

Evaluation of the Curing Process of Polyurethane End-Capped with Trialkoxysilanes by a Boron Trifluoride/Amine Complex and Organotin Compound

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ABSTRACT: Polyurethanes end-capped with some trialkoxysilanes, such as trimethoxysilane, triethoxysilane, tripropoxysilane, and tributoxysilane (silylated polyurethanes), were synthesized. Boron trifluoride/monoethylamine (BF₃-MEA) complex and dibutyltin dimethoxide (DBTDM) were examined as curing catalysts for the obtained silylated polyurethanes to compare their curing speeds. It was found that BF₃-MEA worked as a more efficient catalyst for the condensation reaction of the alkoxyethyl groups in the silylated poly-

urethanes to form the corresponding networked polyurethanes. BF₃-MEA had a great advantage as one of the curing catalysts because it gave a fast curing speed for the silylated polyurethanes having long alkoxyethyl groups (ethoxy, propoxy, and butoxy) in comparison with DBTDM. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 608–616, 2008

Key words: adhesion; catalysts; networks; polyurethanes; silicones

INTRODUCTION

Recently, water-based and solvent-free curable compositions (e.g., adhesives, sealants, and coatings) have received much attention as environmentally friendly products.^{1–6} In particular, so-called volatile organic compounds are the representative inadequacy of typical solvent-based adhesives.^{7–9} On the other hand, elastic adhesives have been used for the adhesion of various materials having different expansion coefficients (e.g., wood and metal, and plastics and metal) because of their good adherence, good property to follow the movement of the substrates, and good vibration suppression.^{10–12}

Recently, we have developed polyurethanes end-capped with alkoxyethyl groups (silylated polyurethanes),^{13–16} which can be applied as base polymers for elastic adhesives in solvent-free systems. The silylated polyurethanes are moisture-curable polymers that can be cured by the condensation reaction of the terminal silyl group in the presence of water.^{17–22} In a previous study,¹⁶ we synthesized silylated polyurethanes from a commercial primary aminosilane [3-aminopropyltri-

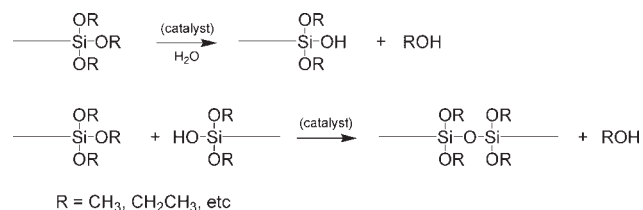
methoxysilane (APTMS)] and evaluated their performance as base polymers for moisture-curable adhesives. The curing process is shown in Scheme 1; it is accelerated in the presence of catalysts (e.g., organotin or organobismuth compounds).^{23,24} In general, various types of catalysts are used for the preparation of adhesives, sealants, and coatings based on the alkoxyethyl-terminated polymers because the curing speed of the polymer without the catalyst is very slow. An important drawback of useful organometallic catalysts is the hazard to human health. Yellow discoloration of the resulting product is another disadvantage in the case of organotin catalysts. Hence, the development of novel environmentally friendly catalysts with high curing efficiency and non-discoloration is eagerly desired.

Boron trifluoride complexes are well known as some of the most conventional strong Lewis acid catalysts. For example, boron trifluoride/diethyl ether complex has been used as a catalyst for cationic polymerization,^{25,26} and boron trifluoride/amine complexes [e.g., boron trifluoride/monoethylamine (BF₃-MEA) complex and boron trifluoride/piperidine complex] have been used as the curing catalysts for epoxy resin.^{27–29} Boron trifluoride complexes are superior from an environmental point of view because the trialkyltin compounds are very hazardous.

The catalytic effect of BF₃-MEA on the condensation reaction of alkoxyethyl groups was reported by Lee et al.,³⁰ although their work was mainly focused

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Scheme 1 Curing process of the alkoxy silane-terminated polymer.

on the thermal and dynamic mechanical properties of thermally cured epoxy-bridged polyorganosiloxanes. However, BF₃-MEA was not used as the curing catalyst of adhesives based on an alkoxy silane-terminated polymer. Therefore, in a previous study,³¹ we reported the contribution of BF₃-MEA for a moisture-curable adhesive based on silylated polyurethane having a trimethoxysilane terminal group with respect to the curing speed, adherence, and heat resistance. It was found that BF₃-MEA was a highly active curing catalyst.

In this study, we again focused on BF₃-MEA as the curing catalyst of alkoxy silane-terminated polymers. The bulkiness of the alkoxy group is related closely to the reactivity of alkoxy silanes, and a longer alkoxy group leads to a slower condensation reaction. The inadequacy motivated us to improve the curing speeds of the slowly curing polymers having a bulky alkoxy silane with BF₃-MEA, a highly active curing catalyst. With this in mind, we compared the effects of BF₃-MEA and dibutyltin dimethoxide (DBTDM) on the curing speed of the silylated polyurethanes having long trialkoxysilyl groups (ethoxy, propoxy, and butoxy).

