). The high molecular weight polymer (M_w 7500) that was identified before the reaction time reached 3 h disappeared when the reaction time reached 8 h (*run 2*). *In run 3, the fact that (1) the polymer had a dimethylsilyl unit and a aromatic unit, which was identified by ^1H and ^{13}C NMR spectroscopy, (2) the high molecular weight polymer had UV absorption at around 340 nm, (3) the polymer was soluble in 5% NaOH aqueous solution, and (4) Ph-p did not homopolymerize to form polysilane assured that the polymer was copolysilane,* not a mere mixture of the two homopolymers, because *dimethylpolysilane homopolymer must be insoluble in 5% NaOH aqueous solution.* The results shown in Figure 1 wherein UV absorption of polysilanes disappeared during synthesis also strongly supported the explanation.

The polymer film began thermal decomposition at around 155 °C, which was determined by TGA and DTA. The thermal decomposition of the Si–Si linkage was supported by UV absorption change after various thermal treatments as shown in Figure 2. There was no change

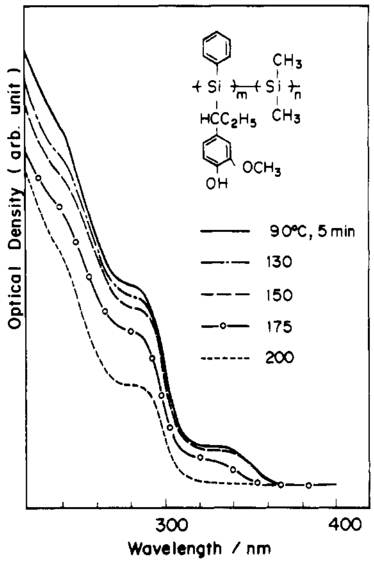


Figure 2. UV absorption change in polysilane after and before heat treatment.

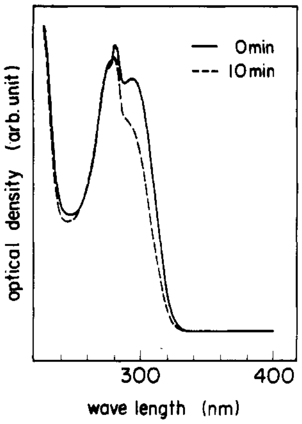


Figure 3. UV spectrum change of P(Me-m-1) in THF before and after UV irradiation.

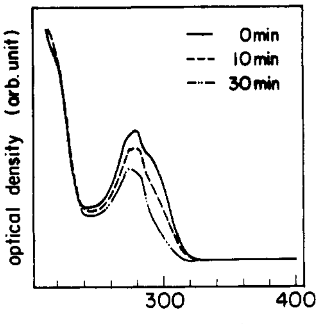


Figure 4. UV spectrum change of P(Me-m-1) in methanol before and after UV irradiation.

up to 130 °C, and the absorption began to decrease above 150 °C, which was consistent with the result obtained by TGA and DTA. The polymer became insoluble in solvents after heat treatment at above 150 °C. Cross-linking might occur.

In contrast to Me-p-1, Me-m-1 could homopolymerized easily (runs 4 and 7). Figures 3 and 4 show the UV absorption of P(Me-m-1) in THF and methanol, after and before UV irradiation. The bleaching was carried out in THF or methanol. Remarkable bleaching shows that this polymer has a polysilane structure. The polymer was purified 3 times in toluene. Before purification, this polymer had three peaks in GPC curve; however, after purification, molecular weight distribution of this polymer was unimodal and the molecular weight was 110 000, as shown in Figure 5. Figure 6 shows the ^{13}C NMR spectrum of P(Me-m-1) in CD_3OD. The fact that each carbon signal was single indicates that the polymer had a regular repeating unit and there were no unknown or isomerized structure in this purified polymer.

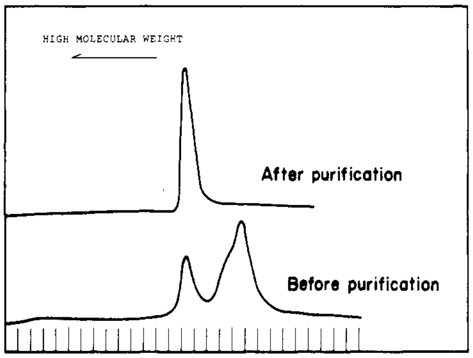


Figure 5. GPC curve of P(Me-m-1) before and after purification.

