

Siloxane Zwitterions: Synthesis and Surface Properties of Crosslinked Polymers

MORTON LITT and TAKEHISA MATSUDA, *Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106*

Synopsis

The aminoalkoxysilanes, γ -aminopropyltriethoxysilane and N-aminoethyl- γ -aminopropyltrimethoxysilane, were chemically modified by ring-opening addition of γ -propanesultone. Surfaces coated with polymers from these new monomers have, at the surface, zwitterionic functions of sulfobetaines which are attached to the polymeric siloxane backbone. They showed good wettability, with critical surface tensions as high as 50 dynes/cm.

INTRODUCTION

Organofunctional silanes are effective and widely used coupling agents and chemical modifiers for glass surfaces. Many organofunctional silanes are produced which have two different kinds of functionality on the same molecule, chloro or alkoxy silane groups which hydrolyze, polymerize, and deposit on the glass surface, perhaps with reaction, combined with an alkyl moiety with a functional substituent. The general structure is $X_3\text{—Si—R}$, where the X groups are either alkoxy or chloro groups. R, in commercial materials, can contain vinyl, glycidyl, ester, amine, etc., functional groups. Lee pointed out that reactive organofunctional silanes could be divided into low-, medium-, and high-polarity monomers on the basis of the critical surface tension of their polymer films; this depends mainly on the type of functionality.¹ Aminoalkoxysilanes are classified as medium polarity despite an amino group of high polarity; that is, the wettability of polymeric aminosiloxanes is not as high as expected.²

In this communication, we wish to report the chemical modification of aminoalkylsilanes by the addition of γ -propanesultone and the high wettability of surfaces coated with these materials. The new polyampholyte, with sulfobetaine zwitterionic functions attached to the polymeric siloxane backbone, provides a high polarity and is easily wettable.

EXPERIMENTAL

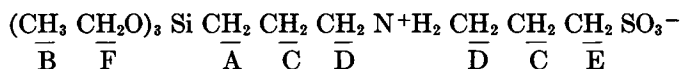
Materials

The materials studied here were γ -aminopropyltriethoxysilane, $\text{H}_2\text{NCH}_2\text{—CH}_2\text{CH}_2\text{Si(OC}_2\text{H}_5)_3$ (Union Carbide, A-1100 silane), and N-aminoethyl- γ -amino-

propyltrimethoxysilane (Dow Corning, Z-6020). The silanes were used without further purification. γ -Propanesultone was purified by distillation under vacuum. Microscope slides (Corning, No. 2947) used for contact angle measurements were cleaned by soaking in concentrated nitric acid-sulfuric acid (HNO₃, 10% by volume) overnight, thoroughly rinsing with water, and air drying at room temperature.

Reaction of Aminoalkoxysilanes with γ -Propanesultone

The equimolar reaction of γ -aminopropyltriethoxysilane (2.21 g; 0.01 mole) and γ -propanesultone (1.06 g; 0.01 mole) in acetone (10 ml) was carried out at room temperature overnight. The fine, white precipitate was filtered, washed with acetone and diethyl ether, and dried under vacuum; yield 92%, mp 218°C. The NMR spectrum in D₂O solution was run at room temperature, with tetramethylsilane as an external standard. The peak assignments, relative integrated intensities (first parenthesis), and multiplicity and coupling constants (second parenthesis) are as follows:



A(2), 8.73 τ , triplet (8 Hz); B(9), 8.26 τ , triplet (6.5 Hz); C(4), 7.70 τ and 7.40 τ , two broad overlapping peaks; D(4), 6.47 τ , broad multiplet; E(2), 5.92 τ , triplet (7 Hz); F(6), 5.60 τ , quartet (6.5 Hz).

Based on the breadth of peaks adjacent to the siloxane units, the monomer probably hydrolyzed and started to polymerize by the time the spectrum was taken.

ANAL. Calcd. for C₁₂H₂₅NO₆SSi: C, 42.8%; N, 4.1%; S, 9.4%. Found: C, 42.8%; N, 6.1%; S, 10.2%.

The reactions of N-aminoethyl- γ -aminopropyltrimethoxysilane with one and two equivalents of γ -propanesultone were carried out in the same manner and gave slightly yellowish powders with yields of 85% and 69%, respectively. They were not analyzed in detail.

Preparation of Polysiloxane Samples

The cleaned microscope slides were placed for a given time at room temperature in 5% aqueous solutions of the silane, adjusted to pH 3.5 with acetic acid. The samples were then removed, rinsed with distilled water, air dried, and baked at 100°C in an oven for 1 hr.

