

## A Polyamine Macromonomer Having Controlled Molecular Weight —Synthesis and Mechanism—

Dedicated to the Memory of the late Professor Ichiro Sakurada

Yoshikuni NABESHIMA, Atsushi MARUYAMA,<sup>†</sup> Teiji TSURUTA,  
and Kazunori KATAOKA\*

Department of Industrial Chemistry, Faculty of Engineering,  
Science University of Tokyo, Kagurazaka,  
Shinjuku-ku, Tokyo 162, Japan

\*Institute of Biomedical Engineering, Tokyo Women's Medical College,  
Kawada-cho, Shinjuku-ku, Tokyo 162, Japan

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**ABSTRACT:** Polyamine macromonomer possessing a polymerizable vinyl group at the chain end was synthesized by lithium amide catalyzed anionic self-polyaddition reaction of *N,N'*-diethyl-*N*-(4-vinylphenethyl)ethylenediamine. To elucidate the reaction mechanism for the macromonomer synthesis, the quantitative analyses were carried out on this reaction using double-wavelength UV method as well as UV fourth order derivative spectra method. The number average molecular weight of the macromonomer was also measured with these UV methods. From these studies, it was concluded that one to one complex consisting of >NH and >NLi played an important role in the successive addition reactions. When the ratio of [>NH] to [>NLi] became smaller to approach unity, there occurred a break point at which the rate of the addition reaction decreased sharply. The number average molecular weight of the macromonomer at the point was expressed by a simple equation (*cf.* eq 7). Thus, it was possible to control the molecular weight of the polyamine macromonomer by adjusting the relative concentrations of >NH to >NLi in the initial mixture for the polyaddition reaction.

**KEY WORDS** Polyamine Macromonomer / Lithium Amide / Anionic Polyaddition Reaction / 1,4-Divinylbenzene / *N,N'*-Diethylmethylenediamine / *N,N'*-Diethyl-*N*-(4-vinylphenethyl)ethylenediamine / Double-Wavelength UV Method / UV Derivative Spectra Method /

It was previously reported<sup>1-9</sup> that a series of new monomers having various amino groups were synthesized by addition reaction of the relevant amines to 1,4-divinylbenzene(1,4-DVB) (1) in the presence of a catalytic amount of lithium alkylamide. By applying a difunctional amine as reactant, we explored novel synthetic method of polyamine macromonomer.<sup>5,9</sup> In a previous paper, we reported

results of study on successive addition reactions of *N,N'*-diethyl-*N*-(4-vinylphenethyl)ethylenediamine (3), which is a one to one addition product between 1,4-DVB (1) and *N,N'*-diethylmethylenediamine (2). The polyamine macromonomer<sup>\*1</sup> was copolymerized with styrene and 2-hydroxyethyl methacrylate to synthesize polyamine graft copolymers, SA and HA, respectively. The poly-

<sup>†</sup> Present address: Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102, Japan.

\*1 Systematic name:  $\alpha$ -(4-vinylphenethyl)- $\omega$ -[(*N*-ethyl)-2-ethylaminoethylamino]poly(ethyliminoethylene-1,4-phenyleneethylene).

amine graft copolymers, SA and HA, were found to exhibit unique biomedical behavior when they came into contact with living cells such as blood platelets or lymphocytes.<sup>10-12</sup>

It was desirable for us to control length of the graft chains in SA or HA copolymers, because their biomedical behavior may depend upon the graft length. Recently, we found an easy method for molecular weight regulation of the macromonomer, which was based on the nature of the lithium catalyzed polymerization reaction. For the measurement of accurate molecular weight of the macromonomer, double wavelength UV method was conveniently applied. With the aid of this method, time dependency of the molecular weight of macromonomers formed was studied in the course of reaction.

The present paper reports as to synthetic method and its mechanism for the polyamine macromonomer having controlled molecular weight.

## EXPERIMENTAL

Most of the experiments were carried out under a purified nitrogen to preclude oxygen and atmospheric moisture.

