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Size-Exclusion Chromatography and Size-Exclusion Chromatography/Fourier Transform Infrared Spectrometry of Reacting Organofunctional Trialkoxysilanes

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Size-exclusion chromatography (SEC), severally and in combination with Fourier transform infrared (FT-IR) spectroscopy, is shown to be uniquely applicable to the investigation of the hydrolysis and condensation reactions of organofunctional trialkoxysilanes. Size-exclusion chromatography provides a method of separation which reveals previously undemonstrated information about the reactions of trialkoxysilanes. Interfacing the chromatography to a FT-IR spectrophotometer with diffuse reflectance optics allows identification of individual reaction products including the silanetriol and the cyclic tetramer. Reaction kinetics are followed for phenyl-triethoxysilane in aqueous tetrahydrofuran. The behavior of the reacting silanes in different media (e.g., aqueous and aqueous-organic) can also be monitored and is demonstrated to be substantially different.

Most analytical techniques have been applied to organofunctional silanes in an attempt to explain their beneficial and

sometimes mysterious behavior in a wide variety of applications (e.g., reinforced polymer composites, liquid crystal orientation, and enzyme immobilization). The reactions of organofunctional trialkoxysilanes are numerous, complex, and depend on a number of interacting variables. Therefore, the investigation of these systems has required the use of many and varied techniques in order to obtain even a preliminary picture of the chemistries involved.

If there is a major class of analysis which has been relatively neglected throughout the 30 or more years of study in this field it would have to be chromatography. Only a few citations are available in which any type of chromatographic separations are used to analyze organofunctional trialkoxysilanes. Plueddemann (1) employed gas chromatography (GC) to separate the lower members of trimethylsilyl end-blocked siloxanes formed from condensing vinylsiloxanols and vinyl siliconates by the Lentz (2) technique. GC has also been used to determine whether a silane adsorbs onto a substrate surface from solution (3). Thin-layer chromatography (TLC), using Rhodamine B dye or Bromocresol Green as developing agents for

vinyl- and (methacryloyl)propyl-functional silanes, has also been shown effective in demonstrating the attraction of silanols for a glass surface and the stability of the silane layers to various solvents (4, 5). Recently, Liptak et al. (6) used GC and SEC to investigate the reactions of vinyltris(2-methoxyethoxy)silane in the presence of aluminum hydroxide.

The primary reactions of organofunctional trialkoxysilanes are hydrolysis and condensation. These reactions determine the solution properties of silanes and their ultimate configuration and structure as low or high polymers. The chemistry of these reactions has been of interest for many years, and numerous analytical techniques have been applied. These include Raman spectroscopy (7), NMR (1, 8), infrared spectroscopy (9–12), gas chromatography (1), extraction (9, 12), UV spectrophotometry (12), and vapor-phase osmometry (1).

In this study, SEC and SEC/FT-IR are employed to determine the individual reaction products and to monitor the reaction kinetics. Other attempts have been made in the past to study the synthesis of oligomerizations by SEC (13–19), and it appears that the integration of other analytical methods with column chromatography will significantly advance the interpretation.

EXPERIMENTAL SECTION

Materials. Trialkoxysilanes, phenyltrimethoxysilane, phenyltriethoxysilane and (γ -(methacryloyl)propyl)trimethoxysilane were purchased from Petrarch Systems, Inc. and analyzed for purity. Aqueous and aqueous-organic silane solutions were prepared by using spectral grade solvents and twice-distilled and deionized water. The reacting solutions were prepared as 3 g of the designated trialkoxysilane in a 50-mL total volume of water or water/tetrahydrofuran mixture and stirred constantly at 25 °C. Aliquots (0.15 mL) of the reacting mixture were withdrawn at specific time intervals, immediately diluted 20 times in THF, and injected into the size-exclusion columns. Phenyldimethylmethoxysilane was purchased from Petrarch Systems, Inc. and polystyrene standards were purchased from Pressure Chemical Co.

Chromatography. Sample injection volume was held constant at 20 μ L. Injection sample concentration was 3.0 g/L, and the weight of injected trialkoxysilane was correspondingly 0.06 mg. The size-exclusion chromatograph consisted of a solvent delivery system (Beckman Model 110), an injection system (Rheodyne Model 7010), a fixed wavelength (254 nm) UV detector (Beckman Model 153), a differential refractometer (Laboratory Data Control RefractoMonitor Model 1107H), and a Digital Equipment Corp. MINC computer. All output data were digitized to facilitate numerical analysis. The chromatograph was operated at room temperature with non-UV stabilized chromatographic grade THF (Fisher Scientific Co.) as the eluting solvent adjusted to a rate of 1.0 mL/min. *o*-Dichlorobenzene (Aldrich Chemical Co., Gold Label) was used as an internal standard. The column series consisted of a Waters Assoc. μ -Stryagel with porosity specification of 500 Å, μ -Stryagel with porosity specification of 100 Å, and Ultrastyragel with porosity specification 100 Å. Individual column dimensions were 7.8 mm i.d. by 30 cm. The packing material was fully porous, highly cross-linked styrene/divinylbenzene copolymer with a particle size less than 10 μ m.

