Preparation and Characterization of Water-Soluble Polysilanes Bearing Chiral Pendant Ammonium Moieties

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ABSTRACT: The preparation and characterization of new amphiphilic polysilanes containing chiral pendant ammonium groups are described. Polyalkylphenylsilanes (alkyl ; C_1—C_8) (**I**) were prepared, and the Friedel–Crafts reaction of **I** was carried out to give p-chloromethylated polysilanes (**II**). **II** were treated with optically active amines such as N, N-dimethyl-α-methylbenzylamine (**1**), N, N-dimethylphenylalaninol (**2**), N, N-dimethyl-O-acethylphenylalaninol (**3**), N, N-dimethyl-iso-leucinol (**4**), N, N-dimethylleucinol (**5**) and N, N-dimethyl-1-phenylethanol (**6**) to give the corresponding amphiphilic polysilanes bearing chiral pendant ammonium moieties. All polymers prepared were soluble in water, ethanol and acetonitrile. The circular dichromic spectra (CD) of the polymers in ethanol showed that the polymer had a screw-sense main chain.
KEY WORDS Water-Soluble Polysilane / Optically Active Pendant / Chloromethylation of Polysilane /

Polysilanes display unique characteristics such as UV absorption and luminescence due to σ-conjugation of the Si–Si main chain. It is important to control the conformation of the Si–Si main chain to develop applications of the polysilanes to functional materials. Attention has been focused on the preparation and characterization of amphiphilic polysilanes carrying ether,[1] phenol,[2] and ammonium moieties[3] in the side chain, since they are expected to have potential for highly orientated structures of the polysilane main chain. Langmuir Blodgett film prepared from a polysilane which has phenollic groups in the side chain shows clear anisotropy in its UV spectra.[2]

There are few reports on the preparation of polysilanes bearing asymmetric moieties.[4,5] Fujiki reported that polysilanes bearing an optically active 2-methylbutyl group exhibited strong UV absorption and luminescence due to the screw-sense conformation of the main chain.[4a] Most functionalized polysilanes, except ammonium functionalized ones,[3] were prepared by the Wurtz reaction using dichlorosilane derivatives bearing optically active groups on silicon.[4] In this method, asymmetric substituents are strictly limited, because they must be stable under the Wurtz coupling conditions.

Introduction of functional groups to a preformed polysilane is another possibility for preparation of functionalized polysilanes. The chloromethylation reaction of phenyl substituted polysilane is expected to be a novel method for the preparation of organofunctional polysilanes,[3,6] since numerous preparative methods of functional materials through chloromethylated polystyrene have been widely developed. We reported the preparation and characterization of poly-n-hexylphenylsilane with an optically active amine, N, N-dimethyl-α-methylbenzylamine (**1**).[7] In this paper, further syntheses of chloromethylated polysilanes and characterization of new polysilanes bearing optically active ammonium derivatives are described.

RESULTS AND DISCUSSION

Preparation of Poly-n-alkylphenylsilane (*I*)

I [R=CH$_3$ (a), C$_2$H$_5$ (b), C$_3$H$_7$ (c), C$_4$H$_9$ (d), C$_5$H$_{11}$ (e), C$_6$H$_{13}$ (f), C$_7$H$_{15}$ (g), C$_8$H$_{17}$ (h)] were prepared by the Wurtz reaction under irradiation of supersonic waves to make the polysilanes monomodal (Scheme 1).[8] The results are shown in Table I. **Ic** and **Id** were obtained as waxy solids, both of which were insoluble in common organic solvents such as toluene, tetrahydrofuran (THF), and benzene. Only **Ib** was yielded in a bimodal molecular weight distribution, and the others were monomodal as expected. The UV spectra of the poly-n-alkylphenylsilanes were measured in chloroform, and the spectra of **If, Ig**, and **Ih** exhibited similar absorption maximum (λ_{max}) and molar absorptivity (ε_{max}).
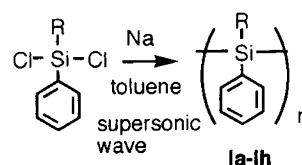
R=CH$_3$ (a), C$_2$H$_5$ (b), C$_3$H$_7$ (c), C$_4$H$_9$ (d), C$_5$H$_{11}$ (e), C$_6$H$_{13}$ (f), C$_7$H$_{15}$ (g), C$_8$H$_{17}$ (h)

Scheme 1. Preparation of polysilanes.

