use of a vacuum line, and the nonvolatile components (XII) were subjected to nucleophilic substitution by treatment with a 0.7 M solution (100 mL) (~25% excess) of sodium trifluoroethoxide in tetrahydrofuran. Water was added to remove sodium chloride and precipitate the polymer. The polymer (XIII) was subjected to sublimation conditions at 70 °C/0.1 Torr for 20 h to remove $[NP(OCH_2CF_3)_2]_3$ formed from unpolymerized trimer.[32] The residue (2.24 g, 43%) was then analyzed. Anal. Calcd for $C_4H_4O_2F_6NP$: C, 19.77; H, 1.66; N, 5.76; P, 12.74. Found: C, 20.00; H, 1.47; N, 5.47; P, 13.00. The reduced specific viscosity of a 1% solution in acetone (containing 0.5% Bu_4NBr) was 0.22, and the estimated $\overline{M}_n$ by gel permeation chromatography was 100 000–400 000. By contrast, samples of $[NP(OCH_2CF_3)_2]_n$ prepared from II had reduced specific viscosities of 2.0 or higher, and $\overline{M}_n$ values ranging from 500 000 to 3×10^6.

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References and Notes

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(15) The ^{31}P NMR sign convention used in this paper is the one recently recommended by I.U.P.A.C., i.e., that upfield shifts from H_3PO_4 are reported as negative values and downfield shifts as positive values. This convention is the opposite of the one used in all previous publications from our laboratory and from most other laboratories in North America. The ^{31}P shift ranges given represent values measured in different solvents and in different experiments using the same solvent.

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(17) Concurrent ligand-exchange reactions may also occur, but these were not studied.

(18) The compounds $N_3P_3(OCH_2CF_3)_6$ and $N_3P_3Cl_2(OCH_2CF_3)_4$ were also detected, but these compounds were present as trace impurities in the starting material. The starting material $N_3P_3Cl(OCH_2CF_3)_5$ was also detected.

(19) This parent peak was determined indirectly from the lower molecular weight fragments and the metastable peaks.

(20) Based on the total chlorine and trifluoroethoxy substituent groups present in the initial trimer.

(21) As pointed out by one of the reviewers, the roughly 2:1:1:2 peak ratio of the main peaks in the ^{31}P NMR spectrum of the copolymer would be compatible with a *random* sequencing of AAA and CCC trimer residues, except for the curiously large shift of the presumed AAC peak (at −10.8 ppm) away from the AAA peak at −18.7 ppm. Two explanations for this anomaly seem plausible: (1) The chemical shift for the AAC sequence may be so close to −18.7 that it lies within the base of the AAA peak. The spectra of some polymer samples do, in fact, show a weak peak near −17 ppm. If this explanation is correct, the peak at −10.8 ppm probably represents ligand exchanged units. (2) The polymer may be composed of an AAA-type main chain, with CCC-type branches. If so, sequences of type AAA, CCC, and perhaps CCA′ (at the branch point) would be detectable, but AAC units would not. The branch points would consist of -N=P(N)-(Cl)- (A′) residues, and the chemical shift of such phosphorus atoms may well lie closer to +8.2 ppm than to +18.7 ppm.

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(31) Good microanalysis data for polyphosphazenes are difficult to obtain because of the resistance of these compounds to complete combustion.

(32) Alternatively, the polymer was dissolved in tetrahydrofuran, treated with a tenfold excess of benzene, and centrifuged.

Silicon Phthalocyanine–Siloxane Polymers: Synthesis and ^1H Nuclear Magnetic Resonance Study

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ABSTRACT: The reaction of silicon phthalocyanine (PcSi) disilanols with bis(ureido)dimethylsilane and bis(ureido)siloxanes yields blue PcSi–siloxane polymers of the general formula $[PcSiOSiMePh(OSiMe_2)_nOSiMePhO]$, where Me = methyl, Ph = phenyl, and n = 2 (IV), 3 (V) and 4 (VI). Reactions which lead to polymers V and VI have been studied via ^1H nuclear magnetic resonance spectroscopy. The dominant shielding effect of the Pc ring which causes clear separation of methyl groups in adjacent siloxane chains facilitated this study. Polymers IV and V have been prepared from $PcSi(OSiMePhOH)_2$ and appropriate bis(ureido)siloxanes. Polymer V was considerably more soluble in organic solvents than polymer IV. Polymer V melted at ca. 65–70 °C, while polymer IV softened at ca. 100 °C (T_g?) but did not melt. Molecular weights for IV (1.4×10^4) and V (1.2×10^4) have been estimated from their NMR spectra.

Since the initial synthesis[2] and subsequent development of silicone polymer chemistry there have been a number of reports concerning modified siloxane polymers. Although polymers based on poly(dimethylsiloxane) offer uncommonly good thermal stability, the polymer backbone tends to form a helical structure which facilitates the formation of cyclosiloxanes at elevated temperatures.[3-5] This led to the synthesis of siloxane copolymers containing modified backbones via addition of organic and inorganic groups. Such groups inhibit reversion to cyclics through steric and/or electronic effects and bring about improved thermal stability. To this end, a variety of arylene–siloxane copolymers, e.g., $(-OSi(CH_3)_2-$

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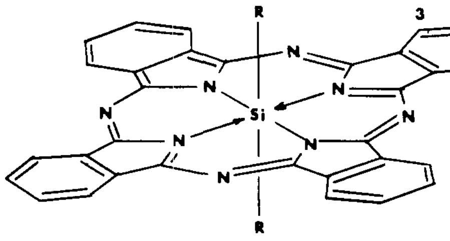


A Silicon Phthalocyanine

Figure 1.