The column plate count was measured using *o*-dichlorobenzene as the plate count standard. The effective plate count calculated from the following equation was 19 000 plates for 90 cm of column.

$$N_{tan} = 0.525(V/W_{tan})^2 \text{ plates/cm}$$

N_{tan} is the plate count, V is the elution volume at the peak apex, and W_{tan} is the base-line peak width established by peak tangents.

The resolution of the column series was calculated from the following equation according to Bly (20).

$$R_s = 2(V_{R2} - V_{R1}) / (\log(M_1/M_2))(W_{B1} + W_{B2})$$

R_s is the elution volume, W_B is the base-line peak width, and M is the molecular weight. Subscripts 1 and 2 refer to polymeric standards of different molecular weight. When polystyrene standards of molecular weights 4000 and 800 were used at an

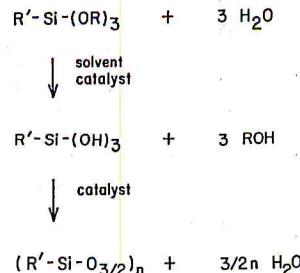


Figure 1. Generalized hydrolysis and condensation reactions of organofunctional trialkoxysilanes.

elution rate of 1.0 mL/min, the measured value of R_s was 1.39. The plate count and resolution appear to be acceptable for the columns and elution conditions employed (19, 21–23).

Spectrophotometry. Diffuse reflectance Fourier transform infrared (DRIFT) measurements were performed on a Digilab FTS-20 spectrophotometer with a hemispherical diffuse reflectance attachment (Digilab DRA-100). A liquid nitrogen cooled mercury cadmium telluride (MCT) detector was employed, and the spectrophotometer was purged with dry nitrogen to reduce atmospheric water vapor. Spectra were collected at a resolution of 2 cm^{-1} with coaddition of 100 scans. Single-beam reflectance data were ratioed against high-purity potassium bromide (KBr), and the Kubelka-Munk (KM) function (24, 25) was calculated. The KM function has the following form where $F(R_\infty)$ represents a ratio between absorption and scattering coefficients and R_∞ is the experimentally measured reflectance spectrum from a semi-infinite specimen.

$$F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$$

Spectral contributions due to nonvolatile solvent residuals were removed by a combination of iterative nonlinear least-squares (26) fitting and digital subtraction.

SEC/FT-IR. The chromatographic and spectroscopic techniques were integrated by the three-step process (1) collection of the chromatographically resolved species, (2) solvent elimination, and (3) solute analysis by DRIFT. The chromatographically resolved species were collected on ground KBr as they eluted from the last detector in series. Samples were collected 5 times per minute with a capacity for collecting 30 samples per minute. Solvent evaporation was completed at room temperature and pressure. The nonvolatile solute on ground KBr was analyzed by the DRIFT technique described above. The presence of nonvolatile residuals in the eluting solvent presents a problem which can be corrected by digital subtraction as described above but emphasizes the necessity for the use of pure solvents.

RESULTS AND DISCUSSION

The generalized hydrolysis and condensation reactions of organofunctional trialkoxysilanes are illustrated in Figure 1. A number of catalysts and inhibitors are known for these reactions, and the rate and completeness of each reaction depend on these and other factors (8, 9, 27).

The final molecular structure, and therefore performance, of these trialkoxysilane systems is extremely dependent on the initial hydrolysis and condensation reactions. Organofunctional trialkoxysilanes may form either low molecular weight caged compounds or high-network polymers, depending only on initial reaction conditions. The necessity of investigating these reactions at early stages is made difficult due to the numerous, yet, chemically similar reaction products and the difficulty of their separation. Size-exclusion chromatography would seem an ideal choice for separation of these condensation polymerization products. However, in the past conventional SEC or gel permeation chromatography could not provide adequate resolution of the low molecular weight species of interest. The advance in separation efficiency now enables the resolution of species in the low molecular weight range (less than 10 000), and an example of this power is illustrated in Figure 2.

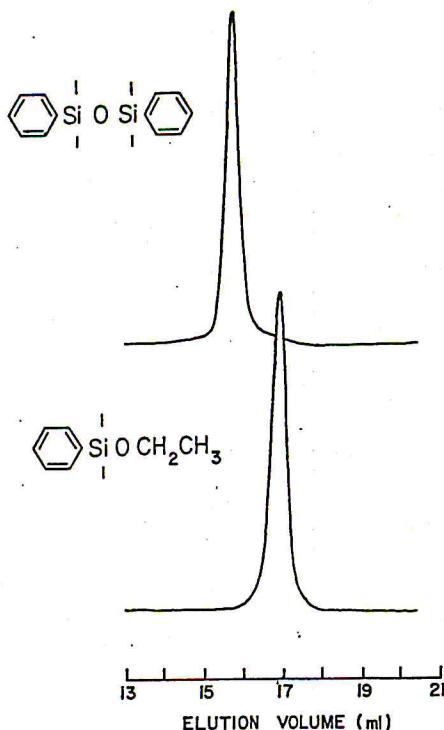


Figure 2. Size-exclusion chromatograms of a monomeric monoalkoxysilane, phenyldimethylethoxysilane, and its corresponding covalent dimer, diphenyltetramethylethoxysiloxane.