EXPERIMENTAL

Materials

The following reagents and materials were used without further purification: poly(propylene oxide) [hydroxyl value = 11.7 (the hydroxyl value is defined as the milligrams of potassium hydroxide required to neutralize the acetic acid capable of combining by acetylation with 1.0 g of a sample), molecular weight = 10,000; PML S 4012, Asahi Glass Urethane Co., Ltd., Kamisu, Japan], isophorone diisocyanate (Sumika Bayer Urethane Co., Ltd., Amagasaki, Japan), methyl acrylate (MA; Toagosei Co., Ltd., Tokyo, Japan), APTMS (Shin-Etsu Chemical Co., Ltd., Tokyo, Japan), 3-aminopropyltriethoxysilane (APTES; Shin-Etsu Chemical), dioctyltin diversate (Nitto Kasei Co., Ltd., Osaka, Japan), DBTDM (Sankyo Organic Chemicals Co., Ltd., Kawasaki, Japan), BF₃-MEA (Wako Pure Chemical Industries, Ltd., Osaka, Japan), dry 1-propanol (Wako Pure Chemical Industries), dry 1-butanol (Wako Pure Chemical Industries),

and dry tetrahydrofuran (THF; Wako Pure Chemical Industries).

Preparation of the aminosilanes

3-Aminopropyltriethoxysilane (APTPS)

APTMS (179.3 g, 1.0 mol) was reacted with dry 1-propanol (300.5 g, 5.0 mol) at 80°C for 3 h. After the reaction, the mixture was cooled to room temperature naturally, and eliminated methanol was evacuated *in vacuo* at room temperature for 1 h. The reaction and evacuation processes were conducted six times. Then, additional dry 1-propanol (300.5 g, 5.0 mol) was added to the reaction mixture, and the reaction and evacuation processes were repeated six times in the same manner. Finally, the remaining 1-propanol was evacuated at 80°C for 2 h to afford APTPS as a colorless, transparent liquid in a 96% yield (252.4 g). The purity was determined by gas chromatography (GC; single peak, retention time: 14.9 min).

The ¹H-NMR spectrum of APTPS is shown later in Figure 2.

IR (NaCl plate): 684, 742, 842, 877, 898, 915, 965, 1015, 1085, 1153, 1189, 1223, 1263, 1303, 1390, 1464, 1578, 2169, 2753, 2877, 2935, 2962, 3297 cm⁻¹.

3-Aminopropyltributoxysilane (APTBS)

APTBS was prepared by the reaction of APTMS (179.3 g, 1.0 mol) with dry 1-butanol (in all, 741.2 g, 10.0 mol) according to the method used for the synthesis of APTPS. The yield was 96% (293.5 g).

Preparation of the silane endcappers

Silane endcapper **1a**

The synthesis of silane endcapper **1a** was conducted by the reaction of APTMS (179.3 g, 1.0 mol) with an equimolar amount of MA (86.1 g, 1.0 mol) according to the method reported previously.¹⁶ The characteristics of the silane endcappers (**1a-1d**) are summarized in Table I.

Silane endcapper **1b**

The synthesis of silane endcapper **1b** was conducted by the reaction of APTES (221.4 g, 1.0 mol) with an equimolar amount of MA (86.1 g, 1.0 mol) in the same manner as **1a**. **1b** was obtained as a colorless, transparent liquid quantitatively. The yield was 99.9% (307.3 g).

Silane endcapper **1c**

The synthesis of silane endcapper **1c** was conducted by the reaction of APTPS (131.8 g, 0.50 mol) with an

TABLE I
Characterization of the Silane Endcappers

Silane endcapper	Silyl group	Total amino group content (%)	Tertiary amino group content (%)	Calculated average molecular weight per reactive amino group ^a	Theoretical molecular weight per reactive amino group ^b
1a	–Si(OCH ₃) ₃	5.30	0.89	317.5	265.4
1b	–Si(OCH ₂ CH ₃) ₃	4.40	0.61	369.4	307.5
1c	–Si(OCH ₂ CH ₂ CH ₃) ₃	4.06	0.50	393.3	349.5
1d	–Si(OCH ₂ CH ₂ CH ₂ CH ₃) ₃	3.80	0.42	414.2	391.6

^a The average molecular weight per reactive amino group was calculated as follows: Average molecular weight = $14 \times 100 / [(Total\ amino\ group\ content) - (Tertiary\ amino\ group\ content)]$. Both primary and secondary amino groups are regarded as the reactive amino groups.

^b The molecular weight of the reaction product of 1 mol of MA with 1 mol of each aminosilane.

equimolar amount of MA (43.1 g, 0.50 mol) in the same manner as **1a**. The yield was 100% (174.9 g).

Silane endcapper **1d**

The synthesis of silane endcapper **1d** was conducted by the reaction of APTBS (152.9 g, 0.50 mol) with an equimolar amount of MA (43.1 g, 0.50 mol) in the same manner as **1a**. The yield was 100% (196.0 g).

