

NMR Spectroscopic Studies of Dimethyldiethoxy Silane Hydrolysis and Polysiloxane Conversion

Ming-Fu Tsai,¹ Yu-Der Lee,² Kan-Nan Chen³

¹Chemical System Research Division, Chung-Shan Institute of Science and Technology, Lung-Tan, Taiwan 325, Republic of China

²Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan 300, Republic of China

³Department of Chemistry, Tamkang University, Tamsui, Taiwan 251, Republic of China

Received 23 November 2001; accepted 30 January 2002

ABSTRACT: The hydrolysis rate of alkoxy silane (dimethyldiethoxy silane, DMDES, etc.) is a linear relationship vs. the reaction time under the moisture flux control. The hydrolysis process results in formation of the linear polysiloxane products by a subsequent condensation reaction. An amidized alkoxy silane (3-(2-aminoethyl)aminopropylmethyl-dimethoxy silane, KLM-602 or γ -aminopropyl-triethoxy silane, γ -APS) serves as an internal standard of DMDES

hydrolysis kinetics measurements. The hydrolysis kinetics of DMDES with the amidized alkoxy silane and the subsequent linear polysiloxanes conversion have been evaluated and characterized by ²⁹Si- and ¹³C-NMR spectroscopic measurements. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 468–477, 2002

Key words: polysiloxane; silane; hydrolysis; NMR

INTRODUCTION

This study is on the hydrolysis reaction of alkoxy silane and its results in the formation of silanol derivatives and polysiloxanes. A larger alkoxy group on silane and a slower hydrolysis rate resulted.^{1–3} These trends are the same in both the acid and base catalytic systems.^{4,5} Various factors, such as pH value,^{6–9} catalyst,^{10,11} solvent,¹² ratio of water to alkoxy silane,¹³ as well as the structure of alkoxy silane,¹⁴ all have effects on the hydrolysis and the sequential siloxane conversion. Hydrolysis rate constant (K_h) of γ -glycidopropyl trimethoxy silane is about 10^4 to $10^5 M^{-1} s^{-1}$,⁸ and its condensation rate constant (K_{cw}) of trimethyl silanol is $10^{-6} M^{-1} s^{-1}$ with a weak base medium.⁹ As for ethyl silicate, its K_h is $10^{-4} M^{-1} s^{-1}$, at a pH value of 2–3.^{15–17}

Chemical shifts of silicone with different bonded groups are distinguishable in ²⁹Si-NMR spectra.^{18–21} For instance, various sizes of cyclic siloxane have a single peak but with different chemical shifts in ²⁹Si-NMR spectra.^{21–23} Furthermore, the hydrolysis mechanism of the silane coupling agent²⁴ and its reaction on the silicate surface are investigated by means of the

measurements of ¹³C-NMR accompanied with ²⁹Si-NMR.^{25–29}

Hydrolysis of alkoxy silane results in cyclic or linear siloxane formation, depending on water quantity. In the case of ethyl silicate solution with a limited amount of water, it comprises a linear diethoxy siloxane at the initial stage of hydrolysis.^{19,30} Under similar conditions, linear polysiloxanes are obtained from a partial hydrolysis of dimethyldiethoxy silane.^{31–35} However, hydrolysis of diethoxy silane with an excess amount of water causes the formation of different silanediols, such as D₄, D₅, D₆, and the cyclic oligomers from the subsequent condensation reaction of silanols.^{36,37}

The hydrolysis of dimethyldiethoxy silane (DMDES) with amidized 3-(2-aminoethyl)aminopropylmethyl-dimethoxy silane (KLM-602) or γ -amino-propyltriethoxy silane (γ -APS) as an internal standard and controlled by the moisture flux. Their hydrolysis and polysiloxane conversion have been investigated by NMR measurements and reported in this article.

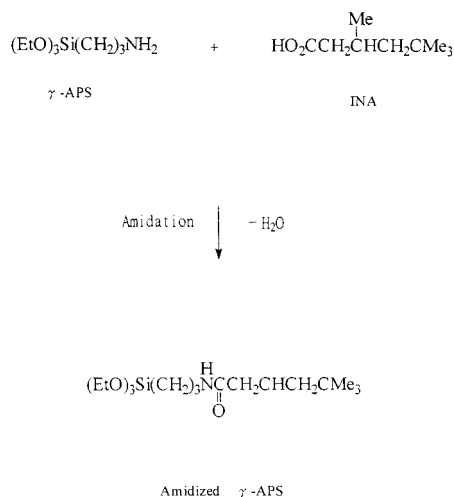
EXPERIMENTAL

Materials

Iso-nonanoic acid (INA) was purchased from Exxon Chemical Co., and is dried over a molecular sieve (4 Å) for 7 days before use. γ -Aminopropyltriethoxy silane (γ -APS) and dimethyldiethoxy silane (DMDES) were purchased from Petrarch System. 3-(2-Aminoethyl)aminopropylmethyl-dimethoxy silane (KLM-602) was obtained from Shin-Etsu Chemical Co., Japan. There were stored in a dry box before use.

Correspondence to: K.-N. Chen (knchen@mail.tku.edu.tw)

