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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Novel Synthesis of a Macromonomer Having Organosilyl and Amino Groups

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**To cite this Article** Nagasaki, Yukio , Honzawa, Eiichi , Kato, Masao , Kihara, Yasuharu and Tsuruta, Teiji(1992) 'Novel Synthesis of a Macromonomer Having Organosilyl and Amino Groups', *Journal of Macromolecular Science, Part A*, 29: 6, 457 – 470

**To link to this Article:** DOI: 10.1080/10101329208052174

**URL:** <http://dx.doi.org/10.1080/10101329208052174>

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## NOVEL SYNTHESIS OF A MACROMONOMER HAVING ORGANOSILYL AND AMINO GROUPS†

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### ABSTRACT

Reaction between dimethyldivinylsilane (**1**) and *N,N'*-diethyl-*N*-lithio-ethylenediamine (**2a**) in the presence of *N,N'*-diethylethylenediamine (**3a**) in THF at 20°C gave a monoadduct, 3,3-dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (**4a**). An anionic self-polyaddition reaction of **4a** in the presence of lithium diisopropylamide (LDA) proceeded to form oligomers. Each of the oligomers thus obtained was found to carry a polymerizable vinylsilane moiety at the oligomer chain terminal. As a result, a new type of macromonomer having alternating repeating units of ethylenediamine and organosilyl groups was synthesized. Acid-base titration showed the macromonomer to have unique characteristics on

†Dedicated to Professor Otto Vogl on the occasion of his 65th birthday.

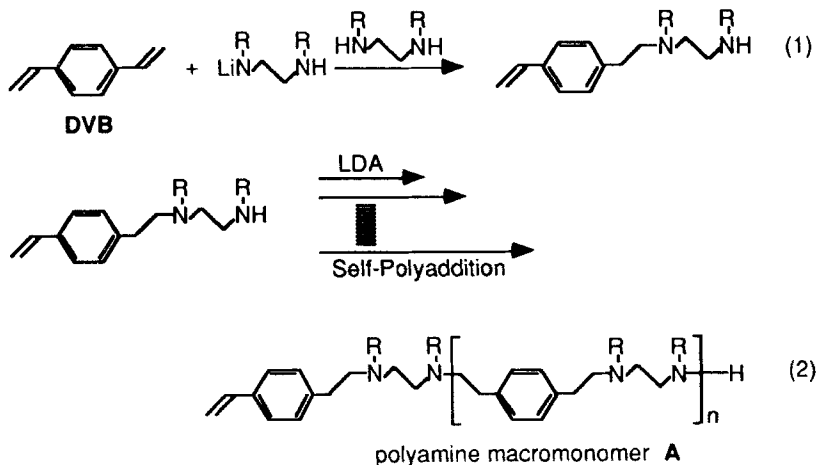
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protonation of diamine moieties. Anionic polyaddition reactions between **1** and *N*-lithio-piperazine (**2b**) in the presence of piperazine (**3b**) also gave a macromonomer consisting of alternating repeating units of piperazine and organosilyl groups (**4b**). Radical copolymerizations of styrene with **5b** gave comblike graft copolymers.

## INTRODUCTION

Organosilicon-containing polymers are of great interest as candidates for new high functional materials such as gas separation membranes [1], resists [2], semiconducting polymers [3], flame retarders [4], etc. Our strategy for the syntheses of organosilicon-containing polymers having new structures is to create a novel synthetic route based on our original reaction design and methodology [5].

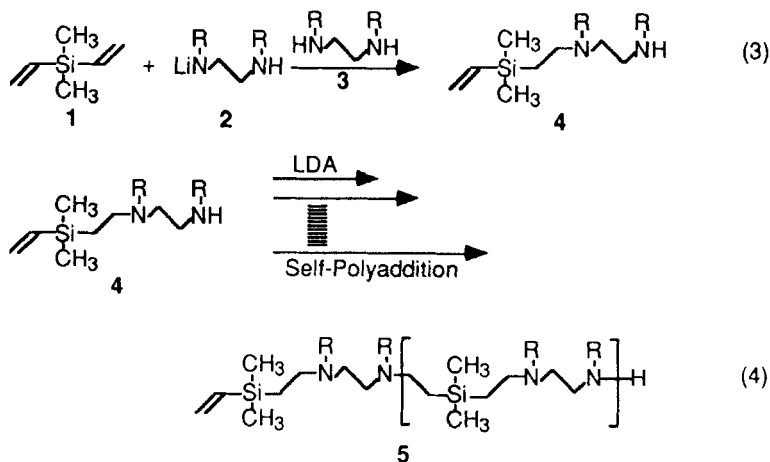
One of the authors, Tsuruta, has been studying addition reactions of lithium alkylamides toward conjugated olefins such as diene, styrene, and divinylbenzene for many years [6]. In the course of the studies, it was found that anionic polyaddition reactions between lithiated diamine and 1,4-divinylbenzene (DVB) form macromonomer [polyamine macromonomer **A**] with alternating repeating units of diamine and divinylbenzene groups [7] as follows:



Polymers having polyamine macromonomer **A** as one component exhibit unique characteristics as functional materials such as biorecognition matrices [8] and pH sensitive gels [9].

