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Synthesis of Stereoregular and Optically Active Polysiloxanes Containing 1,3-Dimethyl-1,3-diphenyldisiloxane as a Constitutional Unit

Motoi Oishi and Yusuke Kawakami*

Graduate School of Materials Science, Japan Advanced Institute of Science and Technology [JAIST], 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

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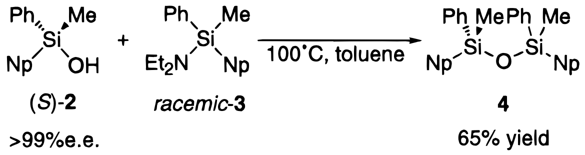
ABSTRACT: Polycondensation reactions of optically active (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol [(*S*,*S*):(*S*,*R*):(*R*,*R*) = 86:14:0] with bis(dimethylamino)dimethylsilane and bis(dimethylamino)diphenylsilane were carried out to give stereoregular and optically active polysiloxanes. The stereoregularity of the polysiloxanes was characterized by ^{1}H and ^{13}C NMR spectroscopy. The polysiloxane (M_n = 51 200, M_w/M_n = 1.85, $[\alpha]^{24}_D$ = +2.3) prepared from (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol and bis(dimethylamino)dimethylsilane was proven to be optically active and rich in diisotacticity. The T_g's of these polymers are influenced by the stereoregularity of the polymers.

Control of stereoregularity and optical activity of polymers has been a challenging theme in the field of polymer synthesis. Configurationally optically active polymers are interesting as well as conformationally optically active polymers.[1] We reported the synthesis of isotactic poly[(methylphenylsilylene)trimethylene] having asymmetric silicon centers by the polyaddition of optically active (*S*)-allylmethylphenylsilane.[2] However, the optically activity itself is lost in the polymer since the asymmetric centers of the resulting polymer are pseudo-asymmetric. One of the practical methods to obtain configurationally optically active polymers is to prepare polymers containing optically active stereorepeating unit of the type A−X*−B (X*, optically active center; A ≠ B). On the basis of this concept, we obtained optically active and isotactic poly[oxy-(*S*)-(1-naphthylphenylsilylene)ethylene(dimethylsilylene)] by polyaddition reaction of (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane, which is the first example of stereoregular and optically active silicon-containing polymer.[3] This polymer was also obtained by ring-opening polymerization.[4] In these cases, X*, A, and B are Si*, O, and CH_2, respectively.

Polysiloxane is a class of important hydrophobic silicon-containing polymer. Poly(dimethylsiloxane)s have been widely used as silicone oil, silicone rubber, main chain for liquid crystalline polymers,[5] and polymer support for metallocene catalyst,[6] as well as other useful materials[7] by taking advantage of their highly flexible structure and high thermal stability. If stereoregularity and optical activity are induced in polysiloxanes, the resulting polymers are expected to exhibit novel unique properties different from those of ordinary polysiloxanes without controlled stereochemistry.

Meanwhile, we recently reported the synthesis of optically active (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol, (*S*,*S*)-**1**.[8] This (*S*,*S*)-**1** is considered suitable as the constitutional units of stereoregular and optically active polysiloxanes. In this report, we describe the synthesis of new stereoregular and optically active polysiloxanes via polycondensation of (*S*,*S*)-**1** with bis(dimethylamino)dialkylsilanes, where X* is (*S*,*S*)- or (*R*,*R*)-MePhSi*OSi*MePh (1,3-dimethyl-1,3-diphenyldisiloxane unit) with A = O and B = $SiMe_2$ or $SiPh_2$.

Scheme 1



Polycondensation reactions of bis(hydroxysilane) with bis(aminosilane) usually afford the polysiloxanes with relatively high molecular weight[9] than those obtained by the reaction with bis(chlorosilane). If the reaction of an aminosilane with a silanol proceeds stereospefically, stereoregular and optically active polysiloxane would be obtained by polycondensation of (*S*,*S*)-**1** with bis(aminosilane)s.

