Efficient Synthesis of Poly(silyl ether)s by Pd/C and $RhCl(PPh_3)_3$-Catalyzed Cross-Dehydrocoupling Polymerization of Bis(hydrosilane)s with Diols

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Received April 6, 1999

Introduction. Poly(silyl ether)s represent a class of promising materials useful as elastomers and plastics,[1,2] conductive polymeric materials,[3] polymer membranes,[4] stimuli-sensitive materials,[5] etc. Although many attempts have been made to synthesize poly(silyl ether)s, general efficient synthetic methods are still not available partly due to the instability of Si−O−C bond under acidic or basic conditions. Early attempts for obtaining high molecular weight linear products by condensation of dichlorosilanes and diols were proven unsuccessful, where cyclic compounds or oligomers (M_n < 2000) were often formed.[6] Instead of dichlorosilanes, using dialkoxy- and diaminosilanes as monomers[1,2,7−9] also seemed undesirable, except diphenoxy- and dianilinosilanes which could afford high molecular weight poly(silyl ether)s; however a high reaction temperature was required in these cases (200−300 °C).[1,2]

Recently, catalytic polyaddition of bis(epoxide)s with dichlorosilanes and the hydrosilylation of bis(silane)s with dicarbonyl compounds opened new pathways to the preparation of poly(silyl ether)s with higher molecular weights.[10,11] The requirements of the specific functional groups (epoxy or carbonyl group) on the monomers, however, limited further application of these methods to the preparation of various poly(silyl ether)s.

We have reported a novel approach to poly[(oxydimethylsilylene)(1,4-phenylene)(dimethylsilylene)] by the treatment of 1,4-bis(dimethylsilyl)benzene (BDMSB) with water in the presence of transition metal catalysts, a catalytic cross-dehydrocoupling polymerization.[12] Similarly, catalytic cross-dehydrocoupling reaction of organosilanes with alcohols[13] would be possibly used for the synthesis of poly(silyl ether)s if the silanes and alcohols are bifunctional. Here, we present our initial results on the successful application of the catalytic cross-dehydrocoupling reaction of bis(hydrosilane)s with several common diols to the synthesis of a new series of poly(silyl ether)s under mild reaction conditions (Scheme 1).

Experimental Section. Measurements. The 500 MHz ^{1}H, 75.3 MHz ^{13}C, and 79.6 MHz ^{29}Si NMR spectra were obtained in $CDCl_3$ on Varian 500 MHz Unity plus, 300 MHz Gemini 2000, and 400 MHz Unity INOVA spectrometers, respectively. Chemical shifts are reported in ppm, referenced to internal $CHCl_3$ (δ 7.26) for ^{1}H, $CDCl_3$ (δ 77.00) for ^{13}C, and external tetramethylsilane (TMS) (δ 0.00) for ^{29}Si. IR spectra were obtained on a JASCO VALOR−III spectrophotometer. Size exclusion chromatography (SEC) analysis was performed on a JASCO HPLC with the combination of Shodex KF-803L (exclusion limit: $M_n = 7 \times 10^4$, polystyrene) and KF-804 (exclusion limit: $M_n = 4 \times 10^5$, polystyrene) columns (linear calibration down to $M_n = 100$, polystyrene) using tetrahydrofuran (THF) as an eluent.

Materials. 1,4-Bis(dimethylsilyl)benzene (BDMSB), 1,3-dihydro-1,1,3,3-tetramethyldisiloxane (DHTMDS), and 1,5-dihydro-1,1,3,3,5,5-hexamethyltrisiloxane (DHHMTS) were offered by Shin-Etsu Chemical Co., Ltd. 1, 2-Bis(dimethylsilyl)ethane (BDMSE) was prepared by the reduction of 1,2-bis(dimethylchlorosilyl)ethane with $LiAlH_4$.

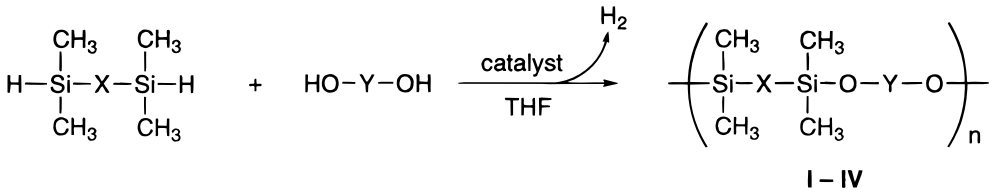
Polymerization. A typical procedure for the preparation of **I** was as follows (**Ib** in Table 1). To a 10 mL flask were added 10% Pd/C (53 mg, 5×10^{-3} mol Pd), ethylene glycol (0.62 g, 0.01 mol), BDMSB (1.94 g, 0.01 mol), and THF (3 mL). After the rapid evolution of hydrogen (an ice−water bath was used to remove the heat generated and the hydrogen generated was released to a balloon) almost ceased (about 30 min), the mixture was heated to 50 °C and maintained for 3 h. Removing the catalyst by Florisil column with $CHCl_3$ eluent, and precipitating into cold methanol (0 °C) gave a white solid (1.87 g, yield 73.1%). SEC: $M_n = 9400$, $M_w/M_n = 1.59$. NMR: ^{1}H, 0.35 (s, 12 H, SiCH_3), 3.66 (s, 4H, OCH_2CH_2O), 7.55 (s, 4 H, C_6H_4); ^{13}C, −1.92 (SiCH_3), 64.20 (OCH_2CH_2O), 132.88, 139.32 (aromatic carbons); ^{29}Si, 8.4. IR (neat): ν 3050−2869, 1254, 1138, 1090 (υ_{SiOC}), 956, 820, 778.