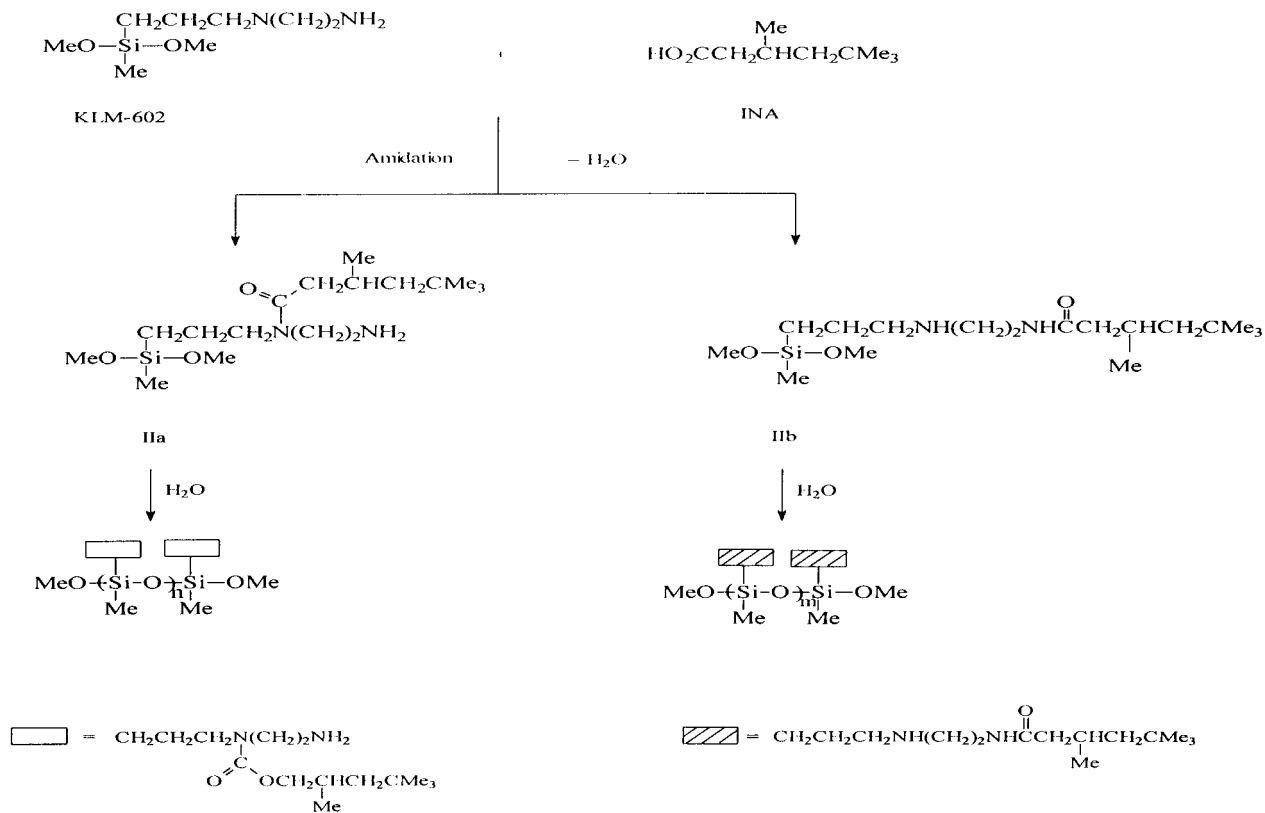
Contract grant sponsor: the development program for specialty chemicals of Chemical System Research Division, Chung-Shan Institute of Science and Technology and the National Science Council, Republic of China.



Scheme 1 Silane amidation of γ -APS with INA.

Preparation of amidized silane

Iso-nonanoic acid (INA, 17.7 g, 0.11 mol) was taken and reacted with 25 g (0.11 mol) of γ -APS or 23.4 g (0.11 mol) of KLM-602. Then the reaction mixture was slowly heated up to 150°C and kept at that temperature for 1 h. These two silane amidation reactions of γ -APS and KLM-602 are shown in Schemes 1 and 2, respectively.



Scheme 2 Silane amidation of KLM-602 with INA.

Hydrolysis of dimethyldiethoxy silane and amidized silane (KLM-602)

A reactor with amidized KLM-602 (IIa) (36.7 g, 0.11 mol) and potassium fluoride (0.1 g) as a catalyst was set up in a water bath at 30°C. Then DMDES (16.28 g, 0.11 mol) was charged for the hydrolysis and the subsequent condensation reaction by means of the moisture flux passing through the reactor. The saturated water vapor contains 1.5×10^{-3} mol of water molecule per liter of air at 28°C. The resulting mixture was diluted with toluene and rinsed twice with water. The organic phase was dried and sampled for the molecular weight measurement by a vapor pressure osmometer.

Alkoxy content was analyzed by means of Zeisel's method during the hydrolysis and the sequential condensation reactions of DMDES and amidized KLM-602 (IIa). Karl Fischer titration was employed to determine the water content in silanol solution during the course of the hydrolysis process.

Hydrolysis kinetics of silane by NMR measurements

NMR spectra were recorded at 27°C on a JEOL FX-90Q with CDCl_3 as the solvent and TMS as the internal standard for proton NMR spectra. The measurements

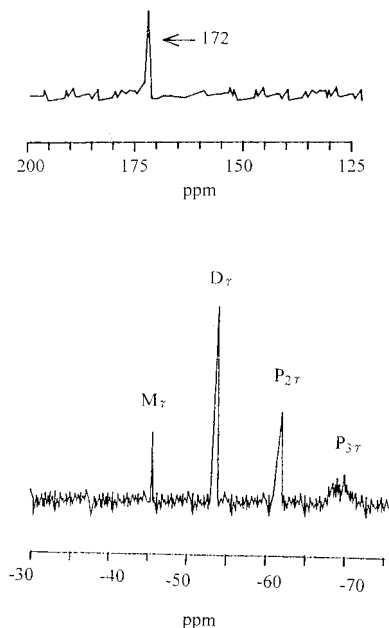


Figure 1 (a) ^{13}C -NMR spectrum of amidized γ -APS. (b) ^{29}Si -NMR spectrum of amidized γ -APS.

of ^{29}Si - and ^{13}C -NMR spectra were taken with the pulse angle of 30° at 17.75 MHz and 22.49 MHz, respectively.

RESULTS AND DISCUSSION

The hydrolysis of DMDDES with the amidized silane (γ -APS or KLM-602) was characterized and monitored by means of ^{13}C - and ^{29}Si -NMR measurements, respectively. ^{13}C -NMR measurement is an effective method to distinguish the methyl groups on different silanes and to identify the amide carbonyl carbon on amidized silane. The different silicone compounds, such as monomer, dimer, and polysiloxane from the amidized γ -APS, are identified by ^{29}Si -NMR spectra. However, the linear polysiloxane is the only product existing in the amidized KLM-602 due to the steric hindrance of the bulky group attached directly on silicone, which is quite different from that in amidized γ -APS.

