Siloxane Equilibration during the Condensation Reactions of Organosilicon Functional Amines and Anhydrides

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ABSTRACT: The condensation reaction between amines and anhydrides in which one or both of the reactants contain siloxane functionality usually affords imide products in which siloxane redistribution has occurred. The reaction is catalyzed by the amic acid intermediate and prevails when geometry is favorable for intramolecular participation. Poly(imide siloxanes) prepared via this type of condensation process will contain scrambled repeat units in the backbone and will produce cyclic siloxanes as coproducts as a result of the redistribution process. The scrambling can be circumvented by employing imides derived from 2-aminopyridylimides in place of anhydrides in the condensation reaction, thereby avoiding the intermediacy of amic acids. Several examples of siloxane redistribution during the preparation of silicone polyimides are presented. Mechanistic studies derived from model reactions are also presented.

Introduction

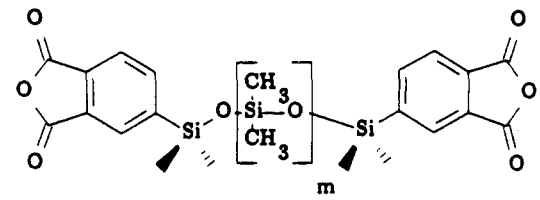
Poly(imide siloxanes) are an interesting class of copolymers which combine the useful properties of two high-performance materials, polyimides and silicones. Although a variety of methods have been described for preparing these polymers,[1] the most frequently employed method involves the condensation polymerization of diamines and dianhydrides in which at least one of the monomers bears siloxane functionality.

In the course of this condensation reaction, amic acid intermediates are produced which cyclodehydrate to produce imides and water. The coexistence of water and acid functionality during this process provides a medium conducive to siloxane equilibration.[2] Surprisingly, this phenomenon has not been previously reported to occur. This paper describes the observation of siloxane equilibration attending the condensation reactions of amines and anhydrides bearing siloxane functionality. The effects of this reaction on the synthesis of poly(imide siloxanes) are discussed in light of the mechanistic information that has been gathered about the process.

Results and Discussion

The cocondensation reaction of 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BPADA) with *m*-phenylenediamine (0.6 equiv) and α,ω-bis(γ-aminopropyl)poly(dimethylsiloxane) (**1b**) (0.4 equiv) in refluxing *o*-dichlorobenzene produces, in addition to the desired high molecular weight copolymer, small amounts of cyclic siloxanes, predominantly hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4). The production of D3 and D4 in this reaction indicates that equilibration of the siloxane backbone occurred during the imidization process (Scheme I).

Further demonstration of siloxane equilibration during the condensation reaction between dianhydrides and diamines was obtained by analysis of the copolymers, **2** and **3**, obtained from the reaction of **1a** and **1b**, respectively, with 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride (**4**) ($m = 0$). The ^{29}Si NMR spectrum of **2** (Figure 1) exhibited four resonances (10.7, 7.6, 0.2, −2.0 ppm) instead of the expected two. The absorptions at 10.7 and −2.0 ppm are ascribed to the presence of the "scrambled" repeat unit **5** produced by siloxane equilibration. In addition, ^{13}C and ^{1}H NMR spectra of this



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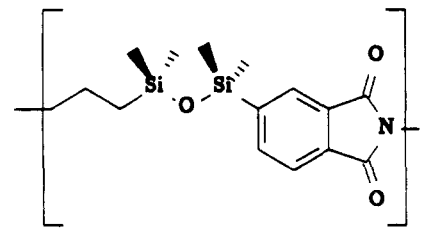

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polymer support the presence of units such as **5** in the backbone. Similarly, the ^{29}Si NMR spectrum of polymer **3** exhibits many more than the expected absorptions (7.7, 0.2, −19.1, −21.9 ppm), the major "extra" ones occurring at 10.7, 7.2, 0.2, 0.1, −1.6, −2.2, and −2.6 ppm. Most of the new peaks are ascribed to equilibration of siloxane groups into **4**. Polymers derived from **4** ($m > 0$) as the only siloxane source exhibit resonances at −1.8, −2.2, and −2.5 ppm for the silicons α to the phenyl ring with varying numbers of siloxane groups adjacent to them, at −17.0 and −19.0 ppm for the β silicons, and at −21.1 to −22.2 ppm for the internal siloxanes. These data establish that siloxane equilibration has occurred during the polymerization reaction.

