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Spectroscopic and Chromatographic Investigation of the Hydrolysis and Condensation of [(*N,N*-Diethylamino)propyl]trimethoxysilane

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The hydrolysis and condensation of [(*N,N*-diethylamino)propyl]trimethoxysilane (NNDE) was monitored by FTIR and ^{1}H NMR spectroscopy, Karl Fischer titration, small-angle X-ray scattering (SAXS), and gel permeation and gas chromatography. Both neat NNDE and methanolic solutions of NNDE were investigated for different water:silane ratios ($R_w = 1.5$ and 3.0). The hydrolysis and condensation behavior of NNDE is typical for base-catalyzed sol−gel systems, the terminal amino group acting as an internal catalyst. The presence of methanol as a solvent retards the consumption of water. Investigation of the hydrolysis kinetics by FTIR showed the reaction order of water being 1.5, due to a preequilibrium between water and the amino group of NNDE. In methanolic solution, octameric species $[Et_2N(CH_2)_3SiO_{3/2}]_8$ are predominantly formed. Dimerization of this species occurs to an appreciable amount in the absence of methanol, but no higher oligomers are observed. A higher R_w results in a faster reaction but does not significantly influence the oligomer distribution.

Introduction

(Aminopropyl)trialkyloxysilanes are the most widely used organofunctional trialkoxysilanes for a variety of applications.[1,2] However, little is known about the nature of the primary products arising from hydrolysis and condensation reactions. Although (aminopropyl)trimethoxysilane is mostly used in practical applications, we chose [(*N,N*-diethylamino)propyl]trimethoxysilane (NNDE) for our study to avoid complications by the NH groups. We investigated the hydrolysis and condensation reaction by a combination of several spectroscopic and chromatographic techniques to provide a comprehensive picture of the early steps of the reaction of (aminopropyl)trialkoxysilanes with water.

Results and Discussion

Commercially available NNDE (95% purity) has an yellowish to brownish color due to oxidation products. When 1.5 equiv of water ($R_w = 1.5$) were added, a slightly exothermic reaction resulted in the initial formation of an emulsion. The emulsion converted into a clear sol after 10 min. However, when freshly distilled, colorless NNDE was hydrolyzed ($R_w = 1.5$ or 3.0), the initially formed emulsion converted into a clear sol after already 2 min. Therefore, unpurified NNDE contains compounds which influence its reactivity. For this reason, freshly distilled NNDE was used for all further investigations reported in this paper. When methanol (9 mol equiv) was added as a solvent, clear solutions or sols were obtained.

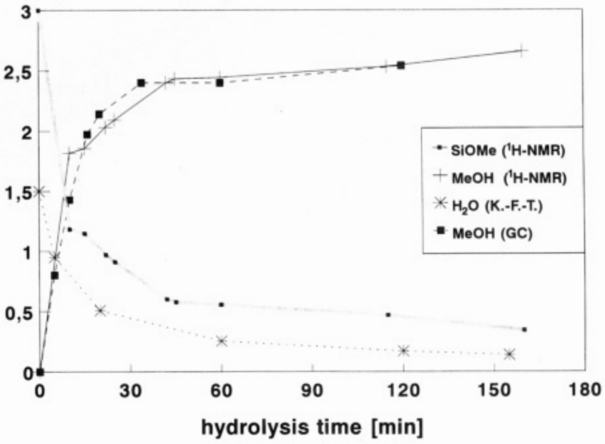

Figure 1. Consumption of water (determined by Karl Fischer titration), disappearance of the Si−OMe groups (^{1}H NMR), and production of methanol (+, ^{1}H NMR; ■, GC) for a solvent-free NNDE sol ($R_w = 1.5$).

The consumption of water and the production of methanol were investigated for solvent-free, freshly distilled NNDE. Water consumption was monitored by Karl Fischer titration, and methanol production by ^{1}H NMR spectroscopy and gas chromatography (Figure 1), both giving the same results within the accuracy of the methods. Simultaneously, the residual Si−OMe groups were determined by ^{1}H NMR spectroscopy. When 1.5 mol equiv of water ($R_w = 1.5$) were added, 1 mol of water was consumed after 20 min, while 2 mol MeOH was produced in the same period (Figure 1). This is typical for base-catalyzed sol−gel systems (the amino group of NNDE acting as the catalyst), in which the produced Si−OH groups immediately condense to Si−O−Si units.

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[1] Rösch, L.; John, P.; Reitmeier, R. In *Ullman's Encylocpedia of Industrial Chemistry;* VCH: Weinheim, 1993; Vol. A24, p 21.

[2] Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem.* **1986**, *98*, 237; *Angew. Chem., Int. Ed. Eng.* **1986**, *25*, 236.

