

NOTES

Stereo-Recognition of Propagating Chain End in the Cross-Dehydrocoupling Polymerization of *meso*-1,3-Dimethyl-1,3-diphenyldisiloxanediol with MethylphenylsilaneMotoi OISHI, Jeong-Yeol MOON,[†] Eiji SHIRAKAWA, and Yusuke KAWAKAMI^{††}Graduate School of Materials Science,
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There are two main strategies for the synthesis of stereoregular polymers. One is the stereospecific or -selective polymerization reactions of prochiral or *racemic* monomers. The other is the polymerization of optically active monomers which proceeds with complete retention or inversion of configuration of chiral centers. By using the latter strategy, we recently reported the synthesis of stereoregular and/or optically active poly(carbosilane),¹ poly(carbosiloxane),² and poly(siloxane),³ which are the first examples of stereoregular and/or optically active silicon-containing polymers.

Stereospecific or -selective polymerization reactions of prochiral or *racemic* organosilicon monomers have been insufficiently studied probably due to the lack of efficient asymmetric reactions for prochiral or *racemic* silicon compounds. Although several attempts on the synthesis of stereoregular poly(silane),⁴ poly(carbosiloxane),⁵ poly(silyl ether),⁶ and poly(siloxane)⁷ by ring-opening polymerization of cyclic organosilicon compounds^{4c,5,7} and transition metal catalyzed dehydrogenative polycondensation of prochiral hydrosilane compounds^{4a,b,6} have been reported, many of them failed to obtain highly stereoregular polymer. To synthesize highly stereoregular silicon-containing polymer, it is important to clarify the nature of the stereo-recognition of propagating chain end in the course of polymerization.

We have recently shown that cross-dehydrocoupling reaction of Si*H and Si*OH in the presence of rhodium catalyst proceeds with retention of configuration at both silicon chiral centers.^{3a} Since, 1,3-dimethyl-1,3-diphenyldisiloxanediol **1**⁸ consisting of stereoisomers of various compositions can be easily prepared, our interest is focused on the stereo-recognition of propagating chain end in the cross-dehydrocoupling polymerization of **1** with prochiral methylphenylsilane **2**.

EXPERIMENTAL

A typical polymerization procedure is as follows. A solution of *meso*-**1** (100% pure) (0.291 g, 1.0 mmol), **2** (0.122 g, 1.0 mol) and triethylamine (0.051 g, 0.5 mmol) was added to RhCl(PPh₃)₃ (0.009 g, 1.0 mol%), and re-

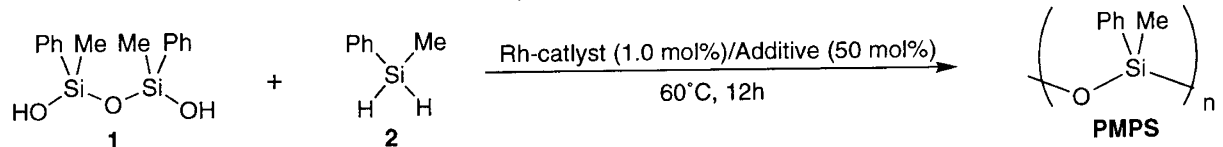
acted at 60°C for 12 h under nitrogen atmosphere. The reaction mixture was filtered on silica gel to remove the catalyst. Removal of the volatile materials afforded a crude polymer. After reprecipitation from Et₂O into methanol, the polymer was collected and dried *in vacuo* (0.191 g, 47% yield). The polymer was identified as poly(methylphenylsiloxane) (PMPS) by ¹H, ¹³C, and ²⁹Si nuclear magnetic resonance (NMR). GPC $M_n = 14000$, $M_w/M_n = 1.9$; ¹H NMR (500 MHz, CDCl₃) δ 0.04, 0.09, and 0.14 (three singlets, 3 H, CH₃, corresponding to *I*, *H*, and *S*, respectively)^{3a}, 7.01–7.18 (br, 2H, phenyl protons), 7.18–7.56 (br, 3H, phenyl protons); ¹³C NMR (125 MHz, CDCl₃) δ -0.47 (*I*), -0.38 (*H*), and -0.29 (*S*)^{3a} (methyl carbons), 127.43 (*S*), 127.49 (*H*), and 127.53 (*I*) (*meta*-phenyl carbons), 127.9 (*para*-phenyl carbon), 133.3 (*ortho*-phenyl carbon), 136.7 (*S*), 136.9 (*H*), 137.1 (*I*) (*ipso*-phenyl carbons); ²⁹Si NMR (99 MHz, CDCl₃) δ -33.8 (singlet); IR (neat, cm⁻¹) 3071, 3050, 3025, 3004, 2962, 2903, 1592, 1429, 1261, 1125, and 1020.

