Synthesis and Characterization of Optically Active Hyperbranched Poly(carbosiloxane)s

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ABSTRACT: An optically pure (*S*,*S*)-1,5-di(1-naphthyl)-1,5-diphenyl-1,5-divinyl-3-methyltrisiloxane (>99% ee) was synthesized by the condensation of (*S*)-lithium (1-naphthyl)phenylvinylsilanolate (>99% ee) with methyldichlorosilane. Hydrosilylation polymerization reactions with various feed ratios of (*S*,*S*)-1,5-di-(1-naphthyl)-1,5-diphenyl-1,5-divinyl-3-methyltrisiloxane (AB_2 monomer, A = Si−H and B = Vi) and 1,1,3,3-tetramethyl-1-vinyldisiloxane (A′B′ monomer) gave optically active hyperbranched poly(carbosiloxane)s in good yield ($M_n = 4320-9370$, $[a]_D^{25} = +13.1$ to $+4.5$, $T_g = -29-34$ °C). Determinations of the composition and degree of branching (0.27−0.43) of the polymers were made by taking advantage of the simplicity of the ^{29}Si NMR spectra of the optically active polymers compared with *meso*/DL polymers. End functionalization of the terminal vinyl groups (Vi) was demonstrated by using either hydrosilylation or hydroboration reactions, affording optically active hyperbranched poly(carbosiloxane)s having silyl chloride (Si−Cl) or hydroxy groups.

Introduction

Highly branched three-dimensional macromolecules such as dendrimers[1] and hyperbranched polymers[2] have recently attracted considerable attention due to the wide applicability to novel macromolecular architecture and functional polymers.[3] Both macromolecules are prepared from AB_n-type monomers, where *n* determines the ideal number of branches per repeating unit,[4] and the resulting macromolecules have a large number of chain end functional groups that are found at the surface of dendrimers or at the termini of the hyperbranched structures. However, the overall structure and method of construction differ substantially. Namely, dendrimers have a regular pattern of branching and are prepared by time-consuming procedures using either a divergent[5] or a convergent method.[6] On the other hand, although with an irregular pattern of branching, hyperbranched polymers can be prepared by a simple step-growth polymerization of AB_n monomers or by a chain-growth polymerization of monomers capable of regeneration of active site[7] in one pot. When A can react only with B, but neither A nor B can react with itself, gelation or formation of microgels is not possible, and macromolecular chains contain one reactive A-functional group at the core in the ideal case. At full monomer conversion, the growth can be terminated either by increasing steric screening on A or B, or depending on the chain flexibility, by ring formation through the intramolecular reaction of A with B in the same macromolecule.[8] Despite irregular pattern of branching, properties of hyperbranched polymers are relatively similar to those of dendrimers, which are quite distinct from analogous linear polymers.

Recently, interest in optically active dendrimers[9] has increased in the development of asymmetric catalysts and the manifestation of the effect of optically active (chiral) units on chiroptical properties. Unfortunately, most optically active dendrimers did not show any special chiroptical property or catalytic activity desired from the structure. For example, Meijeir et al.[9g] reported that poly(propyleneimine) dendrimers with Boc-protected amino acid at terminal groups showed decreasing optical rotation with an increasing number of generations, and it is hardly detectable in the fifth generation. Authors interpreted that this behavior is not caused by racemization, temperature, or solvent but arises from the steric effect of the amino acid moieties that lie closely together; thus, amino acid moieties in a dense packing seem to adopt frozen-in conformations with contributions to the optical rotation that internally cancel each other to give a resulting optical rotation of almost zero. However, this explanation may not be reasonably accepted. On the contrary, approximately constant optical rotation from the first to fifth generation is reported, when flexible alkyl chain was introduced just before the terminal amino acid moiety. Meanwhile, (1*R*,2*S*)-2-aminophenyl-1,3-propanediol, (1*R*,2*S*)-ephedrine, or L-aspartic acid dendrimers with a Cu(I)−Schiff base complex at the core were synthesized and examined as cocatalyst for enantioselective cyclopropanation of styrene with ethyl diazoacetate by Brunner et al.[10] The cyclopropanation of styrene catalyzed by the first generation of dendrimer occurred with 10% ee. When dendrimer with larger branches was used, however, the chemical yields and enantioselectivity did not increase, indicating that catalytic activity depends on the rate of diffusion of both substrates and products to and from catalytic sites. It is also pointed out that chiroptical properties and catalytic activity of the dendrimers strongly depend on the local environments such as position of optical active unit in dendritic structures, number of optically active units, and flexibility of dendritic segments.

Although there have not been many efforts made to create a optically active hyperbranched system,[11] in contrast to the precisely constructed optically active dendrimers, optically active hyperbranched polymers are considered to have the different local environments arisen from irregular pattern of branching, which may make it possible to lead to chiroptical properties and catalytic activity different from those of optically active dendrimers. In addition, optically active hyperbranched

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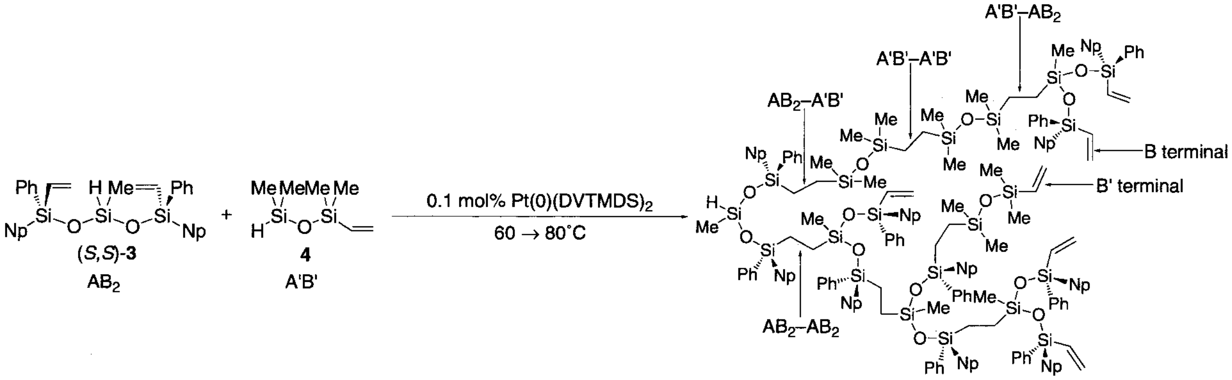
Scheme 1



polymers prepared by a one-pot polymerization of optically active AX*B$_n$-type monomer (where X* is optical active unit) allow the introduction of optically active units and functional groups to the interior and terminal of the molecules which may lead to efficient asymmetric catalysts or chiral recognition. So far, hyperbranched polymers have been regarded as poorly structurally defined by NMR analysis because of their irregular pattern of branching. Recently, we reported the first synthesis of optically active and/or stereoregular poly(siloxane)s[12] and poly(carbosiloxane)s[13] by the polymerization of optically active bifunctional organosilicon monomers (polymerization of AX*B-type monomer or polymerization of AX*A-type with BX*B-type monomers) and showed that thermal properties of these polymers are influenced by the stereoregularity. Furthermore, this approach has enabled us to make exact assignment of the stereoregularity by means of NMR analysis due to the simplicity of the signals originating from the known absolute configuration of monomers and stereospecific polymerization reactions (e.g., highly retention or inversion of configuration of a chiral silicon atom).

Among reported hyperbranched polymers so far, silicon-containing hyperbranched polymers such as poly(carbosilane)s,[14] poly(silyl ether)s,[15] poly(carbosiloxane)s,[16] and poly(siloxane)s[17] are organic–inorganic hybrid polymers that are beginning to attract interests as new functional materials. In particular, the synthesis of siloxane-type (Si–O–Si) hyperbranched polymers with chain end Si–H or Vi groups is an attractive goal, since the chain end group can be chemically modified.[18] Therefore, optically active siloxane-type hyperbranched polymers seem to be suitable for new functional materials such as asymmetric catalysts, liquid crystalline polymers, and materials for chromatography as well as other useful materials by taking advantage of flexible structure and good thermal stability of the siloxane bond.

