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SYNTHESIS AND POLYMERIZATION OF SILYLETHYLENE CONTAINING A STEREOGENIC SILICON CENTER

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Abstract—Hydrosilylation of acetylene with a chiral silane, *R*-(+)-methyl-1-naphthylphenylsilane [*R*-(+)-MeNpPhSi*H], in the presence of $H_2PtCl_6 \cdot xH_2O$ proceeds with retention of the configuration of the stereogenic silicon center and produces a chiral vinylsilane or silylethylene [*S*-(+)-MeNpPhSi*Vi] of high optical purity under mild conditions (50°C) in high chemical yield (85%). Anionic polymerizations of the chiral silylethylene monomer by an achiral initiator *n*-BuLi yield optically active polymers with $[\alpha]_D^{20}$ up to −28.1°, while polymerizations of the racemic monomer by a chiral initiator *n*-BuLi/(−)-sparteine produce polymers with $[\alpha]_D^{20}$ up to +275°. Thus the sign of optical rotation of the polymers can be controlled by different combinations of monomer and catalyst. The magnitude of the optical rotation can be "tuned" by changing the polymerization temperature, with high temperature generally favoring random propagation. All the polymers have low polydispersity indexes (M_w/M_n down to 1.02) or possess narrow molecular weight distributions. Spectroscopic characterization confirms the molecular structure of the polymers to be poly(silylethylene), that is, a polyethylene main chain with a bulky methyl-1-naphthylphenylsilyl side chain. The polymers are thermally stable (onset temperature for weight loss in air: 380°C) and possess a high glass transition temperature (T_g > 380°C).

INTRODUCTION

While great research efforts have been devoted to chiral carbon chemistry, chiral silicon chemistry has received much less attention, and optically active polymers containing stereogenic silicon centers are almost unknown [1–3]. Optically active polymers possess many unique properties which are often difficult or impossible to achieve with optically inactive polymers. For example, optically active polymers are promising candidates for "molecular electronics" materials such as ferroelectric liquid crystals, nonlinear optical assemblies, optical data storage media, etc. [4]. The world's pharmaceutical industry is moving towards manufacturing chiral drugs, and chiral packing materials or stationary phases for chromatographic separation are in great demand. Because of the special importance of organosilicon materials in chromatographic analysis, optically active silicon polymers may find a wide range of applications as chiral stationary phases in the GC- and especially HPLC-based enantioseparation of racemic drug mixtures [5, 6].

We are interested in synthesizing optically active polymers containing stereogenic silicon centers. In 1989, we prepared a chiral silicon-containing polyacetylene and discovered a novel electro-optical application for the optically active polymer in a liquid crystal display system [7–9]. In our previous work, we incorporated the chiral methyl-1-naphthylphenylsilyl group into the acetylene monomer via an alkyl spacer. In this work, we synthesized a chiral silicon-containing vinyl monomer, *S*-(+)-MeNpPhSi*Vi, by direct reaction of a chiral silane with acetylene via platinum-catalyzed hydrosilylation. We here demonstrate that we can synthesize optically active poly(silylethylene)s by polymerizing either the chiral monomer using an achiral initiator (*n*-BuLi) or the corresponding racemic monomer using a chiral initiator [*n*-BuLi/(−)-sparteine].

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EXPERIMENTAL

Materials

Toluene, tetrahydrofuran (THF), dioxane, diethyl ether, and hexane were purchased from Aldrich, dried over molecular sieves, and distilled from sodium benzophenone ketyl immediately prior to use. Chloroform and dichloromethane (both Aldrich) were dried over calcium chloride and distilled from calcium hydride. (*S*, *S*)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (DDB), (+)-camphene, (−)-sparteine (all Aldrich), and dimethoxymethylphenylsilane (United Chemical Technologies) were distilled from calcium hydride. Acetylene gas (Hong Kong Oxygen) was purified by bubbling through sulfuric acid during use. *n*-Butyl lithium, hydrogen hexachloroplatinate (IV) hydrate, 1-bromonaphthalene, (1*R*, 2*S*, 5*R*)-(−)-menthol, lithium aluminium hydride, palladium on activated carbon (Pd 10%), magnesium turnings, and silica gel were all purchased from Aldrich and used as received.

