

^{29}Si NMR study on co-hydrolysis processes in $\text{Si}(\text{OEt})_4$ – $\text{RSi}(\text{OEt})_3$ – EtOH – water – HCl systems ($\text{R} = \text{Me}, \text{Ph}$): effect of R groups

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Hydrolysis and initial polycondensation processes in the $\text{Si}(\text{OEt})_4$ (TEOS)– $\text{RSi}(\text{OEt})_3$ – EtOH – water – HCl systems ($\text{R} = \text{Me}, \text{Ph}$) [$\text{TEOS} : \text{RSi}(\text{OEt})_3 : \text{EtOH} : \text{water} : \text{HCl} = 1 : 1 : 24 : x : y$ ($x = 12, 2/3; y = 2 \times 10^{-3}, 4 \times 10^{-3}, 8 \times 10^{-2}$)] have been investigated by using ^{29}Si NMR spectroscopy. For comparison, the alkoxysilanes [$\text{TEOS}, \text{MeSi}(\text{OEt})_3$ (MTES), $\text{PhSi}(\text{OEt})_3$ (PTES)] were hydrolysed separately in a similar manner. In a water-rich TEOS–MTES system (water : Si = 12 : 1), a silanol-terminated codimer [$\text{Me}(\text{HO})_2\text{SiOSi}(\text{OH})_3$] was detected as well as $(\text{HO})_3\text{SiOSi}(\text{OH})_3$ and $\text{Me}(\text{HO})_2\text{SiOSi}(\text{OH})_2\text{Me}$, suggesting that the hydrolysed monomers were condensed rather randomly. In contrast, in a water-rich TEOS–PTES system, hydrolysed monomers derived from TEOS and those from PTES were condensed independently; a silanol-terminated codimer [$\text{Ph}(\text{HO})_2\text{SiOSi}(\text{OH})_3$] did not form, and only $(\text{HO})_3\text{SiOSi}(\text{OH})_3$ and $\text{Ph}(\text{HO})_2\text{SiOSi}(\text{OH})_2\text{Ph}$ were detected. These observations in the TEOS–PTES system suggest the presence of the association of the phenyl groups. In water-restricted systems (water : Si = 1 : 3), monomers were only partially hydrolysed, and ethoxy-terminated codimers [$\text{R}(\text{EtO})_2\text{SiOSi}(\text{OEt})_3$ ($\text{R} = \text{Me}, \text{Ph}$)] formed in both the TEOS–MTES and the TEOS–PTES systems.

A new family of sol–gel-derived inorganic–organic composite materials called ORMOCERs (organically modified ceramics) [or ORMOSILs (organically modified silicates)] have attracted increasing attention.^{1–3} They can be prepared by two strategies: the co-hydrolysis of tetraalkoxysilane [$\text{Si}(\text{OR})_4$] and organoalkoxysilane [$\text{R}'\text{Si}(\text{OR})_3$ or $\text{R}'\text{R}''\text{Si}(\text{OR})_2$]^{1–3} or the hydrolysis of tetraalkoxysilane in the presence of silanol-terminated poly(dimethylsiloxane).^{4–6} Co-hydrolysis processes are advantageous for the preparation of advanced materials, since trialkoxysilanes where functional groups are covalently attached to silicon can be used; typically chromophores and ligand groups available for coordination to metals have been incorporated into silica matrices by co-hydrolysis processes.⁷ Another recently developed type of material derived from organoalkoxysilanes is the interpenetrating network (IPN), where organic polymers are incorporated into sol–gel glass structures.^{8,9}

When two kinds of alkoxysilanes are co-hydrolysed, the properties of the final xerogels should depend on their homogeneity. If two alkoxysilanes condense mainly independently after their hydrolysis, the products should possess segregated domain structures, while homogeneous materials could be obtained if hydrolysed species are condensed randomly. Solid-state ^{29}Si NMR spectroscopy is capable of investigating the structures of xerogels, so that several solid-state NMR studies have been reported on ORMOCERs.^{10–20} Because of insufficient resolution, however, the discussion on the homogeneity is very limited. Thus, as far as we know, only when the two-dimensional ^1H – ^{29}Si correlation CP MAS NMR technique was applied,^{18,19} could detailed structural information be obtained.

Liquid-state ^{29}Si NMR is also a powerful tool, in particular for the hydrolysis and initial polycondensation process of tetraalkoxysilanes²¹ and organoalkoxysilanes,^{22–35} and it has also been applied to co-hydrolysis processes.^{11,14,16,17,33,35–40} The initial polycondensation process of a tetraethoxysilane [$\text{Si}(\text{OEt})_4$; TEOS]–dimethyldiethoxysilane [$\text{Me}_2\text{Si}(\text{OEt})_2$; DMDES] system has been studied extensively, and the signals due to D–Q [$\text{OSiMe}_2\text{OSi}(\text{O}^-)_3$] bonds have been iden-

tified.^{16,17} In the co-hydrolysis process of the TEOS–methyltriethoxysilane [$\text{MeSi}(\text{OEt})_3$; MTES] system, we have identified two ^{29}Si NMR signals due to $(\text{HO})_2\text{MeSiOSi}(\text{OH})_3$, as well as those due to $(\text{HO})_2\text{MeSiOSiMe}(\text{OH})_2$ and $(\text{HO})_3\text{SiOSi}(\text{OH})_3$.³⁷ Similar results were independently reported for other TEOS–MTES systems.^{39,40} On the other hand, Kim *et al.* studied the co-hydrolysis process of TEOS and a chromophore-tagged trialkoxysilane [N -[3-(triethoxysilyl)propyl]-2,4-dinitrophenylamine; TDP], and revealed that the cross-linking between the TEOS-derived and TDP-derived species was limited.³⁸ Very recently, Babonneau *et al.* utilized liquid-state ^{17}O NMR instead of ^{29}Si NMR spectroscopy, and successfully identified signals due to bridging oxygen for $\text{OSiMe}_2\text{OSi}(\text{O}^-)_3$ (D–Q) and $(-\text{O})_2\text{SiMeOSi}(\text{O}^-)_3$ (T–Q) units.⁴¹

This paper describes the ^{29}Si NMR study on the co-hydrolysis processes of TEOS and organotriethoxysilanes [$\text{RSi}(\text{OEt})_3$; $\text{R} = \text{Me}$ or Ph], and aims to clarify the effect of the R groups on co-condensation between TEOS and $\text{RSi}(\text{OEt})_3$. We focus on the dimer formation behaviour, and discuss the tendency of condensation based on the hydrophobicity of the R groups.