Characterization of amidized silane and its siloxanes

There is only one chemical shift of $\delta = 172$ ppm in ^{13}C -NMR spectrum for amide carbonyl carbon of amidized γ -APS (free acid of INA at $\delta = 179$ ppm is not found) [Fig. 1(a)]. This is the evidence of complete amidation of γ -APS with INA (Scheme 1). From ^{29}Si -NMR spectrum of amidized γ -APS with INA, the chemical shifts in amidized γ -APS mixture can be assigned as the monomer (M_γ , $\delta = -46.0$ ppm), dimer (D_γ , $\delta = -54.2$ ppm), linear polysiloxane (the repeated

siloxane unit) ($P_{2\gamma}$, $\delta = -61.7$ ppm), and T-shape (crosslinked) siloxane structure of γ -APS ($P_{3\gamma}$, $\delta = -68.9$ ppm) [Fig. 1(b) and Table I]. It appears that the ethoxy on γ -APS is not easily hydrolyzed; therefore, some of its monomer (M_γ) and dimer (D_γ) is still found in γ -APS amidation products.

For the silane amidation of KLM-602 with INA (Scheme 2), there are two amide carbonyl peaks in ^{13}C -NMR spectrum [Fig. 2(a)]. One of the chemical shifts is 166 ppm for a compound with a tertiary amide (IIa in Scheme 2), and the other is 172 ppm for a compound with a secondary amide (IIb in Scheme 2) of amidized KLM-602 products. The chemical shift at 172 ppm of compound (IIb) is similar to that of the amidized γ -APS on the ^{13}C -NMR spectrum.

Whereas the amidized KLM-602 with the chemical shifts from -20 to -23 ppm are observed in ^{29}Si -NMR spectrum [Fig. 2(b)], these peaks exhibit the structure of the repeated siloxane units. The methoxy on KLM-602 is apt to be hydrolyzed and then to become polysiloxane from that of ethoxy on γ -APS. During the amidation process of KLM-602 with INA, water is produced as a side product. Then water induces the hydrolysis of the methoxy group in KLM-602 and the copolymers are subsequently formed by the condensation reaction. Therefore, polysiloxane (P_{2k}) is the only major product after the amidation of KLM-602 with INA.

Furthermore, ^{29}Si -NMR spectrum of amidized KLM-602 shown in Figure 2(b) indicates that the intensity of chemical shift at $\delta = -22.8$ ppm is stronger than that at $\delta = -21.0$ ppm. Thus, it is apparent that the siloxane structure of $\delta = -22.8$ ppm is referred to as the siloxane unit of the secondary amide that is shown on the compound IIb of Scheme 2. The siloxane unit of the tertiary amide appears at $\delta = -21.0$ ppm in the ^{29}Si -NMR spectrum, and is represented as the compound IIa of Scheme 2.

DMDDES hydrolysis with amidized KLM-602 as an internal standard

Amidized KLM-602 (P_{2k}) is converted to polysiloxane completely due to water formation as the condensation side product from the amidation of KLM-602 with INA. The hydrolysis of an equal molar ratio of amidized KLM-602 and DMDDES results in the formation of DMDDES derivatives, such as dimer (D_d , $\delta = -1.2$ ppm), polysiloxanes (P_{2d} , $\delta = 0.4$ ppm; P_{2k} , $\delta = -1.6$ ppm), and unreacted DMDDES monomer (M_d , $\delta = -3.7$ ppm) as observed in ^{13}C -NMR spectrum (Fig. 3). The chemical shift of repeated siloxane unit of amidized KLM-602 (P_{2k}) is at -1.6 ppm, which overlaps with that of the dimer (D_d) of DMDDES in the reaction mixture. It is difficult to calculate the amount of each peak representing these two different structures. However, there are two methyl groups on sili-

TABLE I
NMR Chemical Shifts of Alkoxy Silanes

Symbol	Representative	Chemical shift		
		^{13}C -NMR	^{29}Si -NMR	
M_d	Monomer of DMDES		-3.7ppm	-5.0ppm
D_d	Dimer/End capped of DMDES		-1.2ppm	-13.6ppm
P_{2d}	Repeat unit of DMDES		0.4ppm	-22.0ppm
P_{2k}	Repeat unit of KLM-602		-1.6ppm	
M_γ	Monomer of γ -APS			-46.0ppm
D_γ	Dimer/End capped of γ -APS			-54.2ppm
$P_{2\gamma}$	Repeat unit of γ -APS			-61.7ppm
$P_{3\gamma}$	T-shape of γ -APS			-68.9ppm

Note: $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$

$-(\text{CH}_2)_3\text{NH}_2$

cone in DMDES and only one methyl group on silane in KLM-602. The total amount of the methyl group can be measured by the peak area summation from the chemical shifts of -4.0 to 1.0 ppm in the ^{13}C -NMR spectrum (Fig. 3), because the equal mol (0.11 mol) of amidized KLM-602 and DMDES are charged. The total number of methyl groups on these two silanes is deduced as the following:

$$P_{2k} \times 2 = M_d + D_d + P_{2d} \quad (1)$$

The values of P_{2d} and M_d are measured directly from the chemical shifts corresponding to -3.7 and 0.4 ppm, respectively, in the ^{13}C -NMR spectra. Each corresponding peak area is measured from the spectrum by integration. Equation (1) can be rearranged as the following:

$$D_d = P_{2k} \times 2 - (M_d + P_{2d}) \quad (2)$$

The value of P_{2k} (Table II) is calculated by one-third of the total methyl group peak area in the chemical shift

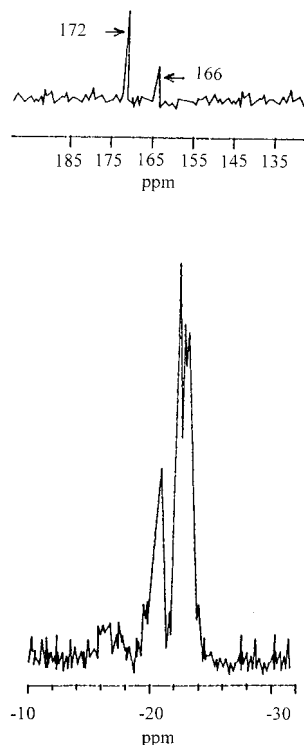


Figure 2 (a) ^{13}C -NMR spectrum of amidized KLM-602. (b) ^{29}Si -NMR spectrum of amidized KLM-602.

range, $\delta = -4.0$ to 1.0 ppm in ^{13}C -NMR spectra at various hydrolysis times (Fig. 4). Then the value of D_d (Table II) is calculated according to eq. (2). Therefore, the siloxane conversion percentage of each hydrolyzed sample is defined as $[(0.5 D_d + P_{2d})/P_{2k} \times 2] \times 100\%$ shown in Table II.

