Macromolecules 1991, *24*, 2682-2688

Synthesis, Characterization, and Solubility Behavior of Polysiloxanes with 4-(Dialkylamino)pyridine Functions

Slawomir Rubinsztajn,[†] **Martel Zeldin,*** **and Wilmer K. Fife**

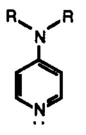
Indiana University-Purdue University at Indianapolis, 1125 East 38th Street, Indianapolis, Indiana 46205

Received August 10, 1990; Revised Manuscript Received November 15, 1990

ABSTRACT: New silane monomers, which contain the 4-(dialkylamino)pyridine (DAAP) function, have been synthesized by hydrosilylation of 4-(*N*-methylallylamino)pyridine with Me$_n$Si(OEt)$_{3-n}$H (n = 0, 1) and 4-(diallylamino)pyridine with Me$_n$Si(OEt)$_{3-n}$H (n = 0–2) using H_2PtCl_6 as a catalyst. Only β-addition products were observed. The products were characterized by elemental analysis, infrared and ^1H and ^{13}C NMR spectroscopy, and gas chromatography–mass spectrometry. Hydrolysis–polycondensation of the respective difunctional monomers with a basic catalyst gave a mixture of linear homopolymer and cyclic oligomers from the monomer with a pendant DAAP residue and only the linear homopolymer from the monomer with the in-chain DAAP residue. The linear homopolymers were trimethylsiloxy end-blocked by reaction with $(Me_3Si)_2NH$ or bis(trimethylsilyl)acetamide. The end-blocked homopolymers were characterized by spectroscopic and thermal analytical methods. Thermal analysis (TGA) of the linear homopolymers indicates remarkable thermal stability (T_d > 400 °C) comparable to that of poly(dimethylsiloxane). Molecular weights for the pendant and in-chain polymers were determined by end-group analysis from the ^1H NMR spectra and exclusion chromatography. The mass spectra of the homopolymers above the degradation temperature indicate depolymerization, giving rise to a cyclic monomer and cyclic oligomeric products. The two linear homopolymers have different and unusual solubility properties in immiscible H_2O/CH_2Cl_2 medium. The effect of pH on solubility and partition behavior of both polymers is discussed. Cross-linked homopolymers were prepared by established procedures.

Introduction

4-(Dialkylamino)pyridines (DAAP; **1**), of which 4-(dimethylamino)pyridine (DMAP; **1**, R = Me) is best known, are widely used, highly effective nucleophilic catalysts for acylation, alkylation, silylation, phosphorylation, ester rearrangement, and polymerization reactions.[1-8] Several investigators have evaluated the catalytic activity of the DAAP group where it is incorporated into soluble and solid-phase polymers.[9-19] Frequently, the polymeric catalysts have exhibited lower levels of activity than DMAP itself. Frechet et al. found that catalytic effectiveness is strongly influenced by the polymer microenvironment at the reactive sites.[19,20] For example, the presence of a three-carbon spacer group between the polymer chain and the DAAP group enhances reactivity of the polymer catalyst to the level of **1a** itself. Since polysiloxanes are known to exhibit significantly different chemical and physical properties (e.g., inherent flexibility, low-temperature elasticity, hydrophobicity, thermooxidative stability) that differ from those of vinyl polymers,[21] it appeared relevant to explore the catalytic behavior of the DAAP moiety upon attachment to the polysiloxane backbone. For example, the DAAP moiety can be attached as a pendant group on silicon, as in polymer **2**, with a typical polysiloxane backbone. Alternatively, the DAAP moiety can be made an integral part of the polymer backbone with siloxane bonds as in polymer **3**. Furthermore, by varying the functionalization of the silane monomers, as in **4b** and **5b** and **5c**, cross-linked homopolymers with a broad range of structural and microenvironmental features can be obtained. In a previous paper,[22] the linear and cross-linked variants, **2**, **3**, **6**, and **7a,b**, were shown to be effective catalysts for the acetylation of 1-methylcyclohexanol with acetic anhydride. The linear in-chain polymer, **3**, exhibited catalytic activity comparable to that of **1** and the most active vinyl-based analogues. We now present a detailed description of (a) the synthesis and structural characterization of monomers **4** and **5**, (b) the polymerization of monomers **4** and **5** by catalytic polycondensation to give linear (**2** and **3**) and cross-linked (**6** and **7a,b**) homopolymers, respectively, (c) the spectroscopic and thermal characterization of the polymers, and (d) a study of the unusual solubility characteristics of polymer **3** relative to polymer **2**.



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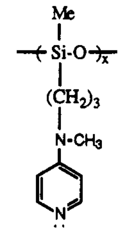

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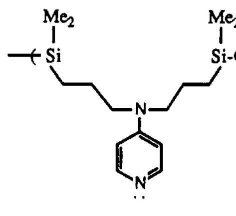

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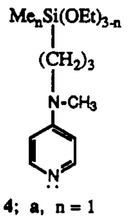
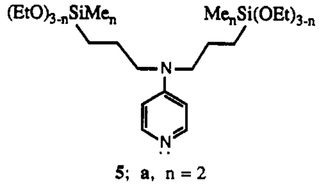


4; **a**, n = 1
b, n = 0



5; **a**, n = 2
b, n = 1
c, n = 0

Experimental Section

Solvents and reagents were purified by drying over suitable dehydrating agents followed by distillation. Infrared spectra were obtained with KBr plates by a Perkin-Elmer 283 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian EM360-A or General Electric QE-300 spectrometer in CCl_4 or $CDCl_3$ with CH_2Cl_2 or TMS as an internal reference. Gas chromatography–mass spectra of the monomeric silanes were obtained

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[†] Visiting scientist on leave from the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences, Lodz, Poland.

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at 50 eV with a Hewlett-Packard 5988A GC–MS system. The mass spectra of the polymers were recorded by direct pyrolysis methods on a Finnigan TSQ 4500 spectrometer in the Aston laboratories of R. G. Cooks (Purdue University, West Lafayette, IN). UV spectra were recorded with a Hewlett-Packard 8450A spectrometer in a 1.00-cm quartz cuvette in MeOH. Thermal analysis was performed under argon on a Perkin-Elmer DSC7 and TGA7 system interfaced with a PE7500 minicomputer. Gas–liquid chromatography was carried out on a Tracor Model 560 chromatograph in the flame-ionization mode with SE20 or SE30 columns. Elemental analyses were obtained from Midwest Microlab (Indianapolis, IN). The molecular weights of the trimethylsiloxy end-blocked polymers were determined by ^{1}H NMR or exclusion chromatography (Waters R401 differential refractometer and ASI (10^3- and 10^4-Å Styragel columns) with *N*,*N*-dimethylacetamide as a mobile phase at 80 °C and by applying a universal calibration with polystyrene standards.