In an effort to further elucidate this process, the reaction between phthalic anhydride and 1-(3-aminopropyl)-1,1,3,3,3-pentamethyldisiloxane (**6**) was carried out in refluxing toluene (Scheme II). This reaction produced nearly equal amounts of the unsymmetrical and symmetrical imide siloxanes, **7** and **8**, along with hexamethyldisiloxane. Control experiments indicated that both the starting amine, **6**, and the unsymmetrical product, **7**, did not undergo equilibration when heated in refluxing toluene even when the toluene was saturated with water. More-

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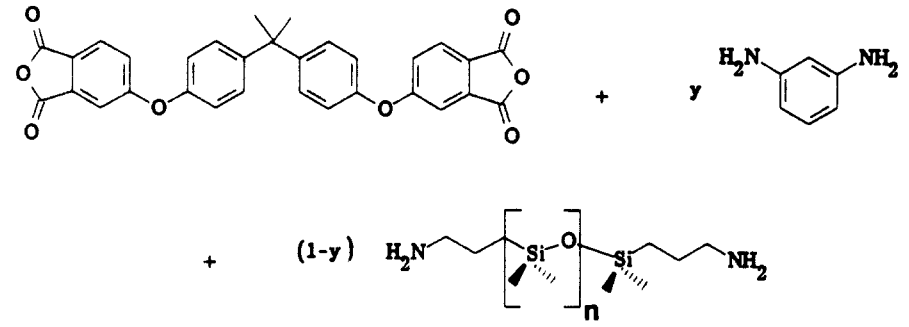
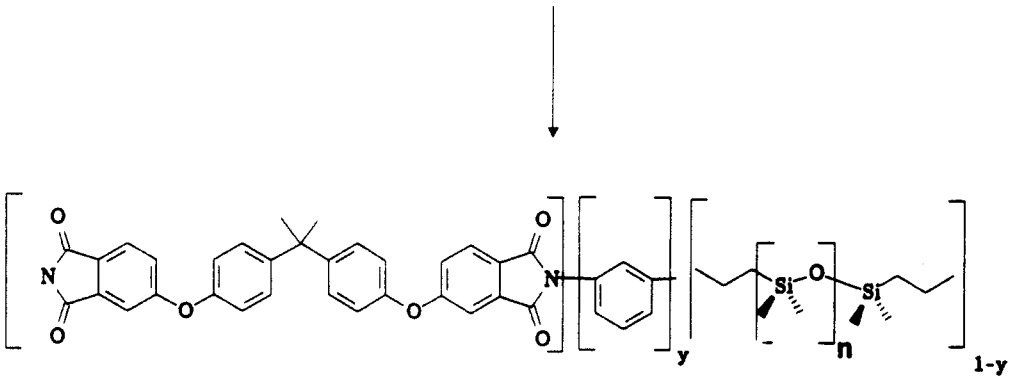
Scheme I



1a: n=1
1b: n=9



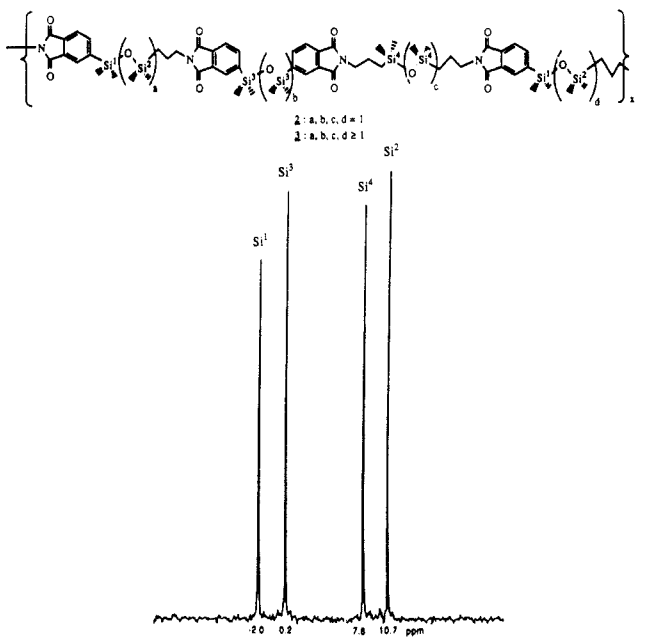
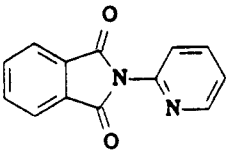


Figure 1. ^{29}Si NMR of copolymer 2 prepared by reaction of 1(n=1) and 4(n=0) showing the presence of the scrambled repeat unit 5.

over, addition of a small amount of the amic acid derived from phthalic anhydride and dimethylamine to these solutions did not catalyze equilibration of these compounds to any appreciable extent. Addition of 6 to phthalic anhydride at 0–5 °C in CH_2Cl_2 afforded the unscrambled amic acid 9 in quantitative yield. Heating 9 in boiling toluene produced 7 and 8 in nearly equal amounts. The data collectively suggest that scrambling occurs during cyclodehydration of the amic acid. The failure of externally added amic acid to induce scrambling implies that the amic acid species does not function merely as an acid catalyst but is an essential intermediate in the equilibration process.