$C_6H_4Si(CH_3)_2OSiR_2-)_x$, were prepared and characterized.[6–8] The extreme thermal stability of carboranes led to the preparation of carborane–siloxane copolymers.[9–12]

Phthalocyanines display a number of interesting properties which would make their incorporation into siloxane polymers of interest. In general, phthalocyanine compounds are noted for their intense colors and high thermal stabilities.[13] In addition, a number of conducting phthalocyanine compounds have recently been reported.[14] Although phthalocyanine compounds are known for their insolubility, several silicon phthalocyanine (PcSi) derivatives (Figure 1) are soluble. We therefore became interested in the synthesis of PcSi monomers for incorporation into siloxane polymers.

This paper reports the synthesis of phthalocyanine–siloxane copolymers from the reaction of appropriate PcSi monomers with bis(ureido)dimethylsilane and bis(ureido)siloxanes. Ureidosilanes were chosen as comonomers due to their successful utilization in the preparation of carborane–siloxane polymers.[11,12] In view of the pronounced shielding effect of the Pc ring,[15–18] ^1H nuclear magnetic resonance (NMR) spectroscopy has been utilized to monitor polymerization reactions and to establish the feasibility of the preparation of tractable phthalocyanine–siloxane polymers.

Experimental Section

General. The IR spectra of all compounds were recorded in KBr pressed pellets on a Perkin-Elmer Model 467 spectrometer. The proton NMR spectra were recorded on a JEOLCO PS-100 spectrometer. Samples were 20–30% solutions by weight in $CDCl_3$ with 1% TMS as internal standard; chemical shifts are reported in ppm vs. Me_4Si (δ). Melting points were determined on a Fisher–Johns apparatus and are uncorrected. The melting points of moisture-sensitive compounds, X–XIII, were determined in sealed capillaries on an Electrothermal melting point apparatus. Elemental analyses were performed by Gailbraith Laboratories, Knoxville, Tenn. Because compounds X–XIII are moisture sensitive, all operations with these compounds were carried out under an atmosphere of dry nitrogen. All solvents and reactants used in this work were dried by standard methods and freshly distilled under nitrogen or under vacuum prior to use. Solution viscosities were obtained in chloroform at 20 °C using a Cannon-Ubbelohde viscometer.

Synthesis. $PcSiCl_2$. This compound was prepared by a modification of the synthesis reported by Kenney et al.[19,20] Silicon tetrachloride (150 g, 0.883 mol) was allowed to react with 1,3-diiminoisoindoline[19] (88 g, 0.607 mol) in 300 mL of tributylamine and 700 mL of tetralin at reflux for 2 h. The purple crystalline product (73.8 g, 0.120 mol, 80% based on 1,3-diiminoisoindoline) was identified as $PcSiCl_2$ by IR and elemental analysis.

$PcSi(OH)_2$. The basic hydrolysis of $PcSiCl_2$ to $PcSi(OH)_2$ was carried out as previously described.[20] In a 2-L flask, $PcSiCl_2$ (44.0 g, 71.7 mmol), NaOH (11 g, 275 mmol), H_2O (1 L), and pyridine (260 mL) were reflexed for 1 h. The product (41.2 g, 71.7 mmol, 100%) was recovered by filtration, washed with water, and dried in vacuo. The compound was identified as $PcSi(OH)_2$ by its IR spectrum and elemental analysis.

$PcSi(OSiMePhOH)_2$ (IB). $PcSi(OH)_2$ (13.50 g, 46.8 mmol) was placed in a 500-mL, three-neck flask along with a magnetic stir bar. The flask was fitted with a serum cap, an inlet for dry nitrogen gas, and a gas outlet tube and bubbler. The flask was then thoroughly purged with dry nitrogen. While a gentle nitrogen purge was maintained, 225 mL of pyridine and 36 mL of tributylamine were added to the flask. Finally, methylphenyldichlorosilane (25 mL, 160 mmol) was injected into the reaction flask with a syringe. A slow nitrogen purge was maintained as the mixture stirred at room temperature for 8 days. The solution was then filtered and the solid obtained was dissolved in 1.2 L of boiling toluene. The hot solution was filtered to remove unreacted $PcSi(OH)_2$. The filtrate was reduced to about 800 mL by continued boiling and finally cooled at 0 °C for 24 h. The product, $PcSi(OSiMePhCl)_2$ (IA), which separated as lustrous dark purple needles (14.93 g, 16.89 mmol, 72.2%) was removed by filtration, washed with 100 mL of dry heptane, and vacuum dried. The melting point of freshly recrystallized IA is 292–3 °C, but the compound is sensitive to atmospheric moisture and will slowly hydrolyze in air (mp after 7 days was 282 °C). The bands in the IR spectrum of IA are: 1611 w, 1523 m, 1475 m, 1430 s, 1337 vs, 1294 s, 1260 m, 1169 m, 1125 vs, 1085 vs, 1045 vs (broad), 915 m, 785 w, 765 m, 735 vs, 700 m, 531 m, 500 m (Si–Cl stretch), 475 w, 427 w. Anal. Calcd for $C_{46}H_{32}N_8O_2Si_3Cl_2$: C, 62.50; H, 3.65. Found: C, 63.58, H, 4.03. Crystals of IA (14.93 g, 16.89 mmol) were placed in a 250-mL flask along with 150 mL of dioxane, 6 mL of pyridine, 6 mL of water, and a magnetic stir bar. After stirring overnight at ambient temperature, the solution was poured slowly into 2.5 L of rapidly stirred water. The blue solid, $PcSi(OSiMePhOH)_2$ (IB), was removed by filtration and dried at 100 °C (14.15 g, 16.70 mmol, 98.9%, mp 380 °C). The bands in the IR spectrum of IB are: 3430 w (broad), 3062 w, 1612 w, 1593 w, 1522 m, 1464 w, 1432 m, 1357 w, 1338 vs, 1296 s, 1262 m, 1173 m, 1128 s, 1052 s, 919 m, 860 w, 768 m, 744 s, 706 w, 578 m, 538 m, 483 w, 432 w, 419 w, 320 vw. Anal. Calcd for $C_{46}H_{34}N_8O_4Si_3$: C, 65.22; H, 4.05; Si, 9.95. Found: C, 65.31; H, 4.18; Si, 10.11.

