

Synthesis of [(Trialkoxysilyl)propyl]imides

Jeffrey H. Wengrovius,* Virginia M. Powell,† and Jimmy L. Webb

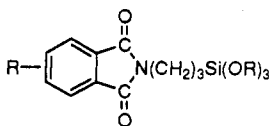
Physical Chemistry Laboratory, GE Corporate Research & Development, 1 River Road, Schenectady, New York 12301

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Imidization reactions between anhydrides and (alkoxysilyl)propylamines containing alkoxy silane groups result in hydrolysis and condensation of the alkoxy silane groups and formation of SiOSi bonds. As a result, the direct reaction of various anhydrides with (γ -aminopropyl)trialkoxysilanes did not afford [(trialkoxysilyl)propyl]imides but instead resulted in insoluble crosslinked materials. A successful two-step synthesis of [(trialkoxysilyl)propyl]imides is reported. In the first step, an intermediate imide was prepared by reaction of an anhydride with 2-aminopyridine. Following removal of the water of imidization, addition of an (γ -aminopropyl)trialkoxysilane resulted in a transimidization equilibrium which favored displacement of 2-aminopyridine and formation of a [(trialkoxysilyl)propyl]imide in high yield. Synthesis of a moisture-curable polyimide containing alkoxy silane endcaps is briefly described.

Introduction

There are several reports in the patent literature regarding the synthesis of [(trialkoxysilyl)propyl]imides, including their use as sizing agents,¹ oxygen bleach activators,² monomers for high-temperature coatings,³ and as adhesion promoters for polyimides.⁴ In all cases, a one-



step synthesis is described in which an anhydride is reacted directly with a (γ -aminopropyl)trialkoxysilane. Unfortunately, our attempts to repeat these procedures have resulted in insoluble solids, due to hydrolysis and condensation of the alkoxy silane groups during the imidization reaction. Here, we wish to further describe reactions between (aminopropyl)trialkoxysilanes and anhydrides and report a successful two-step synthesis of [(trialkoxysilyl)propyl]imides.

Results and Discussion

Reactions of (Aminopropyl)alkoxysilanes with Anhydrides. The reactions shown in Schemes 1 and 2 indicate that hydrolysis and condensation of alkoxy silane groups occur during imidization reactions between anhydrides and (aminopropyl)alkoxysilanes. In the first case, an example from the patent literature⁵ was repeated. Two equiv of (γ -aminopropyl)triethoxysilane and 1 equiv of pyromellitic anhydride were heated together at 100 °C in dry DMSO. After 1 h, the reaction mixture gelled, due to crosslinking of silicone groups via the hydrolysis and condensation of alkoxy silanes. In the second reaction, phthalic anhydride and (γ -aminopropyl)dimethylethoxysilane cleanly reacted to form a bisimide (imide 1) which

contains a SiOSi bond. No evidence of formation of soluble [(alkoxysilyl)propyl]imides was observed in either reaction.

Further demonstration of alkoxy silane hydrolysis and condensation during imidization reactions was observed during the reaction of 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride (known as PADS for phthalic anhydride disiloxane) with (γ -aminopropyl)dimethylethoxysilane (Scheme 3)⁶. The product of this reaction was a silicone polyimide which has redistributed SiOSi bonds (imide 2). The mechanism of siloxane redistribution during this or other imidization reactions has been discussed elsewhere.⁶

Two-Step Synthesis of [(Alkoxysilyl)propyl]imides. [(Alkoxysilyl)propyl]imides have been successfully synthesized in a two-step process in which an anhydride was first reacted with a nonhydrolyzable amine having a relatively low pK_a . After removal of the water of imidization, a transimidization reaction between the intermediate imide and (alkoxysilyl)propylamine gave the desired [(alkoxysilyl)propyl]imide in high yield. This synthesis is summarized in Scheme 4. The transimidization reaction shown in this scheme can be driven toward products by having a large pK_a difference between the (alkoxysilyl)propylamine and the leaving amine.⁷ Additionally, the transimidization equilibrium can be pushed toward the [(alkoxysilyl)propyl]imide by use of an excess of (alkoxysilyl)propylamine and/or by use of a leaving amine with a sufficiently lower boiling point to allow preferential removal.