In this paper, we describe the first synthesis and characterization of optically active hyperbranched poly(carbosiloxane)s based on the Pt-catalyzed hydrosilylation polymerization reactions with various feed ratios of optically active AX*B$_2$ monomer (AB$_2$ monomer) and achiral A′B′ monomer, where AB$_2$ and A′B′ are (*S*,*S*)-1,5-di(1-naphthyl)-1,5-diphenyl-1,5-divinyl-3-methyltrisiloxane (A = (–O)$_2$Me**Si–H** and B = –OPhNpSi–**Vi**) and 1,1,3,3-tetramethyl-1-vinyldisiloxane (A′ = –OMe$_2$**Si–H** and B′ = –OMe$_2$Si–**Vi**), respectively (Scheme 1).

Experimental Section

General. NMR (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{29}Si, 99 MHz) spectra were obtained in CDCl$_3$ on a Varian 500 MHz spectrometer model Unity INOVA. Chemical shifts are reported in ppm, relative to CHCl$_3$ (δ 7.26, ^{1}H), CDCl$_3$ (δ 77.0, ^{13}C), and tetramethylsilane (δ 0.00, ^{29}Si). IR spectra were obtained on a JASCO VALOR-III spectrophotometer. GC and DI EI–mass analyses were carried out on a Shimadzu QP-5000 mass spectrometer. High-resolution electrospray ionization mass (HRESIMS) analyses were carried out on a Bruker DALTONICS Bio-Apex 70 E mass spectrometer. Specific optical rotations were measured with a JASCO DIP-370S digital polarimeter. Size exclusion chromatography (SEC) and HPLC analyses were performed on a HPLC JASCO Gulliver 900 on the combination of Shodex KF-803L and KF-804 columns using tetrahydrofuran as an eluent and on a Daicel Chem. Ind., CHIRALCEL OD [cellulose tris(3,5-dimethylphenylcarbamate)], optically active stationary phase using *n*-hexane as an eluent. Vapor pressure osmometry (VPO) analysis was performed on a Corona Electoric Co., Ltd., model 114 using benzene as solvent. The differential scanning calorimetric (DSC) analysis was performed on a Seiko SSC/5200H instrument at a heating rate of 5.0 °C/min in air. The platinum(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex [Pt(0)(DVTMDS)$_2$] toluene solution (0.01 M) was prepared according to the literature.[19]

(*S*,*S*)-1,5-Di(1-naphthyl)-1,5-diphenyl-1,5-divinyl-3-methyltrisiloxane (3). (*S*)-(–)-(1-Naphthyl)phenylvinylsilanol (**2**)[20] (23.53 g, 49 mmol, >99% optical purity (op)) was converted to (*S*)-lithium (1-naphthyl)phenylvinylsilanolate in Et$_2$O (40 mL) via the reaction with *n*-BuLi (1.59 M in *n*-hexane, 31 mL, 49 mmol). A solution of methyldichlorosilane (2.82 g, 24.5 mmol) in Et$_2$O (5.0 mL) was added to a mixture of (*S*)-lithium (1-naphthyl)phenylvinylsilanolate (49 mmol) and Et$_2$O (40 mL) at 0 °C. The reaction mixture was stirred at room temperature for 5 h. After filtration, the filtrate was extracted with Et$_2$O and washed with water and dried over anhydrous Na$_2$SO$_4$. Removal of the solvent afforded a crude product, which was purified by silica gel column chromatography with *n*-hexane:CHCl$_3$ = 5:1 as an eluent ($R_f = 0.45$) (11.42 g, 79% yield).

(*S*,*S*)-**3**: $[\alpha]^{25}_{D} = +6.8$ ($c = 1.047$, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ 0.09 (d, $J = 1.8$ Hz, 3H), 4.99 (q, $J = 1.8$ Hz, 1H), 5.81 and 5.80 (2dd, $J = 3.6$ and 20.1 Hz, 2H), 6.15 (dd, $J = 3.6$ and 14.7 Hz, 2H), 6.51 and 6.50 (2dd, $J = 14.7$ and 20.1 Hz, 2H), 7.23–7.43 (m, 12H), 7.52 (d, $J = 6.6$ Hz, 4H), 7.72 (d, $J = 6.9$ Hz, 2H), 7.84 (d, $J = 8.1$ Hz, 2H), 7.90 (d, $J = 8.1$ Hz, 2H), 8.06 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (CDCl$_3$): δ 1.4, 125.0, 125.5, 125.8, 127.8, 128.7, 128.9, 129.8, 130.8, 133.2, 133.3, 134.6, 135.4, 135.6, 135.8, 136.1, 136.9. ^{29}Si NMR (CDCl$_3$): δ –33.5, –20.2. IR (neat, cm^{-1}): 3068, 3053, 3010, 2947, 2928, 2855, 2155, 1591, 1505, 1428, 1260, 1115, 1052. EI-MS (*m*/*z*): 594 (M$^+$), 552 ([M–Me–Vi]$^+$), 518 ([M–Ph]$^+$), 466 ([M–Np]$^+$). HRESIMS (*m*/*z*): 617.1757 [calcd for $C_{37}H_{34}O_2Si_3Na$ (M+Na)$^+$: 617.1765].

Synthesis of Hyperbranched Polymers. Polymerization reactions were carried out with various feed ratios of (*S*,*S*)-**3**

and 1,1,3,3-tetramethyl-1-vinyldisiloxane (**4**)[21] [(*S*,*S*)-**3**:**4**=100:0−0:100] to give **P1**−**P6**. As a typical example, homopolymerization reaction of (*S*,*S*)-**3** [(*S*,*S*)-**3**:**4** = 100:0] was given as follows. A solution of Pt(0)(DVTMDS)$_2$ in toluene (0.01 M, 0.2 mL, 0.002 mmol, 0.1 mol %) was added to (*S*,*S*)-**3** (1.186 g, 2.0 mmol) at 60 °C. After 6 h under stirring at the same temperature, the reaction mixture was stirred at 80 °C for a further 6 h. After reprecipitation from $CHCl_3$ into methanol, the precipitate was collected and dried in vacuo to give the hyperbranched poly[{(*S*,*S*)-1,5-di(1-naphthyl)-1,5-(phenyl)-3-methyltrisiloxane-1,5-diyl}ethylene], **P1** (1.030 g, 87% yield).

P1: M_n = 4320 (VPO), M_w/M_n = 2.1 (GPC); $[\alpha]^{25}_D = +13.1$ (c = 0.885, $CHCl_3$); T_g = 34 °C. ^{1}H NMR ($CDCl_3$): δ −0.41−0.22 (CH_3Si), 0.38−1.08 ($CH_2Si(O)_2Me$), 1.08−1.41 (CH_2Si(O)PhNp), 5.51−5.83 (CH_2=CHSi), 5.83−6.19 (CH_2=CHSi), 6.19−6.58 (CH_2 = *CH*Si), 6.80−7.57 (Ph and Np), 7.57−8.43 (Ph and Np). ^{13}C NMR ($CDCl_3$): δ −1.3−1.8 (CH_3Si), 6.5−8.7 ($CH_2Si(O)_2Me$), 8.7−10.8 (CH_2Si(O)PhNp), 124.3−136.8 (C_{Ar} and C_{vi}). ^{29}Si NMR ($CDCl_3$): δ −34.4 (H*Si*Me(O−)$_2$), −21.7 (O*Si*PhNpVi), −20.1, −18.6, and −17.9 (CH_2CH_2*Si*Me(O−)$_2$), −9.6 (O*Si*PhNpCH_2CH_2). IR (neat, cm^{-1}): 3050, 2954, 3010, 2947, 2154, 1590, 1505, 1428, 1259, 1116, 1047.

Characterization data and chemical yields for **P2**−**P6** are described in the Supporting Information.