Table I. Preparation of poly-n-alkylphenylsilanes

Compound	Yield %	M_w $(\times 10^4)^a$	$\lambda_{max}^{\ b}$ nm	ε_{max}
Ia	56	0.9	332	4100
Ib	10	28 (36%),8.0 (64%)^c	341	8500
Ic	17	Insoluble	—	—
Id	18	Insoluble	—	—
Ie	36	14.6	347	12400
If	23	15.0	347	16100
Ig	23	13.6	347	16300
Ih	11	13.2	347	17200

^{a} Polystyrene standard in tetrahydrofuran. ^{b} In CHCl$_3$. ^{c} Bimodal GPC traces appeared.

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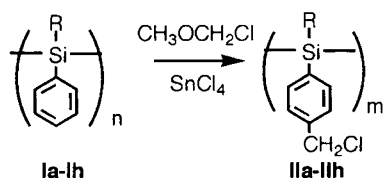
R=CH$_3$ (a), C$_2$H$_5$ (b), C$_3$H$_7$ (c), C$_4$H$_9$ (d), C$_5$H$_{11}$ (e), C$_6$H$_{13}$ (f), C$_7$H$_{15}$ (g), C$_8$H$_{17}$ (h)

Scheme 2. Chloromethylation reaction of **Ia-Ih**.

Table II. Chloromethylation of **I**

Compound	Yield %	Substitution ratio[a] %	M_w ($\times 10^4$)[b]	λ_{max}[c] nm	ε_{max}
IIa	—	—	—	—	—
IIb	87	80	0.7	339	6100
IIc	65	88	43(20%),[d] 2.2(80%)	347	14300
IId	42	68	2.6	347	18200
IIe	49	~100	2.0	345	11100
IIf	90	~100	1.0	346	10500
IIg	63	~100	2.7	347	12200
IIh	55	~100	1.8	346	7800

[a]Estimated from ^{1}H NMR spectrum. [b]Polystyrene standard in tetrahydrofuran. [c]In CHCl$_3$. [d]Bimodal GPC traces appeared.

Scheme 3. Chloromethylation reaction of 2-hexyl-1, 1, 1, 3, 3, 3-hexamethyl-2-phenyltrisilane.

Scheme 4. Reaction of **IIf** with optically active amine.

Chloromethylation Reaction of *I*

Friedel–Crafts chloromethylation using a tin tetrachloride catalyst[6a] was performed to give the corresponding chloromethylated polysilanes (**II**) (Scheme 2). The results are summarized in Table II. Substitution of the chloromethyl group was estimated by the intensity ratio of aromatic protons and methylene protons of the chloromethyl substituent in the ^{1}H NMR of the resulting polysilane derivatives. Although successful preparation of chloromethylated polymethylphenylsilane is described in the literature,[6b] extensive degradation of the polysilane main chain and partial *ipso*-attack to silicon observed in our case (**IIa**) may be due to the relatively higher reaction temperature optimized for complete chloromethylation of **IIf**. Other polysilanes prepared were chloromethylated successfully, although partial cleavage of the polysilane main chain was observed after chloromethylation of **Ib**, **Ie**, **If**, **Ig**, and **Ih**, and the average molecular weight of the corresponding **IIb**, **IIe**, **IIf**, **IIg**, and **IIh** decreased to about one-seventh that of the starting polysilanes. However, it is considered that **IIb**, **IIe**, **IIf**, **IIg**, and **IIh** were appropriate materials to investigate the behavior of the polysilane main chain, because they have over 40 units of the Si–Si bond and there is no detectable increase in the IR spectra around 1100 cm^{-1} absorption due to Si–O–Si. The insoluble polymers, **Ic** and **Id**, were treated with chloromethyl methyl ether in the presence of tin tetrachloride under similar reaction conditions. The reaction mixture became homogeneous at the end of the reaction, although it was heterogeneous at the beginning of the reaction. The usual work-up of the reaction mixture gave soluble **IIc** and **IId**, respectively. These results suggest that the insolubility of **Ic** and **Id** is based not on cross-links but on relatively higher molecular weights of the polysilanes. It is difficult to determine the position of the chlo-