$PcSi(OSiMePhOSiMe_2OH)_2$ (IIB). Dimethyldichlorosilane (0.28 g, 2.47 mmol), 25 mL of benzene, and 0.5 mL of dry pyridine were placed in a 100-mL, three-neck flask equipped with a nitrogen gas inlet, drying tube outlet, stopper, and magnetic stir bar. With a nitrogen purge, a solid addition tube containing IB ($PcSi(OSiMePhOH)_2$) (1.00 g, 1.18 mmol) was substituted for the stopper. While the solution was being stirred, small amounts of IB were gradually added to the reaction mixture. Preliminary NMR experiments revealed that the reaction between IB and dimethyldichlorosilane in the presence of pyridine is quite rapid. The product of this reaction, $PcSi(OSiMePhOSiMe_2Cl)_2$ (IIA), was observed via NMR spectroscopy (Table I) but the compound was not isolated. After being stirred for 20 min at room temperature, 3 mL of water was added and the mixture was stirred another hour. The reaction mixture was extracted with 50 mL of water, and the organic phase was collected and allowed to evaporate in the hood. The residue was dissolved in 5–10 mL of dichloromethane and added dropwise to 200 mL of stirred ligroin. After the solution had partly evaporated, some solid material precipitated. This solid was removed by filtration and the filtrate was allowed to evaporate slowly over a period of 1–2 days. Small dark purple crystals of $PcSi(OSiMePhOSiMe_2OH)_2$ (IIB) (0.69 g, 0.69 mmol, 58.5%, mp 168–9 °C) were deposited. It should be noted that IIB was difficult to obtain pure due to the presence of side products of similar solubility. The bands in the IR spectrum of IIB are: 3440 w, 3078 w, 2968 w, 2599 w, 1615 w, 1594 w, 1526 s, 1477 m, 1435 s, 1360 m, 1340 vs, 1298 s, 1263 s, 1172 m, 1128 vs, 1087 vs, 1033 vs (broad), 920 m, 885 w, 792 m, 769 m, 740 vs, 707 m, 576 m, 533 m, 479 w, 430 w. Anal. Calcd for $C_{50}H_{46}N_8O_6Si_5$: C, 60.33; H, 4.66; Si, 14.11. Found: C, 60.47; H, 4.70; Si, 13.98.

$PcSi(OSiMePhOSiMe_2OSiMe_3)_2$ (III). A 100-mL, three-neck flask was equipped with a nitrogen gas inlet, a gas outlet tube, a septum, and a magnetic stir bar. Dry IIB (1.00 g, 1.00 mmol) and 50 mL of pyridine were added to the flask under a nitrogen purge. *N,O*-Bis(trimethylsilyl)acetamide (1.0 mL, 2.5 mequiv/mL of pyridine solution) was syringed into the flask. A slow nitrogen purge was maintained as the solution stirred at room temperature for 1 h. The solution was then removed under vacuum and the residue was dissolved in 2 mL of dichloromethane. This solution was chromatographed on a 2 × 30 cm column of Alumina (activity III) using ligroin and a 1:3 solution of ligroin and dichloromethane as eluents. A broad blue band eluted first containing $PcSi(OSiMePhOSiMe_2OSiMe_3)_2$ (III) (0.42 g, 0.37 mmol, 37%, mp 103 °C). The identity of compound III was indicated by NMR spectroscopy (Table I). A second blue band was eluted and shown (NMR) to consist of unreacted and partially reacted IIB. The bands in the IR spectrum of III are: 3420 w (broad), 2968 m, 1614 w, 1523 s, 1477 m, 1435 s, 1358 m, 1340 vs, 1296 s, 1262 vs, 1172 m, 1130 vs, 1087 vs, 1034 vs, 919 m, 850 s, 805 s, 768 m, 745 vs, 576 m, 530 m, 428 w, 364 w. Anal. Calcd for $C_{56}H_{42}N_8O_6Si_7$: C, 59.01; H, 5.48. Found: C, 58.87; H, 5.58.

Table I
^{1}H Chemical Shifts for PcSi Monomers and Polymers (22)

	Pc		Ph(Si$_1$)[a]			Ureido		Methyl			
	3,6	4,5	Para	Meta	Ortho	2,5	3,4	Si$_4$	Si$_3$	Si$_2$	Si$_1$
IA	9.61	8.35	6.71	6.36	4.94						−2.14
IB	9.55	8.27	6.63	6.29	4.87						−2.49
IIA	9.55	8.24	6.69	6.33	4.90					−0.74 −0.80	−2.46
IIB	9.49	8.20	6.68	6.30	4.89					−1.13 −1.14	−2.49
III	9.59	8.23	6.69	6.35	4.98				−0.60	−1.18 −1.20	−2.49
IV	9.20	8.05	6.42	5.93	4.36					−2.08	−3.11
V	9.32	8.11	6.53	6.12	4.61				−1.48	−1.67	−2.86
VI	9.42	8.14	6.56	6.19	4.78				−1.09	−1.45	−2.67
VII[b]	9.43	8.24	*c*	6.16	4.71	2.43	1.39			−1.18	−2.89
VIII	9.42	8.20	*c*	6.21	4.83	2.69	1.42		−0.48	−1.47	−2.60
IX	9.50	8.22	*c*	6.27	4.86	2.85	1.46	−0.12	−0.91	−1.30	−2.59

[a] A first-order splitting pattern of *o*-, *m*-, and *p*-Ph(Si$_1$) protons is observed ($J \sim 7$ Hz). The ortho resonance appears as a doublet, while meta and para resonances are triplets. [b] VII, PcSi(OSiMePhOSiMe$_2$Ur)$_2$, was prepared in situ (CDCl$_3$) from IB and Me$_2$SiUr$_2$ so as to aid in assignment of ^{1}H resonances. [c] Complex multiplet due to Ph(Si$_1$) and ortho, meta, and para protons on the phenylureido group.

