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Synthesis of spirosilicates directly from silica and ethylene glycol/ethylene glycol derivatives

Varangkana Jitchum,[a] Sun Chivin,[a] Sujitra Wongkasemjit[a,*] and Hatsuo Ishida[b]

[a]*The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok 10330, Thailand*
[b]*The Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA*

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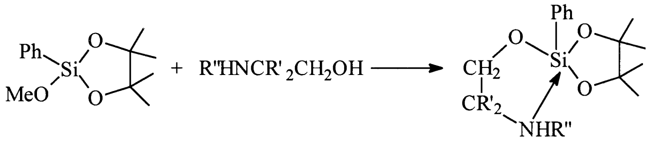
Abstract—Tetracoordinated spirosilicates have been synthesized directly from the reaction of a very inexpensive and plentiful material, SiO_2, and ethylene glycol in the presence of triethylenetetramine (TETA), as catalyst with and without potassium hydroxide as co-catalyst. The reactions are run under nitrogen gas with constant stirring at 200°C, and complete in a reaction time of 10–18 h depending on the catalysts. The reactions using only TETA are complete in 18 h, while with potassium hydroxide the reactions occur much more quickly. When 3-amino-1,2-propanediol, or 2-amino-2-methyl-1,3-propanediol is employed, the reaction must run under vacuum at 0.1mmHg, 160°C, and is complete in 14 and 24 h, respectively. The structures of spirosilicates are fully characterized using FTIR, ^{1}H, ^{13}C, ^{29}Si NMR, FAB^{+}-MS, and TGA. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

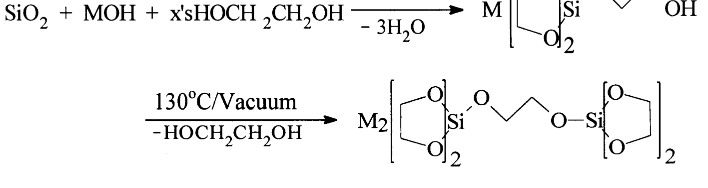
Generally, thermosetting resins undergo a volumetric shrinkage (3–15%) during polymerization even using the best system.[1–3] However, resins without shrinkage would be advantageous for such applications as precision castings, dental composites, rock cracking materials, and high strength composites. The superior mechanical interlocking to a substrate that would be possible with zero shrinkage or expanding materials makes them ideally suited for higher performance adhesives, sealants and coatings.[4–7] Most of the spiroorthocarbonate and spiroorthoester monomers show little or no volume shrinkage or expansion in volume upon polymerization. However, they do provide a few useful applications with low glass transition temperature. Moreover, spiroorthocarbonates and spiroorthoesters can only be synthesized from complicated routes.[8–13]

Frye reported the preparation of spirosiloxane from $Si(OEt)_4$ and ethylene glycol in ethanol with a small amount of NaOMe. The product obtained was polymeric species and in the presence of amine bases, novel pentacoordinated species would be formed (Scheme 1).[14–16]

Laine *et al.* synthesized pentacoordinated and hexacoordinated spiro-silicates directly from silica and ethylene glycol



Scheme 1.



Scheme 2.

Keywords: silica; tetracoordinated spirosilicates; aminospirosilicates.

[*] Corresponding author. Tel.: +66-2-218-4133; fax: +66-2-215-4459; e-mail: dsujitra@chula.ac.th

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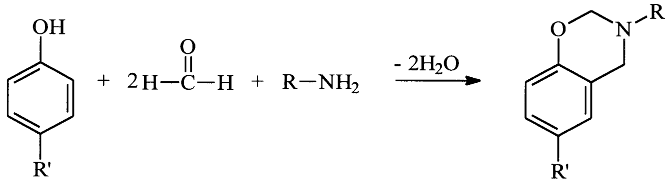


Scheme 3.

in the presence of group I metal hydroxides and II metal oxides.[17–18] These strong bases are expensive and have low environmental stability (Scheme 2).