Synthesis of Model Compounds for Branching Structures. Terminal-Model Compound. A solution of Pt(0)(DVTMDS)$_2$ in toluene (0.01 M, 0.1 mL, 0.001 mmol, 0.1 mol %) was added to a mixture of (*S*,*S*)-**3** (0.593 g, 1.0 mmol) and large excess trimethylvinylsilane (2.005 g, 20.0 mmol) at 50 °C. After 12 h under stirring at the same temperature, excess trimethylvinylsilane was removed. Silica gel column chromatography with *n*-hexane:$CHCl_3$ = 5:1 as an eluent (R_f = 0.43) of crude product gave a pure terminal-model compound, T-model (0.633 g, 91% yield).

T-model: $[\alpha]^{25}_D = +4.4$ (c = 0.685, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ −0.28 (s, 9H, $(CH_3)_3$Si), 0.02 (s, 3H, CH_3Si), 0.12−0.19 (m, 2H, CH_2SiMe_3), 0.24−0.31 (m, 2H $CH_2Si(O)_2Me$) 5.77 (dd, J = 3.3 and 19.8 Hz, 2H, CH_2=CHSi), 6.11 and 6.12 (2dd, J = 3.3 and 14.7 Hz, 2H, CH_2=CHSi), 6.50 and 6.51 (2dd, J = 14.7 and 19.8 Hz, 2H, CH_2=*CH*Si), 7.18−7.42 (m, 12H, Ph and Np), 7.51 (d, J = 6.3 Hz, 4H, Ph), 7.74 (d, J = 6.9 Hz, 2H, Ph and Np), 7.83 (d, J = 8.4 Hz, 2H, Np), 7.89 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H, Np). ^{13}C NMR ($CDCl_3$): δ −2.7 ($(CH_3)_3$Si), −0.81 (CH_3Si) 7.5 ($CH_2Si(O)_2Me$), 9.6 (CH_2SiMe_3), 124.8−136.9 (C_{Ar} and C_{vi}). ^{29}Si NMR ($CDCl_3$): δ −21.9 (O*Si*PhNpVi), −17.8 (CH_2CH_2*Si*Me(O−)$_2$), 3.0 (CH_2CH_2*Si*Me_3). IR (neat, cm^{-1}): 3054, 3009, 2952, 2910, 1591, 1506, 1428, 1258, 1116, 1050. HRESIMS (*m*/*z*): 717.2463 [calcd for $C_{42}H_{46}O_2Si_4Na$ $(M+Na)^+$: 717.2473].

Characterization data and experimental procedures for D-model and L-model are described in the Supporting Information.

End Functionalization. Hydrosilylation Reaction. A solution of Pt(0)(DVTMDS)$_2$ in toluene (0.01 M, 17 μL, 1.7×10^{-4} mmol, 0.1 mol %) was added to a mixture of **P1** (0.1012 g, M_n = 4320 (VPO), M_w/M_n = 2.1 (GPC)) and dimethylchlorosilane (0.2365 g, 2.5 mmol) at room temperature. After 12 h under stirring at the same temperature, excess dimethylchlorosilane was removed under reduced pressure. A solution of 2-propanol (0.0604 g, 1.0 mmol) in Et_3N (0.5 mL) was added to the residue, and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was filtered to remove the formed salt, and removal of the solvent afforded a crude polymer. After reprecipitation from Et_2O into methanol, the precipitate was collected and dried in vacuo to give the polymer **P8**[22] (0.1208 g).

P8: M_n = 4910 (VPO), M_w/M_n = 2.2 (GPC); $[\alpha]^{25}_D = +9.1$ (c = 0.110, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ −0.63−0.22 (CH_3Si), −0.12 ($(CH_3)_2$Si), 0.38−1.18 ($CH_2Si(O)_2Me$), 0.94 ($OCH(CH_3)_2$), 1.18−1.39 (CH_2Si(O)PhNp), 3.77 (OC*H*$(CH_3)_2$), 5.47−5.81 (CH_2=CHSi), 5.81−6.22 (CH_2=CHSi), 6.22−6.53 (CH_2 = *CH*Si), 6.64−7.57 (Ph and Np), 7.57−8.43 (Ph and Np). ^{13}C NMR ($CDCl_3$): δ −2.8−1.1(CH_3Si), 6.3−9.8 (CH_2), 25.6 ($CH(CH_3)_2$), 64.6 (*C*H), 124.3−136.8 (C_{Ar} and C_{vi}). ^{29}Si NMR ($CDCl_3$): δ −21.4 (O*Si*PhNpVi), −20.3 to −18.2 (CH_2CH_2*Si*Me(O−)$_2$), −10.4 to −9.1 (O*Si*Ph$NpCH_2CH_2$), 6.2 (CH_2CH_2*Si*$(Me)_2$OPr-*i*). IR (neat, cm^{-1}): 3054, 2966, 2911, 2874, 2147, 1590, 1507, 1428, 1260, 1115, 10425.

The hydroboration reaction (**P9**) is described in the Supporting Information.

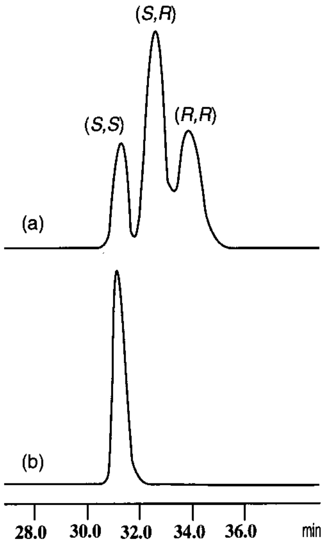
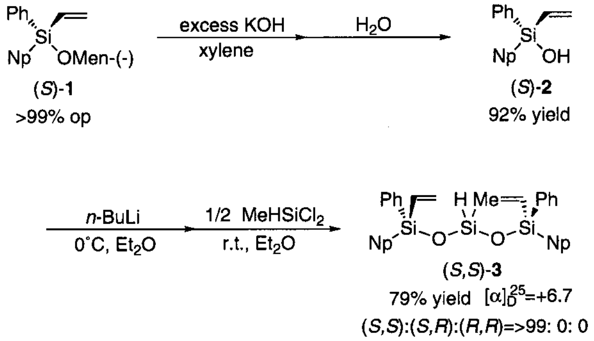


Figure 1. HPLC chromatograms of **3**: (a) *meso*/DL mixture; (b) product from Scheme 2.

Scheme 2. Synthesis of (*S*,*S*)-1,5-Di(1-naphthyl)-1,5-diphenyl-1,5-divinyl-3-methyltrisiloxane (3)



Results and Discussion

Monomer Synthesis and Polymerization. (*S*,*S*)-1,5-Di(1-naphthyl)-1,5-diphenyl-1,5-divinyl-3-methyltrisiloxane, (*S*,*S*)-**3**, was successfully synthesized according to Scheme 2. (*S*)-**2** was prepared by the hydrolysis of (*S*)-**1** (>99% op),[23] obtained by optical resolution of diastereomeric **1**, with excess KOH.[20] Although attempts to determine the enatiomeric excess (ee) of (*S*)-**2** by HPLC failed, this reaction was reported to proceed with 100% retention of configuration of silicon atom.[24] The reaction of methyldichlorosilane ($MeSiCl_2H$) with (*S*)-lithium (1-naphthyl)phenylvinylsilanolate, generated in situ by the lithiation of (*S*)-**2** with *n*-BuLi, afforded (*S*,*S*)-**3** in 79% yield. The stereoisomer ratio of (*S*,*S*)-**3** was found to be (*S*,*S*):(*S*,*R*):(*R*,*R*) = >99:0:0 as determined by HPLC analysis shown in Figure 1. There was no (*S*,*R*) and (*R*,*R*) isomers in **3**, which strongly evidenced that ee of (*S*)-**2** is >99% and that the hydrolysis (*S*)-**1** by excess KOH is a complete retention process of configuration of silicon atom. According to Figure 1a, composition of *meso*/DL-**3** is apparently determined as