Bis(*N*-pyrrolidino-*N*′-phenylureido)dimethylsilane (X). This compound was synthesized in a two-step process.[21] A 5-L, three-neck flask was equipped with a mechanical stirrer, a 250-mL pressure equalizing dropping funnel, and a low-temperature condenser with an outlet to the atmosphere through a drying tube. In place of a stopper, the top of the dropping funnel was fitted with an inlet for dry nitrogen gas. A brisk nitrogen purge of the apparatus was maintained for 30 min before 1.3 L of ethyl ether and 2 mol of butyllithium (2.4 M in hexane) were added to the flask. The flask was cooled in an ice bath and dry ice and acetone were added to the low-temperature condenser. Pyrrolidine (142 g, 2 mol) was placed in the dropping funnel and added dropwise with stirring to the lithio solution. The cooling baths and nitrogen purge were maintained until all the dimethyldichlorosilane had been added. The reaction mixture was allowedto reach room temperature and stirred overnight under nitrogen. Following removal of lithium chloride by filtration under nitrogen the product, bis(pyrrolidinyl)dimethylsilane, was obtained by fractional distillation (153.5 g, 0.774 mol, 77%, bp 105 °C (15.5 mm)). Bis(pyrrolidinyl)dimethylsilane (55.0 g, 0.278 mol) and ethyl ether (150 mL) were placed in a 500-mL flask fitted with a nitrogen gas inlet, a mechanical stirrer, and a dropping funnel with a drying tube gas outlet. A nitrogen purge was maintained throughout the course of the reaction. The flask was cooled with an ice bath and phenyl isocyanate (66.2 g, 0.556 mol) was placed in the dropping funnel and added dropwise to the stirred solution. When addition of the phenyl isocyanate was nearly complete, a white solid began to crystallize. The mixture was allowed to warm slowly to room temperature and stirred overnight. The solid was removed by filtration under nitrogen and dried under vacuum. The product (85.0 g, 0.195 mol, 70%) was recrystallized to constant melting point (107 °C) from dichloromethane–ether. An NMR spectrum of the recrystallized product shows an aromatic multiplet (10 H, Ph) at about δ 7.02, triplet (8 H, Py$_{2,5}$) at 2.90, a triplet (8 H, Py$_{3,4}$) at 1.59, and a sharp singlet (6 H, Si$_1$) at 0.40.[22] From the NMR spectrum, the purity of X is judged to be 95% with the only impurity being the urea, HNPhC(O)NC$_4$H$_8$.

1,3-Bis(*N*-pyrrolidino-*N*′-phenylureido)tetramethyldisiloxane (XI). The intermediate compound in the synthesis of XI (1,3-bis(pyrrolidinyl)tetramethyldisiloxane) (bp 145 °C (21 mm), 60% yield) was prepared by direct reaction of 1,3-(dichloro)tetramethyldisiloxane (Silar) with pyrrolidine in heptane solvent.[23] The NMR spectrum of this colorless liquid intermediate (neat with internal Me$_4$Si) showed a triplet (8 H, Py$_{2,5}$) at δ 2.98, a triplet (8 H, Py$_{3,4}$) at 1.67, and a sharp singlet (12 H, Si$_1$) at 0.04.[22] Following the same procedure described for X above, the addition of phenyl isocyanate to bis(pyrrolidinyl)tetramethyldisiloxane resulted in the formation of the solid, XI (mp 105 °C), in 81% yield. The similar solubilities of XI and urea impurity (identified by NMR as HNPhC(O)NC$_4$H$_8$) made it impossible to obtain XI pure even after several recrystallizations from toluene. The NMR spectrum of XI showed a multiplet (10 H, Ph) at δ 7.10, a triplet (8 H, Py$_{2,5}$) at 2.97, a triplet (8 H, Py$_{3,4}$) at 1.63, and a sharp singlet (12 H, Si$_1$) at 0.08.[22] The NMR spectrum indicated that XI was obtained in 93% purity.

1,5-Bis(*N*-pyrrolidino-*N*′-phenylureido)hexamethyltrisiloxane (XII). Compound XII was synthesized from the corresponding dichlorotrisiloxane (Silar) as described for XI. The intermediate compound 1,5-bis(pyrrolidinyl)hexamethyltrisiloxane, purified by vacuum distillation (bp 170 °C (27 mm)), was obtained as a colorless liquid in 51% yield. The NMR spectrum of this compound (neat liquid with internal Me$_4$Si) showed a triplet (8 H, Py$_{2,5}$) at δ 2.96, a triplet (8 H, Py$_{3,4}$) at 1.65, and two sharp singlets at 0.06 (12 H, Si$_1$) and 0.00 (6 H, Si$_2$). The addition of 2 mol equiv of phenyl isocyanate to the liquid bis(pyrrolidinyl)hexamethyltrisiloxane resulted in the formation of a solid (mp 134 °C, 55% yield), identified as XII by its NMR spectrum: aromatic multiplet (10 H, Ph) at δ 7.26, a triplet (8 H, Py$_{2,5}$) at 3.01, a triplet (8 H, Py$_{3,4}$) at 1.64, and two sharp singlets at 0.27 (12 H, Si$_2$) and −0.32 (6 H, Si$_2$).[22] The product was obtained in 92% purity following a recrystallization from pentane and toluene.