We first studied the stereochemistry of the reaction of optically active (*S*)-(+)-methyl(1-naphthyl)phenylsilanol (**2**) (>99% ee)[10] with *racemic*-methyl(1-naphthyl)phenyl-*(N*,*N*-diethylamino)silane (**3**).[11] The reaction of (*S*)-**2** with *racemic*-**3** was carried out in toluene at 100 °C for 24 h to give 1,3-dimethyl-1,3-di(1-naphthyl)-1,3-diphenyldisiloxane (**4**) in 65% yield (Scheme 1). As shown in the HPLC of the product, the stereoisomer ratio [(*S*,*S*):(*S*,*R*):(*R*,*R*)] of **4** can be easily determined on optically active stationary phase (Daicel Chem. Ind., CHIRALCEL OD, *n*-hexane as an eluent, 0.4 mL/min, 254 nm) to be 46:54:0 (Figure 1). It was proven that this reaction did not give any (*R*,*R*)-**4**; therefore, it was confirmed that the configuration of asymmetric silicon atom of the silanol (*S*)-**2** is not changed in the condensation with aminosilane (i.e., 100% retention of configuration).

The polycondensation of (*S*,*S*)-**1** with bis(dimethylamino)dimethylsilane (**5a**) or bis(dimethylamino)diphenylsilane (**5b**) was carried out under similar reaction conditions with the model reaction (Scheme 2).[12,13] Diastereomer mixtures of **1** and *meso*-**1** were also used as the bis(hydroxysilane) components. The results are summarized in Table 1. The polycondensation reactions

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Scheme 2

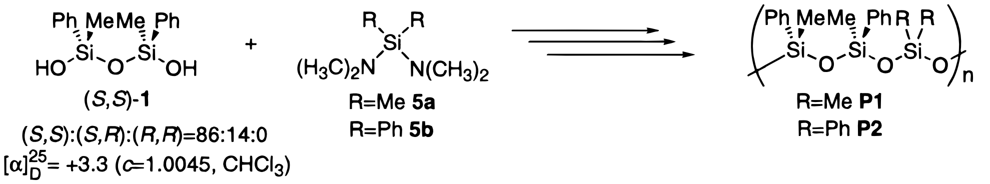


Table 1. Synthesis of Polysiloxanes via Polycondensation of 1 with 5

entry	1	5	polymer	yield (%)[d]	M_n[e]	M_w/M_n[e]	$[\alpha]^{24}_D$	T_g (°C)[h]
1	(*S,S*)[a]	**5a**	(*S,S*)-diisotactic **P1**	48	51 200	1.85	+2.3[f]	−56
2	*meso*[b]	**5a**	*meso*-atactic **P1**	49	50 300	2.10		−53
3	*diastereomers*[c]	**5a**	atactic **P1**	65	74 300	1.51		−54
4	(*S,S*)[a]	**5b**	(*R,R*)-diisotactic **P2**	53	18 400	2.86	−2.0[g]	−2
5	*meso*[b]	**5b**	*meso*-atactic **P2**	38	43 800	2.18		−10
6	*diastereomers*[c]	**5b**	atactic **P2**	51	49 100	1.70		−11

[a] (*S,S*):(*S,R*):(*R,R*) = 86:14:0. [b] Pure isomer. [c] (*S,S*):(*S,R*):(*R,R*) = 25:50:25. [d] Isolated yields after reprecipitation into MeOH. [e] Estimated by GPC (THF as an eluent) with polystyrene standard. [f] $c = 0.870$, $CHCl_3$. [g] $c = 0.820$, $CHCl_3$. [h] Determined by DSC with heating rate of a 5.0 °C min^{-1} on second scan.

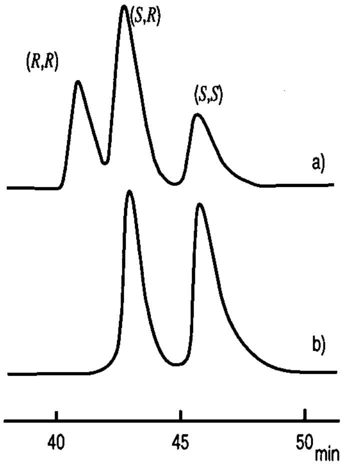


Figure 1. HPLC chromatograms of (a) (*R,R*), (*S,R*), and (*S,S*) mixture **4** and (b) **4** from Scheme 1 (Daicel Chem. Ind., CHIRALCEL OD, *n*-hexane as an eluent, 0.4 mL/min, 254 nm).

gave the polysiloxanes with reasonably high molecular weight (M_n) in all cases.