Ishida, H. et al. synthesized benzoxazine monomers from phenol derivatives, paraformaldehyde, and primary amine derivatives.[19] Benzoxazines have good heat resistant, flame-retardant, and dielectric properties and reduce environmental and health risks. Polybenzoxazines, the ring-opening polymerization phenolic resins, as compared to epoxy resins and conventional phenolics, have indicated excellent glass transition temperatures (T_g), and moduli, low water absorption values, in addition to near-zero shrinkage or slight expansion upon curing (Scheme 3).[20–21]

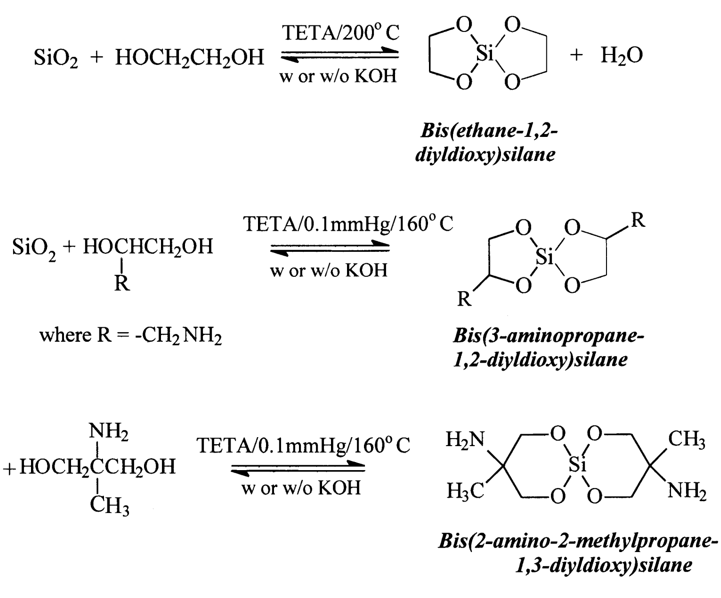
Despite the position of silicon directly below carbon in-group IV, the properties of the two elements are entirely different, for example, Si–O bonds are 22 kCal/mol more stable than C–O bonds. As a result, polymers having recurring Si–O linkages are of interest and importance, because they offer good thermal, oxidative stability, and chemical resistance.[22] We report herein an extension of silicon chemistry by the synthesis of neutral alkoxysilanes, tetracoordinated spirosilicates. In particular, we focus on synthesis starting from an inexpensive and abundant material, silica, and ethylene glycol or 3-amino-1,2-propanediol or 2-amino-2-methyl-1,3-propanediol. Ethylene glycol is of particular interest because it is the prototypical 1,2-diol and the expected product has the same structure as spiro-orthocarbonate and spiroorthoester, which give little shrinkage in volume on polymerization. We thus investigated how to synthesize these spirosilicates. 3-Amino-1,2-propanediol or 2-amino-2-methyl-1,3-propane diol are principally interesting as raw materials for the development of benzoxazine resins containing silicon species.

2. Results and Discussion

2.1. Synthesis

As discovered by Piboonchaisit's et. al [23] that triethylenetetramine (TETA) could be used as an accelerator to dissolve silica, all spirosilicates are thus prepared directly from silica and ethylene glycol, 3-amino-1,2-propanediol, or 2-amino-2-methyl-1,3-propanediol, using TETA as catalyst, in the absence or presence of KOH as co-catalyst according to the reactions in Scheme 4.

Bis(ethane-1,2-diyldioxy)silane is prepared from either fused or fumed silica with >80% overall yield at the boiling point of ethylene glycol in order to remove water and drive equilibrium to products. However, for fused silica, the reaction in the presence of TETA as catalyst and absence of KOH as co-catalyst takes 18 h, which is much longer than that for fumed silica, 6 h, to complete. In this case, fumed silica with a surface area of 280 m^2/g is more reactive than fused silica with a surface area of 182 m^2/g. It is likely that the higher the surface area of silica, the higher the reactivity. When the co-catalyst KOH is present, the reaction employing fumed silica is complete in 4 h while that using fused silica is finished in 10 h. The reason is that the strong base of KOH deprotonates ethylene glycol much faster than the catalyst TETA. If only KOH was used in place of TETA,



Scheme 4.