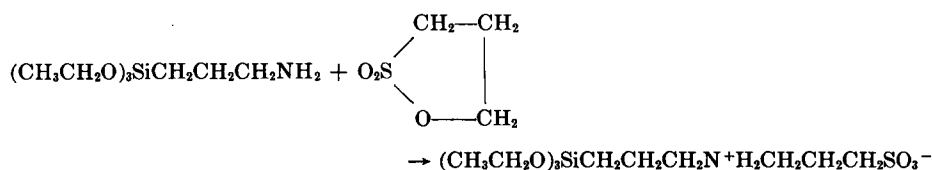
Contact Angle Measurements

Contact angle measurements were made by an NRL C.A. Goniometer, Model A-1100 at constant humidity and temperature (50% R.H., 22.5°C) by the sessile drop technique. The test liquids used to determine the critical surface tension were tridistilled water ($\gamma_{LV} = 72.2$ dynes/cm), 1,1,2,2-tetrabromoethane ($\gamma_{LV} = 49.7$ dynes/cm), 1-bromonaphthalene ($\gamma_{LV} = 44.6$ dynes/cm), and 1,1,2,2-tetrachloroethane ($\gamma_{LV} = 31.7$ dynes/cm).

RESULTS AND DISCUSSION

Ring-Opening Addition of Aminoalkoxysilanes with 1,3-Propanesultone

The reaction of γ -aminopropyltriethoxysilane with γ -propanesultone in acetone at room temperature ran very well. The product was easily soluble in water and methanol, but insoluble in ether and hydrocarbon solvents. The infrared spectrum of the product displayed the characteristic peaks of sulfonic acid³ in the region of 1170–1220 cm^{-1} and 920 cm^{-1} , in addition to the characteristic peaks of silane compounds. The NMR spectrum showed that the peak positions and integrated intensities agreed with those expected for the one-to-one adduct of the aminoalkylsiloxane with γ -propanesultone, as did the elemental analyses. The expected reaction is shown below:



The reactions of N-aminoethyl- γ -aminopropyltrimethoxysilane (Dow Corning Z-6020) with one or two equivalents of γ -propanesultone were carried out in the same manner. The precipitates (mono- and dizwitterions) were soluble in water and methanol, but gradually condensed from solution, forming insoluble materials. This results from the hydrolysis of the alkoxy groups of the sulfobetaines to produce the corresponding trisilanols and their subsequent polycondensation.

Wettability of Treated Glass Surfaces

The wettability of the silane-treated glass surfaces is an important aid in understanding the nature of the deposited polysiloxane. It correlates with the nature and orientation of the functional groups at the surface, and therefore with the chemical reactions at the outermost layer of the polymer. The results of our contact angle measurements of surface coatings on glass slides are shown in Tables I and II. The water contact angle of glass surfaces treated using mono-aminoalkoxysilane (Union Carbide A-1100) was quite high (54°), while the

TABLE I
Contact Angles of Various Probe Liquids on Aminosilane (A-1100)-Treated Glass Surfaces^a

| Treatment time, min | Advancing contact angle, degrees | | | | | | | |
|---------------------|----------------------------------|----|----------------------------------|---|----------------------------------|--------|----------------------------------|--------|
| | Water | | 1,1,2,2-Tetra-bromoethane | | 1-Bromo-naphthalene | | 1,1,2,2-Tetra-chloroethane | |
| | ($\gamma_{LV} = 72.2$ dynes/cm) | | ($\gamma_{LV} = 49.7$ dynes/cm) | | ($\gamma_{LV} = 44.6$ dynes/cm) | | ($\gamma_{LV} = 31.7$ dynes/cm) | |
| | A | B | A | B | A | B | A | B |
| 1 | 32 | 21 | 33 | 7 | 28 | spread | 15 | spread |
| 30 | 40 | 16 | 28 | 6 | 26 | spread | 10 | spread |
| 60 | 54 | 16 | 26 | 8 | 23 | spread | 5 | spread |

^a A: Treated with γ -aminopropyltriethoxysilane (A-1100); B: treated with the adduct of A-1100 and γ -propanesultone. The standard deviation of each measurement was about 2° .

TABLE II
Advancing Contact Angle of Various Probe Liquids on Diaminosilane-Treated Glass Surfaces

| Liquid | A ^a | | | B ^b | | |
|---|---------------------|-------|--------|----------------|-------|--------|
| | 10 sec ^c | 1 min | 30 min | 10 sec | 1 min | 30 min |
| Water ($\gamma_{LV} = 72.2$ dynes/cm) | 17° | 15° | 13.5° | 12° | 10° | 10° |
| Tetrabromoethane ($\gamma_{LV} = 49.7$ dynes/cm) | 3° | 3° | 3° | 1° | 1° | 1° |
| Tetrachloroethane ($\gamma_{LV} = 31.7$ dynes/cm) | spread | | | spread | | |

^a Molar ratio of diaminosilane (Z-6020) to propanesultone = 1.0.

^b Molar ratio of diaminosilane (Z-6020) to propanesultone = 2.0.

^c Treatment time.

corresponding sulfobetaine-treated surface showed a low water contact angle (16°).

