Synthesis of Helical Polymers with a Pentasilane Core

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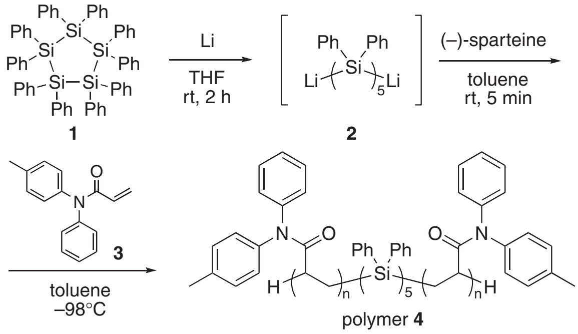
The asymmetric anionic polymerization of *N*-(4-methylphenyl)-*N*-phenylacrylamide was carried out using a new pentasilyl dianion initiator prepared by the reaction of decaphenylcyclopentasilane with lithium. The optically active higher-ordered structure of the pentasilane chain was induced by the helical poly[*N*-(4-methylphenyl)-*N*-phenylacrylamide] segments.

Synthesis of optically active polymers has been extensively carried out over the past few decades because they can be used to form chiral higher-ordered structures such as a helical structure. It is now widely accepted that chiral higher-ordered structures of macromolecules and organisms play a pivotal role in living systems. Many types of optically active polymers, e.g., poly(triphenylmethyl methacrylate)s,[1] poly(*N*,*N*-diphenylacrylamide)s,[1,2] polyisocyanides,[3] and polysilanes,[4] and chirality-responsive helical polymers[5] such as *cis–transoidal* polyacetylenes have been synthesized so far. Optically active polymers are promising materials for use in molecular recognition, chiroptical switching, liquid crystal, circularly polarized luminescence, etc.

Polysilanes have unique properties such as strong UV–vis absorption,[6] luminescence,[6b,7] hole mobility,[8] and UV-irradiated Si–Si bond cleavage.[6b,9] In addition, polysilanes acquire a one-handed helical structure when appropriate chiral alkyl side chains are incorporated. Among them, Sanji, Sakurai, and coworker reported that a helical poly(triphenylmethyl methacrylate) segment in polysilane-*b*-poly(triphenylmethyl methacrylate) block copolymers induced the formation of the one-handed helical structure of the polysilane segment.[10] The control of the helical structure of polysilanes by using an optically active terminal group has also been reported.[11] These polysilanes were successfully prepared by well-controlled anionic polymerization of masked disilenes[12] and not by the Wurtz-type reductive coupling of dihalosilanes.[13]

Cyclic oligosilanes undergo ring-opening due to the nucleophilic attack of alkyl or silyl anions to form the corresponding polysilanes.[14] The ring-opening reaction of cyclic oligosilanes with alkali metals results in the formation of oligosilyl dianions;[15] however, anionic polymerization by means of the oligosilyl dianions has not yet been reported. In this communication, we report a new method for synthesizing helical polymers with a pentasilane core by anionic polymerization of *N*,*N*-diarylacrylamide using the pentasilyl dianion as an initiator and (−)-sparteine as a chiral source and describe the structures of the obtained polymers.



Scheme 1.

We performed anionic polymerization of *N*-(4-methylphenyl)-*N*-phenylacrylamide (**3**)[2d] by using 1,5-dilithiodecaphenylpentasilane (**2**)[15a] as a bifunctional initiator, which was easily prepared from decaphenylcyclopentasilane (**1**) through a reductive Si–Si cleavage reaction with lithium in THF at −98 °C with a N_2(liq)/MeOH bath, as shown in Scheme 1. It is known that monomer **3** is used in asymmetric anionic polymerization to form one-handed helical polymers that have good solubility in organic solvents. After the reaction of **1** with lithium, the reaction mixture was dried and (−)-sparteine in toluene solution was added to it. Then, the toluene solution of **2** was injected into a monomer **3** solution with a syringe to yield the corresponding polymer **4**. Polymerization in THF was also successful; however, the obtained polymer was not optically active owing to the inhibition of the coordination of (−)-sparteine to lithium species in THF. The degree of polymerization (DP) and tacticity were estimated after conversion of polymer **4** to polymer **6** with poly(methyl acrylate) segments via polymer **5** with poly(acrylic acid) segments, as shown in the scheme in Supporting Information. Figures S1 and S4[17] show the ^{1}H NMR spectra of polymers **4** and **6**, respectively. Signals of phenyl groups in the pentasilane core are observed, while methyl signals of 4-methylphenyl groups are not. In addition, GPC curves of polymer **6** show that both ultraviolet (UV, 254 nm) and refractive index (RI) curves are narrow and unimodal (Figure S7).[17] These results indicate that the oligosilane units were not degraded during this transformation. The results of the anionic polymerizations are summarized in Table 1. The DP, tacticity, and specific rotation values of the polymers obtained from runs 1–6 were independent of reaction time, and the polymers with a narrow PDI were formed. The DPs of polymers were higher than the monomer/initiator ratio because of the incomplete initiator, Li–(SiPh$_2$)$_5$–Li, formation. Initiation and propagation of the reaction were very fast,[2e] and thus, the DPs obtained from runs 1–3 were not controlled by the monomer/initiator ratio. We confirmed that the pentasilane unit lay in the middle of the polymer chain by a Si–Si bond cleavage reaction under UV irradiation.[16]