The resulting polymers were characterized by ^1H, ^{13}C, and ^{29}Si NMR. ^{29}Si NMR was not sensitive enough to analyze the stereoregularity of polymers. The ^1H signals of methyl groups of SiPh*Me* of **P1** from **1** and **5a** were relatively broad (Figure 2), reflecting not only the stereochemical relation of the two asymmetric silicon atoms in the disilioxane repeating unit from **1** (Scheme 3a) but also the regularity of the connection of the disiloxane units, which will be discussed later. The **P1** from (*S,S*)-**1** afforded a strong singlet at 0.22 ppm, although the peak is also broadened by the influence of optical purity of disiloxane unit [(*S,S*)-**1**: (*S,S*):(*S,R*) = 86:14]. This singlet is considered to arise from SiPh*Me* of racemic (*S,S*) disiloxane units. Only one singlet at 0.19 ppm was observed in **P1** from *meso*-**1** due to the two equivalent methyl groups in the *meso* repeating disiloxane unit. On the other hand, two sharp peaks at 0.19 and 0.22 ppm in almost equal intensity are observed in **P1** from *diastereomers*-**1**, reflecting the methyl groups from the *meso*- and *racemic*-disiloxane units in equal quantity.

The information about the regularity in the connection of the two successive disiloxane units (stereoregularity) might be obtained by the analysis of ^1H signals of Si*Me*$_2$ sandwiched between (*S* or *R*)-PhMeSi*O and (*S* or *R*)-OSi*MePh [(*S* or *R*)-Si and (*S* or *R*)-Si] in successive units. The **P1**'s from (*S,S*)-**1**, and *meso*-**1** showed basically a singlet at −0.058 ppm [Figure 2a, Scheme 3b (**1**)] and three singlets at −0.015, −0.069, and −0.130 ppm [Figure 2b, Scheme 3b (**2** or **3**)] with higher-order splitting, respectively. The chemical shift of the methyl groups sandwiched by two adjacent silicon atoms of the same configuration of the **P1** from *meso*-**1** (−0.069 ppm) slightly differs from that from (*S,S*)-**1** (−0.058 ppm). The chemical shifts seem to reflect the influence of further neighboring asymmetric silicon centers. As a first approximation, the two methyl groups should appear as a singlet when sandwiched between two silicon atoms of the same absolute configuration and two singlets when sandwiched by two silicon atoms of opposite configuration. The three signals from *meso*-**1**

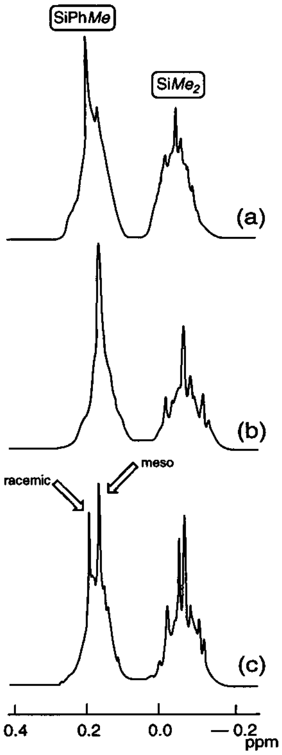
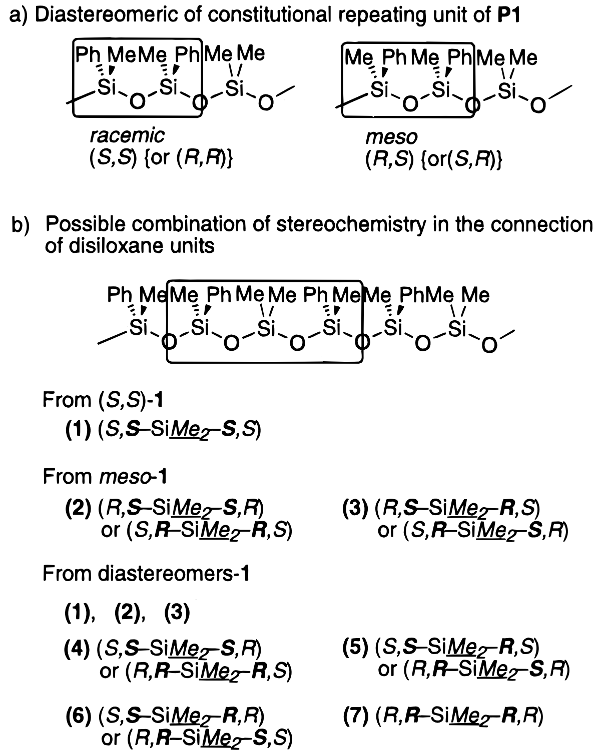


