

# Synthesis of Novel Moisture-Curable Polyurethanes End-Capped with Alkoxysilane and Use as Solvent-Free Elastic Adhesives

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**ABSTRACT:** Novel silane endcappers and novel polyurethanes end-capped with alkoxysilane (silylated polyurethanes) were developed as moisture-curable materials, in which curing reaction occurs under humid conditions in the presence of dioctyltin diversate as a curing catalyst. Two secondary amine-terminated alkoxysilane compounds (silane endcappers) were synthesized by Michael addition reaction of commercially available *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (or *N*-(2-aminoethyl)-3-aminopropylmethyltrimethoxysilane) with methyl acrylate. The resulting silane endcappers were utilized to end-capped isocyanate-terminated polyurethanes, providing the silylated polyurethanes. The physical properties of the moisture-curable silylated polyurethanes derived from several polyols and the silane endcappers were evaluated in terms of 50% modulus, tensile strength at break, elongation at break, and

Shore A hardness after curing. The longer main chain of the silylated polyurethanes led to the lower Shore A hardness, the lower 50% modulus, and the longer elongation at break. In contrast, the tensile strengths at break were almost the same for all silylated polyurethanes, irrespective of the length of the main chain and the structure of the terminal silyl group. The silylated polyurethanes were employed for the preparation of novel solvent-free moisture-curable elastic adhesives, which were evaluated at the tensile shear bond strength. No significant influence of the molecular weight of the polyols and silane endcappers was observed on the tensile shear bond strength. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 236–244, 2008

**Key words:** adhesion; adhesives; elastomers; polyurethanes; silicones

## INTRODUCTION

In recent years, there has been an increasing attention paid to water-based and solvent-free adhesives and coatings, because of recent concerns of environmental protection.<sup>1–7</sup> In particular, the solvent-free adhesives are very useful, since curing shrinkage hardly occurs and so-called VOC's (volatile organic compounds) can be avoided in this system.<sup>8–10</sup> In the solvent-free adhesive field, moisture-curable elastic adhesives, which have the rubber elasticity after curing, have been used for the adhesion of various substrates (e.g., plastics/metal) with different coefficients of linear thermal expansion, because of the good subserviency to the substrates.<sup>11–14</sup>

Generally, the moisture-curable elastic adhesives are utilized so-called modified silicone adhesive

based on polyether having crosslinkable alkoxysilyl group.<sup>15,16</sup> Alkoxysilane-terminated polymers including the modified silicone cure by condensation reaction in the presence of water giving off alcohol compounds, which is accelerated by curing catalyst (e.g., organotin compounds).<sup>17</sup> To synthesize the novel alkoxysilane-terminated polymer, we focused the polyurethanes from industrial view point. Alkoxysilane-terminated polyurethane (silylated polyurethane) can be easily synthesized with isocyanate-terminated polyurethane and end-capping agent having alkoxysilyl group (silane endcapper). In the previous study, we developed several silane endcappers (secondary-aminosilane compounds) derived from 3-aminopropyltrimethoxysilane.<sup>18</sup> In this study, we attempted to synthesize new silylated polyurethanes derived from *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane and *N*-(2-aminoethyl)-3-aminopropylmethyltrimethoxysilane. These silylated polyurethanes can cure with moisture by the condensation reaction of the terminal alkoxysilyl group.

Figure 1 shows our synthetic approach for the novel solvent-free moisture-curable elastic adhesives, which involves four steps. The first step is the synthesis of silane endcapper (**Ia** and **Ib**) by Michael

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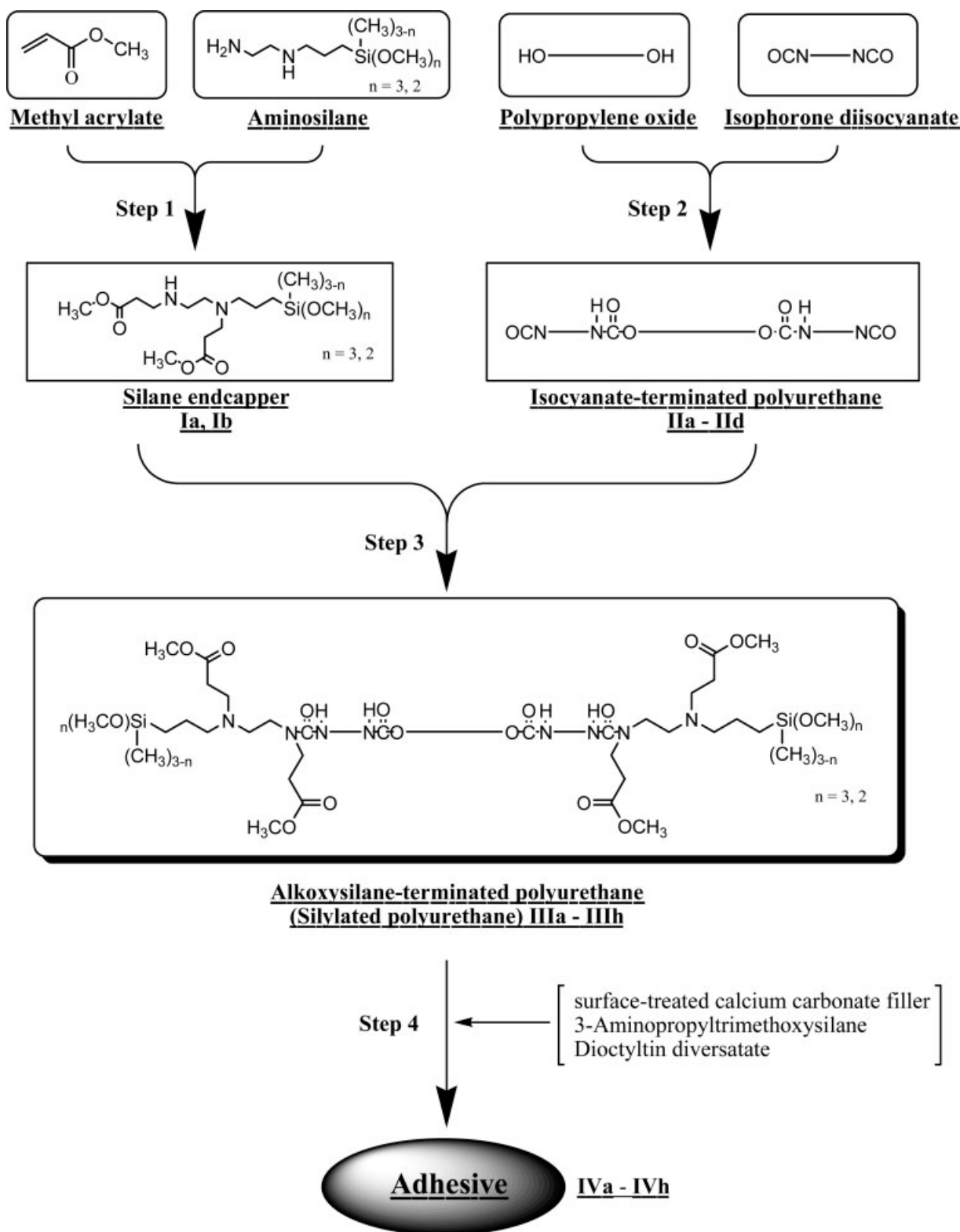


