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Separation of Stereoisomeric Organosilicon Compounds and Synthesis of Stereo-Controlled Polymers

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Chromatographic Separation of Asymmetric Organosilicon Compounds on Chiral Stationary Phase - Stereochemistry of Functional Transformation Reactions

[Background]

The preparation of optically active organosilicon compound was firstly reported in 1959 by Sommer and Frye [1], who successfully resolved diastereomers of methyl(1-naphthyl)phenyl(-)-menthoxysilane. The reduced product, methyl(1-naphthyl)phenylsilane is reported to be optically pure with (*R*) configuration. The stereochemistry of the reduction of alkoxyasilane by lithium aluminum hydride (LiAlH_4) is suggested to be complete retention of the absolute configuration (retention stereochemistry) at the silicon. Since then, synthesis of optically active organosilicon compounds and studies on the stereochemistry at silicon atom in the reactions has been occasionally conducted. However, only the optical purity of the compounds was estimated based on the optical rotation, and enantiomer excess (ee) was not estimated by other quantitative analytical methods.

Recently, our laboratory reported the synthesis of some optically monomers and polymers[2]. However, in the synthesis of optically active organosilicon compounds, problems are often faced in determining the optical purity and ee of the products.

Chromatographic separation in some cases is superior to the preferential crystallization in the point that enantiomerically pure organosilicon compounds might be readily and surely obtained. Although, high-performance liquid chromatography (HPLC) analysis on chiral stationary phase is widely carried out in analyzing the ee of carbon compounds, only little successful analysis on organosilicon compounds was reported [3].

[The outline of dissertation]

HPLC separation of a series of organosilicon compounds by using the CHIRALCEL OD[®] and CHIRALPAK AD[®] was demonstrated, and the chromatographic parameters α , R_s are determined. Chiral recognition ability of CHIRALCEL OD[®] is generally higher than CHIRALPAK AD[®]. Pure hexane as eluent gave the best results.

The importance of hydrogen bonding and π - π interaction between phenyl carbamate function and O-H or N-H, or the phenyl groups of the sample is pointed out for the efficient separation on CHIRALCEL OD[®]. Not only the bulkiness, but also the π - π interaction seems to be playing the important role. Methoxy and bromo substituent on the naphthyl group seems to effect on such interaction.

Specific optical rotation of the organosilicon compounds was determined, and the stereoselectivity at the asymmetric silicon center in functional transformation reactions is quantitatively discussed based on the evaluation of ee. That is, the result the absolute configuration of the silicon atom is completely retained in the reduction of Si-OMen bond by LiAlH_4 .

[References]

- (1) Sommer, L. H.; Frye, C. L. *J. Am. Chem. Soc.* **1959**, *81*, 1013.
- (2) (a) Kawakami, Y.; Takeyama, K.; Komuro, K.; Ooi, O. *Macromolecules* **1998**, *31*, 551. (b) Kawakami, Y.; Takahashi, T.; Yada, Y.; Imae, I. *Polym. J.* **1998**, *30*, 1001. (c) Kawakami, Y.; Nakao, K.; Shinke, S.; Imae, I. *Macromolecules* **1999**, *32*, 6874. (d) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31*, 5592. (e) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32*, 548. (f) Oishi, M.; Kawakami, Y. *Macromolecules* **2000**, *33*, 1960.
- (3) Mori, A.; Toriyama, F.; Kajiro, H.; Hirabayashi, K.; Nishihara, Y.; Hiyama, T. *Chem. Lett.* **1999**, 549.