Reaction of *N*-2-pyridylphthalimide (10) with 6 in refluxing *o*-dichlorobenzene (ODCB) affords mainly the unscrambled imide 7, with less than 5% of the scrambled product 8 being produced. The intermediate in this



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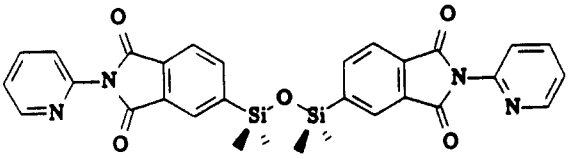

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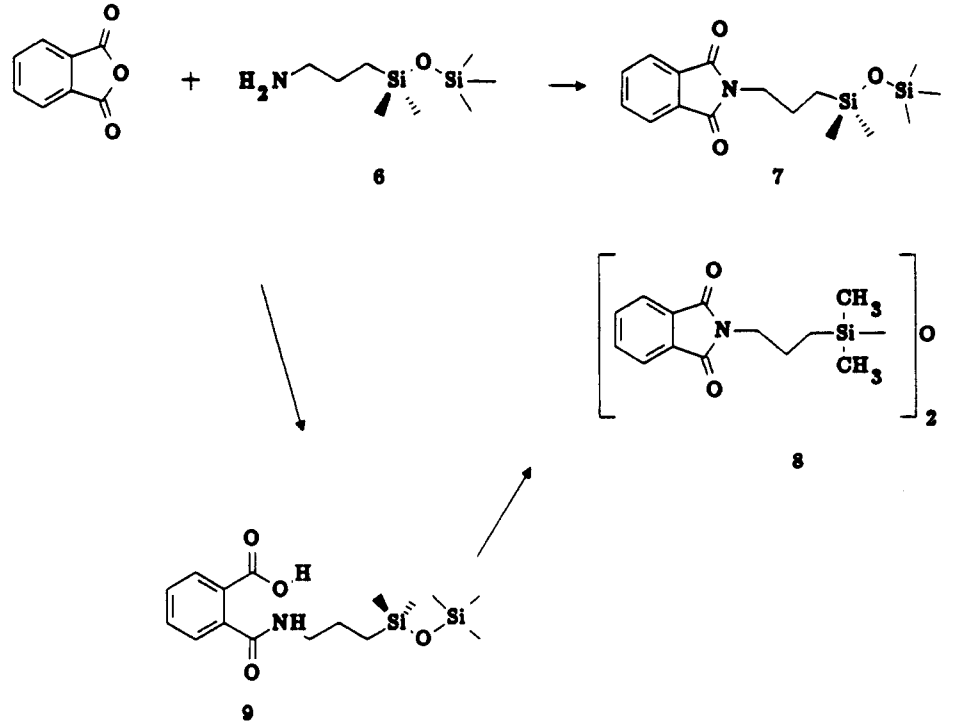
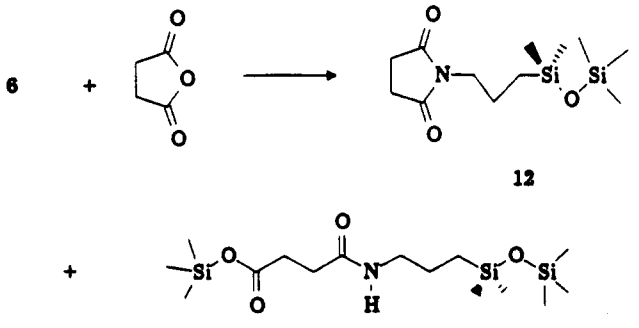
process is not an amic acid but a diamide, which is converted to an imide by explusion of 2-aminopyridine.[3] Similarly, a polymer analogous to 2 was prepared via amine–imide polymerization reaction of 1a with bisimide 11. Analysis of the poly(imide siloxane) 2′ obtained by this process indicated that no scrambling had occurred. Polymer 2′ exhibited only two ^{29}Si resonances, at 7.3 and 0.01 ppm. No evidence of the "scrambled" repeat unit 5 was observed. These experiments demonstrate that amic acid is a required intermediate in the equilibration process.