Experimental

Sample preparation

TEOS, MTES and phenyltriethoxysilane [$\text{PhSi}(\text{OEt})_3$; PTES] were used as received. No hydrolysed products were detected by ^{29}Si NMR spectroscopy. Ethanol was dehydrated by molecular sieves before use. HCl was added as a 0.1 or 1 mol dm^{-3} aqueous solution.

Reactions were conducted in TEOS– $\text{RSi}(\text{OEt})_3$ (MTES or PTES)– EtOH – water ($\text{D}_2\text{O}/\text{H}_2\text{O}$)– HCl systems. Alkoxysilanes were used separately or as 1:1 mixtures; thus five different systems (TEOS–MTES, TEOS–PTES, TEOS, MTES, PTES) were prepared. Two alkoxysilane:water ratios (water:Si = 12:1, 1:3) were applied for every system. When water:Si = 12:1, reactions were conducted in systems with

alkoxysilane:EtOH:water:HCl=2:24:24:y ($y=2 \times 10^{-3}$, 4×10^{-3} , 8×10^{-2}). D₂O and hydrochloric acid were added dropwise to a mixture of alkoxysilanes and ethanol, and the resulting homogeneous solution was stirred for 3 min. For the systems with water:Si=1:3, samples were prepared with alkoxysilane:EtOH:water:HCl=2:24:2/3:4 × 10⁻³. A mixture of ethanol, H₂O and hydrochloric acid was added to the alkoxysilane, and the resulting solution was heated at reflux for 2 days under a protective nitrogen atmosphere.

²⁹Si NMR measurements

Silicon-29 NMR spectra were obtained using a JEOL NM-GSX-400 spectrometer (9.4 T) operated at 79.42 MHz. A sample solution was put in a 10 mm o.d. glass tube and a trace of Cr(CH₃COCHCOCH₃)₃ was added to the sample solution to reduce the ²⁹Si spin-lattice relaxation time (*T*₁). For samples with water:Si=1:3, since no D₂O was used, a small amount of CDCl₃ was added to the sample solution to obtain lock signals. The spectra were essentially similar to those obtained without the addition of CDCl₃. Measurements were performed using inversely gated decoupling. The repetition time was 20 s and π/2 pulses were used. For qualitative measurements in water-rich systems (water:Si=12:1), only 12 FIDs were accumulated, since the distributions of species changed even after 3 h. In contrast, the spectra for qualitative measurements in water-restricted systems (water:Si=1:3) were accumulations of 128 FIDs, since the distributions of species barely changed after refluxing for 2 days with the minimum amount of water. For quantitative analyses of the water-rich systems, 24 (hydrolysis time up to ca. 3 h) and 48 (hydrolysis times ca. 4 and ca. 6 h) FIDs were accumulated. The spectra in water-rich systems were characterized by using the time elapsing from the end of the addition of hydrochloric acid to the middle of the measurement period. Chemical shifts were reported with respect to internal tetramethylsilane.

Results

The environments of the silicon atoms are represented using the number of siloxane bonds and hydroxy groups. For TEOS-derived units, an environment Si(O_{0.5})_n(OH)_m(OEt)_{4-n-m} is represented as Q^{*n*}_(*m*OH). For units derived from MTES and PTES, an environment RSi(O_{0.5})_n(OH)_m(OEt)_{3-n-m} (R=Me, Ph) is expressed as T_M^{*n*}_(*m*OH) (R=Me), T_P^{*n*}_(*m*OH) (R=Ph), or T^{*n*}_(*m*OH) (for both).

Reactions in water-rich systems (water:Si=12:1) were conducted to hydrolyse most of the ethoxy groups before condensation. Thus, condensation should proceed mainly *via* a water-producing reaction:

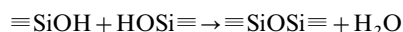


Fig. 1 shows typical ²⁹Si NMR spectra (collected after ca. 3 h hydrolysis) for the five systems (TEOS–MTES, TEOS–PTES, TEOS, MTES and PTES), and enlarged profiles of the T¹ and Q¹ regions are demonstrated in Fig. 2. The signals in the TEOS and MTES systems [Fig. 2(a) and 2(c)] are reasonably assigned to monomers and oligomers on the basis of previous reports (see Table 1).^{21,28} The time evolution of spectra for the PTES system (not shown) is very similar to that of the MTES system,²⁸ although the signal region is shifted considerably upfield from that of the MTES system. Thus, these signals are assigned in the way used for the MTES system.²⁸ Assignments for monomeric species derived from PTES are based on previous work.³² These assignments are summarized in Table 1.