romethyl substituent of the polymer **I** directly, since all NMR spectra of the chloromethylated polysilanes showed broad peaks as usual. Nevertheless, the chloromethylation of the polysilanes, which have a more bulky silane substituent than the model compound, 2-hexyl-1,1,1,3,3,3-hexamethyl-2-phenyltrisilane, may occur at the *p*-position[7] (Scheme 3).
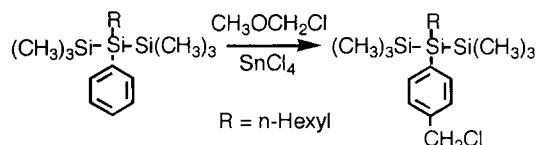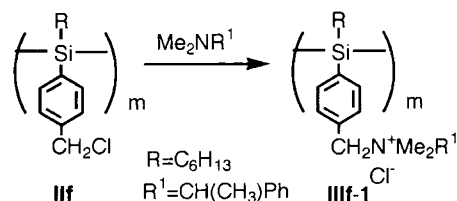
Preparation and Characterization of Ammonium Derivatives of Optically Active N, N-Dimethyl-α-methylbenzylamine

At first, **IIf** was treated with (+)-, (−)-, and (±)-*N*, *N*-dimethyl-α-methylbenzylamine (**1**) to give polysilanes bearing optically active pendant ammonium moieties (**IIIf**-(+)-**1**, **IIIf**-(−)-**1**, and **IIIf**-(±)-**1**), respectively (Scheme 4). All polysilane derivatives obtained were soluble in water, ethanol, and acetonitrile. The UV spectrum of **IIIf**-(+)-**1** showed an absorption due to the Si–Si σ-bonds in the 320 to 355 nm region (λ_{max} 339 nm, ε 6800 in EtOH). The CD spectrum of **IIIf**-(+)-**1** showed a negative broad absorption (λ_{max} 334 nm, ε−0.72 (Si unit) in EtOH) in a similar region to the UV absorption and positive broad absorption around 300 nm (ε+0.65 (Si unit)) probably due to aromatic groups (Figure 1). The CD spectrum of **IIIf**-(−)-**1** exhibited a symmetrical pattern (λ_{max} 336 nm, ε +0.30 (Si unit), and λ_{max} 295 nm, ε− 0.65 (Si unit) in EtOH) to that of **IIIf**-(+)-**1** (Figure 2). No CD absorption was observed in the spectrum of **IIIf**-(±)-**1**. These results indicate that the polysilane main chain of **IIIf**-(+)-**1** and **IIIf**-(−)-**1** has an opposite, one-way screw-like conformation. **IIIf**-(+)-**1** obtained from the reaction of a 50% chloromethylated **IIf** and (+)-**1** gave nearly the same CD spectrum as that of the completely substituted **IIIf**-(+)-**1**. It is apparent that a 50% of the substituent effectively controls the conformation of the polysilane main chain.

Each chloromethylated polysilane (**II**) described in Table II was treated with (+)-**1** to give the corresponding ammonium derivatives (**III**-(+)-**1**). The patterns of the UV and CD spectra of **IIIb**, **IIIc**, **IIId**, **IIIe**, **IIIg**, and **IIIh**-(+)-**1** were similar to that of **IIIf**-(+)-**1**. The value of ε_{max} of **IIIf**-(+)-**1** was largest among the polysilanes prepared here.
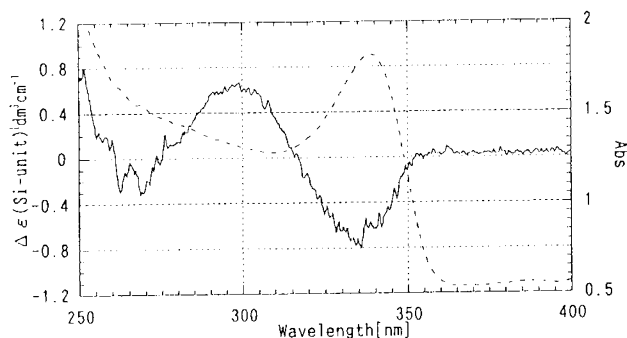
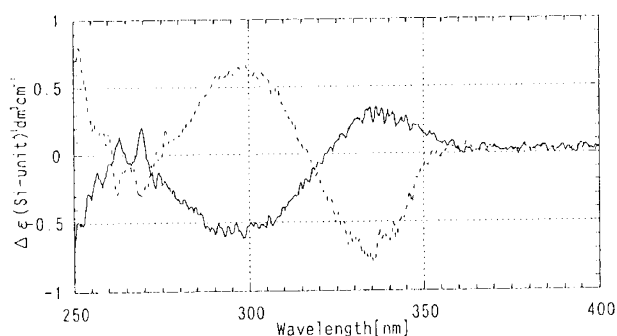**Figure 1.** CD (——) and UV (- - -) spectra of **IIIf-(+)-1** in 99% EtOH.

