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Communications to the Editor

Asymmetric Synthesis of Optically Active Poly(silyl ether)s Having Reactive Si−H Groups by Stereoselective Cross-Dehydrocoupling Polymerization of Bis(silane)s with Diols

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Much attention has been paid in recent years to the fabrication of chiral separation materials based on silicon-containing polymers by incorporating some chiral groups to either the side chain or the main chain.[1] However, chiral separation materials with chirality induced by asymmetric silicon atoms in the main chain have not been reported yet. We have prepared several optically active polymers having asymmetric silicon atoms in the main chain[2−4] and are moving toward finding possible applications of these polymers as a new class of chiral separation materials based on the asymmetry of the silicon atom itself in the polymer backbone, although direct linkage of optically active compounds to the surface of silica was found not always effective in the separation.[5] The method reported previously was the polymerization of optically active organosilicon compounds, which not only are economically unfavorable but also lack diverse structures due to difficulties in obtaining optically active organosilicon monomers. Therefore, the asymmetric synthesis of silicon-containing polymers from racemic or prochiral organosilicon monomers is a more promising way to approach various optically active polymers containing asymmetric silicon atoms in the main chain.

Recently, we found a novel synthetic route to polymers containing silicon−oxygen bonds in the main chain, that is, cross-dehydrocoupling polymerization of organosilanes in the presence of transition metal catalysts.[6−8] Since the dehydrogenative reactions of prochiral organosilanes with alcohols in the presence of chiral catalysts or with optically active alcohols were reported to show some enantioselective feature to afford optically active alkoxysilanes,[9−11] it is highly possible to achieve the asymmetric synthesis of optically active polymers containing the silicon−oxygen bond in the main chain via cross-dehydrocoupling polymerization. Here we report our preliminary observations on the first attempt of asymmetric synthesis of optically active poly(silyl ether)s.

In this study, three bis(silane) monomers, 1,2-bis(phenyldihydridosilyl)ethane (**BSE**), 1,4-bis(phenyldihydridosilyl)benzene (**BSB**), and 1,4-bis(phenyldihydridosilyl)naphthalene (**BSN**), were used to react with optically active diols (2*R*,4*R*)-1,4-pentanediol ((*R*)-PNDOL) and (*R*)-(+)-1,1′-bi-2-naphthol ((*R*)-BINOL) in the presence of $RhCl(PPh_3)_3$ or with an achiral diol cyclohexanediol (CHDOL) in the presence of an optically active catalyst RhCl[(*R*)-BINAP]. If one of the Si−H groups on each silicon atom is stereoselectively reacted, the formed silicon center, −O−Si*(HPh)−X−, would be of enantiomeric excess, and the resulting polymer would be optically active and (*S*,*S*)- or (*R*,*R*)-diisotactic.

Polymers **P1**, **P2**, and **P3** were synthesized as shown in Scheme 1 and Table 1. The cross-dehydrocoupling polymerization reactions of bis(silane)s **BSE**, **BSB**, and **BSN** with (*R*)-PNDOL in the presence of $RhCl(PPh_3)_3$ in benzene were almost completed within 3 h at room temperature, which was confirmed by IR (disappearance of −OH groups), ^{29}Si NMR (disappearance of $-SiH_2$), and SEC (M_n reached plateau). Polymerizations of **BSB** and **BSN** with PNDOL could give polymers **P2a** and **P3a** with relatively high molecular weights in high yields (**P2a**: $M_n = 26\,900$, yield = 87%; **P3a**: $M_n = 6470$, yield = 89%), while in the case of **BSE**, polymer **P1a** with a lower molecular weight in a lower yield ($M_n = 3020$, yield = 65%) was obtained. In contrast to the rigid phenylene and naphthylene groups in **BSB** and **BSN**, the flexible ethylene group in **BSE** might lead to the easy formation of cyclic oligomers in the reaction.