The covalent dimer species, diphenyltetramethylethoxysiloxane, was synthesized from its corresponding monoalkoxysilane, phenyldimethylethoxysilane. The elution volume difference between the monomer and dimer species corresponding to a molecular weight change of 180–280 is greater than 1 mL. This separation was made with one 500-Å Styragel and one 100-Å Ultrastyragel column in series. The resolution of the columns in this molecular weight range according to the method of Bly (20) was 7.6. This indicates the high efficiency of the technique and its applicability to the chemistry involved.

The same analysis as was seen in Figure 2 can be applied to the reactions of trialkoxysilanes. The problem becomes more difficult, however, because the chemical structure of the individual reaction products cannot be specifically assigned based on the chromatographic information alone. Integration of FT-IR with the chromatographic separation allows identification of the reaction products and provides information which is not available by either technique alone. The combination of liquid chromatography and FT-IR was introduced by Griffiths et al. (28) and is beginning to see widespread application (29–32). There are two general approaches to the LC/FT-IR interface which include solvent elimination (28, 33–37) and flow-cell (38, 39) techniques.

For the analysis of organofunctional trialkoxysilanes the SEC/DRIFT method using solvent elimination is optimal due to the low volatility of the solute and the high sensitivity of the DRIFT technique (40). An example of the SEC/DRIFT data is illustrated in Figure 3. Reaction of 0.30 M phenyltrimethoxysilane in THF was catalyzed by water (pH 4.0) at room temperature. Figure 3A is the conventional digitized output from a fixed-wavelength (254 nm) ultraviolet detector of the 7-h reaction product. Figure 3B is the conventional SEC chromatogram constructed from DRIFT-integrated intensity data monitored at 1430 cm⁻¹. The unreacted phenyltrimethoxysilane eluted near 16.0 mL, and, therefore, all the resolved species represent some type of reaction product. The 1430-cm⁻¹ band represents the B_{1'}v₁₃ fundamental phenyl mode of the substituted benzene which should not be strongly affected in intensity or position by the hydrolysis and con-

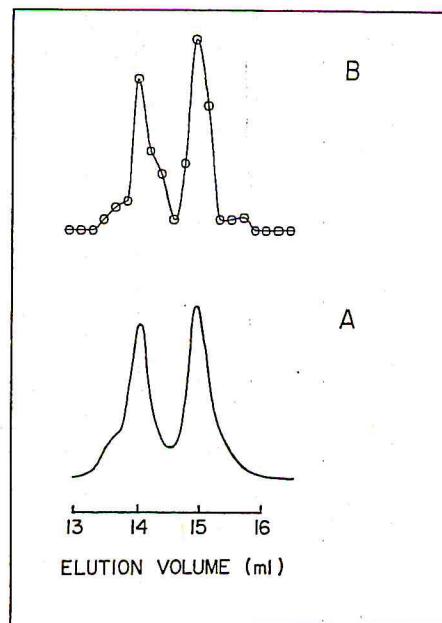


Figure 3. Size-exclusion chromatograms of a reacting solution of phenyltrimethoxysilane in acid-catalyzed aqueous THF at 25 °C. Chromatogram A is the response of a fixed-wavelength (254 nm) UV detector and chromatogram B is constructed from the integrated intensity of a fundamental phenyl mode at 1430 cm⁻¹ as monitored by diffuse reflectance FT-IR. All peaks represent reaction products, and none of the starting material remains.

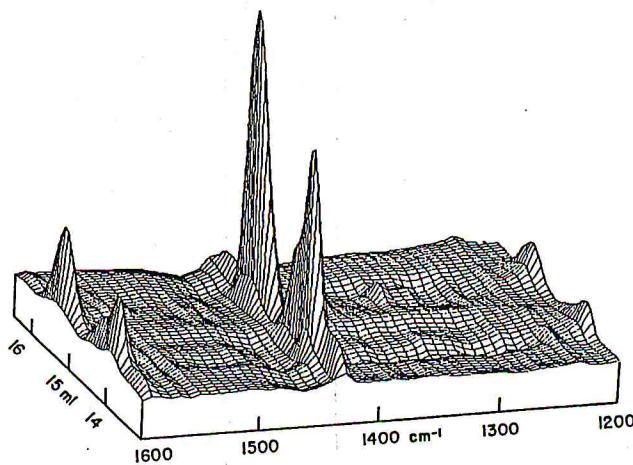


Figure 4. Three-dimensional reconstruction of SEC/DRIFT data in the mid-infrared region 1500–1300 cm⁻¹ for the reacting solution of phenyltrimethoxysilane in acid-catalyzed aqueous THF at 25 °C.

densation reactions of the trialkoxysilane. Figure 3B represents the use of the FT-IR spectrophotometer as an additional fixed-wavelength detector and should correspond exactly to the output from the fixed-wavelength UV detector. For the number of data points recorded the correspondence is quite good. The truly valuable information lies in the complete mid-infrared spectrum recorded for each data point in Figure 3B. This information not only allows identification of individual reaction products but can also potentially resolve individual components which appear as one species in the conventional fixed-wavelength chromatogram.