Scheme II

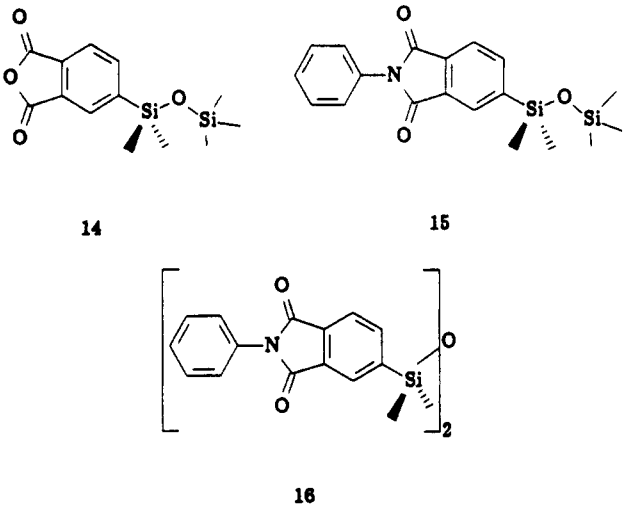


A plausible mechanistic scenario for this amic acid mediated siloxane equilibration reaction involves intramolecular catalysis by the amic acid, leading to siloxane cleavage. Cleavage may occur as a result of inter- or intramolecular nucleophilic attack to afford a silanol and/or a silyl ester. The silanol, once formed, can propagate the equilibration via silanol–silanol condensation or by reaction with another silyl ester (Scheme III).

Evidence for the silyl ester intermediate was obtained from the reaction of amine 6 with succinic anhydride. Very little siloxane scrambling was observed in this reaction, 12 being the major imide product observed. However, examination of the reaction mixture by GC/mass spectrometry revealed that silyl ester, 13 (*m/e* 362, $M^+ - 15$), was produced in this reaction. The formation of 13 demonstrates that amic acid mediated siloxane cleavage can occur under the reaction conditions.

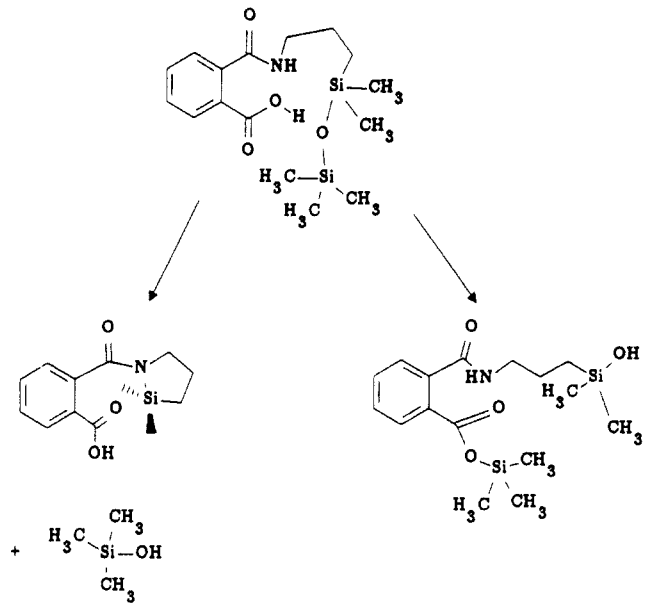


If a silyl ester–amide intermediate is indeed responsible for the siloxane scrambling process, then amine–anhydride combinations which can produce this intermediate intramolecularly should exhibit a greater propensity for scrambling than those which cannot. For example, while the reaction of 6 with phthalic anhydride produces nearly equal amounts of the scrambled and unscrambled products, reaction of anhydride 14 with aniline under identical conditions produces the unscrambled imide 15 plus only trace amounts (<5%) of the scrambled product, 16. In the former case, formation of a silyl ester from the amic acid intermediate can take place intramolecularly while in the latter case it cannot.