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Scheme 1

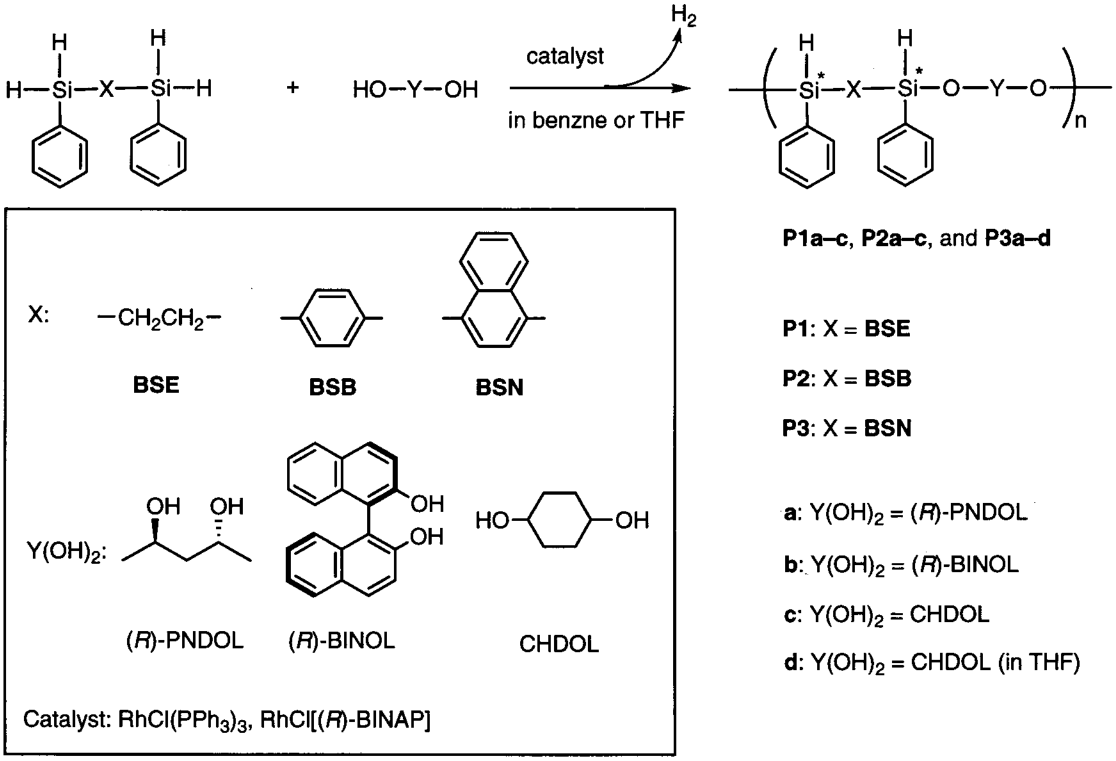


Table 1. Cross-Dehydrocoupling Polymerization of Bis(silane)s with Diols in Benzene[a]

polymer	silane	diol	catalyst	temp, °C	time, h	yield, %[b]	M_n [b]	M_w/M_n [b]
P1a	**BSE**	(*R*)-PNDOL	$RhCl(PPh_3)_3$	r.t.	3	65	3020	1.61
b		(*R*)-BINOL	$RhCl(PPh_3)_3$	50	120	100	950	1.20
c		CHDOL	RhCl[(*R*)-BINAP]	r.t.	24	100	4810	5.41
P2a	**BSB**	(*R*)-PNDOL	$RhCl(PPh_3)_3$	r.t.	3	87	26900	2.58
b		(*R*)-BINOL	$RhCl(PPh_3)_3$	50	24	100	2570	3.01
c		CHDOL	RhCl[(*R*)-BINAP]	r.t.	4	100	gel	
P3a	**BSN**	(*R*)-PNDOL	$RhCl(PPh_3)_3$	r.t.	3	89	6470	1.68
b		(*R*)-BINOL	$RhCl(PPh_3)_3$	50	120	0	*d*	
c		CHDOL	RhCl[(*R*)-BINAP]	r.t.	12	94	18000	2.28
d[c]		CHDOL	RhCl[(*R*)-BINAP]	r.t.	3	94	5150	3.13

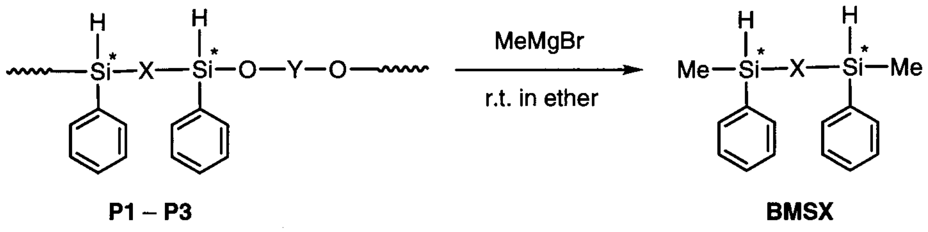
[a] [cat]/[silane] = 0.5% mol. [b] Estimated by SEC with polystyrene standards. [c] In THF. [d] No polymerization.