1,7-Bis(*N*-pyrrolidino-*N*′-phenylureido)octamethyltetrasiloxane (XIII). Compound XIII was prepared from the corresponding (dichloro)octamethyltetrasiloxane (Silar) by the procedure described for XI. The intermediate compound, 1,7-bis(pyrrolidinyl)octamethyltetrasiloxane, purified by vacuum distillation (bp 240 °C (13 mm)), was obtained as a colorless liquid in 52% yield. The NMR spectrum of this compound (50% by volume in CDCl$_3$ with internal Me$_4$Si) showed a triplet (8 H, Py$_{2,5}$) at δ 2.98, a triplet (8 H, Py$_{3,4}$) at 1.70, and two sharp singlets at 0.09 (12 H, Si$_1$) and 0.04 (12 H, Si$_2$).[22] The addition of 2 mol equiv of phenyl isocyanate to the liquid bis(pyrrolidinyl)tetrasiloxane resulted in the formation of XIII, which was obtained in 50% yield following vacuum distillation (204 °C (14 mm)). Compound XIII is a viscous oil which slowly solidifies upon standing in vacuo at room temperature. The NMR spectrum of XIII (50% by volume in CDCl$_3$ with internal Me$_4$Si) showed an aromatic multiplet (10 H, Ph) at δ 7.06, two triplets at 3.02 (8 H, Py$_{2,5}$) and 1.63 (8 H, Py$_{3,4}$), and two sharp singlets at 0.31 (12 H, Si$_1$) and −0.17 (12 H, Si$_2$).[22] Like the other bis(ureido)siloxanes, XIII was contaminated by urea (10%).

(PcSiOSiMePh(OSiMe$_2$)$_2$OSiMePhO) (IV). Xylene (100 mL) was distilled under nitrogen into a 200-mL, three-neck flask equipped with a nitrogen gas inlet, a stopper, and a magnetic stir bar. A nitrogen purge was initiated and IB (2.01 g, 2.37 mmol) was added to the flask. One neck of the flask was fitted with a septum while the stopper was replaced by a water-cooled condenser with drying tube gas outlet. Under a nitrogen atmosphere, a solution of XI was prepared by dissolving 1.540 g in 10.00 mL of tetrachloroethane. A calculated stoichiometric amount of this solution (7.88 mL contained 1.214 g or 2.37 mmol of XI) was then injected into the reaction flask. The reaction mixture was heated to reflux and allowed to stir for 1 h. Because the NMR spectrum of XI showed it contained several percent urea impurity eight more increments (0.079 mL, 0.012 g, 0.024 mmol, or about 1% of the stoichimometric amount necessary for complete reaction) of the bis(ureido)siloxane solution were added to the refluxing reaction mixture, one every 30 min. About 30 min following the final addition of XI the reaction mixture was opened to the atmosphere and allowed to cool to room temperature. The product was precipitated slowly by pouring the reaction mixture into 1 L of stirred methanol. The blue solid (1.95 g, 1.99 mmol, 84%, η_{red} 0.10) was filtered and solvent was removed in vacuo. The bands in the infrared spectrum of IV are: 3078 w, 2968 w, 2598 w, 1616 m, 1594 w, 1525 s, 1478 m, 1434 s, 1410 m, 1359 m, 1340 s, 1297 s, 1264 s, 1172 m, 1128 s, 1084–1008 vs (broad), 920 m, 858 m, 810 s, 768 m, 740 s, 706 m, 654 w, 588 m, 545 m, 492 m, 442 m, 328 w. Anal. Calcd for $C_{50}H_{44}N_8O_5Si_5$: C, 61.43; H, 4.56; Si, 14.36. Found: C, 61.17; H, 4.49; N, 11.33; Si, 14.12.

(PcSiOSiMePh(OSiMe$_2$)$_3$OSiMePhO) (V). This polymer was prepared by the reaction of IB and XII in toluene utilizing the procedure described for IV. A typical reaction utilized IB (0.997 g, 1.18 mmol) and XII (0.699 g, 1.19 mmol) and gave 1.05 g of V (1.01 mmol, 86%, η_{red} 0.13). The bands in the IR spectrum of V are: 3078 w, 2968 w, 2598 w, 1614 m, 1594 w, 1524 s, 1477 m, 1433 s, 1413 m, 1359 m, 1338 s, 1296 s, 1263 s, 1172 m, 1128 s, 1083–1005 vs (broad), 918 m, 855 m, 809 s, 768 m, 738 s, 706 m, 588 m, 544 m, 490 m, 440 m, 328 w. Anal. Calcd for $C_{52}H_{50}N_8O_6Si_6$: C, 59.40; H, 4.79; N, 10.66; Si, 16.03. Found: C, 59.69; H, 4.82; N, 10.57; Si, 16.11.

Results and Discussion

Monomer Synthesis. Two new silicon phthalocyanine disilanols, IB and IIB, have been prepared according to Scheme I. PcSi monomers IB and IIB were chosen for study because of their relatively high solubility. IB and IIB are considerably more soluble than the corresponding compounds containing only methyl groups.[20] IIB even shows modest solubility in pentane. IIB is significantly more soluble and hence of greater utility in monitoring reactions via NMR spectroscopy than is IB. Unfortunately, IIB is difficult to purify by fractional crystallization. For these reasons, IIB has been used primarily in NMR studies of the polycondensations where small amounts of comonomers are sufficient. Disilanol IB has been used in the preparative scale polymerization reactions.