The question of sensitivity often arises for the LC/FT-IR techniques. The SEC/DRIFT technique detected 7×10^{-6} g with a signal-to-noise ratio of approximately 10. This sensitivity was achieved while monitoring a band with only moderate absorptivity and with absolutely no attempt to optimize the detection level. Detection limits as low as 1×10^{-8} g have been reported with HPLC/DRIFT systems (41).

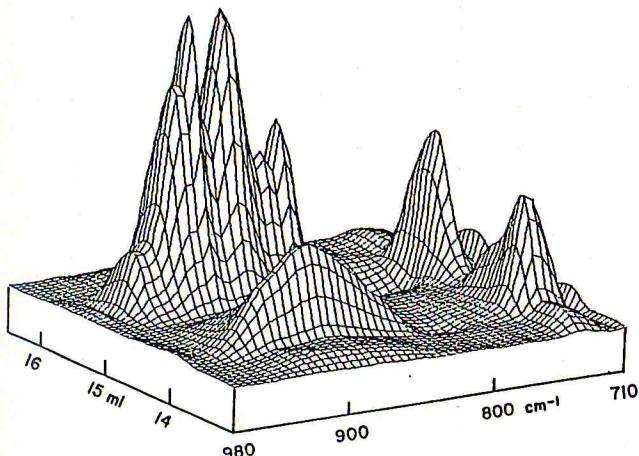


Figure 5. Three-dimensional reconstruction of SEC/DRIFT data in the mid-infrared region $980\text{--}720\text{ cm}^{-1}$ for the reacting solution of phenyltrimethoxysilane in acid-catalyzed aqueous THF at $25\text{ }^{\circ}\text{C}$.

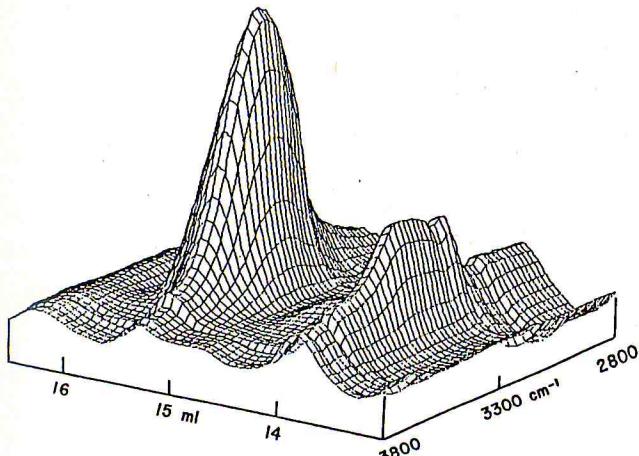


Figure 6. Three-dimensional reconstruction of SEC/DRIFT data in the mid-infrared region $1200\text{--}1000\text{ cm}^{-1}$ for the reacting solution of phenyltrimethoxysilane in acid-catalyzed aqueous THF at $25\text{ }^{\circ}\text{C}$.

Figure 4 shows the information produced by the SEC/DRIFT technique illustrated as a three-dimensional plot of elution volume, frequency, and intensity. Figure 4 plots an infrared region containing only fundamental phenyl modes of the trialkoxysilane-substituted benzene. The changes in Figure 4 are due only to the chromatographic separations since these infrared bands are insensitive to the trialkoxysilane reactions.

Figures 5–7 reveal the complete picture of the reactions involved by depicting the molecular differences between the chromatographically resolved reaction products. Figure 5 illustrates the infrared region from 980 to 710 cm^{-1} . The band near 740 cm^{-1} is again due to a fundamental phenyl mode, but the bands between 960 and 800 cm^{-1} result from the asymmetric stretching, $\nu_{as}(\text{SiO})$, modes of the silanol functionality. The silanol is produced upon hydrolysis of the trialkoxysilane, and it is apparent that the amount of this functionality as well as its structure in the two products are remarkably different.