(*R*)-BINOL was found reluctant to react with **BSE**, **BSB**, and **BSN** in the presence of $RhCl(PPh_3)_3$ in benzene. The reaction of **BSE** with (*R*)-BINOL only gave oligomers (**P1b**, $M_n = 950$) at 50 °C after 5 days, while **BSN** showed almost no reactivity to (*R*)-BINOL. Only **BSB** could afford a polymer **P2b** with a rather low molecular weight ($M_n = 2570$) at 50 °C in 24 h. When using CHDOL, all three organosilanes could produce polymers (**P1c**, **P2c**, **P3c**, and **P3d**) with moderate to high molecular weights and yields in the presence of RhCl[(*R*)-BINAP] under gentle conditions (room temperature, 4−24 h).

Since bis(silane)s **BSE**, **BSB**, and **BSN** have four reactive Si−H groups, selective reaction of only one Si−H on each silicon atom is essential to avoid the formation of branched or cross-linked structures and to achieve a high optical yield. (If two Si−H groups on each silicon were reacted, the formed silyl center would become achiral.) Model reaction of ethylphenyldihydrosilane with cyclohexanol in 1:1 molar ratio, under the same reaction conditions with polymerization, quantitatively gave ethylphenyl(cyclohexyloxy)hydrosilane as the only product, elucidated by gas chromatographic, mass spectrometric, ^{1}H, and ^{29}Si NMR analyses [single peak on GC: 205 (100) ($M^+-C_2H_5$); 156 (117) ($M^+-H-C_6H_5$); 151 (10) ($M^+-C_6H_{11}O$): ^{1}H 4.94, t, $J = 2.50$ Hz, 3.67, m, OC*H*CH$_2$; ^{29}Si −3.19 ppm]. The reaction of **BSE** with cyclohexanol in 1:2 molar ratio under the same condition gave 1,4-bis[phenyl(cyclohexyloxy)hydrosilyl]benzene [single peak on GC: 436 (M^+-2H); 282 ($M^+-2H-2C_6H_5$); 239 (10) ($M^+-H-2C_6H_{11}O$), 204 (90) ($M^+-H-C_{14}H_{21}SiO$); 183 (110) ($M^+-2H-2C_6H_5-C_6H_{11}O$): ^{1}H 4.93, t, $J = 2.50$ Hz, 3.64, m, OC*H*CH$_2$ ^{29}Si −3.86 ppm] in almost quantitative yield with complete consumption of SiH_2 (4.32 ppm) in **BSE** and without formation of 1,1-di(cyclohexyloxy)-substituted product. These facts indicated that the reaction of cyclohexanol with dihydrosilane derivatives occurred selectively with only one Si−H on each silicon atom under the similar conditions with polymerization reaction. All of the polymers except **P2c** were soluble in organic solvents such as benzene, THF, and chloroform and showed almost monomodal SEC profiles in the high molecular weight fraction, indicating that they are primarily linear. The insolubility of **P2c** might be due to the cross-linking structures formed by the dehydrogenative reaction of some side-chain Si−H groups.

The analysis of polymers was conducted under a dry atmosphere since the side chain Si−H groups would react with water in the presence of catalysts (samples

Scheme 2



Average enantiomeric excess (e.e.) of silicon atoms in polymer **P1** – **P3**

$$\approx \text{Average e.e. of } \mathbf{BMSX} = \frac{|[S]-[R]|}{[S]+[R]}\times 100\,\% = \frac{|[S,S]-[R,R]|}{[S,S]+[S,R]+[R,S]+[R,R]}\times 100\,\% = \frac{|[+,+]-[-,-]|}{[+,+]+[+,-]+[-,+]+[-,-]}\times 100\,\% \qquad (1)$$

