AD-A250 637

TION PAGE

Form Approved
OMB No. 0704-0188

D

Pi
g
cc
D

ıerage 1 hour per response, including the time for reviewing instructions, searching existing data sources,
the collection of information. Send comments regarding this burden estimate or any other aspect of this
o Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson
Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
15 May 92

3. REPORT TYPE AND DATES COVERED
Technical Report

4. TITLE AND SUBTITLE
Water Soluble Polysiloxanes with Pendant
1-Oxypyridin-3-yl Groups

5. FUNDING NUMBERS
G-N00014-91-J-1434

6. AUTHOR(S)
Martel Zeldin, Slawomir Rubinsztajn and Wilmer K. Fife

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Indiana University-Purdue University at Indianapolis
Department of Chemistry
Indianapolis, IN 46205

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report
No. 15

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Department of the Navy
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Prepared for publication in the *Journal of Inorganic and Organometallic Polymers*

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

12b. DISTRIBUTION CODE

DTIC
ELECTE
MAY 26 1992
S A D

13. ABSTRACT *(Maximum 200 words)*

Polysiloxanes with 1-oxypyridin-3-yl groups bonded to silicon were prepared by base catalyzed hydrolysis-polycondensation of dialkoxy silane monomers. The polymers were characterized by IR, ^{1}H- and ^{13}C-NMR spectra. Polymers bearing 1-oxypyridin-3-yl functions were soluble in organic solvents like CH_2Cl_2. The solubility in hydrogen bonding solvents, such as H_2O and MeOH, increased with increase in molecular weight. The distribution coefficient for materials with different molecular weight in a water/$CHCl_3$ mixture is reported. Quasi-elastic light scattering data indicate that the Stokes diameter for the polymer with molecular weight 9000 increases in the order $H_2O < MeOH < CH_2Cl_2$. Structural ramifications of the solvent effect are suggested.

14. SUBJECT TERMS
Polysiloxanes, Pyridine 1-oxide, 1-Oxypyridin-3-yl, Quasi-elastic light scattering, Siloxane solubility

15. NUMBER OF PAGES
9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-91-J-1434

R&T Code 4135021

Technical Report No. 15

Water Soluble Polysiloxanes with Pendant 1-Oxypyridin-3-yl Groups

by

Martel Zeldin, Slawomir Rubinsztajn and Wilmer K. Fife

Prepared for Publication

in the

Journal of Inorganic and Organometallic Polymers

Department of Chemistry
Indiana University-Purdue University at Indianapolis
1125 East 38th Street
Indianapolis, IN 46205

May 15, 1992

J. Inorg. Organomet. Polym., in press, 1992

Water Soluble Polysiloxanes with Pendant 1-Oxypyridin-3-yl Groups

Martel Zeldin *, Slawomir Rubinsztajn and Wilmer K. Fife
Indiana University-Purdue University at Indianapolis
1125 East 38th Street
Indianapolis, IN 46205

ABSTRACT

Polysiloxanes with 1-oxypyridin-3-yl groups bonded to silicon were prepared by base catalyzed hydrolysis-polycondensation of dialkoxy silane monomers. The polymers were characterized by IR, ^{1}H- and ^{13}C-NMR spectra. Polymers bearing 1-oxypyridin-3-yl functions were soluble in organic solvents like CH_2Cl_2. The solubility in hydrogen bonding solvents, such as H_2O and MeOH, increased with increase in molecular weight. The distribution coefficient for materials with different molecular weight in a water/$CHCl_3$ mixture is reported. Quasi-elastic light scattering data indicate that the Stokes diameter for the polymer with molecular weight 9000 increases in the order H_2O < MeOH < CH_2Cl_2. Structural ramifications of the solvent effect is suggested

---

Keywords: Polysiloxanes, Pyridine 1-oxide, 1-Oxypyridin-3-yl, Quasi-elastic light scattering, Siloxane solubility