Preparation of isocyanate-terminated polyurethane **2**

The synthesis of isocyanate-terminated polyurethane **2** was conducted by the reaction of PML S 4012 [poly(propylene oxide)] and isophorone diisocyanate with dioctyltin diversatate as a catalyst according to the method reported previously.¹⁶

Preparation of the silylated polyurethanes

Silylated polyurethane **3a**

The synthesis of silylated polyurethane **3a** was conducted by the reaction of silane endcapper **1a** and isocyanate-terminated polyurethane **2** (Fig. 1) according to the method reported previously.¹⁶

Silylated polyurethane **3b**

The synthesis of silylated polyurethane **3b** was conducted by the reaction of silane endcapper **1b** (developed in this study) and isocyanate-terminated polyurethane **2** in the same manner as **3a**. **2** (2092.8 g) and **1b** (143.7 g, equimolar amount of the isocyanate group in **2**) were reacted at 80°C for 30 min under nitrogen to afford **3b** as a colorless, transparent, viscous liquid in a 97% yield (2158.5 g).

Viscosity: 70,000 mPa·s. ¹H-NMR (CDCl₃, δ, ppm): 1.02–1.44 [br, CH₂CH(CH₃)], 3.27–3.44 [br, CH₂CH(CH₃)], 3.44–3.77 [br, CH₂(CH₃)]. ¹³C-NMR (CDCl₃, δ, ppm): 17.0–17.7 [br s, CH₂CH(CH₃)], 18.1

(br s), 18.3 (br s), 18.5 (br s), 58.4 (SiOCH₂), 72.9–73.3 [br, CH₂CH(CH₃)], 75.1–75.4 [br s, CH₂CH(CH₃)], 155.3 [NHC(=O)O], 158.0 [NHC(=O)N], 173.1 [C(=O)OCH₃]. IR (NaCl plate): 665, 834, 867, 931, 1014, 1109, 1254, 1297, 1344, 1373, 145, 1529, 1653, 1721, 2870, 2931, 2971, 3377, 3516, 3578 cm⁻¹.

Silylated polyurethane **3c**

The synthesis of silylated polyurethane **3c** was conducted by the reaction of silane endcapper **1c** and isocyanate-terminated polyurethane **2** in the same manner as **3a**. **2** (1255.6 g) and **1c** (91.6 g, equimolar amount of the isocyanate group in **2**) were reacted at 80°C for 30 min under nitrogen to afford **3c** as a colorless, transparent, viscous liquid in a 96% yield (1296.1 g).

Viscosity: 72,000 mPa·s. ¹H-NMR (CDCl₃, δ, ppm): 0.86–0.98 (m, SiOCH₂CH₂CH₂CH₃), 1.02–1.27 [br, CH₂CH(CH₃)], 1.48–1.64 (m, SiOCH₂CH₂), 3.27–3.44 [br, CH₂CH(CH₃)], 3.44–3.77 [br, CH₂CH(CH₃)]. ¹³C-NMR (CDCl₃, δ, ppm): 10.2 (SiOCH₂CH₂CH₃), 17.0–17.7 [br s, CH₂CH(CH₃)], 18.1 (br s), 18.2 (br s), 18.5 (br s), 25.7 (s, SiOCH₂CH₂), 64.4 (SiOCH₂), 72.9–73.3 [br, CH₂CH(CH₃)], 75.1–75.4 [br s, CH₂CH(CH₃)], 155.3 [NHC(=O)O], 158.0 [NHC(=O)N], 173.1 [C(=O)OCH₃]. IR (NaCl plate): 839, 867, 927, 1014, 1108, 1254, 1297, 1344, 1373, 1454, 1529, 1656, 1720, 2871, 2931, 2970, 3370, 3521 cm⁻¹.

Silylated polyurethane **3d**

The synthesis of silylated polyurethane **3d** was conducted by the reaction of silane endcapper **1d** and isocyanate-terminated polyurethane **2** in the same manner as **3a**. **2** (1569.5 g) and **1d** (120.7 g, equimolar amount of the isocyanate group in **2**) were reacted at 80°C for 30 min under nitrogen to afford **3d** as a colorless, transparent, viscous liquid in a 97% yield (1637.1 g).