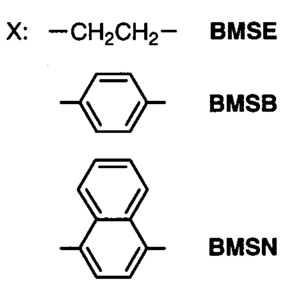


Table 2. Optical Purity of Bis(silane)s BMSX Obtained from Polymers P1−P3

			diastereomers of **BMSX**[a]			
starting polymer	bis(silane) **BMSX**	$[\alpha]^{25}_{D}$ of **BMSX** in hexane	[−,−]	[+,−] or [−,+]	[+,+]	av e.e. of silicon, %[b]
P1a	**BMSE**		18.8	52.9	28.3	9.5
P1c		2.3 (c 4.11)	7.7	44.8	47.5	39.8
P2a	**BMSB**		25.9	47.7	26.4	0.5
P2b		0.1 (c 3.66)	19.6	48.2	32.2	12.6
P2c			26.5	48.5	25.0	1.5
P3a	**BMSN**		32.9	47.9	19.2	13.7
P3c		−0.6 (c 2.12)	31.5	56.4	12.1	19.4
P3d			29.4	48.2	22.4	7.0

[a] The diastereomer concentrations were calculated from the HPLC (on a Daicel CHIRALCEL OD column) results. [b] The definition was described in Scheme 2.

became insoluble when being exposed in air for several days), and all of the polymers were analyzed as obtained without further purification. The ^{1}H and ^{13}C NMR spectra of these polymers are rather complicated, and their ^{29}Si NMR showed some splitting of signals. (The NMR spectra of **P3c** are shown in Figure 1 as examples.) Since there were no unreacted $-SiH_2$ groups in the resulting polymers, the complexity of the NMR spectra was considered due to the oligomers and/or stereochemical splitting (e.g., the existence of both *trans*- and *cis*-structures of the cyclohexane moiety in **P1c** and **P3c**), rather than some side reactions.

As shown in Scheme 1, if the polymerization occurred selectively to form one of the configurations of the asymmetric silicon atom, the resulting polymer would contain bis(silyl ether) moieties with enriched (*R*,*R*) or (*S*,*S*) placement, which would render the polymer optical active and stereoregular. The crude polymer products did show optical activity. However, it is difficult to determine the contribution of the asymmetric silicon atoms in the polymers for the optical activity due to the existence of optically active diol moieties (in **P1a**, **P1b**, **P2a**, **P2b**, and **P3a**) or the unremoved optically active catalysts (in **P1c** and **P3c**). The stereoselectivity of polymerization reactions is usually judged by the tacticity of the resulting polymers using the NMR technique, but the NMR spectra of poly(silyl ether)s prepared here showed too complicated signals to obtain stereochemical information.

The evaluation of the stereoregularity of polymers was thus attempted by a chemical method. The reaction of alkoxysilanes with MeMgBr in ether is known to proceed with almost complete retention of the configuration of silicon atoms and was used for the assessment of the optical purity of alkoxysilanes.[10−13] We employed this reaction as the cleavage reaction of poly(silyl ether)s **P1**−**P3**. The Si−O−C bond in polymers **P1**, **P2**, and **P3** was easily cleaved by MeMgBr in ether at room temperature within 2 h and afforded diastereomeric bis(silane)s **BMSE**, **BMSB**, and **BMSN** (Scheme 2) (even polymer **2c**, a gel-like material, could also be cleaved without difficulty under the same conditions). The (+,+)-, (+,−)-, and (−,−)-isomers of bis(silane)s **BMSB** and **BMSN** were separated easily using an HPLC on an optically active cellulose stationary phase with hexane as an eluent. Although the same column showed poorer resolution for **BMSE**, the separation of diastereomers of **BMSE** was achieved successfully by using a recycling HPLC (after 20 cycles).