INTRODUCTION

Pyridine 1-oxide and organic-polymer variants bearing this moiety are extremely selective nucleophilic catalysts in transacylation reactions of carboxylic and phosphoric acid derivatives.[1-5] Polysiloxanes are organometallic macromolecules well-known for their broadly applicable physical and dynamic mechanical properties (i.e., chain flexibility, low temperature elasticity, hydrophobicity, and thermo-oxidative stability) which differ considerably from vinyl polymers.[6] In an attempt to merge the desirable properties of the siloxane chain with the potentially effective and selective catalytic properties of nucleophilic substituents, we reported the synthesis, characterization and catalytic properties of silane monomers and *low* molecular weight siloxane oligomers with 1-oxypyridin-3-yl groups bonded to silicon.[7] These materials were soluble in organic solvents, but insoluble in water. More recently we described polysiloxanes bearing 'super'-nucleophilic 4-dialkylaminopyridine moieties. These materials, when partially protonated, are water soluble and exhibit a tendency to self-associate as micelle-like species.[7-10] This type of self-aggregation, which is driven by inter- or intramolecular hydrophobic interactions, has led to water soluble polysiloxane catalysts with affinity for lipophobic substrates.[9-11] We now wish to report the synthesis and characterization of higher molecular weight polysiloxanes which contain pendant, polar 1-oxypyridin-3-yl groups and are water as well as organic-solvent soluble.

EXPERIMENTAL

Solvents and reagents were purified by drying over a suitable dehydrating agent followed by distillation. The synthesis of diethoxy(methyl)(3-pyridyl)silane (1) has been described elsewhere.[1] Infrared spectra were obtained with a Perkin-Elmer 282 spectrometer using KBr plates. ^{1}H- and ^{13}C-NMR spectra were recorded on a QE-300 spectrometer in $CDCl_3$ with CH_2Cl_2 or TMS as an internal reference. Molecular weight measurements were determined by size exclusion chromatography using a Waters R401 Differential Refractrometer and ASI (10^3 and 10^4) styragel columns, and, where molecular weights were less that 10,000, by end-group (i.e. $(C\underline{H}_3)_3SiO$: $C\underline{H}_3(3\text{-Py})SiO$ ratio) analysis using integration of the ^{1}H-NMR spectra.

Synthesis of Me₃SiO End-Blocked Poly[(methyl)(1-oxypyridin-3-yl)siloxane]

To a magnetically stirred solution of diethoxy(methyl)(3-pyridyl)silane (1) (2.18 g; 10.3 mmol) diluted with THF (2 mL) in a 25mL round-bottom flask was added H_2O (0.378 g; 21.0 mmol) and Me_4NOH (1.1 μL; 20% in MeOH; 2.3×10^{-6} mol). The mixture was stirred at ambient temperature for 12 h. Volatile materials were removed at 60 °C under vacuum. The temperature was then raised to 140 °C for 20 min to destroy the catalyst. The residual material, the hydroxy end-functional polysiloxane (2), (1.35 g) is a light yellow fluid which is soluble in organic solvents. ^{1}H-NMR (δ, $\Sigma_{1/2}$, H^n, Area): 8.70, 10, $H^{2,6}$, 2; 7.80, 10, H^4, 1; 7.20, 10, H^5, 1; 0.4, 10, H^{SiCH_3}, 3. ^{13}C-NMR (δ, C^n): 153.8, C^2; 151.4, C^6;

---

* To whom all correspondence should be addressed

14.9, C^4; 130.8,C^3; 124.5,C^5; -0.80, C^{Si}. IR (cm^{-1}, int, [assign]): 3400, m,br, [Si-OH]; 1590, s, 1400 s [ring C=C, C=N]; 1260, s, [$Si-CH_3$]; 1100, s,br, [Si-O-Si]; 790, s, [ring C-H].