Figure 2. CD spectra of **IIIf-(+)-1**(- - -) and **IIIf-(−)-1**(——) in 99% EtOH.

$PhCH_2C^*HCH_2OH$ $PhCH_2C^*HCH_2OOCCH_3$
    $N(CH_3)_2$ $N(CH_3)_2$

2   **3**

   CH_3
$CH_3CH_2C^*HC^*HCH_2OH$ $(CH_3)_2CH_2C^*HCH_2OH$
       $N(CH_3)_2$ $N(CH_3)_2$
       4   **5**

$HOC^*HCH_2N(CH_3)_2$
  Ph

6

Figure 3. Optically active amines.

phenyl groups attached to the asymmetric carbon center directly.

EXPERIMENTAL

The NMR spectra were determined at 400 MHz with a Bruker AM400 and ARX400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard or in dimethyl sulfoxide (DMSO)-d_6. UV, CD, and IR spectra were measured with a JASCO V 550 , a J-720 W, and an FT-IR-300E, respectively. Optical rotations were measured with a JASCO DIP-360 polarimeter. Molecular weights were determined by a TOSOH SD-8000 with polystyrene standard. The irradiation of supersonic waves was carried out by a Honda W-221 ultrasound bath. All reactions were performed under an argon atmosphere. Alkylphenyldichlorosilanes were prepared by treating trichlorophenylsilane with appropriate Grignard reagents.

Effects of the Structure of Optically Active Amine

IIf was treated with other optically active amines such as (−)-*N*, *N*-dimethylphenylalaninol (**2**), (+)-*N*, *N*-dimethyl-*O*-acethylphenylalaninol (**3**), (+)-*N*, *N*-dimethyl-*iso*-leucinol (**4**), (+)-*N*, *N*-dimethylleucinol (**5**), or (−)-*N*, *N*-dimethyl-1-phenylethanol (**6**) (Figure 3) to afford the corresponding amphiphilic polysilanes (**IIIf-(−)-2**, **IIIf-(+)-3**, **IIIf-(+)-4**, **IIIf-(+)-5**, and **IIIf-(−)-6**). Amines **1** and **6** have a phenyl group attached to the asymmetric center directly, and **2** and **3** bear a phenyl group on the carbon adjacent to the asymmetric center. Amines **4** and **5** have no phenyl group. All ammonium derivatives obtained were soluble in water, ethanol, and acetonitrile. The CD spectra of the polysilanes bearing these amines in ethanol are shown in Figure 4.

All polysilanes bearing optically active ammonium moieties showed negative Cotton effects around 330 nm based on the Si–Si σ conjugation in their CD spectra (Figure 4). This means that all chiral pendant ammonium moieties control the conformation of the polysilane main chains effectively.

Broad positive Cotton effects around 300 nm were observed in the CD spectra of **IIIf-(+)-1** (Figure 1) and **IIIf-(−)-6** (Figure 4e) in which phenyl groups were attached to the asymmetric center directly. However, absorption was not found in the spectra of **IIIf-(+)-4** (Figure 4c) and **IIIf-(+)-5** (Figure 4d) which did not have a phenyl group in the optically active amines. Positive absorption was also not found in those of **IIIf-(−)-2** (Figure 4a) and **IIIf-(+)-3** (Figure 4b) even though the amines had a phenyl group. These results suggest that the broad positive Cotton effects around 280—300 nm come from the
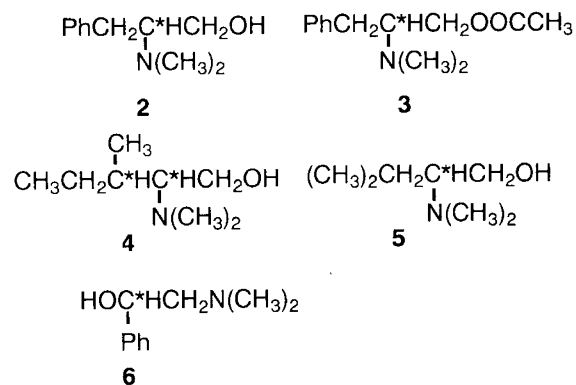
Preparation of Polysilanes