Figure 2. ^1H NMR (500 MHz) spectra of the SiPh*Me* and Si*Me*$_2$ of **P1**: (a) (*S,S*)-diisotactic; (b) *meso*-atactic; (c) atactic.

Scheme 3



are assignable to Si*Me*$_2$ sandwiched between (*S*)-Si and (*S*)-Si or (*R*)-Si and (*R*)-Si, and (*S*)-Si and (*R*)-Si or (*R*)-Si and (*S*)-Si centers with different asymmetric silicon centers next to them. There is only one possible combination of the configuration of (*S*)-Si−Si*Me*$_2$−(*S*)-Si for **P1** from (*S*,*S*)-**1**; thus, the methyl groups of the **P1** from (*S*,*S*)-**1** gave basically a singlet. This polymer is considered to be rich in (*S*,*S*)-diisotacticity together with the analysis of the stereochemistry of the disiloxane unit. In the case of **P1** from *meso*-**1**, there are two possible combinations of the configuration for adjacent two silicon atoms. Thus, the methyl groups of the **P1** showed three singlets. This fact indicates that (*R*,*S*) and (*S*,*R*) structures were connected randomly in the polymer chain; hence, this polymer is considered to be *meso*-atactic **P1**. The methyl signals of **P1** from *diastereomers*-**1** (Figure 2c) are basically overlapped signals of Figure 2a and Figure 2b, and this polymer is considered to be atactic **P1**. However, the ^{1}H NMR signals are too complicatedly split, reflecting the higher-order regularity of the connection of disiloxane units in the polymer chain. It seems necessary to prepare purely diisotactic **P1** starting from enantiomerically pure (*S*, *S*)-**1** to quantitatively evaluate the regularity.

Further evidence for the tacticity of **P1** is given by the peak of *meta*-Si*Ph*Me carbon splitting in ^{13}C NMR (Figure 3). The peaks at 127.75 and 127.72 ppm could be assigned to *meso*- and *racemic*-disiloxane repeating unit, respectively. From ^{1}H and ^{13}C NMR spectra, **P1** formed from (*S*,*S*)-**1** with **5a** is concluded as a polymer rich in diisotacticity. Unfortunately, in the case of **P2** from **1** and **5b**, no appreciable difference was observed in ^{1}H, ^{13}C, and ^{29}Si NMR. However, we believe that **P2** formed from (*S*,*S*)-**1** is also diisotactic similar to the diisotactic **P1** because the model reaction proceeded with 100% retention of configuration of the silicon atom of the (*S*)-**2**. The diisotactic **P1** showed the positive optical rotation ($[\alpha]^{24}_{D} = +2.3$, entry 1), whereas that of diisotactic **P2** showed negative optical rotation ($[\alpha]^{24}_{D} = -2.0$, entry 4). The results of the model reaction suggested that absolute configuration of diisotactic **P1** and diisotactic **P2** are (*S*,*S*) and (*R*,*R*), respectively.