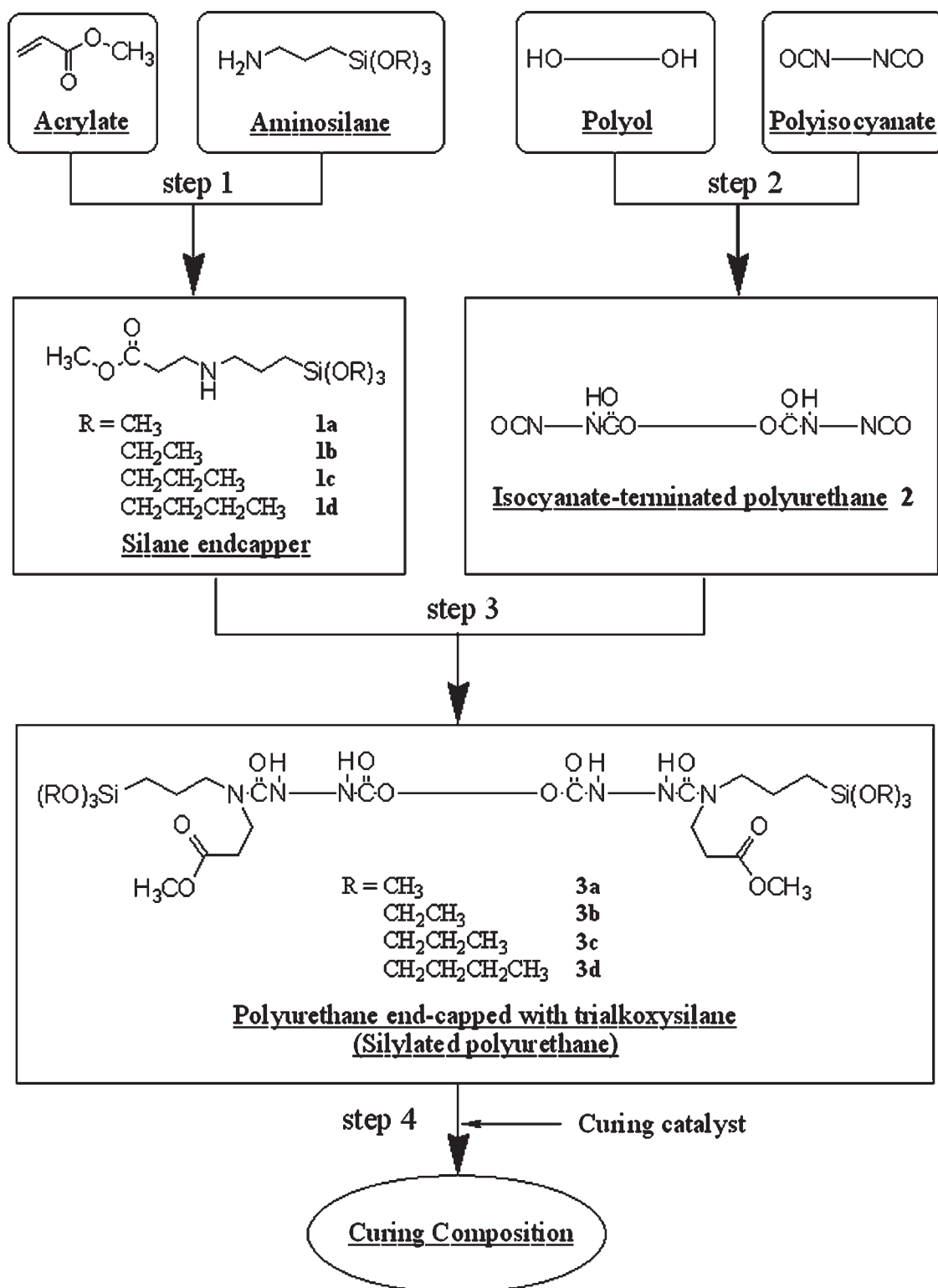


Figure 1 Pathway for preparing curing compositions based on silylated polyurethane.

Viscosity: 72,000 mPa·s. ¹H-NMR (CDCl₃, δ, ppm): 0.89–0.96 (m, SiOCH₂CH₂CH₂CH₃), 1.02–1.27 [br, CH₂CH(CH₃)], 1.33–1.43 (m, SiOCH₂CH₂CH₂), 1.48–1.58 (m, SiOCH₂CH₂), 3.27–3.44 [br, CH₂CH(CH₃)], 3.44–3.77 [br, CH₂CH(CH₃)]. ¹³C-NMR (CDCl₃, δ,

ppm): 13.8 (SiOCH₂CH₂CH₂CH₃), 17.0–17.7 [br s, CH₂CH(CH₃)], 18.1 (br s), 18.2 (br s), 18.5 (br s), 18.9 (s, SiOCH₂CH₂CH₂), 34.6 (s, SiOCH₂CH₂), 62.5 (SiOCH₂), 72.9–73.3 [br, CH₂CH(CH₃)], 75.1–75.4 [br s, CH₂CH(CH₃)], 155.3 [NHC(=O)O], 158.0

[NHC(=O)N], 173.1 [C(=O)OCH₃]. IR (NaCl plate): 669, 734, 834, 867, 927, 1014, 1108, 1254, 1297, 1344, 1373, 1456, 152, 1654, 1719, 2870, 2931, 2970, 3362 cm⁻¹.

Preparation of the curable composition based on silylated polyurethane

The catalyst DBTDM or BF₃-MEA (2.0 mmol) was dissolved in 2.0 mL of THF to afford the catalyst solution. Each catalyst solution was mixed in silylated polyurethanes **3a–3d** (200 g) at room temperature for 10 min *in vacuo* to afford the curable composition for the measurement of the film formation time to compare the curing speed. The curable composition was subdivided into hermetically closed cartridges and left to rest at 50°C for 3 days and additionally at 23°C for 1 day before the measurement of the film formation time.