We recently found the reactivity of lithium diethylamide toward the double bond of dimethyldivinylsilane (**1**) ( $k_1 = 31.2 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  in THF at  $30^\circ\text{C}$  [10]) was of the same order as that of DVB ( $k_{\text{DVB}} = 30.4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  in THF at  $30^\circ\text{C}$  [11]). Actually, the reaction between **1** and lithium diethylamine gave the monoadduct 2-(*N,N*-diethylamino)ethyl dimethylvinylsilane along with the diadduct bis[2-(*N,N*-diethylamino)ethyl dimethylsilane] [10]. When lithiated diamine was used as the reactant instead of monoamine, anionic polyaddition reactions between **1** and diamine resulted in the formation of a new type of macromonomers having alternating repeating units of diamine and organosilyl groups.

This paper deals with synthesis and pH dependency of silicon-containing polyamine macromonomers.



where R : C<sub>2</sub>H<sub>5</sub> for a  
R-R : CH<sub>2</sub>-CH<sub>2</sub> for b

## EXPERIMENTAL

All procedures were carried out under purified nitrogen or argon to eliminate oxygen and moisture.

### Materials

Commercial tetrahydrofuran (THF), cyclohexane (cHx), *N,N'*-diethylethylenediamine (3a), piperazine (3b) diisopropylamine, and dimethyldivinylsilane (1), were purified by conventional methods [12]. Butyllithium was used as the hexane solution, the concentration of which was determined by Gilman's double titration method [13].

### Addition Reaction between Dimethyldivinylsilane (1) and *N,N'*-Diethyl-*N*-lithio-ethylenediamine (2a) in the Presence of *N,N'*-Diethylethylenediamine (3a)

One of the representative procedures for addition reactions of 2a toward 1 is described. To a stirred THF solution of 3a, hexane solution of butyllithium was added by using a syringe. After a few minutes agitation to complete formation of 2a, 1 was added by using a syringe ([1]<sub>0</sub> = 0.5 mol/dm<sup>3</sup>; [2a]<sub>0</sub> = 0.05 mol/dm<sup>3</sup>; [3a]<sub>0</sub> = 0.5 mol/dm<sup>3</sup>). The mixture was stirred at 20°C, and an aliquot of the mixture was sampled every few minutes and analyzed directly by gas chromatography. The monoadduct obtained, 3,3-dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (4a), was purified by fractional distillation under reduced pressure (bp: 63°C/0.5 mmHg). The 4a thus obtained was analyzed by <sup>1</sup>H-NMR and mass spectroscopy.

### Anionic Self-Polyaddition Reactions of 3,3-Dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (4a)

One of the representative procedures for anionic self-polyaddition reactions of **4a** is described. To a stirred THF solution of lithium diisopropylamide (0.05 mol/dm<sup>3</sup>), **4a** (1.0 mol/dm<sup>3</sup>) was added by using a syringe. The mixture was allowed to react at 30°C for 24 h, and then a small amount of methanol was added to quench the reaction. The macromonomer (**5a**) was obtained after removing low boiling materials under reduced pressure at 60°C. The **5a** thus obtained was analyzed by <sup>1</sup>H NMR, GPC, and acid-base titration.

### Radical Copolymerization of Styrene with Organosilicon-Containing Macromonomer (5b)

To an ethanol solution of 2,2'-azobis(2,4-dimethylvaleronitrile) (V-65; 10<sup>-2</sup> mol/dm<sup>3</sup>) in a glass tube, styrene (1.0 mol/dm<sup>3</sup>) and the macromonomer (the same sample as Run 1 in Table 2 was used; 0.1 mol/dm<sup>3</sup>) were added. After sealing off the tube, the mixture was allowed to react at 45°C for 20 h. Then the tube was opened and the reaction mixture was poured into methanol. Precipitates thus obtained were purified by three successive reprecipitations from THF solution into methanol. The polymer sample thus obtained was freeze-dried with benzene to remove the solvents employed.

### Acid-Base Titration of Silicon-Containing Macromonomer (5a)

To a stirred water solution (30 mL) of **5a** (0.115 g; 1.0 mmol as N-atom), 15 mL of mol/dm<sup>3</sup> HCl aqueous solution was added. A titration curve was obtained by potentiometric titration using 0.1 mol/dm<sup>3</sup> NaOH aqueous solution as the titrant at 23°C. Turbidity of the macromonomer solution was recorded simultaneously during titration using a UV/Visible spectrometer.