Figure 1 Pathway to prepare silylated polyurethane-based adhesives.

addition reaction of the aminosilane and acrylate. Independently, isocyanate-terminated polyurethane (**IIa–IIId**) is synthesized by the reaction of a diol with a diisocyanate (the second step). The third step is

the reaction of the isocyanate-terminated polyurethane with the silane endcapper, resulting in the formation of the silylated polyurethane (**IIIa–IIIh**). Finally, the silylated polyurethane is applied as a

base polymer, which is mixed with filler, adhesion promoter, and curing catalyst to afford a silylated polyurethane-based adhesive.

In this study, the polyurethanes end-capped with trimethoxysilane ( $n = 3$ ) or methyltrimethoxysilane ( $n = 2$ ) were evaluated. Our attention was also focused on the effect of the length of the main chain (molecular weight of material polyol (MW) = 4000, 5500, 10,000, and 15,000), in addition to the influence of the alkoxy functionality ( $n = 2$  and 3) of the terminal silyl group on adhesive properties. And further, we tested the bonding abilities with polycarbonate plate (PC) and aluminum plate (Al), which are commodity plastics and metal with different coefficient of linear thermal expansion (PC:  $72.4 \times 10^{-6}/^{\circ}\text{C}$  and Al:  $24 \times 10^{-6}/^{\circ}\text{C}$ )<sup>19</sup> each other, to study the feasibility of the new silylated polyurethanes.

## EXPERIMENTAL

### Materials

The following reagents and materials were used without further purification: polypropylene oxide (PPO, Preminol S 4104, hydroxyl value = 27.6, MW = 4000, viscosity = 930 mPa · s, Asahi Glass Urethane Co., Ltd., Hydroxyl value is defined as the number of mg of potassium hydroxide required to neutralize the acetic acid capable of combining by acetylation with 1.0 g of sample.), PPO (Preminol S 4006, hydroxyl value = 20.2, MW = 5500, viscosity = 1400 mPa · s, Asahi Glass Urethane), PPO (Preminol S 4011, hydroxyl value = 11.1, MW = 10,000, viscosity = 4400 mPa · s, Asahi Glass Urethane), PPO (Preminol S 4015, hydroxyl value = 7.6, MW = 15,000, viscosity = 12,000 mPa · s, Asahi Glass Urethane), isophorone diisocyanate (IPDI, Desmodur I; Sumika Bayer Urethane), dioctyltin diversate (DOTDV, Neostann U-830; Nitto Kasei), methyl acrylate (MA, Toagosei), *N*-(2-aminoethyl)-3-aminopropyl trimethoxysilane (KBM-603; Shin-Etsu Chemical), *N*-(2-aminoethyl)-3-aminopropylmethyltrimethoxysilane (KBM-602; Shin-Etsu Chemical), 3-aminopropyltrimethoxysilane (KBM-903; Shin-Etsu Chemical), surface-treated calcium carbonate filler (Hakuenka CCR-B; Shiraishi Calcium Kaisha).

### Preparation of silane endcappers **Ia** and **Ib**

After MA (172.2 g, 2.0 mol) was dropped into 1.0 mol of aminosilanes (222.4 g of KBM-603 for **Ia**, 206.4 g of KBM-602 for **Ib**) with stirring at room temperature for 1 h under nitrogen, the mixture was kept at 40°C for additional 7 days to afford **Ia** and **Ib** as pale yellow transparent liquid. The average molecular weight per a reactive amino group is utilized for the calculation of the feed in the reaction of the isocyanate-terminated polyurethane with the silane endcapper.

The silane endcappers was used to end-cap the isocyanate-terminated polyurethanes without purification.