Table 1. FTIR assignments of bis(ethane-1,2-diyldioxy)silane, **1**, bis-(3-aminopropane-1,2-diyldioxy)silane, **2**, and bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, **3**

Products	Wave number (cm^{-1})	Assignment
1	3386, broad	–OH: water absorbed by the product
	2949–2882	C–H stretching
	1085, 966 and 883	Si–O–C stretching
2	3397, broad	–OH: water absorbed by the product; $-NH_2$
	2955–2889	C–H stretching
	1090, 966 and 872	Si–O–CH stretching
3	3406, broad	–OH: water absorbed by the product; $-NH_2$
	2953–2868	C–H stretching
	1082, 962 and 883	Si–O–CH stretching

according to Laine et al.'s work,[17–18] pentacoordinated spirosilicates were resulted.

As for the aminospirosilicate products of bis(3-aminopropane-1,2-diyldioxy)silane and bis(2-amino-2-methylpropane-1,3-diyl dioxy)silane, the reactions need to be carried out under vacuum at high temperature owing to the high boiling points of starting materials, 3-amino-1,2-propanediol (264°C/739 mmHg) and 2-amino-2-methyl-1,3-propanediol (151°C/10 mm Hg). TETA, which has the boiling point 266°C/760 mm Hg close to the boiling points of those aminodiols, is thus used as both solvent and catalyst. To obtain the highest yields of the products, the reactions must distill off the by-product H_2O along with the solvent TETA. As a result, the starting materials, aminodiols, were also distilled off while the reaction was running. This is why a high amount of both aminodiols must be employed to achieve the highest percentage yields of the products. Both products are synthesized directly from fumed silica with >70% and >80% overall yields, respectively. The first product was obtained in 10 and 14 h with and without KOH, respectively. On the other hand, the second product takes a longer time of 14 h with KOH and 24 h without the catalyst. This is due to the higher boiling point of the second aminodiol, 2-amino-2-methyl-1,3-propanediol, requiring longer reaction time to complete the reaction.

2.2. Characterization

The structures of spirosilicate products were identified by FTIR, ^1H, ^{13}C, and ^{29}Si NMR, TGA, and FAB^+-MS.

The FTIR spectra of all spirosilicates show similar bands at 3386 cm^{-1} due to the combined hydrogen bonded N–H stretching modes and the intermolecularly hydrogen bonded O–H stretching modes,[24] 2949–2882 cm^{-1} corresponding to the C–H group, 1085, 966, and 883 cm^{-1} belonging to the Si–O–C stretching. The results are summarized in (Table 1).