Characterization and evaluation

GC was performed with a GC-14B gas chromatograph (Shimadzu Corp., Kyoto, Japan). Thermal Conductivity Detector (TCD) detector with UA1-15W-1.5F (length = 15 m, i.d. = 0.53 mm, film = 1.5 μm). The initial temperature was 50°C, which was held for 2 min, and then the temperature was increased at 10°C/min to reach 300°C; the final retention time at the final temperature was 5 min. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet Avatar 360 FTIR spectrometer system (Thermo Fisher Scientific K. K., Yokohama, Japan). ¹H-NMR, ¹³C-NMR, ¹⁵N-NMR, and ²⁹Si-NMR (400 MHz) spectra were measured on a JEOL ECX-400 spectrometer (Tokyo, Japan) with tetramethylsilane (0 ppm for ¹H-NMR, ¹³C-NMR, and ²⁹Si-NMR) and nitromethane (378.4 ppm for ¹⁵N-NMR)³² as an internal standard. The nitrogen contents of the primary, tertiary, and total amino groups in the silane endcappers were measured by titration with an AT-510 automatic potentiometric titrator (Kyoto Electronics Manufacturing Co., Ltd., Kyoto, Japan). The estimation of the nitrogen content was conducted with perchloric acid (acetic acid solution) pursuant to JIS K 7245 ("Plastics—Amine Epoxide Hardeners—Determination of Primary, Secondary and Tertiary Amine Group Nitrogen Content"). The content of the isocyanate group of the isocyanate-terminated polyurethane was determined from the amount of dibutylamine reacted with the isocyanate-terminated polyurethane by titration (amine equivalent method) with an AT-510 automatic potentiometric titrator (Kyoto Electronics Manufacturing). The viscosity was measured with a B-type viscometer (no. 7 rotor, 10 rpm, model BH), Tokimec Inc. (Tokyo, Japan) at 23°C. The curing speed of the adhesives was eval-

uated as the film formation time at 23°C under 50% relative humidity. To confirm the film formation time, the curable composition was exposed at 23°C under 50% relative humidity, and the surface of the exposed sample was evaluated by contact with a spatula. The time when the surface was not stuck on the spatula was regarded as the film formation time.

RESULTS AND DISCUSSION

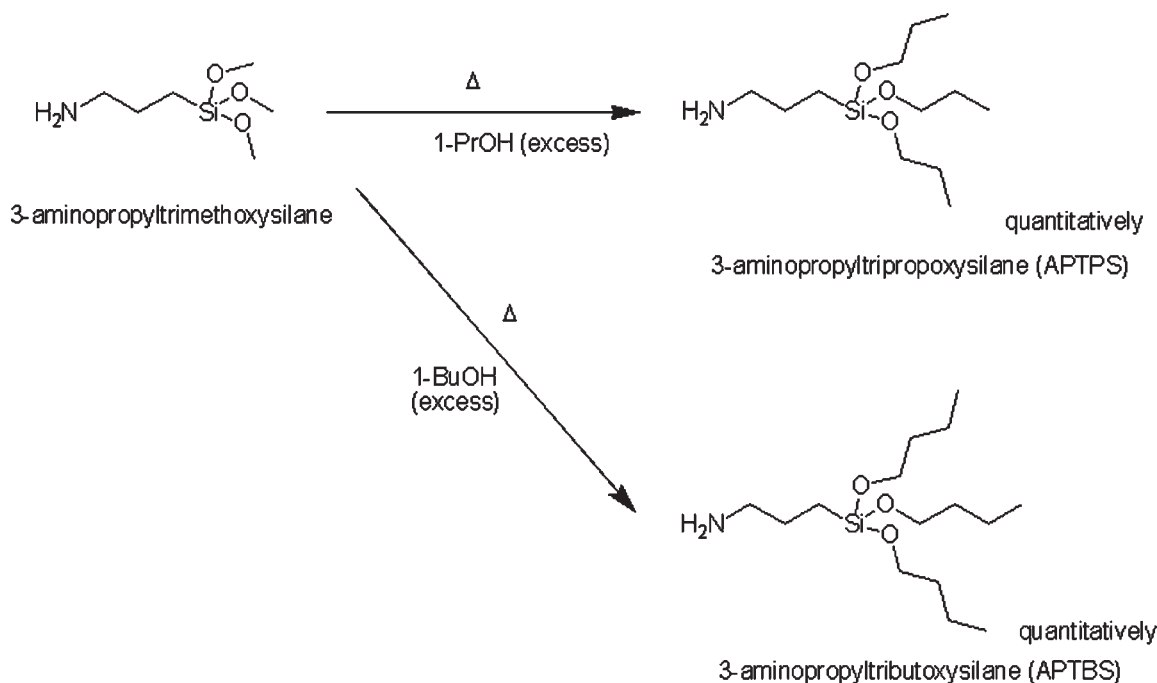
Synthesis and characterization of the aminosilanes

Alkoxysilane compounds having bulky alkoxy groups, APTPS and APTBS, were synthesized through the alkoxy exchange reaction from APTMS with 1-propanol and 1-butanol, respectively (Scheme 2). The repetition process of the reaction and evacuation was conducted with a careful selection of the reaction conditions (temperature = 80°C, time = 3 h) and evacuation condition (room temperature). APTPS and APTBS were obtained quantitatively when a large excess of 1-propanol or 1-butanol was used for the reaction and methanol produced as a byproduct was successively evacuated. The resulting APTPS and APTBS were characterized with ¹H-NMR and GC. According to ¹H-NMR spectra shown in Figure 2, the peaks of NCH₂ (b) and SiCH₂ (d) were observed in both spectra. Additionally, new peaks were generated by comparison with APTMS, and they were attributed to CH₂ and CH₃ of the propoxysilyl group and butoxysilyl group. Furthermore, their purities were determined with GC, and only a single peak was observed in each GC chart (retention time: 14.9 min for APTPS and 17.6 min for APTBS).