When the 1:1 mixture of TEOS and MTES is hydrolysed, the spectrum is not a simple overlay of the spectra of the TEOS and MTES systems; two new intense signals (AB1 and AB2) are clearly observed in Fig. 2(b), and are assigned to T_M¹_{(2OH)Q}¹_(3OH).³⁷ In contrast, the spectrum for the TEOS–PTES system [Fig. 2(d)] is essentially an overlay of those of the TEOS and PTES systems [Fig. 2(c) and 2(e)]; no detectable new signals appear in the T_P¹ and Q¹ regions. Even

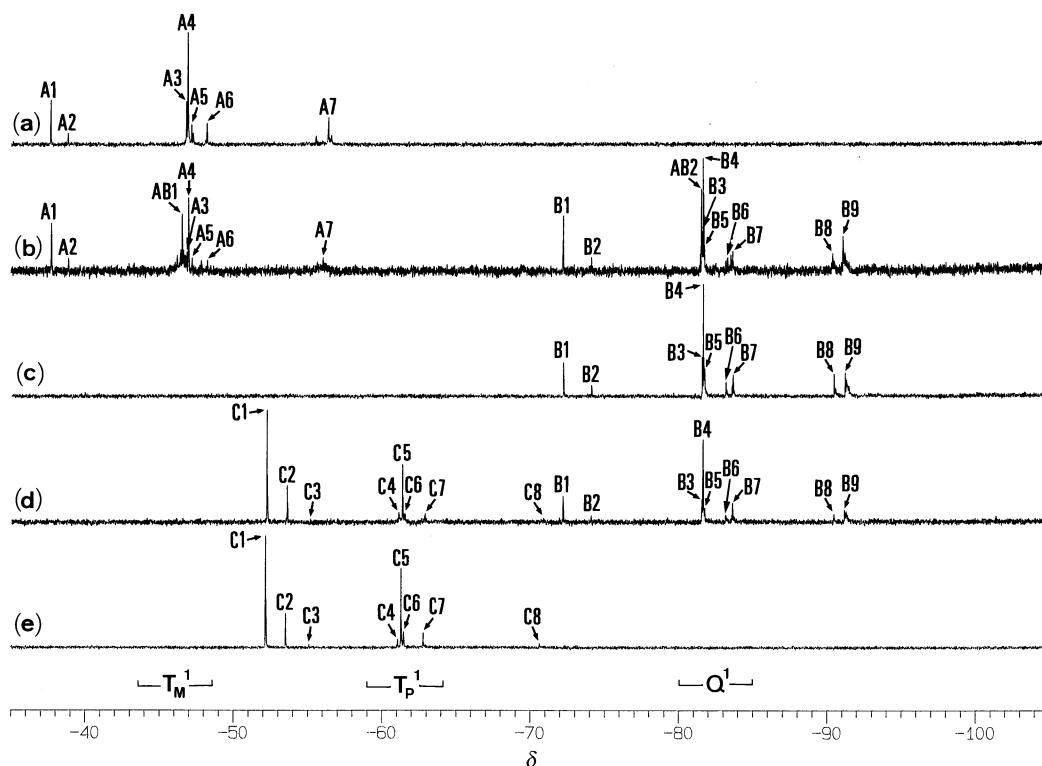


Fig. 1 Silicon-29 NMR spectra of the solution in the system with alkoxysilane:EtOH:D₂O/H₂O:HCl=2:24:24:4 × 10⁻³ after hydrolysis for ca. 3 h. (a) MTES only; (b) MTES:TEOS=1:1 mixture; (c) TEOS only; (d) PTES:TEOS=1:1 mixture; (e) PTES only.

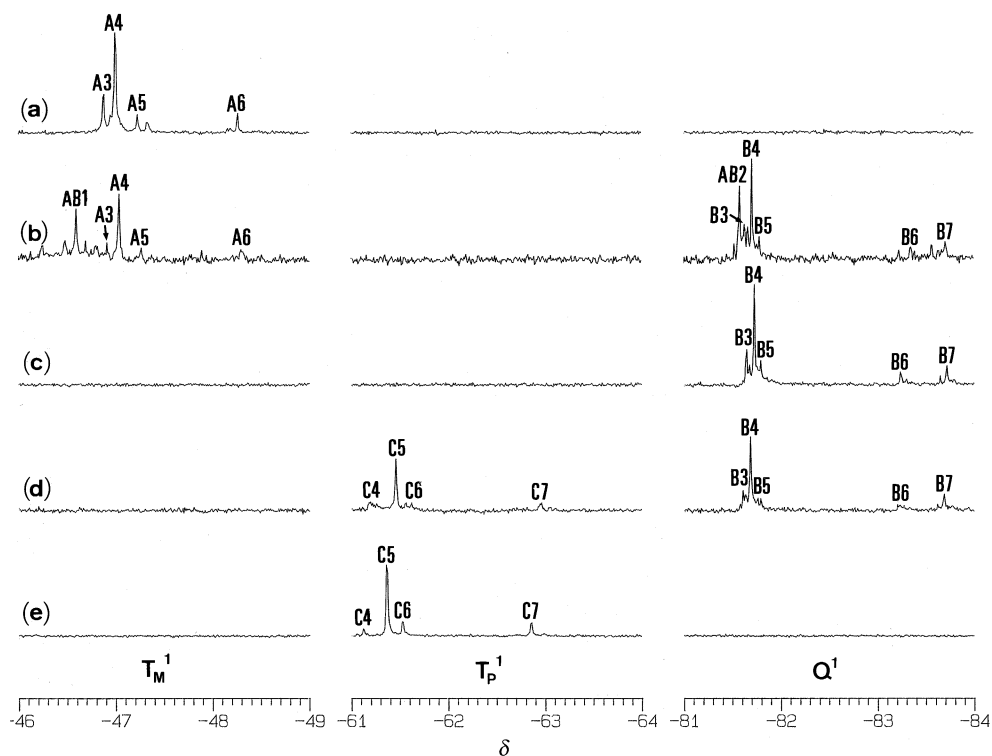


Fig. 2 Enlarged profile (T^1 and Q^1 region) of Fig. 1. (a) MTES only; (b) MTES:TEOS = 1:1 mixture; (c) TEOS only; (d) PTES:TEOS = 1:1 mixture; (e) PTES only.