Polymer 2 (Scheme 1) (1.35 g) was dissolved in CH_2Cl_2 (5 mL) in a 25 mL round-bottom flask. Bis(trimethylsilyl)acetamide (BSA, 2 mL; $8.1x10^3$ mol) was added and the mixture was stirred for 12 h at room temperature. The volatile materials were removed under vacuum at 90 °C for 24 h to give a viscous yellow fluid which is soluble in chlorinated hydrocarbons and methanol but insoluble in water and hexane. The product (3, 1.13 g) was precipitated from methanol solution with hexane. ^1H-NMR (δ, $\Sigma_{1/2}$, H^n, Area): 8.70, 12, $H^{2,6}$, 2; 7.80, 10, H^4, 1; 7.20, 10, H^5, 1; 0.35, 15, H^{SiCH_3}, 3; 0.00, 3, $H^{Si(CH)_3}$, 0.3. ^{13}C-NMR (δ, C^n): 154.0, C^2; 151.9, C^6; 141.3, C^4; 131.2, C^3; 123.9, C^5; -0.06, $C^{(CH_3)_3Si}$. IR (cm^{-1}, int, [assign]): 1590, s, 1400 s [ring C=C, C=N]; 1260, s, [$Si-CH_3$, $Si(CH_3)_3$]; 1100, s,br, [Si-O-Si]; 790, s, [ring C-H]. The number average molecular weight (M_n), which is estimated from the area ratio of end-group to in-chain methyl protons, is 8500. Gel permeation chromatographic (GPC) data indicate a bimodal distribution for the material first isolated from the synthesis. Purification giving a single-peak chromatogram is accomplished by precipitation of the product from methanol solution with addition of hexane; M_n, 9000; polydispersity, 2.7 (relative to polystyrene standards).

Polymer 3 (MW_{GPC} = 9000; 0.90 g) was dissolved in CH_2Cl_2 (10 mL) in a 25 mL round-bottom flask. *m*-Chloroperoxybenzoic acid (1.25 g, $5.8x10^{-3}$ mol) dissolved in CH_2Cl_2 (10 mL) was added. fter 16 h of stirring at room temperature, Et_3N (2 mL) and then hexane (40 mL) were added. A white precipitate (suspension) instantly formed. After 15 min a light brown oil (4) collected at the bottom of the flask. The suspension was decanted. The oil was dissolved in CH_2Cl_2 and precipitated by addition of hexane. The dissolution-precipitation procedure was repeated two more times. Solvents were removed under vacuum at 70 °C for 24 h to yield a clear, brown, glassy material (4, 0.78 g) which is soluble in chlorinated hydrocarbons, methanol and water. The solid is hygroscopic and gains 15% by weight of water in 2 h to become a viscous brown fluid. ^1H-NMR (δ, $\Sigma_{1/2}$, H^n, Area): 8.28, 30, $H^{2,6}$, 2; 7.38, 30, $H^{4,5}$, 2; 0.40, 30, H^{SiCH_3}, 3; 0.05, 3, $H^{Si(CH)_3}$; ^{13}C-NMR (δ, C^n): 142.2, C^2; 140.4, C^6; 134.0, C^4; 130.3, C^3; 126.4, C^5; 0.0, $C^{(CH_3)_3Si}$. IR (cm^{-1}, int, [assign]): 1210, s,br, [$Si-CH_3$, $Si(CH_3)_3$]; 1100, s,br, [Si-O-Si]; 925, m, [N^+-O^-]; UV (solvent, $\neg_{max}$ (nm)): H_2O, 208, 256; CH_3OH, 268; CH_2Cl_2, 278.

The organic solvent/water distribution coefficient for 4 was determined by ^1H-NMR in $CDCl_3$ and UV spectroscopy at 267 nm in $CHCl_3$. For example, 4 (80 μg) was placed in a 5 mm NMR tube with $CDCl_3$ (500 μL) and toluene (2 μL). After the spectrum was recorded, D_2O (500 μL) was added and the mixture was vigorously mixed by shaking for 30 min at ambient temperature (22-23 °C). The phases were allowed to separate and the NMR spectrum of the organic and water layers was recorded. Table 1 summarizes the data for 4 (M_n, 9000, 5300, >1000), 3-trimethylsilylpyridine 1-oxide (monomer, 5), and 1,1,3,3-tetramethyl-1,3-*bis*(1-oxypyridin-3-yl)disiloxane (dimer, 6). The NMR data were compared to the results obtained from the UV spectral studies. In the latter experiment, a 1.0 μL sample of the organic and water phases was withdrawn separately and each was injected into a quartz cuvette containing MeOH

(3.00 mL). The spectrum of each was taken and a comparison of the absorbances at 267 nm permitted the calculation of the partition coefficient.

