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Control of the Stereochemical Structure of Silicon-Containing Polymers

Yusuke Kawakami

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

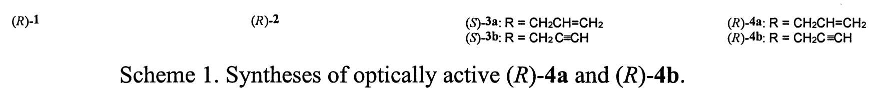
SUMMARY: Various optically pure organosilicon compounds were synthesized or separated on HPLC. Stereoregular silicon-containing polymers, poly(carbosilane)s, poly(carbosiloxane)s and poly(siloxane)s were synthesized from these compounds as monomer. Stereochemistry of the elementary reactions to give stereoregular polymers was elucidated.

Introduction

Increasing interest has been paid in recent years in silicon-containing polymers applicable as electrical and optical materials, ceramic precursors, etc.[1,2] We synthesized poly[(methylphenylsilylene)(trimethylene)] by polyaddition *via* hydrosilylation[3] of optically active (*R*)-allylmethylphenylsilane and quantitatively evaluated the regioselectivity of the reaction and the tacticity of the polymer.[4,5] The optical activity itself, however, is lost in the resulting pseudo asymmetric polymer.

Optically active (*R*)-methylphenylpropargylsilane and (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyl-3-hydro-1,3-disiloxane were synthesized to obtain optically active poly(carbosilane)[6] and poly(carbosiloxane).[7] Poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxan-1,3-diyl}ethylene] of well-controlled molecular weight and stereoregularity was synthesized by ring-opening polymerization.[8] Synthesis of stereoregular and/or optically active poly(siloxane)s is also described.[9-11]

Results and Discussion



Scheme 1. Syntheses of optically active (*R*)-**4a** and (*R*)-**4b**.

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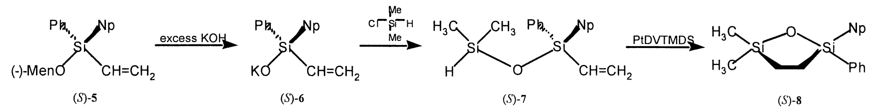
(*R*)-**1** can be obtained by optical resolution,[13] and whose optical purity was confirmed to be higher than 99.9 % by HPLC on optically active stationary phase and by ^{1}H NMR.[5] The reaction of (*R*)-**2** with allylmagnesium bromide or propargylmagnesium bromide gave allylated[4] or propargylated product.[6]



Scheme 2. Synthesis of optically active (*S*)-7 and (*S*)-**8**.

(*S*)-7 was synthesized from optically pure (*S*)-**5** (>99% de).[14] Dilute solution of (*S*)-7 was added drop wise to PtDVTMDS in xylene to obtain pure (*S*)-**8**.[8]

Polyaddition reactions of (*R*)-**4a** and (*R*)-**4b**, and (*S*)-7 were carried out in the presence of PtDVTMDS, and (*S*)-**8** was polymerized by anionic mechanism. The polymerization to give poly[(*R*)-**4a**] proceeded through β-selective hydrosilylation. The methyl signals at 0.120, 0.125, and 0.131 ppm were assigned to isotactic (*I*), heterotactic (*H*), and syndiotactic (*S*) triad, respectively. The calculated concentration of each triad starting from monomer with 76.5 % ee assuming complete retention of Si stereochemistry is $S : H : I = 1.0 : 2.0 : 6.6$. The actual triad evaluated is 1.0 : 2.0 : 7.0. There was no racemization in allylation, reduction step to synthesize (*R*)-**4a** and in polymerization.

In order to keep the configurational optical activity derived from the chiral silicon atom, polymerization of (*R*)-**4b** was studied. Poly[(*S*)-**4b**] showed optical activity ($[\alpha]_D^{23}$ = -2.74° (*c* 3.43, $CHCl_3$). Poly[(*S*)-7] is also formed

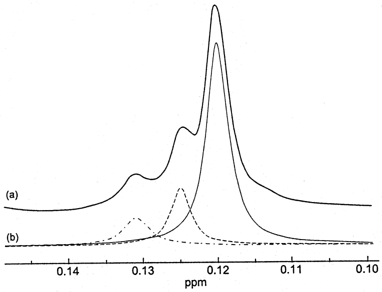


Figure 1. ^{1}H NMR spectra of poly[(*R*)-**4a**] obtained from the optically active monomer having $[\alpha]_D^{26}$ = +24.0°. (a) actual spectrum, (b) individual component plots; Isotactic (solid), Heterotactic (dashed), Syndiotactic (dash-dot).