Synthesis and characterization of the silane endcappers

The conjugate addition reaction is known as a process in which an amino group reacts quantitatively with an α,β-unsaturated carbonyl group under mild conditions.³³ In this study, the conjugate addition technology was applied to synthesize silane endcappers by the reaction of primary aminosilanes and MA, as shown in Scheme 3. The resulting trialkoxysilane compound, having mainly secondary amine groups, could be successfully used as an end-capping agent for the terminal isocyanate groups of the isocyanate-terminated polyurethane. Four aminosilanes having different alkoxysilyl groups were employed, including APTMS, APTEs, APTPS, and APTBS, to confirm the catalytic effect on the curing process.

In our approach, 1 mol of MA was reacted with 1 mol of each aminosilane under mild conditions (Scheme 3). In all cases, the reaction was conducted



Scheme 2 Synthesis of APTPS and APTBS.

without any solvent. The resulting silane endcappers were characterized with $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, GC, and titration as previously reported,¹⁶ and the titration data are listed in Table I. MA was converted quantitatively because the disappearance of the vinyl groups was confirmed by $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra of silane endcappers **1a–1d**. On each GC chart of silane endcappers **1a–1d**, three peaks were observed,

which most likely corresponded to the raw material aminosilanes (retention time: 8.9, 11.8, 14.7, and 17.4 min), the secondary aminosilanes (retention time: 15.6, 17.5, 19.7, and 21.8 min), and the tertiary aminosilanes (19.5, 21.0, 22.7, and 24.4 min), for **1a**, **1b**, **1c**, and **1d**, respectively. The concentrations of the secondary aminosilanes calculated from the areas of the GC charts were 70, 76, 77, and 82 mol % for **1a**,

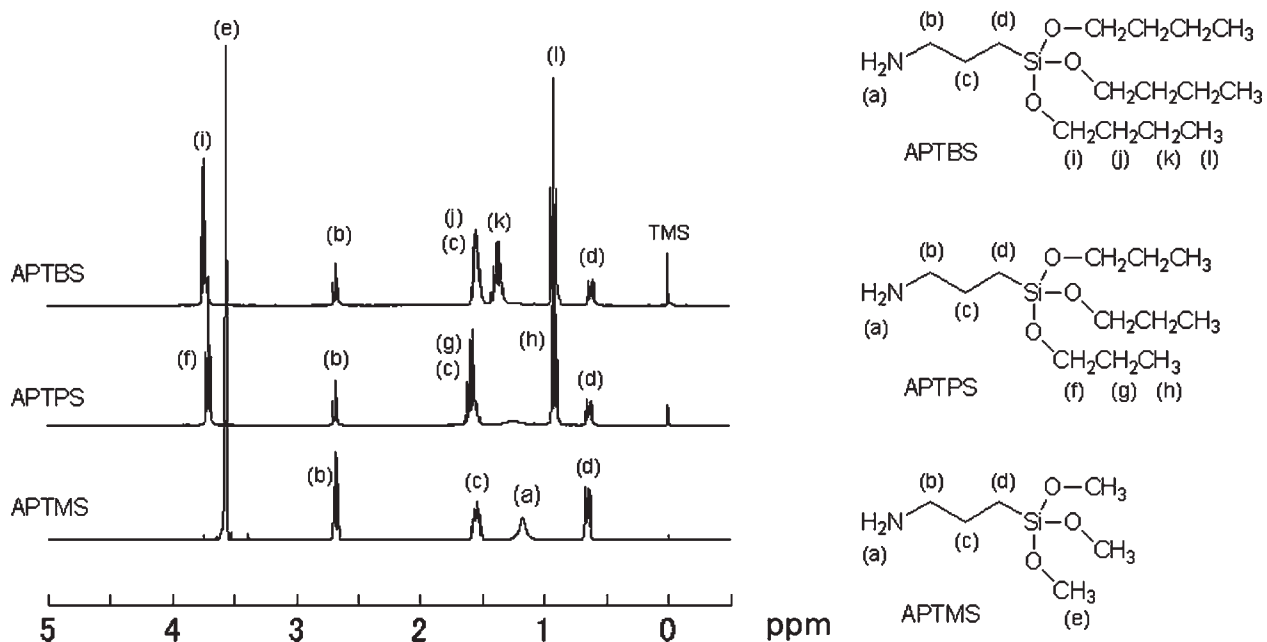
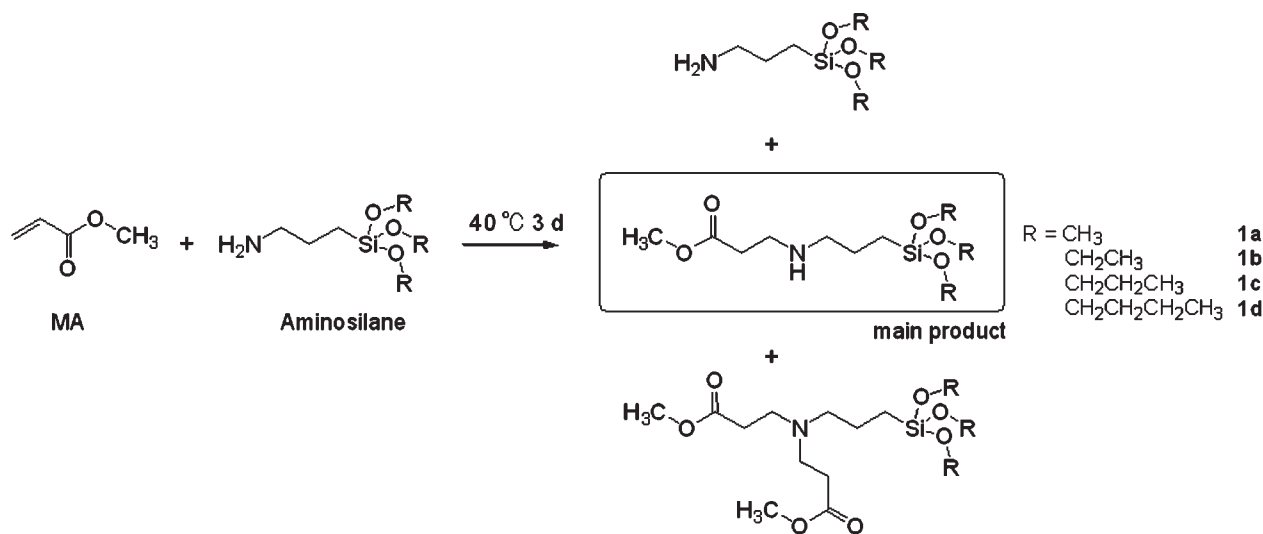