A representative procedure is described. A solution of dichlorohexylphenylsilane (12.0 g, 45.9 mmol) in dry toluene (12 mL) was added by syringe to a mixture of sodium dispersion prepared from sodium (2.11 g, 91.9 mmol) in dry toluene (60 mL) under high speed stirring and irradiation of supersonic waves. The mixture was stirred for 1 h and then dry 2-propanol (15 mL) was added to the mixture. The reaction mixture was added to 2-propanol (250 mL) with stirring. Precipitated mixture was collected by filtration. Toluene (200 mL) was added to the mixture and washed with water (100 mL) three times. The organic layer was dried (Na_2SO_4). The solvent was evaporated. Toluene (5 mL) was added to the residue, and the solution was added to 2-propanol (100 mL). The precipitate was separated by filtration to give a white powder in 2.04 g (23%) yield. ^1H NMR ($CDCl_3$) δ −0.5—1.4 (broad, 13H, C_6H_{13}), 5.9—7.2 (broad, 5H, Ar).

Preparation of Chloromethylated Polysilanes

A representative procedure is described. Tin tetrachloride (1.0 g, 3.84 mmol) was added to a solution of **If** (1.0 g, 5.25 mmol/phenyl group) and large excess of chloromethyl methyl ether (10 mL) in chloroform (15 mL) by syringe at 0℃. The mixture was stirred at 0℃ for 6 h and 12 h at room temperature. The reaction mixture was washed with water several times. The water was ex-
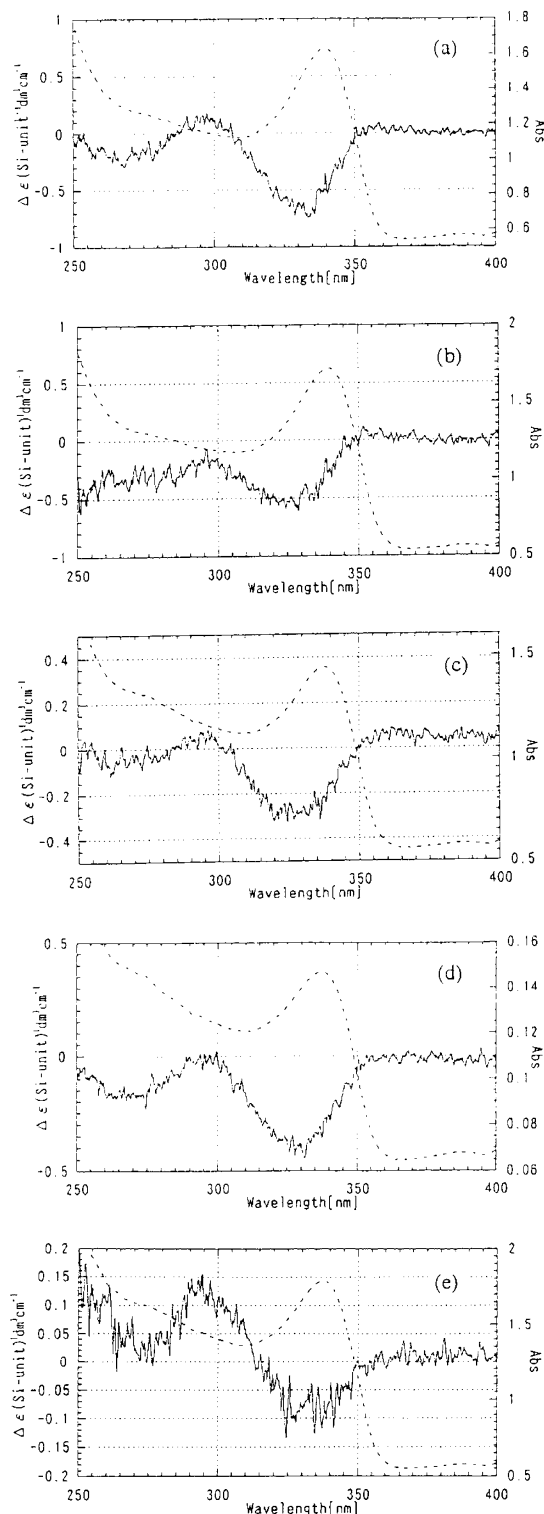
Figure 4. CD (—) and UV (- - -) spectra of **IIIf**-(−)-**2** (a), **IIIf**-(+)-**3** (b), **IIIf**-(+)-**4** (c), **IIIf**-(+)-**5** (d), and **IIIf**-(−)-**6** (e) in 99% EtOH.

tracted with chloroform (5 mL) three times. The combined chloroform solution was dried (Na$_2$SO$_4$). The solvent was removed and THF (2 mL) was added to the residue. The THF solution was added to methanol (200 mL). The precipitate was separated by filtration to give **IIf** (white powder) in 1.13 g (90%) yield. ^{1}H NMR (CDCl$_3$) δ−0.5—1.4 (broad, 13H, C$_6$H$_{13}$), 4.46 (broad s, 2 H, CH$_2$Cl), 5.9—7.2 (broad, 5H, Ar).