Preparation of [(Alkoxysilyl)propyl]imides via Transimidization. A number of heterocyclic and non-heterocyclic amines were screened for their ability to undergo transimidization reactions. For several reasons, including low boiling point (204–210 °C), availability, and low basicity (favorable transimidation equilibrium, $pK_a = 6.82^8$), 2-aminopyridine (2-AP) was chosen as the leaving

* GE Silicones, 260 Hudson River Road, Waterford, NY 12188.

† Abstract published in *Advance ACS Abstracts*, April 15, 1994.

(1) Holub, F. F.; Evans, M. L. U. S. Patent 3,576,031 (GE Company), 1971 and U.S. Patent 3,755,354 (GE Company), 1973.

(2) Lo, S. J.; Swihart, T. J.; Ward, A. H. U. S. Patents 4,906,399 and 4,956,472 (Dow Corning Corp.), 1990.

(3) Kim, Y. K. U. S. Patent 3,901,913 (Dow Corning Corp.), 1975.

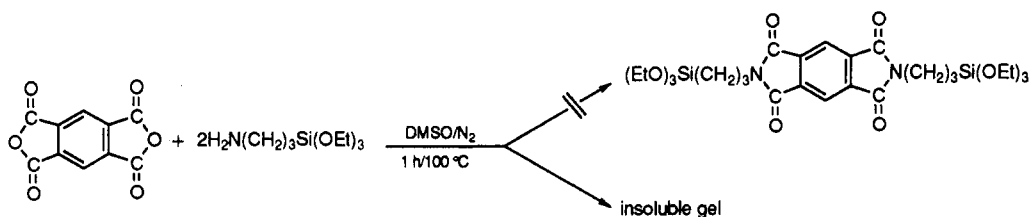
(4) Darms, R.; Beyeler, H.; Haug, F. U. S. Patent 4,562,119 (Ciba-Geigy), 1985.

(5) Example 4 from ref 3.

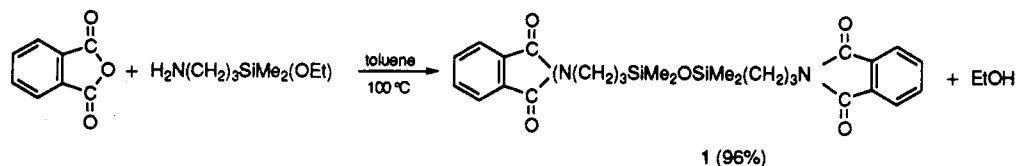
(6) Cella, J. A.; Grade, M. M.; Nye, S. A.; Van Valkenburgh, V. M.; Wengrovius, J. H. *Macromolecules* 1992, 23, 6355.

(7) The effects of pK_a and steric factors on the extent of transimidization equilibria has been extensively studied by T. Takekoshi, GE Corporate R&D. U. S. Patents 3,847,870 and 3,850,885 (GE Company), 1974; *Proceeding from Recent Advances in Polyimides and Other High Performance Polymers*, ACS Division of Polymer Chemistry, Jan 1990, San Diego, CA, E-1.