### Materials

1,4-Divinylbenzene (**1**) (supplied by Asahi Chemical Co.) was purified by fractional distillation over calcium hydride *in vacuo*. Commercial *N,N'*-diethylethylenediamine (**2**) was purified by two subsequent distillations over calcium hydride *in vacuo*. bp 69°C at 60 mmHg. *n*-Butyllithium was used as a cyclohexane solution and the concentration of the solution was determined by double titration. Other reagents and solvents were purified by usual methods.

### Synthesis of *N,N'*-Diethyl-*N*-(4-vinylphenethyl)ethylenediamine (**3**)

As described previously,<sup>5</sup> 100 mmol of **1** was added to a benzene solution (100 ml) of **2** (100

mmol) and *n*-butyllithium (5 mmol). After 15 min, the reaction was ceased by adding of a small amount of water. After the precipitates of lithium hydroxide were filtered off, the solution was treated with drierite (calcium sulfate). The drierite in the solution was filtered off and the solvent and other low boiling point materials were removed by evaporation. The product was separated by fractional distillation *in vacuo*. bp 70°C at 0.006 mmHg. IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra of the product corresponded the structure of **3**.

### Synthesis of 1,4-Bis(*N,N'*-diethylethylene-diaminoethyl)benzene (**5**)

To a THF solution (60 ml) prepared from 100 mmol of **2** and 5 mmol of *n*-butyllithium, 20 mmol of **1** were added at 20°C. The mixture was stirred for 24 h, followed by the addition of a small amount of water. After the solvent was removed by evaporation, the product was isolated by fractional distillation *in vacuo*. bp 158°C at 0.006 mmHg. IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra of the product corresponded to the structure of **5**.

### Synthesis of *N,N'*-Diethyl-*N*-phenethyl-ethylenediamine (**6**)

To a benzene solution (100 ml) of **2** (100 mmol), *n*-butyllithium (5 mmol) and styrene (100 mmol) were added successively and stirred for 5 h. The reaction was stopped by the addition of a small amount of water. Product formed was isolated by fractional distillation *in vacuo*. bp 80°C at 40 mmHg. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the product were confirmed to correspond to the structure of **6**.

### Synthesis of the Polyamine Macromonomer<sup>5</sup>

To a THF solution of *n*-butyllithium and diisopropylamine with a given quantity, **3** was added and placed in a thermostatted bath at 20°C. After an appropriate reaction time, the reaction was ceased by the addition of a small amount of water. After precipitates of lithium hydroxide were filtered off, the solvent and

other low boiling point materials were removed by evaporation and dried under vacuum. The product was analyzed by GPC and UV.

#### Kinetic Study of the Self-Polyaddition Reaction

The reaction mixture was prepared by the same method as described above. The reaction was quenched after various time intervals by sampling a portion of the solution and adding to it a small amount of water. The products were subjected directly to UV and GPC measurements.

#### UV Measurement

UV spectra of **4** in THF (UV measurement grade) were recorded on Hitachi 557 double wavelength-double beam spectrophotometer by a quartz cell (path length 1 cm).

#### GPC Measurement

Gel permeation chromatograms of **4** were recorded on Hitachi 655 liquid chromatograph, equipped with TSK gel G4000, G3000 and G2500 (Toyo Soda Co.) as column. Products were detected with a differential re-

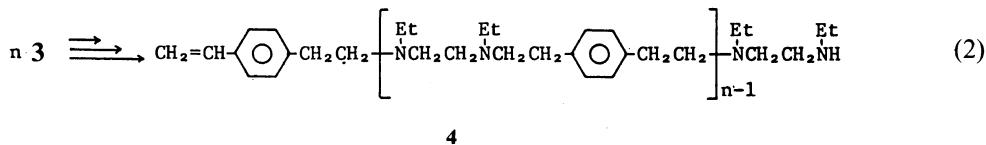
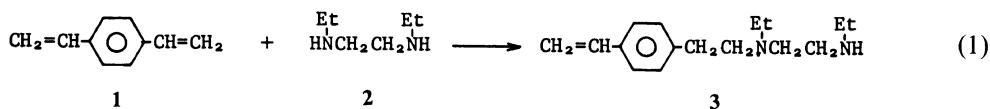
fractometer (Shodex RI SE-31, Showa Denko Co.) and Hitachi variable wavelength UV monitor. The elution volume-molecular weight calibration curves of **4** was plotted by making use of the peak separation for low molecular weight fraction ( $n=1-9$ ) and of the polystyrene standard calibration curve for high molecular weight fraction ( $n \geq 9$ ).