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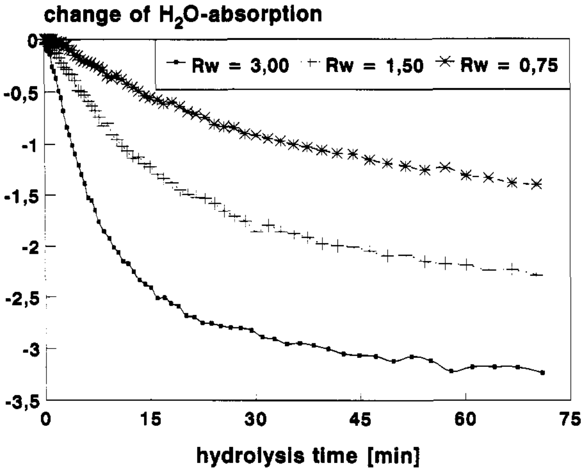

Figure 2. Change of the H_2O absorption in the FTIR spectrum of methanolic NNDE (1700–1616 cm^{-1}).

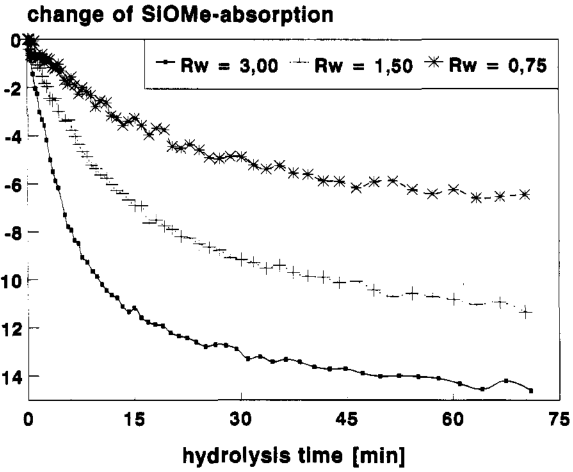

Figure 3. Change of the SiOMe absorption in the FTIR spectrum of methanolic NNDE (1100–1059 cm^{-1}).

However, even after 6 weeks, hydrolysis and condensation were not complete, with 0.15 mol of water and 2.7 mol of MeOH then being present in the reaction mixture.

Water consumption was also monitored for modified reaction conditions. In the presence of 9 mol equiv of methanol, the concentration of unreacted water was slightly higher (0.23 mol after 190 min, compared with 0.15 mol in the absence of methanol; $R_w = 1.5$). This agrees with the results found for $Si(OEt)_4$.[3] Less Si–OMe groups are present in the equilibrium state in the absence of methanol as a solvent. The addition of NH_4OH did not change the rate of the water consumption. This shows that no external catalyst is needed due to the basic character of NNDE itself.

The hydrolysis reaction was also monitored by FTIR spectroscopy for different R_w ratios. This method allows the simultaneous measurement of the intensities of characteristic H_2O, SiOMe, SiOH, and SiOSi bands for the kinetic investigation of the hydrolysis and condensation reactions.

The distinct influence of R_w on both the hydrolysis and condensation rate is obvious from Figures 2–5. The maximum concentration of Si–OH groups is reached after about 10 min.

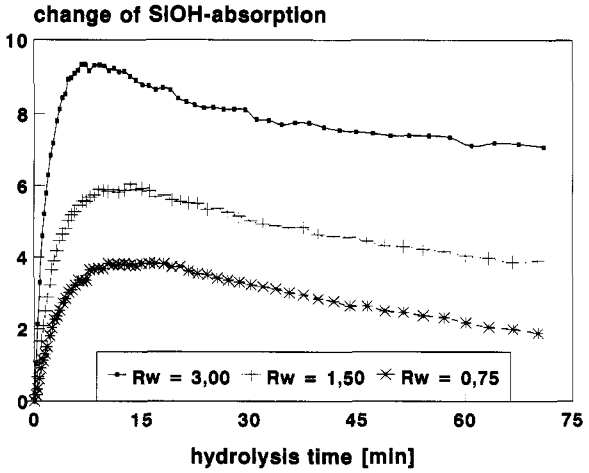

Figure 4. Change of the SiOH absorption in the FTIR spectrum of methanolic NNDE (950–873 cm^{-1}).

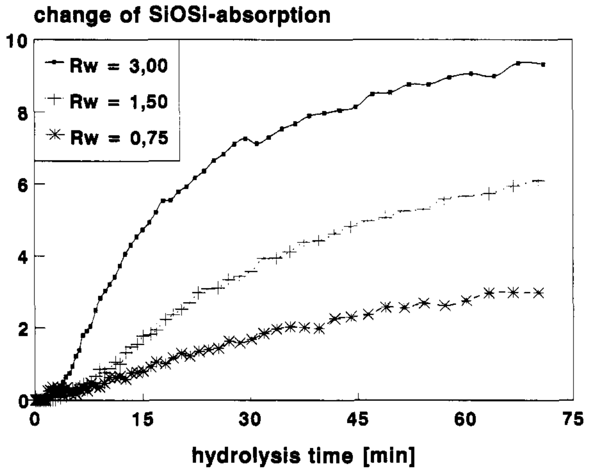

Figure 5. Change of the SiOSi absorption in the FTIR spectrum of methanolic NNDE (1153–1100 cm^{-1}).