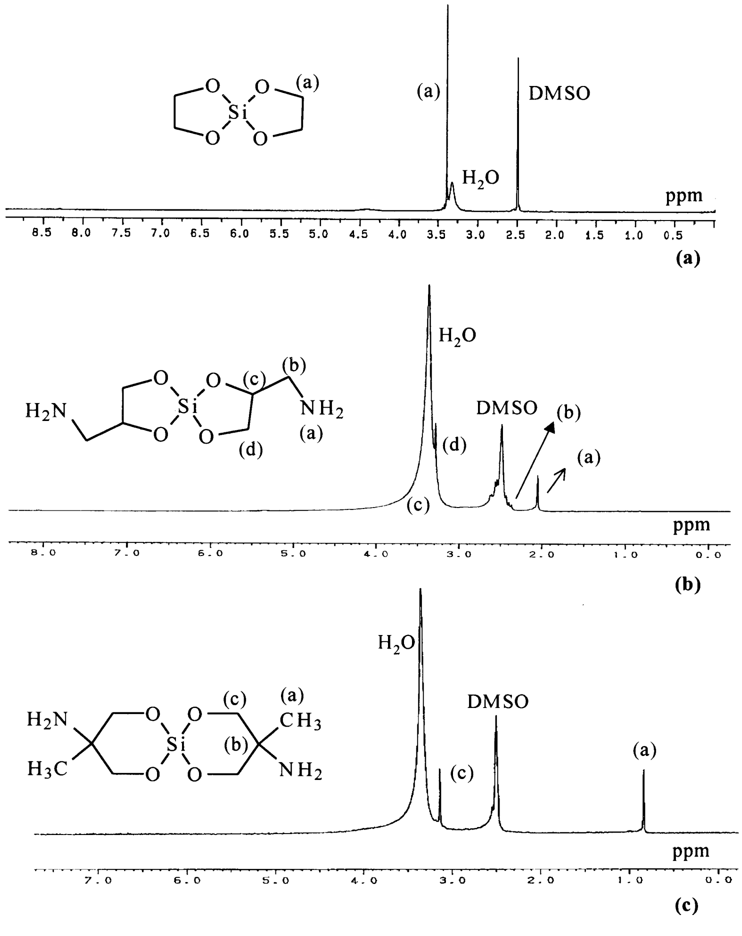


Figure 1. ^1H NMR Spectra of a) bis(ethane-1,2-diyldioxy)silane, b). bis(3-amino propane-1,2-diyldioxy)silane, and c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

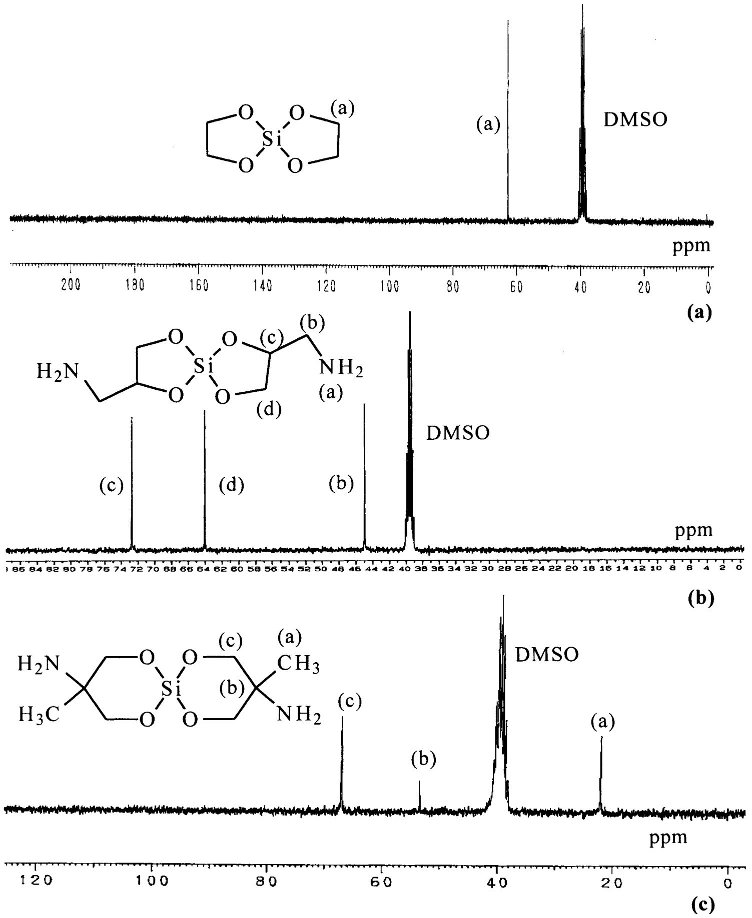


Figure 2. ^{13}C NMR Spectra of (a) bis(ethane-1,2-diyldioxy)silane, (b) bis(3-amino propane-1,2-diyldioxy)silane, and (c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

The ^{1}H NMR spectra, as illustrated in Fig. 1, show resonances that belong to the corresponding products. They all show the H_2O contained in deuterated DMSO and absorbed by the product at $\delta=3.27$ ppm, in agreement with the FTIR results. For bis(ethane-1,2-diyldioxy)silane, there appears to be a singlet at $\delta=3.38$ ppm, resulting from the four hydrogen atoms (4H) of CH_2–O–Si. For bis(3-aminopropane-1,2-diyldioxy)silane, the ^{1}H NMR spectrum shows a singlet at $\delta=2.05$ ppm corresponding to the 4H of $-NH_2$, multiplet at $\delta=2.45$ ppm belonging to the 4H of CH_2–N, doublet at $\delta=3.29$ ppm referring to the 4H of CH_2–O–Si. The 2H of CH–O–Si is unfortunately overlapped with the H_2O peak. This, however, can be confirmed by ^{13}C NMR data. The ^{1}H NMR spectrum of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane shows clearer chemical shifts at $\delta=0.83$ ppm belonging to $-CH_3$ and $\delta=3.13$ ppm corresponding to CH_2–O–Si.