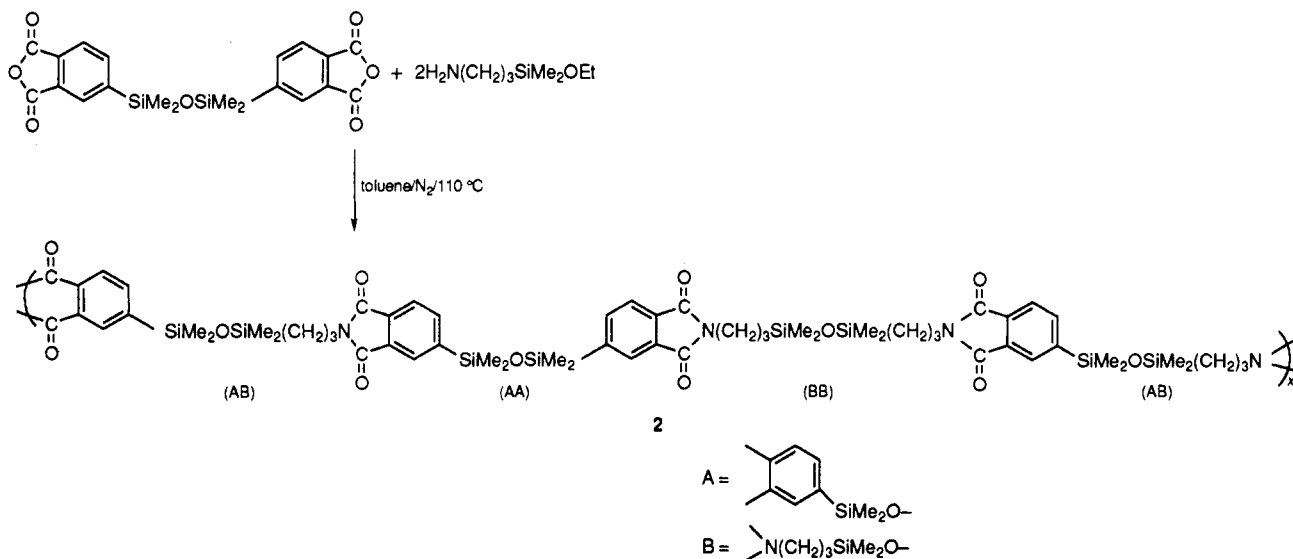
Scheme 1



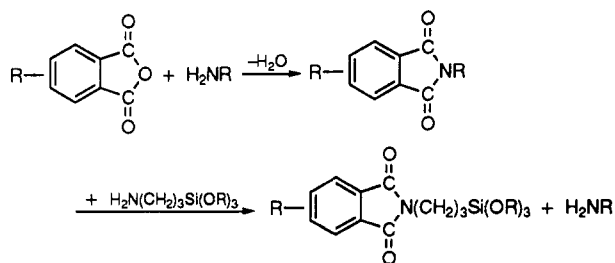
Scheme 2



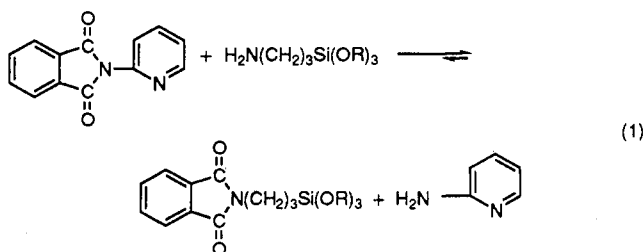
Scheme 3



Scheme 4. Two-Step Process for the Preparation of [(Alkoxy)silyl]propyl]imides



amine in the preparation of (alkoxy)silylpropylimides via the transimidation reaction shown in eq 1. The high $\text{p}K_a$ of (γ -aminopropyl)trialkoxysilane ($\text{p}K_a$ approximately



10.7^8) should result in complete transimidization to the [(alkoxy)silyl]propyl]imide.⁷ To test this hypothesis, a variety of (2-aminopyridyl)imides were prepared by reaction of 2-AP with the appropriate anhydride or dianhydride in refluxing toluene. The water of imidization was then removed by azeotropic distillation, and the imides or bisimides (imides 3–6) were purified by recrystallization from toluene/hexane. These intermediates were characterized by ^1H NMR, ^{13}C NMR, FDMS, melting point, and elemental analysis.