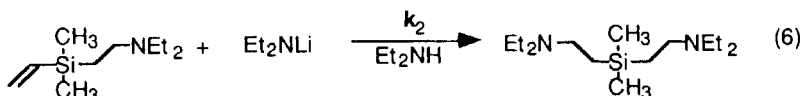
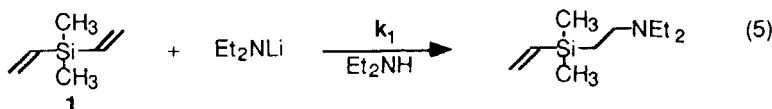
### Measurements

Gas chromatograms were taken with a Shimadzu GC-14A gas chromatograph (Column: glass capillary column OV-1 50m). GC/mass spectra were obtained using a Hewlett-Packard 5890 Series II equipped with a 5971A Mass Selective Detector. For GPC measurements, a Shimadzu LC 6A Liquid Chromatograph was used with the equipment of a RI detector (RID 6A; Column: TSK-Gel G4000H8 + G3000H8 + G2500H8). To eliminate possible adsorption of amino-containing polymer onto polystyrene gel as packing, THF containing low molecular weight amine was used as the eluent (2 vol% dimethylbenzylamine in THF). <sup>1</sup>H-NMR spectra were observed on JEOL FX 90Q and Varian VXR-500S spectrometers at room temperature by using a 5-mm glass tube containing a solution of the polymer sample in CDCl<sub>3</sub> (1.0 g/dL). Chloroform was used as the internal reference for the measurements. Potentiometric titration was carried out using a HORIBA pH Meter F11. Turbidity was monitored with visible light at 500 nm using a Hitachi 557 UV/Visible spectrometer.

## RESULTS AND DISCUSSION

1. Reaction between *N,N'*-Diethyl-*N*-lithio-ethylenediamine (**2a**) in the Presence of *N,N'*-Diethylethylenediamine (**3a**)

To obtain polymers having the desired molecular mass through polyaddition reactions, we isolated the monoadduct of the two reactants as the starting material for the polyaddition reaction. As we reported previously, reactivity of **1** toward lithium dialkylamide was strongly dependent on the reaction media [10]. For example, the rate constant for the first step of the addition reaction of **1** toward lithium diethylamide in THF ( $k_1$  in Eq. 5) was 10 times larger than that of the second step ( $k_2$  in Eq. 6), while the ratio of  $k_1/k_2$  obtained in cyclohexane was only 2.6. Consequently, THF is a suitable solvent to obtain the monoadduct in high yield. Actually, the yield of monoadduct was as high as 78% in the reaction between lithium diethylamide and **1** in THF [10].



To get information on the reactivity of **1** toward lithiated diamine (**2**), reactions between **1** and *N,N'*-diethyl-*N*-lithio-ethylenediamine (**2a**) in the presence of *N,N'*-diethylethylenediamine (**3a**) in THF were carried out. A gas chromatogram of the reaction mixture (Fig. 1) shows a new product appearing around 8 min. From the GC/mass analysis shown in Fig. 2, the fragment ion pattern of the product was favorable for the formation of the monoadduct 3,3-dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (**4a**), although the intensity of the parent ion peak was very weak.

Figure 3 shows time-dependent changes in the yield of **4a**. As compared to the reaction between **1** and lithium diethylamide, the maximum yield of **4a** was lower (49.4%) owing to the consumption of **4a** through anionic polyaddition reactions. Actually, nonvolatile materials remained after evaporation of low boiling materials and **4a** under reduced pressure.

2. Anionic Polyaddition Reaction of 3,3-Dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (**4a**)

Anionic polyaddition reactions of **4a** were carried out in the presence of lithium diisopropylamide. The reaction proceeded smoothly, and colorless nonvolatile materials remained after evaporation of the low boiling materials. The oligomers thus obtained were soluble in a variety of solvents such as benzene, toluene, hexane, THF, dioxane, ether, chloroform, carbon tetrachloride, methanol, ethanol, acetone, acidic water, etc. Figure 4 shows gel permeation chromatograms of the oligomers formed. As shown in the figure, the oligomers formed had molecular weights that ranged from a few hundred to 5000. By using a calibration curve based on a