The initial reaction rates v_0 are obtained from the tangent to the concentration vs time curve for $t = 0$. $v_0 = -k_{\mathrm{exp}}[\mathrm{SiOMe}]_0^x[\mathrm{H_2O}]_0^y$, x and y being the reaction orders of the two components ($R_w = 0.75$: $v_0 = 1.923 \times 10^{-4}\ \mathrm{s}^{-1}$; $R_w = 1.50$: $v_0 = 5.263 \times 10^{-4}\ \mathrm{s}^{-1}$; $R_w = 3.00$: $v_0 = 13.888 \times 10^{-4}\ \mathrm{s}^{-1}$). Since the silane concentration was not varied and the reaction order of the alkoxysilane should be 1 under basic conditions, v_0 is $-k'[\mathrm{H_2O}]_0^y$. When $\log v_0$ is plotted vs $\log [\mathrm{H_2O}]_0$, a straight line with a slope of 1.5 is obtained. The slope corresponds to y.

For the preequilibrium $R'NEt_2 + H_2O \rightleftharpoons R'NEt_2H^+ + OH^-$ (where $R'NEt_2$ is NNDE) the equilibrium constant K is $[OH^-]^2/[H_2O]$, since there was a constant concentration of NNDE in all experiments, and $[OH^-] = [R'NEt_2H^+]$.

The rate law for the base-catalyzed hydrolysis of the Si–OMe groups can be assumed to be

$$-\mathrm{d}[\mathrm{SiOMe}]/\mathrm{d}t = k_{\mathrm{h}}[\mathrm{OH^-}][\mathrm{H_2O}][\mathrm{SiOMe}]$$

as found for $Si(OEt)_4$.[4] With $[OH^-] = K^{0.5}[H_2O]^{0.5}$:

$$-\mathrm{d}[\mathrm{SiOMe}]/\mathrm{d}t = k_{\mathrm{h}}K^{0.5}[\mathrm{H_2O}]^{1.5}[\mathrm{SiOMe}]$$

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(3) Chojnowski, J.; Cypryk, M.; Kazmierski, K.; Rozga, K. *J. Non-Cryst. Solids* **1990**, *125*, 40.

(4) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science;* Academic Press: New York, 1990.

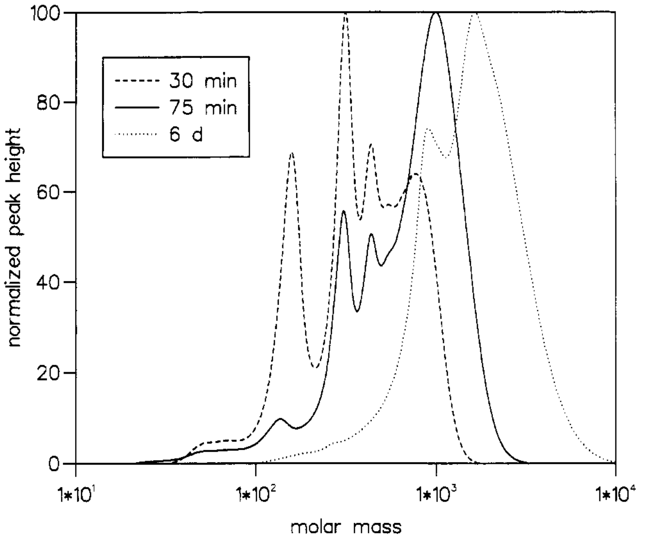

Figure 6. Gel permeation chromatograms of a solvent-free NNDE sol ($R_w = 1.5$, (– – –) 30 min; (—) 75 min; (···) 6 days).