RESULTS AND DISCUSSION

Cross-dehydrocoupling polymerization reactions of **1** consisting of different stereoisomers (*meso/dl*-**1**; (*S,S*) : (*S,R*) : (*R,R*) = 25 : 50 : 25, *dl* rich **1**; (*S,S*) : (*S,R*) : (*R,R*) = 35 : 30 : 35, and *meso*; 100% pure) with **2** were carried out in bulk at 60°C for 12 h. The results are summarized in Table I. Triad tacticity of the resulting PMPS's was evaluated by the integral ratio of *ipso*-carbon peaks in ¹³C NMR.^{3a} Calculated triad tacticity was obtained assuming no stereoselection by propagating chain end in the polymerization.

The polymerization of *meso*-**1** gave PMPS's rich in syndiotactic triad (*rr* = 18–20%) compared with calculated value (*rr* = 8%) (entries 5 and 6) when catalyzed by RhCl(PPh₃)₃. Contrary to the fact that triad tacticity was almost identical to the calculated value in the polymerization of *meso/dl*-**1** and *dl* rich **1** (entries 1–4). This is an interesting fact indicating that the polymerization of **1** with **2** proceeded with stereo-recognition by propagating chain end for *meso*-**1**, and without stereo-recognition when *meso* content in the monomer is less than 50%.

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Table I. Cross-dehydrocoupling Polymerization of **1** with **2**


Entry	1	Catalyst	Additive	Yield/% ^b	M_n^c	M_w/M_n^c	triad tacticity		pentad tacticity ^g	
							obsd. ^e	calcd. ^f	$mmmm : mrrm : mrrm$	$mm : mr : rr^d$
1	<i>meso/dl</i> ^h	RhCl(PPh ₃) ₃	Et ₃ N	46	6700	1.1	25 : 49 : 26	25 : 50 : 25		
2			(-)-Sp	55	11000	2.4	26 : 45 : 29			
3	<i>dl</i> rich ⁱ	RhCl(PPh ₃) ₃	Et ₃ N	49	7200	2.7	23 : 47 : 30	18 : 50 : 32		
4			(-)-Sp	60	12000	1.9	23 : 46 : 31			
5	<i>meso</i> ^j	RhCl(PPh ₃) ₃	Et ₃ N	47	14000	1.9	32 : 48 : 20	42 : 50 : 8	28 : 12 : 60	
6			(-)-Sp	35	5400	1.2	26 : 49 : 25		26 : -1(-0) : 75	
7		RhCl[(S)-BINAP]	Et ₃ N	46	8600	2.5	34 : 46 : 20			
8			(-)-Sp	41	5200	1.7	29 : 44 : 27			
9		RhCl[(R,R)-DIOP]	Et ₃ N	38	12000	3.2	39 : 43 : 18			
10			(-)-Sp	trace	7000	1.2	30 : 44 : 26			

^a The polymerization reactions were carried out at 60°C for 12 h. ^b Isolated yields after reprecipitation into MeOH. ^c Estimated by GPC with polystyrene standard (THF as an eluent). ^d Determined by ¹³C NMR at ipso carbon. ^e The error is about $\pm 1\%$. ^f Calculated triad tacticity was obtained assuming no stereoselection by propagating chain end. ^g Calculated from triad tacticity. ^h (S,S) : (S,R) : (R,R) = 25 : 50 : 25. ⁱ (S,S) : (S,R) : (R,R) = 35 : 30 : 35. ^j 100% pure.