Synthesis of Monomers. Synthesis of 4-[*N*-[3-(diethoxymethylsilyl)propyl]-*N*-methylamino]pyridine (4a): Compound **4a** was prepared by hydrosilylation of 4-(*N*-methylallylamino)pyridine (8) with diethoxymethylsilane, $(EtO)_2MeSiH$. Compound 8 was obtained by reaction of 4-chloropyridine and *N*-methylallylamine. For example, 4-chloropyridine (11.4 g, 0.10 mol) and *N*-methylallylamine (7.1 g, 0.10 mol) were placed in a glass ampule. The mixture was degassed under vacuum, and the vessel was sealed. The ampule was heated for 3 days at 120 °C. The ampule was then opened, and the contents were dissolved in water and neutralized with 10% aqueous NaOH. The aqueous solution was extracted with several portions of diethyl ether. The ether extracts were combined and filtered. The solvent was evaporated, and the fluid residue was distilled under vacuum to give 8 [11.1 g, 75%; bp 70 °C (0.1 Torr)]. Anal. Calcd: C, 72.97; H, 8.11; N, 18.92. Found: C, 72.18; H, 7.89; N, 18.93. IR (cm^{-1}, intensity, assignment): 1595 s, 1505 s, 1380 s (ring C═C, C═N), 985 s (–C═CH$_2$). ^{1}H NMR (multiplet, *J* (Hz), area, assignment): δ 8.20 (d, 4, 2, H^{2,6}), 6.47 (d, 4, 2, H^{3,5}), 5.78 (m, 3, 1, H$^{CH{=}CH_2}$), 5.16 (q, 5, 2, H$^{CH_2{=}CH}$), 3.95 (d, 5, 2, H$^{CH_2CH{=}CH_2}$), 2.97 (s, 3, 1, H^{NCH_3}). ^{13}C NMR (assignment): δ 153.7 (C^4), 149.9 (C^{2,6}), 131.9 (C$^{CH{=}CH_2}$), 116.5 (C$^{CH_2{=}CH}$), 106.7 (C^{3,5}), 56.7 (C^{NCH_3}), 37.2 (C^{CH_2}). MS (%, ion): *m/e* 148 (62, M$^{+\bullet}$), 147 (30, (M – 1)$^+$), 133 (26, (M – 15)$^+$), 121 (100, (M – 27)$^+$), 78 (22, Py$^+$). Compound 8 (4.45 g, 0.030 mol), $MeSiH(OEt)_2$ (6.7 g, 0.050 mol), and H_2PtCl_6 (60 μL, 0.080 mol/L in *i*-PrOH; 4.8 × 10^{-6} mol) were combined and heated under vacuum in a sealed vessel for 10 h at 130 °C. The vessel was opened, and the products were removed and distilled to give compound **4a** as a colorless liquid [6.3 g, 74%; bp 122–127 °C (0.05 Torr)]. Anal. Calcd: C, 59.6; H, 9.22; N, 9.93. Found: C, 58.8; H, 9.09; N, 9.78. IR (cm^{-1}, intensity, assignment): 1595 s, 1510 m, 1390 m (ring C═C, C═N); 1255 s, (SiCH$_3$); 1100 s, 1075 s, 980 m, 950 m (SiOEt); 800 br, 760 m (ring CH). ^{1}H NMR (multiplet, *J* (Hz), area, assignment): δ 8.19 (d, 4, 2, H^{2,6}), 6.45 (d, 4, 2, H^{3,5}), 3.72 (q, 6, 4, H^{OCH_2}), 3.30 (t, 6, 2, H^{NCH_2}), 2.93 (s, 3, H^{NCH_3}), 1.63 (m, 6, 2, H^{CH_2}), 1.19 (t, 6, 6, H^{CH_3}), 0.50 (t, 6, 2, H^{SiCH_2}), 0.10 (s, 3, H^{SiCH_3}). ^{13}C NMR (assignment): δ 153.3, (C^4), 149.8 (C^{2,6}), 106.4 (C^{3,5}), 58.1 (C^{OCH_2}), 54.1 (C^{NCH_2}), 37.4 (C^{NCH_3}), 20.0 (C^{CH_2}), 18.4 (C^{CH_3}), 11.0, C^{SiCH_2}), –4.9 (C^{SiCH_3}). MS (%, ion): *m/e* 282 (4, M$^{+\bullet}$), 237 (2, (M – 45)$^+$), 133 (5, $(CH_3)(OEt)_2Si^+$), 121 (100, 4-PyN(CH$_3$)(CH$_2$)$^+$).

Synthesis of 4-[*N*-[3-(triethoxysilyl)propyl]-*N*-methylamino]pyridine (4b): In a similar manner, compound **4b** was prepared and characterized [40%; bp 135–140 °C (0.05 Torr)]. Anal. Calcd: C, 57.7; H, 8.97; N, 8.97. Found: C, 57.3; H, 9.10; N, 8.87. IR (cm^{-1}, intensity, assignment): 1595 s, 1510 m, 1390 m (ring C═C, C═N); 1100 s, 1075 s, 980 m, 950 m (OEt); 800 br, 750 m (ring CH). ^{1}H NMR (multiplet, *J* (Hz), area, assignment): δ 8.16 (d, 4, 2, H^{2,6}), 6.42 (d, 4, 2, H^{3,5}), 3.78 (q, 6, 6, H^{OCH_2}), 3.25 (t, 6, 2, H^{NCH_2}), 2.9 (s, 3, H^{NCH_3}), 1.64 (m, 6, 2, H^{CH_2}), 1.18 (t, 6, 9, H^{CH_3}), 0.55 (t, 6, 2, H^{SiCH_2}). ^{13}C NMR (assignment): δ 153.5, (C^4), 149.7 (C^{2,6}), 106.4 (C^{3,5}), 58.4 (C^{CH_3}), 53.8 (C^{NCH_2}), 37.3 (C^{NCH_3}), 19.9 (C^{CH_2}), 18.2 (C^{CH_3}), 7.41 (C^{SiCH_2}). MS (% ion): *m/e* 312 (3, M$^{+\bullet}$), 267 (2, (M – 45)$^+$), 163 (2, $(EtO)_3Si^+$), 121 (100, 4-PyN(CH$_3$)(CH$_2$)$^+$).