In a second step, each of these (2-aminopyridyl)imides were reacted with an excess of $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ or $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ in refluxing toluene. After 12 h, GC analysis of the resulting transimidization equilibria showed quantitative formation of 2-AP. Removal of the solvent, 2-AP, and excess (γ -aminopropyl)trialkoxysilane was achieved by vacuum distillation leaving behind [(trialkoxysilyl)propyl]imides. These products (imides 7–12) were isolated as moisture-sensitive, off-white oils that were analytically pure. Table 1 lists several [(trialkoxysilyl)propyl]imides, their ^{29}Si NMR data, and their parent (2-aminopyridyl)imides. These compounds were further characterized by ^1H NMR, ^{13}C NMR, FDMS, and elemental analysis.

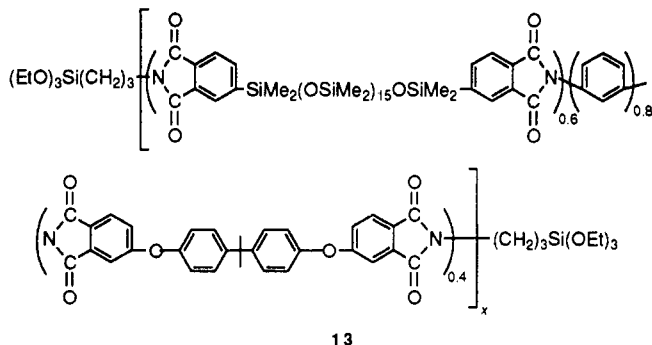
A moisture-curable silicone polyimide endcapped with [(trialkoxysilyl)propyl]imide groups was also prepared by transimidization. This synthesis was accomplished in three steps: (1) reaction of two dianhydrides, PADS

(8) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworth: London, 1965.

Table 1. (2-Aminopyridyl)imide Intermediates and [(Alkoxysilyl)propyl]imide Products

(2-aminopyridyl)imide intermediates	[(alkoxysilyl)propyl]imide products	²⁹ Si NMR (ppm)
		-42.8
		-42.8
		0.0, -43.1 (R = Me); -0.2, -46.2 (R = Et)
		-2.5, -19.7, -21.6, -21.7, -46.2
		-2.5, -19.7, -21.3, -21.6, -21.9, -46.2
		-2.5, -19.7, -21.3, -21.6, -21.9, -46.2

containing 15 internal dimethylsilicone groups and [(1-methylethylidene)bis(1,4-phenyleneoxy)]bis-1,3-isobenzofurandione (known as BPADA for bisphenol A dianhydride) with a deficiency of *meta*-phenylenediamine yielded an anhydride endcapped polyimide, (2) reaction of these anhydride endcaps with 2-aminopyridine gave a polyimide with (2-aminopyridyl)imide endcaps, and (3) finally, transimidation with (γ -aminopropyl)triethoxysilane gave the moisture-curable silicone polyimide (imide 13) shown below. ^{29}Si NMR indicated that this polymer was endcapped with triethoxysilyl groups.



This polyimide was crosslinked by exposing a solution of this polyimide mixed with an alkoxy silane hydrolysis and condensation catalyst, $\text{Bu}_2\text{Sn}(\text{acac})_2$ (acac is acetylacetonate),⁹ to atmospheric moisture. An insoluble polyimide was formed after evaporation of the organic solvent.

Conclusions

Attempts to prepare [(alkoxysilyl)propyl]imides by direct reaction of (γ -aminopropyl)alkoxysilanes with anhydrides resulted in hydrolysis and condensation of alkoxy silane groups and the formation of insoluble imides. Successful preparation of [(trialkoxysilyl)propyl]imides was achieved in a two-step synthesis. In the first step, (2-aminopyridyl)imides were synthesized by reaction of 2-aminopyridine with various anhydrides. After removal of the water of imidization, the (aminopyridyl)imides were reacted with (γ -aminopropyl)trialkoxysilanes. The resulting transimidation equilibria gave nearly quantitative yields of the desired [(alkoxysilyl)propyl]imides which were then isolated by removal of the liberated 2-aminopyridine.