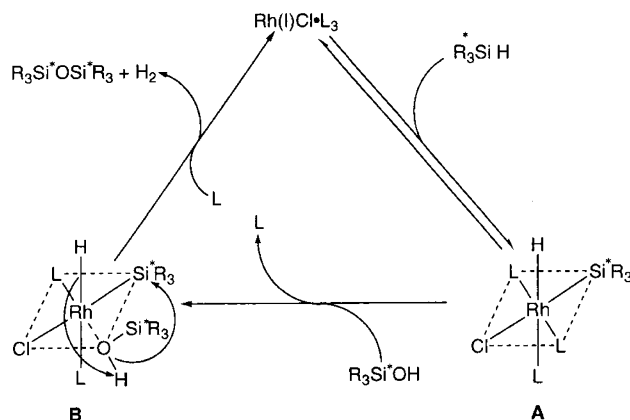


Figure 1. Tentative reaction mechanism of Rh-catalyzed cross-dehydrocoupling reaction of R_3Si^*H with R_3Si^*OH .

Stress will be put on this point in the discussion.

Polymerization reactions with optically active Rh-catalysts such as RhCl[(S)-BINAP] and RhCl[(R,R)-DIOP] gave PMPS's with triad tacticity [$rr = 20\%$ (entry 7), and $rr = 18\%$ (entry 9)] similar to that of PMPS catalyzed by RhCl(PPh₃)₃ (entry 5), suggesting no effect of the optically active Rh-catalyst on stereo-recognition of propagating chain end. Use of (-)-spartein ((-)-Sp) instead of triethylamine (Et₃N) as the additive showed somewhat higher syndiotactic triad ($rr = 26\text{--}27\%$, entries 6, 8, and 10).

Tentative reaction mechanism for Rh-catalyzed cross-dehydrocoupling reaction of R_3Si^*H with R_3Si^*OH in the presence of an amine is proposed in Figure 1 considering the generally accepted Wilkinson catalyst reaction mechanism. The mechanism involves the oxidative addition of Si^*H to Rh (I) to form Rh (III) intermediate **A**, followed by the coordination of Si^*OH to give intermediate **B**. Attack of Rh-H bond on silanol hydrogen gives hydrogen molecules, and following reductive elimination gives $R_3Si^*OSi^*R_3$. It was reported that configuration of silicon atom of Si^*OH is completely retained, and there

is some racemization of Si^*H chiral center depending on the reaction conditions, although the stereochemistry of Si^*H in oxidative addition is basically retention of configuration.^{3a} Tilley proposed a two step σ -bond metathesis reaction mechanism for the condensation of two PhSiH₃ molecules catalyzed by zirconocene or hafnocene with evolution of hydrogen gas.⁹

Figure 2 illustrates the possible stereo-sequence formation in the polymerization to give PMPS. The configuration of Si^*H terminal is determined in the reaction with Si^*OH terminal to give mm or mr triad Si^*H terminal. Since prochiral silicon atom of **2** is attacked twice by two chiral Si^*OH terminals when being incorporated into the polymer chain, stereochemistry of silicon atom derived from **2** is affected twice by the reaction with two Si^*OH of propagating chain end from **1** to give five consecutive silicon chiral centers. Accordingly, stereoregularity of PMPS obtained from *meso*-**1** and **2** should be discussed based on the pentad tacticity.

Population in percentage of possible pentad sequences $mmmm$, $mrrm$, and $mrrm$ were estimated from the data of triad tacticity for entries 5 and 6 in Table I. When x , y , and z are defined as the population of $mmmm$, $mrrm$, and $mrrm$, respectively, the population of isotactic triad (mm), heterotactic triad (mr), and syndiotactic triad (rr) can be calculated by $[mm] = x + y/3$, $[mr] = 2y/3 + 2z/3$, and $[rr] = z/3$. Only $mrrm$ pentad among the possible three pentad sequences can afford the syndiotactic triad rr . For the polymer obtained in the presence of Et₃N (Table I, entry 5, $mm : mr : rr = 32 : 48 : 20$), the population of $mrrm$ pentad, namely, z , is calculated as 60% by using the equation of $[rr] = 20\% = z/3$. The population of $mrrm$, y , is calculated as 12% from $z = 60\%$ and $[mr] = 48\% = 2y/3 + 2z/3$. As a result, the population of $mmmm$ pentad, x , is calculated as 28%.