#### Kinetics of the Addition Reaction of **6** to Styrene

Into a given quantity of THF placed in a round-bottomed flask equipped with a three-way stop cock, given quantities of **6**, dodecane, *n*-butyllithium and styrene were added. The reaction was quenched after various time intervals by sampling a portion of the solution and adding to it a small amount of water. The products were analyzed by GC.

## RESULTS AND DISCUSSION

As reported previously,<sup>5</sup> **1** reacts with **2**, in the presence of a lithium alkylamide, to form a one to one addition product **3** in an excellent yield.



It was also shown that the self-polyaddition reaction of **3** in the presence of lithium diisopropylamide proceeded according to a stepwise addition mechanism.

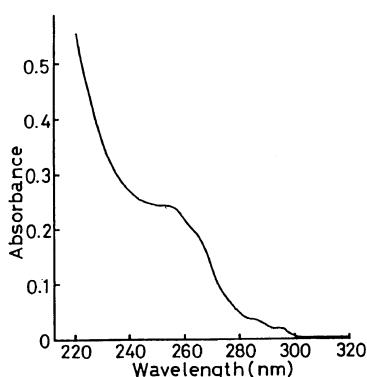
Number average of the degree of polymerization ( $\bar{P}_n$ ) and number average molecular weight ( $\bar{M}_n$ ) of the macromonomer can be

expressed by eq 3 and 4, respectively.

$$\bar{P}_n = \frac{[\text{phenylene}]}{[\text{vinylphenethyl}]} + 1 \quad (3)$$

$$\bar{M}_n = \bar{P}_n \times M \quad (M = \text{Molecular weight of } \text{3}) \quad (4)$$

Figure 1 shows the absorption spectrum of



**Figure 1.** Absorption spectrum of **4** (Systematic name is shown in footnote \*1). Solvent, THF; temp, room temp;  $[4]=1.91 \times 10^{-5} \text{ mol l}^{-1}$ ;  $\bar{P}_n=3.62$ .

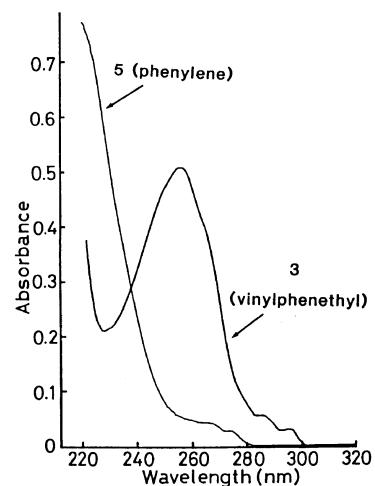
polyamine macromonomer. This spectrum is made up by the absorbances arising from both vinylphenethyl and phenylene groups which are the constitutional units of **4**. The concentrations of phenylene and vinylphenethyl groups were determined as follows.

#### UV Analysis for Addition Products

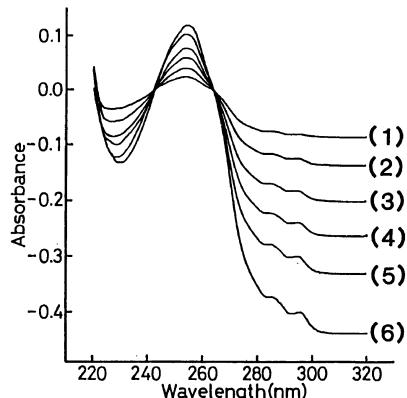
*UV Analysis for Phenylene Group.* Absorption spectra of two model compounds, **3** for vinylphenethyl group and **5** for phenylene group, are shown in Figure 2. The absorption spectrum of **3** showed strong red-shift compared to that of **5**.