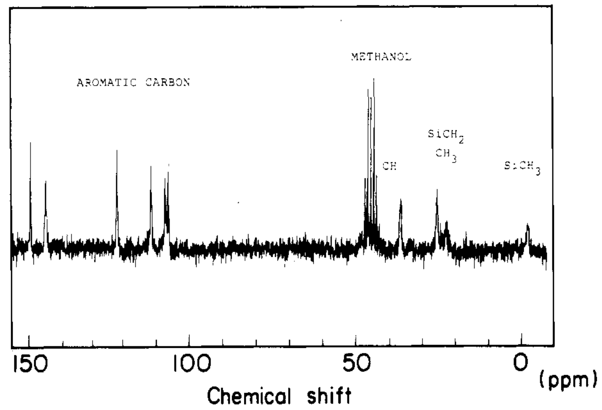


Figure 6. ^{13}C NMR spectrum of P(Me-m-1) in CD_3OD.

There was a possibility that this polymer might contain an aromatic carbon–Si–Si linkage, because the UV absorption of this linkage also bleaches after UV irradiation.[16] However, this possibility was denied by the fact that the six carbon signals of the aromatic ring were single and there was no carbon signal assigned to aromatic carbon adjacent to a Si–Si linkage.

Usually, poly(alkylsilanes) have maximum UV absorption in the range from 280 to 310 nm, except for symmetrical dialkylsilanes, like poly(di-*n*-hexylsilane).[5,11,17] On the other hand, polysilanes with aromatic groups adjacent to Si have rather red-shifted maximum UV absorption in the range between 330 and 350 nm, due to the orbital interaction between the delocalized $3d_{Si-Si}$ MO and the p–π^* MO of the aryl group.[11,23] In P(Me-m-1), the phenyl group is separated by two carbons from Si; therefore, it is assumed that there is no orbital interaction between them. Therefore, UV absorption of Si–Si linkage in P(Me-m-1) is similar to that for asymmetric polysilane, which absorbs UV light in the range between 280 and 300 nm. Since the phenol group absorbs UV light in the range from 260 and 270 nm, the UV absorption of the phenol group overlapped with that of the Si–Si linkage. Zhang et al. reported the UV spectra of poly[methyl(β-phenethyl)silane] whose phenyl group is separated by two carbons from Si.[6] The polymer has UV absorption maximum at 305 nm and a small absorption assigned to benzenoid band of phenyl group is seen at 265 nm. Since the phenol moiety has a larger molecular extinction coefficient (ϵ 1450, 270 nm) than benzene (230 at 255 nm), the UV absorption of the Si–Si linkage against that of the phenol moiety looks less remarkable than those of poly(methylphenylsilane) and poly[methyl(β-phenethyl)silane].

The absorption of Si–Si linkage blue-shifted in methanol, compared with in THF. Polarity of solvent might cause conformational changes of the Si–Si linkage. Further consideration was carried out on this phenomena. The overlap of UV absorption of the phenol group and Si–Si linkage was also suggested by the fact that, especially in methanol, the UV absorption in the range from 260 to 300 nm decreased after UV irradiation, UV absorption of phenol group remaining.

Me-p-1 did not polymerize to polysilane, but Me-m-1 did (runs 4 and 7). There were two distinctions between the two monomers, namely, whether the ether moieties were substituted at para and meta positions or at the meta position only and whether the aromatic moiety was separated from Si by one carbon or two carbon. Therefore, the reasons why Me-p-1 did not homopolymerize were considered to be pertinent to the following two points. One is that methylene linking Si of Me-p-1 is easily attacked by Na, because Me-p-1 has a $Si-CH_2$ linkage and a methylene of a benzyl moiety, both of which are well-known to be labile against ionic and radical species. The other is that the ether structure, substituted at the para position of the benzene ring, might be easily attacked by Na.

In order to examine the former possibility, monomer Ps-3 and monomer Ps-1 were prepared and polymerized. *Both Ps-3 and Ps-1 gave polysilane (runs 12 and 14), which indicated that whether a SiCHPh or $SiCH_2CHPh$ linkage was present was not the dominant reason. However, these polymers have small SiH absorption in IR spectra, suggesting that chain-termination reactions are molecular weight limiting. Since it would be thermodynamically unfavored for a Si radical to abstract hydrogen from the toluene solvent, the SiH termination most likely comes from chain termination on monomer or by "back-biting" reactions on the polymer.*

The monomer Ps-2 did not polymerize to give polysilane (run 13), which shows that the substitution position of the ether determines whether or not homopolysilane can be synthesized. Only a monomer with a meta ether structure could homopolymerize to give polysilane. The fact that polysilanes could not be obtained from other monomers having para ether structures like Ph-p-3, Ph-p-2, Me-p-2, and *Me-m-2* further confirms the conclusion (runs 8, 9, 10, and *11*).