Table 1 Assignments of labelled ^{29}Si NMR signals for monomeric and oligomeric species obtained by the hydrolysis of alkoxy silanes (water: Si = 12:1)

signal	structure	formula
A1	$T_M^0(3\text{OH})$	$\text{MeSi}(\text{OH})_3$
A2	$T_M^0(2\text{OH})$	$\text{MeSi}(\text{OH})_2(\text{OEt})$
A3	$T_M^1(2\text{OH})T_M^2(1\text{OH})T_M^1(2\text{OH})$	$\text{Me}(\text{HO})_2\text{Si}(\text{OMe})(\text{HO})\text{SiOSi}(\text{OH})_2\text{Me}$
A4	$T_M^1(2\text{OH})T_M^1(2\text{OH})$	$\text{Me}(\text{HO})_2\text{SiOSi}(\text{OH})_2\text{Me}$
A5	$T_M^1(2\text{OH})T_M^1(1\text{OH})$	$\text{Me}(\text{HO})_2\text{SiOSi}(\text{OH})(\text{OEt})\text{Me}$
A6	$T_M^1(2\text{OH})T_M^1(1\text{OH})$	$\text{Me}(\text{HO})_2\text{SiOSi}(\text{OH})(\text{OEt})\text{Me}$
A7	$T_M^1(2\text{OH})T_M^2(1\text{OH})T_M^1(2\text{OH})$	$\text{Me}(\text{HO})_2\text{Si}(\text{OMe})(\text{HO})\text{SiOSi}(\text{OH})_2\text{Me}$
B1	$Q^0(4\text{OH})$	$\text{Si}(\text{OH})_4$
B2	$Q^0(3\text{OH})$	$\text{Si}(\text{OH})_3(\text{OEt})$
B3	$Q^1(3\text{OH})Q^2(2\text{OH})Q^1(3\text{OH})$	$(\text{HO})_3\text{Si}(\text{O})(\text{HO})_2\text{SiOSi}(\text{OH})_3$
B4	$Q^1(3\text{OH})Q^1(3\text{OH})$	$(\text{HO})_3\text{SiOSi}(\text{OH})_3$
B5	$Q^1(3\text{OH})Q^1(2\text{OH})$	$(\text{HO})_3\text{SiOSi}(\text{OH})_2(\text{OEt})$
B6	$[\text{Q}^2(2\text{OH})]_{3\text{cyc}}$	$[(\text{HO})_2\text{SiO}]_3$
B7	$Q^1(3\text{OH})Q^1(2\text{OH})$	$(\text{HO})_3\text{SiOSi}(\text{OH})_2(\text{OEt})$
B8	$[\text{Q}^2(2\text{OH})]_{4\text{cyc}}$	$[(\text{HO})_2\text{SiO}]_4$
B9	$Q^1(3\text{OH})Q^2(2\text{OH})Q^1(3\text{OH})$	$(\text{HO})_3\text{Si}(\text{O})(\text{HO})_2\text{SiOSi}(\text{OH})_3$
C1	$T_P^0(3\text{OH})$	$\text{PhSi}(\text{OH})_3$
C2	$T_P^0(2\text{OH})$	$\text{PhSi}(\text{OH})_2(\text{OEt})$
C3	$T_P^0(1\text{OH})$	$\text{PhSi}(\text{OH})(\text{OEt})_2$
C4	$T_P^1(2\text{OH})T_P^2(1\text{OH})T_P^1(2\text{OH})$	$\text{Ph}(\text{HO})_2\text{Si}(\text{OPh})(\text{HO})\text{SiOSi}(\text{OH})_2\text{Ph}$
C5	$T_P^1(2\text{OH})T_P^1(2\text{OH})$	$\text{Ph}(\text{HO})_2\text{SiOSi}(\text{OH})_2\text{Ph}$
C6	$T_P^1(2\text{OH})T_P^1(1\text{OH})$	$\text{Ph}(\text{HO})_2\text{SiOSi}(\text{OH})(\text{OEt})\text{Ph}$
C7	$T_P^1(2\text{OH})T_P^1(1\text{OH})$	$\text{Ph}(\text{HO})_2\text{SiOSi}(\text{OH})(\text{OEt})\text{Ph}$
C8	$T_P^1(2\text{OH})T_P^2(1\text{OH})T_P^1(2\text{OH})$	$\text{Ph}(\text{HO})_2\text{Si}(\text{OPh})(\text{HO})\text{SiOSi}(\text{OH})_2\text{Ph}$
AB1	$T_M^1(2\text{OH})Q^1(3\text{OH})$	$\text{Me}(\text{HO})_2\text{SiOSi}(\text{OH})_3$
AB2	$T_M^1(2\text{OH})Q^1(3\text{OH})$	$\text{Me}(\text{HO})_2\text{SiOSi}(\text{OH})_3$

when the amount of HCl was increased to 8×10^{-2} (not shown), no evidence for the presence of codimer was obtained.

Fig. 3 illustrates the quantitative results for the systems of the 1:1 mixtures of alkoxy silanes [TEOS:MTES (or PTES):EtOH:water:HCl = 1:1:24:24: 2×10^{-3} ; Fig. 3(a) and (c) for the TEOS–MTES system and Fig. 3(b) and (d) for the TEOS–PTES system]. After hydrolysis for 19 min, the amounts of oligomers are very small [Fig. 3(c)]. At this point, nearly 70% of the MTES is completely hydrolysed to form $T_M^0(3\text{OH})$, while less than 50% of the TEOS is present as $Q^0(4\text{OH})$

[Fig. 3(a)]. For the TEOS–PTES system [Fig. 3(b)], the hydrolysis behaviour of TEOS is similar to that of the TEOS–MTES system. In contrast, hydrolysis of PTES is slower than that of MTES, and only *ca.* 40% of the PTES is hydrolysed completely to form $T_P^0(3\text{OH})$ after 19 min hydrolysis.