Quasi-elastic Light Scattering Experiment

Quasi-elastic light scattering measurements on polymers 1 and 2 were carried out on a Brookhaven B12030AT Light Scattering System with 72 channel real-time correlator and Joden laser (power, 15mW). A 90° scattering angle was used and the polymers were dissolved in water, methanol and methylene chloride to a concentration of 5 g/L. The apparent Stokes diameters, D_S^{app} (nm) for polymer 4 (M_n, 9000) in different solvents is as follows (solvent, D\s(app,s) (nm)): water, 5.0±1; MeOH, 7.0±1; CH_2Cl_2, 9.5±1. D_S^{app}.

RESULTS AND DISCUSSION

We have recently shown that low molecular weight, linear oligomeric siloxanes, which contain pendant 3-pyridinyl and 1-oxypyridin-3-yl groups, can be prepared by the alkaline hydrolysis of the corresponding difunctional chlorosilane monomers.[7,12,13] ^{1}H-NMR, GPC and Direct Injection Probe-MS data suggest that the predominant products from the hydrolysis are low molecular weight linear and cyclic species with degree of polymerization (DP) between 3 and 15. The problems encountered using chlorosilanes as polymer intermediates are moderate-to-poor product yield, decomposition of the monomer during purification by distillation, difficulty in transferring and handling extremely moisture-sensitive intermediates, multiple substitutions which result in by-products that are difficult to separate from the primary product, and the ubiquitous presence of HCl which complexes with the pyridinyl function and makes purification difficult. In an effort to prepare polymer chains of sufficiently high molecular weight for potential applications as catalytically active fluids, films, resins and elastomers, we have used diethoxy(methyl)(pyridin-3-yl)silane (1) as the monomer precursor.[14] Polymer 2 was prepared by hydrolytic polycondensation of monomer 1 in the presence of catalytic quantities (1×10^{-3} mol/dm^3) of a strong base, preferably, Me_4NOH (Scheme 1) in a THF-water solution. Polymerization is complete within 1 hour. In contrast, uncatalyzed hydrolytic polymerization of 1 in the same solvent mixture is slow, giving less than 10% conversion in 6 hours and low molecular weight species.

Polymer 2 is a clear pale-yellow viscous fluid which is soluble in chlorinated hydrocarbons. The infrared spectrum of 2 exhibits a strong, broad absorption at 1100 cm^{-1} characteristic of the Si-O stretching vibration of the siloxane chain and an intense broad band at 3400 cm^{-1} assigned to the terminal Si-OH vibration.[15] The ^{1}H-NMR spectrum of 2 exhibits three broad unresolved resonances in the aromatic region (8.7 to 7.2 ppm) comparable to shifts found in the monomer. The methyl group protons appear as multicenter singlets at ~0.4 ppm corresponding to the various structural arrangements due to different tacticities. Similar observations have been noted for poly[methyl(phenyl)siloxane].[16] The ^{13}C-NMR spectrum of 2 consists of five peaks which appear at positions expected for pyridinyl carbons with a 3-substituent in addition to methyl group carbons on silicon.

Upon end-blocking with BSA, polymer 3 is formed. Polymer 3 is a pale-yellow viscous fluid which is soluble in chlorinated hydrocarbon solvents and THF. The solubility of 3 in alcohols and water depends on molecular weight. The only change in the infrared spectra of 3 relative to 2 is the disappearance of the O-H band at 3400 cm^{-1}. The ^{13}C-NMR spectrum of 3 is similar to 2. The ^{1}H-NMR spectrum of 3 is the same as 2 with the exception of a small singlet at ~0 ppm which has been assigned to the end-group methyl protons.[7] The area ratio of the end-group to in-chain methyl signals can be used to estimate the molecular weight of oligomers (e.g., $A^{Me}/A^{Me_3} \cong 10$; $x \cong 60$; $M_n \sim 8500$). The GPC data for 3, which is obtained directly from material in the reaction medium, indicate a bimodal distribution. The lower molecular weight material, which represents about 5% of the product, has M_n less than 600 and is assumed to be a mixture of cyclic oligomers, which is consistent with the appearance of sharper ^{1}H-NMR lines in the aliphatic region. On removal of the low molecular weight oligomers, which is accomplished by precipitation of the higher molecular weight material from methanol solution with hexane, polymer 3 has $M_n \cong 9000$ (relative to polystyrene standards) and a polydispersity of 2.7.