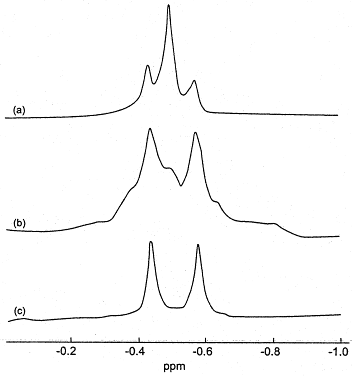


Figure 2. ^{13}C NMR spectra of (a) poly[*rac*-7], (b) poly[(*S*)-7], and poly[(*S*)-**8**].

predominantly by β-addition (> 99%). The polymer showed optical activity ($[\alpha]_D^{25}$= +2.2° (*c* 1.88, $CHCl_3$)) as expected. ^{13}C NMR spectra of the $Si(CH_3)_2$ region showed different splitting patterns depending on the tacticity. Atactic polymer showed three peaks (-0.427, -0.503, and -0.564 ppm), while optically active polymer showed mainly two peaks (-0.427 and -0.564 ppm).

There are four possible dyads depending on the asymmetric silicon centers: *S-S, S-R, R-S*, and *R-R*. Two methyl carbons in both *S-S* and *R-R* dyad are in different environments and therefore should have different chemical shifts. On the contrary, in *S-R* (or *R-S*) dyad, two methyl groups are in very similar environments, so that their carbon resonance appear at almost same position. $Si(CH_3)_2$ in poly[*rac*-**7**], therefore, would be split into three peaks with an intensity of 1 : 2 : 1. Poly[(*S*)-**7**], containing only the *S-S* dyad, would show two peaks of methyl carbons. The obtained optically active poly[(*S*)-**7**] showed two distinct peaks of methyl carbons, indicating the polymer is highly isotactic. In order to avoid cyclic oligomer formation, ring-opening polymerization of (*S*)-**8** was carried out. Poly[(*S*)-**8**] gave nicely split two singlets.

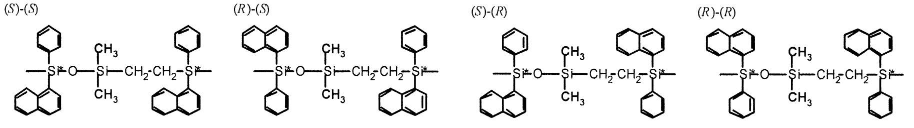


Figure 3. Possible dyads of poly[7].

The attack of a nucleophile could occur on the *Si*(Me)$_2$ or *Si*(NpPh) of (*S*)-**8**, that would result in head-to-tail (H–T), head-to-head (H–H), and tail-to-tail (T–T) structures in the propagation step. The two major peaks at -1.2 and -0.9 ppm in ^{29}Si NMR of the initial product are assigned to the *Si*(NpPh)OH and *Si*Me$_2$Ph, respectively. A very small peak at 18.5 ppm is considered to be the *Si*(Me)$_2$OH. The integral ratio of *Si*(NpPh)OH and *Si*(Me)$_2$OH is about 92/8. It can be concluded