As the reactions proceed, hydrolysed monomers are involved in condensation reactions to form oligomers and polymers. In the time range investigated, T^1 , T^2 , Q^1 and Q^2 environments are mainly detected as condensed ones, and branched environ-

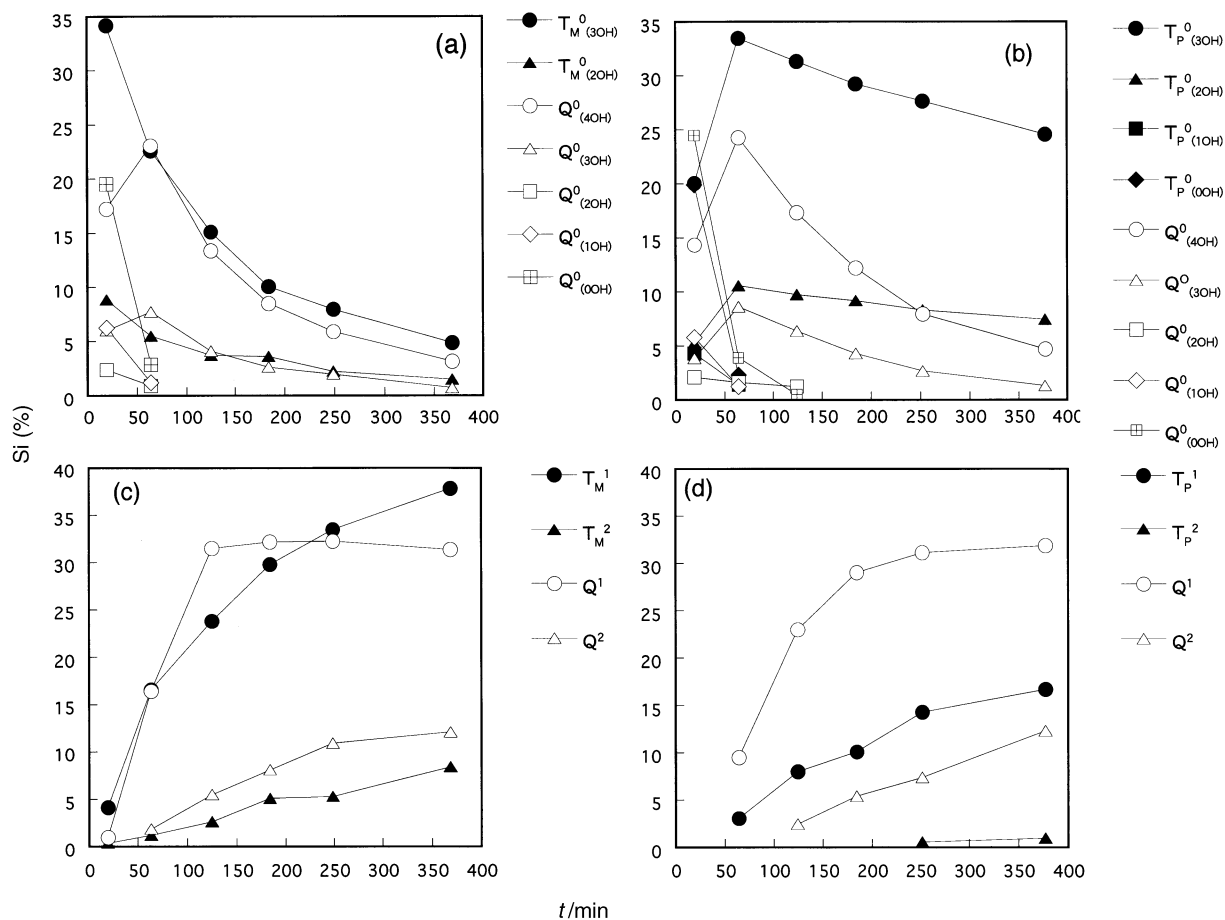


Fig. 3 Time evolution of signals due to monomeric and condensed species in the system with TEOS:RSi(OEt)₃:EtOH:D₂O/H₂O:HCl=1:1:24:24:2 × 10⁻³. (a) monomeric species for the MTES:TEOS=1:1 mixture; (b) monomeric species for the PTES:TEOS=1:1 mixture; (c) condensed species for the MTES:TEOS=1:1 mixture; (d) condensed species for the PTES:TEOS=1:1 mixture.

ments (T^3 , Q^3 and Q^4) are hardly detected. From the results presented in Fig. 3(b) and (d), we can calculate the average number of siloxane bonds per silicon atom, as shown in Fig. 4. Clearly, the condensation rate of PTES-derived species is much lower than those of TEOS- and MTES-derived species.

We also prepared dimers with a minimum amount of water (water:Si=1:3). Fig. 5 represents the whole ²⁹Si NMR spectra of the five systems, and their enlarged profiles for the T¹ and Q¹ regions are shown in Fig. 6. Since the amount of silanol groups is very restricted, the alcohol-producing condensation should be dominant, thus ethoxy-terminated species should

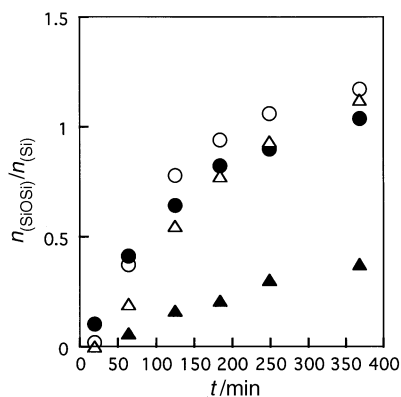
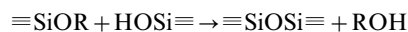