Method of double-wavelength spectrophotometry was applied to a quantitative determination of phenylene group in **4**. Two wavelengths  $\lambda_1$  and  $\lambda_2$ , at which vinylphenethyl group shows the same absorbance irrespective of its concentration, were selected. In other words, intensity difference,  $\Delta A_{\lambda_1-\lambda_2}$ , between the absorbances at  $\lambda_1$  and  $\lambda_2$  is always equal to zero. Figure 3 shows the absorption spectra of **3** in several concentrations with  $\lambda_1$  fixed at 242.0 nm and  $\lambda_2$  scanned, wherefrom 266.3 nm was settled as the wave number of  $\lambda_2$ . Figure 4 shows a straight line relationship between the concentration of phenylene group and  $\Delta A_{\lambda_1-\lambda_2}$  in the binary systems of **3** and **5**.

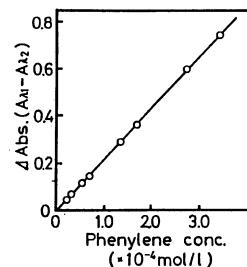
#### UV Analysis for Vinylphenethyl Group



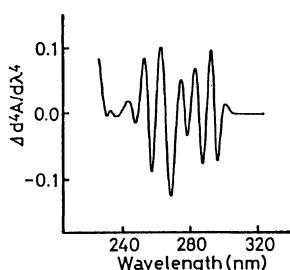
**Figure 2.** Absorption spectra of **5** (phenylene) and **3** (vinylphenethyl). Solvent, THF; temp, room temp;  $[5]=7.20 \times 10^{-5} \text{ mol l}^{-1}$ ;  $[3]=2.68 \times 10^{-5} \text{ mol l}^{-1}$ .



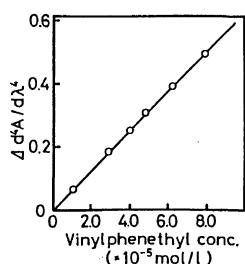
**Figure 3.** Absorption spectra with  $\lambda_1$  fixed (242.0 nm) and  $\lambda_2$  scanned. Solvent, THF; concentration of **3** ( $\times 10^5 \text{ mol l}^{-1}$ ), (1) 5.77; (2) 4.34; (3) 3.76; (4) 2.62; (5) 1.79; (6) 1.10.



**Figure 4.** Relationship between concentrations of **5** (phenylene) and absorbance difference,  $\Delta A_{\lambda_1-\lambda_2}$ , where  $\lambda_1=242.0 \text{ nm}$  and  $\lambda_2=266.3 \text{ nm}$ .



**Figure 5.** Spectrum of the fourth-order differential coefficient of absorbance of **3** (vinylphenethyl). Solvent, THF; temp, room temp;  $[3] = 2.85 \times 10^{-5} \text{ mol l}^{-1}$ .



**Figure 6.** Relationship between vinylphenethyl concentration and fourth-order derivative absorbance at 298–296 nm. Solvent, THF.

Quantitative analysis of vinylphenethyl groups in **4** was carried out in the range of 284–296 nm by using UV derivative spectra method. Figure 5 shows a curve of the fourth-order differential coefficient of absorbance of **3** as model compound with vinylphenethyl group. It is known that the distance between the maximum and minimum of the differential coefficient on the absorption band was in proportion to the amount of a chemical species.<sup>13</sup> Figure 6 shows a calibration curve for vinylphenethyl analysis by using the fourth-order derivative spectra.

#### *Self-Polyaddition Reaction of **3***

To obtain an insight into the nature of the polyaddition reaction, a series of study on the self-polyaddition reaction of **3** was carried out at 20°C in THF in the presence of lithium diisopropylamide.  $\bar{M}_n$  was determined by using UV method which was described in the preceding section.