Besides the deuterated DMSO peak, the ^{13}C NMR spectra, as shown in Fig. 2, show only one resonance at $\delta=62.7$ ppm (CH_2–O–Si) for bis(ethane-1,2-diyldioxy)silane; chemical shift for bis(3-aminopropane-1,2-diyldioxy)silane at $\delta=44.9$ ppm (CH_2–N), $\delta=64.0$ ppm (CH_2–O–Si) and $\delta=72.7$ ppm (CH–O–Si); and also 3 resonances for bis-(2-amino-2-methylpropane-1,3-diyldioxy)silane at $\delta=22.0$ ppm ($-CH_3$), $\delta=53.5$ ppm (C) and $\delta=67.1$ ppm (CH_2–O–Si).

The results of ^{29}Si NMR spectra (Fig. 3) support that we have obtained tetracoordinated spirosilicate products, although the first two products showed the resonances at $\delta=-104$ and -103 ppm, respectively, which are assigned to pentacoordinated species,[17,25] The reason is simply that the ^{29}Si NMR spectra were carried out using the reaction solution containing TETA. Therefore, there is a partial bonding between the product and TETA. Intermolecular bonding between the second product, which contains amino groups is also possible to form pentacoordinated species, as described previously by Frye.[15] The ^{29}Si NMR spectrum of the last product indicates tetracoordinated species at $\delta=-77$ ppm. In this case, there is no partial bonding between this product with TETA or the product with itself due to the steric hindrance of the structure.

FAB^{+}-MS results are shown in Tables 2–4 for bis(ethane-1,2-diyldioxy)silane, bis(3-aminopropane-1,2-diyldioxy)-silane and bis(2-amino-2-methylpropane-1,3-diyldioxy)-silane, respectively. The proposed structures according to their fragmentation also indicated the desired products.

The other results, which support that the synthesized spirosilicates are truly the tetracoordinated not pentacoordinated species, were obtained by TGA (Table 5). They gave ceramic yields in close agreement with the calculated values based on the tetracoordinated species.

