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SYNTHESIS AND PROPERTIES OF SILETHYNYLENE–SILOXANE ALTERNATING COPOLYMERS

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Abstract—A series of novel silethynylene–siloxane alternating copolymers with variation of siloxane contents and substituents on the silicon atoms has been prepared. Reactions of bis(hydroxydiphenylsilyl)-ethyne with bis(*N*-methylacetamido)diphenylsilane or bis(*N*-ethylacetamido)dimethylsilane in THF gave polymers with molecular weights in the range of 5800 to 23,000. The polymers for which all substituents on the silicon atoms are phenyl groups have T_ms at 155–174° and 10% weight loss temperatures at 503–521°.

INTRODUCTION

Recently considerable interest has developed in polymers consisting of silicon and ethynylene moieties in the main chain [1–5]. Almost all polymers in this class so far reported contain only silicon and carbon atoms in the backbone, probably because their intended applications are as ceramic precursors and conducting polymers. Among them, poly(diphenylsilethynylene) is reported to be spinnable, film-forming and thermally stable but with a relatively low melting temperature (T_m, 135°) [6].

We thought that a combination of this poly(diphenylsilethynylene) and the very rigid poly(diphenylsiloxane) [7] could afford a polymer which has a satisfactory T_m (close to or higher than 200°) and good processability together with high thermal stability. There have been few reports dealing with polymers containing both silethynylene and siloxane building blocks. Komarov *et al.* reported syntheses of disiloxane and trisiloxane species with ethynyl groups [8]. Frisch and Young suggested hydrolysis of bis(dichlorosilyl)ethynes to form silethynylene–siloxane copolymers but no example was shown [9]. Bortolin *et al.* proposed ring-opening copolymerization of cyclic silethynylenes and cyclic siloxanes to form random copolymers using a lithium salt as a catalyst [10].

We now report the synthesis and properties of alternating copolymers consisting of silethynylene units and di-, tetra- and hexasiloxane units, with focus on the perphenylated species.

EXPERIMENTAL PROCEDURES

General

All synthetic experiments were performed in a dry argon atmosphere using vacuum-heat-dried glassware unless otherwise stated. Tetrahydrofuran (THF) was distilled from a purple solution of sodium/benzophenone/THF. Diethyl ether (Et_2O) was stored over lithium aluminum hydride and distilled. Toluene was stored over molecular sieves and distilled from sodium. Diphenylsilanediol was dried under high vacuum for 24 hr at room temperature. Butyllithium (BuLi, in hexanes), sodium, benzoyl peroxide (BPO) and chlorosilanes were used as purchased. Bis(*N*-ethylacetamido)-dimethylsilane was obtained from Dow Corning Toray Silicone Co. Ltd and purified by distillation. Other reagents were distilled and stored over activated molecular sieves.

Measurements

Quantitative ^1H,- ^{13}C- and ^{29}Si-NMR spectra were obtained using a Bruker AC-P 300 spectrometer from $CDCl_3$ solutions [300.13 MHz for ^1H, reference: $CHCl_3$ or Me_4Si for ^1H; $CDCl_3$ for ^{13}C; external Me_4Si for ^{29}Si, relaxation agent: $Cr(acac)_3$ (0.02 M)]. Gas chromatography-mass spectrometric (GC-MS) data were obtained using a Shimadzu GCMS-QP1000EX gas chromatograph-mass spectrometer. Molecular weights of polymers relative to standard poly(dimethylsiloxane) samples were determined using a Shodex GPC System 11 equipped with a series of KF-80M and KF-802 columns (eluent: THF, flow: 1.0 ml/min, detector: refractometer). Melting temperatures of monomers and polymers were determined using a Mettler FP 82HT hot stage and an optical microscope. Differential scanning calorimetry was also used for observing the melting behaviour of polymers with a Rigaku DSC 8230D. Thermogravimetric analyses were carried out using a Rigaku TG 8101D.

Bis(N-methylacetamido)diphenylsilane (2)

Diamidosilane **2** [13] was prepared from a sodium salt of *N*-methylacetamide and diphenyldichlorosilane in toluene. The crude solid was purified by recrystallization in hexane (yield: 58%).

Bis(diphenylsilyl)ethyne

Bis(diphenylsilyl)ethyne was prepared from trichloroethene, BuLi and chlorodiphenylsilane in THF/Et_2O using the procedure of Barton *et al.* [6]. The crude solid was recrystallized from ethanol to give white, needle-like crystals. Yield: 74%. m.p.: 84.5–86°, ^1H-NMR: δ (ppm) 7.69–7.66 (m, 4H); 7.36–7.34 (m, 6H); 5.24 (s, 1H), ^{29}Si-NMR: δ (ppm) −41.1, GC-MS *m/e* (% relative intensity): 390 (M^+, 16); 389 (M^+-H, 7); 388 (M^+-2H, 5); 312 (M^+-C_6H_6, 100); 259 (87); 207 (46); 181 (50); 105 (88); 53 (21). Elemental analysis: found C 80.14 H5.59%; calcd for $C_{26}H_{22}Si_2$ C 79.94 H 5.68%.