Table 1. Polymerization Reactions with Various Feed Ratio of (*S*,*S*)-3 (AX*B$_2$) and 4 (A′B′)

entry	feed ratio (*S*,*S*)-**3**:**4**	polymer	yield (%)^a	M_n^{b}	M_w/M_n^{c}	polymer composition^d (*S*,*S*)-**3**:**4**	DB (obsd)	DB (theor)^e	$[\alpha]^{25}_D$ (deg)	T_g (°C)^f
1	100^g:0	*meso*/DL-**P1**	90	3970	1.8	100:0	0.45	0.50		26
2	100:0	**P1**	87	4320	2.1	100:0	0.43	0.50	+13.1	34
3	66:34	**P2**	89	4530	2.4	63:37	0.38	0.48	+9.8	22
4	50:50	**P3**	86	6240	2.5	49:51	0.35	0.44	+8.3	10
5	34:66	**P4**	82	6850	3.2	33:67	0.31	0.38	+5.9	−12
6	25:75	**P5**	72	9370	3.6	26:74	0.27	0.32	+4.5	−29
7	0:100	**P6**	71	4700^c	1.8	0:100				−49

(*S*,*S*):(*S*,*R*):(*R*,*R*) = 28:46:26 due to partial overlapped peaks. Hydrosilylation polymerization reactions with various feed ratios of (*S*,*S*)-**3** (AB$_2$ monomer) and **4** (A′B′ monomer) were carried out in bulk at 60−80 °C for 12 h in the presence of 0.1 mol % of Pt(0)(DVTMDS)$_2$ to give optically active hyperbranched polymers with chain end Vi functional groups (Table 1). For comparison, homopolymerization reactions of *meso*/DL-**3** and **4** were also carried out to give optically inactive hyperbranched polymer, *meso*/DL-**P1** and **P6**, respectively. All hyperbranched poly(carbosiloxane)s (**P1**−**P5**) were obtained in good yield with moderate molecular weight that does not vary significantly upon the second addition of the monomer. These results probably suggest a formation of a globular molecule for which further growth is limited by the lower reactivity of the functional group B caused by the steric hindrance in the bulky ViNpPhSi− group. As the feed ratio of **4** was increased, increase in the molecular weight was observed due to the somewhat relaxed steric hindrance.

Structure and Composition of the Hyperbranched Polymers. In no case did DEPT ^{13}C NMR spectroscopy show CH− carbon signals arisen from α-addition, indicating that the hydrosilylation reaction yielded selective *β*-addition products. A similar conclusion was reached in the reported polymerization reactions of (1*S*)-1-(1-naphthyl)-1-phenyl-1-vinyl-3,3-dimethyldisiloxane,[13c] (*S*)-allylmethylphenylsilane,[25] and (*R*)-methylphenylpropargylsilane[26] which yielded only the *β*-addition polymer. In addition, the existence of Si−H groups in **P1** was confirmed by means of ^{1}H NMR (4.51−4.83 ppm, [Si−H]:[Vi] = 1:9) and IR (2154 cm^{-1}). The apparent degree of polymerization (DP) for **P1** is calculated as about 8 (calcd M_n = 4700), which agrees with the M_n (=4320) determined by VPO. These results indicate that intramolecular cyclization of Si−H groups with Vi groups seldom took place during the polymerization and that Si−H groups at the core remain when the polymerization is terminated.

^{1}H and ^{13}C NMR spectra of **P1**−**P5** are complex and are not sensitive to analyze the polymer composition and branching structure. On the other hand, ^{29}Si NMR spectra of *meso*/DL-**P1**, **P1**, **P3**, and **P5** shown in Figure 2 gave evidence for the proposed structures in Scheme 1. ^{29}Si NMR chemical shifts of typical structures ($\mathbf{Si^1}$−$\mathbf{Si^6}$) used for the assignment of chemical shifts of polymers are listed in Table 2. ^{29}Si NMR spectrum of *meso*/DL-**P1** showed the three broad signals at around −34.4, −21.7, and −9.6 ppm and a multiplet signal at −21.1 to −18.0 ppm (Figure 2a). The chemical shifts −34.4, −21.7, and −9.6 ppm are quite close to those of $\mathbf{Si^2}$ (−33.5 ppm), $\mathbf{Si^1}$(−20.2 ppm), and $\mathbf{Si^3}$ (−10.7 ppm) in Table 2, respectively, indicating that the signals at −34.4, −21.7, and −9.6 ppm can be reasonably assigned to terminal H$\mathbf{Si^2}$Me(O−)$_2$, −O$\mathbf{Si^1}$PhNpVi, and −O$\mathbf{Si^3}$NpPhCH$_2$CH$_2$− silicon atoms in polymer structure, respectively. A rather complex multiplet signal at −21.1to −18.0 ppm arises from −CH$_2$CH$_2$$\mathbf{Si^\dagger}$Me(O−)$_2$ silicon atom of *meso*/DL-**P1**. The −CH$_2$CH$_2$$\mathbf{Si^\dagger}$Me(O−)$_2$ signals for **P1** prepared from (*S*,*S*)-**3** are split into basically well-separated three peaks at −20.1, −18.6, and −17.9 ppm (Figure 2b). This difference in the complexity of the signals between optically active- and *meso*/DL-**P1** is caused by the difference in stereochemical relation of the branching silicon atom ($\mathbf{Si^\dagger}$) sandwiched by two asymmetric silicon atoms ($\mathbf{Si^1}$ and $\mathbf{Si^3}$). The silicon atoms labeled [$\mathbf{Si^1}$ and $\mathbf{Si^3}$] and [$\mathbf{Si^2}$ and $\mathbf{Si^\dagger}$] represent the [unreacted and reacted] silicon atoms that were originally bonded to vinyl and hydrogen in the starting monomer **3**, respectively. Since the integral ratio of each silicon atoms was determined to be −O$\mathbf{Si^1}$PhNpVi:−O$\mathbf{Si^3}$NpPhCH$_2$CH$_2$−:H$\mathbf{Si^2}$Me(O−)$_2$:−CH$_2$CH$_2$$\mathbf{Si^\dagger}$Me(O−)$_2$ = 34:30:4:32, the ratio of ($\mathbf{Si^1}$ + $\mathbf{Si^3}$):($\mathbf{Si^2}$ + $\mathbf{Si^\dagger}$) was calculated as 1.8:1, which is almost in accordance with the theoretical value in the starting monomer **3** ($\mathbf{Si^1}$:$\mathbf{Si^2}$ = 2:1), indicating that **P1** has principally the proposed structure formed via the *β*-addition reaction.

Assignment of the signals of hyperbranched copolymers **P2**−**P5** consisting of various (*S*,*S*)-**3** and **4** units was also performed. Poly[(1,1,3,3-tetramethyldisiloxane-1,3-diyl)ethylene], **P6**, prepared by homopolymerization of **4** gave a sharp signal at 8.1 ppm (Figure 2e and Table 2 ($\mathbf{Si^6}$)). Therefore, signals at around 8.2 ppm of **P2**−**P5** are assignable to −O$\mathbf{Si^6}$Me$_2$CH$_2$CH$_2$− silicon atom originated from the **4** unit. The signals at around −4.1 ppm have a close chemical shift with **4** ($\mathbf{Si^4}$ = −5.8 ppm in Table 2), and the relative intensity of the signals increased with the increasing in the feed ratio of **4** (Figure 2, c vs d), indicating that signals at −4.1 ppm arise from the terminal −O$\mathbf{Si^4}$Me$_2$Vi silicon atom originated from **4** unit in **P2**−**P5**. The signal for terminal −O$\mathbf{Si^5}$Me$_2$H, originating from **4**, which should appear at −1.8 ppm ($\mathbf{Si^5}$ in Table 2), was not detected. As a consequence of the above assignment and integral ratio, the polymer composition (AB$_2$ unit:A′B′ unit) for **P2**−**P5** could be determined as 63:37 (**P2**), 49:51 (**P3**), 33:67 (**P4**), and 26:74 (**P5**) by eq 1, which almost agreed with the monomer feed ratio.

$$(S,S)\text{-}\mathbf{3}:\mathbf{4} = \frac{\mathbf{Si^1} + \mathbf{Si^2} + \mathbf{Si^3} + \mathbf{Si^\dagger}}{3} : \frac{\mathbf{Si^4} + \mathbf{Si^6}}{2} \quad (1)$$