Synthesis of 4-[*N*,*N*-bis[3-(dimethylethoxysilyl)propyl]amino]pyridine (5a): Compound **5a** was prepared by hydrosilylation of 4-(diallylamino)pyridine (**9**) with dimethylethoxysilane, $(EtO)Me_2SiH$. Compound **9** was obtained by reaction of 4-chloropyridine with diallylamine. Thus, in an experiment similar to that described above, 4-chloropyridine (11.4 g, 0.10 mol) and diallylamine (14.6 g; 0.15 mol) were combined in an ampule, degassed under vacuum, sealed, and heated for 3 days at 130 °C. The product mixture was dissolved in water, neutralized with 10% NaOH, and extracted with several portions of diethyl ether. The ether solution was filtered, the solvent was evaporated, and the residue was distilled to give compound **9** [11.3 g, 65%; bp 92 °C (0.25 Torr)]. Compound **9** (5.2 g, 0.030 mol), $(EtO)Me_2SiH$ (8.3 g, 0.080 mol), and H_2PtCl_6 (60 μL, 0.080 mol/L in *i*-PrOH; 4.6 × 10^{-6} mol) were combined as described above and heated for 10 h at 130 °C. After reaction, the product mixture was distilled under vacuum to give **5a** as a colorless liquid [5.75 g, 50%; bp 142–146 °C (0.05 Torr)]. Anal. Calcd: C, 59.7; H, 9.95; N, 7.33. Found: C, 59.2; H, 10.54; N, 7.16. IR (cm^{-1}, intensity): 1585 s, 1505 m, 1360 m (ring C═C, C═N); 1250 s (SiCH$_3$); 1100 s, 1075 s, 980 m, 965 m (SiOEt); 830 br, 800 (ring CH). ^{1}H NMR (multiplet, *J* (Hz), area, assignment): δ 8.19 (d, 6, 2, H^{2,6}), 6.42 (d, 6, 2, H^{3,5}), 3.65 (6, 4, H^{OCH_2}), 3.26 (t, 6, 4, H^{NCH_2}), 1.61 (m, 6, 4, H^{CH_2}), 1.18 (t, 6, 6, H^{CH_3}), 0.56 (t, 6, 4, H^{SiCH_2}), 0.11 (s, 12, H^{SiCH_3}). ^{13}C NMR (assignment): δ 152.3 (C^4), 149.9 (C^{2,6}), 106.3 (C^{3,5}), 58.3 (C^{OCH_3}), 57.1 (N^{CH_2}), 20.7 (C^{CH_2}), 18.5 (C^{CH_3}), 13.5 (C^{SiCH_2}), –2.1 (C^{SiCH_3}). MS (%, ion): *m/e* 382 (7, M$^{+\bullet}$), 367 (1, (M – 15)$^+$), 337 (1, (M – 45)$^+$), 251 (58, PyN[(CH$_2$)$_3$Si(CH$_3$)$_2$(OEt)](CH$_2$)$^+$), 207 (60, PyN[(CH$_2$)$_3$Si(CH$_3$)$_2$H](CH$_2$)$^+$), 103 (100, $(CH_3)_2(OEt)Si^+$), 75 (48, $(CH_3)_2(OH)Si^+$), 59 (14, $(CH_3)_2HSi^+$).

Synthesis of 4-[*N*,*N*-bis[3-(methyldiethoxysilyl)propyl]amino]pyridine (5b) and 4-[*N*,*N*-bis[3-(triethoxysilyl)propyl]amino]pyridine (5c): In a similar manner, compounds **5b** and **5c** were prepared and characterized. **5b** [25%; bp 164–165 °C (0.05 Torr)]. Anal. Calcd: C, 57.0; H, 9.50; N, 6.33. Found: C, 56.9; H, 9.65; N, 6.46. IR (cm^{-1}, intensity): 1590 s, 1510 m, 1390 m (ring C═C, C═N); 1255 (SiOEt); 1100 s, 1070 s, 980 m, 945 m (SiOEt); 800 br, 760 m (ring CH). ^{1}H NMR (multiplet, *J* (Hz), area, assignment): δ 8.15 (d, 4, 2, H^{2,6}), 6.43 (d, 4, 2, H^{3,5}), 3.75 (q, 6, 8, H^{OCH_2}), 3.26 (t, 6, 4, H^{NCH_2}), 1.65 (m, 6, 4, H^{CH_2}), 1.20 (t, 6, 12, H^{CH_3}), 0.57 (t, 6, 4, H^{SiCH_2}), 0.11 (s, 6, H^{SiCH_3}. ^{13}C NMR (assignment): δ 152.3 (C^4), 150 (C^{2,6}), 106.3 (C^{3,5}), 58.2 (C^{OCH_2}), 52.8 (C^{NCH_2}), 20.3 (C^{CH_2}), 18.4 (C^{CH_3}), 11.0 (C^{SiCH_2}), –4.9 (C^{SiCH_3}). MS (%, ion): *m/e* 442 (5, M$^{+\bullet}$), 427 (1, (M – 15)$^+$, 281 (60, PyN[(CH$_2$)$_3$Si(EtO)$_2$(CH$_3$)](CH$_2$)$^+$), 237 (78, PyN[(CH$_2$)$_3$Si(OEt)(CH$_3$)(H)](CH$_2$)$^+$), 133 (100, $CH_3(OEt)_2Si^+$), 105 (20, $CH_3(OEt)(OH)Si^+$), 89 (28, $CH_3(OEt)HSi^+$). **5c** [20%; bp 174–180 °C (0.05 Torr)]. Anal. Calcd: C, 55.0; H, 9.16; N, 5.58. Found: C, 54.9; H, 9.27; N, 5.69. IR (cm^{-1}, intensity): 1590 s, 1510 m, 1390 m (ring C═C, C═N); 1100 s, 1075 s, 985 m, 955 s (SiOEt), 800 br (ring CH). ^{1}H NMR (multiplet, *J* (Hz), area, assignment): δ 8.12 (d, 4, 2, H^{2,6}), 6.44 (d, 4, 2, H^{3,5}), 3.79 (q, 6, 12, H^{OCH_2}), 3.24 (t, 6, 4, H^{NCH_2}), 1.66 (m, 6, 4, H^{CH_2}), 1.19 (t, 6, 18, H^{CH_3}), 0.57 (t, 6, 4, H^{SiCH_2}). ^{13}C NMR (assignment): δ 152.5 (C^4), 149.8 (C^{2,6}), 106.3 (C^{3,5}), 58.4 (C^{OCH_2}), 52.4 (C^{NCH_2}), 20.2 (C^{CH_2}), 18.2 (C^{CH_3}), 7.41 (C^{SiCH_2}). MS (%, ion): *m/e* 502 (6, M$^{+\bullet}$), 311 (77, (M – 191)$^+$, 267 (100, (M – 235)$^+$), 163 (58, $(EtO)_3Si^+$), 119 (39, $(EtO)_2HSi^+$).

Synthesis of Polymers. Linear polymer 2: To a magnetically stirred solution of **4a** (1.06 g, 0.0028 mol) diluted with THF/*i*-PrOH (1 mL) in a 25-mL round-bottom flask under a dry inert gas was added H_2O (99 μL, 0.0055 mol) and Me_4NOH (2 μL, 20% in MeOH; 4.4 × 10^{-6} mol). The mixture was stirred for 12 h at room temperature. Volatile materials were removed by heating to 60 °C for 12 h under vacuum. The residue, which is a colorless viscous fluid, was dissolved in CH_2Cl_2 (5 mL) and excess hexamethyldisilazane (or bis(trimethylsilyl)acetamide, BSA) was added. The mixture was stirred at room temperature for 12 h. Volatile materials were removed under vacuum, and the polymeric product was heated under vacuum at 60 °C for 12 h. The temperature was then raised to 140 °C for 20 min. The product (**2**; 0.35 g, 60%) was purified by precipitation three times from CH_2Cl_2 solution with excess hexane and is a pale yellow, viscous fluid. The molecular weight was determined either by end-group analysis with ^{1}H NMR or by exclusion chromatography in *N*,*N*-dimethylacetamide at 80 °C. Regarding the former, the number-average degree of polymerization (M_n) can be obtained from ^{1}H NMR spectra using the equation DP = $9A_{CH_2}/(A_{CH_3} - 1.5A_{CH_2})$, where A_{CH_3} and A_{CH_2} are the integrated areas of the protons of the methyl and methylene groups, respectively, bonded to silicon; M_n(NMR) = 2900. The GPC data indicate a bimodal mass