### Preparation of isocyanate-terminated polyurethanes **Ia–IId**

PPO was reacted with IPDI (NCO/OH molar ratio = 2.0) in the presence of catalyst DOTDV (0.0050 wt % for PPO) at 80°C for 3 h under nitrogen in the same manner as our previous report<sup>18</sup> to afford **Ia–IId** as colorless viscous liquid as crude products. The combinations of PPO, the yields, the viscosities, and the isocyanate contents are summarized in Table II.

### Preparation of silylated polyurethanes **IIIa–IIIh**

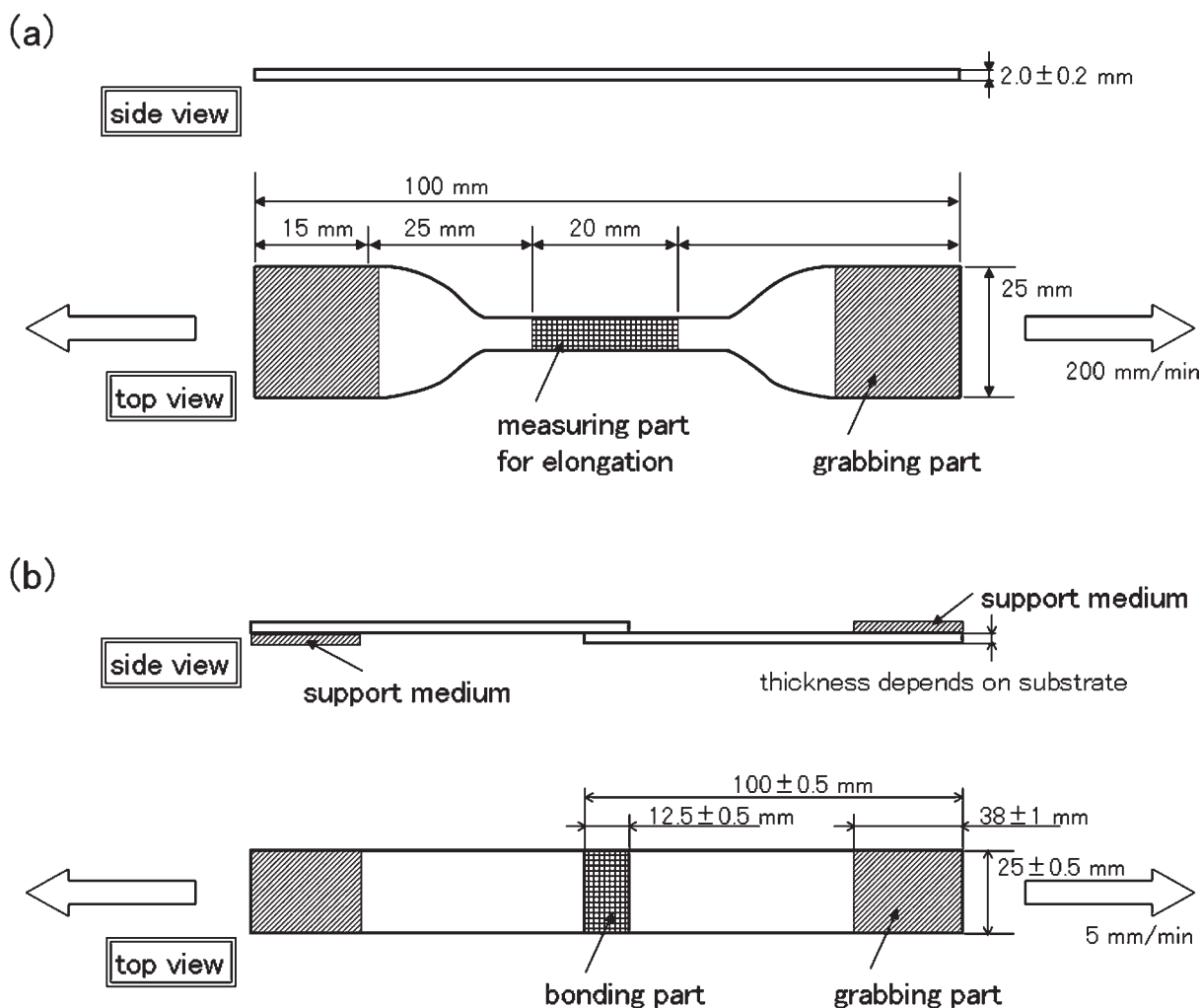
Isocyanate-terminated polyurethanes **Ia–IId** were reacted with silane endcappers **Ia** and **Ib** (equimolar amount of NCO group in **Ia–IId**) at 80°C for 30 min under nitrogen in the same manner as our previous report<sup>18</sup> to afford **IIIa–IIIh** as pale yellow transparent viscous liquids. The combinations of reactants, the yields, and the viscosities are summarized in Table III.

### Sample preparation for measurement of physical properties

Cured sheets of the silylated polyurethane were prepared for the investigations of the physical properties of the silylated polyurethanes obtained in this study. The silylated polyurethane (100 g) and curing catalyst (DOTDV, 1.0 g) were mixed *in vacuo* at 50°C for 10 min. The mixture was aged on polypropylene plate at 23°C under 50% relative humidity for 1 day, and then 50°C under 95% relative humidity for 1 day to be cured thoroughly. The cured silylated polyurethane sheet (thickness: ~ 2.0 mm) was employed for the analysis of the physical properties. The physical properties of the cured silylated polyurethanes, including the 50% modulus, the tensile strength at break, and the elongation at break, were measured using dumbbell no. 3 of Japan Industrial Standard, JIS K 6251 (Fig. 2) with an AUTOGRAPH AGS-100B (Shimadzu Corp.) at a tensile speed of 200 mm/min. Shore A hardnesses of the cured silylated polyurethanes were measured with Type-A durometer pursuant to JIS K 7215. All data of physical properties were on the averages of the measurements of three different specimens.