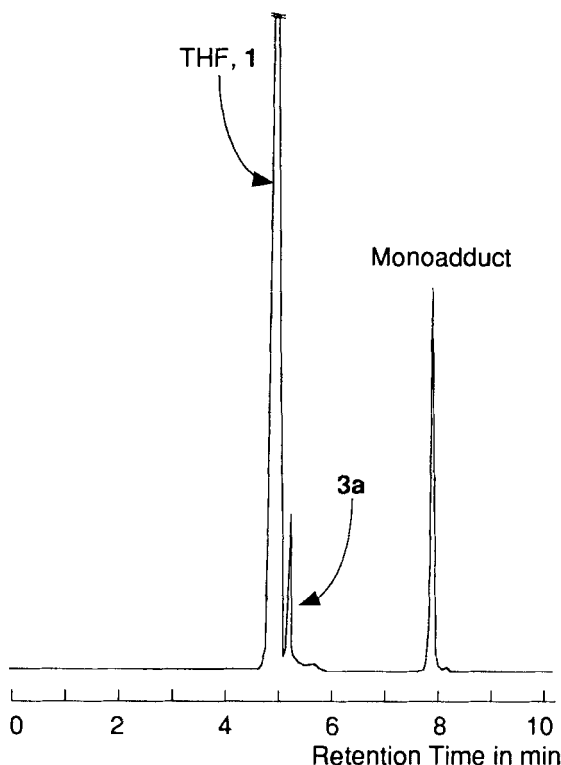


FIG. 1. Gas chromatogram of the product obtained from the reaction between dimethyldivinylsilane (**1**) and *N,N'*-diethyl-*N*-lithio-ethylenediamine (**2a**) in the presence of *N,N'*-diethylethylenediamine (**3a**).

standard polystyrene sample, the number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of the oligomers were determined to be 900 and 1680, respectively ( $M_w/M_n = 1.86$ ).

Figure 5 shows the  $^1\text{H-NMR}$  spectra of the **4a** oligomers formed together with the 1:1 adduct, **4a**. By using trimethylvinylsilane, 2-(*N,N*-diethylamino)ethyl-dimethylvinylsilane, diethylamine, and triethylamine as reference compounds, assignments of the signals of **4a** and **4a** oligomers were made, the results of which are described in the figure. The ratio of the peak intensities of the signals appearing in Fig. 5(A) was as follows:

$$\mathbf{a}:\mathbf{a}':\mathbf{b}:\mathbf{c}:\mathbf{c}':\mathbf{e}:\mathbf{e}':\mathbf{f} = 41.0:6.0:30.5:46.8:3.0:94.7:4.0:3.0$$

Because the intensity of the  $\alpha$ -end protons of the oligomers, **a'** (6.0) and **f** (3.0), agreed stoichiometrically with those of  $\omega$ -end protons, **c'** (3.0) and **e'** (4.0), it was confirmed that the oligomers thus obtained had one polymerizable vinyl group at the end of the polymer chain and were regarded as a macromonomer (**5a**). Further results obtained in the anionic self-polyaddition reactions are summarized in Table 1. Under appropriate reaction conditions, the molecular weight of **5a** was controllable in the range between 1000 to 3000.

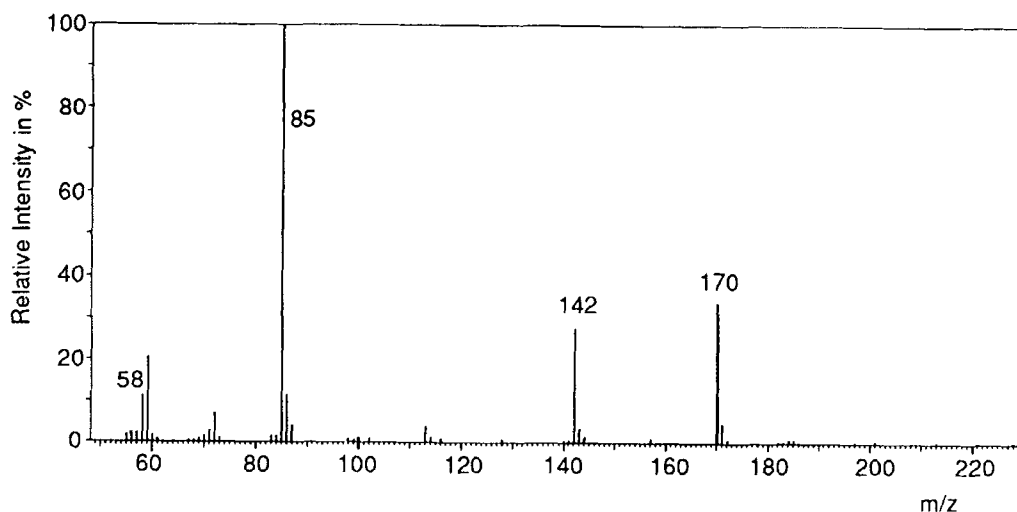
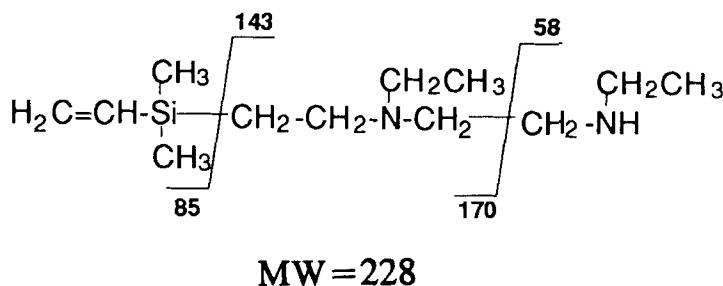


FIG. 2. Mass spectrum of the monoadduct of dimethyldivinylsilane (**1**) and *N,N'*-diethylethylenediamine (**3a**), 3,3-dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (**4a**).