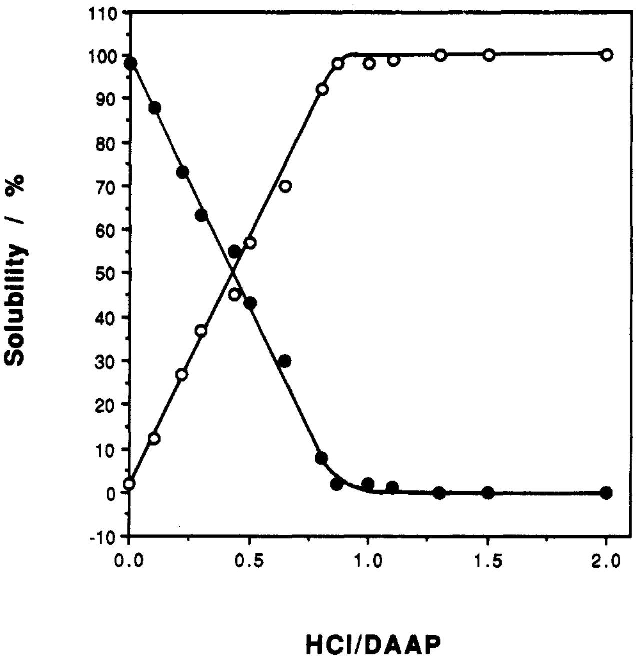


Figure 1. Dependence of solubility on the HCl/DAAP ratio of polymer **2** in a two-phase system containing CH_2Cl_2 (●) and H_2O (○).

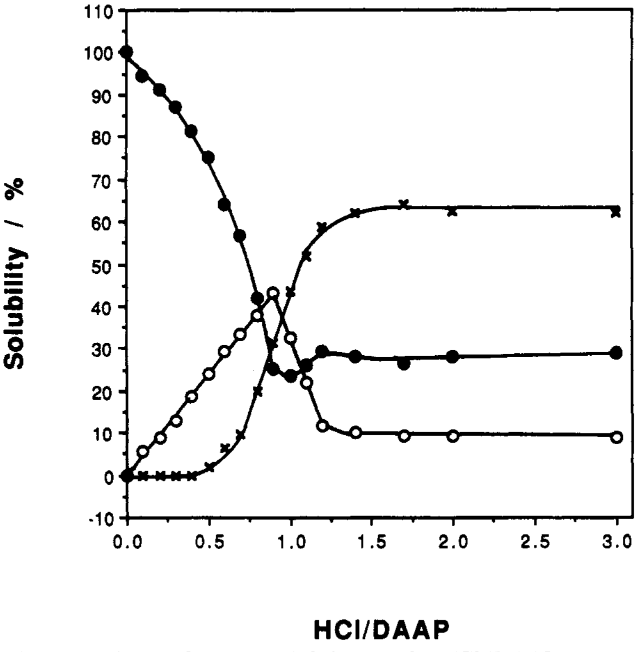


Figure 2. Dependence of solubility on the HCl/DAAP ratio of polymer **3** in a two-phase system containing CH_2Cl_2 (●) and H_2O (○); third phase (×) data from mass balance.

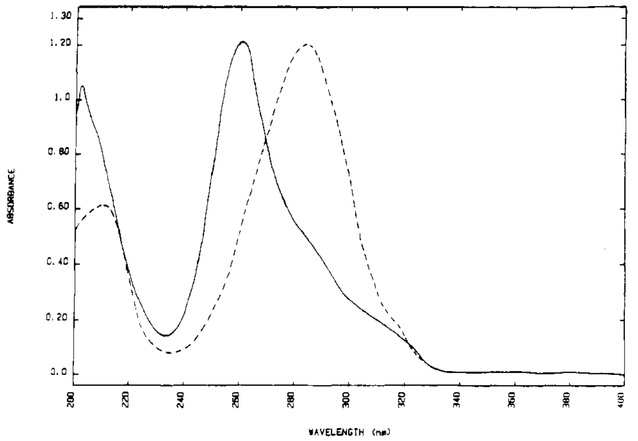


Figure 3. UV spectra of unprotonated polymer **2** sampled from CH_2Cl_2 (—) and fully protonated polymer **2** sampled from H_2O (- -). Concentration of DAAP residues = 7.4 × 10^{-5} mol dm^{-3} in MeOH.

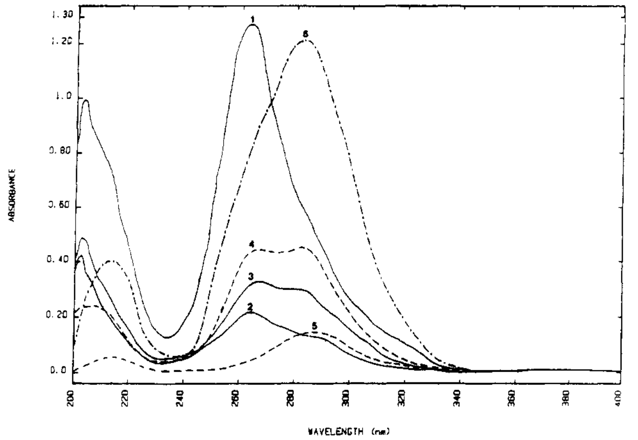
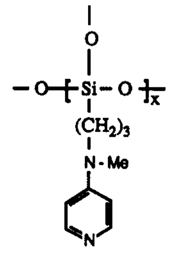


Figure 4. UV spectra of polymer **3** sampled from CH_2Cl_2 (—) [(1) HCl/DAAP = 0; (2) HCl/DAAP = 1; (3) HCl/DAAP = 3] and sampled from H_2O (- -) [(4) HCl/DAAP = 1; (5) HCl/DAAP = 3]. Starting concentration of DAAP residues = 7.4 × 10^{-5} mol dm^{-3}. (6) (- · -) Spectrum of fully protonated material (third phase) in MeOH.

distribution; for peak 1, M_n(GPC) = 2000; for peak 2, M_n = 800. The molecular weight is dependent on the ratio of monomer to catalyst and reaction conditions (i.e., solvent mixture, temperature). Polymer **2** is soluble in CH_2Cl_2, THF, and methanol. Anal. Calcd: C, 56.7; H, 7.94; N, 12.5. Found: C, 55.0; H, 7.68; N, 12.1. IR (cm^{-1}, intensity): 1590 s, 1410 m, 1385 m (ring C=C, C=N), 1255 s ($SiCH_3$), 1070 s, br (SiOSi), 795 br (ring CH). ^1H NMR (multiplet, area, assignment): δ 8.17 (m, 2, $H^{2,6}$), 6.42 (m, 2, $H^{3,5}$), 3.22 (m, 2, H^{NCH_2}), 2.95 (m, 3, H^{NCH_3}), 1.58 (m, 2, H^{CH_2}), 0.45 (m, 2, H^{SiCH_2}), 0.08 (m, 3.5, H^{SiCH_3}). ^{13}C NMR (assignment): δ 154.0 (C^4), 149.8 ($C^{2,6}$), 106.4 ($C^{3,5}$), 54.2 (C^{NCH_2}), 37.5 (C^{NCH_3}), 20.1 (C^{CH_2}), 17.8 (C^{SiCH_2}), 0.00 (C^{SiCH_3}). UV (unprotonated): e_{max}, 17 500; λ_{max}, 262 nm. UV (protonated): λ_{max}, 282 nm. T_d(TGA): 375 °C (10% residue at 600 °C).