Equipment

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques in vacuum line systems or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the resulting polymers, which was done in an open atmosphere. The 300-MHz ^{1}H NMR spectra were recorded on a Brucker ARX300 spectrometer in deuterated chloroform solutions with or without added tetramethylsilane (TMS). Chemical shifts were reported in parts per million (ppm) on the δ scale referenced to TMS or chloroform, and coupling constants (J) were expressed in Hz. Mass spectra were obtained with the use of a Finnigan TSQ7000 triple quadrupole mass spectrometer operating in an electron impact (EI) or a chemical ionization (CI) mode. FTIR spectra were recorded on Perkin-Elmer 16PC spectrophotometer using KBr pellets or liquid films. Optical rotation was measured on a Perkin-Elmer 241 polarimeter using a sodium D line in hexane, THF, or dioxane solutions. Molecular weights of the polymers were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Waters 510 HPLC pump, a Rheodyne 7725i injector with a stand kit, a set of Styragel columns covering molecular weights down to 100 g/mol, a column temperature controller, a Waters 486 tunable UV/VIS detector, a Waters 410 differential refractometer, and a system DMM/scanner with an 8 channel scanner option. All the polymer solutions were prepared in THF (ca. 2 mg/ml) and filtered through 0.45 μm PTFE syringe-type filters, before being injected into the GPC system. THF was used as eluent at a flow rate of 1.0 ml/min. The column temperature was maintained at 40°C and the working wavelength of the UV/VIS detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) were used for calibration purposes. A DuPont 951 thermogravimetric analyzer (TGA) and a DuPont 901 differential scanning calorimeter (DSC) equipped with a Thermal Analyst 2100 System were used to study the thermal behavior of the polymers at a heating rate of 10°C/min in air or under nitrogen.

Monomer synthesis

Racemic methyl-1-naphthylphenylsilane (MeNpPhSiH) was prepared by coupling $MePhSi(OMe)_2$ with 1-naphthylmagnesium bromide followed by reduction with $LiAlH_4$ according to Sommer's procedure [10]. The chiral silane *R*-(+)-MeNpPhSi*H was prepared by converting the racemic silane to diastereomeric methyl-1-naphthylphenyl-(−)-menthoxysilanes followed by reduction of one of the resolved diastereomers (−)-MeNpPhSi*-(−)-OMen by $LiAlH_4$ [11]. The racemic silylethylene monomer MeNpPhSiVi was prepared by a Pt-catalyzed hydrosilylation according to Gevorgyan's procedure [12].

The preparation of the chiral silylethylene *S*-(+)-MeNpPhSi*Vi by hydrosilylation has not been reported and we thus carried out hydrosilylation of acetylene by the chiral silane *R*-(+)-MeNpPhSi*H and fully characterized the reaction product spectroscopically. A 1.0 g sample of *R*-(+)-MeNpPhSi*H [$[\alpha]_D^{20}$ + 31.4° (*c* 0.90, cyclohexane)] was dissolved in 10 ml toluene, to which 1 mg of $H_2PtCl_6 \cdot xH_2O$ was added. Acetylene gas was freed from acetone by passing through two Drechsel bottles half-filled with concentrated sulfuric acid, and bubbled through the silane solution at 50°C until no unreacted silane was detected by TLC analysis. After removal of the solvent, the product was first isolated by a silica-gel column using hexane as eluent and further purified by distillation under reduced pressure (132–134°C/0.075 mmHg). Yield: 0.93 g (85%). $[\alpha]_D^{20}$ + 1.21° (*c* 8.40, hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (TMS, ppm) 0.78 (s, 3H, Si-CH_3), 5.82 (dd, 1H, *a*-H, J_{ac} 16.5 Hz, J_{ab} 3.3 Hz), 6.21 (dd, 1H, *b*-H, J_{bc} 1.08 Hz, J_{ab} 3.3 Hz), 6.64 (dd, 1H, *c*-H, J_{bc} 10.8, J_{ac} 16.5 Hz), 7.33–7.96 (m, 12H, Si-C_6H_5, Si-$C_{10}H_7$). Positive-ion CI-MS (NH_3) *m/z*: 275.1 (MH^+), 259.1 (M^+-CH_3), 247.1 (M^+-$CH{=}CH_2$), 196.1 (M^+-Ph), 147.1 (M^+-Np).