Similarly, the population of pentad tacticity for entry 6 in Table I ($mm : mr : rr = 26 : 49 : 25$) was calculated as $mmmm = 26$, $mrrm = -1(\sim 0)$, and $mrrm = 75\%$ in the presence of (-)-Sp.

Since the concentration of $mrrm$ pentad is higher than

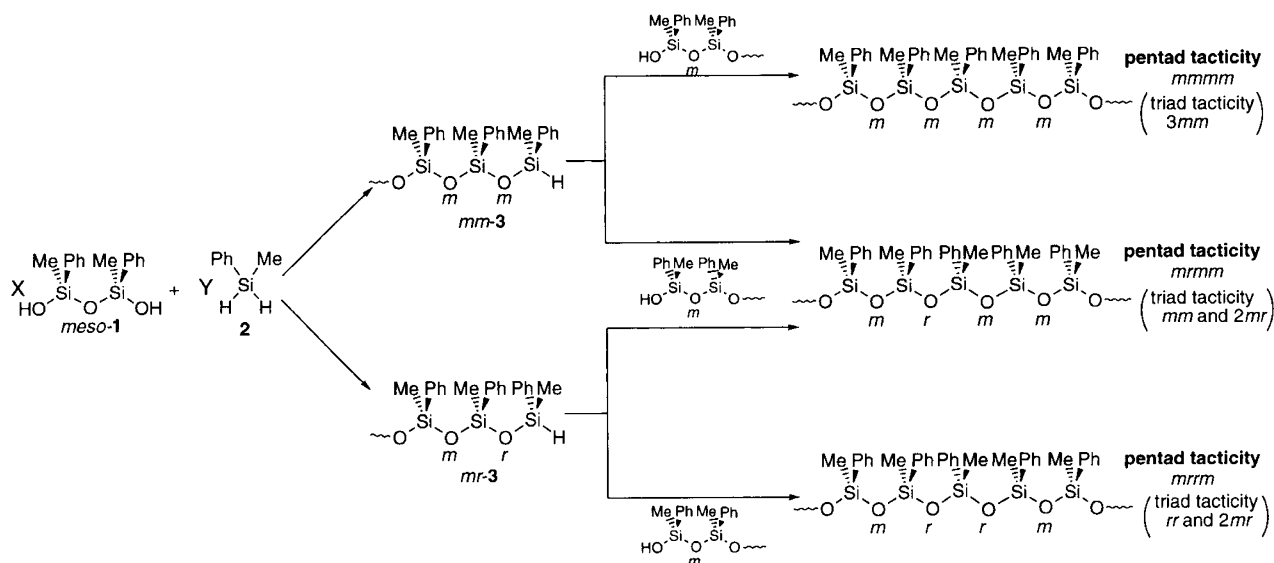


Figure 2. Possible stereo-sequences of PMPS in the polymerization of *meso*-1 with **2**.