Similarly, because the chemical shift of this labeling carbon ($-\text{CH}_2$) in the structure of $\text{Si}-\text{O}-\text{CH}_2\text{CH}_3$ is $\delta = 55.6$ ppm, the peak area induced from the labeling carbon is available in comparison with that of P_{2k} on the amidized siloxane (KLM-602). The ethoxy silane content is measured by the peak area ratio of labeling carbon to amidized KLM-602 during the hydrolysis process. The plot of ethoxy content (determined by Zeiel's method in Table III) is taken in logarithm against the hydrolysis time, and it appears a linear relationship (Fig. 5).

Effect of water content in alkoxy silane hydrolysis

By controlling the equivalent ratio of $\text{H}_2\text{O}/\text{Si}-\text{OR}$ and results in various condensation reaction products. The reaction mixture contains insufficient water, and the resulting system comes to be a $\text{Si}-\text{OR}$ terminated polymer formation.

An alkoxy silane, DMEDES, is hydrolyzed with amidized silane (KLM-602) under moisture flux control. Water in the reaction mixture is exhausted almost as soon as water diffuses into the system during the

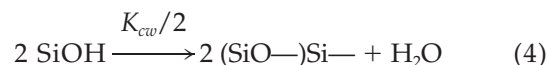
hydrolysis of alkoxy silane. A linear relationship of the siloxane conversion and the ethoxy ($\text{Si}-\text{OCH}_2\text{CH}_3$) content from DMEDES vs. the hydrolysis time is observed (Fig. 5). Hence, it is possible to monitor the hydrolysis process and its consequence condensation reaction of DMEDES in this moisture flux system.

Hydrolysis and condensation kinetics of DMEDES

When water is in contact with DMEDES with a catalyst (potassium fluoride) in the hydrolysis process, it results in silanol formation on the first stage as follows:



Once silanol is formed, it condenses further with SiOH or SiOEt and produces water or alcohol in the system. These are expressed as in eqs. (4) and (5).



According to eqs. (3) and (5), the amount of SiOR disappearing with respect to the hydrolysis time is:

$$\begin{aligned} d(\text{SiOEt})/dt = & -K_h(\text{SiOEt})(\text{H}_2\text{O}) \\ & - (K_{ca}/2) (\text{SiOH})(\text{SiOEt}) \quad (6) \end{aligned}$$

Because the disappearance of SiOH is related to eqs. (3), (4), and (5), the amount of SiOH vanished vs. the hydrolysis time can be expressed as follows:

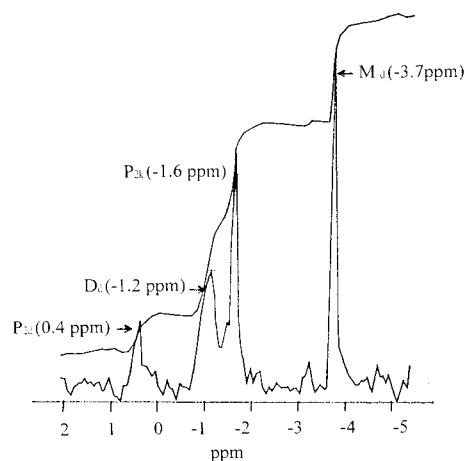


Figure 3 ^{13}C -NMR spectrum of DMEDES with amidized KLM-602.

TABLE II
Siloxane Conversion of Silanes Hydrolysis^a

Sample no.	Hydrolysis time (min) ^b	¹³ C-NMR (ppm) Peak Intensity ^c				Siloxane conversion (%) ^d
		<i>M_d</i> -3.7	<i>D_d</i> -1.2	<i>P_{2d}</i> +0.4	<i>P_{2k}</i> -1.6	
1	40	8.7	4.4	—	6.5	17.0
2	100	3.0	8.7	2.0	6.8	46.3
3	160	2.6	5.0	8.0	7.8	67.3
4	220	—	1.8	8.6	5.3	91.3
5	280	—	1.1	6.5	3.8	92.7

^a Silanes are the mixture of DMES and Amidized KLM-602.

^b Hydrolysis reaction is carried out at 30°C with potassium fluoride as a catalyst.

^c The peak intensity based on each peak area in ¹³C-NMR spectra. The repeated siloxane units of DMEDES and amidized KLM-602 are represented as *P_{2d}* and *P_{2k}*, respectively.

^d Siloxane conversion (%) = $[(0.5 D_d + P_{2d})/P_{2k} \times 2] \times 100\%$.

$$d(\text{SiOH})/dt = K_h (\text{SiOEt})(\text{H}_2\text{O}) - (K_{cw}/2) (\text{SiOH})^2 - (K_{ca}/2) (\text{SiOH})(\text{SiOEt}) \quad (7)$$

From eqs. (4) and (5), the rate of siloxane conversion is shown as follows:

$$d[(\text{SiO—})\text{Si—}]/dt = K_{cw}(\text{SiOH})^2 + K_{ca}(\text{SiOH})(\text{SiOEt}) \quad (8)$$

Both water and alcohol are the by-products of DMEDES hydrolysis. The rates of water and alcohol formation can be expressed as in eqs. (9) and (10), respectively.

$$d(\text{H}_2\text{O})/dt = -K_h (\text{SiOEt})(\text{H}_2\text{O}) + (K_{cw}/2) (\text{SiOH}) \quad (9)$$

$$d(\text{EtOH})/dt = K_h (\text{SiOEt})(\text{H}_2\text{O}) + (K_{ca}/2) (\text{SiOH})(\text{SiOEt}) \quad (10)$$