### 3. Synthesis of Organosilicon-Containing Macromonomer Having Other Diamine Repeating Units

To synthesize another type of organosilicon-containing macromonomer, reactions between **1** and *N*-lithio-piperazine (**2b**) were carried out. Because **2b** was not soluble in THF, anionic polyaddition reactions were carried out without separation of the monoadduct between **1** and **2b**, and the results obtained are summarized in Table 2. As shown in Table 2, anionic polyaddition reactions proceeded smoothly in the reaction between **1** and **2b**. The oligomers obtained were soluble in such common organic solvent as benzene, toluene, THF, dioxane, ether, chloroform, carbon tetrachloride, methanol, and ethanol, and were insoluble in acetone. The molecular weights of the oligomers were in the range between 2000 and 6000. Figure 6 shows the <sup>1</sup>H-NMR spectrum of the oligomers formed. The assignment of the signals in Fig. 6 was carried out using **5a** and piperazine (**2b**) and is described in the figure. As the polymerizable vinyl protons at the end of the polymer chain remained as in the case of **4a**, the oligomers formed were regarded as a macromonomer (**5b**).

To examine the polymerization ability of the macromonomer, copolymeriza-



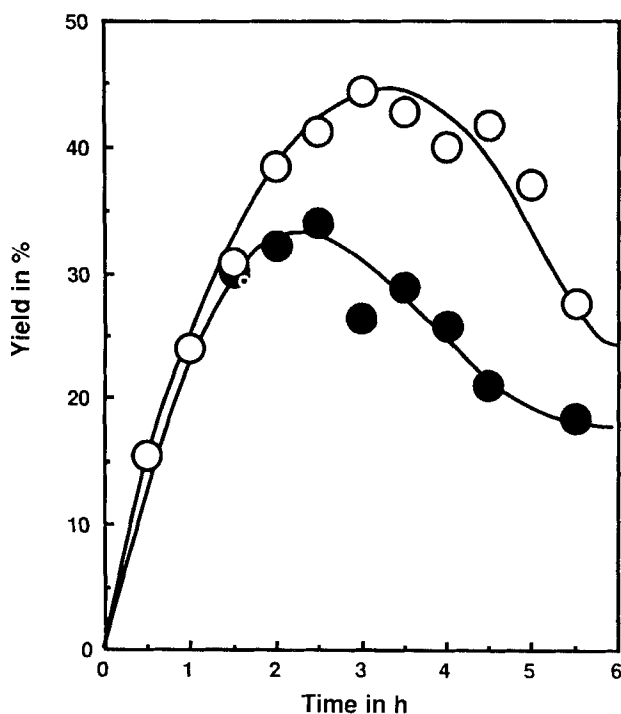


FIG. 3. Time-conversion curve for the addition reaction between dimethyldivynylsilane (**1**) and *N,N'*-diethyl-*N*-lithio-ethylenediamine (**2a**) in the presence of *N,N'*-diethylethylenediamine (**3a**). (O):  $[\text{Dimethyldivynylsilane}]_0 = 0.5 \text{ mol/dm}^3$ ;  $[\text{N,N'-diethylethylenediamine}]_0 = 0.5 \text{ mol/dm}^3$ ;  $[\text{N,N'-diethyl-N-lithio-ethylenediamine}]_0 = 0.05 \text{ mol/dm}^3$  in THF at 20°C. (●):  $[\text{Dimethyldivynylsilane}]_0 = 0.25 \text{ mol/dm}^3$ ;  $[\text{N,N'-diethylethylenediamine}]_0 = 0.125 \text{ mol/dm}^3$ ;  $[\text{N,N'-diethyl-N-lithio-ethylenediamine}]_0 = 0.125 \text{ mol/dm}^3$  in THF at 20°C.

tion with styrene was carried out. Radical copolymerization of styrene with **5b** (see Experimental part) gave a polymer which was soluble in benzene, chloroform, THF, and acetone, and insoluble in methanol. From the  $^1\text{H-NMR}$  spectrum of the polymer purified by reprecipitation using methanol as a nonsolvent (Fig. 7), it was found that the polymer formed had both starting monomer units.

#### 4. Protonation Behavior of Silicon-Containing Polyamine Macromonomer

To estimate the response of **5a** to a pH change, acid-base and turbidity titrations of the macromonomer were carried out. As shown in Fig. 8, a typical two-stage titration curve of **5a** was observed. This was attributable to the two-stage deprotonation process of ethylenediamine structure as reported previously [14] (Eq.