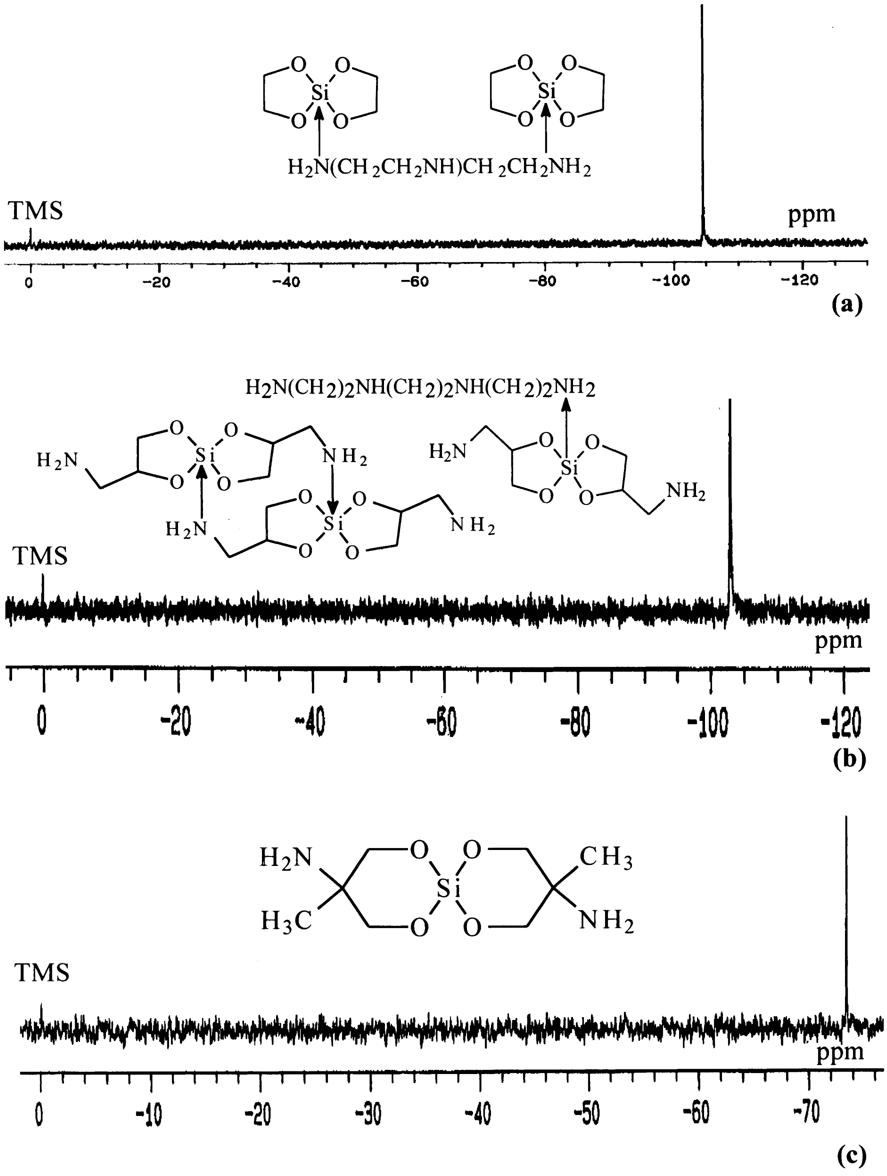


Figure 3. ^{29}Si NMR Spectra of (a) bis(ethane-1,2-diyldioxy)silane, (b) bis(3-aminopropane-1,2-diyldioxy)silane, and (c) bis(2-amino-2-methylpropane-1,3-diyldioxy)silane.

3. Conclusions

Spirosilicates have been successfully synthesized directly via an one step process from very inexpensive materials, silica and ethylene glycol/its derivatives in the presence of

Table 2. The proposed structure and fragmentation of bis(ethane-1,2-diyldioxy) silane

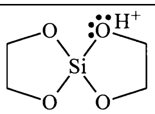
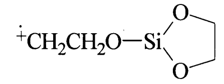
m/e	Intensities	Proposed Structure
149	7.00	
132	31.57	
72	9.11	$^{\cdot+}CH_2CH_2O$-Si
58	100	$^{\cdot+}CH_2O$-Si
44	80.94	$^{\cdot+}O$-Si

Table 3. The proposed structure and fragmentation of bis(3-aminopropane-1,2-diyldioxy)silane

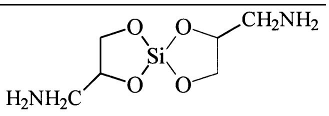
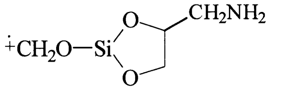
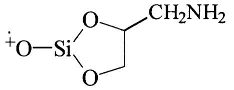
m/e	Intensities	Proposed Structure
206	0.77	
147	17.62	
133	100	
58	4.94	$^{\cdot+}CH_2O$-Si
44	42.28	$^{\cdot+}O$-Si

Table 4. The proposed structure and fragmentation of bis(2-amino-2-methylpropane-1,3-diyldioxy)silane

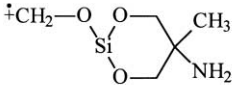
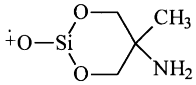
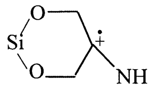
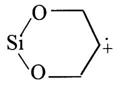
m/e	Intensities	Proposed Structure
161	0.8	
147	1.2	
116	13	
100	28	
74	46	$^{\cdot+}CH_2O{-}Si$
58	54	$^{\cdot+}CH_2O{-}Si$
44	100	$^{\cdot+}O{-}Si$

Table 5. % Ceramic yields of bis(ethane-1,2-diyldioxy)silane, **1**, bis(3-aminopropane-1,2-diyldioxy)silane, **2**, and bis(2-amino-2-methylpropane-1,3-diyldioxy)silane, **3**

	% Ceramic yield	
Product	Calculation	Experiment
1	40.5	40.8
2	29.1	30.4
3	25.4	26.9

triethylenetetramine, as catalyst/solvent with/without potassium hydroxide, as co-catalyst. The reactions are much faster when the co-catalyst and silica with a higher surface area are employed.