Linear polymer 3: In an experiment similar to that described above, monomer **5a** (0.85 g, 0.0030 mol) was dissolved in THF/*i*-PrOH (1 mL). H_2O (108 μL, 0.0060 mol) and Me_4NOH (2 μL, 20% in MeOH; 4.4 × 10^{-6} mol) were added, and the mixture was stirred for 12 h at room temperature. Volatile materials were removed by heating under vacuum at 60 °C for 12 h. The resulting viscous fluid was dissolved in CH_2Cl_2, and hexamethyldisilazane (1 mL) was added. The mixture was stirred for 8 h, and then the volatile materials were removed under vacuum at 60 °C for 12 h. The temperature was raised to 140 °C for 20 min. The product was purified by precipitation from CH_2Cl_2 solution with excess hexane. The pale yellow, viscous product (**3**; 0.83 g, 90%) has a molecular weight dependent on the ratio of monomer to catalyst and reaction conditions. The number-average degree of polymerization can be obtained from ^1H NMR spectra using the equation DP = $4.5A_{CH_2}/(A_{CH_3} - 3A_{CH_2})$, where A_{CH_3} and A_{CH_2} are the integrated areas of the protons of the methyl and methylene groups, respectively, bonded to silicon: M_n(NMR) = 3500, M_n(GPC-monomodal) = 3200, M_w = 6600. Polymer **3** is soluble in CH_2Cl_2, THF, ether, toluene, and methanol. $M_n \cong 3.5 \times 10^3$. Anal. Calcd: C, 57.7; H, 9.19; N, 8.64. Found: C, 57.0; H, 9.10; N, 8.49. IR (cm^{-1}, intensity): 1590 s, 1420 m, 1385 m (ring C=C, C=N); 1255 s ($SiCH_3$); 1070 s, br (SiOSi); 795 br (ring CH). ^1H NMR (multiplet, area, assignment): δ 8.19 (d, 2, $H^{2,6}$), 6.40 (d, 2, $H^{3,5}$), 3.22 (t, 4, H^{NCH_2}), 1.58 (m, 4, H^{CH_2}), 0.49 (t, 4, H^{SiCH_2}), 0.09 (s, 12, H^{CH_3}), ^{13}C NMR (assignment): δ 152.0 (C^4), 149.1 ($C^{2,6}$), 106.0 ($C^{3,5}$), 52.9 (C^{NCH_2}), 20.3 (C^{CH_2}), 15.1 (C^{SiCH_2}), 0.0 (C^{SiCH_3}). UV (unprotonated): e_{max}, 17 300; λ_{max}, 262 nm. UV (protonated): λ_{max}, 284 nm. T_d(TGA): 427 °C (3% residue at 600 °C).

Cross-linked polymers: Monomers **4b**, **5b**, and **5c** were each hydrolyzed in THF/*i*-PrOH/H_2O solvent media for 12 h at 60 °C with catalytic amounts of Me_4NOH in a manner similar to that described above. Volatile materials were removed under vacuum at 90 °C for 12 h. The polymeric residue was then heated at 110 °C for 6 h. The products (**6**, **7a**, and **7b**, respectively) are yellow-brown solids. Polymer **6** is soluble in MeOH and CH_2Cl_2. Anal. Calcd: C, 52.4; H, 7.11; N, 12.0. Found: C, 50.5; H, 6.60; N, 11.5. IR (cm^{-1}, intensity): 3200 br (SiOH); 1590 s, 1420 m (ring C=C, C=N) 1390 m (NCH_3); 1100 br (SiOSi). ^{1}H NMR (multiplet, area, assignment): δ 8.18 (br s, 2, $H^{2,6}$), 6.40 (br s, 2, $H^{3,5}$), 3.22 (br s, 2, H^{NCH_2}), 2.90 (br s, 3, H^{CH_3}), 1.50 (br s, 2, H^{CH_2}), 0.55 (br s, 2, H^{CH_2}), 0.05 (s, 1, H^{SiCH_3}). T_d(TGA): 423 °C (38% residue at 600 °C). Polymer **7a** is insoluble in common organic solvents. Anal. Calcd: C, 53.1; H, 7.48; N, 9.52. Found: C, 51.9; H, 7.66; N, 8.62. IR (cm^{-1}, intensity): 3300–3000 br (SiOH); 1590 s, 1410 m (ring C=C, C=N); 1250 m ($SiCH_3$); 1000–1050 br s (SiOSi). T_d(TGA): 460 °C (54% residue at 600 °C). Polymer **7b** is insoluble in common organic solvents. Anal. Calcd: C, 47.1; H, 5.71; N, 10.0. Found: C, 39.0; H, 6.27; N, 7.59. IR (cm^{-1}, intensity): 3300–3000 br (SiOH); 1590 s, 1420 m (ring C=C, C=N); 1250 m ($SiCH_3$); 1050–1100 br s (SiOSi). T_d(TGA): 486 °C (47% residue at 600 °C).



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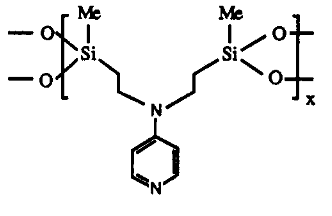
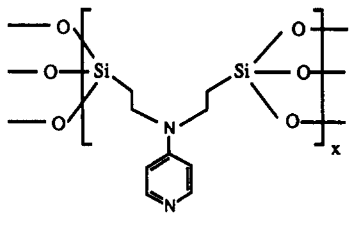