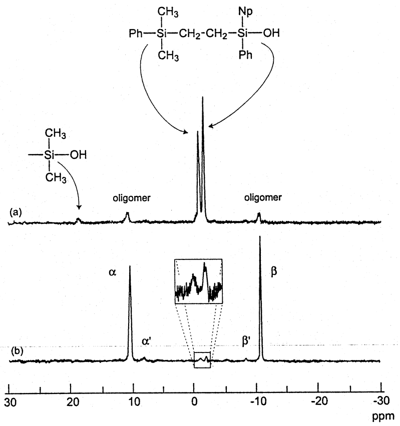


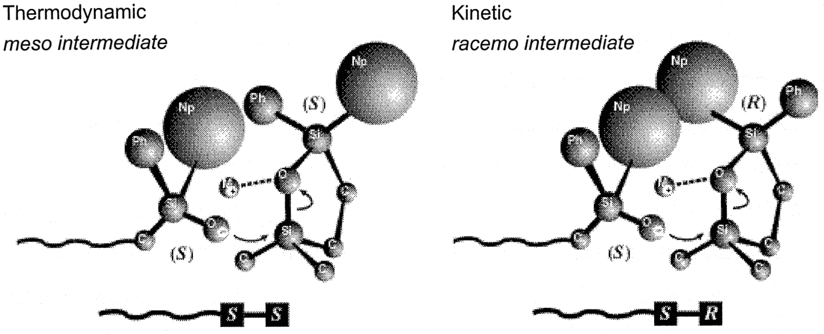
Figure 4. ^{29}Si NMR spectra of (a) model compounds by the reaction of **8** and initiator of 1 to 1 molar ratio, and (b) poly[**8**].

that the initiation step using PhLi is highly regioselective, *i.e.*, PhLi predominantly attacked the silicon atom of *Si*$(Me)_2$ rather than the *Si*(NpPh).

In the spectrum of poly[**8**], the major signals at -10.7 and 10.4 ppm can be undoubtedly assigned to the H–T structure. The two peaks at -1.9 and -1.2 ppm of polymer clearly correspond to the peaks at -1.2 and -0.9 ppm of the initial product, and are therefore assigned to be the chain end *Si*(NpPh)OH and the initiating terminal *Si*Me_2Ph, respectively. Because there is no visible chain end, *Si*$(Me)_2OH$, in poly[**8**], the propagation step seems to proceed highly regioselectively to give the *Si*(NpPh)OH chain end.

The peaks at -8.4 and 8.1 ppm were ascribed to the H–H and T–T structure, respectively. Consequently, the H–T content of the polymer is calculated to be 98.7 %. The counter cation of the initiator influences the H–T content of the polymer [Li^+ (97.6 %) > Na^+ (89.4 %) >K^+ (79.2 % (at 10 min)].

Interestingly, the calculated integral ratio of *racemo* and *meso* dyads (*r* / *m*) of poly[*rac*-**8**] was 64 / 36 , which apparently varied from that of a random sequence distribution (*r* / *m* = 50 / 50), suggesting the rich syndiotacticity of this polymer. When a mixture of (*S*)-**8** and *rac*-**8** was used, the *r* / *m* ratio of the resultant poly[**8**] decreased from 58 / 42 at the early stage to 51 / 49 at the later stage, indicating the faster *racemo* dyad formation over the *meso* dyad formation. The changes of the optical purity of the remaining monomer during the polymerization further confirmed this tendency.[15] It is tentatively considered that the propagating chain ends and the approaching monomers form diastereomeric intermediates. Differences in the size and association ability of the counter cation, chirality of chain end, etc. may lead to the different outcomes of the stereoregulation.

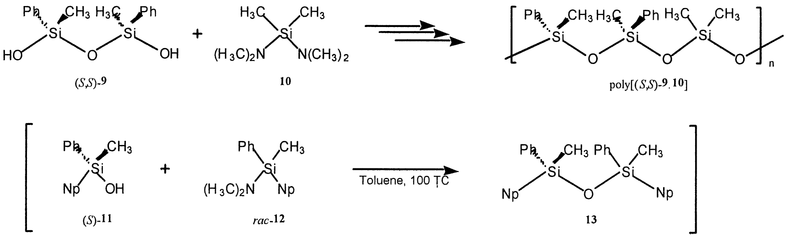

Thermodynamic
meso intermediate

Kinetic
racemo intermediate

Figure 5. Stereo-selection of (*S*)-**8**.

Preparation of stereoregular poly(unsymmetrically dialkyl-substituted siloxane)s have been limited to anionic ring-opening polymerization of *cis*-1,3,5-trimethyl-1,3,5-triphenyl cyclotrisiloxane[19] or *cis*-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane[3] using alkali metal silanolate as an initiator.