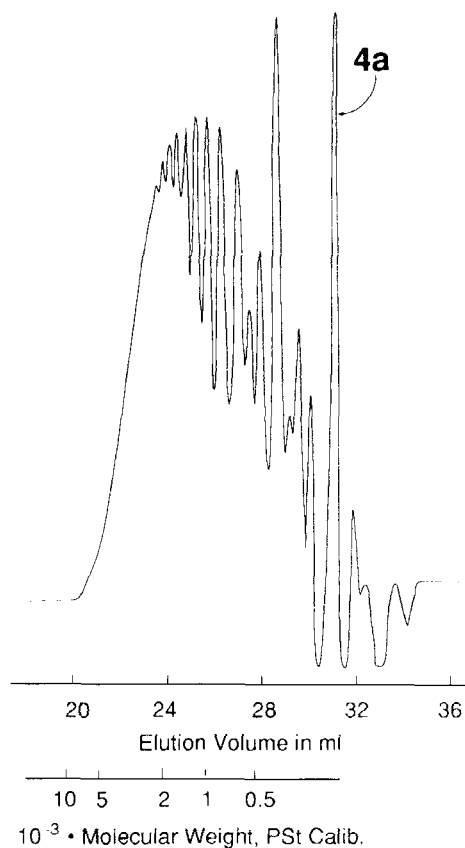
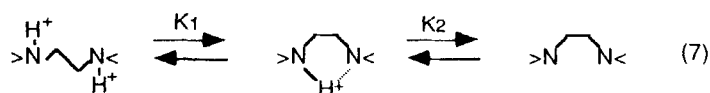


FIG. 4. Gel permeation diagrams of the **5a** formed in the anionic self-polyaddition reaction of **4a** in the presence of lithium diisopropylamide in THF. The same reaction conditions as for Run 5 in Table 2.

7). As the second-stage deprotonation of protonated **5a** proceeded, turbidity of the solution increased drastically. The same was observed for polyamine macromonomer **A** (shown in Eq. 2) [14].



Apparent  $pK$  values of the macromonomer, as determined from the acid-base titration curve (Table 3), suggest the protonated structure of the diamine units in **5a** is more stable than the one in polyamine macromonomer **A**. These phenomena may be attributable to the organosilicon-moiety structure of macromonomer **5a**. Detailed studies on the properties of the macromonomer having both organosilicon and diamine repeating units will be published elsewhere.

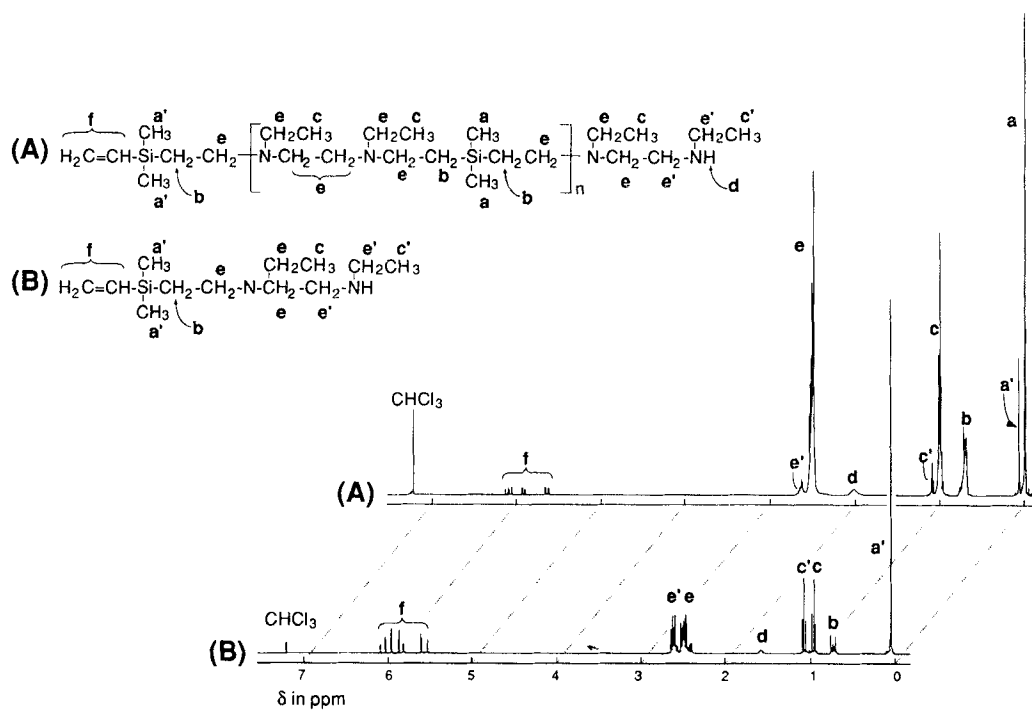


FIG. 5.  $^1\text{H}$ -NMR spectra. (A): The **5a** formed in the anionic self-polyaddition reactions of **4a** (the same sample as in Fig. 4). (B): 3,3-Dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (**4a**).