Experimental Section

General. PADS was obtained from Jonathan Rich (GE/CRD)¹⁰ and was recrystallized from hot toluene. BPADA was obtained from GE Plastics, Mt. Vernon, IN. All other starting materials were purchased. NMR spectra were obtained at a frequency of 59.6 MHz for ^{29}Si and 75.4 MHz for ^{13}C spectra. All spectra were obtained in CDCl_3 and are referenced to Me_4Si . Elemental analyses were performed by Schwarzkopf Microanalytical Labs, Woodside, NY. GC analyses were obtained using a thermal conductivity detector and a 6-ft \times 1/8-in. column packed with 3% OV-17 on an inorganic support. All melting points are uncorrected.

Reaction of Pyromellitic Anhydride with 2 Equiv of (γ -Aminopropyl)triethoxysilane. The procedure followed for this reaction was identical to example 4 in US Patent 3,901,913.⁵ Dry

(9) Some Sn-based alkoxy silane hydrolysis and condensation catalysts are described in: Wengrovius, J. H.; Hallgren, J. E.; Stein, J.; Lucas, G. M. U. S. Patent 4,863,992 (GE Company), 1989.

(10) (a) Rich, J. D. U. S. Patent 4,709,054 (GE Company), 1987. (b) Rich, J. D. *J. Am. Chem. Soc.* 1989, 111, 5886.

pyromellitic anhydride (13.25 g, 60.7 mmol), $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ (25.4 g, 115 mmol), and dry DMSO (50.8 g) were heated for 1 h at 100 $^\circ\text{C}$ under N_2 . After 45 min, the entire reaction mixture gelled. GC analysis revealed a substantial amount of ethanol indicating that hydrolysis and condensation of alkoxy silane groups had occurred.

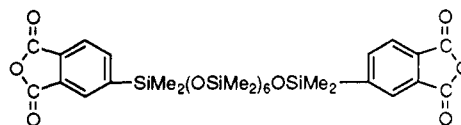
Reaction of Phthalic Anhydride with (γ -Aminopropyl)-dimethylethoxysilane. Preparation of Imide 1. A mixture of phthalic anhydride (15.10 g, 62 mmol) and $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiMe}_2(\text{OEt})$ (10 g, 62 mmol) was refluxed in 100 mL of toluene for 6 h under N_2 . About 0.5 mL of water was collected by azeotropic distillation. The remainder of the solvent was removed in vacuo, yielding a white solid (9.18 g, 96% yield). This crude product was purified by recrystallization from CH_2Cl_2 /pentane, followed by column chromatography (silica gel using CH_2Cl_2 /pentane) affording a white crystalline product (10.9 g, 69% yield): mp 123–124 $^\circ\text{C}$; ^1H NMR δ 7.78 (AA'BB', 4 H), 3.67 (t, $J = 7.4$ Hz, 2 H), 1.70 (m, 2 H), 0.55 (m, 2 H), 0.06 (s, 6 H); ^{13}C NMR δ 168.2, 133.6, 132.0, 122.9, 40.7, 22.4, 15.2, 0.1; ^{29}Si NMR δ +7.6; FD-MS m/z 508 (M^+), 493 ($\text{M}^+ - \text{Me}$). Anal. Calcd for $\text{C}_{28}\text{H}_{32}\text{O}_5\text{N}_2\text{Si}_2$: C, 61.39; H, 6.34; N, 5.51. Found: C, 61.52; H, 6.13; N, 5.35.