The chromatographically separated structure at higher elution volume is assigned as the crystalline phenylsilanetriol. It is comprised of bands near 908 , 885 , 861 , and 847 cm^{-1} which have previously been assigned to the $\nu_{as}(\text{SiO})$ modes and combinations and overtones (42) of the silanetriol. The phenylsilanetriol also shows characteristic bands near 1035 cm^{-1} in Figure 6 due to the SiOH in-plane bending mode (44) and the strong OH stretching mode near 3225 cm^{-1} in Figure 7. The apparent stability of this species in the solid state is in agreement with previous findings (44, 45) even though

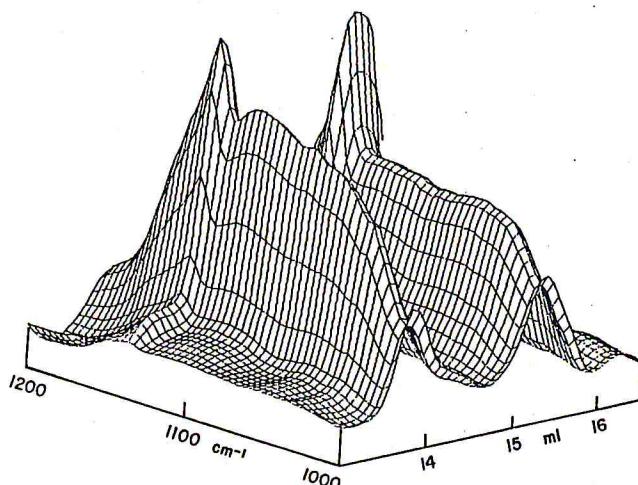


Figure 7. Three-dimensional reconstruction of SEC/DRIFT data in the mid-infrared region $3800\text{--}2800\text{ cm}^{-1}$ for the reacting solution of phenyltrimethoxysilane in acid-catalyzed aqueous THF at $25\text{ }^{\circ}\text{C}$.

almost all organofunctional silanetriols are extremely unstable in the solid state and undergo rapid siloxane formation.

The phenylsilanetriol elutes earlier than the unhydrolyzed trialkoxysilane. We believe this to be caused by intermolecular association of the silanetriol forming a hydrogen bonded dimer species in solution. Other explanations might include solvation of the hydroxy-containing product or interaction between the silanol groups and the gel material. However, when different reaction conditions are used, a hydrolyzed product can be isolated which elutes at a greater elution volume (smaller hydrodynamic volume) than the trialkoxysilane. The elution volume of the phenylsilanetriol also corresponds approximately to the expected volume of the hydrogen-bonded dimer based on calibration with poly(dimethylsiloxanes). Therefore, the structure is a strongly hydrogen-bonded dimer in solution which crystallizes to a hydrogen-bonded network upon evaporation of the solvent.

The phenylsilanetriol species appears to be slightly convoluted with a reaction product containing small amounts of a covalent siloxane bond. This is indicated by the contribution in the infrared spectrum near 1100 cm^{-1} seen in Figure 6. This contribution is not seen in the purified phenylsilanetriol product (38). There is also a small corresponding decrease in intensity of the bands due to the silanol groups compared to the purified product. It is approximated that the chromatographically resolved peak is 86% phenylsilanetriol based on quantitative analysis of the infrared spectra. The remaining 14% is likely to be the covalent dimer.

Figure 5 shows that the crystallinity present in the phenylsilanetriol is not present in the chromatographically resolved species at lower elution volume. There is also a substantial decrease in intensity much greater than that reflected by the reaction insensitive phenyl mode near 740 cm^{-1} . This decrease in silanol functionality between the two products is also reflected by the broad OH stretching mode centered near 3225 cm^{-1} in Figure 7.

Quantitative analysis of the normalized amount of silanol functionality in the two reaction products indicates that the lower elution volume product contains 32% of the silanol functionality in the phenylsilanetriol. This analysis was based on the integrated intensity of the OH stretching mode near 3225 cm^{-1} (Figure 7). Often this region of the infrared spectrum is not used for quantitative analysis due to contributions of water and hydrogen bonding. However, it is appropriate in this analysis because water is chromatographically separated and, therefore, does not contribute to this or other regions of the spectrum. Also, the OH stretching mode in both products is centered at 3225 cm^{-1} , indicating

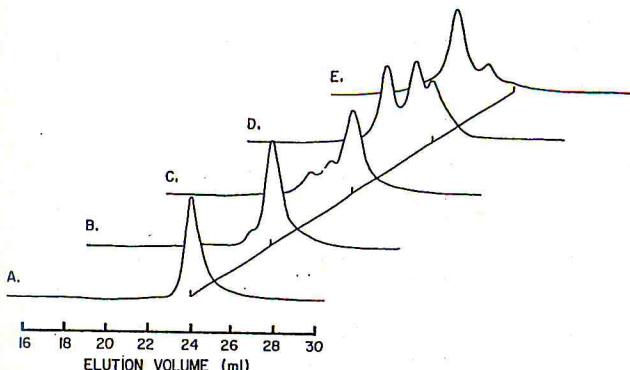


Figure 8. Size-exclusion chromatograms monitoring the reactions of phenyltriethoxysilane in aqueous THF at 25 °C; (A) 0 h, (B) 4.5 h, (C) 8.0 h, (D) 48 h, (E) 168 h.

a consistent degree of hydrogen bonding of the silanol functionality. The chromatographically resolved shoulder at the lowest elution volume best seen in Figure 3 contains only 10% of the silanol functionality observed in the phenylsilanetriol.