TABLE 1. Results of Anionic Self-Polyaddition Reactions of 3,3-Dimethyl-6-ethyl-3-sila-6,9-diaza-1-undecene (**4a**) in the Presence of Lithium Diisopropylamide (LDA)<sup>a</sup>

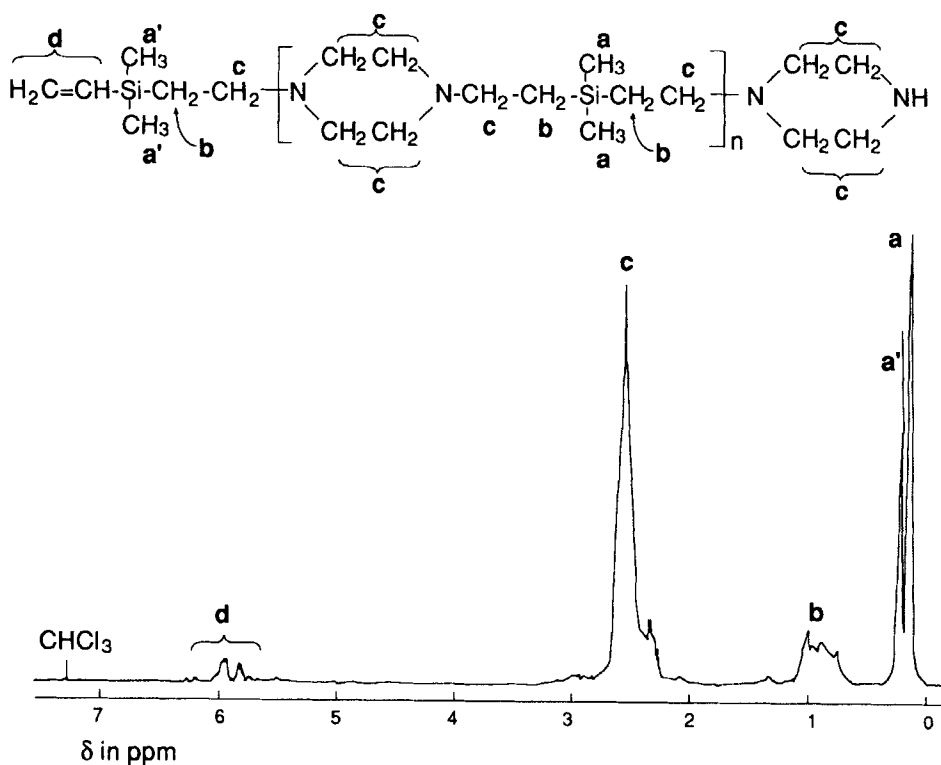
Run	[ <b>4a</b> ] <sub>0</sub>	10 <sup>2</sup> × [LDA] <sub>0</sub>	Solvent	10 <sup>3</sup> × <i>M<sub>n</sub></i> <sup>b</sup>
1	1.0	10.0	THF	1.3
2	1.0	7.5	THF	2.0
3	1.0	5.0	THF	3.2
4	1.0	10.0	cHx	1.2
5	0.87	5.0	THF	1.9

<sup>a</sup>Temperature, 30°C; time, 24 h.

<sup>b</sup>Determined from  $^1\text{H}$  NMR results.

TABLE 2. Results of Anionic Polyaddition Reactions between Dimethyldivinylsilane (**1**) and *N*-Lithio-piperazine (**2b**)<sup>a</sup>

Run	$10^2 \times [\mathbf{2b}]_0$ in mol/dm <sup>3</sup>	Solvent	Time, h	Temperature, °C	Yield, %	$10^3 \times M_{\text{GPC}}^b$
1	5.0	THF	6	30	48.7	2.3
2	2.5	THF	24	30	80.3	5.9
3	5.0	Bz	96	50	65.6	2.1
4	2.5	Bz	96	50	64.8	6.2

<sup>a</sup>[**1**]<sub>0</sub> = [piperazine]<sub>0</sub> = 0.50 mol/dm<sup>3</sup>.<sup>b</sup>Determined from GPC results.FIG. 6. <sup>1</sup>H-NMR spectrum of the **5b** formed in the reaction between dimethyldivinylsilane (**1a**) and *N*-lithio-piperazine (**2b**).