Bis(chlorodiphenylsilyl)ethyne

A flask fitted with a reflux condenser and a mechanical stirrer was charged with carbon tetrachloride (100 ml), bis(diphenylsilyl)ethyne (30 g, 77 mmol) and BPO (2.6 g, 11 mmol). The solution was mixed under reflux and the

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conversion by GC reached 100% after 18 hr of reaction. The solvent was evaporated *in vacuo* and the crude solid was recrystallized from petroleum ether to give white crystals. Yield: 84%, purity by GC: >99%, ^{29}Si-NMR: δ (ppm) −19.8, GC-MS *m/e* (% relative intensity): 458 (M^+, 11); 460 ($M^+ + 2$, 7); 462 ($M^+ + 4$, 2); 380 (M^+-C_6H_6, 5); 283 (100); 181 (12); 63 (11).

Bis(hydroxydiphenylsilyl)ethyne (1)

Disilanol **1** was prepared by hydrolysis of bis (chlorodiphenylsilyl)ethyne in Et_2O in the manner as described previously [14]. White-yellow crystals, m.p.: 124–126°. Yield: 94%, ^{1}H-NMR: δ (ppm) 7.77–7.74 (m, 4H); 7.47–7.24 (m, 6H); 3.01 (broad s, 1H), ^{29}Si-NMR: δ (ppm) −31.6. Elemental analysis: found C 73.77 H 5.29%; calcd for $C_{26}H_{22}O_2Si_2$ C 73.89 H 5.25%.

Polymerizations

The following shows a typical polymerization method (run 2 in Table 1). A flask fitted with a dropping funnel was charged with THF (10 ml) and **2** (1.96 g, 6.00 mmol). With magnetic stirring at room temperature, **1** (2.60 g, 6.15 mmol) in THF (10 ml) was dropwise added over 3 hr. The reaction mixture was stirred for a further 2 hr and then poured into methanol (500 ml). The precipitated polymer was separated by centrifugation and washed with methanol three times and once with acetone. Evaporation at 80° *in vacuo* gave white powder (3.2 g, 89% yield).

Solubility of the polymers

3, **4** and **5** were soluble in THF and $CHCl_3$ but insoluble in acetone, toluene, diethyl ether, hexane and methanol. **6** was soluble in THF, $CHCl_3$, acetone, toluene and diethyl ether but insoluble in hexane and methanol.

Typical ^{13}C- and ^{1}H-NMR chemical shifts of the polymers

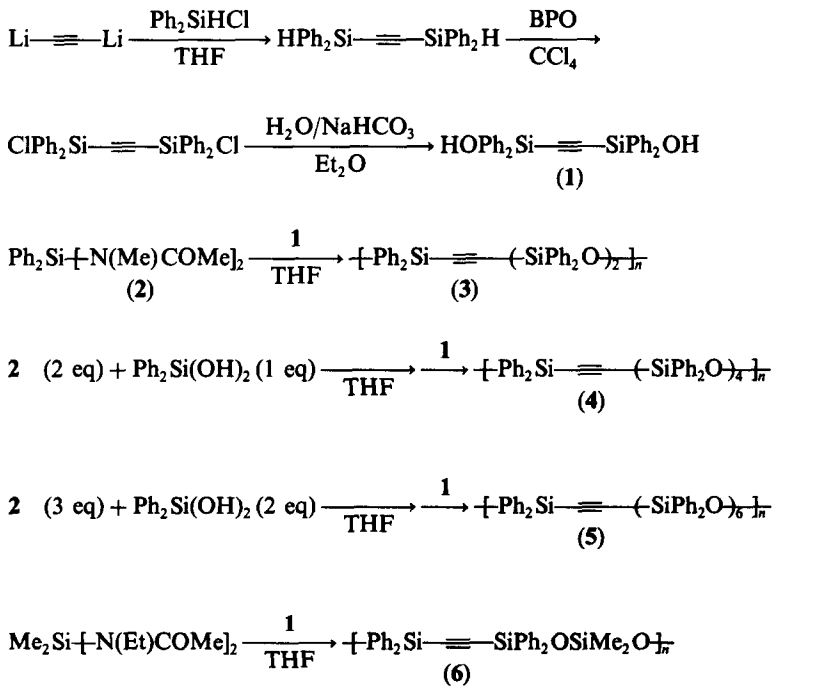
^{13}C (ppm): 134.0, 129.2 and 127.5 (phenyl carbons); 112.0 (ethynylene carbons); 0.9 (methyl carbons). ^{1}H (ppm): 7.7–6.9 (phenyl protons); 0.2 (methyl protons).