7a



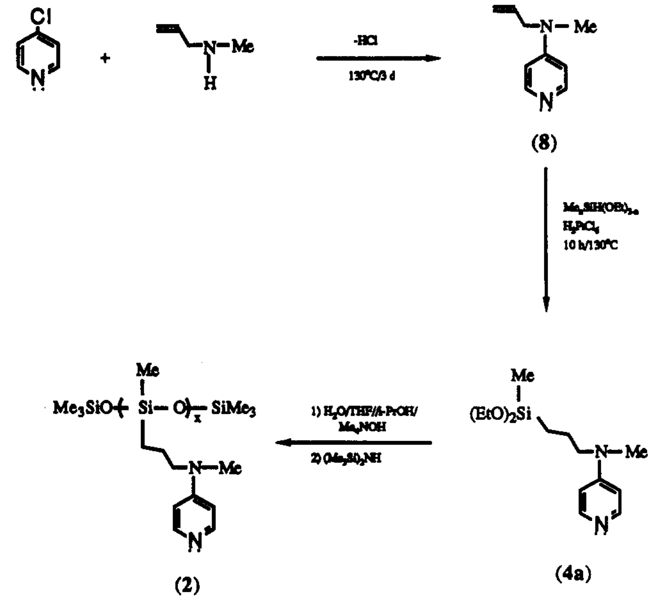
7b

Solubility Studies of Linear Polymers. Solubility studies of linear polymers **2** and **3** were carried out in a two-phase system composed of CH_2Cl_2 and H_2O. For example, 1.0 mL of 0.10 M solution of the polymer in CH_2Cl_2 was combined with an equal volume of water. The mixture was stirred vigorously for 10 min. When the stirring was stopped, the suspension separated into component layers by centrifugation at 10 000 rpm for 15 min. Each layer was sampled with a syringe, and the concentration of the polymer in each phase was determined by UV spectroscopy (i.e., monitored at 262 nm for the unprotonated polymer and 284 nm for the protonated polymer). The dependence of water solubility on the degree of polymer protonation was determined in the same fashion by titration with 0.50 M HCl(aq). After addition of 1.5 equiv (based on DAAP residues) of acid, a fluid third phase appeared at the CH_2Cl_2/H_2O interphase. On standing at ambient temperature for 3 weeks, the third phase becomes gelatinous. The gelatinous material was isolated by separately withdrawing the aqueous and organic phases with a syringe. The results for polymers **2** and **3** are summarized in Figures 1–4.

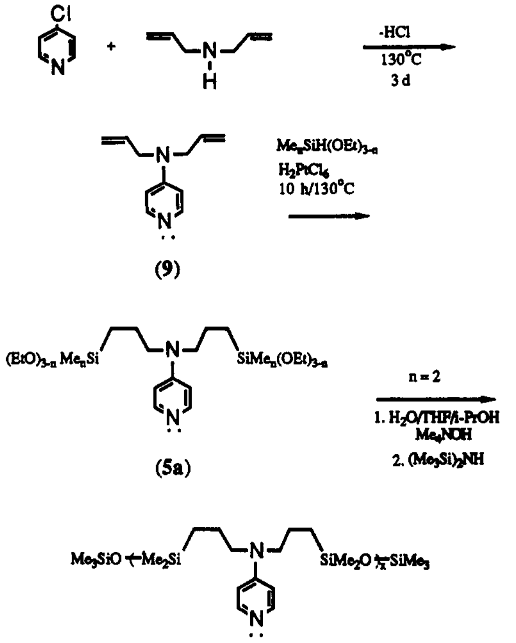
Results and Discussion

Monomers **4a,b** and **5a–c** were prepared by hydrosilylation of compounds **8** and **9** with $Me_nSiH(OR)_{3-n}$. Compounds **8** and **9** were obtained by reaction of 4-chloropyridine with the corresponding allylamine (Schemes I and II).[23] Hydrosilylation was carried out under vacuum in a sealed ampule at 130 °C for at least 10 h, with chloroplatinic acid as a catalyst. When R is Me, both α and β products are obtained; however, when R is Et, only the less sterically hindered β isomer is found. Although the yield of **4a** and **5a** is relatively good (74% and 50%, respectively), only modest to poor yields of **4b** (40%) and **5b,c** (25%, 20%) were obtained. The boiling points of the latter species are very high. Low yields in the latter cases appear to be a result of lower reactivity of the silanes, difficulty in separating mono- from dihydrosilylation product, and thermal decomposition of the high-boiling monomeric products during purification by distillation. All the monomers were colorless or pale yellow liquids and soluble in aliphatic, aromatic, and halogenated hydrocarbons, alcohols, and ethers.

Scheme I



Scheme II



The compositions of monomers **4a,b** and **5a–c** were confirmed by elemental analyses. Infrared spectra of all the monomers exhibit absorptions that are characteristic of assigned structures; i.e., heterocyclic ring bands at 1380–1600 and 700–800 cm^{-1}, SiOC mode at 1000–1200 cm^{-1}, and a sharp MeSi band at 1250–1255 cm^{-1}.[24]

^{1}H and ^{13}C NMR spectra of the monomers are consistent with the structural assignments. The protons of methyl groups attached to silicon appear as a sharp singlet at

0.10–0.11 ppm. The ethoxy group protons exhibit a normal quartet/triplet pattern at 1.18–1.20 and 3.72–3.80 ppm, respectively. The chemical shifts, assignments, and coupling constants in the region 3.6–0.5 ppm for the three methylene group protons indicate that only the less sterically hindered product is formed. The proton of the methyl group attached to nitrogen is a sharp singlet at 2.9 ppm, and the pattern of resonances attributed to the pyridine ring is typical for 4-DAAP compounds (i.e., an A_2B_2 coupling). In the ^{13}C NMR spectra, methyl carbon bonded to silicon is slightly upfield from TMS. Replacement of methyl with ethoxy groups further increases the chemical shift. A similar effect is noted for CH_2 bonded to Si, which appears at 7.4–13.5 ppm. The remaining resonances (CH_2's, ethoxy, and pyridine carbons) appear at expected positions.

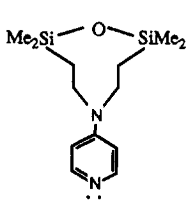
The mass spectra of **4a** and **4b** indicate small molecular ions (m/e 282 (4%), m/e 312 (3%), respectively). Contrary to most Me–Si bonded silanes,[25] monomer **4a** has a very small $(M - Me)^+$ ion (m/e 267 (0.4%)). The dominant ion from both monomers results from C–C bond fragmentation of the propylene spacer group with the resonance-stabilized 4-aminopyridinyl species, $NC_5H_4N(Me)(CH_2)^+$ (m/e 121 (100%), rather than the silicon species carrying the ion current. Compounds **5a–c** also give small molecular ions (m/e 382 (7%), m/e 442 (5%), m/e 502 (6%), respectively) and, where the Me–Si group is present, a very small $(M - Me)^+$ ion. The fragmentation pattern of **5a–c** is considerably more complex. For example, for **5a** and **5b**, the silicon species carry most of the ion current (i.e., $Me_2Si(OEt)^+$ and $MeSi(OEt)_2^+$, respectively). The mass spectrum of **5c**, on the other hand, gives rise to numerous fragments from both simple C–C (m/e 267; $PyN[(CH_2)_3Si(OEt)_2H]CH_2^+$; 100%) and Si–C bond scission (m/e 163, $(EtO)_3Si^+$, 58%).

Difunctional monomers **4a** and **5a** were converted to the linear homopolymers (**2** and **3**, Schemes I and II, respectively) by base-catalyzed hydrolytic polycondensation reaction in a THF/i-PrOH/H_2O solvent mixture at ambient temperature using methods described in the literature.[22] ^1H NMR spectra of the polymers verified the absence of residual SiOEt groups. The resulting hydroxyl-terminated polymers are colorless viscous fluids that were end-blocked with either $(Me_3Si)_2NH$ or bis(trimethylsilyl)acetamide (BSA) to give a pale yellow, viscous fluid product soluble in chlorinated hydrocarbons, THF, and alcohols but insoluble in water. The number-average molecular weight (M_n) of polymers **2** and **3** was determined by ^1H NMR end-group analysis and exclusion chromatography. GPC analysis of **2** indicates a bimodal mass distribution ($M_n(a) \cong 2000$, $M_n(b) \cong 800$), which probably arises from the formation of both linear and cyclic ($M_n \cong 800$) siloxanes. Hydrolysis of monomers with bulky pendant groups is well-known to afford principally cyclic oligomers.[26] These data are consistent with NMR results, which, because of the presence of cyclic materials, are expected to give an inflated value of molecular weight (viz., $M_n \cong 2900$). The GPC data of polymer **3** are monomodal with $M_n = 3200$, $M_w = 6600$, and $\rho = 2.1$. The ^1H NMR data ($M_n = 3500$) are in excellent agreement with chromatography and suggest insignificant quantities of cyclic material.