In a typical condensation reaction there would be a variety of individual oligomerization products which might show approximately 2/3 conversion of the reactive functionality. These would also separate chromatographically based on the number of repeat units. In the case of phenyltrimethoxysilane a single species with 2/3 silanol conversion elutes as a single species at a molecular weight less than 800 by polystyrene standards and is assigned as the cyclic tetrol, specifically, 2,4,6,8-tetraphenylcyclotetrasiloxanetetrol. The asymmetric siloxane stretching mode, $\nu_{as}(\text{SiOSi})$, of this species in Figure 6 shows a single band near 1105 cm⁻¹ convoluted by the $\nu_{as}(\text{SiO})$ mode near 1035 cm⁻¹. This assignment is in close agreement with that of the purified crystalline tetrol product (44).

In addition to the cyclic tetrol, the elution volume of the reaction product with 90% silanol conversion which is seen as a shoulder near 13.6 mL in Figure 3 corresponds to a molecular weight of less than 800 by polystyrene standards. This emphasizes the small hydrodynamic volume of these products formed under the specified reaction conditions even at such high extents of reaction. The phenomena is caused by a cyclization tendency and specificity of reaction (44) which causes the formation of small molecules from a trifunctional monomer.

SEC can also be used to monitor reactions as they proceed and obtain kinetic information. Figure 8 illustrates this technique by using all three SEC columns described previously in series. Phenyltriethoxysilane at a concentration of 0.25 M in THF and diluted to 0.0125 M in THF elutes as a single chromatographic separation near 24.0-mL elution volume as seen in Figure 8A. Under the specified constraints of this experiment, introduction of H₂O produced two new chromatographically distinct species as well as a corresponding loss of the starting material (chromatograms B–E). The new peaks appear at elution volumes near 23.0 and 21.5 mL. Near neutral (pH 6.0) water was used in this case to ensure that the reactions, both hydrolysis and condensation, would be moderately slow.

Kinetic information is available from quantitative analysis of the chromatographic separations. The relative concentrations of each chromatographically resolved species are plotted as a function of time in Figure 9. The curves are typical for reactions proceeding through an intermediate. The concentration of the reactant (A) decays and the concentration of the product (C) increases throughout the course of the reaction. The concentration of the intermediate (B) rises from zero to a maximum and then falls off. The predominance of

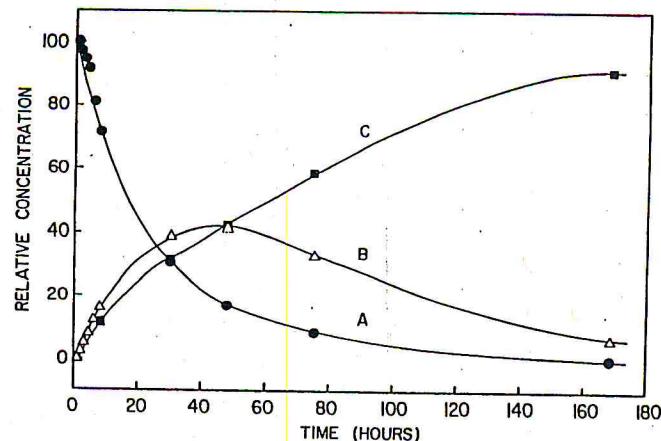


Figure 9. Relative concentration of the starting material (A) and products (B, C) in the reactions of phenyltriethoxysilane in aqueous THF at 25 °C as monitored by size-exclusion chromatography.

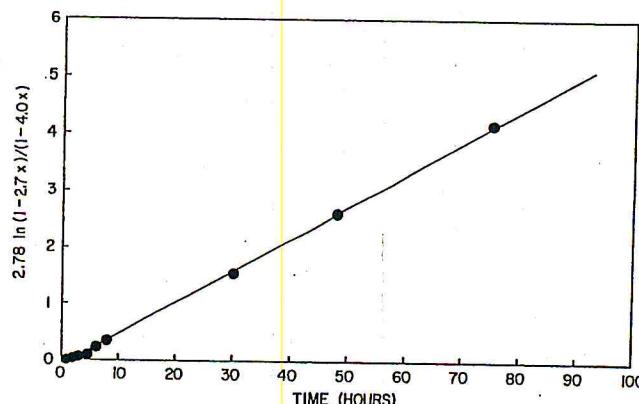


Figure 10. Plot of the integrated rate law for the general second-order reaction $A + 3B \rightarrow P$ as it applies to the loss of the starting material in the reactions of phenyltriethoxysilane in aqueous THF at 25 °C. The initial concentration of the reactants was 0.25 M in phenyltriethoxysilane and 1.11 M in water. "X" represents the concentration of products.

the structure in solution eluting near 21.5 mL (C) was maintained with time up to 1250 h (2 months). Relative comparison of the elution volumes of these chromatographically resolved reaction products as well as infrared examination of the bulk reaction products indicates that products B and C are the previously described phenylsilanetriol and cyclic tetrol, respectively. The cyclic tetrol is more stable in this case due to lack of an acidic or basic catalyst which would promote condensation.