### Preparation of silylated polyurethane-based adhesives

The silylated polyurethane **IIIa** (100 g), surface-treated calcium carbonate filler (Hakuenka CCR-B, 50 g), adhesion promoter (3-aminopropyltrimethoxysilane, 5.0 g), and curing catalyst (DOTDV, 1.0 g) were mixed at room temperature for 1.0 min to afford **IVa** as a white viscous paste. The same proce-



**Figure 2** Illustrations of (a) dumbbell no. 3 specimen for physical properties measurements (JIS K 6251) and (b) specimen for tensile shear bond strength measurement (JIS K 6850).

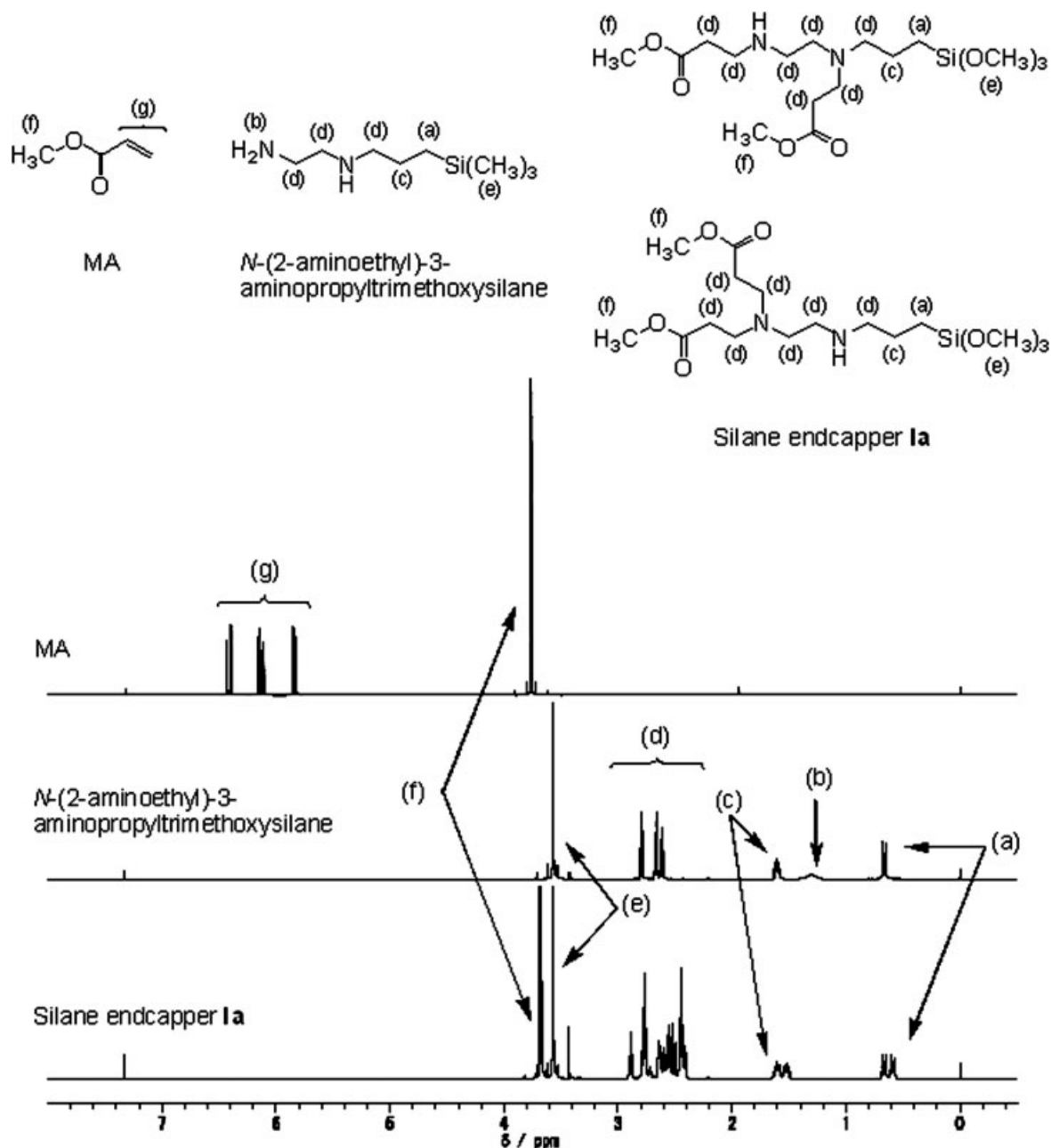
ture was employed to prepare adhesives **IVb–IVh** from **IIIb–IIIh**. The tensile shear bond strengths of **IVa–IVh** were evaluated.

#### Sample preparation for measurement of bond strengths

The substrates ( $25 \times 100 \text{ mm}^2$ ) for the tensile shear bond strength measurement were plastic plate (polycarbonate, thickness = 3.0 mm) and metal plate (A1050 aluminum, thickness = 2.0 mm). All substrates were used without any surface treatment. The bonded test pieces adhered with the adhesives **IVa–IVh** were aged at  $23^\circ\text{C}$  under 50% relative humidity for 1 day and then additionally aged at  $50^\circ\text{C}$  under 95% relative humidity for 1 day to cure fully enough to test. After aging, the tensile shear bond strength was measured with AUTOGRAPH AG-50kNE (Shimadzu Corp.) at a tensile speed of 5.0 mm/min, pursuant to JIS K 6850 (Fig. 2). The tensile shear bond strength was the average of the measurement of three different specimens.