Preparation of Optically Active Amines

Optically active *N*, *N*-dimethylamines were prepared as described in the literature.[9] A representative procedure is described. (+)-α-Methylbenzylamine (14.5 g, 0.12 mol) ([α]$_D$+37.3° (c1, EtOH); lit.[9] [α]$_D$+40.3° (neat)) was slowly added to formic acid (98% solution) (28.5 mL, 0.6 mol). Formaldehyde (37% aqueous solution) (31.5 mL, 0.36 mol) was added to the mixture. The reaction mixture was warmed to start decarboxylation reaction. The mixture was then made to stand at room temperature till spontaneous degradation was finished. The mixture was stirred at 100℃ for 8 h. Four molar hydrochloric acid (60 mL) was added to the mixture, and the solvent was evaporated. To the residue 18M NaOH (42 mL) was added. The reaction mixture was extracted with benzene (30 mL) three times. The combined organic layer and extracts was dried (K$_2$CO$_3$). Evaporation and distillation gave **1** in 13.9 g (77%) yield. Bp 85℃/22 Torr. ^{1}H NMR (CDCl$_3$) δ 1.37 (d, *J*=7.1 Hz, 3H, CCH3), 2.19 (s, 6H, NCH3), 3.24 (q, *J*=7.1 Hz, 1H, PhCH), 7.2—7.4 (m, 5 H, Ar). [α]$_D$+47.6 (c10, EtOH).

2; Yield 94%. Bp 140℃/3 Torr. [α]$_D$−2.1° (c1, EtOH). ^{1}H NMR (CDCl$_3$) δ 2.25—2.28 (m, 1H, CH), 2.35 (s, 6H, NCH$_3$), 2.75—3.0 (m, 2H, PhCH$_2$), 3.22 (broad s, 1H, OH), 3.24—3.45 (m, 2H, OCH$_2$), 7.0—7.4 (m, 5H, Ar). **3**; Yield 83%. Bp 170℃/22 Torr. [α]$_D$+28.9° (c1, EtOH). ^{1}H NMR (CDCl$_3$) δ 2.01 (s, 3H, C(=O)CH$_3$), 2.39 (s, 6H, NCH$_3$), 2.44—2.66 (m, 1H, CH), 2.87—3.10 (m, 2H, PhCH$_2$), 3.95—4.22 (m, 2H, OCH$_2$), 7.1—7.4 (m, 5H, Ar). **4**; Yield 88%. Bp 110℃/7 Torr. [α]$_D$ + 20.8° (c1.7, EtOH). ^{1}H NMR (CDCl$_3$) δ 0.80 (d, *J*=7.0 Hz, 3H, C* CH$_3$), 0.90 (t, 3H, *J*=7.3 Hz, CCH$_3$), 1.15—1.30 (m, 1H, NCCH), 1.35—1.55, 1.55—1.75 (m, 2H, MeCH$_2$), 2.38 (s, 6H, NCH$_3$), 2.35—2.5 (m, 1H, NCH), 3.29 (t, *J*=10.2 Hz, 1H, OCH$_2$), 3.51 (q, *J*=5.5 Hz, 1H, OCH$_2$). **5**; Yield 65%. Bp 115℃/37 Torr. [α]$_D$+35.2° (c1.7, EtOH). ^{1}H NMR (CDCl$_3$) δ 0.90 (t, *J*=7.1 Hz, 6H, CH$_3$), 0.85—1.05, 1.20—1.40 (m, 2H, NCCH$_2$), 1.40—1.60 (m, 1H, MeCH), 2.24 (s, 6H, NCH$_3$), 2.55—2.77 (m, 1H, C*H), 3.21 (t, *J*=10.6 Hz, 1H, OCH$_2$), 3.49 (q, *J*=4.8 Hz, 1H, OCH$_2$). **6**; Yield 83%. Bp 100℃/ 2 Torr. [α]$_D$−12.3° (c1, EtOH). ^{1}H NMR (CDCl$_3$) δ 2.34 (s, 6H, NCH$_3$), 2.3—2.6 (m, 2H, NCH$_2$), 3.99 (broad s, 1H, OH), 4.68 (dd, *J*=10.2 Hz, 3.9 Hz, PhCH), 7.2—7.5 (m, 5H, Ar).