Scheme I

$$\mathrm{PcSiCl_2 + 2NaOH \rightarrow PcSi(OH)_2 + 2NaCl} \quad (1a)$$

$$\mathrm{PcSi(OH)_2 + 2MePhSiCl_2 + 2py \rightarrow \underset{IA}{PcSi(OSiMePhCl)_2} + 2pyHCl} \quad (1b)$$

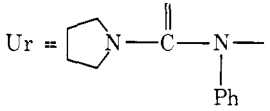
$$\mathrm{IA + 2H_2O \rightarrow \underset{IB}{PcSi(OSiMePhOH)_2} + 2HCl} \quad (1c)$$

$$\mathrm{IB + 2Me_2SiCl_2 + 2py \rightarrow \underset{IIA}{PcSi(OSiMePhOSiMe_2Cl)_2} + 2pyHCl} \quad (1d)$$

$$\mathrm{IIA + 2H_2O \rightarrow \underset{IIB}{PcSi(OSiMePhOSiMe_2OH)_2} + 2HCl} \quad (1e)$$

The bis(ureido)siloxane comonomers were prepared by a method similar to that previously reported[21] for compound X, $Me_2Si(NPhC(O)NC_4H_8)_2$ (see Scheme II). Compounds XI–XIII were synthesized from commercially available dichlorosiloxanes. The separation of bis(ureido)siloxanes from urea by-product $HNPhC(O)NC_4H_8$ proved extremely difficult due to the formation of urea whenever the bis(ureido)siloxane encountered trace amounts of moisture and the similar solubilities of urea and bis(ureido)siloxanes. Although the urea was present as a minor impurity in all of the bis(ureido)siloxane samples used in the disilanol condensation reactions, it was a noninterfering by-product of these reactions and did not appear to affect significantly the polymerization process.

Scheme II



XI, n = 0; XII, n = 1; XIII, n = 2

$$\mathrm{ClSiMe_2(OSiMe_2)_{\it n}OSiMe_2Cl + 4HN(CH_2)_4 \rightarrow [(CH_2)_4NMe_2Si](OSiMe_2)_{\it n}[OSiMe_2N(CH_2)_4] + 2(CH_2)_4NHCl} \quad (2a)$$

$$\mathrm{[(CH_2)_4NMe_2Si](OSiMe_2)_{\it n}[OSiMe_2N(CH_2)_4] + 2PhNCO \rightarrow (UrMe_2Si)(OSiMe_2)_{\it n}(OSiMe_2Ur)} \quad (2b)$$

As comonomers in the polycondensations with disilanols IB and IIB, compounds X–XIII provide a means of preparing PcSi–siloxanes with varying numbers of dimethylsiloxy groups between PcSi rings. The effect of increasing the length of the dimethylsiloxy chain segments on the properties of these PcSi–siloxanes is discussed below.

^{1}H NMR Studies. General. ^{1}H NMR spectroscopy was used extensively in the early stages of this work to monitor the course of the PcSi disilanol–bis(ureido)siloxane condensation reactions. Spectroscopic identification of monomers, intermediates, and products was facilitated as a result of the effective shielding of the Pc ring. The movement of electrons in the planar aromatic Pc macrocycle causes a large shielding effect, resulting in pronounced high-field chemical shift values for protons on R groups adjacent to the Pc ring. Kenney's group has reported in detail on this ring current effect.[15-18] They found that the closer a group is to the PcSi macrocycle, the farther upfield is its chemical shift. Our results confirm these observations. The dominant effect of the PcSi group on proton chemical shifts may be seen in Table I. Si_1Me protons[22] are found to high field ($\delta > -2$); Si_2Me protons are seen close to or above δ −1; Si_3Me protons (exception V) are found close to or less than δ −1.

The NMR spectra of some of the PcSi monomers, intermediates, and polymers reported in this work display another interesting feature, viz., two separate absorptions for the two methyl groups on Si_2. For a given compound, the separation between the two signals varies with the solvent. The peak separations (in Hz) in various solvents for the Si_2Me groups of several PcSi compounds are: IIA, 6 in $CDCl_3$/pyridine, 8 in benzene/pyridine; IIB, 0.5 in CD_2Cl_2, 1 in $CDCl_3$, 4 in CCl_4, 6 in pyridine-d_5; V, 0.5 in $CDCl_3$, 4 in 1,2-dichloroethane; VIII, 0.5 in $CDCl_3$, and 3 in 1,2-dichloroethane. The observed signal separation is due to the presence of an asymmetric center at Si_1 which makes the methyl groups on Si_2 chemically inequivalent. It has been demonstrated[24,25] that an asymmetric center may bring about observable inequivalency in another group even though the two groups may be separated by a bivalent atom such as oxygen. Solvent effects are often observed in such systems. In the PcSi–siloxanes prepared in this study the effect of solvent on the chemical shift of the inequivalent methyl groups on Si_2 is quite marked. The NMR studies of polymerization reactions discussed below were carried out in $CDCl_3$ so that separate resonances for the Si_2Me protons were not observed.