When the hydrolysis occurs under moisture flux, then obviously the water content in the hydrolysis mixture cannot be defined in eq. (9), and the yield of ethanol in

eq. (10) is also ambiguous. However, the hydrolysis of DMEDES can be estimated as the SiOEt content decreases according to eq. (6). For considering SiOEt content (Table III), eq. (6) can be rewritten as follows:

$$d(\text{SiOEt})/(\text{SiOEt}) = -[K_h (\text{H}_2\text{O}) - (K_{ca}/2) (\text{SiOH})]dt \quad (11)$$

Both sides of the above equation are integrated with the result of

$$\ln (\text{SiOEt}) = -[K_h (\text{H}_2\text{O}) - (K_{ca}/2) (\text{SiOH})]t \quad (12)$$

There is a linear relationship for the siloxane conversion against the hydrolysis time (below 90% conversion) as shown in Figure 5. It shows that a constant rate of polycondensation occurs in hydrolysis under moisture flux control, because the concentration of [SiOH] is quite low (9×10^{-3} to 4.6×10^{-2} M shown in Table IV) during the hydrolysis process. Therefore, the term of [SiOH] can be ignored and eq. (8) can be reduced to the following:

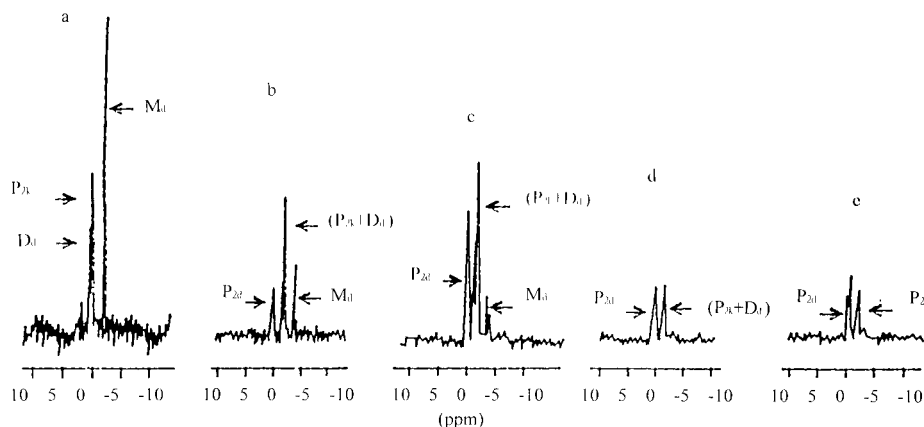


Figure 4 ¹³C-NMR spectra of the products from the hydrolysis of DMEDES with amidized KLM-602 at various reaction times. (a) 40 min; (b) 100 min; (c) 160 min; (d) 220 min; (e) 280 min.

TABLE III
Ethoxy Silane Content during the Hydrolysis of Silanes^a

Sample no.	Peak's Area ^b		Peak area ratio (B/2P _{2k}) % ^c	—OEt % by ¹³ C-NMR ^d	—OEt % by Zeisel's method	-ln[—OEt] ^e
	Amidized KLM-602 P _{2k}	Si—O—C ₁ —C ₂ C ₁ of —OEt B				
1	6.5	12.0	92.3	19.2	18.5	-0.89
2	6.8	11.0	80.9	16.8	15.0	-1.10
3	7.8	6.0	38.5	8.0	7.5	-1.79
4	5.2	—	—	—	3.2	-2.65
5	3.8	—	—	—	1.0	-3.82

^a The hydrolysis process of DMEDES with amidized KLM-602 and its theoretical wt % of the total Si-OEt charged initially from DMEDES is calculated as following:

$$90 \div \{[(\text{MW of INA}) + (\text{MW of KLM-602}) + (\text{MW of DMEDES})] - [18 + 31 \times 2]\} = 20.8\%$$

^b The corresponding chemical shifts of amidized KLM-602 and C₁ of —OEt (from DMEDES) are located at -1.6 and -55.6 ppm; respectively in ¹³C-NMR spectra.

^c The peak area ratio of these two peaks are calculated according to the following equation:

$$(\text{Peak's area of C-1 at —OEt}) \div (\text{Peak's area of P}_{2k} \times 2) \times 100\%$$

^d The estimation of Si—OEt content is based on ¹³C-NMR peak area ratio of these two peaks and its calculation is based on the following equation:

$$\text{—OEt \%} = 0.21 \times (\text{total charged SiOEt wt \% of DMEDES}) \times (\text{peak area ratio}).$$

^e The values of ln[—OEt] are obtained from the concentration [M] of SiOEt.

$$d[(\text{SiO—})\text{Si—}]/dt = K_{ca}(\text{SiOH})(\text{SiOEt}) \quad (13)$$

Therefore, K_{ca} can be calculated from eq. (13) by using the data listed in Table IV. The average value of K_{ca} is $2.44 \times 10^{-1} \text{ M}^{-1} \text{ m}^{-1}$ for further calculation. From the slope in Figure 6, K_h can be estimated from eq. (14).

$$\frac{\Delta \ln(\text{SiOEt})}{\Delta t} = -[K_h(\text{H}_2\text{O}) - K_{ca}/2(\text{SiOH})] \quad (14)$$

Thus, the K_h value of sample No.5 in Table V is taken at the end of hydrolysis; it has the least value of $2.0 \times 10^{-2} \text{ M}^{-1} \text{ m}^{-1}$ ($3.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$). This value is still larger than that of DMEDES hydrolysis with NH_3 as the catalyst ($K_h < 1.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$).¹⁵ This may

be caused by a trace amount of SiOEt residue that remained in the solution, and its hydrolysis is depressed by the phase separation in the KF-H₂O/siloxane system. The K_h value is $1.03 \text{ M}^{-1} \text{ m}^{-1}$ ($1.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$) on Table V under $8 \times 10^{-3} \text{ M}$ water content. In fact, the water concentration solution exerts an influence on the hydrolysis rate (K_h) as shown in Figure 6.