Information regarding the sequence of (*S*,*S*)-**3** (AB$_2$) and **4** (A′B′) in polymers should be obtained by the analysis of −O$\mathbf{Si^3}$NpPhCH$_2$CH$_2$− signal of AB$_2$ and −O$\mathbf{Si^6}$Me$_2$CH$_2$CH$_2$− signal of A′B′. There are four possible monomer diad sequences **AB$_2$**−AB$_2$, **AB$_2$**−A′B′, **A′B′**−A′B′, and **A′B′**−AB$_2$ in **P2**−**P5** (Figure 3). Unfortunately, analysis of −O$\mathbf{Si^6}$Me$_2$CH$_2$CH$_2$− signal of A′B′

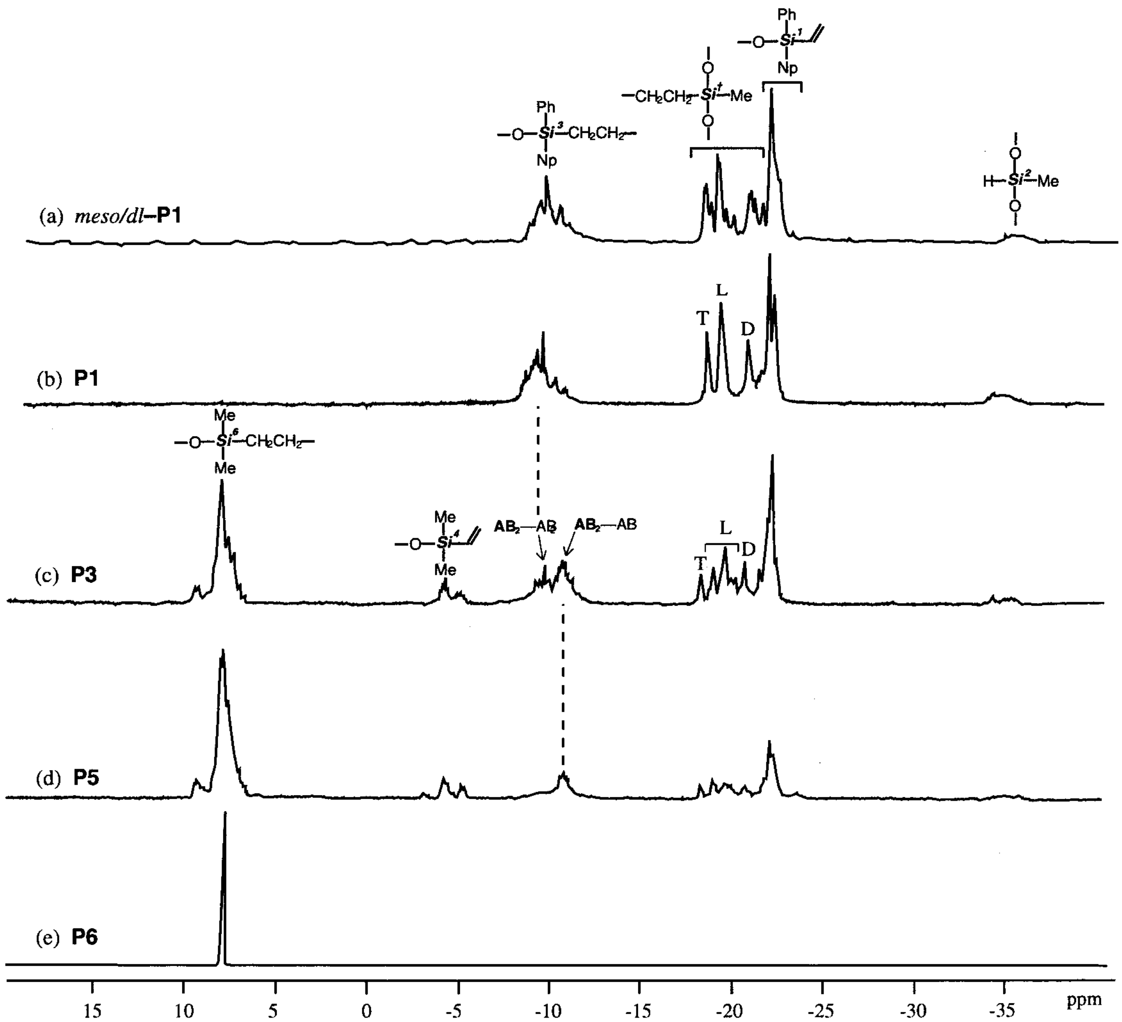


Figure 2. ^{29}Si NMR spectra of poly(carbosiloxane)s (**P1**, **P3**, **P5**, and **P6**) prepared from: (a) *meso*/DL-**3**; (b) (*S*,*S*)-**3**; (c) (*S*,*S*)-**3** and **4** (50:50); (d) (*S*,*S*)-**3** and **4** (25:75); (e) **4**.

Table 2. ^{29}Si NMR Chemical Shifts of Typical Structures

Compounds	Chemical shifts (ppm)	
ViNpPhSi^1OSi^2(Me)(H)OSi^1PhNpVi (**3**)	$Si^1 = -20.2$	$Si^2 = -33.5$
$-[OSi^3(Ph)(Np)CH_2CH_2Si(Me)_2]_n-$ [a] (**PM**)	$Si^3 = -10.4$	
ViMe$_2$$Si^4OSi^5Me_2$H (**4**)	$Si^4 = -5.8$	$Si^5 = -1.8$
$-[CH_2CH_2Si^6(Me)_2OSi^6(Me)_2]_n-$ [b] (**P6**)	$Si^6 = 8.1$	

[a] See ref 13c. [b] Prepared by homopolymerization of **4**.

did not give clear information about the sequences of **A′B′**−A′B′ and **A′B′**−AB$_2$. On the other hand, the −O**Si^3**NpPhCH$_2$CH$_2$− signal of AB$_2$ gave the information about the sequences of **AB$_2$**−AB$_2$ and **AB$_2$**−A′B′. Namely, the −OSi^{3}NpPhCH$_2$CH$_2$− signals of **P1** showed basically one broad peak at −10.2 to −8.3 ppm (Figure 2b) arisen from the **AB$_2$**−AB$_2$ sequence, whereas **P3** showed two broad peaks at −11.7 to −10.1 and −10.1 to −8.2 ppm (Figure 2c). As the feed ratio of **4** was increased, increase in the intensity of the peak at −11.7 to −10.1 ppm was observed (**P5**: Figure 2d), indicating that this peak is assignable to the **AB$_2$**−A′B′ sequence. From the integral ratio of −O**Si^3**NpPhCH$_2$CH$_2$− signals at −11.7 to −10.1 and −10.1 to −8.2 ppm, the ratio of **AB$_2$**−AB$_2$ and **AB$_2$**−A′B′ sequences (FAB$_2$−AB$_2$:FAB$_2$−A′B′) for **P2**−**P5** could be roughly determined as 64:36 (**P2**), 44:56 (**P3**), 31:69 (**P4**), and 25:75 (**P5**), which almost agreed with the both polymer composition (d[AB$_2$]: d[A′B′]) and monomer feed ratio ([AB$_2$]:[A′B′]). Namely,

$$[AB_2]:[A'B'] = X = d[AB_2]:d[A'B'] = FAB_2{-}AB_2:FAB_2{-}A'B'$$

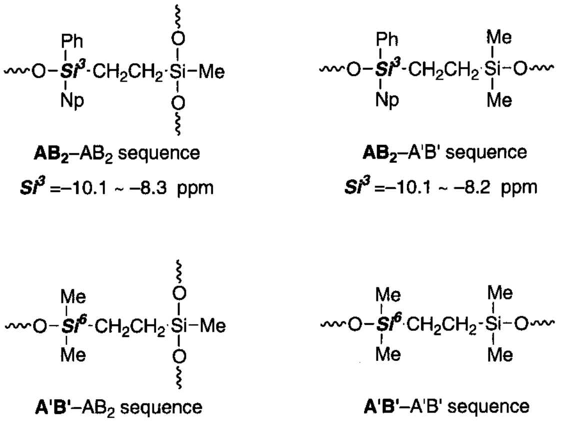


Figure 3. Structures and ^{29}Si NMR chemical shifts of possible monomer diad sequences of AB$_2$ and A′B′.