Reaction of PcSi Disilanol IIB with Bis(ureido)silane X. When PcSi disilanol IIB and bis(ureido)silane comonomer X were dissolved in $CDCl_3$ the reaction could be monitored via ^{1}H NMR spectroscopy over a period of hours (Figure 2). Spectra A and B show the SiMe region (δ 1 to −4) for comonomers IIB and X, respectively. Spectrum C was recorded 10 min after addition of 0.5 mol equiv of disilanol IIB to silane X. The absence of peaks for disilanol IIB in this spectrum indicates X has rapidly reacted with IIB. The three new high-field absorptions in 2:2:1 relative intensity are assigned (Table I) to the ureido terminated PcSi species VIII, $PcSi[OSiMePhOSiMe_2OSiMe_2(Ur)]_2$ (Scheme III, eq 3a). The

Scheme III

$$\mathrm{IIB + 2X \rightarrow \underset{VIII}{PcSi(OSiMePhOSiMe_2OSiMe_2Ur)_2} + 2UrH} \quad (3a)$$

$$\mathrm{IB + 2XI \rightarrow VIII} \quad (3b)$$

$$\mathrm{VIII + H_2O \rightarrow PcSi(OSiMePhOSiMe_2OSiMe_2OH)_2 + 2UrH} \quad (3c)$$

$$\mathrm{VIII + IIB \rightarrow \underset{V}{(—PcSiOSiMePh(OSiMe_2)_3OSiMePhO—)_{\it n}} + UrH} \quad (3d)$$

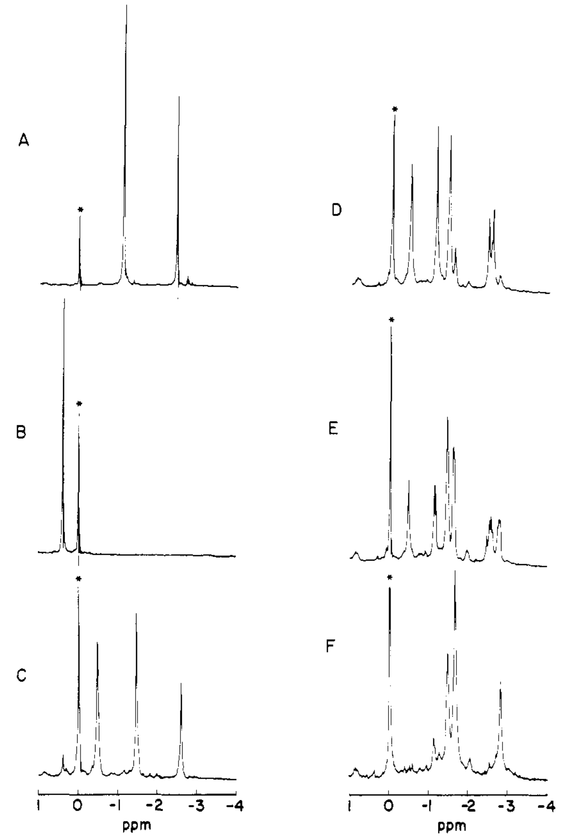


Figure 2. ^1H NMR spectra for disilanol IIB (A), bis(ureido)silane X (B), bis(ureido) intermediate VIII (C), intermediates in the reaction of VIII with IIB (D, E), and PcSi-siloxane polymer V (F).

presence of a small peak at δ 0.40 in spectrum C shows there is a slight excess of X present. In the absence of reactive hydroxy groups intermediate VIII is stable in solution for days. If exposed to the atmosphere, VIII will react rapidly with water to give the corresponding silanol (eq 3c). Compound VIII could also be prepared from the reaction of disilanol IB with bis(ureido)siloxane XI (eq 3b).

Spectrum D (Figure 2) was recorded on the solution prepared from IIB and X described above ca. 10 min after addition of enough disilanol IIB to make the mole ratio of comonomers close to 1:1. The peaks for disilanol IIB are plainly observed at δ −2.12 (12 H) and −2.49 (6 H) showing that the reaction of ureido terminated VIII with IIB is slow. Nevertheless, small high-field peaks at −1.67 and −2.86 mark the beginning of oligomer formation (eq 3d). Spectrum E shows the same mixture approximately 1 h after mixing. With the exception of the peak at δ −1.47 all of the peaks due to monomer IIB and the intermediate VIII have decreased in intensity as polymerization continues. The peak at δ −1.47 remains relatively unchanged since one of the peaks for intermediate VIII is coincident with one of the peaks for polymer V. As the concentration of VIII decreases, the concentration of V increases at the same rate, and the intensity of the peak at δ −1.47 remains unchanged. The NMR spectrum of the same reaction mixture 5 h after mixing is shown in Figure 2F. The peaks due to monomer IIB and intermediate VIII have almost completely disappeared, and the three SiMe singlets of 1:2:1 intensity indicative of polymer V are now observed (Table I). Only slight changes occur in the spectrum during an additional period of 2–3 days.

Reaction of Disilanol IIB with Bis(ureido)disiloxane XI. This reaction was also followed via ^1H NMR spectroscopy and representative spectra are shown in Figure 3. The NMR spectrum of the bis(ureido)disiloxane XI is shown in Figure 3A. Addition of 0.5 mol of IIA to the solution of XI rapidly produces the bis(ureido) intermediate IX (Figure 3B) with absorption intensities in the expected 1:2:2:2 ratio. It is interesting to note that the shielding effect of the PcSi macrocycle is sufficiently strong that Si_4Me protons are still shifted to high field of Me_4Si. Additional disilanol IIB was added to this solution so as to make the mole ratio of comonomers 1:1. Figure 3C shows the NMR spectrum of this solution 2 h after mixing. The reaction is nearly complete as the peaks due to intermediate IX and disilanol IIB have almost disappeared. The three SiMe singlets for polymer VI are observed in the anticipated 1:2:2 ratio.