#### Characterization methods

Gas chromatography (GC) was performed with a GAS CHROMATOGRAPH GC-14B (Shimadzu Corp., detector; TCD) with UA1-15W-1.5F (Length; 15 m, I.D.; 0.53 mm, Film;  $1.5 \mu\text{m}$ ). The initial temperature was  $50^\circ\text{C}$ , which was held for 2 min, and then the temperature was increased at  $10^\circ\text{C}$  per min, to keep at  $300^\circ\text{C}$  and the final retention time at the final temperature was 5 min. FTIR spectra were recorded with a Nicolet AVATAR 360 FTIR spectrometer system.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were measured on a JEOL ECX-400 spectrometer or a Varian Inova-500 spectrometer using tetramethylsilane as an internal standard. Titration was performed with an Automatic Potentiometric Titrator AT-510 (Kyoto Electronics Manufacturing). The content of the amino groups of the silane endcappers was estimated by titration pursuant to JIS K 7245. The content of the isocyanate groups of the isocyanate-terminated polyurethane was estimated by titration pursuant to JIS K 1556. The viscosity was measured



**Figure 3**  $^1\text{H-NMR}$  spectra ( $\text{CDCl}_3$ ) of MA, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane, and silane endcapper **Ia**.

ured with a B-type viscometer (No. 7 rotor, 10 rpm, Model BH or BS) at 23°C.

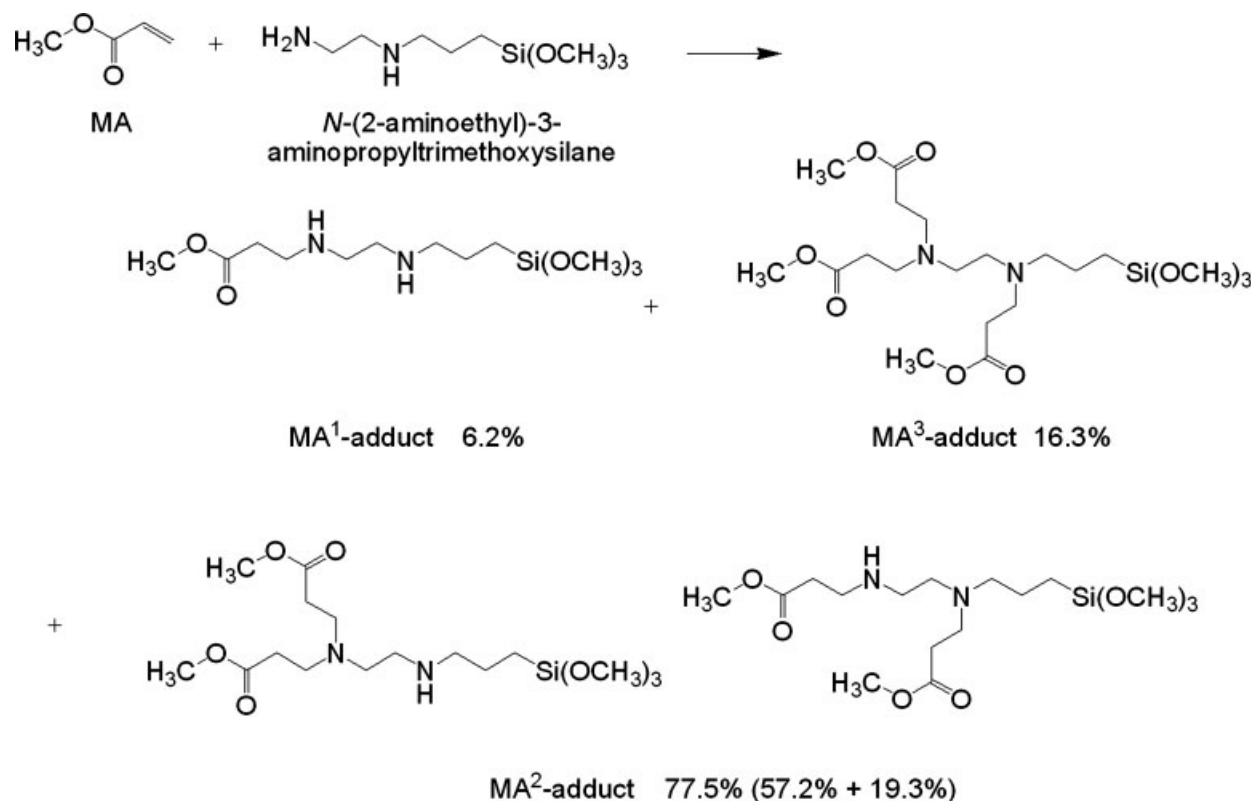
## RESULTS AND DISCUSSION

### Synthesis and characterization of silane endcapper

As shown in Figure 3, complete conversion of MA was confirmed by the disappearance of vinyl peak (g) at around 5.82–6.43 ppm and  $\text{NH}_2$  peak (b) at around 1.18 ppm in  $^1\text{H-NMR}$  spectroscopy. Furthermore, new peaks (d) are seen at 2.40–2.92 ppm, which correspond to  $\text{CH}_2$  groups in the  $\alpha$ -position to the N atom and in the  $\alpha$ -position to the carbonyl

group. The integration of the peak (d) was compared with the intensity of peak (a) attributed to the  $\text{CH}_2$  group in the  $\alpha$ -position of the Si atom of the endcapper **Ia**. The observed ratio ( $d/a = 6.76$ ) is approximately consistent with the theoretical value (7.00). Moreover, the ratios of the intensity of peak (a) to intensity of peak (e) attributed to  $\text{Si}(\text{OCH}_3)_3$  and peak (f) attributed to  $\text{COOCH}_3$ ,  $e/a = 4.44$  and  $f/a = 3.10$ , are also consistent with the theoretical values (4.50 and 3.00). The complete conversion was also confirmed by the disappearance of the  $^{13}\text{C-NMR}$  signals at 128.1 and 130.3 ppm, corresponding to the vinyl peak. The same tendency was observed on GC,





Scheme 1 Synthesis of silane endcapper **Ia**.