If the reactivity of each monomer is determined by the reactivity of the monomer Si−H and Vi groups as a whole, apparent reactivity of each monomer might be calculated assuming the Mayo−Lewis equation as a first

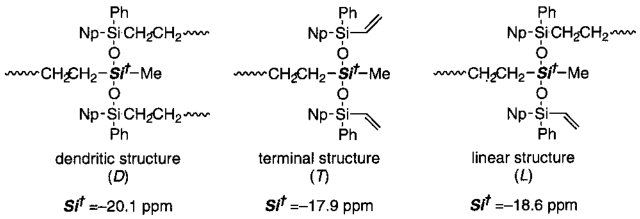


Figure 4. Possible branching structures in **P1** and their ^{29}Si NMR chemical shifts of **Si**†.

approximation. In the case $[AB_2]:[A'B'] = d[AB_2]:d[A'B']$, the feed ratio can be written as $[AB_2]:[A'B'] = X = (r_{A'B'} - 1):(r_{AB_2} - 1)$, where r indicates the monomer reactivity ratio. The composition $FAB_2-AB_2:FAB_2-A'B'$ is written as $FAB_2-AB_2:FAB_2-A'B' = d[AB_2]\cdot PAB_2-AB_2:d[AB_2]\cdot PAB_2-A'B'$. The probabilities of the formation of homo- and cross-diad sequence are defined as

$$P_{AB_2-AB_2} = r_{AB_2}X/(r_{AB_2} + 1), \quad P_{AB_2-A'B'} = 1/(r_{AB_2} + 1)$$

When these relations are substituted into the experimental fact, the following equation can be derived.

$$X = [AB_2]:[A'B'] = F_{AB_2-AB_2}:F_{AB_2-A'B'} = P_{AB_2-AB_2}:P_{AB_2-A'B'} = r_{AB_2}X$$

This relation concludes $r_{AB_2} = 1$. This also reach a conclusion of $r_{A'B'} = 1$.

Thus, AB_2 and $A'B'$, whose reactivity is determined by the Si−H and Vi functional groups, seem to have apparently almost equal overall reactivity in the polymerization. A little more insight into the relative reactivity of vinyl group can be estimated from the amount of remaining vinyl groups in the polymerization. For example, the ratio of unreacted vinyl groups for AB_2 and $A'B'$ in **P3** is $B:B' = 70:30$, which is somewhat higher than that of ratio 66:34 calculated from statistical consideration (calcd $B:B' = ([L] + 2[T]):[T_l]$, $D:L:T:L_l:T_l = 22:22:6:33:17$).[27] The vinyl group of $A'B'$ seems to have a little higher reactivity than that of AB_2. The apparently equal reactivity of AB_2 and $A'B'$ in the polymerization may indicate higher reactivity of the Si−H group of AB_2 than that of $A'B'$.

Degree of Branching. The information about the branching structures for **P1** was obtained by ^{29}Si NMR analysis of $-CH_2CH_2\mathbf{Si}^{\dagger}Me(O-)_2$ signals at −20.1, −18.6, and −17.9 ppm, reflecting the branching structures such as dendritic (D), terminal (T), and linear (L) units as shown in Figure 4. To clarify the branching structure, some model compounds (D-model, T-model, and L-model) were synthesized as shown in Scheme 3. The hydrosilylaion reaction of (*S*,*S*)-**3** with large excess trimethylvinylsilane afforded T-model as the *β*-addition product in 91% yield after purification. Similarly, hydrosilylation reactions of T-model with a large excess of 1,1,1,3,5,5,5-heptamethyltrisiloxane (**5**) afforded D-model in 77% yield after purification, whereas the use of 1.0 equiv of **5** afforded a mixture of L-model, T-model, and D-model compounds. The obtained D-model, T-model, and L-model compounds were used as models for D, T, and L units, respectively. ^{29}Si NMR spectra of branching silicon atom **Si**† region of T-model, D-model, and a mixture of L-model, T-model, and D-model compounds are shown in Figure 5. The **Si**† signals for T-model (**Si**†, Figure 5a) and D-model (**Si**†, Figure 5c) appeared at −17.8 and −19.1 ppm, respectively. In addition, **Si**† signals for a mixture of L-model, T-model, and D-model compounds appeared at −17.8, −18.3, and −19.1 ppm, indicating that the signal at −18.3 ppm can be attributed to L-model **Si**† atom (Figure 5b). Examination of the ^{29}Si NMR spectrum of **P1** reveals good correlation between the chemical shifts of branching silicon atoms **Si**† for model compounds and the three peaks observed at −17.9, −18.6, and −20.1 ppm for **P1**.

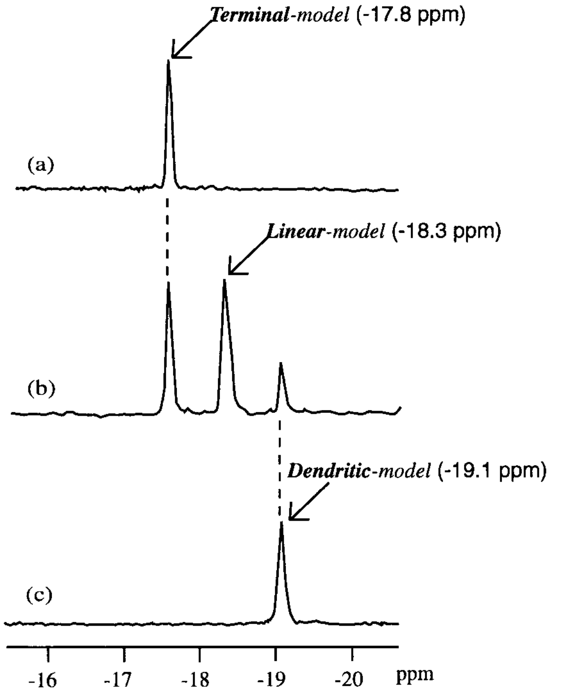
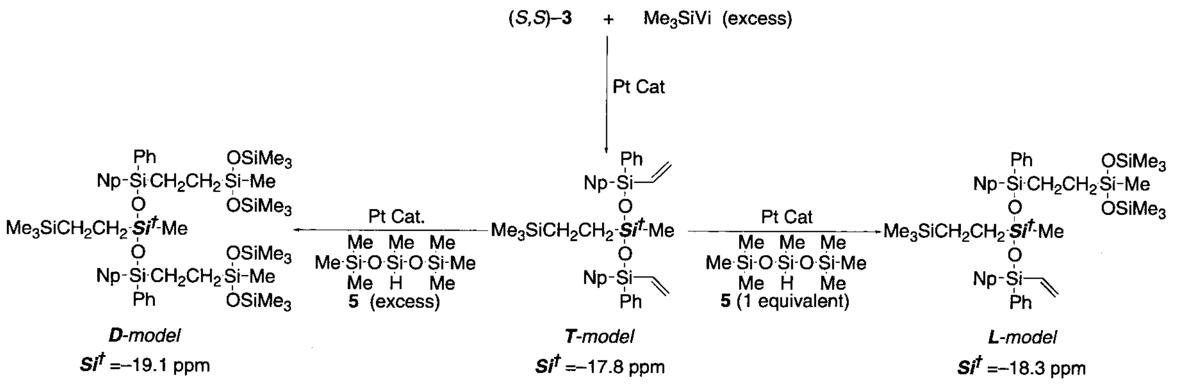


Figure 5. ^{29}Si NMR spectra of branching silicon atoms **Si**† of model compounds: (a) D-model; (b) mixture of L-model, T-model, and D-model; (c) D-model.