Polymerization

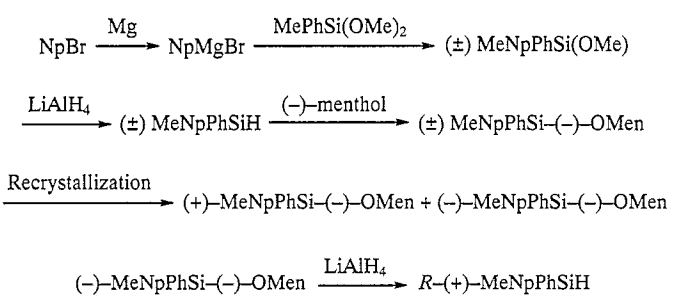
All polymerization reactions were conducted in Schlenk tubes under an atmosphere of oxygen-free dry nitrogen. In a typical run, 0.63 ml of a 1.6 M hexane solution of *n*-BuLi was admixed with 4.37 ml of freshly distilled toluene in a baked 10-ml Schlenk tube. In another Schlenk tube a monomer solution was prepared by dissolving 0.55 g of *S*-(+)-MeNpPhSiVi in 0.44 ml toluene, to which 0.5 ml of the pre-prepared catalyst solution was added using an hypodermic syringe. After stirring at 40°C under nitrogen for 24 hr, the polymerization was terminated by adding one drop of methanol to the reaction mixture. After diluting with 3 ml of toluene, the reaction mixture was added to a large amount (30 ml) of methanol with stirring. The precipitated polymer was filtered through a fine glass filter and dried under vacuum to a constant weight. White powder; yield: 0.16 g (29%). M_n (by GPC on the basis of a polystyrene calibration): 3220; M_w/M_n: 1.04. $[\alpha]_D^{20}$ − 28.1° (*c* 1.25, THF). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) −0.8–2.5 (br, aliphatic protons in CH_3, CH_2, and CH), 5.8–8.3 (br, aromatic protons in Ph and Np).

RESULTS AND DISCUSSION

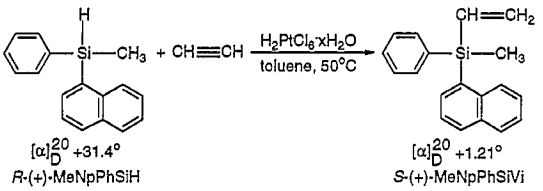
Stereochemistry in hydrosilylation

While addition of various silanes to alkynes has been extensively studied, there have been no reports on hydrosilylation of alkynes by optically active silanes [12, 13]. In 1992, Gevorgyan *et al.* carried out hydrosilylation of alkynes by racemic MeNpPhSiH in the presence of Pt catalysts [12], but the stereochemistry of the hydrosilylation remains unknown because of the racemic nature of the silane starting material they used. Hydrosilylation of alkynes by chiral silanes would lead to a variety of optically active silylalkene monomers, and it is of interest to know whether the reactions proceed with retention or inversion of the configuration of the stereogenic silicon center. We thus prepared a chiral silane *R*-(+)-MeNpPhSi*H according to Sommer and Holt's procedures [10, 11], which involve the following five steps: (i) coupling of dimethoxymethylphenylsilane with 1-naphthylmagnesium bromide; (ii) reduction of methoxymethylphenylsilane by $LiAlH_4$; (iii) diastereomerization of racemic MeNpPhSiH by (1*R*, 2*S*, 5*R*)-(−)-menthol; (iv) resolution of the diastereomers by recrystallization; and (v) reduction of one of the resolved diastereomers by $LiAlH_4$ (Scheme 1). Optical rotation of the resulting *R*-(+)-MeNpPhSi*H was found to be +31.4°, close to the value (+34.6°) reported by Sommer [14].