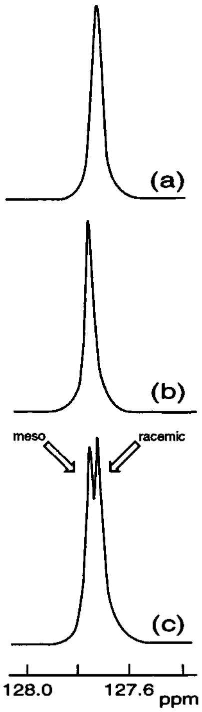


Figure 3. ^{13}C NMR (75 MHz) spectra of the *meta*-Si*Ph*Me carbon of **P1**: (a) (*S*,*S*)-diisotactic; (b) *meso*-atactic; (c) atactic.

The effect of the stereochemistry on physical properties of **P1** and **P2** can be demonstrated by DSC (differential scanning calorimeter) analysis. All the polysiloxanes exhibited only one glass transition temperature without any other transitions. The T_g's found for (*S*,*S*)-diisotactic **P1**, atactic **P1**, and *meso*-atactic **P1** were −56, −54, and −53 °C, respectively, namely, almost no difference in T_g for **P1**'s with different stereoregularity. On the other hand, different T_g's of −2, −11, and −10 °C, for (*R*,*R*)-diisotactic **P2**, atactic **P2**, and *meso*-atactic **P2** were observed, respectively. Although the T_g generally depends on the molecular weight of polymer, the (*R*,*R*)-diisotactic **P2** (M_n = 18 400) with lower molecular weight exhibited a slightly higher T_g than that of atactic **P2** (M_n = 49 100) and *meso*-atactic **P2** (M_n = 43 800). Thus, it is considered that the T_g's of these polymers are influenced by the difference in the stereoregularity of the polymers.

In conclusion, we have demonstrated the first example of optically active and diisotactic polysiloxanes via polycondensation of (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol (**1**) with bis(dimethylamino)dimethylsilane (**5a**) or bis(dimethylamino)diphenylsilane (**5b**). The polysiloxane **P1** prepared from (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol (**1**) and bis(dimethylamino)dimethylsilane (**5a**) was proven to be diisotactic and optically active. The T_g's of these polymers are influenced by the stereoregularity of the polymers. Further studies on the synthesis of syndiotactic poly(methylphenylsiloxane) by the polycondensation of (*S*,*S*)-**1** with optically active 1,3-di(*N*,*N*-diethylamino)-1,3-dimethyl-1,3-diphenyldisiloxane and application to functionality materials such as catalyst, liquid crystalline polymer, and materials for chromatography would be also interesting.

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(12) Experimental procedure and NMR and IR data for (*S,S*)-diisotactic **P1**: A solution of **5a** (0.1057 g, 0.74 mmol) in toluene (0.74 mL) was added to (*S,S*)-**1** (0.2158 g, 0.74 mmol). The reaction mixture was stirred at 100 °C for 24 h with N_2 bubbling. After pouring into methanol, the precipitate was collected and dried in vacuo to give the polymer (0.1232 g, 48% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ −0.18 to 0.04 (br, 6H), 0.19 (minor) and 0.22 (major) (2s, 6H), 7.11−7.23 (br, 4H), 7.23−7.34 (br, 2H), 7.36−7.56 (br, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.27, 0.99, 127.7, 130.0, 133.5, 137.5. ^{29}Si NMR (79 MHz, $CDCl_3$): δ −34.3, −20.3. IR (neat, cm^{-1}): 3093, 3072, 3026, 2963, 2765, 1593, 1429, 1125, 1097, 1021.

(13) NMR and IR data for (*R,R*)-diisotactic **P2**: ^{1}H NMR (500 MHz, $CDCl_3$): δ -0.23−0.14 (br, 6H), 6.74−7.11 (br, 8H), 7.11−7.46 (br, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.51, 127.6, 127.7, 129.6, 129.9, 133.5 (overlap), 134.5, 134.6. ^{29}Si NMR (79 MHz, $CDCl_3$): δ −46.8, −33.5. IR (neat, cm^{-1}): 3071, 3051, 3026, 3004, 2962, 2904, 1592, 1429, 1126, 1024.

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