Polymer 3 can be oxidized to the 1-oxypyridinyl derivative (4) by treatment with *m*-chloroperoxybenzoic acid in CH_2Cl_2 at room temperature. Product 4 is a brown, glass-like, hygroscopic substance which is soluble in chlorinated hydrocarbons, alcohols *and* water. The IR spectrum of 4 gives direct evidence for the presence of the N^+-O^- bond with a characteristic strong stretching vibration at 1210 cm^{-1} and a medium intensity deformation band at 925 cm^{-1}.[17] The ^{1}H-nmr spectrum of 4 exhibits two broad, unresolved resonances in the aromatic region resulting from the merging of H^2 and H^6, and H^4 and H^5 protons, respectively. A similar effect has been noted with other 3-substituted pyridines.[18] The high-field methyl group proton signals are similar to those in 3. The ^{13}C-NMR spectrum of 4 is very complex, perhaps reflecting structural variations associated with chain conformations, tacticity and the effect of the highly polar N-O bond. The DSC and TGA of 4 is similar to that reported earlier for oligomers.[7]

The solubility properties of 4 are very interesting and depend on molecular weight. The monomer model, 3-trimethylsilylpyridine 1-oxide (5) and the dimer, 1,1,3,3-tetramethyl-1,3-*bis*(1-oxypyridin-3-yl)disiloxane (6), are essentially insoluble in water and have very small distribution coefficients in a water-$CHCl_3$ partitioning experiment (i.e., 0.05/0.95 and 0.09/0.91, respectively; Table 1). The low molecular weight oligomer (M_n, >1000), is sparingly soluble in water and has a distribution coefficient of 0.40/0.60. The higher molecular weight materials (viz., M_n, 5300 and 9000) have increasing solubility in water and appreciable partitioning into the water phase (0.69/0.31 and 0.87/0.13, respectively) with increasing molecular weight. The high solubility in water is presumably a result either of the flexible siloxane backbone assuming a conformation in which the polar N^+-O^- moieties can interact strongly with water (i.e., hydrophilic surface with hydrophobic core; Scheme 2, **A**) or self-association of the chains into a bilayer-like structure mediated by inter- or intramolecular hydrophobic interactions of the hydrophobic methylsiloxyl units coupled with strong hydrophilic interaction of the polar group with water. The solubility in the organic phase could then correspond to reorganization of the polymer chain, for example, to achieve a conformation which maximizes hydrophobic interaction with the solvent (e.g., hydrophobic surface with hydrophilic core where water is present; Scheme 2, B). In the absence of water, it is expected that polymer 4 will have a random-coil structure (C) owing to the high flexibility of the siloxane backbone. Similar unusual solubility effects have been observed with siloxanes bearing charged 4-aminopyridine residues.[10] Evidence for conformational variation with solvent has been obtained from quasi-elastic light scattering studies in the various solvents. Thus, it has been found that the Stokes diameter for the water-soluble polymer increases with a decrease in the solvent's hydrophobicity in the order H_2O (5.0 nm) < MeOH (7.0 nm) < CH_2Cl_2 (9.5 nm).

Acknowledgement: The authors wish to acknowledge support for this work by the Office of Naval Research. We appreciate the help of Prof. Paul Dubin and Dr. Jiulin Xia for carrying out the light scattering experiments and their helpful discussion of the data.