Figure 2 $^1\text{H-NMR}$ spectra (CDCl_3) of APTMS, APTPS, and APTBS.



Scheme 3 Synthesis of silane endcappers.

1b, **1c**, and **1d**, respectively. All of the silane endcappers (**1a–1d**) have the approximately the same calculated average molecular weight per reactive amino group (within plus 20% at maximum) as the theoretical one. From the results of the concentrations of the secondary aminosilanes and the calculated average molecular weight per reactive amino group, the main products, the secondary aminosilanes, should play a key role in the curing process, whereas the contribution from the minor products may be negligible because of the low content.

Synthesis and characterization of the silylated polyurethanes

The pathway for the synthesis of the silylated polyurethanes is shown in Figure 1 (step 3). The isocyanate-terminated polyurethane was reacted with each silane endcapper at 80°C for 30 min under nitrogen without a reaction solvent, and the resulting product was characterized with ¹³C-NMR, FTIR, and viscosity measurements according to the previously reported method.¹⁶ All silylated polyurethanes had no NCO peak in the IR chart, and the peaks of

NHCOO, NHCON, >C=O, and alkoxy-silyl groups were observed in the ¹³C-NMR spectrum of each silylated polyurethane. The viscosity of the silylated polyurethanes are shown in Table II. The viscosity and appearance of all silylated polyurethanes (**3a–3d**) were almost the same, regardless of the structures of the alkoxy-silyl group.

Comparison of the curing speeds of BF₃-MEA and DBTDM

The curing speed of the curable composition was compared by the film formation time: 2.0 mmol of BF₃-MEA or DBTDM was added to 200 g of silylated polyurethanes **3a–3d**. Figure 3 shows the film formation time of **3a–3d** with each catalyst, and Figure 4 presents a magnification of the area from 4 to 20 min with BF₃-MEA. Although DBTDM is one of the most active curing catalysts, the film formation

TABLE II
Characterization of the Silylated Polyurethanes

Silylated polyurethane	Silyl group	Viscosity (mPa·s) ^a
3a	–Si(OCH ₃) ₃	61,000
3b	–Si(OCH ₂ CH ₃) ₃	70,000
3c	–Si(OCH ₂ CH ₂ CH ₃) ₃	72,000
3d	–Si(OCH ₂ CH ₂ CH ₂ CH ₃) ₃	72,000

^a Measured with a B-type viscometer (no. 7 rotor, 10 rpm, model BH) at 23°C.

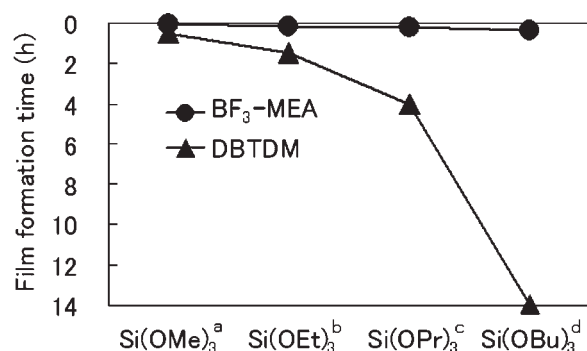


Figure 3 Film formation time of **3a–3d** with a catalyst. Superscripts a, b, c, and d indicate samples **3a**, **3b**, **3c**, and **3d**, respectively (see Table II).