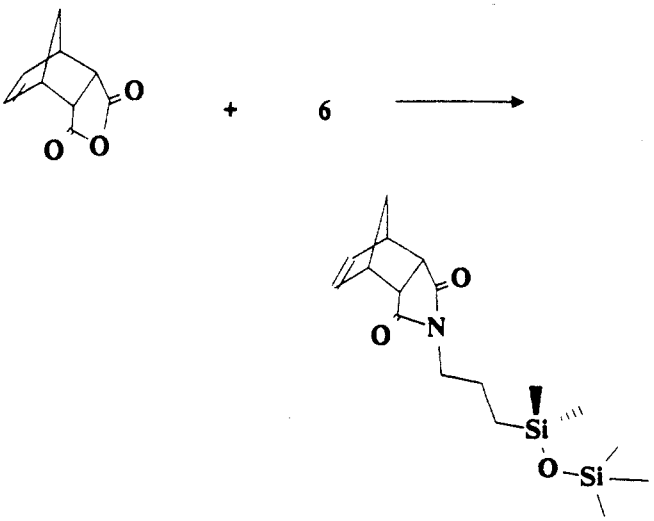


Similarly, the reaction of 6 with nadic anhydride affords only the unscrambled imide 17, suggesting that intramolecular silylation of the amic acid is not facile in this case. The formation of a silyl ester and a silanol from an amic acid is, in effect, a siloxane cleavage process. If scrambling results only from a recombination of these species, then little or no crossover should occur when imidization is carried out in the presence of nonparticipating siloxanes. Indeed, reaction of 1a with phthalic anhydride (2.1 equiv) in refluxing toluene in the presence of 2 equiv of hexamethyldisiloxane (HMDS) affords 8 (>90%) plus only 5–10% of the crossover product, 7. Similarly, reaction of 4 ($m = 0$) with aniline (2.1 equiv) under the same conditions in the presence of HMDS affords 16 without a trace of the crossover product, 15. The extent to which scrambling occurs in these reactions thus depends on a subtle balance between the rates of imidization and intramolecular silylation of the amic acid intermediates.

Scheme III



As a consequence of the scrambling phenomena described in this report, amine–anhydride combinations which give rise to siloxane equilibration during the imidization process (combinations of phthalic anhydride and (3-aminopropyl)siloxane derivatives are certainly among these) will likely produce siloxane cyclics (D3 and D4 predominantly) and modified siloxane segments in the polymer backbone. Since the amic acid enjoys only a transient existence during the imidization process, the extent of equilibration may be relatively insignificant. The use of an imidization catalyst should likewise diminish the probability of equilibration by increasing the rate of imidization relative to scrambling. In cases where it is desirable to completely avoid siloxane equilibration during the preparation of poly(imide siloxanes), use of the amine imide exchange[3] reaction is recommended.



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Experimental Section

General Procedures. Gel permeation chromatography (GPC) was performed on a Waters Associates liquid chromatograph using either a bank of Waters μ-Styragel columns (500, 10^3, 10^4, and 10^5 Å) in series or a Varian TSK mixed-bed column. Chloroform containing 1% ethanol was the eluant. Gas chromatography was carried out on a Varian Vista Series gas chromatograph equipped with a flame ionization detector using a 6 ft × 1/8 in. glass column packed with 3% OV-17 on an inorganic support. Helium was used as the carrier gas at a flow rate of 30 mL/min. Liquid chromatography was carried out on a Shimadzu LC-4A chromatograph using a Whatman C-18 reverse-phase column with a solvent gradient from 50 to 95% acetonitrile/water. NMR spectra were determined on a Varian XL-300 instrument operating at a frequency of 59.6 MHz for ^{29}Si and 75.4 MHz for ^{13}C spectra. Mass spectra were determined using a Varian MAT 731 high-resolution double-focusing mass spectrometer. Differential scanning calorimetry was performed on a Mettler DSC 20. Intrinsic viscosities were determined in chloroform. BPADA was obtained from GE Plastics, Mt. Vernon, IN. 1,3-Bis(3-aminopropyl)tetramethyldisiloxane (**1a**) was purchased from Silar Laboratories, Scotia, NY. Dianhydride **4** was obtained from Jonathan Rich (GE/CRD).[4] Siloxane diamine (**1b**) was obtained from the reaction of **1a** with octamethylcyclotetrasiloxane catalyzed by tetramethylammonium hydroxide.[5]

Preparation of Copolymer 2. A 250-mL three-necked flask was charged with **1a** (5.83 g, 23.4 mmol), **4** (10.0 g, 23.4 mmol), (dimethylamino)pyridine (DMAP) (0.06 g, 0.47 mmol), and toluene (100 mL). The resulting heterogeneous mixture was heated to reflux under nitrogen for 2 h. The reaction mixture became homogeneous, and water of imidization was removed by azeotropic distillation into a Dean–Stark trap. The remaining volatiles were removed in vacuo, and the resulting yellow elastomeric solid was dried in a vacuum oven to afford 14.5 g (97% yield) of copolymer **2**. ^{29}Si NMR ($CDCl_3$) δ 10.2, 7.6, 0.2, −2.0. ^{13}C NMR ($CDCl_3$) δ 168.7, 168.5, 168.4, 168.3, 148.0, 147.8, 147.1, 146.9, 138.5, 138.4, 132.8, 132.7, 132.6, 132.5, 131.0, 130.9, 127.0, 122.1, 40.7, 40.6, 22.4, 15.2, 0.6, 0.1. ^{1}H NMR ($CDCl_3$) δ 7.94–7.76 (m, 3, ArH), 3.61 (t, 2, J_{ab} = 7.06 Hz, $NCH_2CH_2CH_2Si$), 1.65 (m, 2, $NCH_2CH_2CH_2Si$), 0.55 (m, 2, $NCH_2CH_2CH_2Si$), 0.40, 0.36, 0.08, 0.03 (s, 3, 3, 3, 3, $SiCH_3$). GPC M_n = 13 200. IV ($CHCl_3$) = 0.483 dL/g. Anal. Calcd for $C_{30}H_{42}O_6N_2Si_4$: C, 56.39; H, 6.62; N, 4.38. Found: C, 56.25; H, 6.08; N, 4.63.