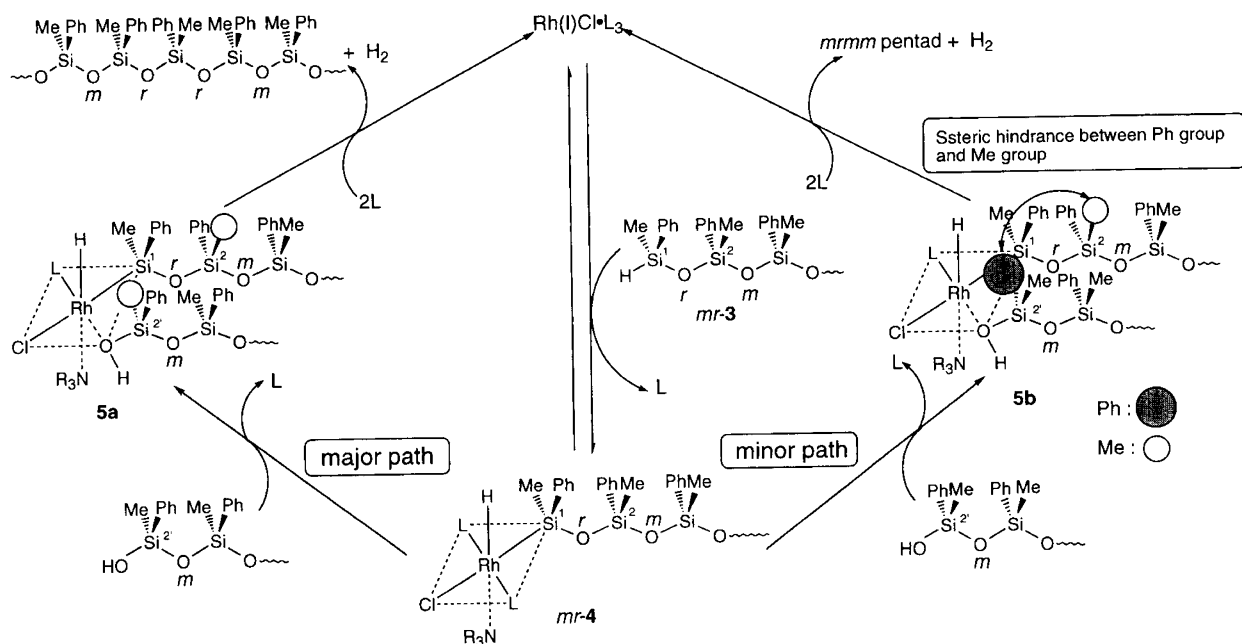


Figure 3. Plausible mechanism of stereo-recognition of propagating chain end in polymerization of *meso*-1 with **2**.

the calculated one, *mr* triad Si*H (*mr*-3) terminal seems to be preferentially formed as the propagating chain end in the initial coupling of **2** with Si*OH terminal as shown in Figure 2. Coupling between this *mr*-3 terminal and Si*OH terminal with same configuration gives *mrrm* pentad as the major stereo-sequence. The *mmmm* pentad is formed by the coupling of *mm* triad Si*H (*mm*-3) terminal, as the minor chain end, with Si*OH terminal with opposite configuration. Coupling between *mm* or *mr* triad Si*H and Si*OH with same or opposite configuration gives *mrrm* pentad in low concentration in the presence of Et₃N.

Stereo-recognition of propagating chain end in the polymerization of *meso*-1 with **2** is interpreted based on the reaction mechanism proposed in Figure 1 (Figure 3). The oxidative addition of preferentially formed *mr* triad Si*H

chain end, *mr*-3, affords intermediate *mr*-4, to which Si*OH chain end with same configuration with Si*H terminal of *mr*-3 preferentially coordinates to give intermediate **5a**. Formation of **5a** may be favored by the absence of steric hindrance between substituents on the Si¹ or Si² and Si² atoms in the polymer chain in the coordination step, alternatively, the reductive elimination from **5a** may be favored to produce *mrrm* pentad. Coordination of Si*OH chain end with opposite configuration to *mr*-3 seems less favorable because of the steric interaction resulting in the formation of *mrrm* pentad as the minor sequence.

Reaction of *mm*-4 with Si*OH with opposite configuration to that of Si*H of *mm*-3 seems favored to produce *mmmm* pentad over *mrrm* pentad, which is produced by the reaction of *mm*-3 with Si*OH with same configu-

ration.

In other words, Si*H propagating chain end preferentially reacts with Si²OH chain end with opposite configuration of the penultimate Si² of *mr-3* or *mm-3* to produce *mrrm* or *mmmm* pentad over *mrrm* pentad regardless of whether the SiH chain end is (*S*)- or (*R*)-configuration. Thus, existence of *m* diad derived from *meso-1* seems the most important factor for the stereo-recognition in the polymerization. On the contrary, *r* diad derived from *dl-1* does not exhibit any stereo-recognition resulting in triad tacticity in accordance with the calculated value.

The difference in stereo-selection between the reactions in the presence of Et₃N and (–)-Sp (entries 5 and 6 in Table I) may be due to the existence or non-existence of racemization of Si*H terminal of *mr-3* or *mm-3* in the reversible oxidative addition step to form *mr-4* or *mm-4*.^{3a} The role of bulky (–)-Sp is considered to suppress the racemization of *mr-4* or *mm-4* by the existence at the apical position of rhodium center. The effect of the molecular weight of the polymer on stereo-recognition in the polymerization of *meso-1* with **2** was considered not significant (entries 5–10 in Table I). Thus, polymerization of *meso-1* with **2** was found to proceed with preferentially formation of *mrrm* pentad sequence.