Linear polysiloxane conversion from DMEDES hydrolysis

Hydrolysis of DMEDES with Amidized KLM-602

In the case of DMEDES reacting with silicate, the chemical shifts at -20 and -100 ppm on ²⁹Si-NMR spectra

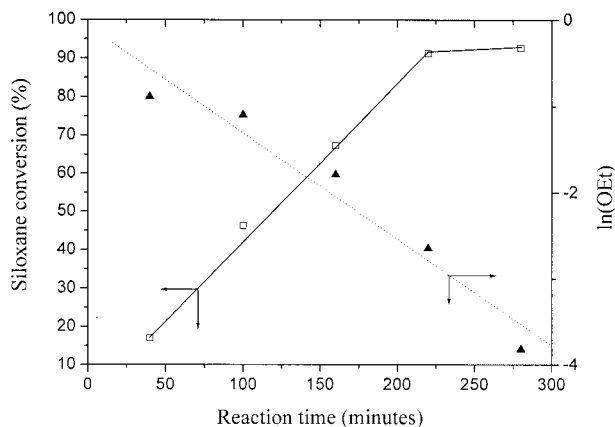


Figure 5 Ethoxy silane content and siloxane conversion during DMEDES hydrolysis at various reaction times.

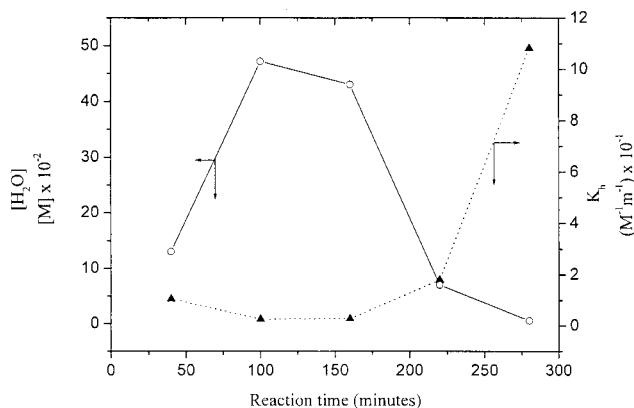


Figure 6 Hydrolysis rate constant and water content of DMEDES at various reaction times.

TABLE IV
Siloxane Conversion of DMDDES Hydrolysis

Sample no.	[SiOH] [M] $\times 10^{-1}$	[SiOR] [M]	[SiOH][SiOR] [M] $\times 10^{-1}$	$d[\text{Si-O-Si}]/dt$ $M/m \times 10^{-2}$	$K_{ca} M^{-1} m^{-1} \times 10^{-1}$
1	0.09	4.11	0.37	1.98	5.38
2	0.46	3.34	1.53	1.98	1.29
3	0.42	1.66	0.70	1.98	2.83
4	0.10	0.71	0.07	1.04	1.45
5	0.35	0.23	0.08	1.04	1.28

are observed. However, for methyltriethoxy silane instead of DMDDES, the chemical shifts is found between -65 and -100 ppm.²⁵ During the catalytic hydrolysis of DMDDES and KLM-602 using potassium fluoride as a catalyst, DMDDES prefers to bond with amidized KLM-602 (compound IIa) rather than reacting with itself. This is due to the methoxy in amidized KLM-602 hydrolyzing faster than that of the ethoxy group in DMDDES (Scheme 3).

Thus, the end groups of SiOMe and SiOH attached on amidized KLM-602 have been exhausted, and are converted to the structure of EtO—Si(Me)-Amidized KLM-602 (compound III in Scheme 3). This indicates that only the ethoxy group is left on the initial hydrolysis stages of DMDDES addition as shown in ²⁹Si-NMR spectra [Fig. 7(a) and (b)]. When the moisture flux is applied for controlling the hydrolysis, only the methoxy group reacts with water moisture and results in silanol formation and then it reacts with SiOEt of DMDDES to obtain a linear polysiloxane by the stepwise condensation reaction. It is possible to form a linear polysiloxane because of the concentration of silanol (9×10^{-3} to 4.6×10^{-2} M, which is shown in Table IV) is too low to form a cyclic compound by self-condensation.

The chemical shifts on P_{2d} and P_{2k} of the polycondensation products (Table I) represent the repeated siloxane unit of DMDDES and amidized KLM-602, respectively. These chemical shifts overlapped each other in the range of -20 to -23 ppm in ²⁹Si-NMR spectrum. The overlapping area broadens in the spectrum not only due to the different chemical structure, but also by the various molecular weight distributions inherent on polymerization. Therefore, the area corresponding to P_{2d} and P_{2k} cannot be clearly identified in

NMR spectrum. Even though the hydrolysis of DMDDES with KLM-602 still can be investigated from the various amount of DMDDES monomer (M_d) and its dimer (D_d) for which comprises different chemical shifts at -5.0 and -13.6 ppm on ²⁹Si-NMR [Fig. 7(a)]. During the DMDDES hydrolysis process, the monomer content decreases as the dimer content increases with increasing the hydrolysis time. There is a small amount of DMDDES monomer (M_d) and a maximum amount of DMDDES dimer (D_d) found after 2 h hydrolysis [Fig. 7(c)]. The chemical shift of D₂ disappeared after 3.6 h hydrolysis but formed the repeat trf units of DMDDES siloxane (P_{2d}). Finally, only the chemical shifts of P_{2d} and repeated units of amidized KLM-602 (P_{2k}) is shown in the ²⁹Si-NMR spectrum [Fig. 7(e)]. These final products have been treated with toluene and washed by water. The number-average molecular weight (M_n) of the final product is around 2000, which is measured by a vapor pressure osmometer. This indicates that the linear copolymer III (Scheme 3) can be one of the polycondensation products from the hydrolysis of DMDDES with amidized KLM-602.