References

1. W. K. Fife and Y. Xin, *J. Am. Chem. Soc.*, 109, 1278 (1987).
2. W. K. Fife and Z.-d. Zhang, *J. Org. Chem.*, 51, 3744 (1986).
3. W. K. Fife and Z.-d. Zhang, *Tetrahedron Lett.*, 27, 4933 (1986).
4. W. K. Fife and Z.-d. Zhang, *ibid.*, 27, 4937 (1986).
5. L. J. Mathias and R. A. Vaidya, *J. Am. Chem. Soc.*, 108, 1093 (1986).
6. E. G. Rochow, "Silicon and Silicones," Springer-Verlag, Berlin, (1987).
7. M. Zeldin, W. K. Fife, C.-x. Tian and J.-m. Xu, *Organometallics*, 7, 470 (1988).
8. S. Rubinsztajn, M. Zeldin and W. K. Fife, *Macromolecules*, 23, 4026-4027 (1990).
9. K. K. Kasem, W. K. Fife, M. Zeldin and C. R. Leidner, *Journal of Electroanalytical Chemistry*, 296, 221-231 (1990).
10. S. Rubinsztajn, M. Zeldin and W. K. Fife, *Macromolecules*, 24, 2782 (1991).
11. W. K. Fife, S. Rubinsztajn and M. Zeldin, *J. Am. Chem. Soc.*, 113 ~~xxx~~, 8535 xxx (1991).
12. W. K. Fife, M. Zeldin and C.-x. Tian, in "Advances in Silicon-Based Polymer Science," G. Fearon and J. Zeigler, Eds., No. 224, American Chemical Society, 1990; Chapter 5.
13. M. Zeldin, W. K. Fife, C.-x. Tian and Y. Xin, in "Inorganic and Organometallic Polymers," M. Zeldin, K. J. Wynne and H. R. Allcock, Eds., ACS Symposium Series No. 360, 1988; Chapter 15.
14. S. Rubinsztajn, M. Zeldin and W. K. Fife, *Syn.& React. Inorg. & Metal-Orgn. Chem.*, 20(4), 495-502 (1990).
15. E. Maslowsky, Jr., "Vibrational Spectra of Organometallic Compounds," Wiley-Interscience: New York, 1977; pp 111-116.
16. L. S. Bresler, V. P. Mileshkevich, Yu. A. Yuzhelevskii and N. P. Timofeeva, *Zh. Strukt. Khim.*, 3, 453 (1978).

17. G. V. Kireev, V. B. Leontev, Yu. V. Kurbatov, O. S. Otroshchenco and A. S. Sadyleov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 5, 1034 (1980).
18. C. J. Pouchert and R. J. Campbell, "The Aldrich Library of NMR Spectra," Aldrich Chemical Co., Milwaukee, 1974; Vol. IX.

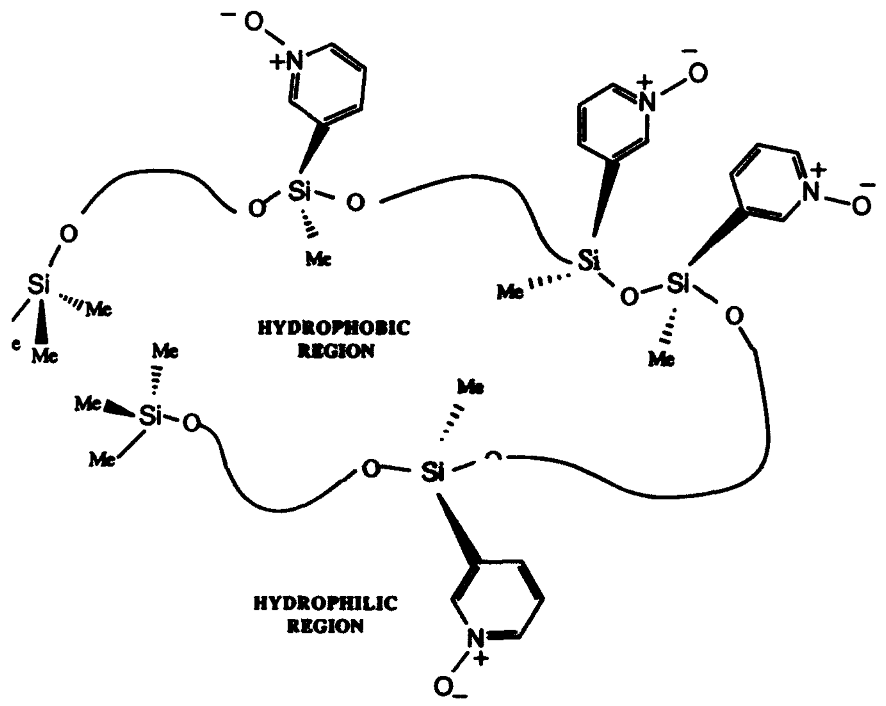
Table 1. Distribution Coefficient of Pyridine 1-Oxide Species (Monomer, Dimer, Oligomer and Polymers) Between H_2O and $CHCl_3$ Phases