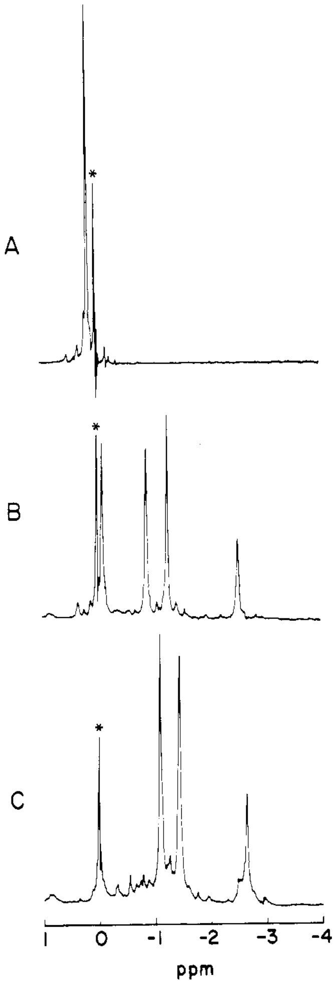


Figure 3. ^1H NMR spectrum of bis(ureido)disiloxane XI (A), intermediates IX (B), and PcSi-siloxane polymer VI (C).

Polymer Synthesis. After NMR studies demonstrated the feasibility of utilizing the reaction of PcSi disilanol and bis(ureido)silane/siloxane comonomers to obtain soluble PcSi-siloxane polymers, gram quantities of polymers IV and V were synthesized. This was accomplished through the reaction of disilanol IB with bis(ureido)siloxanes XI and XII at reflux in xylene or toluene, respectively. The polymeric products were precipitated by pouring reaction mixtures into methanol. Polymer V which has one more $OSiMe_2$ group separating the PcSi rings was considerably more soluble in typical organic solvents than polymer IV. In addition, polymer V melted at 65–70 °C, while polymer IV softened at ~100 °C (T_g?) but did not melt.

Polymer V exhibited an NMR spectrum similar to that shown in Figure 2F. However, many of the small peaks seen in Figure 2F which are due to low molecular weight oligomers and intermediates are of much diminished intensity or are not observed. Polymer IV exhibited two peaks in the expected 1:2 ratio (Table I).

It is interesting to note the shift to high field for the Si_1Me peak in proceeding from IV to VI (Table I). As the length of the siloxy chain segment separating the PcSi rings decreases, the shielding experienced by the intervening Si_1Me groups increases resulting in a $\Delta\delta_{Si_1Me}$ (IV–VI) of 0.44. A related effect was observed by Kenney in a study of the unique ring stacked oligomers $Me_3SiO(PcSiO)_xSiMe_3$.[18] For these molecules the ^1H chemical shift values for the terminal groups increased with increasing number of intervening PcSi rings.

The accentuated chemical shift of Si_1Me groups which are "sandwiched" between Pc rings in the polymers has an interesting consequence. Si_1Me end groups experience the shielding of only one PcSi group and are observable as separate resonances close to the chemical shifts found for Si_1Me in compounds such as IB and IIB, δ ca. -2.5. Thus inspection of a number of spectra for polymer V (prepared from IB and XII) showed a broad peak of low intensity at δ -2.6 which is assigned to terminal Si_1Me groups.[26] The breadth of this peak is probably due to overlapping absorptions from end groups containing one or four silicon atoms. Similarly, a set of peaks centered at δ -2.7 are observed for IV.

The end group Si_1Me resonance(s) are not as clearly separated from the internal Si_1Me resonances as the ^{29}Si resonances found for disiloxanols.[27] Nevertheless, adequate separation of terminal and internal Si_1Me resonances exists in the NMR spectra of IV and V to allow an estimate of $\overline{DP}$ utilizing eq 4, where A and B are the integrated intensities for terminal and internal Si_1Me resonances, respectively.

$$\overline{DP} = B/A - 1 \qquad (4)$$

In our hands the synthesis of IV from IB and XI yielded a polymer with a $\overline{DP}$ of 14.0, while a $\overline{DP}$ of 11.0 was obtained for V. These low $\overline{DP}$'s belie the molecular size of the polymer as the repeat units have a high molecular weight (IV 977.4; V 1051.6). Thus for IV $M_n = 1.4 \times 10^4$ while $\eta_{red} = 0.10$; the corresponding values for V are 1.2×10^4 and 0.13.

Conclusions

The present investigation has shown the feasibility of preparing novel PcSi-siloxane polymers. More importantly these polymers have been shown to be tractable and capable of being studied in solution. Our results in this regard stand in contrast to those of Meyer and Wohrle[28] who prepared a number of PcSi–organic polymers. These polymers which were synthesized from diols and dicarboxylic acids and $PcSiCl_2$ or $PcSi(OH)_2$ were reported to be too insoluble for solution studies.

However, it is clear that improvements are needed to increase the modest molecular weights obtained for the PcSi-siloxane polymers prepared form ureido siloxanes. We are currently investigating alternative synthetic routes which will simplify the synthesis of PcSi–siloxanes and provide higher molecular weight materials.

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(22) The following notation is used in the assignment of proton chemical shifts: $Py_{2,5}$ refers to protons on carbons 2 and 5 in the pyrrolidine ring (see Scheme II) of the pyrrolidinyl- and ureido-siloxanes; $Py_{3,4}$ refers to protons on carbons 3 and 4 in the pyrrolidine ring of the pyrrolindinyl- and ureido-siloxanes. Ph refers to protons on the phenyl groups. Si_1, Si_2, etc., refer to the first, second, etc., silicon atoms in siloxy groups attached to the PcSi macrocycle, e.g., the methyl group on silicon adjacent to the PcSi group is designated Si_1Me.

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(26) End group peaks for V prepared in situ from IIB and X can be seen in Figure 2F (δ -2.52 to -2.68). The principal peak in this group at δ -2.52 is assigned to Si_1Me in a $PcSiOSiMePhOSiMe_2OH$ end group. The remaining smaller peaks at higher field (more clearly evident in the original unreduced spectrum) are probably due to ureido terminated end groups.

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