II−**IV** were prepared similarly (for polymerization conditions, see Table 1). Data for **IIc** (white solid) follow. SEC: $M_n = 9700$; $M_w/M_n = 1.44$. NMR: ^{1}H, 0.27 (s, 12 H, SiCH_3), 6.91 (d, 4H, $J = 8.4$ Hz), 7.39 (d, 4H, $J = 8.4$ Hz); ^{13}C, −0.64 (SiCH_3), 120.22, 127.80, 134.59, 153.60 (aromatic carbons); ^{29}Si, −12.3. IR (neat): ν 3062−2906, 1606, 1497, 1267, 1168, 1068 (υ_{SiOC}), 920, 828, 804. Data for **IIIc** (brown liquid) follow. SEC: $M_n = 12\,200$; $M_w/M_n = 1.99$. NMR: 0.078 (minor), 0.083 (minor), 0.10 (minor), 0.12 (major), 0.25 (major), 6.93 (d, 4 H, $J = 8.5$ Hz), 7.39 (d, 4 H, $J = 8.5$ Hz); ^{13}C, −0.66 (major), 0.78 (major), 0.84 (minor), 0.90 (minor), 115.59, 120,15, 127.77, 134.44, 153.74; ^{29}Si, −13.15 (major), −13.41, −19.56 (major), −20.49, −21.64, −21.76. IR (neat): ν 3035−2905, 1606, 1411, 1406, 1261, 1168, 1048 (υ_{SiOC}), 922, 802, 719. Data for **IVc** (white solid) follow. SEC: $M_n = 6800$; $M_w/M_n = 1.39$. NMR: 0.28 (s, 12 H, SiCH_3), 0.76 (t, 4H, SiCH_2CH_2Si, $J = 2.8$ Hz), 6.86 (m, 4 H), 7.39 (m, 4 H); ^{13}C, −2.12 (SiCH_3), 7.75 (SiCH_2CH_2Si), 120.26, 127.78, 134.21, 154.44 (aromatic carbons); ^{29}Si, 20.1. IR (neat) ν 3061−2789, 1605, 1498, 1406, 1252, 1168, 1136, 1053, 910, 830, 790, 716.

Results and Discussion. Four typical commercially available or easily prepared bis(hydrosilane)s (BDMSB, DHTMDS, DHHMTS, and BDMSE) and two typical diols (ethylene glycol and 4,4′-bisphenol) were chosen as monomers (Table 1). Initial attempts to obtain polymer **I** were made by the reaction of BDMSB with ethylene glycol in the presence of tris(dibenzylideneacetone)dipalladium(0)−chloroform ($Pd_2(dba)_3$), which was found to be a very efficient catalyst for the cross-dehydrocoupling polymerization of BDMSB with water as reported in our previous paper.[12] However, in this case, only low molecular weight products were obtained (**Ia**, $M_n = 3600$), although the early stage of this reaction was very fast (violent evolution of H_2). It was found that when the monomers and $Pd_2(dba)_3$ were mixed together in THF, the color of the mixture changed quickly from purple to black, and after 30 min, large black particles

10.1021/ma990511+ CCC: $18.00
Published on Web 09/11/1999

Scheme 1



I – IV

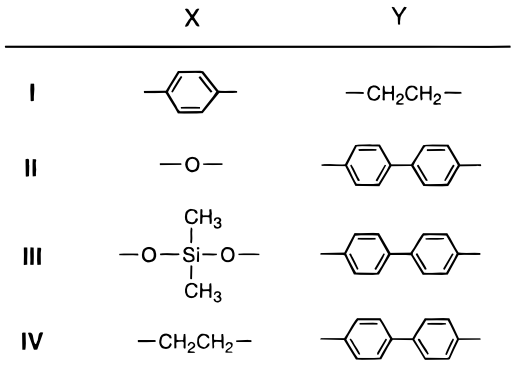
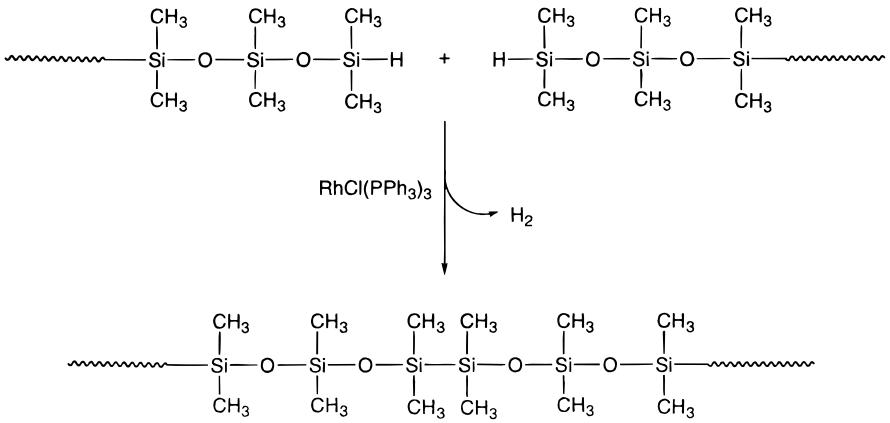