Optically active (*S*,*S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol, (*S*,*S*)-**9**[16] is considered suitable as the constitutional units of stereoregular and optically active polysiloxanes. Polycondensation reactions of bis(hydroxysilane) with bis(aminosilane) usually afford the polysiloxanes with relatively high molecular weight.[17] If the reaction proceeds stereospefically, stereoregular and optically active polysiloxane would be obtained by polycondensation of (*S*,*S*)-**9** with bis(aminosilane)s. Model reaction has proven that the configuration of asymmetric silicon atom of the silanol (*S*)-**11** is not changed in the condensation. Polycondensation of (*S*,*S*)-**9** with bis(dimethylamino)dimethylsilane **10** was carried out under the similar reaction conditions with the model reaction (Scheme 3).[9]



Scheme 3. Synthesis of optically active polysiloxane.

The signals of methyl groups of SiPh*Me* and Si*Me*$_2$ of poly[(*S*,*S*)-**9.10**] (M_n=170000, M_w/M_n=1.1, $[\alpha]_D^{25}$=+3.4) appeared as nearly singlet peaks at 0.22 and –0.058ppm, respectively, reflecting the same absolute configuration of asymmetric silicon atoms in disiloxane unit, accordingly, only one combination of (*S*)-Si*O-Si*Me*$_2$-OSi*-(*S*) stereochemistry. The configuration of silicon atoms of (*S*,*S*)-**9** was not affected during the polycondensation, and poly[(*S*,*S*)-**9.10**] is completely diisotactic and optically pure. Further evidence for the isotacticity of poly[(*S*,*S*)-**9.10**] is given by the peak of *meta*-Si<u>*Ph*</u>Me carbon splitting in ^{13}C NMR. The peaks at 127.75 and 127.72 ppm could be assigned to the carbon signals of *meso*- and *racemic*- disiloxane repeating unit, respectively.

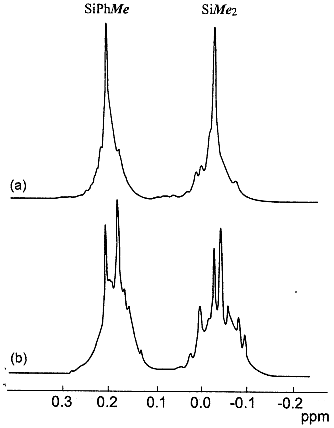
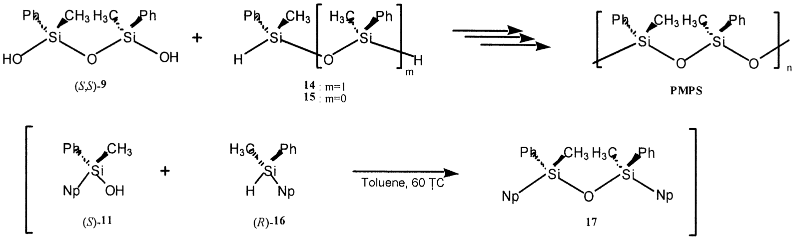


Figure 6. ^{1}H NMR spectra of the SiPh*Me* and Si*Me*$_2$ of (a) diisotactic and (b) atactic poly[**9.10**].

We recently reported the transition metal-catalyzed cross-dehydrocoupling polymerization reaction of bis(hydro)silane and water, which is a facile method to obtain various polymers containing silicon-oxygen bond with relatively high molecular weight under mild conditions.[18]