**Table I.** Time course of polyaddition reaction of **3** at 20°C in THF<sup>a</sup>

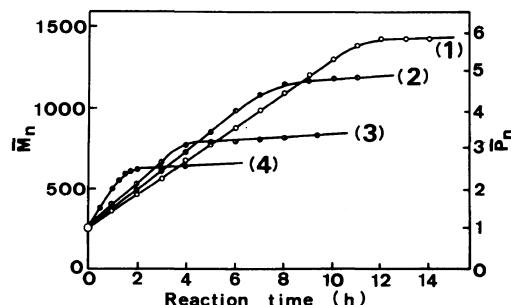
Time/h	$\bar{M}_n^b$	$\bar{P}_n^c$	$p^d$
1.0	380	1.39	0.28
2.0	480	1.93	0.48
3.0	600	2.44	0.59
4.0	720	2.92	0.66
5.0	850	3.46	0.71
6.0	990	4.01	0.75
7.0	1090	4.44	0.77
8.0	1150	4.68	0.79
9.0	1170	4.74	0.79
10.0	1180	4.81	0.79
11.0	1190	4.84	0.79

<sup>a</sup>  $[3]_0 = 1.00 \text{ mol l}^{-1}$ ;  $[\text{iPr}_2\text{NH}]_0 = 0.10 \text{ mol l}^{-1}$ ;  $[\text{n-butyl-lithium}]_0 = 0.10 \text{ mol l}^{-1}$ .

<sup>b</sup> Determined by UV measurement.

<sup>c</sup> Calculated by eq 4.

<sup>d</sup> Calculated by eq 5.



**Figure 7.** Time course of anionic self-polyaddition reaction of **3** at various concentrations of lithium species in THF at 20°C.  $[3]_0 = 1.00 \text{ mol l}^{-1}$ ;  $[\text{iPr}_2\text{NLi}]_0$  (mol l<sup>-1</sup>); ○ (1) 0.08; □ (2) 0.10; ▲ (3) 0.15; ◆ (4) 0.20.

Table I shows  $\bar{M}_n$ ,  $\bar{P}_n$  and extent of reaction  $p$  with respect to vinyl ( $\text{CH}_2=\text{CH}-$ ) or secondary amino ( $>\text{NH}$ ) group at several reaction times.

In earlier stages of this reaction, a straight line was obtained between  $\bar{P}_n$  and reaction time as shown in Figure 7 (2), a fact which indicates the reaction to proceed in accordance with the Flory theory<sup>14</sup>:

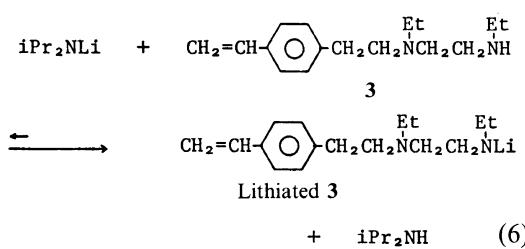
$$\bar{P}_n = \frac{1}{1-p} = kt + 1 \quad (5)$$

But the remarkable feature of this reaction was

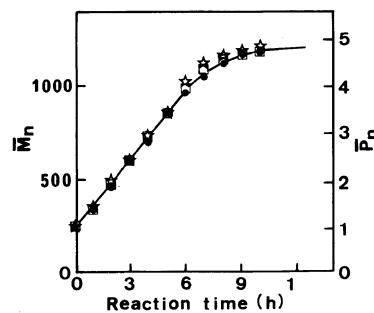
the presence of a sudden break, at which the rate of reaction became very small.

Four runs of experiment were carried out in the presence of various concentrations of lithium diisopropylamide with the initial concentration of **3** kept unchanged. Results obtained as also shown in Figure 7. Straight line relationship was found again to hold between  $\bar{P}_n$  and reaction time for every run in earlier stages. A significant difference from the corresponding plots for the conventional polycondensation reactions was that every straight line in this self-polyaddition system possessed a sudden break.  $\bar{P}_n$  of polymers when coming a sudden break was found to be larger with lower initial concentration of lithium diisopropylamide.