Preparation of Ammonium Derivatives

A representative procedure is described. A mixture of **IIf** (100 mg, 0.42 mmol/silicon) and (+)-**1** (312 mg, 2.09 mmol) in 2-propanol (1 mL) was refluxed for 12 h in the dark, followed by the addition of hexane (100 mL). The precipitated polymer was separated by filtration to give a white solid (**IIIf**-(+)-**1**) in 144 mg (88%) yield. ^{1}H NMR (DMSO-d_6) δ 0—1.5 (13H, C$_6$H$_{13}$), 1.7—2.2 (3H, NCCH$_3$), 2.4—3.2 (6H, NCH$_3$), 4.0—5.0 (2H, NCH$_2$), 5.0—6.0 (1H, NCH), 7.0—8.1 (9H, Ar). **IIIb**-(+)-**1** (white solid); Yield quant. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (5H, C$_2$H$_5$), 1.7—2.2 (3H, NCCH$_3$), 2.4—3.2 (6H, NCH$_3$), 4.0—5.0 (2H, NCH$_2$), 5.0—6.0 (1H, NCH), 7.0—8.1 (9H, Ar). **IIIc**-(+)-**1** (white solid); Yield 91%. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (7H, C$_3$H$_7$), 1.7—2.2 (3H, NCCH$_3$), 2.4—3.2 (6H, NCH$_3$), 4.0—5.0 (2H, NCH$_2$), 5.0—6.0 (1H, NCH), 7.0—8.1 (9H, Ar). **IIId**-(+)-**1** (white solid); Yield 96%. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (9H, C$_4$H$_9$), 1.7—2.2 (3H,

NCCH$_3$), 2.4—3.2 (6H, NCH$_3$), 4.0—5.0 (2H, NCH$_2$), 5.0 —6.0 (1H, NCH), 7.0—8.1 (9H, Ar). **IIIe-(+)-1** (pale yellow solid); Yield quant. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (11H, C$_5$H$_{11}$), 1.7—2.2 (3H, NCCH$_3$), 2.4—3.2 (6H, NCH$_3$), 4.0—5.0 (2H, NCH$_2$), 5.0—6.0 (1H, NCH), 7.0— 8.1 (9H, Ar). **IIIg-(+)-1** (white solid) ; Yield 88%. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (15H, C$_7$H$_{15}$), 1.7—2.2 (3H, NCCH$_3$), 2.4—3.2 (6H, NCH$_3$), 4.0—5.0 (2H, NCH$_2$), 5.0 —6.0 (1H, NCH), 7.0—8.1 (9H, Ar). **IIIh-(+)-1** (white solid) ; Yield 82%. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (17H, C$_8$H$_{17}$), 1.7—2.2 (3H, NCCH$_3$), 2.4—3.2 (6H, NCH$_3$), 4.0 —5.0 (2H, NCH$_2$), 5.0—6.0 (1H, NCH), 7.0—8.1 (9H, Ar). **IIIf-(−)-2** (white solid) ; Yield quant. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (13H, C$_6$H$_{13}$), 2.4—3.2 (6H, NCH$_3$), 3.7— 4.5 (4H, PhCH$_2$, OCH$_2$), 4.4—5.3 (1H, NCH), 7.0—8.1 (4 H, Ar). **IIIf-(+)-3** (white solid); Yield 98%. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (13H, C$_6$H$_{13}$), 1.7—2.2 (3H, C(=O) CH$_3$), 2.4—3.2 (6H, NCH$_3$), 3.7—4.5 (4H, PhCH$_2$, OCH$_2$), 4.4—5.3 (1H, NCH), 7.0—8.1 (4H, Ar). **IIIf-(+)-4** (pale yellow solid); Yield quant. ^{1}H NMR (DMSO-d_6) δ 0.0— 1.5 (21H, C$_6$H$_{13}$, C$_2$H$_5$, CH$_3$), 2.0—2.4 (1H, MeCH), 2.4— 3.2 (6H, NCH$_3$), 3.5—4.5 (2H, OCH$_2$), 4.4—5.3 (1H, NCH), 7.0—8.1 (4H, Ar). **IIIf-(+)-5** (pale yellow solid); Yield 97%. ^{1}H NMR (DMSO-d_6) δ 0.5—1.5 (19H, C$_6$H$_{13}$, CH$_3$), 1.5—2.0 (3H, CH-CH$_2$), 2.4—3.2 (6H, NCH₃), 3.5 —4.5 (2H, OCH$_2$), 4.4—5.3 (1H, NCH), 7.0—8.1 (4H, Ar). **IIIf-(−)-6** (pale yellow solid); Yield quant. ^{1}H NMR (DMSO-d_6) δ 0.0—1.5 (19H, C$_6$H$_{13}$), 2.4—3.2 (6H, NCH$_3$), 3.2—3.5 (2H, NCH$_2$), 5.0—5.5 (1H, PhCH), 7.0—8.1 (9 H, Ar).