Gevorgyan used a H_2PtCl_6(cyclohexanone) complex to catalyze the hydrosilylation of acetylene by the racemic silane MeNpPhSiH. We directly used a commercially available $H_2PtCl_6 \cdot xH_2O$ catalyst to hydrosilylate acetylene by the chiral silane (Scheme 2). The reaction went smoothly under mild heating (50°C) and an optically active silylethylene was obtained in high yield (85%). Optical rotation of the silylethylene was found to be +1.21°. According to Corriu and Royo's correlation [15], the absolute configuration of the silylethylene is *S*; that is, the hydrosilylation proceeds with retention of the configuration of the stereogenic center. Corriu and Royo prepared the *S*-(+)-MeNpPhSi*Vi by coupling



Scheme 1



Scheme 2

(−)-NpPhViSi*Cl with MeMgI, and the optical rotation value of their product was +0.75° [15]. They also carried out reactions of MeLi with (+)-NpPhViSi*H, (+)-NpPhViSi*OMe and (+)-NpPhViSi*F, and the optical rotation values of the resulting *R*-(−)-MeNpPhSi*Vi were −1.0, −0.6 and −0.55, respectively [15]. Although the starting material we used was not 100% optically pure (vide supra), the hydrosilylation product had a higher $[\alpha]_D^{20}$ value than those prepared by Corriu and Royo using the above-mentioned reactions, implying that insertion of the Pt center into the Si*–H bond proceeds with a high degree of retention of configuration at Si* and that product formation also takes place in a highly stereospecific manner. In other words, the hydrosilylation is a better way for preparing the chiral silylethylene with higher optical purity.

Polymerization of chiral monomer by achiral initiator

We first used the racemic silylethylene monomer MeNpPhSiVi to test polymerization conditions. We attempted to polymerize the monomer using typical radical initiators such as AIBN and BPO, but failed to obtain even a trace amount of polymeric product either in bulk or in solution over a wide temperature range. The monomer was not susceptible to radical polymerization. *n*-BuLi is a commonly used initiator for anionic polymerization. We tried to polymerize the silylethylene at low temperature (−78 to 0°C), but again failed to isolate any polymeric product. However, when we carried out the anionic polymerization at 20°C for 24 hr, a methanol-insoluble, white powdery polymer was isolated in 48% yield (Table 1, no. 2). GPC analysis of the polymer gave a sharp peak, from which M_n and M_w/M_n of the polymer were estimated (relative to polystyrene) to be 8933 and 1.14, respectively. When we increased the polymerization temperature to 55°C, the polymer yield increased to 87% and the polydispersity index decreased to 1.03. Further increase in the polymerization temperature further increased the polymer yield and narrowed the molecular weight distribution, although M_n of the polymer decreased undesirably.

It has become clear that the silylethylene monomer undergoes *n*-BuLi-initiated anionic polymerization at around ambient temperatures. We thus investigated anionic polymerization of the chiral monomer by the achiral initiator. The chiral monomer did undergo polymerization at 25°C but, much to our surprise, both the yield and M_n of the polymer were rather low. However, the polymer was optically active, and its $[\alpha]_D^{20}$ was found to be −15.8° (Table 1, no. 5). Both the polymer yield and M_n increased when the polymerization temperature was increased to 40°C and, even better, the polymer had a narrower molecular weight distribution and a higher optical rotation value. Further increase in temperature, however, had undesirable effects on the polymerization reaction: the polymer yield and M_n decreased, the polydispersity broadened, and the optical rotation also decreased. This is probably due to the instability of the active center at the high temperature, which favors random polymerization and lowers tacticity of the resulting polymer. It is noteworthy that the polymerization behavior of the chiral monomer was markedly different from that of its racemic counterpart. Further study on the reaction mechanisms should help us understand the stereochemistry involved in the polymerizations.

Polymerization of racemic monomer by chiral initiator

It is attractive to synthesize optically active polymers from racemic monomers by chiral

Table 1. Anionic polymerization of (methyl-1-naphthylphenylsilyl)-ethylene initiated by *n*-BuLi[a]

No.	Temperature (°C)	Yield (%)	M_n[b] (g/mol)	M_w/M_n[b]	$[\alpha]_D^{20}$[c] (°)
Racemic monomer					
1	0	0			
2	20	48	8933	1.14	
3	55	87	5490	1.03	
4	60	93	4118	1.02	
Chiral monomer[d]					
5	25	15	927	1.14	−15.8
6	40	29	3220	1.04	−28.1
7	55	27	1006	1.27	−9.5

[a]In toluene for 24 hr; $[M]_0 = 2$ M, [catalyst] = 0.1 M.
[b]Determined by GPC on the basis of polystyrene calibration.
[c]In THF.
[d]$[\alpha]_D^{20} + 1.21°$.