In order to obtain polysilanes by using a monomer substituted with a para ether moiety, copolymerization with dimethyldichlorosilane was available. However, in that case, much care should be paid to reaction temperature and time, as mentioned before (run 3).

P(Me-m-1) was stable even at 200 °C, which was a large difference when compared with P(Ph-p)(SiMe) (decomposition temperature, 150 °C). Ph-m, which did not homopolymerize, could be copolymerized with dimethyldichlorosilane (run 6). Copolymer P(Ph-m)(SiMe) was also stable at 200 °C, and there was not disappearance of UV absorption of polysilane even at 200 °C. Namely, polysilanes with a *m*-hydroxyphenyl moiety had heat stability more than those with a *p*-hydroxyphenyl moiety.

The reason why polysilane with a *p*-hydroxyphenyl-moiety is difficult to synthesize might be explained as follows. *In a monomer with a meta ether structure, like Me-m-1, chain termination at SiCH on the monomer or the polymer would not become dominant, however, in the monomer with a para ether structure such as Me-p-1, para oxygen would activate the SiCH moiety and chain termination would be dominant. The degree of activation against H transfer would vary by whether the structure is SiCH– or $SiCH_2CH$. The chain termination might also take place at OCH_3. In both explanations, the presence of a para ether structure is significant.* In addition, thermal instability of P(Me-p-1) would be pertinent to the reason.

Copolymerization was started at a equimolar ratio (monomer:dimethyldichlorosilane = 1:1). However, the monomer unit was larger than the dimethylsilyl unit in the copolymer (runs 2, 6, and 10). The reason is explained by the assumption that homopolymer, formed by rapid polymerization of dimethyldichlorosilane, was not soluble in solvents like toluene and xylene, and monomer ratio was gradually deviated during polymerization. The polydimethylsilane was removed as precipitate from the homogeneous reaction mixture or as insoluble matter in dilute NaOH aqueous solution.

In the case of monomer Ph-p-3, 30% of the OCH_2O group remained, even after base treatment.

Photolysis. Polymers P(Ph-p)(SiMe), P(Ph-m)(SiMe), and P(Me-m-1) photodecomposed to form oligomers and the UV absorption from 300 to 350 nm disappeared during photolysis. The phenomena were the same as for conventional polysilanes reported previously.[2,7] Most intriguing was determining whether or not the OH moiety in the polymer seriously affected photolysis behavior. The reason is that silylene was reported to be released by photodecomposition of polysilanes, which reacted with alcohols to form silyl ethers by inserting into the O–H bond.[18-20]

In order to examine the effect of the OH moiety, the quantum efficiencies for scission Φ(S) and cross-linking Φ(X) were determined by the following equations:[21-22]

$$\frac{1}{\bar{M}_n} = \frac{1}{\bar{M}_n^{\,0}} + (\Phi(S) - \Phi(X))\frac{D}{N_A} \qquad \frac{1}{\bar{M}_w} = \frac{1}{\bar{M}_w^{\,0}} + \left(\frac{\Phi(S) - 4\Phi(X)}{2}\right)\frac{D}{N_A}$$

where Φ(S) is the quantum efficiency for scission, Φ(X) is the quantum efficiency for cross-linking, N_A is Avogadro's number, and D is the absolute dose.

The ratio Φ(S)/Φ(X) for P(Me-m-1) was 5.2, which was almost the same as that for methylphenylsilane (4.7).[23] The ratio Φ(S)/Φ(X) for P(Ph-m)(SiMe) was infinite. Therefore, facility of photodegradation could be improved by copolymerization with alkyldichlorosilane. The results show that the OH moiety did not affect the molecular weight decrease and cross-linking during photolysis. Since the copolymer of (Ph-p) with dimethyldichlorosilane did not cross-link, cross-linking might have occurred by a reaction between the phenyl group and silyl radical or silylenes.

Summary

Hydrophilic high molecular weight polysilanes containing phenol moieties were synthesized. The substitution position of the ether structure in the phenol group and the number of carbons between phenyl and Si determined whether or not the polysilanes could be prepared. Stability against heat and molecular weight (110 000) were almost the same as for conventional polysilanes with hydrophobic moieties, such as alkyl and aromatic groups. The distinctive difference between them was solubility. Polysilanes with phenol moieties are soluble in hydrophilic solvents such as alcohols, ketones, and ethers. However, polysilanes with alkyl and aromatic moieties are insoluble

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in these solvents. OH moieties did not affect the molecular weight decrease and cross-linking during photolysis.