Scheme 3. Model Compounds for Branching Structures in Figure 4 and Their ^{29}Si NMR Chemical Shifts of Si†



The relative percentages of each branching silicon atom can be determined by assigning these signals to the corresponding silicon atoms of the T (−17.9 ppm), D (−20.1 ppm), and L (−18.6 ppm) units in **P1**, respectively. The relative percentage of T:L:D in **P1** is found to be 20:57:23 by the integral ratio of three peaks at −17.9, −18.6, and −20.1 ppm. The degree of branching (DB)[28] of hyperbranched polymers is defined as eq 2.

$$\mathrm{DB}_{\mathrm{AB}_2} = \frac{\mathrm{T} + \mathrm{D}}{\mathrm{T} + \mathrm{L} + \mathrm{D}} \tag{2}$$

From the ratio of T:L:D, DB's for **P1** and *meso*/DL-**P1** were determined to be 0.43 and 0.45, respectively. The DB's of **P2**−**P5** were determined by integral ratio of the signals of the five different branching units such as T, D, L, $\mathrm{L_l}$ ($-\mathrm{O}\mathbf{Si^6}\mathrm{Me_2CH_2CH_2}-$), and $\mathrm{T_l}$ ($-\mathrm{O}\mathbf{Si^4}\mathrm{Me_2Vi}$) based on eq 3.[28,29]

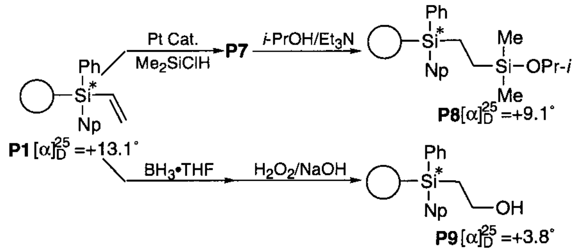
$$\mathrm{DB}_{\mathrm{AB}_2/\mathrm{AB}} = \frac{\mathrm{T} + \mathrm{D}}{\mathrm{T} + \mathrm{L} + \mathrm{D} + \mathrm{L_l}} \tag{3}$$

The DB's were determined as 0.38 (**P2**), 0.35 (**P3**), 0.31, (**P4**), and 0.27 (**P5**), which are somewhat smaller than the theoretical value[27,28] in Table 1. The difference in DB between observed and theoretical values is most likely the result of the lower reactivity of Vi groups in ViNpPhSi− groups of $\mathrm{AB_2}$ compared with that of $\mathrm{ViMe_2Si}-$ groups of A′B′, especially, the reactivity of the second ViNpPhSi− groups (L-structure) is considered lower to form dendritic structure owing to the larger steric hindrance caused by already formed polymer chain.

Chiroptical Properties of the Hyperbranched Polymers. All polymers were also characterized concerning their optical rotation power in chloroform. **P2**−**P5** showed the optical rotation [α] with the same positive sign as the (*S*,*S*)-**3** used for polymerization. This is in accordance with the expectation that in hydrosilylation polymerization proceeded with 100% retention of configuration, in which chiral silicon center remains unaffected.[13c,25] As feed ratio of **4** was increased, decrease in the value of [α] was observed due to the existence of higher achiral fraction in the polymer (optical dilution effect).

The absolute value of [α] (13.1°) observed for **P1** having 14−16 chiral silicon atoms is higher than that of monomer (6.9°) and linear poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene] (**PM**)[13b] having 17−18 chiral silicon atoms (8.5°, M_n = 5900, M_w/M_n = 1.15). This behavior is different from optically active hyperbranched poly(glycerol)s with narrow polydispersities (M_w/M_n < 1.5) of which absolute values of [α] are almost similar to that of monomer and linear polymers;[11] e.g., each chiral center behaves like an isolated molecule. One possibility of the difference in absolute values of [α] between **P1**, (*S*,*S*)-**3**, and **PM** is the formation of local chiral conformations inside the **P1**. To clarify this point, CD spectrum of **P1** was measured, but the Cotton effect of **P1** was not observed. Therefore, chiroptical properties of **P1** seem to be generated by the effect of irregular pattern of branching, e.g., local environments are quite distinct at the each chiral center. However, a more detailed study is needed by using [Φ]/*n* (molar optical rotation divided by number of optically active units) of **P1** with various molecular weight.

Scheme 4



Thermal Properties. The effect of the optical activity, polymer composition, and branching structure on thermal properties of **P1**−**P5** can be demonstrated by means of DSC analysis. As listed in the last column in Table 1, all hyperbranched polymers exhibited only one glass transition temperature without any other transitions. Different T_g's of 34 and 26 °C for **P1** and *meso*/DL-**P1** were observed, respectively. It is considered that the T_g's of **P1** and *meso*/DL-**P1** were influenced by the difference in the stereochemical structure (optical activity) of the polymers. As expected, significant decrease in T_g was observed for **P2**−**P5** with increasing in composition of **4** in polymer, indicating that this is due to the effect of introducing flexible Si−O−Si linkages into hyperbranched polymer backbone. The T_g of **P1** (34 °C) was significantly lower than that of **PM** (M_n = 11 300, M_w/M_n = 1.12, 47 °C), suggesting that branching structure have made the polymer chain more compact compared with linear structure having the same molecular weight.

End Functionalization. One of the most appealing characteristics of hyperbranched polymers (**P1**−**P5**) is the possibility to functionalize their terminal Vi groups. End functionalization of **P1** was accomplished by using either hydrosilylation or hydroboration as illustrated in Scheme 4. Hydrosilylation reaction of **P1** with dimethylchlorosilane was carried out at room temperature for 12 h in the presence of $\mathrm{Pt(0)(DVTMDS)_2}$ to give new hyperbranched polymer (**P7**) having Si−Cl groups that are amenable to further modification with a variety of nucleophilic reagents. To determine the degree of functionalization (*f*), Si−Cl end functional groups of **P7** were capped with excess 2-propanol, and *f* of the resulting polymer (**P8:** M_n = 4910 (VPO), $[\alpha]^{25}_{\mathrm{D}} = +9.1°$) was found to be 72% as determined by the integral ratio of remaining vinyl (5.47−6.53 ppm) and methine (3.77 ppm) protons in ^{1}H NMR.

Hydroboration reaction has been used frequently for quantitative hydroxylation of carbon double bonds of dendrimers to give dendritic polyols as the precursor for liquid crystalline dendrimers.[30] Hydroboration reaction of **P1** with the $\mathrm{BH_3{\cdot}THF}$ complex was carried out at room temperature for 12 h to give new hyperbranched polymer having −OH groups (**P9**) in good yield without cleavage of siloxane bond. Evidence for the existence of hydroxy group was given by IR (−OH: 3418 cm^{-1}). The *f* of the **P9** (M_n = 4410 (VPO), $[\alpha]^{25}_{\mathrm{D}} = +3.8°$) was found to be 89% as determined by the integral ratio of remaining vinyl (5.47−6.63 ppm) and methylene (3.22−3.66 ppm) protons in ^{1}H NMR.

Conclusions

The first example of optically active hyperbranched poly(carbosiloxane)s (**P1**−**P5**) by the hydrosilylation polymerization reactions with various feed ratios of optically pure (*S*,*S*)-1,5-di(1-naphthyl)-1,5-diphenyl-1,5-

divinyl-3-methyltrisiloxane (**3**) ($>$99% ee) and 1,1,3,3-tetramethyl-1-vinyldisiloxane (**4**) was demonstrated. Use of an optically pure (S,S)-**3** for the polymerization allowed quantitative evaluation of hyperbranched structure of polymers by means of ^{29}Si NMR analysis. The values of DB (degree of branching) of the polymers (**P1**−**P5**) are 0.27−0.43. End functionalization of the terminal vinyl groups (Vi) was demonstrated by using either hydrosilylation or hydroboration, affording optically active hyperbranched poly(carbosiloxane)s having silyl chloride groups (**P7**: Si−Cl, degree of functionalization = 72%) or hydroxy groups (**P9**: degree of functionalization = 89%).

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Supporting Information Available: Characterization data and experimental procedures for compounds **P2**−**P6**, **P9**, D-model, and L-model. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For recent reviews, see: (a) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99,* 1665. (b) Newkome, G.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99,* 1689. (c) Fisher, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38,* 885. (d) Fréchet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci., Pure Appl. Chem.* A **1996**, *33,* 1399. (e) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165,* 193.