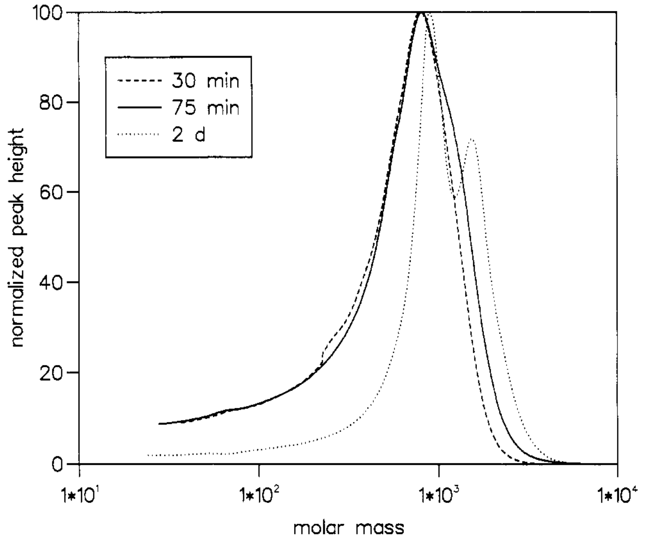

Figure 7. Gel permeation chromatograms of a solvent-free NNDE sol ($R_w = 3.0$, (– – –) 30 min; (—) 75 min; (···) 2 days).

The experimentally observed rate constant $k_{exp} = 1.46 \times 10^{-4}$ L$^{1.5}$/(mol$^{1.5}$ s) therefore is proportional to the product of the hydrolysis rate constant k_h and the square root of the equilibrium constant K is the pre-equilibrium.

Gel permeation chromatography (GPC) for the solvent-free system with $R_w = 1.5$ (Figure 6) showed the presence of monomers ($M_p = 160$ for the unhydrolyzed monomer, 18%) and small oligomers $[RSiO_{3/2}]_n$ (dimer, $M_p = 318$, 26%; trimer, $M_p = 439$, 15%; tetramer, $M_p = 546$, 10%; octamer, $M_p = 775$, 31%) after 30 min. The assignment of the octamer is based on the assumption that no pentamers, hexamers, and heptamers are formed.[5] (The apparent molecular weight of the octamer may be due to its cagelike structure or may result from the low purity of the peak at the beginning of the reaction. The peak shifts to higher values during the reaction). After 2 days, only octamers and higher oligomers with masses centered around $M_p = 1660$ (probably $[RSiO_{3/2}]_{16}$, R = $Et_2N(CH_2)_3$) were left. The polydispersity index (PI) was rather constant (decrease from 1.53 after 30 min to 1.45 after 10 days).

A higher R_w value promoted hydrolysis and condensation, as expected. At 30 min after the addition of 3.0 mol equiv of water, only octamers were identified in the GPC (Figure 7). However, since the baseline of the chromatogram was shifted for lower M_p, ionic species or species with a high number of Si–OH groups interacting with the column must be present, which cannot be identified separately.

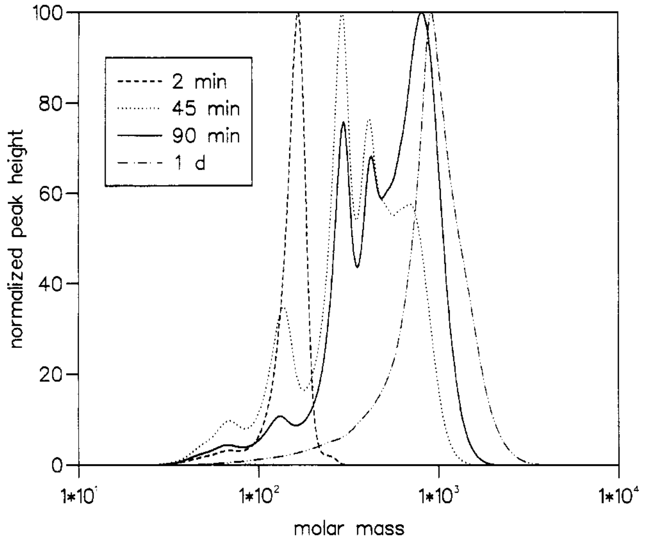

Figure 8. Gel permeation chromatograms of a NNDE sol containing 9 mol equiv of methanol ($R_w = 1.5$, (– – –) 2 min; (—) 45 min; (···) 90 min, (–·–) 1 day).

When methanol is added as a solvent, the reaction stops with the formation of octamers (Figures 8 and 9). Species with $n = 16$, which in the solvent-free systems are preferentially formed within the same period, only appear to a minor extent. The equilibrium between $n = 8$ and $n = 16$ is shifted to the cubic octamer, probably by alcoholysis of the "dimer". This has also been observed for the base-catalyzed hydrolysis and condensation of $Si(OEt)_4$.[6] Due to this fact the mean molecular mass after 24 h is slightly smaller ($M_w = 971$ for $R_w = 1.5$, and 870 for $R_w = 3.0$, respectively), compared to the solvent-free system ($M_w = 1151$ for $R_w = 3.0$).

The influence of R_w on the development of the oligomer distribution upon hydrolysis of methanolic NNDE solutions is once more shown in Figures 10 and 11. A higher initial concentration of water resulted in the quicker appearance of the octamers (i.e., the quicker disappearance of the smaller oligomers), due to a more rapid hydrolysis reaction. Both curves indicate that the systems are close to equilibrium after about 3 h. The formed sols are stable for months; within that period no gelation occurs.