Table 1. Synthesis of Polymers I–IV by Cross-Dehydrocoupling Polymerization[a]

polymer	catalyst	time, h	yield, %[b]	M_n[b]	M_w/M_n[b]
Ia	$Pd_2(dba)_3$	24	90.8	3600	1.65
Ib	10%Pd/C	3	94.1	7400 (9400)	1.67 (1.59)
Ic	$RhCl(PPh_3)_3$	48	~0		
Id	$RhCl(PPh_3)_3$	24	92.8 (71.8)	7600 (9500)	2.10 (1.66)
Ie	$PdCl_2(PPh_3)_3$	48	95.0	4400	1.75
If	5%Rh/C	24	92.8	3800	4.71
IIa	$Pd_2(dba)_3$	36	72.5	2100	1.44
IIb	10%Pd/C	48	35.7	800	1.18
IIc	$RhCl(PPh_3)_3$	36	82.3 (70.0)	5000 (9700)	1.95 (1.44)
IIIa	$Pd_2(dba)_3$	48	46.6	1400	1.22
IIIb	10%Pd/C	48	~0		
IIIc	$RhCl(PPh_3)_3$	48	74.8 (46.6)	6100 (12200)	2.53 (1.99)
IVb	10%Pd/C	48	~0		
IVc	$RhCl(PPh_3)_3$	60	90.0 (57.4)	5400 (6800)	1.93 (1.39)

[a] Polymerization conditions: [catalyst]/[silane] = 5×10^{-3}, solvent: THF, temperature: 50 °C (except **Id**, room temperature). [b] Estimated by SEC with polystyrene standards before (after) reprecipitation; yields in parentheses are isolated values.

Scheme 2



began to precipitate from the reaction solution. Thus, it was considered that the dba ligands are removed from the Pd center and the resulting naked Pd(0) metal may coagulate to the less active particles.

On the other hand, palladium dispersed on carbon (10% Pd/C) was a good catalyst, giving a polymer with $M_n = 7400$ in 3 h at 50 °C (**Ib**). When the reaction was conducted at 50 °C using $RhCl(PPh_3)_3$ as a catalyst, the reaction mixture changed quickly from dark brown ($RhCl(PPh_3)_3$'s color) to yellow, but no polymer was produced at all even over 48 h (**Ic**). Interestingly, a high molecular weight polymer (**Id**, $M_n = 7600$) was produced after reaction for 24 h at room temperature. $PdCl_2(PPh_3)_3$ and 5% Rh/C did not give high molecular weight products (**Ie** and **If**).

In the case of the reaction of 4,4′-bisphenol with DHTMDS, DHHMTS, and BDMSE, neither $Pd_2(dba)_3$ nor 10% Pd/C is an efficient catalyst, giving only oligomers in low yields (**IIa,b**, **IIIa,b**, and **IVb**). On the other hand, $RhCl(PPh_3)_3$ afforded high molecular weight polymers **IIc** ($M_n = 9700$), **IIIc** ($M_n = 12\,200$), and **IVc** ($M_n = 6800$).

NMR analysis indicated clearly that polymers **I**, **II**, and **IV** have the identical regular structure as shown in Scheme 1. However, the NMR spectra of polymer **IIIc** prepared by $RhCl(PPh_3)_3$ are relatively complicated. Major peaks at −13.15 ppm and −19.56 ppm in the ^{29}Si NMR spectrum of this polymer were assigned to two kinds of silicon atom in the regular repeating unit (refer to Scheme 1). Other peaks at −13.41, −20.49, −21.64, and −21.76 ppm were considered to be arisen from some irregular structures formed by some side reactions, such as the Si−Si containing units which might be formed by the dehydrocoupling reaction of SiH's (Scheme 2).[14]

Acknowledgment. This work was supported in part by a grant in aid for Scientific Research (08455438), a grant in aid for "New Polymers and Their Nano-Organized Systems" (10126222), and a grant in aid for Scientific Research in Priority Areas (10133220) from the Ministry of Education, Science, Sports, and Culture of Japan.

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MA990511+