<sup>1</sup>H and <sup>13</sup>C-NMR spectra of the silane endcapper **Ib**, indicating that MA was converted quantitatively.

Silane endcappers obtained in this study were a mixture of single MA-adducted aminosilane, double MA-adducted aminosilane (two structural isomers), and triple MA-adducted aminosilane. The silane endcappers were characterized by GC, titration, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR. Scheme 1 shows the synthesis of silane endcapper **Ia**. The reaction products of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane with MA are single MA-adducted (MA<sup>1</sup>-adduct), double MA-adducted (MA<sup>2</sup>-adduct), and triple MA-adducted (MA<sup>3</sup>-adduct), and silane endcapper **Ia** was mixture of them. MA<sup>2</sup>-adduct has two structural isomers (MA<sup>2</sup>-adduct-A and MA<sup>2</sup>-adduct-B), depending on the position of Michael reaction to

NH group. There were four peaks in the GC chart 19.0 min, 22.4 min, 22.6 min, and 25.1 min in the retention time. The yields of them determined by GC were 6.2 mol %, 57.2 mol %, 19.3 mol %, and 16.3 mol %, as shown in Scheme 1. The feed ratio of the silane endcapper **Ia** for the synthesis of the silylated polyurethane was estimated with the average molecular weight per a reactive amino group calculated the reactive amino group content by titration (Table I).

#### Synthesis and characterization of silylated polyurethanes

The pathway to prepare the silylated polyurethane is shown in Figure 1 (step 3). The isocyanate-termi-

TABLE I  
Characterization of Silane Endcappers

	Yield (%)	Amino group content (%) <sup>a</sup>				Average molecular weight per a reactive amino group <sup>b</sup>
		Primary	Secondary	Tertiary	Total	
<b>Ia</b>	99	n.d. <sup>c</sup>	3.30	3.66	6.96	424.5
<b>Ib</b>	99	n.d. <sup>c</sup>	3.50	3.76	7.26	400.0

<sup>a</sup> The contents of primary, tertiary (A), and total (B) amino groups in the silane endcappers were estimated by titration. The content of secondary (C) amino group was calculated as follows: C = B - A.

<sup>b</sup> The average molecular weight per a reactive amino group (D) was calculated as follows: D = 14 × 100/C. Both primary and secondary amino groups are regarded as the reactive amino groups.

<sup>c</sup> Not detected.

**TABLE II**  
Characterization of Isocyanate-Terminated Polyurethanes

	Reactant PPO <sup>a</sup>	Yield (%)	Viscosity <sup>b</sup> (mPa s)	Isocyanate content <sup>c</sup> (wt %)
<b>IIa</b>	PML S 4104	99	12,000	1.63
<b>IIb</b>	PML S 4006	99	17,000	1.31
<b>IIc</b>	PML S 4011	98	70,000	0.76
<b>IId</b>	PML S 4015	97	150,000	0.52

<sup>a</sup> NCO/OH molar ratio = 2.0.

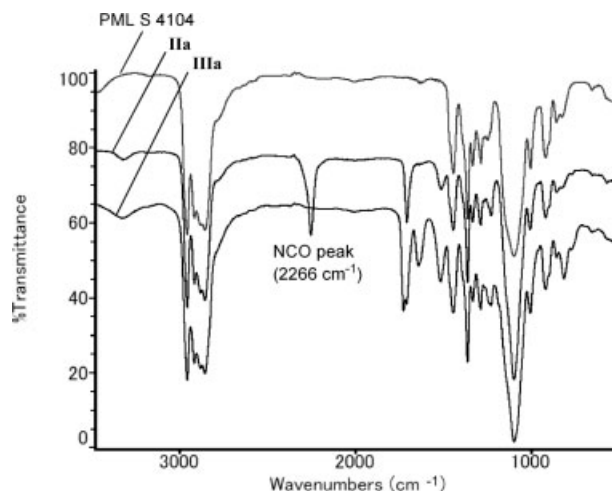
<sup>b</sup> Measured by B-type viscometer (at 23°C).

<sup>c</sup> Calculated by titration.

nated polyurethane was reacted with the secondary amino groups in the silane endcapper at 80°C for 30 min under nitrogen in the bulk condition, and the resulting product was characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FTIR, and viscosity measurements. Note that polyols having different chain lengths (MW = 4000, 5500, 10,000, and 15,000) were employed for the synthesis of the isocyanate-terminated polyurethanes, which were required to evaluate the effect of the chain length on various properties (Tables II and III).

Figure 4 shows FTIR spectra of PPO (PML S 4104) used as a starting diol, isocyanate-terminated polyurethane **IIa**, and silylated polyurethane **IIIa**. The isocyanate (NCO) peak at 2266 cm<sup>-1</sup> disappeared in the FTIR spectrum of the silylated polyurethane **IIIa**, suggesting that terminal isocyanate groups of **IIa** were capped completely with the trimethoxysilyl groups.