1-(3-Aminopropyl)-1,1,3,3,3-pentamethyldisiloxane (6). To a solution of 48.6 g (300 mmol, 7.5 equiv) of hexamethyldisiloxane and 10.258 g (40 mmol) of 1,3-bis(3-aminopropyl)-tetramethyldisiloxane was added 2.25 mL of a 1.225 M solution of the potassium (3-aminopropyl)dimethylsilanolate–DMSO complex (prepared from **1a** and KOH in 3/2 DMSO/toluene with azeotropic water removal). The mixture was heated at reflux overnight. The cooled reaction mixture was quenched by the addition of 10 mL of 0.373 N HCl in methanol. The quenched solution was diluted with 2 volumes of ether, transferred to a separatory funnel, and washed with 2 × 200 mL of H_2O and brine (150 mL). The washed solution was filtered through a cone of anhydrous $CaSO_4$ (Drierite), and solvent was removed in vacuo. The residue (16.58 g) was distilled under house vacuum (15 mm), affording 12.20 g of a colorless liquid (bp 100–102 °C). Redistillation afforded 8.11 g (98.9%) of the pure disiloxane. Mass spectrum (field desorption) m/e 206 (M^+) and 191 (M − 15). ^{1}H NMR ($CDCl_3$) δ 2.67 (t, 2, $NCH_2CH_2CH_2Si$), 1.43 (pentuplet, 2, $NCH_2CH_2CH_2Si$), 1.06 (s, 2, NH_2), 0.47 (m, 2, CH_2Si), 0.075 (s, 15, $SiCH_3$).

1-(3-*N*-Phthalimidopropyl)-1,1,3,3,3-pentamethyldisiloxane (7). A solution of 1.016 g (2.0 mmol) of 1,3-bis(3-phthalimidopropyl)-1,1,3,3-tetramethyldisiloxane (**8**) (from **1a** and 2 equiv of phthalic anhydride), 16.2 g (100 mmol) of hexamethyldisiloxane, and 0.05 mL of concentrated H_2SO_4 in 10 mL of 1,2-dichloroethane was stirred for 3 days at room temperature. Occasional additions of 2–3 g of hexamethyldisiloxane (HMDS) were made during this period. Progress of the reaction was monitored by liquid chromatography, and when the reaction was judged to be complete, the solution was diluted with 50 mL of CH_2Cl_2 and washed with H_2O (2 × 50 mL) and brine. Evaporation of the solvent and excess HMDS afforded 1.4 g of an oil which solidified on standing to a low-melting solid. ^{1}H NMR ($CDCl_3$) δ 8.00 (m, 4, ArH), 3.90 (t, 2, NCH_2), 1.95 (m, 2, NCH_2CH_2), 0.76 (m, 2, CH_2Si), 0.28 (s, 15, $SiCH_3$).

Reaction of 6 with Phthalic Anhydride. A 50-mL flask equipped with a magnetic stirrer and condenser with an N_2 inlet was charged with 1.025 g (5.0 mmol) of **6**, 0.748 g (5.05 mmol) of phthalic anhydride, and 10.0 mL of toluene. The mixture was heated to reflux, and progress of the reaction was monitored by liquid chromatography. After about 5 h, analysis indicated that

imidization of the phthalic anhydride was complete and that two products, 7 and 8, were produced in nearly equivalent amounts. Removal of solvent and volatile products (HMDS) from the mixture afforded a solid mixture of the two imides. The ratio of these products was determined by ^{1}H NMR to be near unity.

Preparation of 10. A 250-mL flask fitted with a Dean–Stark trap and condenser with a nitrogen inlet was charged with 14.8 g (0.1 mol) of phthalic anhydride, 7.4 g (0.1 mol) of 2-aminopyridine, and 120 mL of ODCB. The mixture was heated to 140 °C for 1 h, and the temperature was raised until water and ODCB codistilled. When no more water was collected, the mixture was heated at reflux for an additional 2 h and then allowed to cool. The imide separated as a white powder. Mass spectrum (FDMS) *m/e* 224 (M^+). Mp 232 °C (DSC).