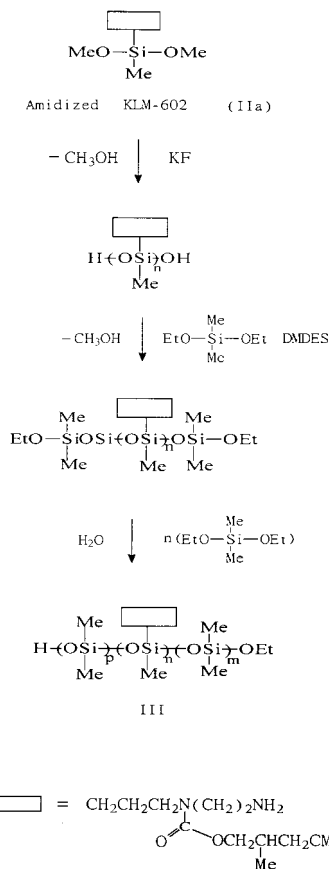
Hydrolysis of DMDDES with amidized γ -APS

The chemical shifts of -4.5 , -12.5 , and -22.0 ppm in ²⁹Si-NMR spectra corresponding to monomer (M_d), dimer (D_d), and the repeat siloxane unit of DMDDES (P_{2d}). On the other hand, the corresponding species on chemical shifts of -46.0 , -53.5 , and -68.0 ppm are monomer (M_γ), dimer (D_γ), linear polysiloxane (P_{2 γ}), and three-dimensional siloxane (P_{3 γ}), respectively, from the hydrolysis and the subsequent condensation reaction of amidized triethoxy silane (γ -APS) [Fig. 8(a)]. There are two peaks in the chemical shift range

TABLE V
Hydrolysis Rate Constant of DMDDES

Sample no.	[H ₂ O] [M] $\times 10^{-2}$	$d \ln[\text{SiOR}]/dt \times 10^{-3}$	$K_{ca}[\text{SiOH}]/2 \times 10^{-3}$	$K_h (M^{-1} m^{-1}) \times 10^{-1}$
1	4.5	-1.4	-1.1	2.9
2	0.8	-1.4	-5.7	10.3
3	0.9	-1.4	-5.1	9.4
4	7.9	-1.4	-1.2	1.6
5	49.5	-1.4	-4.3	0.2

K_{ca} value of $2.44 \times 10^{-1} M^{-1} m^{-1}$ is taken for K_h value calculation.



Scheme 3 Hydrolysis of DMEDES with amidized KLM-602.

of -20 to -22 ppm in the ^{29}Si -NMR spectrum [Fig. 8(d)] are found. One chemical shift centered at -20 ppm, represents as $\text{P}_{2d'}$ and the other chemical shift centered at -22 ppm assigned as P_{2d} . The intensity of $\text{P}_{2d'}$ is enhanced after the hydrolysis solution of Figure 8(c) is heated at 50°C for another half hour [Fig. 8(d)]. It may be due to the polysiloxane (P_{2d}) possess active groups (e.g., ethoxy silane), which react with the third ethoxy silane functional group on $\text{P}_{2\gamma}$ of amidized γ -APS. Thus, the chemical shift of P_{2d} (at -22 ppm) shifts to -20 ppm, and it is assigned as $\text{P}_{2d'}$. Meanwhile, the chemical shift of $\text{P}_{2\gamma}$ disappeared [Fig. 8(c)], and that of $\text{P}_{3\gamma}$ was enhanced [Fig. 8(d)]. Because of the remaining ethoxy silane groups of the repeated siloxane unit of amidized γ -APS, ($\text{P}_{2\gamma}$) condensed further to form three-dimensional amidized γ -APS ($\text{P}_{3\gamma}$). It is obvious that these polysiloxanes have the capability for further condensation reaction. Therefore, these polysiloxanes from DMEDES hydrolysis should be linear but not cyclic because the cyclic polymer is a dead polymer. Besides, the cyclic siloxane possesses a single peak in ^{29}Si -NMR spectrum that is completely different from that of linear polysiloxane. The products obtained from the hydrolysis and the subsequent condensation of DMEDES with amidized γ -APS is linear, and the three-dimensional siloxane moiety con-

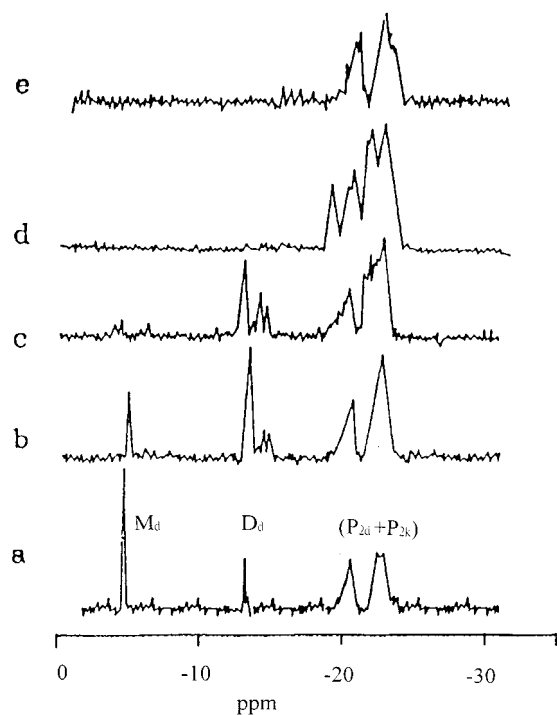


Figure 7 ^{29}Si -NMR spectra of the products from the hydrolysis of DMEDES with amidized KLM-602 at various reaction times. (a) 40 min; (b) 100 min; (c) 160 min; (d) 220 min; (e) 280 min.