Figure 1 shows the circular dichroism (CD) spectra of polymer **4** (DP = 115, PDI = 1.16) in CHCl$_3$/CF$_3$CO$_2$H (v/v = 100:1) at room temperature. The UV spectra of **4** are shown in Figure S8A,[17] which exhibit π–π^* transition bands of phenyl and tolyl groups at around 260 nm and a σ–σ^* transition band at around 290 nm as a shoulder peak. As shown in Figure 1, a strong Cotton effect is observed at around 260 nm; this suggests that aromatic rings in the poly[*N*-(4-methylphenyl)-*N*-phenyl-

Table 1. Asymmetric anionic polymerization of *N*-(4-methylphenyl)-*N*-phenylacrylamide (**3**) by Li–$(SiPh_2)_5$–Li initiator **2**

Entry	[Monomer]/[Initiator]	Time	Yield/%	DP[a]	PDI[a]	Isotacticity[b]/%	$[\alpha]^{25}_{365}$[c]/°
1	10	1 min	36	118	1.09	70	+618
2	15	1 min	81	126	1.13	71	+762
3	20	1 min	73	115	1.16	77	+748
4	20	5 min	81	113	1.18	75	+622
5	20	20 s	60	111	1.11	78	+778
6	20	20 s	44	191	1.08	93	−2.0

[a] DP (degree of polymerization) and PDI (polydispersity index) were calculated from GPC (THF eluent, polystyrene standards) after their conversion to poly(acrylic acid) derivatives **6**. [b] Calculated from ^{1}H NMR spectra of polymer **6**. [c] Measured in $CHCl_3/CF_3CO_2H$ (v/v = 100:1, *c* 0.5).

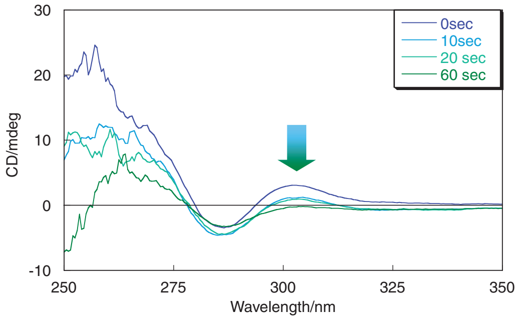


Figure 1. CD spectra of polymer **4** in $CHCl_3/CF_3CO_2H$ (v/v = 100:1, 1.0×10^{-5} M) at room temperature under UV irradiation.

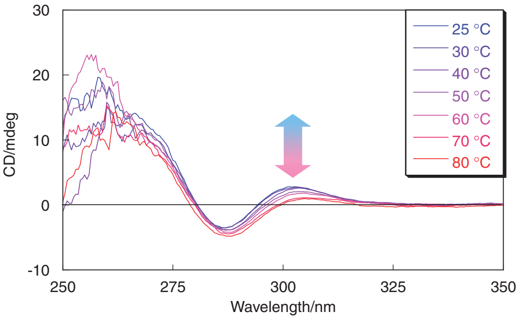


Figure 2. Thermochromism of CD spectra of polymer **4** in $CHCl_3/CF_3CO_2H$ (v/v = 100:1, 1.0×10^{-5} M).

acrylamide] and pentasilane segments exist in a chiral environment. In addition, the Cotton effect observed at 300 nm indicates the existence of an optically active higher-ordered structure of the pentasilane chain induced by the poly[*N*-(4-methylphenyl)-*N*-phenylacrylamide] segments.

A significant decrease in the CD signal intensity was observed at 300 nm during the photoirradiated Si–Si bond degradation using a low-pressure mercury lamp (60 W) (Figure 2). The CD Cotton signal of the pentasilane unit disappears completely owing to the UV irradiation for 60 s, and that of poly[*N*-(4-methylphenyl)-*N*-phenylacrylamide] units decreased simultaneously. Figure 2 shows the variable-temperature CD spectra of polymer **4**, which responded to temperatures of 25–80 °C (Figure S9A).[17] As the temperature increased from 25 to 80 °C, the CD signal at 300 nm continuously decreased and showed a slight red-shift, which was derived from the helical to random coil conformation of the pentasilane unit. The CD Cotton signal of π–π^* transition bands of aryl groups also depended on temperature, and its intensity decreased as the temperature increased, owing to the partial cancellation of the helical structure of the pentasilane core. On the other hand, the conformation change of the pentasilane unit was found to be reversible after four heating/cooling cycles between 80 and 25 °C, as shown in Figure S10.[17]

In summary, we carried out the asymmetric anionic polymerization of *N*-(4-methylphenyl)-*N*-phenylacrylamide using a new pentasilyl dianion initiator obtained from a reaction of decaphenylcyclopentasilane with lithium. Polymerization proceeded smoothly and produced the corresponding poly[*N*-(4-methylphenyl)-*N*-phenylacrylamide] with a pentasilane core. Formation of the optically active higher-ordered structure in the pentasilane chain was induced by the poly[*N*-(4-methylphenyl)-*N*-phenylacrylamide] segments. The CD Cotton signal of the pentasilane core in poly[*N*-(4-methylphenyl)-*N*-phenylacrylamide] responded to temperatures reversibly.

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16 GPC charts are shown in Figure S11 in Supporting Information.
17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.