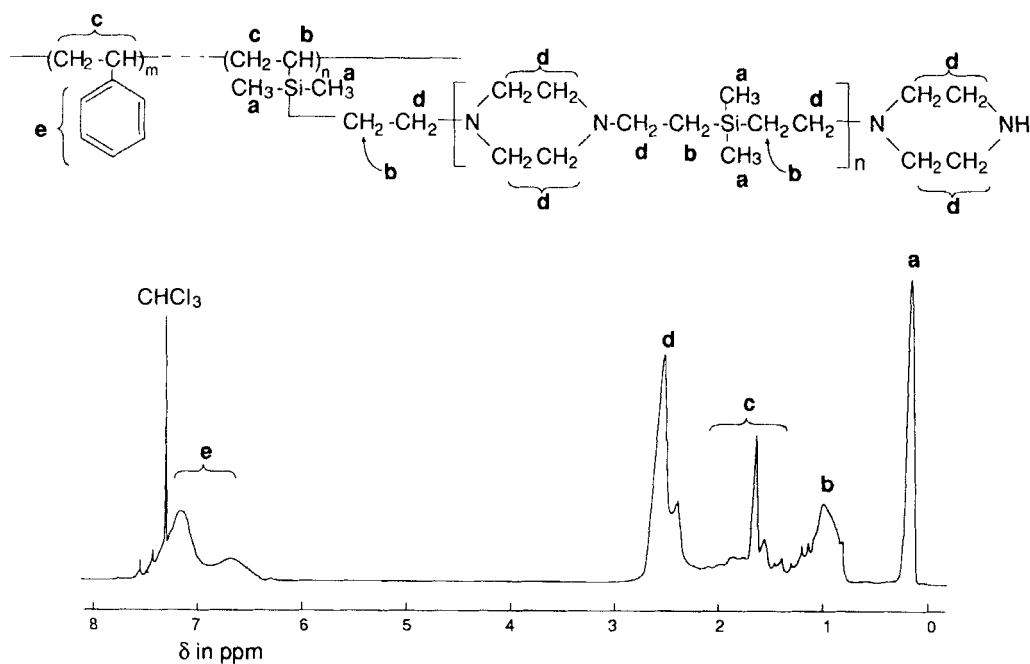


FIG. 7.  $^1\text{H-NMR}$  spectrum of the copolymer formed in the radical copolymerization of styrene with **5b**.

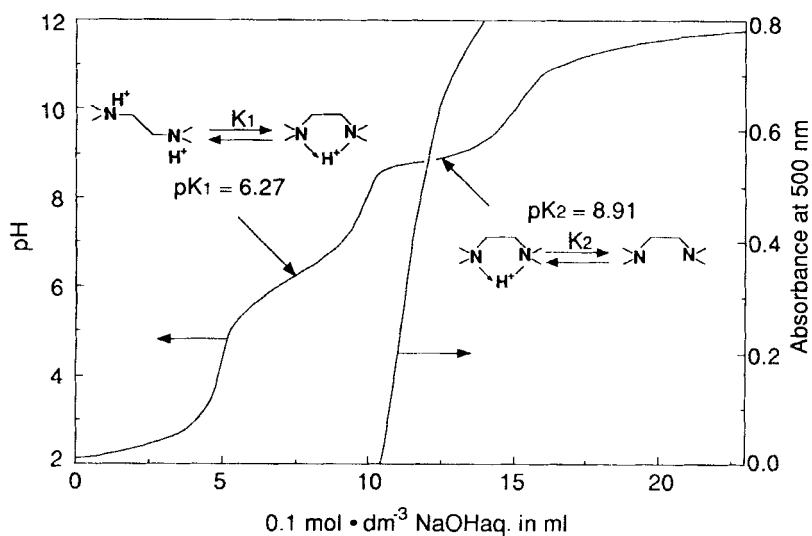
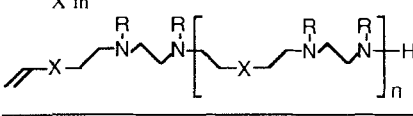
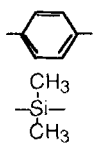
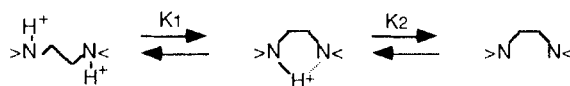


FIG. 8. Acid-base and turbidity titration curve of **5a** at  $23^\circ\text{C}$ .

TABLE 3. Apparent pK Value of Polyamine Macromonomer at 23 °C<sup>a</sup>

X in	pK <sub>1</sub>	pK <sub>2</sub>	Reference
	5.0	7.5	[15]
	6.3	8.9	This work
Tetraethylethylenediamine <sup>b</sup>	5.8	10.2	[15]

a



b Model Compound

### ACKNOWLEDGMENTS

One of the authors (Y.N.) would like to express his sincere appreciation to ICI Japan Foundation for financial support of a part of this research. A part of this work was supported financially by a Grant-in-Aid for Scientific Research on Priority Areas (Synthetic Process and Control of Functionality Materials, Reaction Design for Synthesis of Functionality Materials), The Ministry of Education, Science and Culture, Japan.

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Received August 2, 1991

Revision received October 24, 1991