In addition to linear polymers, a variety of cross-linked homopolymers were obtained by hydrolytic polycondensation of polyfunctional **4b**, **5b**, or **5c**. The cross-linked polymers from **5b** (**7a**) and **5c** (**7b**) are insoluble resins, whereas the material from **4b** (**6**) is soluble in MeOH and CH_2Cl_2. This suggests that the latter may have either a ladderlike structure comparable to the sesquisiloxanes,[27] which are obtained by hydrolysis of trifunctional silanes, or a drumlike structure, which is obtained by condensation of organostannoic acid with a carboxylic acid,[28] or it may be a low molecular weight oligomer.

The polymers were characterized by IR, ^1H and ^{13}C NMR, and UV spectra, as well as elemental analysis, thermal analysis, and thermodegradative mass spectra. The IR spectra of **2** and **3** are similar to their respective monomers with the addition of a new strong band in the 1050–1100-cm^{-1} region, which is attributed to the SiOSi stretching vibration in siloxanes.[24] The ^1H NMR spectra of both polymers exhibit broad unresolved signals in the aromatic and aliphatic regions. Broad lines are consistent with magnetic nonequivalence of the pyridine, methylene, and methyl protons resulting from a mixture of triad and higher assembly tacticities. The ^{13}C NMR spectra of **2** and **3** have signals corresponding to all the assignable carbons present in the monomer species.

Both linear polymers thermally decompose (TGA) at about 430 °C. Polymer **2** leaves a small residue (<10%) at 900 °C; however, polymer **3** degrades completely. The combination of a low residue fraction and a smooth appearance of the TGA curve of **3** suggests that the weight loss occurs by depolymerization to volatile components, presumably cyclic oligomers, as is observed for poly(dimethylsiloxanes).[29] Polymers **2** and **3** are more thermally stable than poly[(diallylamino)pyridine], which exhibits a 20% weight loss at 200–300 °C.[14] In order to determine the nature of the decomposition products, both polymers were studied by direct-pyrolysis mass spectrometry.[30] For example, thermolysis of **2** at 800 °C in the spectrometer exhibits mainly a trimeric species (m/e 624 (22%)), along with principal fragment ions corresponding to [tetramer-121]$^+$ (m/e 711 (33%)), [trimer-121]$^+$ (m/e 503 (100%)), and $[(CH_2)(CH_3)NC_5H_4N]^+$ (m/e 121 (49%)) ions, the latter, presumably, resulting from C–C bond scission. Polymer **3** is remarkably stable for a species that contains bis(trimethylene)amine units in the backbone. The mass spectrum of **3** upon thermolysis reveals fragments corresponding to the cyclic monomer ion (m/e 308 (27%)), as well as ions due to [dimer+1], [dimer−1] (**10**; m/e 617, 615 (100%), respectively), and trimer (**11**; m/e 924 (<5%)).



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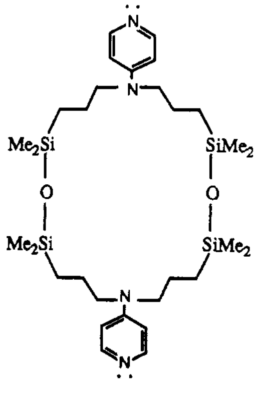

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The two homopolymers differ significantly in their distribution between immiscible solvents, CH_2Cl_2 and H_2O, when titrated with hydrochloric acid (Figures 1 and 2). For example, polymer **2** ($M_n \sim 2000$) is soluble in CH_2Cl_2 and partitions only slightly (<5%) into the aqueous phase (pH = 7). However, the solubility in water is directly proportional to the number of pendant DAAP residues that are protonated on titration with HCl(aq) (Figures 1 and 3). This is consistent with the conversion of the organic soluble strong base to its water-soluble conjugate acid. Polymer **3** ($M_n \sim 3500$), which has DAAP and hydrocarbon segments along the polymer backbone, is soluble in CH_2Cl_2 and insoluble in water. Upon treatment with aqueous HCl (Figure 2), the solubility of polymer **3** in CH_2Cl_2 goes through a minimum of about 22% at a HCl/DAAP ratio of 1.0 with only a small portion of the base residues protonated (Figure 4). With additional acid (i.e., up to 3.0 equiv) the solubility in the organic phase increases to about 28% with more than half the DAAP residues protonated. Concomitantly, the solubility in the aqueous phase increases, with the degree of protonation reaching a maximum at 1.0 equiv of added acid. At this point only 45% of the polymer is in the aqueous phase, and, in contrast to polymer **2**, approximately half of the DAAP residues are protonated. Interestingly, with additional acid (up to 3.0 equiv), the solubility in water decreases to about 10%. It is noteworthy that, upon addition of more than 1 equiv of acid, a third phase separates at the CH_2Cl_2/H_2O interphase. The third phase becomes gelatinous on standing at room temperature for 3 weeks. The UV spectrum of the isolated third-phase material, which is soluble in methanol, indicates partial protonation of the DAAP residues. Partial protonation is also observed for the aged gelatinous material, which does not completely dissolve in methanol.

The unusual pH-solubility behavior of polymer **3** may be explained by structural changes of the chain resulting from protonation. For example, in organic solvent the neutral polymer probably has a random orientation of aminopyridyl functions. At low degree of protonation **3** is still soluble in the CH_2Cl_2. In order to stabilize charge in low dielectric medium, an interaction between protonated and unprotonated DAAP residues (viz., hydrogen bonding) occurs. The macromolecule assumes a conformation with a hydrophobic surface and a hydrophilic core where the charged moieties reside. As the degree of protonation increases, electrostatic forces on **3** become appreciable, and water solubility increases; i.e., the macromolecule undergoes a conformational inversion to a hydrophilic surface and hydrophobic core. At high degree of protonation, the charge density becomes considerable and the molecule extends into a rodlike structure having a lipophilic backbone interspersed with hydrophilic groups. Macromolecules of this type have a tendency to self-associate as micelles, bilayers, etc.,[31] which may be the reason for the appearance of the third phase. The gelatinous material may be a result of cross-linking arising from interchain hydrogen-bonding interactions between protonated and unprotonated DAAP residues and/or interchain chloride ion bridging between protonated residues. A detailed investigation of this fascinating and unusual phenomenon is worthy of further investigation since it appears related to the pH-dependent changes in conformation or aggregation and could provide a measure of control over surfactant and catalytic activity of these materials. Significantly, addition of aqueous NaOH completely solubilizes the gel in the organic solvent, thus demonstrating that this is a reversible phenomenon.