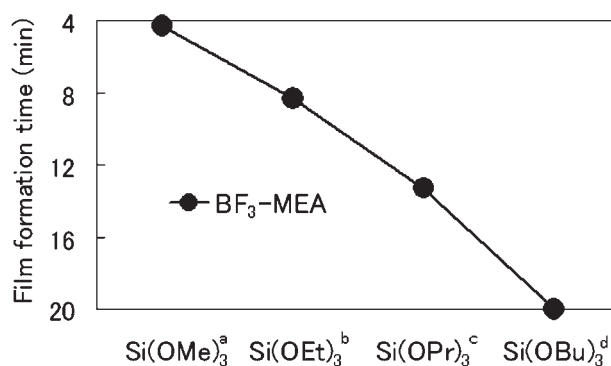
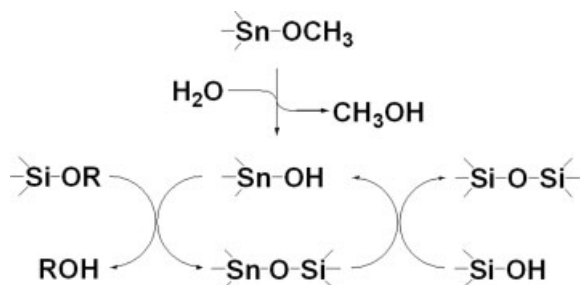


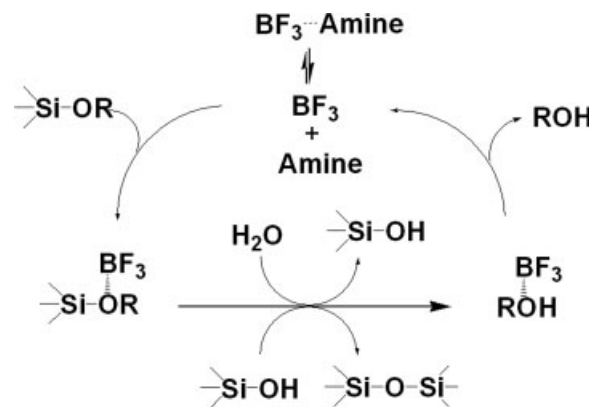
Figure 4 Higher magnification figure taken from the area between 4 and 20 min in Figure 3. Superscripts a, b, c, and d indicate samples **3a**, **3b**, **3c**, and **3d**, respectively (see Table II).

time of the silylated polyurethanes in the presence of $\text{BF}_3\text{-MEA}$ was much shorter than that with DMTDM, as shown in Figure 3. The result indicates that $\text{BF}_3\text{-MEA}$ is obviously more active than DBTDM. In a previous publication,³¹ $\text{BF}_3\text{-MEA}$ was reported to be a very active curing catalyst for silylated polyurethane terminated with a trimethoxysilyl group. In this study, it was also confirmed that $\text{BF}_3\text{-MEA}$ worked as a remarkable curing agent for silylated polyurethanes terminated with even longer alkoxy-silyl groups (ethoxy, propoxy, and butoxy). It is known that the curing speeds of silylated polyurethanes terminated with longer alkoxy-silyl groups are slower in the presence of an organometallic catalyst.³⁴ A similar tendency was observed in this study, as shown in Figure 3. The high performance of $\text{BF}_3\text{-MEA}$ is an extraordinary effect in this field.

The reason for the high performance of $\text{BF}_3\text{-MEA}$ possibly involves different condensation processes of the alkoxy-silyl groups and differences in the strength of Lewis acidity. A possible condensation process with an tin carboxylate compound has been reported.²³ In the case of DBTDM, the condensation process is considered to follow Scheme 4. On the contrary, the postulated condensation process with



Scheme 4 Catalytic cycle of the organotin methoxide catalyst.



Scheme 5 Postulated catalytic cycle of the $\text{BF}_3\text{-amine}$ complex catalyst.

$\text{BF}_3\text{-MEA}$ is shown in Scheme 5. In both processes, the trigger of the condensation is H_2O , which is moisture in the air. In the case of DBTDM, the conversion from $-\text{SnOCH}_3$ to $-\text{SnOH}$ is necessary before the catalytic cycle. In contrast, $\text{BF}_3\text{-MEA}$ will interact with $-\text{Si}-\text{O}-\text{R}$ beforehand, and the catalytic cycle can start immediately after being triggered with H_2O . BF_3 is known to be a strongly oxophilic Lewis acid,³⁵ and the acidity of $\text{BF}_3\text{-MEA}$ is decreased by the basicity of monoethylamine. However, $\text{BF}_3\text{-MEA}$ still has strong Lewis acidity, which is applicable as a curing catalyst for epoxy resin.²⁷⁻²⁹ In other words, $\text{BF}_3\text{-MEA}$ has enough oxophilicity for complexation with oxygen atoms. The strong Lewis acidity should accelerate the catalytic cycle. Anyway, the film formation time is the only parameter to characterize the curing reaction. The evaluation of the generation of the film is very important for obtaining more useful data about the curing mechanism. Further study on this point will be reported separately.

CONCLUSIONS

In this study, polyurethanes end-capped with different trialkoxy-silanes, including trimethoxysilane, triethoxysilane, tripropoxysilane, and tributoxysilane, were synthesized to compare the curing effects of $\text{BF}_3\text{-MEA}$ and DBTDM. $\text{BF}_3\text{-MEA}$ was significantly superior to DBTDM in terms of the curing speed. The curing process by $\text{BF}_3\text{-MEA}$ is possibly different from that by DBTDM because of the large difference in the film formation time. Polyurethanes end-capped with long alkoxy-silyl groups, which are generally regarded as slowly curing polymers, could be cured very quickly with $\text{BF}_3\text{-MEA}$.

$\text{BF}_3\text{-MEA}$ can extend the possibility of these polymers and can be successfully employed for the pre-

paration of one-component, solvent-free elastic adhesives based on silylated polyurethanes.

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