RESULTS AND DISCUSSION

As a preliminary study, conventional condensation methods were tried for obtaining alternating copolymers. A dehydrochlorination between bis-(hydroxydiphenylsilyl)ethyne (**1**) and diphenyldichlorosilane or between diphenylsilanediol and bis-(chlorodiphenyl-silyl)ethyne in the presence of pyridine gave only oligomers with molecular weights <2000. From these results, it was deduced that the steric hindrance caused by the diphenyl groups is quite significant. Attempted dehydrogenative condensation between **1** and diphenylsilanediol did not proceed when dibutyltin dilaurate or tetrabutyl titanate was used as catalyst. When butyllithium was used as catalyst for this dehydrogenation, a rearrangement reaction of **1** cleaving the silicon–acetylene bonds took place.

Dvornic and Lentz reported preparation of silphenylene–siloxane alternating copolymers employing a bis(hydroxysilyl)benzene and a bisureidosilane [11]. Similarly, Babu and Newmark reported reactions between a bis(hydroxysilyl)benzene and a bis-(dimethylamino)silane for the same purpose [12]. In the latter reaction it was necessary to carry out the reaction stepwise (once low boiling material was evaporated before the final condensation) probably in order to drive the condensation reaction toward completion by removing dimethylamine.

Thus, it was concluded that a siloxane bond formation reaction with evolution of a neutral compound such as acetamide, i.e. a reaction between a disilanol and a diamidosilane, would be suitable for obtaining a satisfactory polymer. The polymers synthesized in this way are shown in Scheme 1 along with the synthetic routes.



Scheme 1

Table 1. Results of polymerization

Run	1	2	3	4	5	6
Polymer	**3**	**3**	**4**	**5**	**6**	**6**
Addition method[a]	A	B	B	B	A	B
Temperature	rt	rt	Reflux	Reflux	rt	rt
Yield (%)	94	89	91	60	69	71
$M_n \times 10^{-3}$[b]	2.4	12.4	8.3	13.6	3.8	6.8
$M_w \times 10^{-3}$[b]	5.8	17.9	18.6	20.1	9.0	23.0
Appearance[c]	C	C	C	C	D	D

[a]A, Diamidosilane added to disilanol; B, disilanol added to diamidosilane.
[b]Relative to standard poly(dimethylsiloxane) samples.
[c]C, White powder; D, yellow gummy solid.

Table 2. NMR data for polymers

	Polymer			
	3	**4**	**5**	**6**
^{29}Si				
δ(OSiC≡C)(ppm)	−37.9	−38.3	−38.4	−38.6
δ(OSiO)[a](ppm)	−43.4	−44.8	−44.9	−14.7
δ(OSiO)[b](ppm)		−45.8	−45.8	
δ(OSiO)[c](ppm)			−46.1	
OSiC≡C/OSiO[d]	2.2	0.65	0.52	2.0
(theoretical)	(2.0)	(0.67)	(0.4)	(2.0)
^{13}C				
Ph/C≡C	5.8	11	13	4.0
(theoretical)	(6.0)	(12)	(14)	(4.0)
^{1}H				
Ph/Me				2.0
(theoretical)				(2.0)

[a]C≡CSiOSiOSiC≡C unit.
[b]C≡CSiOSiOSiOSiOSiC≡Cunit.
[c]C≡CSiOSiOSiOSiOSiOSiOSiC≡C unit.
[d]Integral ratio of C≡CSiO silicons to all OSiO silicons.

The results of the polymerizations are shown in Table 1. Polymers with moderately high molecular weights were obtained in fairly good yield. Polymers **3**, **4** and **5** are white powders and polymer **6** is a yellow gummy solid. It is noteworthy that polymers **3** and **4** are film-forming and spinnable although the resulting films and fibres are brittle. A comparison of runs 1 and 2 indicates that the order of addition of the reactants affected the resulting molecular weights of the products. The higher molecular weight was obtained when disilanol **1** was added dropwise to diamidosilane **2**. This tendency was also seen when the reactions were carried out under reflux (data not shown). Whereas no good explanation for this phenomenon has been made, the reproduciblility is demonstrated in the difference between runs 5 and 6.

Without reflux, satisfactory polymers were not obtained regardless the order of the addition for preparation of **4** and **5**. When the reaction was carried out at room temperature, the resulting M_w was <2000.