Table 2. Anionic polymerization of (methyl-1-naphthylphenylsilyl)-ethylene initiated by chiral catalysts[a]

No.	Temperature (°C)	Yield (%)	M_n[b] (g/mol)	M_w/M_n[b]	$[\alpha]_D^{20}$[c] (°)
n-BuLi/(+)-DDB[d]					
1	20	0			
2	40	0			
n-BuLi/(+)-camphene					
3	20	20	1237	1.23	0
4	40	56	1481	1.26	0
n-BuLi/(−)-sparteine					
5	20	21	nd[e]	nd[e]	+275[f]
6	40	50	4349	1.06	+1.7
7	60	83	4751	1.04	0

[a]In toluene for 24 hr; $[M]_0$ = 2 M, [*n*-BuLi] = 0.1 M, [R*] = 0.12 M.
[b]Determined by GPC on the basis of polystyrene calibration.
[c]In THF except no. 5.
[d](*S*, *S*)-(+)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane.
[e]Not determined (insoluble in THF).
[f]For dioxane-soluble fraction.

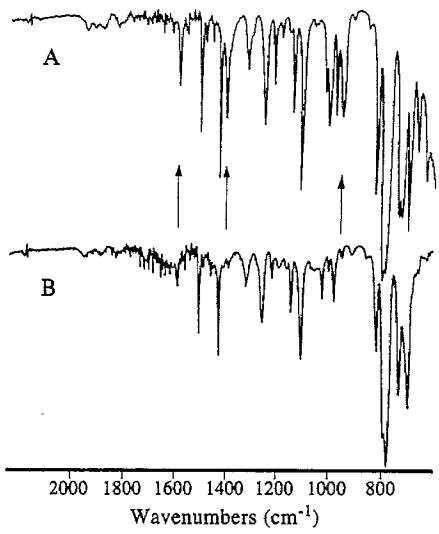


Fig. 1. IR spectra of (A) (methyl-1-naphthylphenylsilyl)ethylene monomer and (B) its polymer (KBr, RT; sample from Table 1, no. 2).

initiators. *n*-BuLi/(+)-DDB is an effective chiral initiator for the stereoelective polymerization of some methacrylates [16], but did not work for the polymerization of our racemic silylethylene monomer. Neither of the attempted polymerizations carried out at 20 and 40°C succeeded (Table 2, nos 1 and 2). *n*-BuLi/(+)-camphene could polymerize the racemic monomer, but the resulting polymers were optically inactive. When *n*-BuLi/(−)-sparteine was used at 20°C, a small amount of polymer was isolated. Unfortunately, however, the polymer was insoluble in THF. This is probably because the chiral active center preferentially polymerizes one enantiomer, thus forming a polymer chain with a tightly packed helical conformation. This hypothesis was supported by the high optical rotation power of the polymer: The polymer was partially soluble in dioxane, and the filtered dioxane solution exhibited an $[\alpha]_D^{20}$ value as high as +275° (Table 2, no. 5). When the polymerization temperature was increased to 40°C, the polymer yield increased but the optical rotation of the polymer decreased dramatically. This might be because the stereospecificity of the active center decreases with increasing temperature, allowing another enantiomer to participate in the propagation reaction, thus increasing the yield but decreasing the $[\alpha]_D^{20}$. At 60°C, more polymer was produced but the resulting polymer was completely inactive optically, although its molecular weight distribution remained very narrow.

Structure and properties

The molecular structure of the polymers was characterized spectroscopically. The silylethylene monomer absorbed at 1590, 1402 and 956 cm^{-1} due to C=C stretching, $=CH_2$ scissoring and =C–H wagging vibrations, respectively. While the contribution from the aromatic absorption remained, the polymer showed no olefinic absorption bands in its IR spectrum (Fig. 1). The absorption peaks at 5.82, 6.21 and 6.64 ppm from the olefinic protons in the monomer completely disappeared in the ^1H NMR spectrum of the polymer (Fig. 2). New peaks from methine (CH) and methylene (CH_2) protons in the polymer backbone appeared in the range 0.7–2.5 ppm. The absorption peak of the methyl ($Si-CH_3$) protons shifted upfield because of the loss of the deshielding effect of the vinyl group. We carefully compared the spectroscopic data for the racemic and chiral polymers, but found no noticeable difference.