The stepwise growth of the oligomers, including the condensation of $R_8Si_8O_{10}(OH)_2$ units, corresponds to the growth mechanism proposed by Brown et al. for the condensation of cyclohexyl- and phenylsilanetriole.[7] Cubic octamers were identified or isolated as very stable entities for a variety of silsesquioxanes.[8] Due to the overlap of the GPC peaks, the intermediate appearance

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(5) Piana, K.; Schubert, U. *Chem. Mater.* **1994**, *6*, 1504.

(6) Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 3.

(7) Brown, J. F.; Vogt, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 4313. Brown, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 4317.

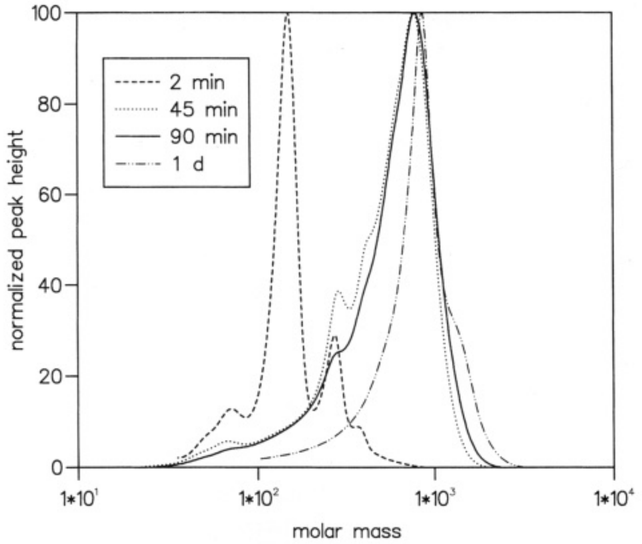

Figure 9. Gel permeation chromatograms of a NNDE sol containing 9 molar equivalents of methanol (R_w = 3.0, (− − −) 2 min; (···) 45 min; (—) 90 min; (−·−) 1 day).

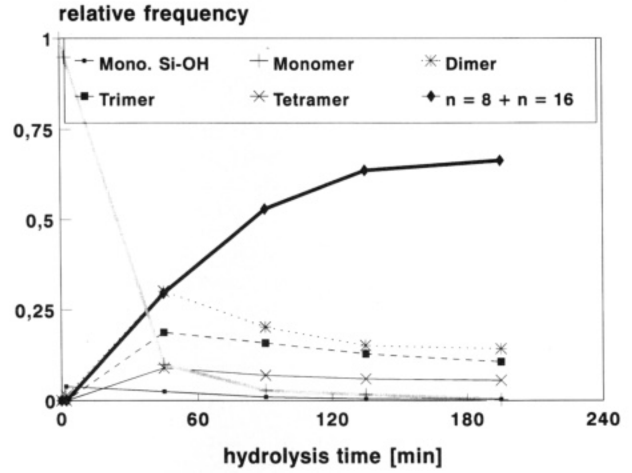

Figure 10. Development of the oligomer distribution by the time on hydrolysis of a methanolic NNDE solution (R_w = 1.5).

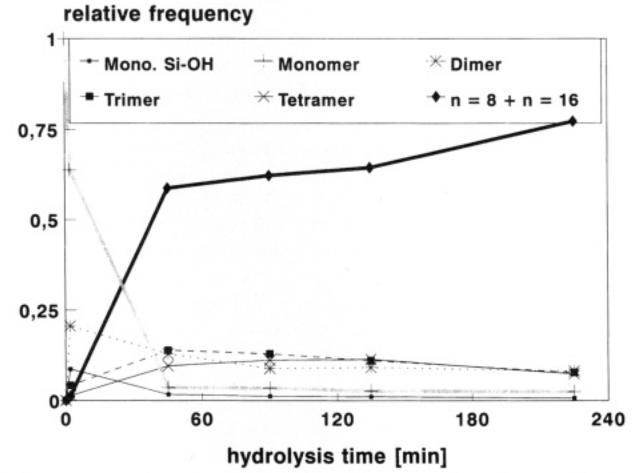

Figure 11. Development of the oligomer distribution by the time on hydrolysis of a methanolic NNDE solution (R_w = 3.0).

of $[RSiO_{3/2}]_n$ species with $n = 5-7$ in minor concentrations cannot be totally excluded in the NNDE hydrolysis reaction.