In conclusion, we observed stereo-recognition by terminal disiloxane silanol with *m* diad in Rh-catalyzed cross-dehydrocoupling polymerization of *meso-1,3*-dimethyl-1,3-diphenylsiloxanediol **1** with methylphenylsilane **2** in the presence of triethylamine or (–)-Sp. 75% *mrrm* pentad of PMPS was obtained, when (–)-Sp was used as the additive. Further study on the synthesis of highly stereoregular poly(siloxane) by polymerization of prochiral or *racemic* silicon monomers is now in progress.

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REFERENCES

1. a) Y. Kawakami, K. Nakao, S. Shinke, and I. Imae, *Macromolecules*, **32**, 6874 (1999). b) Y. Kawakami, T. Takahashi, Y. Yada, and I. Imae, *Polym. J.*, **30**, 1001 (1998). c) Y. Kawakami, K. Takeyama, O. Ooi, and K. Komuro, *Macromolecules*, **31**, 551 (1998).
2. a) Y. Li and Y. Kawakami, *Macromolecules*, **32**, 548 (1999). b) Y. Li and Y. Kawakami, *Macromolecules*, **31**, 5592 (1998).
3. a) M. Oishi, J.-Y. Moon, W. Janvikul, and Y. Kawakami, *Polym. Int.*, in press. b) M. Oishi and Y. Kawakami, *Macromolecules*, **33**, 1960 (2000).
4. For poly(phenylsilane) rich in syndiotacticity, see: a) N. Choi, S. Onozawa, T. Sakakura, and M. Tanaka, *Organometallics*, **16**, 2765 (1997). b) J. P. Banovertz, K. M. Stein, and R. M. Waymouth, *Organometallics*, **10**, 3430 (1991). For poly(methylphenylsilane) rich in heterotacticity, see: c) E. Fossum and K. Matyjaszewski, *Macromolecules*, **28**, 1618 (1995).
5. Y. Li and Y. Kawakami, *Macromolecules*, **33**, 1560 (2000).
6. Y. Li, M. Seino, and Y. Kawakami, *Macromolecules*, **33**, 5311 (2000).
7. For poly(methylphenylsiloxane) rich in isotacticity, see: a) B. Momper, Th. Wanger, U. Maschke, M. Ballauff, and E. W. Fisher, *Polym. Commun.*, **31**, 186 (1990). b) S. J. Clarson, J. A. Semlyen, and K. Dodgson, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **31**, 563 (1990). c) M. D. Curtis, S. Thanedar, and M. Ejshiek, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **25**, 224 (1984). d) T. N. Baratova, V. P. Mileshkevich, and V. I. Gurari, *Poly. Sci. USSR*, **25**, 2899 (1983). e) T. N. Baratova, V. P. Mileshkevich, and V. I. Gurari, *Poly. Sci. USSR*, **24**, 27 (1982). f) L. S. Bresler, V. P. Mileshkevich, Yu. A. Yuzheleskii, and N. P. Timofeeva, *Zh. Struct. Khim. SSSR*, **19**, 453 (1978). g) E. A. Bostik, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **10**, 877 (1969). For poly[methyl(3,3,3-trifluoropropyl)siloxane] rich in isotacticity, see: h) K. P. Battjes, C.-M. Kuo, R. L. Miller, and J. C. Saam, *Macromolecules*, **28**, 790 (1995). i) C.-M. Kuo, J. C. Saam and R. B. Taylor, *Polym. Int.*, **33**, 2663 (1994).
8. a) M. Oishi and Y. Kawakami, *Org. Lett.*, **1**, 549 (1999). b) A. W. P. Jarvie, A. Holt, J. Homer, and H. J. Hickton, *J. Chem. Soc. Sect B*, 978 (1969). c) W. H. Daudt and J. F. Hyde, *J. Am. Chem. Soc.*, **74**, 386 (1952).
9. T. D. Tilley, *Acc. Chem. Res.*, **26**, 22 (1993).