Substance [a]	Fraction (in H_2O)	Fraction (in $CHCl_3$)
Monomer	0.05	0.95
Dimer	0.09	0.91
Oligomer (<1000)	0.40	0.60
Polymer (5300)	0.69	0.31
Polymer (9000)	0.87	0.13
	(0.92	0.08)[b]

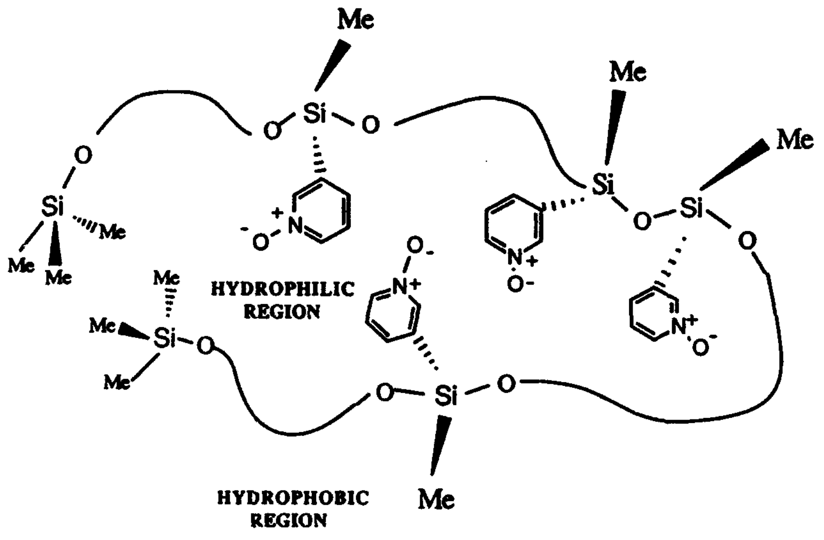
---

a. Monomer = 4-trimethylsilylpyridine 1-oxide; Dimer = 1,1,3,3-tetramethyl-1,3-*bis*(1-oxypyridin-3-yl)disiloxane

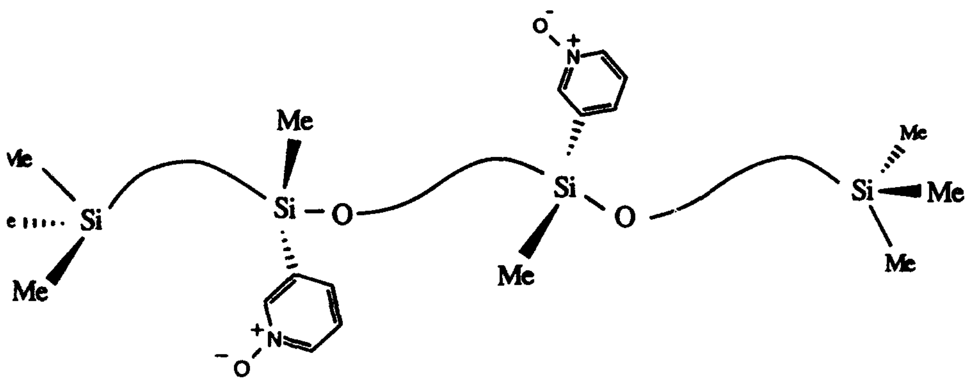
b. In CH_2Cl_2


HYDROPHOBIC REGION
HYDROPHILIC REGION

A


HYDROPHILIC REGION
HYDROPHOBIC REGION

B



C