When the quantitative loss of the starting material, phenyltriethoxysilane, is fitted to the rate equation, the reaction is found to proceed as a second-order reaction in aqueous-organic solution. The second-order kinetics are illustrated in Figure 10 by a plot of the integrated rate law for the generalized reaction $A + 3B \rightarrow C$. The observed second-order rate constant at 25 °C calculated from the slope in Figure 10 is 1.6×10^{-5} L mol⁻¹ s⁻¹. The linear correlation coefficient for the least-squares fit of the actual experimental data is 0.9996.

The hydrolysis and condensation reactions of organofunctional trialkoxysilanes are also heavily dependent on the reaction medium and the organofunctional group involved. This is illustrated by the series of chromatograms in Figure 11. Chromatograms A through E represent the reaction of (γ -(methacryloyl)propyl)trimethoxysilane in aqueous solution near neutral pH (pH 6.0) and 25 °C. As with phenyltriethoxysilane, the unhydrolyzed species is separated as a single peak near an elution volume of 24.0 mL. With time, reaction products appear near 25.1 and 22.2 mL in a manner quite different than observed for phenyltriethoxysilane. One of the

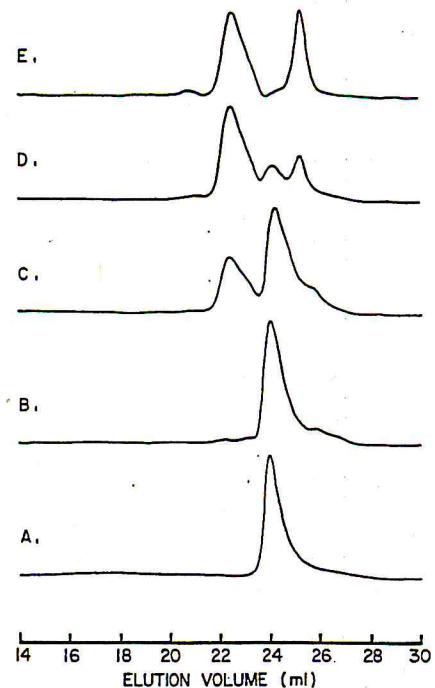


Figure 11. Size-exclusion chromatograms monitoring the reactions of (γ -(methacryloyl)propyl)trimethoxysilane in aqueous solution near neutral pH and 25 °C; (A) 0 h, (B) 0.5 h, (C) 0.8 h, (D) 1.2 h, (E) 1.6 h.

reaction products has an elution volume greater than the starting material, indicating a smaller hydrodynamic volume. This is likely to be the free silanetriol. The peak near 22.2 mL appears to be an incompletely resolved convolution of at least two distinct condensation products. The free silanetriol also appears to be relatively stable once formed under these solution conditions and is probably in equilibrium with the other products.

ACKNOWLEDGMENT

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Registry No. Phenyltrimethoxysilane, 2996-92-1; phenyltriethoxysilane, 780-69-8; (γ -methacryloyl)propyl)trimethoxysilane, 60319-98-4; diphenyltetramethylsiloxane, 56958-44-2; phenyl-dimethylethoxysilane, 1825-58-7; phenylsilanetriol, 3047-74-3; 2,4,6,8-tetraphenylcyclotetrasiloxanetetrol, 3450-18-8.

LITERATURE CITED

- (1) Pluedemann, E. P. *Proc. Annu. Conf.—Reinf. Plast./Compos. Div., Soc. Plast. Ind.* 1969, 24, Section 19-A.