Scheme 4. Synthesis of syndiotactic PMPS

The cross-dehydrocoupling reaction of (*S*)-**11** (>99% ee)[10] with (*R*)-**16** (>99%ee),[10] as a model reaction did not proceed at room temperature. All the reactions proceeded by heating to 60°C, but the yield of **17** was not high. The stereo-selectivity[10] of reaction catalyzed by $RhCl(PPh_3)_3$ and $[RhCl(C_8H_{14})_2]_2$ were almost identical to that of $[RhCl(cod)]_2$. $[RhCl(cod)]_2$-catalyzed reactions with LiH or Et_3N proceeded at room temperature with 99%, or 96% retention of configuration at silicon atom, respectively. The Rh-catalyzed cross-dehydrocoupling polymerization of optically pure (*S,S*)-**9** with **14** [(*S,S*):(*S,R*):(*R,R*)=84:16:0] was carried out. Diastereomer mixture of *meso*/*dl*-**9** and *meso*/*dl*-**14** were also polymerized to prepare atactic poly(methylphenylsiloxane) **PMPS**. The ^1H NMR of methyl group of atactic **PMPS** showed three singlets at 0.04, 0.09, and 0.14ppm arisen from triad tacticity. The singlet at 0.09ppm was assigned to the heterotactic triad (*H*). **PMPS** from (*S,S*)-**9** and **14** [(*S,S*):(*S,R*):(*R,R*)=84:16:0] also showed three singlet peaks. Since the model reaction indicated the retention of configuration at silicon atoms of silanol, the **PMPS** prepared from (*S,S*)-**9** with **14** can be considered to be rich in syndiotacticity. Namely, the two

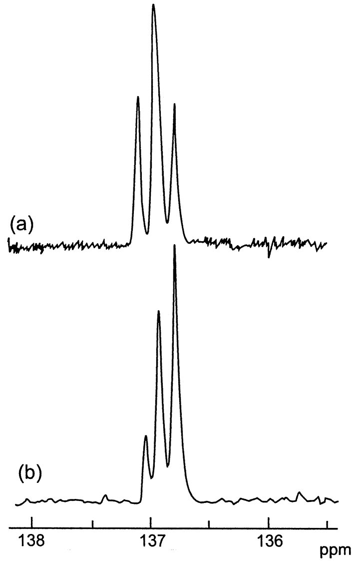


Figure 7. ^{13}C NMR spectra of **PMPS** (a) run 1 and (b) run 2 in Table 1.

singlets at 0.04 and 0.14ppm are assigned to isotactic (*I*) and syndiotactic (*S*) triad, respectively. Methyl carbon peaks (*I*=-0.47, *H*=-0.38, *S*=-0.29ppm) and *meta*-carbon peaks (*I*=127.53, *H*=127.49, *S*=127.43ppm), in particular, *ipso*-carbon peaks (*I*=137.1, *H*=136.9, *S*=136.7ppm) showed definite splitting based on the triad tacticity. The triad tacticity of **PMPS** prepared from (*S,S*)-**9** and **14** [(*S,S*):(*S,R*):(*R,R*)=84:16:0] in the presence of Et_3N was estimated as *S*:*H*:*I*=60:32:8 and *S*:*H*:*I*=38:37:25 in the presence of LiH from the *ipso*-carbon peaks. Although the cross-dehydrocoupling polymerization of optically pure (*S,S*)-**9** with **14** [(*S,S*):(*S,R*):(*R,R*)=84:16:0] in the presence of Et_3N afforded **PMPS** rich in syndiotacticity, some apparent decrease in syndiotacticity of **PMPS** was noticed compared with the calculated value (*S*:*H*:*I*=84:10:6) from the model reaction. This is due to the racemization of **14** during the polymerization.

Table I. Rh-catalyzed cross-dehydrocoupling polymerization of **9** with **14**.

run	**9**	**14**	yield [%]^a	M_n x 10^3	M_w/M_n	*S* : *H* : *I* ^{b} calcd.	*S* : *H* : *I* ^{b} obs.	T_g [ŢC]
1	*meso* / *dl*		23	7.7	1.5	25:50:25	31:42:27	-24
2	(*S*,*S*)^c	(*S*,*S*)^d	23	2.4	1.7	88:8:4	60:32:8	-22

[a]Isolated yields after reprecipitation into methanol based on compound 9. [b]determined by ^{13}C NMR. [c](*S*,*S*) = 100 %. [d](*S*,*S*) : (*S*,*R*) : (*R*,*R*) = 84 : 16 : 0