4. Experimental

4.1. Materials

All reactions were equilibrium reactions and products were sensitive to either moisture or air. Thus, all glassware used for these experiments was dried in an oven at 100°C overnight. All reactions were carried out in an inert atmosphere (Nitrogen gas).

Fused silicon dioxide (HI-SIL 927 silica, SiO_2 with surface area of 182 m^2/g) was donated by PPG Siam Silica Co., Ltd. Fumed silica, 3-amino-1,2-propanediol and 2-amino-2-methyl-1,3-propanediol were purchased from Aldrich Chemical Co., Inc. (USA), used without purification and kept under nitrogen atmosphere. Triethylenetetramine (TETA) was also purchased from Facai Polytech. Co., Ltd. and was used as received. Sodium hydroxide and potassium hydroxide were purchased from Merck Company Co., Ltd., and used as received. Ethylene glycol, acetonitrile and isooctane were purchased from Lab-Scan Company Co., Ltd., purified by standard methods under nitrogen atmosphere and kept in sealed flasks. Methanol was purchased from J.T. Baker Company Co., Ltd., and purified by distillation over magnesium activated with iodine.

4.2. Instruments

Mass spectra (MS) were obtained using a VG Autospec model 7070E from Fison Instruments with VG data system. Samples were run in the positive fast atomic bombardment (FAB-MS$^+$) mode using glycerol as the matrix, cesium gun as initiator and cesium iodine (CsI) as a reference. Thermograms were obtained using thermogravimetric analysis (TGA) mode on a Du Pont model TGA 2950 with a ramp rate of 10°C/min from 25° to 750°C in N_2 atmosphere. FTIR spectra were recorded using a FRA 106/s Bruker instrument with a spectral resolution of 4 cm^{-1}. The samples were mixed with KBr at an approximate ratio of sample:KBr of 1:20. ^1H and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer at room temperature using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent and reference for chemical shift measurements. ^{29}Si NMR spectra were obtained using a Bruker 500 MHz spectrometer, DMSO-d_6 as solvent and tetramethylsilane (TMS) as reference for chemical shift measurements.

4.3. Syntheses

4.3.1. Preparation of bis(ethane-1,2-diyldioxy)silane. A mixture of 12.5 mmol silica (SiO_2), (0.75 g, surface area of 320 cm^2/g or 182 cm^2/g), 15 mL of ethylene glycol (EG), and 15.63 mmol TETA (2.29 g) with/without potassium hydroxide (KOH) at 10 mole percent equivalent to silica, was placed in a 50 mL two-neck round bottomed flask. The mixture was heated to the boiling point of ethylene glycol under nitrogen with constant magnetic stirring, to distill ethylene glycol and water formed as by-product. The reaction was complete, when it turned clear. The mixture was allowed to cool overnight. The product was filtered, washed with a 5% of dried methanol in acetonitrile, and dried overnight at room temperature under vacuum, 0.1 mmHg.

4.3.2. Preparation of bis(3-aminopropane-1,2-diyldioxy)-silane and bis(2-amino-2-methyl propane-1,3-diyldioxy)-silane. A mixture of 5 mmol fumed silica, (0.3 g, surface area of 320 cm^2/g), 7 mL TETA, and 30 mmol 3-animo-1,2-propanediol (2.73 g) or 30 mmol 2-amino-2-methyl-1,3-propanediol (3.1 g) with/without potassium hydroxide (10 mol% equivalent to silica), was placed in a 50 mL two-neck round bottomed flask. The mixture was heated under vacuum at 0.1mm/Hg, 160°C with constant stirring, to distill TETA, 3-amino-1,2-propanediol or 2-amino-2-methyl-1,3-propanediol, and water formed as by product. The product was precipitated and purified, as described above.

Acknowledgements

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