The poly(silylethylene)s were thermally stable. As can be seen from Fig. 3, the onset temperature for weight loss from the polymer in air was as high as 380°C. The high thermal stability of the polymer might be due to the so-called "jacket effect" of the side chain [17]. The polymer main chain "wears" a "jacket" of side chains consisting of bulky methyl-1-naphthylphenylsilyl groups, which protects the polyethylene backbone from the attack of thermal and/or oxidative decomposition. When the temperature becomes so high as to break the protective "jacket", the polyethylene backbone would rapidly

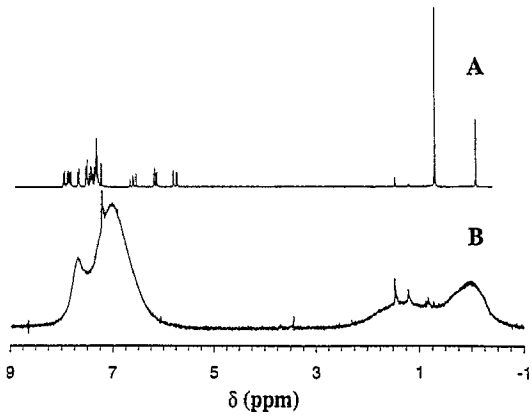


Fig. 2. ^1H NMR spectra of (A) (methyl-1-naphthylphenylsilyl)ethylene monomer and (B) its polymer ($CDCl_3$, RT; sample from Table 1, no. 2).

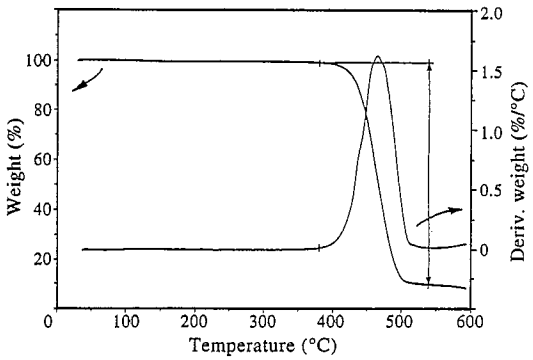


Fig. 3. TGA thermogram of poly[(methyl-1-naphthylphenylsilyl)ethylene] (in air, heating rate 10°C/min; sample from Table 1, no. 2).

decompose, as evidenced by the sharp slope of the TGA curve in the high temperature range. No glass transition temperature was detected by DSC analysis. This might again be because of the rigid "jacket", which forces the polymer main chain to take a stiffened conformation, preventing the segmental movements from occurring.

CONCLUSION

In this study, we have synthesized a silylethylene of high optical purity through platinum-catalyzed hydrosilylation of acetylene using a chiral silane *R*-(+)-MeNpPhSi*H. By identifying the absolute configuration of the silylethylene to be *S*-(+)-MeNpPhSi*Vi, we have revealed that the hydrosilylation proceeds with retention of the configuration of the stereogenic silicon center. We have synthesized optically active poly(silylethylene)s by polymerizing either the chiral monomer using an achiral initiator (*n*-BuLi) or the racemic monomer using a chiral initiator [*n*-BuLi/(−)-sparteine]. All the polymers possess very narrow molecular weight distributions (M_w/M_n down to 1.02). The sign (+ or −) and magnitude of the optical rotation of the polymers can be "tuned" by changing the catalyst system and the polymerization temperature. The polymers are thermally stable, possess a high glass transition temperature, and may find a wide range of "hi-tech" applications as specialty materials. For example, the optically active polymers may be used as chiral dopants in nonlinear optical systems and chiral commanders in liquid crystalline display devices. Different from the optically active poly(methacrylates) that are used in HPLC chiral separation but suffer from hydrolysis of the ester bonds, the poly(silylethylene)s we synthesized here are chemically stable and resistant to hydrolysis, making them promising candidates for chiral stationary phases in chromatographic enantioseparation.

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