The critical surface tensions (γ_c) of polymeric γ -aminopropyltriethoxysilane (A-1100) and N-aminoethyl- γ -aminopropylalkoxysilane (Z-6020) were reported to be 35 and 33.5 dynes/cm, respectively, using a series of polyethylene glycol liquids.⁴ The present experiment using nonhydrogen-bonded liquids gave γ_c of about 31 dynes/cm for A-1100, using a Zisman plot.⁵ The low critical surface tensions of polymeric mono- and diaminosilane film surfaces imply that the surface has a hydrocarbon nature rather than the polar or ionic type one might expect in this case, since the reaction was catalyzed using acetic acid. The polarity of the surface is similar to that of polypropylene oxide ($\gamma_c = 32$ dynes/cm)⁵ and that of polyethylene ($\gamma_c = 31$ dynes/cm).⁵ This result, though reported before,² is contrary to expectation because the ammonium group is hydrophilic with a high water-solvation energy (16.8 kcal/mole); the carboxylate anion is not as high (7.4 kcal/mole). Hydroxyl groups are the least interacting (5.7 kcal/mole).^{6,7} Therefore, our conclusions are that very few amino or ammonium groups are exposed at the air/polysiloxane interface. The hydrocarbon character of the aminosilane surface is probably due to the tendency for the formation of heavily crosslinked mixed silazane-siloxane polymers. Most of amino groups have probably reacted with silanol groups under the curing conditions, $>100^\circ\text{C}$, eliminating water.

The internal chelate proposed by Plueddeman² to explain the solubility of the polymer and its low critical surface tension cannot operate here. At pH 3.5, where the polymerization was carried out, all the amines are in salt form, and the silanols cannot interact readily. This is seen more easily with our sulfobetaines, which precipitated from solution, indicating crosslinking.

Once the aminosiloxane is cured, the amino groups are not available for any reaction. Treatment of the surface with acid or base did not change its wettability. Even treatment of a base cured coating with γ -propanesultone did not affect its critical surface tension or wettability. It seems reasonable to conclude, therefore, that the amino groups, at least after curing at 100°C , are chemically rather than physically bound in the crosslinked network. Another observation which supports this conclusion is that coatings remain insoluble and bound to the surface though somewhat swollen even after one week of soaking in water.

TABLE III
Approximate Critical Surface Tensions of Chemically Modified Glass Surfaces

| Surface | Water advancing contact angle, degrees | γ_c , dynes/cm |
|---|--|------------------------|
| Nontreated, cleaned with HNO ₃ /H ₂ SO ₄ | 4 | >70 |
| Monoaminosilane treated (Union Carbide A1100) | 54 | 31 (35) ^a |
| Monoaminosilane sulfobetaine | 16 | ≈ 50 |
| Diaminosilane treated (Dow Corning Z-6020) | 49 | 32 (33.5) ^a |
| Z-6020, Monosulfobetaine (average) | 14 | ≈ 50 |
| Z-6020, Disulfobetaine | 10 | ≈ 50 |

^a Reference 4.

On the other hand, the surface prepared using A-1100 reacted with γ -propanesultone is highly wettable and hydrophilic. The critical surface tension was estimated to be about 50 dynes/cm. Thus, the ionic character of the polymeric zwitterion remained intact. Similar treatment of glass surfaces with Z-6020 reacted with one or two equivalents of γ -propanesultone showed similar results. The greater concentration of polar groups on this diaminosilane resulted in lower water contact angles and higher critical surface tensions than that obtained using monoaminosilanebetaine. The data are shown in Table II. For the dizwitterion, the advancing water contact angle was only 10°; the surface did not dewet. When contact angles were measured using nonhydrogen-bonded liquids, the surface was almost wetted with tetrabromoethane ($\gamma_{LV} = 49.7$ dynes/cm, contact angle 1°). The data are in Table III. This surface is the most polar one we have made and may be the most polar polysiloxane created so far.

The much improved wettability must be directly due to the nature of the zwitterion produced. Ordinary salts with acetic acid allow loss of the acid by vaporization during curing because the low dielectric constant of the matrix promotes reversion to the neutral compounds. Here, the sulfonic acid is so much stronger than acetic acid that the salts remain as such. The ammonium ion is not able to interact with the silanol. Thus, when the polymerization is complete, each residue still has a zwitterionic group attached. With such a high concentration of polar groups, many must be at the surface, making it a polar surface. The detailed study of the polymeric siloxane zwitterions is now in progress.

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References

1. L. H. Lee, Society of Plastic Industry, Technical Conference, 9-D, 1968.
2. E. P. Plueddemann, Society of Plastic Industry, Technical Conference, 19-A, 1969.
3. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., Wiley, New York, 1958, p. 350.
4. L. H. Lee, *J. Colloid Interfac. Sci.*, **27**, 751 (1968).
5. W. A. Zisman, *Advan. Chem. Ser.*, **43**, 1 (1964).
6. I. C. Watt, R. H. Kenett, and J. F. P. James, *Text. Res. J.*, **29**, 975 (1959).
7. J. D. Leeder and I. C. Watt, *J. Phys. Chem.*, **69**, 3280 (1965).

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