Reaction of 10 with 6. A 25-mL flask fitted with a condenser was charged with 0.210 g (1.028 mmol) of 6, 0.230 g (1.028 mmol) of 10, and 2.0 mL of ODCB. The mixture was refluxed for 3 h. Liquid chromatographic analysis of the reaction mixture indicated that the unscrambled imide, 7, was produced in >95% yield while only a trace (<5%) of the scrambled imide 8 was formed. The reaction of 6 with phthalic anhydride under identical conditions afforded a 3/2 mixture of 7/8.

Preparation of 11. A 500-mL three-necked flask equipped with a mechanical stirrer and Dean–Stark trap with condenser and nitrogen inlet was charged with dianhydride 4 (50.0 g, 0.117 mol), 2-aminopyridine (22.1 g, 0.235 mol), and toluene (250 mL). The resulting solution was stirred at reflux for 12 h with azeotropic removal of water. The product was isolated by concentration of the reaction mixture to afford a white powder, 65.4 g (96%). ^{1}H NMR ($CDCl_3$) δ 8.75–7.36 (m, 6, ArH), 0.48 (s, 6, $SiCH_3$). ^{13}C NMR ($CDCl_3$) δ 166.6, 166.3 (C=O), 149.3, 147.7, 145.9, 138.8, 137.9, 132.3, 130.6, 127.7, 123.1, 122.7, 121.8 (Ar), 0.3 ($SiCH_3$). ^{29}Si NMR ($CDCl_3$) δ 0.4. Anal. Calcd for $C_{30}H_{28}N_4O_5Si_2$: C, 62.26; H, 4.53; N, 9.68. Found: C, 62.17; H, 4.47; N, 9.58.

Preparation of Polymer 2′. A 25-mL two-necked flask equipped with a short-path still head was charged with 0.510 g (0.882 mmol) of 11, 0.219 g (0.882 mmol) of **1a**, and 6 mL of ODCB. The mixture was stirred at reflux for 6 h and then heated under vacuum (~40 mm) for 20 h with distillative removal of 2-aminopyridine. ^{29}Si NMR ($CDCl_3$) δ 8.20, 0.77.

Preparation of Polymer 3. A 500-mL three-necked flask equipped with a mechanical stirrer and Dean-Stark trap with condenser and nitrogen inlet was charged with 20.76 g (48.68 mmol) of 4, 18.08 g (19.87 mmol) of **1b**, and 120 mL of ODCB. The resulting mixture was stirred at 100 °C until it became homogeneous. Then 3.22 g (29.80 mmol) of *p*-phenylenediamine, 0.29 g (1.99 mmol) of phthalic anhydride, and 0.30 g (1.36 mmol) of DMAP in 100 mL of ODCB were added. The reaction mixture was heated at reflux for 7 h while water of imidization was continuously removed. After cooling, the mixture was poured into approximately 5 volumes of methanol in a blender, and the precipitated polymer was collected by filtration. The polymer was redissolved in $CHCl_3$ and reprecipitated into methanol. The final material was dried in a vacuum oven at 120 °C for 18 h. ^{29}Si NMR ($CDCl_3$) δ 10.2, 7.2, 0.2, 0.1, −1.6, −2.2, −19.1, −20.8, −21.9, −22.2.

Preparation of 4-(((Trimethylsilyl)oxy)dimethylsilyl)-phthalic Anhydride (14). A solution of 2.13 g (5 mmol) of 4 (*m* = 0) in 40 mL of toluene was azeotropically dried, allowed to cool, and treated with 23 g (140 mmol) of hexamethyldisiloxane and 250 μL of trifluoromethanesulfonic acid. The mixture was stirred for 24 h at ambient temperature and the resulting solution was washed with equal volumes of water and brine. The washed solution was passed through a cone of anhydrous $CaSO_4$ (Drierite), and volatiles were removed under vacuum. The residue was a crystalline solid obtained in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 8.20 (s, 1, ArH), 8.0 (q, 2, ArH), 0.40 (s, 6, $ArSiCH_3$), 0.1 (s, 9, OTMS). ^{13}C NMR ($CDCl_3$) δ 163.1, 163.0 (C=O), 151.7, 140.4, 130.57, 130.21, 129.84, 124.50 (aromatic), 1.89, 0.75 ($SiCH_3$).