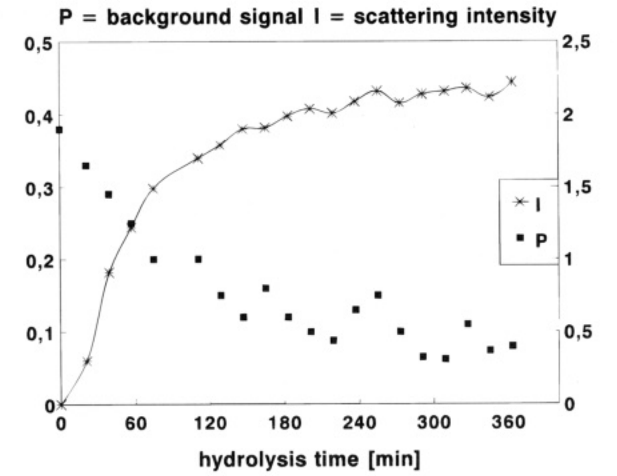

Figure 12. Development of the scattering intensity by the time (methanolic NNDE sol, R_w = 1.5). I = scattering intensity of the particles; P = scattering intensity of the background.

Removal of all volatiles from a methanolic NNDE sol (R_w = 3.0) in vacuo resulted in a clear, viscous oil. Its GPC was identical with that of the methanolic sol, i.e., the composition of the sol particles was not changed. The infrared spectrum of this oil showed a band at 1130 cm^{-1} typical for the cubic octamers $[RSiO_{3/2}]_8$.[9] There were no signals for Si−OMe or Si−OH groups in the ^{1}H NMR spectrum. The sharpness of the signals strongly indicated the presence of molecular species instead of polymers. Complete condensation is also consistent with an elemental analysis, which fits very well to the composition $[Et_2N(CH_2)_3SiO_{3/2}]_n$. In the mass spectrum the most prominent peaks corresponded to singly and doubly ionized $[Et_2N(CH_2)_3SiO_{3/2}]_8$. Molecular peaks of some higher oligomers were additionally observed with low intensity.

Combining all pieces of evidence, the conclusion is that the cubic octamer is predominantly formed, which is rather resistent against further oligomerization.

The observation that a higher ratio of smaller oligomers was formed with methanol as a solvent compared to neat NNDE, was supported by the results of X-ray small-angle scattering (SAXS) experiments. The radius of gyration (which corresponds to the average of all detectable species) after 12 h was 0.51 ± 0.02 nm, compared with 0.55 ± 0.02 nm for the solvent-free systems.

For one sample (methanolic solution of NNDE; R_w = 1.5) the condensation process was followed by SAXS (Figure 12). The increase of the radius of gyration (R_g) followed an exponential time law. Already 110 min after the addition of water R_g was 0.47 ± 0.02 nm. There was a linear relation between $\ln[I_0/(I_0 - I)]$ (I = scattering intensity of the particles) and the time. From that a pseudo-first-order rate constant of $k_P = 0.013 \pm 0.001$ min^{-1} was calculated. Simultaneously, the intensity of the scattering background signal (P) decreased exponentially, $\ln P/P_0 = -k_P t$ with $k_I = 0.0066 \pm 0.001$ min^{-1}. This scattering is caused by small species (probably monomers or dimers) being outside the detection range.

A pseudo-first-order rate law is typical for dimerization reactions. However, the rate constant found for the

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(8) Voronkov, M. G.; Lavrent'yev V. I. *Top. Curr. Chem.* **1982**, *102*, 199. Martynova, T. N.; Korchkov, V. P.; Semyannikov, P. P. *J. Organomet. Chem.* **1983**, *258*, 277. Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *379*, 33.

(9) Anderson, D. R. In *The Analysis of Silicon;* Smith, A. L., Ed.; Wiley: New York, 1974.

appearance of the "dimer" (derived from the scattering intensity I) is twice that of the disappearance of the "monomer" (derived from the scattering intensity P). This can be explained by a preequilibrium by which the "monomers" are formed. The scattering curve (I in Figure 12) is nearly identical with the appearance of the octamers in GPC (Figure 10). We therefore assume that the "dimerization" process observed by the SAXS measurements is the formation of the octamers from the tetramers. The diameter ($d = 2r$) of spherical particles can be calculated from R_g ($R_g = \sqrt{(3/5)}r$). The calculated value of 1214 pm agrees quite well with the lengths of the Si–Si diagonals in cubic octamers $[RSiO_{3/2}]_8$ determined by X-ray crystallography (R = OMe: 1559 pm; R = Me: 1460 pm).[10] It should be noted that by SAXS measurements only the inorganic part of the oligomers can be "seen", since R_g for the primary particles of sols obtained from different aminoalkyl-substituted alkoxysilanes with different lengths of the alkyl chain were found to be the same.[11]

When NNDE was hydrolyzed with $R_w = 3.0$ instead of 1.5, only the increase of the number of particles with $R_g = 0.5$ nm could be detected. At 20 min after the addition of water, the intensity of the background signal was no longer detectable. Therefore, determination of the kinetic parameters of the reaction was not possible. The radius of gyration after 2 h was about the same as for the sols with $R_w = 1.5$.