Fig. 4 Time evolution of the average number of SiOSi bonds formed per Si atom in the system with TEOS:RSi(OEt)₃:EtOH:D₂O/H₂O:HCl=1:1:24:24:2 × 10⁻³ (R=Me, Ph). ●, T_M; ○, Q (TEOS-MTES); ▲, T_P; △, Q (TEOS-PTES).

mainly form:



Since only weak signals are observed in the T² and Q² regions, and no signals are detected in the T³ and Q³ regions, monomers and dimers are the dominant species in these systems. In the separate alkoxy silane systems, unhydrolysed monomers [a1, T_M⁰(_{0OH}); b1, Q⁰(_{0OH}); c1, T_P⁰(_{0OH})] are clearly detected. In addition, one intense signal is observed for each system in the T¹ and Q¹ regions, and should be ascribed to ethoxy-terminated dimers [a2, T_M¹(_{0OH})T_M¹(_{0OH}); b2, Q¹(_{0OH})Q¹(_{0OH}); c2, T_P¹(_{0OH})T_P¹(_{0OH})] which can form by condensation between an unhydrolysed monomer and a hydrolysed species possessing one hydroxy group [from T⁰(_{0OH}) and T⁰(_{1OH}) or from Q⁰(_{0OH}) and Q⁰(_{1OH})]. In the spectrum of the TEOS-MTES system, in addition to the signals observed in the TEOS and MTES systems, two new intense signals appear, and are assigned to an ethoxy-terminated codimer [T_M¹(_{0OH})Q¹(_{0OH})].⁴⁰ Similarly, two new signals are detected for the TEOS-PTES system (cb1 and cb2), which should also be ascribed to an ethoxy-terminated codimer [T_P¹(_{0OH})Q¹(_{0OH})]. Table 2 summarizes these assignments.

Discussion

When the water:Si ratio is 12:1, the hydrolysis and condensation behaviour in the TEOS-MTES system is different from that in the TEOS-PTES one. The hydrolysis rate of MTES is much larger than those of TEOS and PTES. Under acidic conditions, the hydrolysis of alkoxy silanes is reported to be initiated by the fast protonation of a leaving alkoxy group,

Table 2 Assignments of labelled ^{29}Si NMR signals for monomeric and dimeric species obtained by the hydrolysis of alkoxysilanes (water: Si = 1:3)

signal	structure	formula
a1	$\text{T}_\text{M}^0_{(0\text{OH})}$	$\text{MeSi}(\text{OEt})_3$ (MTES)
a2	$\text{T}_\text{M}^1_{(0\text{OH})}\text{T}_\text{M}^1_{(0\text{OH})}$	$\text{Me}(\text{EtO})_2\text{SiOSi}(\text{OEt})_2\text{Me}$
b1	$\text{Q}^0_{(0\text{OH})}$	$\text{Si}(\text{OEt})_4$ (TEOS)
b2	$\text{Q}^1_{(0\text{OH})}\text{Q}^1_{(0\text{OH})}$	$(\text{EtO})_3\text{SiOSi}(\text{OEt})_3$
c1	$\text{T}_\text{P}^0_{(0\text{OH})}$	$\text{PhSi}(\text{OEt})_3$ (PTES)
c2	$\text{T}_\text{P}^1_{(0\text{OH})}\text{T}_\text{P}^1_{(0\text{OH})}$	$\text{Ph}(\text{EtO})_2\text{SiOSi}(\text{OEt})_2\text{Ph}$
ab1	$\text{T}_\text{M}^1_{(0\text{OH})}\text{Q}^1_{(0\text{OH})}$	$\text{Me}(\text{EtO})_2\text{SiOSi}(\text{OEt})_3$
ab2	$\text{T}_\text{M}^1_{(0\text{OH})}\text{Q}^1_{(0\text{OH})}$	$\text{Me}(\text{EtO})_2\text{SiOSi}(\text{OEt})_3$
cb1	$\text{T}_\text{P}^1_{(0\text{OH})}\text{Q}^1_{(0\text{OH})}$	$\text{Ph}(\text{EtO})_2\text{SiOSi}(\text{OEt})_3$
cb2	$\text{T}_\text{P}^1_{(0\text{OH})}\text{Q}^1_{(0\text{OH})}$	$\text{Ph}(\text{EtO})_2\text{SiOSi}(\text{OEt})_3$

and subsequent nucleophilic attack of water molecule leads to a five-coordinate transition state.^{42,43} The substitution of an alkoxy group with an alkyl group increases the hydrolysis rate by stabilizing the development of positive charge by providing electrons (the so-called polar effect). In addition, if the transition state becomes sterically more crowded, the hydrolysis rate is reduced (the so-called steric effect). Thus, the substitution of the ethoxy groups with methyl groups should result in increased hydrolysis rates according to the polar effect.⁴² In contrast, substitution with the bulky phenyl group has very little effect on the hydrolysis rate, probably because of the combination of these two effects.

The acid-catalysed condensation rates of TEOS- and MTES-derived species are comparable, whereas that of PTES-derived species is much lower (Fig. 4). Acid-catalysed condensation reactions can involve protonated silanol groups ($\equiv\text{SiOH}_2^+$); thus, the polar effect can change the condensation rates.⁴² Since the steric effect is reported to be important for condensation reactions of silanol groups,^{42,43} however, the condensation reactions in the present system appear to be controlled sterically. Thus, the observed slow condensation rate of PTES-

derived species should be ascribed to the bulkiness of the phenyl groups.

When only one alkoxysilane is hydrolysed with sufficient water, the distribution of dimers reflects the distribution of monomers.^{27,28} In the TEOS–MTES system, although MTES is hydrolysed faster than TEOS, fully hydrolysed monomers [$\text{Q}^0_{(4\text{OH})}$ and $\text{T}_\text{M}^0_{(3\text{OH})}$] are the dominant monomeric species. As dimers, $\text{T}_\text{M}^1_{(2\text{OH})}\text{T}_\text{M}^1_{(2\text{OH})}$, $\text{Q}^1_{(3\text{OH})}\text{Q}^1_{(3\text{OH})}$ and $\text{T}_\text{M}^1_{(2\text{OH})}\text{Q}^1_{(3\text{OH})}$ are mainly observed, consistent with the monomer distribution; thus monomeric species are condensed rather randomly in this system.