(2) For recent reviews, see: (a) Sunder, A.; Heinemann, J.; Frey, H. *Chem. Eur. J.* **2000**, *6,* 2499. (b) Feast, W. J.; Cacialli, F.; Daik, R.; Friend, R. H.; Herzog, E.; Heywood, B. R.; Hobson, L.; Megson, J. L.; Snowden, D. *Macromol. Symp.* **1999**, *143,* 81. (c) Kim, Y. H. *Polym. Mater. Sci. Eng.* **1999**, *80,* 61. (d) Malmstroem, E.; Hult, A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37,* 555. (e) Turner, S. R. *Polym. Mater. Sci. Eng.* **1995**, *73,* 77. (f) Voit, B. I.; Turner, S. R. *Angew. Makromol. Chem.* **1994**, *223,* 13.

(3) For examples, see: (a) Kleij, A. W.; Gossage, R. A.; Jastrzebski, J. T. B. H.; Boersama, J.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39,* 176. (b) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature (London)* **1998**, *391,* 161. (c) Jansen, J. F. G. A.; de Brabander van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266,* 1226. (d) Fréchet, J. M. J. *Science* **1994**, *263,* 1710.

(4) Flory, P. J. In *Principles of Polymer Chemistry*; Cornnel University Press: Ithaca, NY, 1953.

(5) For examples, see: (a) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, C.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19,* 2466. (b) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, C.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17,* 117. (c) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50,* 2003.

(6) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112,* 7638.

(7) For examples, see: (a) Kadokawa, J.; Kaneko, Y.; Yamada, S.; Ikuma, K.; Tagaya, H.; Chiba, K. *Macromol. Rapid Commun.* **2000**, *21,* 362. (b) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32,* 4240. (c) Fréchet, J. M. J.; Hemmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269,* 1080. (d) Hawker, C. J.; Fréchet, J. M. J.; Grubss, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117,* 10763. (e) Suzuki, M.; Ii, A.; Saegusa, T. *Macromolecules* **1992**, *25,* 7071.

(8) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74,* 2718.

(9) For examples, see: (a) Peerlings, H. W. I.; Struijk, M. P.; Meijer, E. W. *Chirality* **1998**, *10,* 46. (b) Thomas, C. W.; Tor, Y. *Chirality* **1998**, *10,* 53. (c) Seebach, D.; Rheiner, P. B.; Greiveldinger, G.; Butz, T.; Sellner, H. *Top. Curr. Chem.* **1998**, *197.* (d) McElhanon, J. R.; McGrath, D. V. *J. Am. Chem. Soc.* **1998**, *120,* 1647. (e) Peerlings, H. W. I.; Meijer, E. W. *Chem. Eur. J.* **1997**, *3,* 1563. (f) Chang, H.-T.; Chen, C.-T.; Kondo, T.; Siuzdak, G.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35,* 182. (g) Jansen, J. F. G. A.; Peerlings, H. W. I.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34,* 1206.

(10) Brunner, H.; Altmann, S. *Chem. Ber.* **1994**, *127,* 2285.

(11) Sunder, A.; Mülhaupt, R.; Haag, R.; Frey, H. *Macromolecules* **2000**, *33,* 253.

(12) (a) Oishi, M.; Moon, J.-Y.; Janvikul, W.; Kawakami, Y. *Polym. Int.* **2001**, *50,* 135. (b) Oishi, M.; Kawakami, Y. *Macromolecules* **2000**, *33,* 1960. (c) Oishi, M.; Moon, J.-Y.; Shirakawa, E.; Kawakami, Y. *Polym. J.* **2000**, *32,* 980. (d) Oishi, M.; Kawakami, Y. *Org. Lett.* **1999**, *1,* 549.

(13) (a) Murano, M.; Li, Y.; Kawakami, Y. *Macromolecules* **2000**, *33,* 3940. (b) Li, Y.; Kawakami, Y. *Macromolecules* **1999**, *32,* 548. (c) Li, Y.; Kawakami, Y. *Macromolecules* **1998**, *31,* 5592.

(14) For examples, see: (a) Xiao, Y.; Wong, R. A.; Son, D. Y. *Macromolecules* **2000**, *33,* 7232. (b) Schlenk, C.; Kleij, A. W.; Frey, H.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39,* 3445. (c) Lach, C.; Frey, H. *Macromolecules* **1998**, *31,* 2381. (d) Whitmarsh, C. K.; Interrante, L. V. *Organometallics* **1991**, *10,* 1336.

(15) Muzafarov, A. M.; Golly, M.; Möller, M. *Macromolecules* **1995**, *28,* 8444.

(16) For examples, see: (a) Miravet, J. F.; Fréchet, J. M. J. *Macromolecules* **1998**, *31,* 3461. (b) Rubinsztajn, S.; Stein, J. *J. Inorg. Organomet. Polym.* **1995**, *5,* 43. (c) Rubinsztajn, S. *J. Inorg. Organomet. Polym.* **1994**, *4,* 61. (d) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113,* 4043.

(17) (a) Paulasaari, J. K.; Weber, W. P. *Macromolecules* **2000**, *33,* 2005. (b) Paulasaari, J. K.; Weber, W. P. *Macromol. Chem. Phys.* **2000**, *201,* 1585.

(18) Marciniec, B. In *Comprehensive Handbook on Hydrosilylation;* Pergamon: New York, 1993.

(19) (a) Oishi, M.; Kawakami, Y. *Polym. J.* **2001**, *33,* 765. (b) Chandra, G.; Lo, P. Y.; Hitchcock, P. B.; Lappert, M. F. *Organometallics* **1987**, *6,* 191. (c) Karstedt, B. D. U.S. Patent 3,775 452, 1973.

(20) Corriu, R. J. P.; Royo, G. *J. Organomet. Chem.* **1968**, *14,* 291.

(21) Shintani, K.; Ooi, O.; Mori, A.; Kawakami, Y. *Polym. Bull. (Berlin)* **1996**, *37,* 705.

(22) Exchange reaction between the 2-propoxy group attached to silicon atom and methanol did not occur during the reprecipitation procedure, since ^{1}H NMR spectrum of **P8** did not show methoxy peak.

(23) The de was determined by means of HPLC analysis (Daicel Chem. Ind., CHIRALCEL OD, *n*-hexane as an eluent, 0.4 mL/min, 254 nm).

(24) Sommer, L. H.; Frey, C. L.; Parker, G. A. *J. Am. Chem. Soc.* **1964**, *86,* 3276.

(25) (a) Kawakami, Y.; Takahashi, T.; Yada, Y.; Imae, I. *Polym. J.* **1998**, *30,* 1001. (b) Kawakami, Y.; Takeyama, T.; Ooi, O.; Komuro, K. *Macromolecules* **1998**, *31,* 551.

(26) Kawakami, Y.; Nakao, K.; Shinke, S.; Imae, I. *Macromolecules* **1999**, *32,* 6874.

(27) (a) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48,* 30. (b) Kim, Y. H. *Macromol. Symp.* **1994**, *77,* 21. (c) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113,* 4583.

(28) Frey, H.; Höltre, D. *Acta Polym.* **1999**, *50,* 67.

(29) Möck, A.; Burgath, A.; Hanselmann, R.; Frey, H. *Macromolecules* **2001**, *34,* 7692.

(30) (a) Terunuma, D.; Kato, T.; Nishio, R.; Matsuoka, K.; Kuzuhara, H.; Aoki, N.; Noshira, H. *Chem. Lett.* **1998**, 59. (b) Lorenz, K.; Hölter, D.; Frey, H.; Stühn, B. *Polym. Mater. Sci. Eng.* **1997**, *77,* 168. (c) Lorenz, K.; Hölter, D.; Stühn, B.; Mülhaupt, R.; Frey, H. *Adv. Mater.* **1996**, *8,* 414. (d) Frey, H.; Lorenz, K.; Mülhaupt, R.; Rapp, U.; Mayer-Posner, F. J. *Macromol. Symp.* **1996**, *102,* 19. (e) Lorenz, K.; Mülhaupt, R.; Frey, H.; Rapp, U.; Mayer-Posner, F. J. *Macromolecules* **1995**, *28,* 6657.

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