To judge the optical purity of bis(silane)s, **BMSE**, **BMSB**, and **BMSN**, and their corresponding polymers **P1**, **P2**, and **P3**, an average enantiomeric excess (e.e.) of silicon atoms was defined as eq 1 (Scheme 2). The cleavage of polymers by MeMgBr could be considered

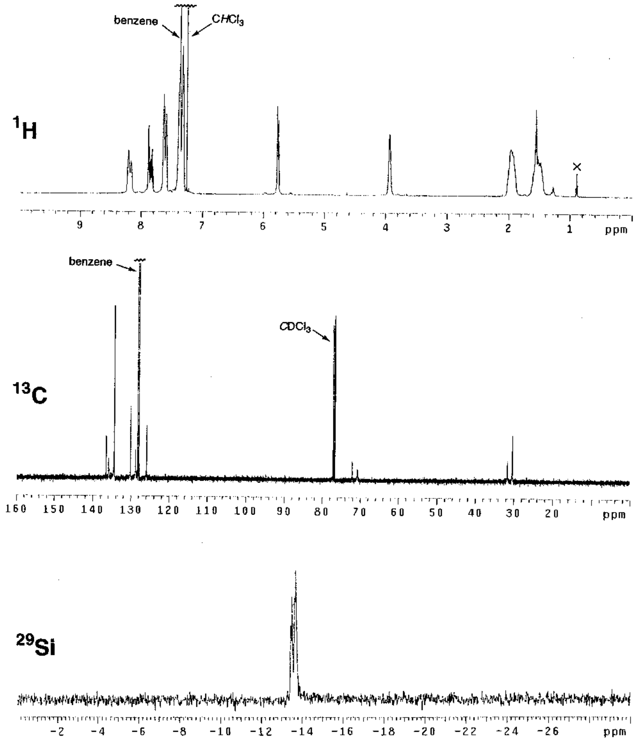


Figure 1. NMR spectra of polymer **P3c**.

complete retention of the configuration of silicon atoms; therefore, the average e.e. values of bis(silane)s should be approximately equal to the optical purity of their corresponding polymers and could be used to evaluate the stereoselectivity of the polymerization reactions. Although the absolute configurations of these stereoisomers have not been determined, their average e.e. values could be calculated from the concentrations of diastereomers obtained by HPLC analysis, since the (*S*,*S*), (*S*,*R*) (or (*R*,*S*)), and (*R*,*R*) isomers should correlate to the (+,+), (+,−) (or (−,+)), and (−,−) isomers. According to the average e.e. values of the reduced products **BMSE** and **BMSN**, the average e.e. values of **P1a** and **P3a** were about 9.5% and 13.7%, respectively, indicating that optically active (*R*)-PNDOL showed some extent of stereoselective effect on the polymerization reactions with bis(silane)s **BSE** and **BSN** (Table 2). On the other hand, the polymerization of **BSB** with (*R*)-PNDOL exhibited almost no stereoselection, affording polymer **P2a** with 0.5% e.e. of optical purity at silicon atoms, while the use of a C_2-symmetric diol (*R*)-BINOL could slightly improve the optical purity of the resulting polymer (**P2b**: 12.6% e.e.).

The polymerization of **BSB** with an achiral diol, CHDOL, in the presence of an optically active catalyst [RhCl((*R*)-BINAP)], exhibited almost negligible stereoregulation (**P2c**: 1.5% e.e.). On the other hand, polymer **P3c** obtained from **BSN** apparently had a higher e.e. value (19.4%). Interestingly, when the reaction was conducted in THF, the optical purity of the resulting polymer **P3d** decreased to 7.0% e.e., indicating that the polarity of solvents exerted some influence on the stereoselectivity. Among the polymerization reactions investigated here, the highest stereoselectivity was observed in the polymerization of **BSE** with CHDOL in the presence of [RhCl((*R*)-BINAP)] in benzene, which afforded a polymer **P1c** with an optical purity of 39.8% e.e. of silicon atoms. Although the results obtained here are still not satisfactory, higher stereoselectivity can be expected upon choosing appropriate monomers, catalysts, and reaction conditions.

Poly(silyl ether)s prepared here possess reactive SiH groups on the side chain. The reaction of the side chain Si−H groups of these polymers with some bifunctional compounds such as water or divinyl compounds will form cross-linked structures containing asymmetric silicon centers. The resulting optically active networks will have potential applications as enantiorecognitive separating membranes or chiral column packing materials.

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Supporting Information Available: Experimental details of the synthesis of bis(silane)s and polymers and the cleavage of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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