In the TEOS–PTES system, the fully hydrolysed monomers [$\text{Q}^0_{(4\text{OH})}$ and $\text{T}_\text{P}^0_{(3\text{OH})}$] are also dominant when dimers start to form. Although the condensation rate of the PTES-derived species is much slower, the estimated $\text{Q}^0_{(4\text{OH})}/\text{T}_\text{P}^0_{(3\text{OH})}$ values range from 1.4 (after 64 min) to 2.4 (after 184 min) at the initial stage. Moreover, based on the steric hindrance to the condensation of PTES-derived species, the formation of $\text{T}_\text{P}^1_{(2\text{OH})}\text{Q}^1_{(3\text{OH})}$ should be much easier than that of $\text{T}_\text{P}^1_{(2\text{OH})}\text{T}_\text{P}^1_{(2\text{OH})}$. Thus, if we assume random condensation in the TEOS–PTES system, the observed distribution of the dimers [the absence of $\text{T}_\text{P}^1_{(2\text{OH})}\text{Q}^1_{(3\text{OH})}$ and the presence of $\text{T}_\text{P}^1_{(2\text{OH})}\text{T}_\text{P}^1_{(2\text{OH})}$] cannot yet be interpreted.

Since phenyl groups are highly hydrophobic, immiscible solutions were obtained for a wide range of compositions in the TEOS–PTES system. With the present composition (TEOS:PTES:EtOH:water:HCl = 1:1:24:24:4 $\times 10^{-3}$), a certain amount of water should be still present with ethanol (only 7 mol of water is consumed for the complete hydrolysis of 1 mol of TEOS and 1 mol of PTES), and additional water forms from the condensation of two silanol groups. Compared with silicic acid [$\text{Q}^0_{(4\text{OH})}$; $\text{Si}(\text{OH})_4$], $\text{T}_\text{P}^0_{(3\text{OH})}$ [$\text{PhSi}(\text{OH})_3$] is highly hydrophobic because of the presence of the phenyl groups. Thus, the hydrophobic effect of the phenyl groups should lead to their association. Hence, although a homogeneous solution was obtained with the present composition, PTES-derived species appear to be associated and the formation of $\text{T}_\text{P}^1_{(2\text{OH})}\text{Q}^1_{(3\text{OH})}$ is very limited.

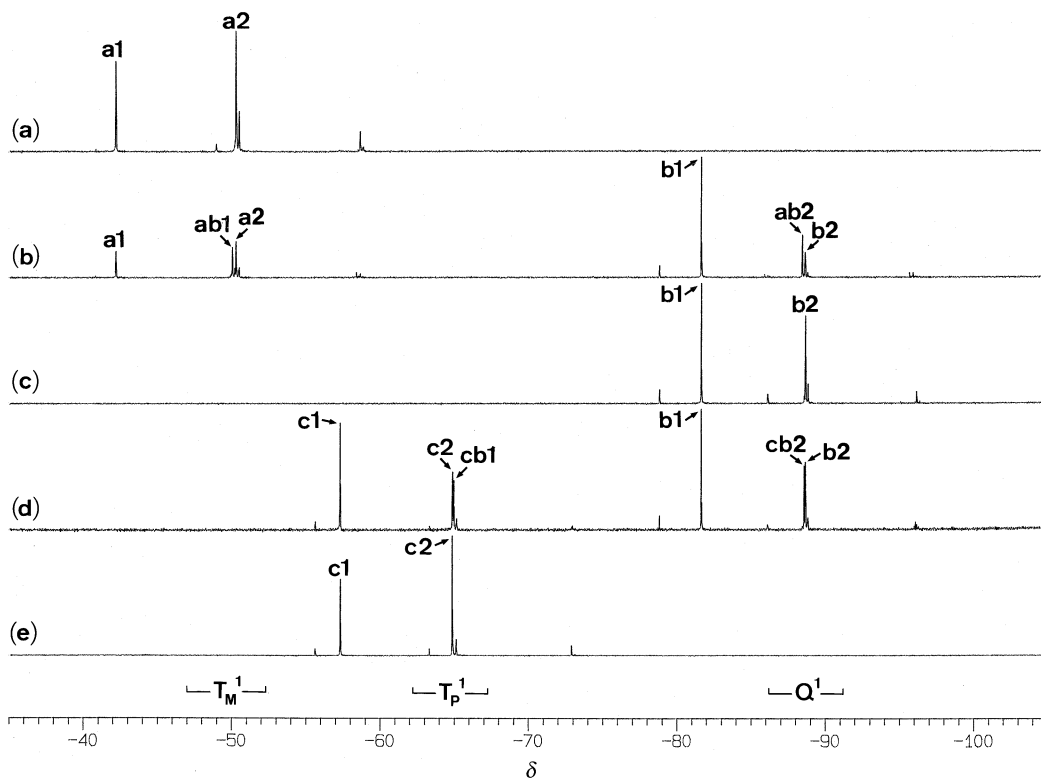


Fig. 5 Silicon-29 NMR spectra of the solution in the system with alkoxysilane: EtOH: D₂O/H₂O: HCl = 2:24:2/3:4 $\times 10^{-3}$ after refluxing for 2 days. (a) MTES only; (b) MTES:TEOS = 1:1 mixture; (c) TEOS only; (d) PTES:TEOS = 1:1 mixture; (e) PTES only.