Cross-dehydrocoupling polymerization reactions of **9** consisting of different stereoisomer compositions (*meso*/*dl*; (*S,S*):(*S,R*):(*R,R*)=25:50:25, *dl*-rich ; (*S,S*):(*S,R*):(*R,R*)=35:30:35, and *meso*; 100% pure) with **15** were carried out in the presence of Rh-catalyst and Et_3N or (-)-spartein [(-)-Sp]. In the polymerization of *meso*/*dl*-**9** and *dl*-rich-**9** catalyzed by $RhCl(PPh_3)_3$, triad tacticity was almost identical with calculated value, which indicated that these polymerization proceeded without stereo-recognition by propagating chain end when *meso*

Table II. Cross-dehydrocoupling polymerization of 9 with 15.^{a}

run	**9**	Catalyst	Additive	Yield (%)^b	M_n^{c}	M_w/M_n^{c}	tiad tacticity *mm*:*mr* :*rr* ^{d} obsd.	tiad tacticity *mm*:*mr* :*rr* ^{d} calcd.
1	*meso*/*dl* : (*S*,*S*):(*S*,*R*):(*R*,*R*)=25:50:25	$RhCl(PPh_3)_3$	Et_3N	46	6700	1.1	25 : 49 : 26	25 : 50 : 25
2			(-)-Sp	55	11000	2.4	26 : 45 : 29	
3	*dl*-rich : (*S*,*S*):(*S*,*R*):(*R*,*R*)=35:30:35	$RhCl(PPh_3)_3$	Et_3N	49	7200	2.7	23 : 47 : 30	18 : 50 : 32
4			(-)-Sp	60	12000	1.9	23 : 46 : 31	
5	*meso* : 100% pure	$RhCl(PPh_3)_3$	Et_3N	47	14000	1.9	32 : 48 : 20	42 : 50 : 8
6			(-)-Sp	35	5400	1.2	26 : 48 : 26	
7		RhCl[(*S*)-BINAP]	Et_3N	46	8600	2.5	34 : 46 : 20	
8			(-)-Sp	41	5200	1.7	29 : 44 : 27	
9		RhCl[(*R*,*R*)-DIOP]	Et_3N	38	12000	3.2	39 : 43 : 18	
10			(-)-Sp	trace	7000	1.2	30 : 44 : 26	

[a] The polymerization reactions were carried out at 60ŢC for 12hr. [b] Isolated yields after reprecipitation into MeOH. [c] Estimated by GPC with polystyrene standard (THF as an eluent). [d] Determined by ^{13}C NMR at *ipso* carbon.

content is less than 50%. Interestingly, polymerization of *meso*-**9** with **15** gave **PMPS** rich in syndiotactic triad (*S*=20%) compared with the calculated value (*S*=8%). Use of the (-)-Sp as the additive showed somewhat higher syndiotactic triad (*rr*=26-27%). Possible pentad stereo-sequences of **PMPS** from *meso*-**9** with **15** are shown. Since the polymerization afforded **PMPS** rich in syndiotacticity, Si-OH propagating chain end with *m* diad stereo-sequence seems preferentially react with prochiral SiH_2 to give Si-H propagating chain end with *mr* triad sequence. The formed Si-H propagating chain end with *mr* triad sequence reacts with *meso*-**9** to produce Si-OH propagating end with *mrrm* pentad stereo-sequence (D), almost selectively. On the other hand, Si-H end with *mm* triad, the minor stereo-sequence, reacts with Si-OH to produce *mmmm* pentad (A). Polymerization with (-)-Sp forms only sequence (A) and (D) without any other stereo-sequences. The difference in stereo-selection between Et_3N and (-)-Sp may be due to the existence or non-existence of racemization of Si-H propagating chain end in the polymerization.[3a]

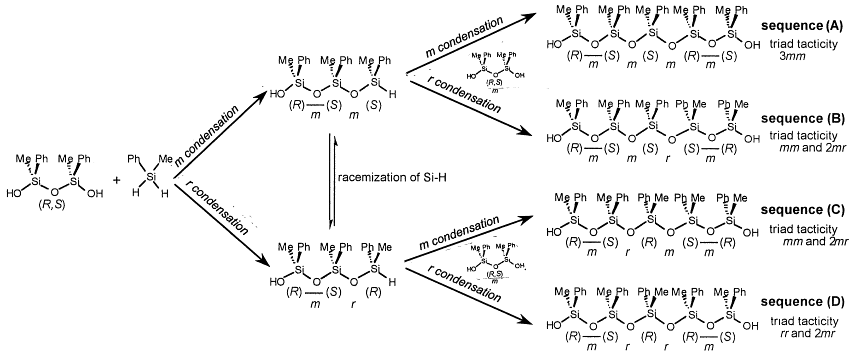


Figure 8. Pentad sequence of **PMPS**.