The <sup>1</sup>H-NMR spectrum of the silylated polyurethane **IIIa** showed main-chain signals (CH, CH<sub>2</sub>, and CH<sub>3</sub>) clearly at 0.81–1.33 ppm and 3.22–3.82 ppm. The signals of the terminal silyl groups which should be observed at 3.57 ppm were hard to identify, because of overlapping by main-chain signals. On the other hand, <sup>13</sup>C-NMR spectrum of silylated polyurethane **IIIa** shows the existence of trimethoxy-



**Figure 4** FTIR spectra of polypropylene oxide (PML S 4104), isocyanate-terminated polyurethane **IIa**, and silylated polyurethane **IIIa**.

silyl group around 50 ppm, suggesting the predominant silylation of the isocyanate-terminated polyurethane **IIa** (Fig. 5). Clear signals (e.g., carbon atoms of IPDI) were hardly detected due to the relatively long main chains of the products ( $M_n$  of isocyanate-terminated polyurethane > 4000), whereas the peaks of NHCOO (b), NHCON (c), >C=O (d), and SiOCH<sub>3</sub> (e) were detected in the <sup>13</sup>C-NMR spectrum of the silylated polyurethane **IIIa**.

In the same process, no NCO peaks were observed on the FTIR spectra of all silylated polyurethanes **IIIb–IIIh**. The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the silylated polyurethanes **IIIb–IIIh** were comparable with those of **IIIa**. The viscosities of the silylated polyurethanes **IIIa–IIIh** were influenced by the main chain length, as shown in Table III. The longer main chain of the silylated polyurethanes led to higher viscosity.

**TABLE III**  
Characterization of Silylated Polyurethanes

Silylated polyurethane	Reactants <sup>a</sup>		Yield (%)	Viscosity <sup>b</sup> (mPa s)	50% Modulus (MPa)	Tensile strength at break (MPa)	Elongation at break (%)	Shore A hardness
	Isocyanate-terminated polyurethane/ molecular weight of polyol	Silane endcapper/ functionality <sup>c</sup> ( <i>n</i> )						
<b>IIIa</b>	<b>IIa</b> /4,000	<b>Ia</b> /3	98	42,000	0.72	0.76	55.0	46
<b>IIIb</b>	<b>IIb</b> /5,500	<b>Ia</b> /3	98	53,000	0.61	0.67	62.6	42
<b>IIIc</b>	<b>IIc</b> /10,000	<b>Ia</b> /3	97	215,000	0.52	0.77	83.2	40
<b>IIId</b>	<b>IId</b> /15,000	<b>Ia</b> /3	96	425,000	0.49	0.67	89.5	38
<b>IIIe</b>	<b>IIa</b> /4,000	<b>Ib</b> /2	98	47,000	0.64	0.76	71.6	44
<b>IIIf</b>	<b>IIb</b> /5,500	<b>Ib</b> /2	98	54,000	0.62	0.76	76.3	42
<b>IIIg</b>	<b>IIc</b> /10,000	<b>Ib</b> /2	97	225,000	0.51	0.71	123.9	36
<b>IIIh</b>	<b>IId</b> /15,000	<b>Ib</b> /2	96	400,000	0.43	0.76	149.6	31

<sup>a</sup> NCO/NH molar ratio = 1.0.

<sup>b</sup> Measured by B-type viscometer (at 23°C).

<sup>c</sup> Trimethoxysilyl type ( $n = 3$ ), and methyldimethoxysilyl type ( $n = 2$ ).