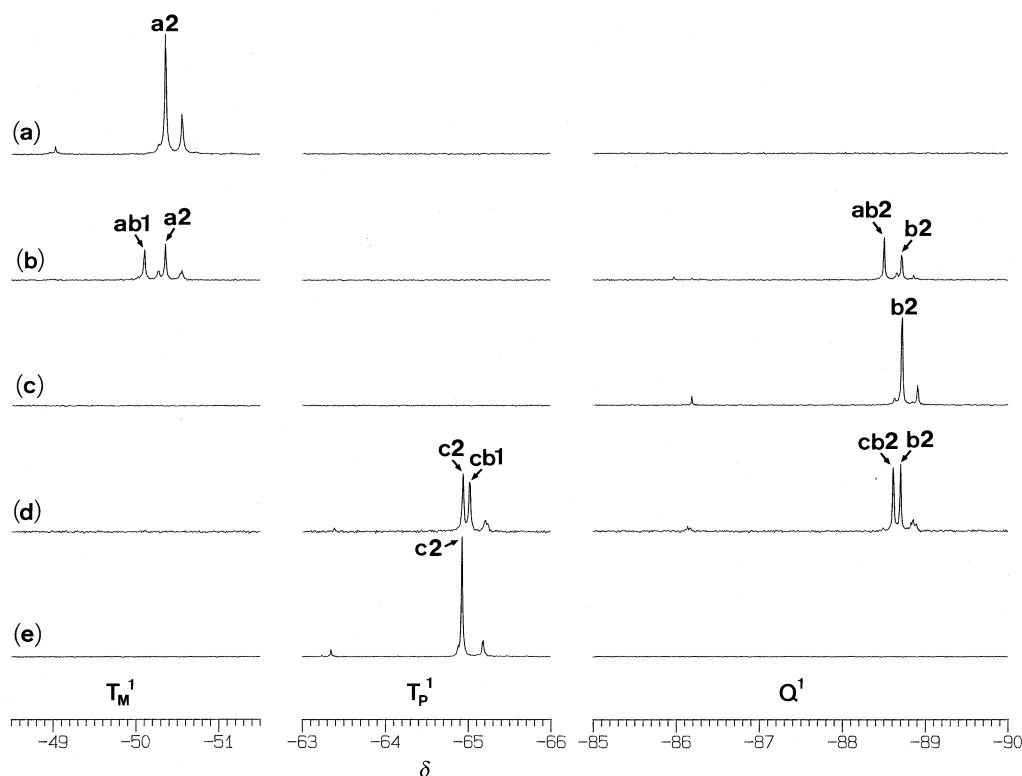


Fig. 6 Enlarged profile (T^1 and Q^1 region) of Fig. 5. (a) MTES only; (b) MTES:TEOS=1:1 mixture; (c) TEOS only; (d) PTES:TEOS=1:1 mixture; (e) PTES only.

This assumption is supported by the results for water-restricted systems. In addition to $T^1_{(\text{OOH})}T^1_{(\text{OOH})}$ and $Q^1_{(\text{OOH})}Q^1_{(\text{OOH})}$ codimers, $T^1_{(\text{OOH})}Q^1_{(\text{OOH})}$ dimers are clearly detected in both the TEOS–MTES and TEOS–PTES systems. In these systems, most of the water is consumed and is finally converted into ethanol *via* condensation. Moreover, the average number of hydroxy groups attached to silicon is very small, thus all the species should be hydrophobic. These conditions can allow the homogeneous distribution of the monomers in the solutions and random condensation should occur even in the TEOS–PTES system.

These results indicate that, if a large amount of water is present (water:Si=12:1) in the TEOS–PTES system, hydrolysed monomers tend to aggregate as reactions proceeded. Thus, although a homogeneous gel was obtained by ageing the uncovered water-rich solution of the TEOS–PTES systems, a segregated domain structure may form. Two-dimensional ^1H – ^{29}Si correlation CP MAS NMR has been applied to both the TEOS–MTES and the TEOS–PTES systems, and homogeneous structures were suggested based on the clear evidence for the presence of coupling between Q^4 silicon and organic protons (those of methyl and phenyl groups).^{18,19} In the reported TEOS–PTES system,¹⁹ the amount of water is equivalent to that of alkoxy groups. Thus, in contrast to the present water-rich TEOS–PTES system, co-condensation can frequently occur and a certain amount of T_P – Q bonds formed.

Conclusions

We have investigated the hydrolysis and initial polycondensation process of $\text{Si}(\text{OEt})_4$ – $\text{RSi}(\text{OEt})_3$ – EtOH – water – HCl systems ($R=\text{Me}, \text{Ph}$), and have discussed the effect of the R groups on condensation reactions on the basis of the dimer formation behaviour. In the TEOS–MTES system, irrespective of the amount of water, the dimers possessing T_M – Q bonds [$(-\text{O})_2\text{SiMeOSi}(\text{O}-)_3$] are formed as well as those possessing T_M – T_M [$(-\text{O})_2\text{SiMeOSiMe}(\text{O}-)_2$] and Q – Q [$(-\text{O})_3\text{SiOSi}(\text{O}-)_3$] bonds. On the other hand, in

the TEOS–PTES system with the large amount of water (TEOS:PTES:EtOH:water=1:1:24:24), the dimer possessing T_P – Q bonds [$(-\text{O})_2\text{SiPhOSi}(\text{O}-)_3$] is not detected, and only those with T_P – T_P and Q – Q bonds are detected. If the amount of water is very small (TEOS:PTES:EtOH:water=1:1:24:2/3), however, the dimer possessing T_P – Q bonds is also obtained. These results suggest that, in the water-rich system, the hydrophobic phenyl groups are associated in solution, while the methyl groups appear to be randomly dispersed. Hence, in the co-hydrolysis processes of alkoxy silanes, compositions, in particular the amount of water, should be selected carefully based on the hydrophobicity of the organic groups attached to silicon.

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