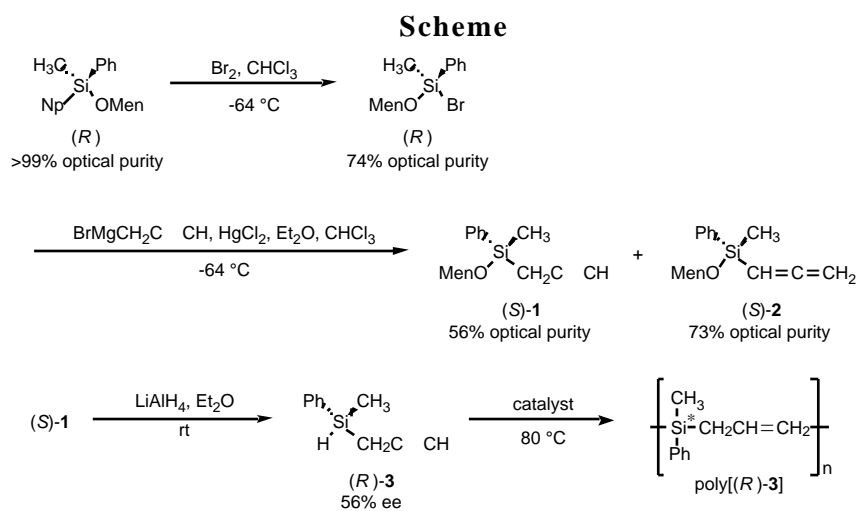
Synthesis and Polyaddition Reaction of Optically Active Alkynylsilane

[Background]

Ring-opening polymerization of silacyclobutane or disilacyclobutane derivatives and polyaddition reaction of hydrosilyl compounds with unsaturated compounds have been conducted to prepare a variety of poly(carbosilane)s [1-3]. Our laboratory has reported the stereoregular poly[(methylphenylsilylene)(trimethylene)] synthesized from optically active allylmethylphenylsilane via self-polyaddition reaction[3]. The stereoregularity of the polymer estimated by ^1H NMR indicated that this polymerization proceeded through β -selective hydrosilylation in which stereochemistry of silicon atom was retained, but the optical activity itself was lost in the resulting polymer since the silicon atoms in the formed polymer are not chiral any more. In order to keep the configurational optical activity derived from the chiral silicon atom, it is necessary to distribute the optically active silicon moiety connected with different constitutional units in the polymer chain. Here, I report the synthesis and polymerization of optically active (*R*)-methylphenyl(2-propynyl)silane, (*R*)-**3** to obtain optically active poly(carbosilane), poly[(*R*)-**3**]. Such stereoregular and optically active unsaturated poly(carbosilane)s will find potential applications as reactive polymer precursors for the synthesis of variety of new optically active branched polymers, typically star-type, comb-shaped, and hyperbranched polymers.

[The outline of dissertation]

Optically active (*S*)-methylphenyl(2-propynyl)silane, (*R*)-**1** (56% ee) was synthesized from (*S*)-methylphenyl(2-propynyl)-(+)-menthoxy silane, (*S*)-**1** (56% optical purity) via (*R*)-methyl(1-naphthyl)phenyl-(+)-menthoxy silane, (*R*)-**3**. Polyaddition reactions of (*R*)-**3** using Pt-DVTMDS gave polymers (Scheme). Poly[(*R*)-**3**] obtained by Pt-DVTMDS showed optical activity, i.e.



$[\alpha]_D^{23} -2.74$ (c 3.43, CHCl_3). This is the first example of optically active poly(carbosilane). And keep the configurational optical activity derived from the chiral silicon atom in the polymer.

The geometry of the double bond formed in the polymer chain depended on the catalyst used. And hydrosilylation of propynyl group could proceed in β -addition mode, elucidated by ^1H , ^{13}C NMR and DEPT spectra. These signals can be assigned to *cis* or *trans* vinylene protons. It is known that the hydrosilylation of C=C bond by $[\text{Rh}(\text{cod})_2]\text{BF}_4/2\text{PPh}_3$, $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhBr}(\text{PPh}_3)_3$ proceeds in *syn* addition mode. Interestingly, the geometry of the polymer from optically active propynylsilane was dependent on the catalyst and reaction conditions.

[References]

- (1) (a) Cundy, C. S.; Eaborn, C.; Lappert, M. F. *J. Organometal. Chem.* **1972**, *44*, 291. (b) Liao, C. X.; Weber, W. P. *Polym. Bull.* **1992**, *28*, 281. (c) Matsumoto, K.; Yamaoka, H. *Macromolecules* **1995**, *28*, 7029.
- (2) (a) Curry, J. W. *J. Am. Chem. Soc.* **1956**, *78*, 1686. (b) Boury, B.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J. M.; Vioux, A. *Organometallics* **1991**, *10*, 1457. (c) Pang, Y.; Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1993**, *26*, 5671.
- (3) Kawakami, Y.; Takeyama, K.; Komuro, K.; Ooi, O. *Macromolecules* **1998**, *31*, 551.