Reaction of PADS with 2 Equiv of (γ -Aminopropyl)-dimethylethoxysilane. Preparation of Polyimide 2. PADS (6.61 g, 15.5 mmol) and $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiMe}_2\text{OEt}$ (5.0 g, 31 mmol) were refluxed in 100 mL of toluene for 15 h under N_2 . A small quantity of water was collected by azeotropic distillation. The remainder of the solvent was removed in vacuo, yielding a straw colored, amorphous polymer (9.50 g, 96% yield). NMR spectroscopy (^1H , ^{13}C , ^{29}Si) showed that this product was identical to a polymer prepared by the reaction of the same dianhydride with 1 equiv of $\text{H}_2\text{N}(\text{CH}_2)_3\text{SiMe}_2\text{OSiMe}_2(\text{CH}_2)_3\text{NH}_2$ (polyimide 2). The characterization of polyimide 2 has previously been reported.⁶

Synthesis and Characterization of (2-Aminopyridyl)-imides. Bisimide 3. BPADA (50 g, 96.2 mmol), 2-aminopyridine (18.1 g, 192 mmol), and 250 mL of toluene were refluxed under N_2 for 12 h while water was collected by azeotropic distillation into a Dean-Stark trap. Analytically pure product precipitated from solution on cooling (62.5 g, 97% yield): mp 222–223 $^\circ\text{C}$; ^1H NMR δ 8.74–7.01 (m, 11 H), 1.79 (s, 3 H); ^{13}C NMR δ 166.1, 163.8, 152.6, 149.5, 147.4, 146.1, 138.1, 134.1, 128.8, 128.7, 125.8, 124.9, 123.3, 123.1, 121.9, 120.1, 119.8, 111.9, 42.4, 30.9; FD-MS m/z 672 (M^+). Anal. Calcd for $\text{C}_{41}\text{H}_{26}\text{O}_6\text{N}_4$: C, 73.21; H, 4.20; N, 8.33. Found: C, 73.17; H, 3.97; N, 8.42.

Bisimide 4. PADS (50 g, 0.117 mol), 2-aminopyridine (22.1 g, 0.235 mol), and 250 mL of toluene were refluxed under N_2 for 12 h while water was collected by azeotropic distillation into a Dean-Stark trap. Crystallization was induced by addition of hexane affording a white crystalline solid (65.4 g, 96% yield): ^1H NMR δ 8.75–7.36 (m, 7 H), 0.48 (s, 6 H); ^{13}C NMR δ 166.6, 166.3, 149.3, 147.7, 145.9, 138.8, 137.9, 132.2, 130.6, 127.7, 123.1, 122.7, 121.8, 0.3; ^{29}Si NMR δ +0.4; FD-MS m/z 578 (M^+). Anal. Calcd for $\text{C}_{30}\text{H}_{26}\text{O}_6\text{N}_4\text{Si}_2$: C, 62.26; H, 4.53; N, 9.68. Found: C, 62.17; H, 4.47; N, 9.58.

Bisimide 5. A PADS-based dianhydride containing six internal SiMe_2O groups was prepared by acid-catalyzed ring-opening equilibration of octamethylcyclotetrasiloxane (D_4) with PADS (structure shown below). The experimental procedure

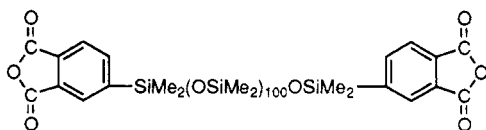


employed is described elsewhere.¹¹ This silicone dianhydride (5.85 g, 6.74 mmol), 2-aminopyridine (1.3 g, 13.5 mmol), and 100 mL of toluene were refluxed together for 15 h under N_2 . The water of imidization was removed by azeotropic distillation. The solvent was then removed in vacuo yielding a straw-colored oil (7.1 g, 95% yield). This product was characterized by ^1H NMR δ 8.70–7.20 (m, 7H), 0.39 (s, 6 H), 0.09 (s, 18 H).

Bisimide 6. A PADS-based dianhydride having the following structure was prepared in a similar fashion as the precursor of

(11) Nye, S. A.; Swint, S. A. *J. Appl. Pol. Sci.* 1991, 43, 1539.

bisimide 5.¹¹ This silicone dianhydride (74.7 g, 9.6 mmol),



2-aminopyridine (1.8 g, 19.2 mmol), and 250 mL of toluene were refluxed for 15 h under N₂. The water of imidization was removed by azeotropic distillation. The solvent was then removed in vacuo yielding a straw-colored oil (75.6 g, 97% yield). ¹H NMR indicated that the imidization reaction was complete.