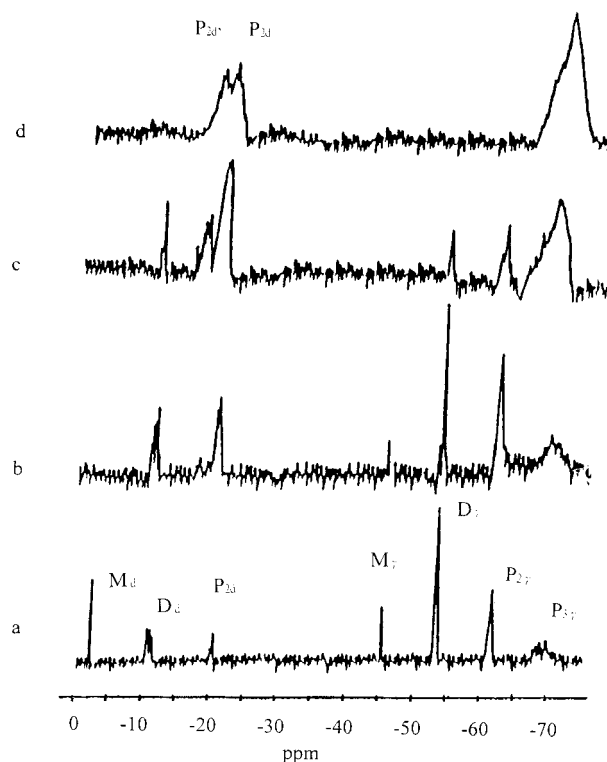


Figure 8 ^{29}Si -NMR spectra of the products from the hydrolysis of DMEDES with amidized γ -APS at various reaction conditions. (a) $30^\circ\text{C}/30$ min; (b) $30^\circ\text{C}/120$ min; (c) $30^\circ\text{C}/180$ min; (d) $30^\circ\text{C}/180$ min then $50^\circ\text{C}/30$ min.

taining copolymer is shown in the ^{29}Si -NMR spectrum [Fig. 8(d)].

CONCLUSION

The catalytic hydrolysis of DMDES with amidized silane under moisture flux control results in the formation of linear siloxane copolymers that are proved by ^{13}C - and ^{29}Si -NMR spectra. The hydrolysis and its subsequent condensation of DMDES is a linear relationship vs. the hydrolysis time. The rate constants of DMDES hydrolysis (K_h) and subsequent condensation (K_{ca}) are also investigated by NMR measurements and amidized silane (γ -APS or KLM-602) as an internal standard. This hydrolysis or siloxane conversion rate constant (K_h or K_{ca}) measurement on the DMDES hydrolysis process may be the useful information for helping understand the mechanism of silica-immobilization,³⁸ adhesion promotion,³⁹ sol-gel hybridization,⁴⁰ etc.

The authors wish to acknowledge the financial supports by the development program for specialty chemicals of Chemical System Research Division, Chung-Shan Institute of Science and Technology and also by National Science Council, Republic of China.

References

- Hyde, J. F. *J Am Chem Soc* 1953, 75, 2166.
- Kantor, S. W. *J Am Chem Soc* 1953, 75, 2712.
- Sprung, M. M.; Gaenter, F. O. *J Am Chem Soc* 1955, 77, 6045.
- Aelion, R. A.; Eirich, F. *J Am Chem Soc* 1950, 72, 5705.
- van Blaaderen, A. *J Noncryst Solids* 1992, 149, 161.
- McNeil, K. J. *J Am Chem Soc* 1980, 102, 1859.
- Masaguki, Y.; Satoru, I.; Atsuo, T. *J Noncryst Solids* 1984, 63, 13.
- Pohl, E. R.; Osterholtz, F. D. *Polym Preprints* 1983, 24, N-1 200.
- Grubb, W. T. *J Am Chem Soc* 1954, 76, 3408.
- Zerta, T. W.; Artaki, I.; Jones, J. J. *Noncryst Solids* 1986, 81, 365.
- Apope, E. J.; MacKenzie, J. D. *J Noncryst Solids* 1986, 87, 185.
- Artaki, I.; Zerda, T. W.; Jones, J. J. *Noncryst Solids* 1986, 81, 381.
- Pouxviel, J. C.; Boilot, J. P. *J Noncryst Solids* 1987, 89, 345.
- Noll, W. *Chemistry and Technology of Silicones*, 2nd ed.; Academic Press: New York, 1968.
- Schmidt, H.; Hcholze, H.; Kaiser, A. *J Noncryst Solids* 1984, 63, 1.
- Aekion, R.; Loebel, A.; Eirich, F. *J Am Chem Soc* 1950, 72, 5705.
- Chojnowski, J.; Cypryk, M.; Kazmierski, K.; Rozga, K. *J Noncryst Solids* 1990, 125, 40.
- Artaki, I.; Bradley, M.; Zerda, T. W.; Jones, J. *J Phys Chem* 1985, 89, 4399.
- Larochelle, R. W.; Cargioli, J. D.; Williams, E. A. *Macromolecule* 1976, 9, 85.
- Horn, H. G.; Marsmann, H. C. *Makromol Chem* 1972, 162, 255.
- Harris, R. K.; Robins, M. L. *Polymer* 1978, 19, 1123.
- Magi, M.; Lippmaa, E. *J Organomet Chem* 1973, 54, 115.
- Engelhardt, G.; Jancke, H. *ibid* 1971, 28, 293.
- Norihiro, N.; Kozo, H. *J Appl Polym Sci* 1987, 34, 1619.
- Sindorf, D. W.; Maciel, G. E. *J Am Chem Soc* 1983, 105, 3767.
- Sindorf, D. W.; Maciel, F. W. *J Am Chem Soc* 1981, 103, 4263.
- Sindorf, D. W.; Maciel, F. W. *J Phys Chem* 1982, 86, 5208.
- Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J Chromatogr* 1981, 205 438.
- Sindorf, D. W.; Maciel, F. W. *J Phys Chem* 1983, 87, 5516.
- Sakka, S.; Kamiya, K. *J Noncryst Solids* 1982, 48, 31.
- Sprung, M. M.; Guenther, F. O. *J Am Chem Soc* 1955, 77, 3990.
- Sprung, M. M.; Guenther, F. O. *J Am Chem Soc* 1955, 77, 3996.
- Sprung, M. M.; Guenther, F. O. *J Am Chem Soc* 1955, 77, 4173.
- Fletcher, H. J.; Hunter, M. J. *J Am Chem Soc* 1949 71, 2918.
- Fletcher, H. J.; Hunter, M. J. *J Am Chem Soc* 1949 71, 2922.
- Al Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Lickiess, P. D. *J Organometal Chem* 1989, 362, 17.
- Brunet, F. *J Noncryst Solids* 1998, 231, 58.
- Khatib, I. S.; Parish, R. V. *J Organometal Chem* 1989, 369, 9.
- Cayless, R. A.; Perry, D. L. *J Adhesion* 1988, 26, 113.
- Lichtenhan, J. D.; Schwab, J. J. *Polym Preprints (ACS)* 2000, 41, 527.