The results of NMR analyses of the polymers are summarized in Table 2. Good agreement is seen between the theoretical molar ratios and the observed integral ratios for polymers **3**, **4** and **6**, while there is a discrepancy for polymer **5** with regard to the OSiC≡C/OSiO ratio. The ^{29}Si-NMR spectra of **4** and **5** are shown Fig. 1. As can be seen, the spectrum of **5** indicates existence of certain kinds of silicon atoms which were not expected. For example, the signal at *ca* −43 ppm can be attributed to octaphenylcyclotetrasiloxane and the broad one at *ca* −46.5 ppm is assignable to linear poly(diphenylsiloxane). On the other hand, the spectrum of **4** contains only negligible amounts of signals due to unexpected species. These observations suggest that **5** contains by-products. Their presence might be explained by formation of molecules with distribution of molecular weights in the first stage of the preparation (Scheme 2).

The thermal properties of the polymers are listed in Table 3. It is seen that the perphenylated polymers (**3**, **4** and **5**) have clear T_ms both in the visual observations and in the DSC, though all are below

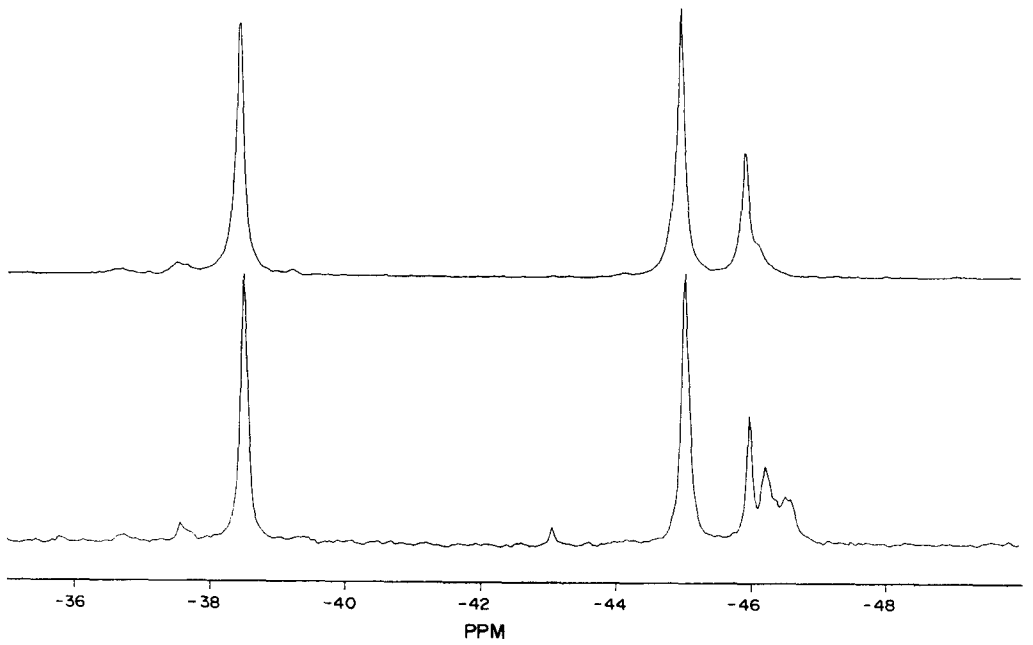


Fig. 1. ^{29}Si-NMR spectra of polymers (in $CDCl_3$); upper: **4**, lower: **5** (see Scheme 1).

$$Ph_2Si(NMA)_2(3\ eq) + Ph_2Si(OH)_2(2\ eq) \rightarrow$$

$$NMA\text{-}(\text{-}Ph_2SiO\text{-})_4SiPh_2NMA + NMA\text{-}(\text{-}Ph_2SiO\text{-})_aSiPh_2NMA + \boxed{(\text{-}Ph_2SiO\text{-})_4}$$

(intended) ($a = 1, 2, 3, 5, \ldots$)

(NMA: methylacetamido)

Scheme 2

the optimal T_m of 200°. The low T_m of **5** compared with that of **4** seems contradictory to the higher diphenylsiloxane content, but is reasonable when the presence of by-products is taken into account. Polymer **6** is considered to be amorphous and no distinct peak was found in the DSC thermogram in the range 20 to 300°.

All the polymers exhibited excellent thermal stability as shown by TGA results (in N_2 or air, rate: 10°/min). The temperature at which the weight loss of each perphenylated polymer reaches 10% is >500° in N_2. The 10% weight loss temperature of **4** in air is as high as 509°. These values can be regarded as in the highest class among those of thermoplastic polymers.

Table 3. Thermal properties of polymers

	Polymer			
	3	**4**	**5**	**6**
T_m (°C)				
Obs.	161–164	170–176	155–160	50–70[a]
DSC	154	174	155	—
TGA[b] (N_2)				
5% wt loss (°C)	476	478	496	452
10% wt loss (°C)	503	506	521	487
Residue at 800°(%)	41	30	61	41
TGA[b] (air)				
10% wt loss (°C)	495	509	471	—

[a]Softening point.
[b]Rate: 10°/min.

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