References

1. (a) Miller, R.D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (b) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; p 1207. (c) *Silicon-Containing Polymers*, Richard, G.J., Ed.; The Royal Society of Chemistry, Cambridge, 1995. (d) Birot, M.; Pillot, J.; Dunognes, J. *Chem. Rev.* **1995**, *95*, 1443.
2. (a) Yajima, S.; Hayashi, J.; Omori, M. *Chem. Lett.* **1975**, 931. (b) Yajima, S.; Okamura, K.; Hayashi, J. *Chem. Lett.* **1975**, 1209.
3. Curry, J. W. *J. Am. Chem. Soc.* **1956**, *78*, 1686.
4. Kawakami, Y.; Takeyama, K.; Komuro, K.; Ooi, O. *Macromolecules* **1998**, *31*, 551.
5. Kawakami, Y.; Takahashi, T.; Yada, Y.; Imae, I. *Polym. J.* **1998**, *30*, 1001.

6. Kawakami, Y.; Nakao, K.; Shinke, S.; Imae, I. *Macromolecules* **1999**, *32*, 6874.
7. Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592.
8. Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 548.
9. Oishi, M.; Kawakami, Y. *Macromolecules* **2000**, *33*, 1960.
10. Oishi, M.; Moon, J.-Y.; Janvikul, W.; Kawakami, Y. submitted to *Polym. Int.*
11. Oishi, M.; Moon, J.-Y.; Kawakami, Y. in preparation.
12. (a) Sommer, L.H.; Frey, C.L. *J. Am. Chem. Soc.* **1959**, *81*, 1013. (b) Corriu, R.J.P.; Lanneau, G.F.; Leard, M. *J. Organomet. Chem.* **1974**, *64*, 79.
13. Shinke, S.; Kawakami, Y. in preparation.
14. Corriu, R.J.P., Royo, G. *J. Organometal. Chem.* **1968**, *14*, 291.
15. Li, Y.; Kawakami, Y. *Macromolecules* **2000**, *33*, 5.
16. Oishi, M., Kawakami, Y. *Macromolecules* **1999**, *1*, 549.
17. (a) Pike, R.M.; *J. Polym. Sci.* **1961**, *50*, 151. (b) Stewart, D.D.; Deters, E.N.; Bead, C.D.; Dunks, G.B.; Hedaya, E.; Kwiatkowski, G.T.; Moffitt, R.B.; Bohan, J. *Macromolecules* **1979**, *12*, 373. (c) Babu, G.N.; Newmark, R. A. *Macromolecules* **1991**, *24*, 4503.
18 (a) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 3540. (b) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 6871. (c) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 8768.
19. a) Momper, B.; Wanger, Th.; Maschke, U.; Ballauff, M.; Fisher, E. W. *Polym Commun.* **1990**, *31*, 186. (b) Clarson, S.J.; Semlyen, J.A.; Dodgson, K. *Polym Prepr (Am Chem Soc Div Polym Chem)* **1990**, *31*, 563. (c) Curtis, M.D.; Thanedar, S.; Elshiek, M. *Polym Prepr (Am Chem Soc Div Polym Chem)* **1984**, *25*, 224. (d) Baratova, T.N.; Mileshkevich, V.P.; Gurari, V.I. *Poly Sci USSR* **1983**, *25*, 2899. (e) Baratova, T.N.; Mileshkevich, V.P.; Gurari, V.I. *Poly Sci USSR* **1982**, *24*, 27. (f) Bresler, L.S.; Mileshkevich, V.P.; Yuzhelevskii, Yu.A.; Timofeeva, N.P. *Zh Strukt Khim SSSR* **1978**, *19*, 453. (g) Bostik, E.A. *Polym Prepr (Am Chem Soc Div Polym Chem)* **1969**, *10*, 877.