Reaction of 14 with Aniline. A solution of 0.093 g (1.0 mmol) of aniline with 0.294 g (1.0 mmol) of 14 in 5 mL of toluene was heated to reflux for 3 h. Liquid chromatographic analysis of the solution indicated the formation of a single major product (>90% yield), identified as the unscrambled imide **15** by comparison with an authentic sample. Compound **15**: ^{1}H NMR ($CDCl_3$) δ 8.2 (s, 1, ArH), 8.0 (2, AB quartet, ArH), 7.5 (m, 5, ArH), 0.4 (s, 6, $ArSiCH_3$), 0.15 ppm (s, 9, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 168, 167 (C=O), 149, 139, 132, 131, 129, 128, 127.9, 127.7, 126.5, 122.6 (aromatic carbons), 1.2, 1.0 ($SiCH_3$). Mass spectrum (field desorption) *m/e* 369 (M^+). A small amount of the scrambled imide **16** was also produced and identified by comparison with an authentic sample prepared from 4 and aniline. Compound **16**: Mass spectrum (field desorption) *m/e* 576 (M^+), 288 (M^{+2}).

Reaction of 1a with Phthalic Anhydride in the Presence of Hexamethyldisiloxane. A mixture of 2.49 g (10 mmol) of **1a**, 2.96 g (20 mmol) of phthalic anhydride, and 8.10 g (50 mmol) of hexamethyldisiloxane in 50 mL of toluene was heated to reflux for 2.5 h with continuous water removal via a Dean–Stark trap. Removal of solvent afforded a white solid residue which consisted of a 3/1 mixture of 8/7, as judged by NMR analysis.

Reaction of 4 (*m* = 0) with Aniline in the Presence of Hexamethyldisiloxane. A mixture of 2.13 g (5.0 mmol) of 4, 0.93 g (10.0 mmol) of aniline, and 4.05 g (25 mmol) of hexamethyldisiloxane in 30 mL of toluene was heated at reflux for 3 h with continuous water removal via a Dean–Stark trap. Removal of solvent under vacuum afforded a quantitative yield of a white solid identified as **16** by comparison with an authentic sample.

Reaction of 6 with Succinic Anhydride. A 25-mL round-bottomed flask was charged with 0.1 g (1 mmol) of succinic anhydride, 0.205 g (1 mmol) of 6, and 4 mL of toluene. The mixture was refluxed for 1 h, and then solvent was removed under vacuum, affording a solid residue consisting of three components in a 4:1:1 ratio. The major product was identified by its mass spectrum as the unscrambled imide, **12**. Mass spectrum *m/e* (relative abundance) 272 (55%) [M^+ − 15], 147 (100%) [$Me_5Si_2O^+$]). The minor products were identified as the scrambled bisimide (authentic sample prepared from **1a** and succinic anhydride; mass spectrum *m/e* (relative abundance) 397 (15%) [M^+−15], 272 (100%) [M−$(CH_2)_3$-succinimide$^+$]) and a silylated amic acid, tentatively identified as **13** (mass spectrum *m/e* (relative abundance) 362 (15%) [M^+ − 15], 147 (100%) [$Me_5Si_2O^+$]).

Reaction of 6 with Nadic Anhydride. A 50-mL flask was charged with 0.164 g (1.0 mmol) of nadic anhydride, 0.205 g (1.0 mmol) of 6, and 4.0 mL of toluene. The mixture was refluxed for 1 h and then solvent was removed under vacuum. The residue, a white solid, consisted of a single component by gas chromatographic analysis. ^{1}H NMR analysis indicates this material to be the unscrambled imide **17**. ^{1}H NMR ($CDCl_3$) δ 6.33 (s (br), 2, vinyl H), 3.88 (t, 2, NCH_2), 3.4, 3.0, 2.2–1.2 (m, 10, aliphatic and ring H's), 0.1 (s, 15, $SiCH_3$).

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Registry No. **1a**/**4** (copolymer), 123565-16-2; **1a**/11 (copolymer), 142721-77-5; **1b**/**4**/ODCB/*p*-phenylenediamine (copolymer), 142761-37-3; **6**, 23029-21-2; **7**, 142721-69-5; **8**, 91859-19-7; **10**, 59208-49-0; **11**, 142721-70-8; **12**, 142721-71-9; **14**, 142721-72-0; **15**, 142721-73-1; **16**, 142721-74-2; **17**, 142721-75-3; $Me_3SiOSiMe_3$, 107-46-0; $PhNH_2$, 62-53-3; 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 2469-55-8; phthalic anhydride, 85-44-9; 2-aminopyridine, 504-29-0; succinic anhydride, 108-30-5; nadic anhydride, 129-64-6.