Influence of the concentration of diisopropylamine on the rate of polymerization was examined under various concentrations of diisopropylamine with the initial concentrations of **3** and lithium species kept unchanged. A sudden break point was observed again for every run of the experiments in which excess diisopropylamine present in the reaction system, as shown in Figure 8. The rate of the polyaddition reaction of **1** to **2** was not influenced by the diisopropylamine concentration in the reaction system. From these results, it was considered that a diamine having secondary amino group like **3** binds lithium ion stronger than diisopropylamine. So the rightwards reaction of eq 6 is expected to be fast enough and the equilibrium be shifted strongly to the right-hand side.

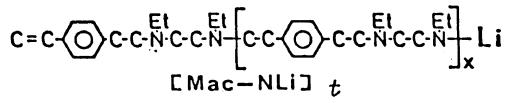
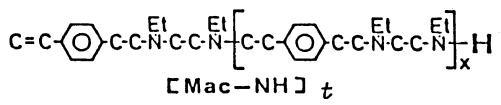


### Change in the concentration of each chemi-



**Figure 8.** Effect of the concentration of  $[iPr_2NH]$  on time course of the polyaddition reaction at  $20^\circ C$ .  $[3]_0 = 1.00 \text{ mol l}^{-1}$ ;  $[n\text{-butyllithium}]_0 = 0.10 \text{ mol l}^{-1}$ ;  $[iPr_2NH]_0 (\text{mol l}^{-1})$ :  $\star$ , 0.50;  $\square$ , 0.20;  $\bullet$ , 0.10.

cal species was observed in the course of reaction for the polymerization of **3**. There are three types of chemical species, diisopropyl-amine,  $[Mac-NH]$ , and  $[Mac-NLi]$ , at time  $t$  in the reaction system, where  $[Mac-NH]$ , and  $[Mac-NLi]$ , denote the following species, respectively.



The initial concentrations of lithium diisopropylamide and **3** are denoted as  $[>\text{NLi}]_0$  and  $[3]_0$ , respectively. As stated above, most of lithium ions are located only at the end of **4** to form  $[\text{Mac-NLi}]$ , so that  $\bar{P}_n$  at that time can be expressed by eq 7.

$$\bar{P}_n = \frac{[3]_0}{[\text{Mac-NH}]_t + [\text{Mac-NLi}]_t} \quad (7)$$

Table II shows the results of the calculation at the time of break point for the samples shown in Figure 8. It is seen from Table II that the break takes place when the ratio of  $[Mac-NH]_t$  to  $[Mac-NLi]_t$  decreases down to the unity.

**Table II.** Relative concentration of chemical species,  $[Mac-NH]_t$ , and  $[Mac-NLi]_t$ , at the break point

$[>NLi]_0^a$	Time	$[Mac-NLi]_t$	$[Mac-NH]_t^b$	$\frac{[Mac-NH]_t}{[Mac-NLi]_t}$
mol l <sup>-1</sup>	h	mol l <sup>-1</sup>	mol l <sup>-1</sup>	
0.20	2.0	0.20	0.20	1.00
0.15	4.0	0.15	0.17	1.13
0.10	8.0	0.10	0.11	1.10
0.08	12.0	0.08	0.09	1.13

<sup>a</sup>  $[3]_0 = 1.00 \text{ mol l}^{-1}$  in THF at 20°C.<sup>b</sup> Calculated by eq 7.

From the break point shown in Figure 7, the growth reaction was essentially stopped, so that the molecular weight of **4** could be controlled by adjusting the relative concentrations of  $>\text{NH}$  to  $>\text{NLi}$  in the initial mixture for the polyaddition reaction. Several samples of the macromonomer prepared are shown in Table III. Observed values for  $\bar{M}_n$ , which were obtained by end-group determination by UV measurement, are very close to  $\bar{M}_n$  values calculated by eq 7.