The scattering curves of both sols ($R_w = 1.5$ or 3.0) after 1 day were identical within the experimental accuracy. They can be described by a Guinier approximation for the scattering vector $q > 0.1$ Å^{-1}. Deviations from this approximation were observed for smaller angles, due to interference phenomena known for concentrated solutions.[12] In the Porod regime the scattering curves corresponded to a q^{-3} behavior. (Due to the slit geometry of the aperture, the scattering exponent is 10 times larger than for an aperture with point geometry, where a q^{-4} behavior would be observed.) The particles therefore have a smooth surface, as has been observed for the base-catalyzed hydrolysis of $Si(OEt)_4$ in aqueous solutions.[13]

Conclusions

The reactivity of NNDE is strongly influenced by impurities. Therefore, only freshly distilled NNDE should be used to achieve reproducible results. This should particularly be kept in mind for practical applications of (aminoalkyl)trialkoxysilanes.

The hydrolysis and condensation behavior of NNDE is the same as typically found for alkoxysilanes in the presence of a base catalyst. The amino group of NNDE therefore acts as a kind of internal catalyst. The reaction order of 1.5 for water can be explained by a preequilibrium between the two bases OH^- and the $-NEt_2$ group. Strong hydrogen bonds between silanol groups and the NH_2 group of (aminopropyl)trialkoxysilanes were previously found by FTIR, Raman, and NMR studies[14] and are consistent with this picture.

Without an external catalyst and without methanol as a solvent, only small oligomers are formed (n = 8 and 16). While the rate of formation of these primary particles strongly depends on the water:silane ratio (R_w value), the degree of oligomerization is hardly affected.

Hydrolysis is accelerated and the intermediate concentration of species with Si–OH groups is increased by a high R_w. These species quickly condense. A similar influence of R_w on hydrolysis and condensation was observed for (3-glycidoxypropyl)trimethoxysilane.[5] Contrary to that, the degree of oligomerization of NNDE is not influenced by R_w. The predominant oligomer resulting from hydrolysis and condensation of NNDE is $[Et_2N(CH_2)_3SiO_{3/2}]_8$. Only without methanol as a solvent dimerization of this species occurs to an appreciable amount. The formation of real polymers was never observed under base-catalyzed conditions. All spectroscopic and chromatographic evidence suggests that growth of the oligomers is as proposed by Brown et al.[6] for the condensation of cyclohexyl- or phenylsilanetriole, hydrolysis being the rate-determining step.

Experimental Section

Materials and Reactions. [(*N*,*N*-Diethylamino)propyl]trimethoxysilane (NNDE) was obtained from Petrarch and was freshly distilled before use. Deionized water [0.15 mol (2.70 g) or 0.30 mol (5.40 g), pH = 5.5) was added at 25 °C to 0.10 mol (23.54 g) of NNDE. When methanol was used as a solvent, NNDE was dissolved in 0.90 mol (28.80 g) of methanol before addition of the water. The mixtures were stirred in a closed vessel and then kept.

For the spectroscopic and analytical investigations, the methanolic sol with $R_w = 3.0$ was held at high vacuum for 3 days to remove all volatiles. A clear, viscous oil was obtained. IR (KBr, film) 2800 (NCH), 1130 cm^{-1} (SiOSi). ^1H NMR δ (JEOL FX90Q, $CDCl_3$) 2.49 (m, 6H, NCH_2), 1.03 (quint, 2H, $CH_2C\mathit{H}_2CH_2$), 0.95 (t, 6H, CH_3), 0.86 (m, 2H, $SiCH_2$). Mass spectrum (70 eV) 664.6 (12.2%, $[C_7H_{16}NSiO_{1.5}]_n$, $n = 8$ [M^{2+}]), 1329 (14.8%, $[C_7H_{16}NSiO_{1.5}]_n$, $n = 8$ [M^+]), 1495 (0.7%, $n = 9$), 1662 (3.7%, $n = 10$), 1828 (0.1, $n = 11$), 1994 (0.2%, $n = 12$). Anal. Calcd for $C_7H_{16}NSiO_{1.5}$: C, 50.48; H, 9.26; N, 8.41. Found: C, 49.50; H, 9.53; N, 8.24.

Karl Fischer Titration. Pyridine-free Karl Fischer solutions K and U of Merck and a Mettler DL 18 titrator were used.

Gel Permeation Chromatography. Samples were taken from the reaction mixtures and dissolved in 1 mL of THF (not stabilized, obtained from Promochem) per 20 μL of sol. Toluene was used as an internal standard. At 5 min after addition of the solvent the solution was filtered and gel chromatographed.