REFERENCES

1. a) C. H. Yuan and R. West, *Macromolecules*, **26**, 2645 (1993). b) O. Greszta and K. Matyajaszewski, *Macromolecules*, **26**, 6231 (1993). c) K. Oka, N. Fujiue, S. Nakanishi, T. Tanaka, T. Dohmaru, C. H. Yuan, and R. West, *Chem. Lett.*, 875 (1995). d) K. Oka, N. Fujiue, T. Dohmaru, C. H. Yuan, and R. West, *J. Am. Chem. Soc.*, **119**, 4074 (1997).
2. a) R. Kani, Y. Nakano, Y. Majima, S. Hayase, C. H. Yuan, R. West, and I. Keminek, *Macromolecules*, **27**, 1911 (1994). b) R. Horiguchi, Y. Onishi, and S. Hayase, *Macromolecules,* **21**, 304 (1988).
3. a) I. Keminek, E. Brynda, and W. Achnabel, *Eur. Polym. J.*, **27**, 1073 (1991). b) I. Kminek, Y. Yagci, and W. Schmabel, *Polym. Bull.*, **29**, 277 (1992). c) T. Seki, T. Tamaki, and K. Ueno, *Macromolecules*, **25**, 3825 (1992). d) T. Seki, A. Tohnai, T. Tamaki, and K. Ueno, *J. Chem. Soc. Chem. Commun.*, 1876 (1993). e) T. Seki, T. Tamaki, K. Ueno, and Y. Tanaka, *Thin Solid films*, **243**, 625 (1994). f) T. Seki, N. Tanigaki, K. Yase, A. Kaito, T. Tamaki, K. Ueno, and Y. Tanaka, *Macromolecules*, **28**, 5609 (1995). g) T. Seki, A. Tohnai, T. Tamaki, and A. Kaito, *Chem. Lett.*, 361 (1996). h) T. Seki, A. Tohnai, T. Tamaki, and A. Kaito, *Macromolecules*, **29**, 4813 (1996). i) T. Seki, A. Tohnai, N. Tanigaki, K. Yase, T. Tamaki, and A. Kaito, *Macromolecules*, **30**, 1768 (1997).
4. a) M. Fujiki, *J. Am. Chem. Soc.*, **116**, 6017 (1994). b) M. Fujiki, *J. Am. Chem. Soc.*, **116**, 11976 (1994). c) M. Fujiki, *Polyme. Prepr., Am. Chem. Soc,. Div. Polym. Chem*, **37**, 454 (1996). d) M. Fujiki and H.Takigawa, *Polym. Prepr. Jpn.*, **46**, 3939 (1997). e) K. Obata and M. Kira, *Macromolecules*, **31**, 4666 (1998).
5. K. Shinohara, T. Aoki, T. Kaneko, and E. Oikawa, *Chem. Lett.*, 361 (1997). b) K. Obata, C. Kubota, and M. Kira, *J. Am. Chem. Soc.*, **119**, 11345 (1997).
6. a) H. Ban, K. Sukegawa, and S. Tagawa, *Macromolecules*, **20**, 1775 (1987). b) R. Jones, R. Benfild, A. Swain, S. Webb, and M. Went, *Polymer*, **36**, 393 (1995).
7. D. Terunuma, K. Nagumo, N. Kamata, K. Matsuoka, and H. Kuzuhara, *Chem. Lett.*, 681 (1998).
8. K. Matyjaszewski, D. Greszta, J. S. Hekach, and H. K. Kim, *Macromolecules*, **28**, 59 (1995).
9. H. Nohira, M. Kai, M. Nohira, J. Nishikawa, T. Hoshiko, and K. Saigo, *Chem. Lett.*, 951 (1981).