Synthesis and Characterization of [(Alkoxysilyl)propyl]imides. All of the [(alkoxysilyl)propyl]imides were prepared by mixing a pure (2-aminopyridyl)imide with a 25–50% molar excess of either H₂N(CH₂)₃Si(OMe)₃ or H₂N(CH₂)₃Si(OEt)₃ in dry toluene. The reactions were heated at reflux for 10–15 h under N₂. Gas chromatography was used to monitor the progress of the transimidization equilibria. The reaction mixtures were then vacuum distilled to remove solvent, 2-aminopyridine, and excess (γ-aminopropyl)trialkoxysilane. The desired (alkoxysilyl)propylimides remained as the least volatile product.

Imide 7. The precursor of imide 7, (2-aminopyridyl)phthalimide, was synthesized as previously described.⁶ Imide 7 was isolated as a colorless liquid in an 81% yield (after purification). The scale of the reaction was 0.223 mol. This product was distilled at 115–120 °C/ <0.1 mm vacuum: ¹H NMR δ 7.73 (AA'BB', 4 H), 3.63 (t, *J* = 7.1 Hz, 2 H), 3.52 (s, 9 H), 1.77 (m, 2 H), 0.65 (m, 2 H); ¹³C NMR δ 167.2, 132.9, 131.2, 122.0, 49.5, 39.4, 21.0, 5.6; ²⁹Si NMR δ -42.8; FD-MS *m/z* 309 (M⁺), 278 (M⁺ - OMe). Anal. Calcd for C₁₄H₁₉O₅NSi: C, 54.35; H, 6.19; N, 4.53. Found: C, 53.98; H, 6.09; N, 4.91.

Bisimide 8 was isolated as a straw-colored, viscous liquid in a near-quantitative yield. The scale of the reaction was 30 mmol. Upon standing, this material hardened into a glass. However, gentle heating transformed the product into a pourable liquid: ¹H NMR δ 7.94–6.96 (m, 7 H), 3.68 (t, *J* = 7.1 Hz, 2 H), 3.58 (s, 9 H), 1.77 (m, 5 H), 0.65 (m, 2 H); ¹³C NMR δ 167.4, 162.9, 152.5, 147.0, 134.2, 128.3, 128.0, 125.2, 124.6, 122.0, 119.5, 118.7, 111.2, 50.1, 42.1, 40.1, 30.6, 21.5, 6.3; ²⁹Si NMR δ -42.8; FD-MS *m/z* 842 (M⁺), 811 (M⁺ - OMe). Anal. Calcd for C₄₃H₅₀O₁₂N₂Si₂: C, 61.26; H, 5.98; N, 3.32. Found: C, 60.57; H, 5.85; N, 3.69.

Bisimide 9 was isolated as an off-white liquid in a 97% yield. The scale of the reaction was 34.5 mmol: ¹H NMR δ 7.95–7.84 (m, 3 H), 3.69 (t, *J* = 7.2 Hz, 2 H), 3.56 (s, 9 H), 1.81 (m, 2 H), 0.68 (m, 2 H), 0.44 (s, 6 H); ¹³C NMR δ 167.7, 167.4, 146.2, 137.7, 132.4, 130.6, 126.4, 121.4, 49.6, 39.6, 21.2, 5.9, -0.2; ²⁹Si NMR δ 0.0 (1 Si), -43.1 (1 Si); FD-MS *m/z* 718 (M⁺ - OMe). Anal. Calcd for C₃₂H₄₈O₁₁N₂Si₄: C, 51.31; H, 6.46; N, 3.74. Found: C, 51.06; H, 6.07; N, 4.11.