Analytical chromatograms were obtained with a HPLC system operated at a temperature of 38 °C. A bank of three 300 × 8 mm columns packed with polystyrene–divinylbenzene gel (permeabilities 10^2, 10^3, 10^5 Å; pore size 5 μm) was employed. The mobile phase was nonstabilized, N_2-saturated THF (Promochem), and its flow rate was 1.0 mL/min. An injection volume of 20 μL was used. A UV detector (LCD 500 of GAT operated at 230 nm) was used.

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(10) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Miller, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262.

(11) Rouseau, F. Ph.D. Thesis, University of Grenoble, 1990.

(12) Glatter, O.; Kratky, O. *Small Angle X-Ray Scattering;* Academic Press: New York, 1982.

(13) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62. Matsoukas, T.; Gulari, E. *J. Colloid Interface Sci.* **1988**, *124*, 252.

(14) Ishida, H.; Chiang, C.; Koenig, J. L. *Polymer* **1982**, *23*, 251. Ishida, H.; Naviroj, S.; Tripathy, S. K.; Fitzgerald, J. J.; Koenig, J. L. *J. Polymer Sci.* **1982**, *20*, 701. Vrancken, K. C.; van der Voort, P.; Gillis-D'Hamers, I.; Vansant, E. F. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3197.

(15) Ishida, H.; Koenig, J. L. *J. Colloid Interface Sci.* **1978**, *64*, 555. Ishida, H.; Chiang, C. L.; Koenig, J. L. *Polymers* **1982**, *23*, 253. Benesi, H. A.; Jones, A. C. *J. Chem. Soc.* **1959**, *63*, 179. Smith, A. L. In *The Analysis of Silicon;* Smith, A. L., Ed.; Wiley: New York, 1974.

The peak maxima are given as polystyrene equivalents (M_p). A calibration curve was generated from the chromatograms of 16 nearly monodisperse polystyrene standards with molecular masses ranging from 162 to 1.55 × 10^6. The oligomer distribution was determined by integration of the chromatograms. The percentage of a particular oligomers therefore rather corresponds to the relative peak area of the corresponding band.

SAXS Measurements. A Kratky compact camera of Paar KG with a location-sensitive detector Braun OED50M (0.1–60 nm) was used. The samples were sealed in glass capillaries with a diameter of 1 mm and a wall thickness of 10 μm. The solvent-free sols were diluted with 9 mol equiv of MeOH before the measurements to avoid interference effects.

FTIR Spectroscopy. The FTIR measurements were measured with a Nicolet 60SX spectrometer (ATR mode, ZnSe crystal, 4000–650 cm^{-1}) using a circle cell (Spectra Tech, 0.65 mL cell volume, film volume 16 μL) and a stopped-flow device (flow 5 mL/min, dead volume 50 μL). The characteristic bands of the different groups were integrated within the following limits:[15] H–OH 1700–1616 cm^{-1} (maximum at 1635), Si–OSi 1153–1100 cm^{-1} (maximum at 1130), Si–OMe 1100–1059 cm^{-1} (maximum at 1080), Si–OH 950–873 cm^{-1} (maximum at 910).

The starting concentrations, and the extinctions of the Si–OMe and H_2O band are given in Table 1. Concentrations were calculated from the integrated extinctions, assuming that the Lambert–Beer law is valid, by the linear relation $E_0 = c_0a + b$, with a = 4.8073 and b = 24.6140. The validity of this assumption is shown by the nearly identical E_0/c_0(Si–OMe) values for the three reactions. There is no linear relation for the H_2O band. Therefore, the calculations were based on the ration $\Delta c_{Rw=1.50}/\Delta c_{Rw=3.00} = 0.717$ ($\Delta E_{Rw=1.50}/\Delta E_{Rw=3.00} = 0.720$), determined by Karl Fischer titration after 1 h. Since this is a linear relation, the concentrations were calculated by $\Delta E/1.39$.

Table 1. Starting Concentrations and the IR Extinctions of the Si–OMe and H_2O Band for Different R_w (Indexes Refer to 0 and 60 min, Respectively; Concentrations in mol/L)

R_w	0.75	1.50	3.00
$[H_2O]_0$	1.20	2.35	4.50
$[NNDE]_0$	1.60	1.56	1.50
$[Si\text{-}OMe]_0$	4.80	4.69	4.50
$[MeOH]_0$	14.08	14.08	13.51
E_0(SiOMe)	48.174	47.170	46.247
E_0/c_0	10.036	10.053	10.28
$E_0 = E_{60}$	5.987	10.82	14.32
$E_0(H_2O)$	2.949	5.081	9.131
E_0/c_0	2.458	2.166	2.029
$E_0 - E_{60}$	1.44	2.29	3.18
KF titration (after 1 h)		1.72	2.40

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