#### Model Reaction—Addition Reaction of **6** to Styrene

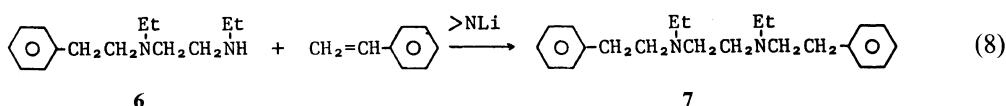
It was suspected whether or not microgel formation might have happened to the later stage of reaction, which could be responsible for the diminished rate of polymerization. We carried out a model reaction, in which possi-

**Table III.** Synthesis of **4** with controlled molecular weight<sup>a</sup>

Run	$[>NLi]_0$	Time	$\bar{M}_n$ , calc <sup>b</sup>	$\bar{M}_n$ , obsd <sup>c</sup>
	mol l <sup>-1</sup>	h		
1	0.12	7	1030	990
2	0.06	18	2050	2100
3	0.03	45	4100	4230
4	0.02	85	6150	6060

<sup>a</sup>  $[3]_0 = 1.00 \text{ mol l}^{-1}$  in THF at 20°C.<sup>b</sup> Calculated by eq 7, by using the relation  $[Mac-NH]_t = [Mac-NLi]_t = [>NLi]_0$  at the break point.<sup>c</sup> Observed values from the end-group determination by UV measurement.

bility of forming microheterogeneity could be eliminated. **6** and styrene were chosen as reactants in the model reaction as shown in eq 8.

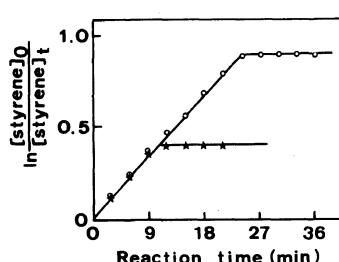


All experimental conditions were adjusted to be the same as those in the polyaddition reaction of **3**. Figure 9 shows the first-order analysis for reaction 8.

These results show the rate of reaction 8 to be proportional to the concentration of styrene in the earlier stage of reaction, as shown in eq 9.

$$-\frac{d[\text{styrene}]}{dt} = k'[\text{styrene}] \quad (9)$$

It was found again that every straight line possessed a break point when the ratio of concentration of **6** ( $[>\text{NH}]$ ) versus lithiated **6** ( $[>\text{NLi}]$ ) attained to the value of unity, which means the presence of the break point to be



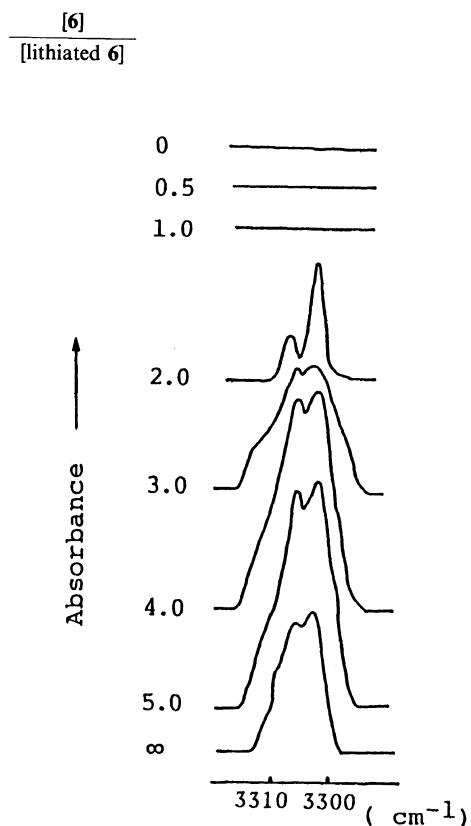
**Figure 9.** First-order analysis of the reaction of lithiated **6** with styrene.  $[>\text{NLi}] = 0.2 \text{ mol l}^{-1}$  in THF at  $20^\circ\text{C}$ ;  $\bigcirc$   $[6] = 1.0 \text{ mol l}^{-1}$ ;  $[\text{styrene}] = 1.0 \text{ mol l}^{-1}$ ;  $\blacksquare$   $[6] = 0.6 \text{ mol l}^{-1}$ ;  $[\text{styrene}] = 0.6 \text{ mol l}^{-1}$ .

explained by another mechanism than that of forming microheterogeneity.