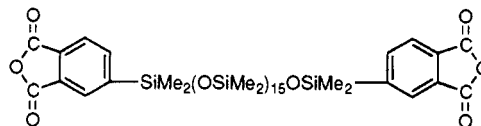
Bisimide 10 was isolated as an off-white liquid in a 97% yield. The scale of the reaction was 3.5 mmol. This product crystallized upon standing: ¹H NMR δ 7.97–7.84 (m, 3 H), 3.87 (q, *J* = 7.0 Hz, 6 H), 3.69 (t, *J* = 7.1 Hz, 2 H), 1.82 (m, 2 H), 1.22 (t, *J* = 7.0 Hz,

9 H), 0.66 (m, 2 H), 0.43 (s, 6 H); ¹³C NMR δ 168.5, 168.2, 146.9, 138.3, 132.8, 131.1, 127.0, 122.1, 58.2, 40.3, 22.0, 18.1, 7.7, 0.5; ²⁹Si NMR δ 0.2 (1 Si), -46.2 (1 Si); FD-MS *m/z* 832 (M⁺), 787 (M⁺ - OEt). Anal. Calcd for C₃₈H₆₀O₁₁N₂Si₄: C, 54.78; H, 7.26; N, 3.36. Found: C, 53.97; H, 6.68; N, 3.74.

Bisimide 11 was isolated as a straw-colored liquid in a near-quantitative yield: ¹H NMR δ 7.97–7.74 (m, 3 H), 3.76 (q, *J* = 7.1 Hz, 6 H), 3.64 (t, *J* = 7.3 Hz, 2 H), 1.76 (m, 2 H), 1.17 (t, *J* = 7.0 Hz, 9 H), 0.61 (m, 2 H), 0.36 (s, 6 H), 0.06, 0.05, 0.04, 0.03, 0.02 (s, 18 H); ²⁹Si NMR δ -2.5 (1Si), -19.7, -21.3, -21.6, -21.9 (s, 3 Si), -46.2 (1 Si).

Bisimide 12 was isolated as a straw-colored, viscous liquid in a near-quantitative yield: ²⁹Si NMR δ -2.5 (1 Si), -19.7, -21.3, -21.6, -21.9 (50 Si), -46.2 (1 Si).

Synthesis of Moisture-Curable Polyimide 13. A PADS-based dianhydride containing 15 internal SiMe₂O groups (structure shown below) was prepared as described elsewhere.¹¹ A



polyimide endcapped with 2-aminopyridyl groups was prepared by reacting this PADS-based dianhydride (10 g, 6.84 mmol), *meta*-phenylenediamine (0.99 g, 9.17 mmol), BPADA (2.37 g, 4.56 mmol), and (dimethylamino)pyridine imidization catalyst (0.07 g, 0.5% by weight) in refluxing *o*-dichlorobenzene (ODCB) for 2 h. Water was removed by azeotropic distillation with the aid of a Dean-Stark trap. 2-Aminopyridine (0.45 g, 4.79 mmol) was then added, and the reaction mixture was refluxed for an additional 12 h. The remaining water and a portion of ODCB was removed by distillation. The polymer was precipitated into methanol and dried in a vacuum oven. FT-IR analysis indicated that no unreacted anhydride groups were present. A mixture of this polymer (5 g, 0.828 mmol) and (γ-aminopropyl)triethoxysilane (0.55 g, 2.49 mmol) was dissolved in ODCB. After the mixture was stirred for 2 h under N₂, GC analysis showed the formation of 2-aminopyridine. The reaction was driven to completion by removal of the reaction volatiles by vacuum distillation. The product was a tan polyimide (5.1 g): ²⁹Si NMR δ -2.5, -19 to -22, -46.2.

This alkoxy silane-endcapped polyimide was dissolved in a minimal amount of CHCl₃, and an alkoxy silane hydrolysis and condensation catalyst, Bu₂Sn(acac)₂⁹ (0.2 g), was added. On exposure to atmospheric moisture, and after evaporation of the solvent, a tough, brittle, insoluble, crosslinked polymer was obtained.

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