Work is currently underway to prepare linear and less densely cross-linked copolymers with different solubility, film (membrane), and swellability characteristics for examination of solubility properties and effectiveness in a variety of other transacylation reactions. Attention will be directed to the influence of polymer backbone (vinyl vs siloxane), mode of DAAP attachment (pendant vs intrachain), and microstructural constraints on solubility and catalytic activity.

Acknowledgment. Support for this work came from the Office of Naval Research. We thank the National Science Foundation for financial support enabling the purchase of the thermal analysis equipment (Grant CHE84-10776) and Prof. R. G. Cooks (Purdue University, West Lafayette, IN) for the mass spectra and interpretation of the data.

References and Notes

(1) Hofle, G.; Steglich, W.; Vorbrungen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.

(2) Scriven, E. *Chem. Soc. Rev.* **1983**, *12*, 129.

(3) (a) Kirichenko, A. I.; Litvinenko, L. M.; Dotsenko, I. N.; Kotenko, N. G.; Nikkel'sen, E.; Berrestetskaya, V. D. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1979**, *101*, 6020. (b) Litvinenko, L. M.; Savelova, V. A.; Solomoichenko, T. N.; Zaslavskii, V. G.; Ved, T. V. *Org. React. (Tartu)* **1986**, *22*, 162.

(4) Steglich, W.; Hofle, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 981.

(5) Rubinsztajn, S.; Cypryk, M.; Chojnowski, J. *J. Organomet. Chem.* **1989**, *367*, 27.

(6) Cypryk, M.; Rubinsztajn, S.; Chojnowski, J. *J. Organomet. Chem.* **1989**, *377*, 197.

(7) Kellner, H. A.; Schneiderwind, R. G. K.; Eckert, H.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 577.

(8) Mansson, P.; Westfelt, L. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1509.

(9) (a) Hierl, M. A.; Gamson, E. P.; Klotz, I. M. *J. Am. Chem. Soc.* **1979**, *101*, 6020. (b) Delaney, E. J.; Wood, L. E.; Klotz, I. M. *J. Am. Chem. Soc.* **1982**, *104*, 799. (c) Klotz, I. M.; Massil, S. E.; Wood, L. E. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 575.

(10) Shinkai, S.; Tsuji, H.; Hara, Y.; Manabe, O. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 631.

(11) (a) Tomoi, M.; Akada, Y.; Kakiuchi, H. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 537. (b) Tomoi, M.; Goto, M.; Kakiuchi, H.; Noguchi, Y. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 397. (c) Tomoi, M.; Goto, M.; Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 77. (d) Tomoi, M.; Arita, Y.; Kakiuchi, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2455. (e) Tomoi, M.; Ishigaki, S.; Arita, Y.; Kakiuchi, H. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2251.

(12) (a) Guendouz, F.; Jacquier, R.; Verducci, J. *Tetrahedron Lett.* **1984**, *25*, 4521. (b) Guendouz, F.; Jacquier, R.; Verducci, J. *Tetrahedron* **1988**, *44*, 7095.

(13) (a) Verlaan, J. P.; Alferink, P. J. T.; Challa, G. *J. Mol. Catal.* **1984**, *24*, 235. (b) Koning, C. E.; Eshuis, J. J. W.; Viersen, F. J.; Challa, G. *React. Polym.* **1986**, *4*, 293. (c) Koning, C.; Jongsma, T.; Brinkhuis, R.; Challa, G. *React. Polym., Ion Exch., Sorbents* **1988**, *9*, 19. (d) Koning, C.; Viersen, F.; Challa, G.; Reedijk, J. *J. Mol. Catal.* **1988**, *44*, 245.

(14) (a) Mathias, L. J.; Vaidya, R. A.; Bloodworth, R. H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 289. (b) Mathias, L. J.; Vaidya, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 1093. (c) Vaidya, R. A.; Mathias, L. J. *J. Am. Chem. Soc.* **1986**, *108*, 5514.

(15) Menger, F. M.; McCann, D. J. *J. Org. Chem.* **1985**, *50*, 3928.

(16) (a) Narang, S. C.; Remharack, R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 147. (b) Narang, S. C.; Ventura, S.; Ramharack, R. In *Chemical Reactions on Polymers*; ACS Symposium Series 364; Benham, J., Kinstle, J., Eds.; American Chemical Society: Washington, DC, 1988; pp 72–84.

(17) Shai, Y.; Jacobson, K. A.; Patchorik, A. *J. Am. Chem. Soc.* **1985**, *107*, 4249.

(18) Storck, W.; Manecke, G. *J. Mol. Catal.* **1985**, *30*, 145.

(19) (a) Frechet, J. M. J.; Deratani, A.; Darling, G. D.; Lecavalier, P.; Li, N. H. *Macromol. Chem. Symp.* **1986**, *1*, 91. (b) Deratani, A.; Darling, G. D.; Horac, D.; Frechet, J. M. J. *Macromolecules* **1987**, *20*, 767.

(20) Frechet, J. M. J.; Darling, G. D.; Hsuno, S.; Lu, P.-Z.; Vivas de Meftahi, M.; Rolls, W. A., Jr. *Pure Appl. Chem.* **1988**, *60*, 353.

(21) Mark, J. E. In *Silicon-Based Polymers*; Advances in Chemistry Series 224; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990; Chapter 2.

(22) Rubinsztajn, S; Zeldin, M.; Fife, W. K. *Macromolecules* **1990**, *23*, 4026.

(23) Pentimalli, L. *Gazz. Chim. Ital.* **1964**, *94*, 902.

(24) Launer, P. J. In *Silicon Compounds Register and Review*; Petrarch Systems: Bristol, PA, 1987; pp 69–72.

(25) Litzow, M. R.; Spalding, T. R. *Mass Spectrometry of Inorganic and Organometallic Compounds*; Elsevier Scientific Publishing Co.: Amsterdam, The Netherlands, 1973.
(26) Voronkov, M. G.; Mileshkevich, V. P.; Yuzheleveskii, Yu. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978; Chapter 3.
(27) Helminiak, T. E.; Berry, G. C. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 107.
(28) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Schmid, C. G.; Swamy, K. C. K.; Holmes, J. M. In *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington, DC, 1989; Chapter 38.
(29) Zeldin, M.; Kang, D.; Rajaendran, G. P.; Qian, B.; Choi, S. J. *Sci. Total Environ.* **1988**, *73*, 71.
(30) Cooks, R. G.; Majumdar, T. K., private communication. See: Kaiser, R. E., Jr.; Louris, J. N.; Amy, J. W.; Cooks, R. G. *Rapid. Commun. Mass Spectrom.* **1989**, *3*, 225.
(31) Dubin, P., Ed. *Microdomains in Polymer Solutions*; Plenum Press: New York, 1985.

Registry No. **4a**, 128823-43-8; **4b**, 128823-45-0; **5a**, 128823-46-1; **5b**, 128823-47-2; **5c**, 128823-48-3; **8**, 128823-44-9; **9**, 97464-44-3; diethoxy(methyl)silane, 2031-62-1; 4-chloropyridine, 626-61-9; *N*-methylallylamine, 627-37-2; dimethyl(ethoxy)silane, 14857-34-2; diallylamine, 124-02-7.