To obtain information which may explain the nature of break point, infrared spectroscopic analysis was carried out with a mixture of **6** and lithiated **6**. FT-IR spectra of the binary systems consisting of **6** and lithiated **6** shows absorptions at  $3280 \text{ cm}^{-1}$ — $3300 \text{ cm}^{-1}$  when the mole ratio of  $[6]/[\text{lithiated } 6]$  is kept larger than one as shown in Figure 10. These absorptions are assignable to the free N—H stretching frequencies. It is seen from the Figure 10 that the shape of absorption curves changes gradually with decreasing the value of  $>\text{NH}$  to  $>\text{NLi}$ . The absorptions are no longer observable when the  $[>\text{NH}]/[>\text{NLi}]$  ratio become less than one, which suggests a possible formation of a one to one complex of **6** with lithiated **6**.

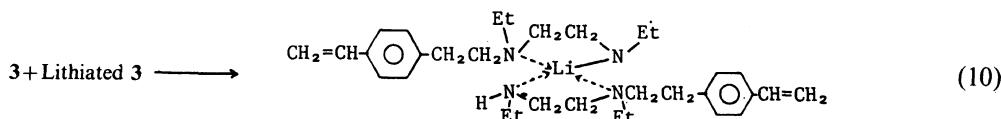
#### A Possible Mechanism of Self-Polyaddition Reaction of **3**

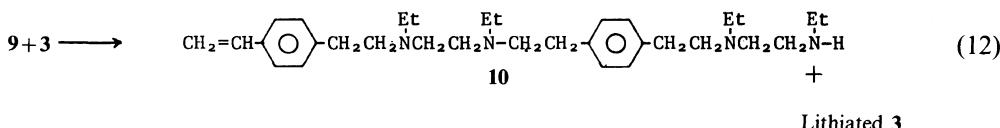
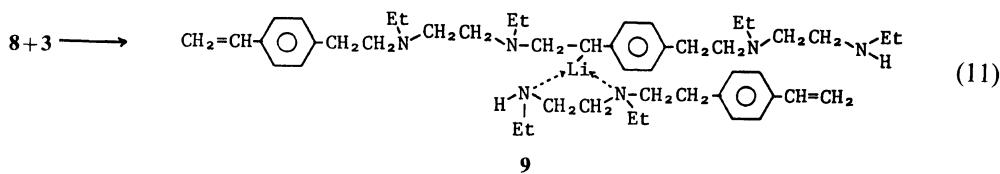
The one to one complex, **8**, consisting of **3** and lithiated **3** is considered to have an activated  $>\text{NLi}$  bond (eq 10). The polyaddition reaction will be initiated by a reaction between



**Figure 10.** FT-IR spectra of binary systems consisting of **6** and lithiated **6** in THF, where  $[\text{lithiated } 6] = 0.2 \text{ mol l}^{-1}$ .

the activated  $>\text{N—Ni}$  of **8** and the double bond of styrene moiety of the second molecule of **3** to form **9** (eq 11). We assume a third molecule of **3** to be required for the addition reaction to proceed. A metal exchange reaction between **10** and the third molecule of **3** will give dimer and a new lithiated **3** molecule, the latter of which will form a new one to one complex with any of  $>\text{NH}$  groups present in the reaction system (eq 12).





The repetition of this cycle will continue until the reaction system contains no more  $\text{>NH}$  group which is available to the metal exchange reaction with the one to one complex.

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- The repetition of this cycle will continue until the reaction system contains no more  $\text{>NH}$  group which is available to the metal exchange reaction with the one to one complex.

*Acknowledgment.* A part of this study was financially supported by the Ministry of Education, Science and Culture, Japan (Special Project Research "Design of Multi-phase Biomedical Materials").

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