Stereo-Controlled Synthesis of Optically Active Poly(siloxane)

[Background]

Poly(siloxane)s consist of $(\text{SiRR}'\text{O})_n$ repeating unit, a class of unique organic-inorganic hybrid polymers, have been extensively used as one of the most important thermally stable rubbery, weather resistance and insulating materials [1]. Especially, poly(dimethylsiloxane)s has been widely used as silicone oil, silicon rubber, and main chain for liquid crystalline polymers because of drape hydrophobic methyl substituent over helical structure [2].

Polycondensation is considered suitable for preparation of well-defined polymers. Cross-coupling reactions of organosilanols, Si-OH with hydrosilane, H-Si or aminosilanes, $\text{H}_2\text{N-Si}$ are particularly convenient to synthesize poly(siloxane)s. Hydrogen or low molecular weight amine as by-product can be used for forming and easily removed.

Configurational optical active poly(siloxane)s is expected to exhibit novel unique properties different from those of ordinary poly(siloxane)s without controlled stereochemistry without controlled stereochemistry. It will be very interesting to correlation of the stereoregularity of poly(siloxane) and their physical characteristics. However, there are only few reports on the control of the stereochemistry of Si atom in the polymer main chain as optically active poly(carbosilane) [3], poly(siloxane)s [4], and etc.

[The outline of dissertation]

Deaminative polycondensation of optically pure organosilicon compounds $\{(R, R)\text{-}1,3\text{-dimethyl-}1,3\text{-[diphenyl or di(1-naphthyl)]-}1,3\text{-disiloxanediol}$ with bis(dimethylamino)dimethylsilane and bis(dimethylamino)methylsilane obtained the optically active linear poly(siloxane)s having function group Si-H.

Cross-dehydro-coupling reaction of optically pure methyl(1-naphthyl)-phenylsilane, **4** with triphenylsilanol was carried out, and the results were summarized in Table. And, I proved that the stereochemistry of the cross-dehydrocoupling reaction by $\text{B}(\text{C}_6\text{F}_5)_3$ is inversion by the reaction of optically pure $(R)\text{-4}$ with $(-)$ -menthol.

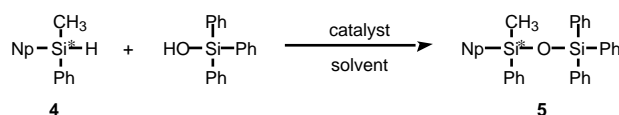


Table 2. Cross-dehydrocoupling Reaction of Hydrosilane with Triphenylsilanol in the presence of Catalyst

silane of 4	catalyst (mol%)	solvent	time (h)	yield (%) of 5^b	% ee of 5^c
<i>R</i> , >99% ee	$\text{B}(\text{C}_6\text{F}_5)_3$ (0.4)	toluene	6	71	64
<i>R</i> , >99% ee	$\text{B}(\text{C}_6\text{F}_5)_3$ (0.1)	— ^d	0.3	74	65
<i>S</i> , >99% ee	$\text{B}(\text{C}_6\text{F}_5)_3$ (0.4)	toluene	6	86	76
<i>R</i> , >99% ee	AuCl_3 (10)	dioxane	4	7 ^e	23
<i>R</i> , >99% ee	AuCl_3 (10)	toluene	72	no reaction	
<i>R</i> , >99% ee	$\text{AuCl}_3/\text{AgOTf}$ (10)	dioxane	18	16	43
<i>R</i> , 96% ee	AgSbF_6 (10)	dioxane	19	10 ^e	30
<i>R</i> , >99% ee	AgSbF_6 (10)	toluene	96 ^f	3	29
<i>R</i> , >99% ee	AgOTf (10)	dioxane	20	29	28

^a Equimolar **3a** with silanol was stirred at room temperature. ^b Determined by ¹H NMR.

^c Determined by HPLC. ^d 55°C/300Pa. ^e Isolated yield. ^f **4** was 31% converted.