Registry No. Ph-p, 111351-17-8; Ph-p (homopolymer), 111351-25-8; Ph-p (SRU), 111351-32-7; Me-p-1, 111495-40-0; Me-p-1 (homopolymer), 111351-33-8; Me-p-1 (SRU), 111351-26-9; Ph-m, 111351-18-9; Ph-m (homopolymer), 111351-34-9; Ph-m (SRU), 111351-27-0; Me-m-1, 111351-19-0; Me-m-1 (homopolymer), 111556-64-0; Me-m-1 (SRU), 111524-60-8; Me-p-2, 111351-20-3; Me-p-2 (homopolymer), 111351-35-0; Me-p-2 (SRU), 111351-28-1; Ph-p-2, 111351-21-4; Ph-p-3, 111351-22-5; Me-m-2, 111351-23-6; Me-m-2 (homopolymer), 111351-36-1; Me-m-2 (SRU), 111351-29-2; Ps-2, 111351-24-7; Ps-2 (homopolymer), 111351-39-4; Ps-2 (SRU), 111351-30-5; Ps-3 (homopolymer), 111351-40-7; Ps-3 (SRU), 111351-31-6; (Ph-p)(Me_2SiCl_2) (copolymer), 111351-41-8; (Ph-m)(Me_2SiCl_2) (copolymer), 111351-42-9; (Ph-p-2)(Me_2SiCl_2) (copolymer), 111378-53-1; (Ph-p-3)(Me_2SiCl_2) (copolymer), 111351-43-0; $PhSiHCl_2$, 1631-84-1; 3-$Me_3SiOC_6H_4CH{=}CHMe$, 111351-14-5; $MeSHCl_2$, 75-54-7; 4-$Me_3SiOC_6H_4CH{=}CHMe$, 25195-80-6; $PhCH{=}CH_2$, 100-42-5; 4-$MeOC_6H_4CH{=}CHCH_3$, 104-46-1; ($MeSiCl_2CH(Ph)CH_2CH_3$)($MeSiCl_2CH_2CH(Ph)Me$) (copolymer), 111351-38-3; 1-[4-[(trimethylsilyl)oxy]-3-methoxyphenyl]-1-propene, 6689-41-4; eugenol trimethylsilyl ether, 4515-52-0; isosafrole trimethylsilyl ether, 111351-15-6; isosafroeugenol trimethylsilyl ether, 111351-16-7.

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Surface-Selective Hydroxylation of Polypropylene

Kang-Wook Lee and Thomas J. McCarthy*

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003.

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ABSTRACT: Room-temperature oxidation of polypropylene film with chromium(VI) oxide in acetic acid/acetic anhydride introduces hydroxyl groups, olefins, ketones, and esters to a thin layer at the surface of the film. Analysis using a combination of analytical techniques (UV–vis, XPS, ATR IR, contact angle, and gravimetric analysis) indicates that the density of functionality increases over the first 4 h of reaction and remains essentially constant thereafter. Gravimetric analysis reveals an initial mass gain (over the first 4 h) and subsequent mass loss, indicating the gradual dissolution of modified polymer and the maintenance of a modified layer on the order of 100 Å thick. SEM reveals no changes in surface topography at the limits of resolution: all film surfaces appear flat. Treatment of the oxidized polypropylene with borane reduces the ketones, the esters, and more slowly, the olefins and increases the density of hydroxyl groups. Hydroxyl groups on oxidized and oxidized/reduced polypropylene were labeled (for XPS and ATR IR identification) by reaction with heptafluorobutyryl chloride.

Introduction

Isotactic polypropylene (PP) film is widely used, often in laminates, as a barrier polymer due to its moisture-resistant properties.[1] Its relatively low surface energy and relatively high chemical resistance impede its materials applications, particularly those which require an adhesive bond between PP and another condensed phase (ink, metal, another polymer, inorganic filler). This problem has led to copious research associated with PP surface chemistry and an extensive literature of PP surface modification techniques. Gas discharge treatments[2,3] in air and other atmospheres introduce a range of functionality. Sulfuric acid[4] and chromic–sulfuric acid[4–6] introduce sulfonic acid, carboxylic acid, and likely other less oxidized functional groups. Photohalogenation[7–9] produces printable surfaces. Hydroperoxide-catalyzed oxidation[10] introduces hydroperoxide groups. Ozone treatment[11,12] renders wettable surfaces. Graft polymerizations from free radical sites generated on the surface give access to a range of surface functionality.[12–15] A thin layer of vapor-deposited copper catalyzes surface autoxidation.[16] Radical addition reactions with maleic anhydride produce maleated polypropylene.[17]

We are interested in developing an understanding of the molecular basis (at the functional group level) for macroscopic polymer surface properties. For this study, we need unreactive polymers containing surface-confined versatile organic functional groups. Ideally, the substrates should contain an array of a single functional group covalently attached and located in a position (the surface) where each

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