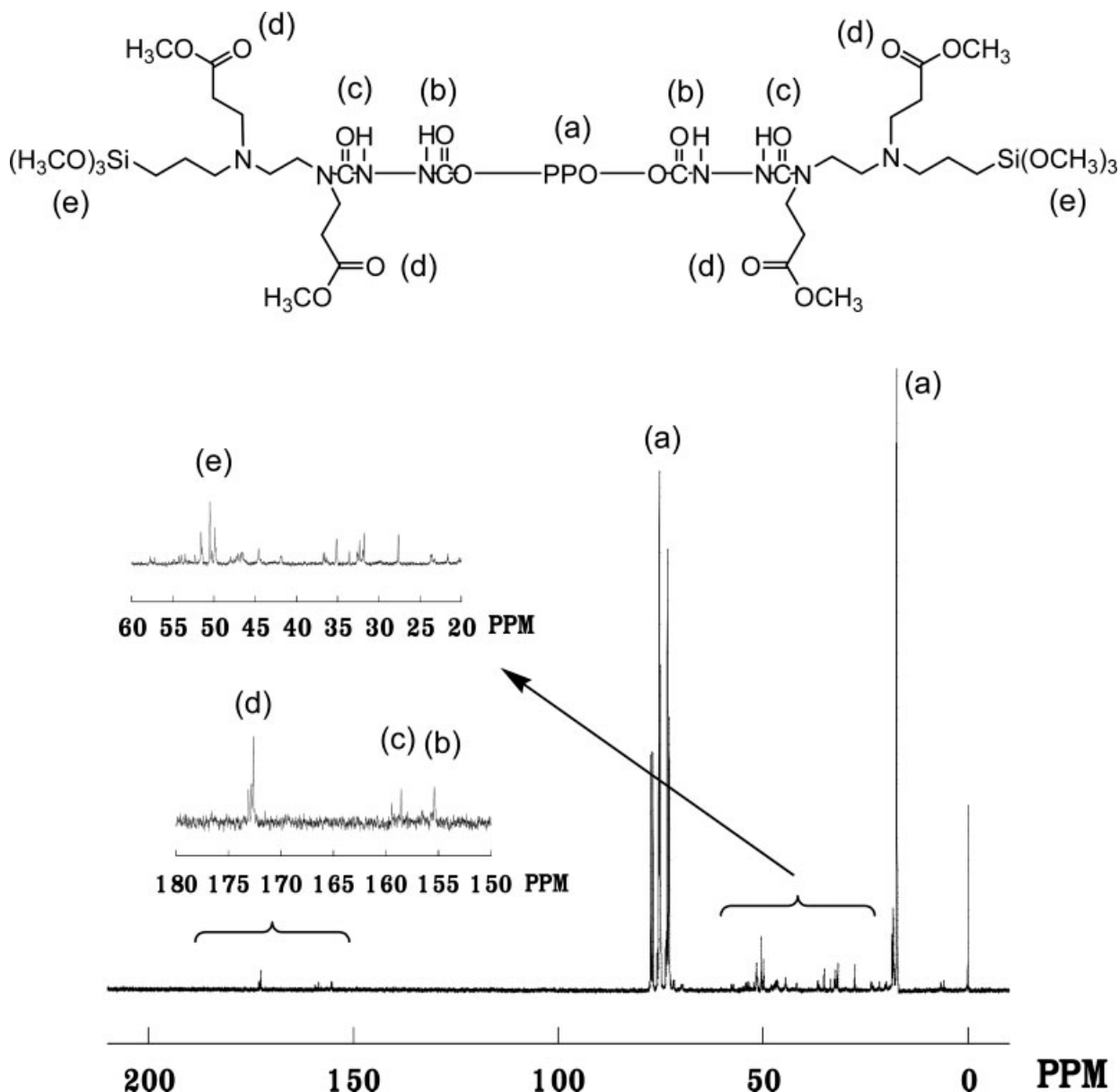


Figure 5  $^{13}\text{C}$ -NMR spectrum ( $\text{CDCl}_3$ ) of the silylated polyurethane IIIa.

### The physical properties of cured silylated polyurethanes

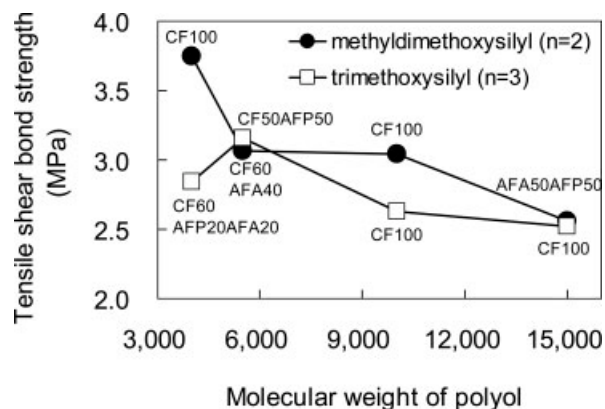
The physical properties of the cured silylated polyurethanes IIIa–IIIh were investigated to clarify the effects of the main chain length of the silylated polyurethanes and the alkoxy functionality of the terminal silyl group. The physical properties involving the 50% modulus, the tensile strength at break, the elongation at break, and the Shore A hardness were evaluated, as can be seen in Table III. The longer main chain of the silylated polyurethanes led to the lower Shore A hardness, the lower 50% modulus, and the longer elongation at break. In contrast, the tensile strengths at break were almost the same for all silylated polyurethanes (IIIa–IIIh), irrespective of the

length of the main chain and the structure of the terminal silyl group. In other words, the silylated polyurethanes can be possibly change the elongation with almost the same tensile strength at break by the combination of the functionality ( $n = 3$  and 2).

### Evaluation of the silylated polyurethane-based adhesives

Figure 6 shows the tensile shear bond strength (PC/Al) of the adhesives IVa–IVd prepared from *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane and IVe–IVh prepared from *N*-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane. Overall, there was a tendency that the silylated polyurethanes with longer





**Figure 6** Comparison of the tensile shear strengths (PC/Al) of the silylated polyurethanes IVa–IVh. CF, cohesion failure; AFP, adhesion failure on the PC side; AFA, adhesion failure on the Al side. The number after CF, AFP, and AFA indicates the percentage of each failure condition.

main chain had lower tensile shear bond strength, which may be due to the low modulus. However, only the shortest trimethoxysilyl type silylated polyurethane IVa (MW of polyol = 4000) showed different from the tendency. This is probably due to the balance of adherence, tensile strength at break, and elongation at break. Insufficient adherence (CF60AFP20AFA20) and subservency attributing the short elongation at break could be dominant over the good tensile strength at break, resulting in the low tensile shear bond strength than silylated polyurethane IVb. Nevertheless, all of the adhesives show enough tensile shear bond strengths, suggesting that the silylated polyurethane synthesized in this study have a possibility to apply as the base polymer of the moisture-curable elastic adhesives.

## CONCLUSION

Novel silane endcappers were synthesized by Michael addition reaction of commercially available primary aminosilanes, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane and *N*-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, with MA. The silane endcappers were successfully used to synthesize the polyurethanes end-capped with alkoxy silane (sily-

lated polyurethane) without purification, which could be employed as the base polymer for the solvent-free moisture-curable elastic adhesives. The viscosities, physical properties, and the tensile shear bond strength were found to be controlled by the length of the main chain and the structure of the silane endcapper in the silylated polyurethanes. The silylated polyurethanes can be easily synthesized, and this approach may lead to further development of solvent-free moisture-curable elastic adhesives, which can be tailored according to the required performance.

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