[References]

- (1) (a) Riresiduald, G. J.; Wataru, A.; Julian, C. *Silicon-Containing Polymers*; Kluwer Academic Publications: Dordrecht, 2000. (b) Michael, A. B.; *Silicon in Organic, Organometallic, and Polymer Chemistry*; John Wiley and Sons: New York, 2000. (c) Mark, J. E. *Acc. Chem. Res.* **2004**, *37*, 946.
- (2) (a) Kawakami, Y.; Itoh, Y.; Toida, K. *Macromolecules* **1993**, *26*, 1177. (b) Kawakami, Y.; Toida, K. *Macromolecules* **1995**, *28*, 816. (c) Komuro, K.; Kawakami, Y. *Polym. Bull. (Berlin)* **1999**, *42*, 669.
- (3) (a) Uenishi, K.; Imae, I.; Shirakawa, E.; Kawakami, Y. *Macromolecules* **2002**, *35*, 2455. (b) Kawakami, Y.; Nakao, K.; Shinke, S.; Imae, I. *Macromolecules* **1999**, *32*, 6874. (c) Kawakami, Y.; Omote, M.; Imae, I.; Shirakawa, E. *Macromolecules* **2003**, *36*, 7461.
- (4) (a) Oishi, M. Kawakami, *Macromolecules* **2000**, *33*, 1960. (b) Oishi, M.; Moon, J. Y.; Janvikul, W.; Kawakami, Y. *Polym. Int.* **2001**, *50*, 135.

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[Publications]**Original Articles**

1. Kawakami, Y.; Nakao, K.; Shinke, S.; Imae, I. "Synthesis and Polyaddition Reaction of Optically Active Methylphenylpropargylsilane" *Macromolecules* **1999**, *32*, 6874-6876.
2. Shinke, S.; Kawakami, Y. "Chromatographic Separation of Asymmetric Organosilicon Compounds on Cellulose and Amylose Stationary Phases. The Stereochemistry of Functional Transformation Reactions", *Chromatographia* **2001**, *53*, 140-146.
3. Shinke, S.; Tsuchimoto, T.; Kawakami, Y. "Stereospecific Cross-Dehydrocoupling Reaction of Optically Active Methyl(1-naphthyl)phenylsilane with Triphenylsilanol or Alcohol by Lewis Acid Catalyst", in preparation.

Supplementary Publication

Kawakami, Y.; Takeyama, K.; Shinke, S.; Uenishi, K.; Park, S.-Y.; Kakihana, Y. "Catalytic Synthesis and Characterization of Stereoregular and Optically Active Polycarbosilanes", *Design. Monom. Polym.* **2004**, *7*(1/2), 119-126.

Reviews

1. 上西和也, 新家悟之, 表正克, 川上雄資, 「光学活性ケイ素化合物の単離と立体規則性ポリマーへの展開(1)」, *高分子加工* **2001**, *50*, 439-450.
2. 上西和也, 新家悟之, 表正克, 川上雄資, 「光学活性ケイ素化合物の単離と立体規則性ポリマーへの展開(2)」, *高分子加工* **2001**, *50*, 482-485.

Contributions to Conferences and Meetings

1. 新家悟之, 今栄一郎, 川上雄資, 「立体規則性かつ光学活性なポリ[(メチルフェニルシリレン)(2-プロペニレン)]の合成」, 第49回高分子討論会(仙台)2000年9月29日. Satoshi Shinke, Ichiro Imae, and Yusuke Kawakami, "Synthesis of Stereoregular and Optically Active Poly[(methylphenylsilylene)(2-propenylene)]", *Polymer Preprints, Japan* **2000**, *49*, 1273.
2. Satoshi Shinke, Ichiro Imae, and Yusuke Kawakami, "Synthesis, Separation and Polyaddition of Optically Active Methylphenylpropargylsilane", Poly Millennium 2000 (Hawaii), December 9, 2000.
3. 新家悟之, 今栄一郎, 川上雄資, 「キラルカラムを用いるケイ素化合物の分析」, 日本化学会第79回春期年会(神戸)2001年3月29日. Satoshi Shinke, Ichiro Imae, and Yusuke Kawakami, "HPLC Analysis of Chiral Organosilicon Compounds by Use of Chiral Stationary Phase", *Chemical*

Society of Japan Conference, Spring 2001, 79, 15.