- (2) Lentz, C. W. *Inorg. Chem.* 1964, 3, 574.
- (3) Stucker, N. E. "Enjay Butyl LM-430 Sealants. A Compounding Guide EPL-7204597"; Enjay Polymer Labs: Linden, NJ, 1984.
- (4) Holtmann, R. *Proc. Annu. Conf.—Reinf. Plast./Compos. Inst., Soc. Plast. Ind.* 1966, 21, Section 13-C.
- (5) Ashmead, B. V.; Owen, J. J. *J. Polym. Sci., Polym. Phys. Ed.* 1971, 9, 331.
- (6) Liptak, P.; Rado, R.; Mlejnek, O.; Lacuska, M. *Polym. Commun. (Peking)* 1984, 25, 126.
- (7) Shih, P. T. K.; Koenig, J. L. *Mater. Sci. Eng.* 1975, 20, 137.
- (8) Pohl, E. R.; Osterholz, F. D. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1983, 24, 200.
- (9) Pohl, E. R. *Proc. Annu. Conf.—Reinf. Plast./Compos. Inst., Soc. Plast. Ind.* 1983, 38, Section 4-B.
- (10) Ishida, H.; Koenig, J. L. *Appl. Spectrosc.* 1978, 32, 469.
- (11) Ishida, H.; Koenig, J. L. *Appl. Spectrosc.* 1978, 32, 462.
- (12) McNeill, K. J.; DiCaprio, J. A.; Walsh, D. A.; Pratt, R. F. *J. Am. Chem. Soc.* 1980, 102, 1859.
- (13) Sotobayashi, V. H.; Lie, S. L.; Springer, J.; Veherreiter, K. *Makromol. Chem.* 1968, 111, 172.
- (14) Heitz, W. "Separation of Oligomers by Use of Gel Chromatography", Abstracts, Third Prague Microsymposium, IUPAC, September 1968.
- (15) Robertson, A. B.; Cook, J. A.; Gregory, J. T. *Adv. Chem. Ser.*, No. 128, 1973, 258.
- (16) Kuzayev, A. I. *Polym. Sci. USSR (Engl. Transl.)* 1980, 22, 1260.
- (17) Barzykina, R. A.; Radugin, V. S.; Kuzayev, A. I.; Estrin, Y. I. *Polym. Sci. USSR (Engl. Transl.)* 1982, 24, 1636.
- (18) Gaziev, G. A.; Filinovskii, V. Y.; Yanovskii, M. I. *Kinet. Katal.* 1963, 4, 688.
- (19) Kuo, C.; Prover, T. In "Size Exclusion Chromatography (GPC)"; Prover, T., Ed.; American Chemical Society: Washington DC, 1980; ACS Sympos. Ser. No. 138, pp 207–224.
- (20) Bly, D. D. *J. Polym. Sci., Part C* 1968, 21, 13.
- (21) Yau, W. W.; Kirkland, J. J.; Bly, D. D. In "Modern Size-Exclusion Liquid Chromatography"; Wiley-Interscience: New York, 1979; p 111.
- (22) Vivileccia, R. V.; Colter, R. L.; Limpert, R. J.; Thimof, N. A.; Little, N. J. *J. Chromatogr.* 1974, 99, 407.
- (23) Dark, W. A.; Limpert, R. J.; Carter, J. D. *Polym. Eng. Sci.* 1975, 15, 831.
- (24) Kubelka, P.; Munk, F. Z. *Tech. Phys.* 1931, 12, 593.
- (25) Kubella, P.; Munk, F. J. *Opt. Soc. Am.* 1948, 38, 448.
- (26) Marquadt, D. M. *J. Soc. Ind. Appl. Math.* 1963, 11, 431.
- (27) Miller, J. D.; Hoh, K.; Ishida, H. *Polym. Compos.* 1984, 5, 18.
- (28) Kuehl, D. T.; Griffiths, P. R. *Anal. Chem.* 1980, 52, 1394.
- (29) Azarraga, L. V. *Appl. Spectrosc.* 1980, 34, 224.
- (30) Azarraga, L. V.; Brackett, J. M.; Castles, M. A.; Rogers, L. B. *Appl. Spectrosc.*, In press.
- (31) Jinno, K.; Fujimoto, C.; Uematsu, G. *Am. Lab. (Fairfield, Conn.)* 1984, 16 (2), 39.
- (32) Combelles, C.; Bayart, H.; Jasse, B.; Caude, W.; Rosset, R. J. *Chromatogr.* 1983, 259, 211.
- (33) Fuller, M. P.; Griffiths, P. R. *Am. Lab. (Fairfield, Conn.)* 1978, 10 (10), 69.
- (34) Kuehl, D. T.; Griffiths, P. R. *J. Chromatogr. Sci.* 1979, 17, 471.
- (35) Fujimoto, C.; Jinno, K.; Hirata, Y. *J. Chromatogr.* 1983, 258, 81.
- (36) Jinno, K.; Fujimoto, C.; Hirata, Y. *Appl. Spectrosc.* 1982, 36, 67.
- (37) Jinno, K.; Fujimoto, C.; Ishii, D. *J. Chromatogr.* 1982, 239, 625.
- (38) Brown, R. S.; Taylor, L. T. *Anal. Chem.* 1983, 55, 1492.
- (39) Johnson, C. C.; Taylor, L. T. *Anal. Chem.* 1983, 55, 436.
- (40) Miller, J. D.; Ishida, H. *Surf. Sci.*, In press.
- (41) Conroy, C. C.; Griffiths, P. R.; Jinno, K., Abstracts on the Pittsburgh Conference, 1984, No. 653.
- (42) Ishida, H.; Koenig, J. L. *Appl. Spectrosc.* 1978, 32, 5.
- (43) Tyler, L. J. *J. Am. Chem. Soc.* 1955, 77, 7701.
- (44) Brown, J. F., Jr. *J. Am. Chem. Soc.* 1965, 87, 4317.

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