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The Hydrolysis/Condensation Behaviour of Methacryloyloxyalkylfunctional Alkoxysilanes: Structure-Reactivity Relations

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Summary. Various methacryloyloxymethylalkoxysilanes have been synthesized by nucleophilic substitution reactions starting from chloromethylalkoxysilanes under phase transfer catalysis conditions. The compounds thus obtained show an exceptionally high degree of reactivity with regard to hydrolysis and condensation both under acidic as well as under basic conditions compared to the established 3-methacryloyloxypropyltrimethoxysilane. A mechanistic model for this high reactivity by intramolecular activation is discussed.

Keywords. Acrylics; Hydrolysis; Kinetics; NMR spectroscopy; Organofunctional silanes.

Introduction

Organofunctional silanes, characterized by both organic functional groups and an inorganic reactive center prone to hydrolysis, are commercially used since the 1950's and demand is growing steadily (Fig. 1).

Major application fields of organofunctional silanes are filler/material treatment and utilization as adhesion promoters or crosslinkers, respectively. This wide range of applications relies on the bifunctionality of the organofunctional silanes, giving rise to the possibility to form chemical bonds to both inorganic and organic substrates and also between two organofunctional silane molecules [1].

For example, an aminoalkylfunctional silane can react with an inorganic material bearing surface-bonded hydroxy groups and with an organic resin bearing *e.g.* epoxy groups, thus forming a permanent link between the two different matrices (Fig. 2).

In this context, methacryloyloxyalkylfunctional silanes bearing hydrolyzable groups on the silicon atom are of special interest for

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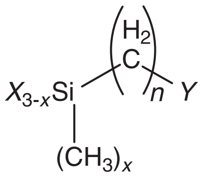


X = *e.g.* MeO-, EtO-, iPrO-, PhO-, Cl-, -OAc,...
$x = 0, 1, 2$
Y = *e.g.* $-NH_2$, $-NHCH_2CH_2NH_2$, epoxy, -SH, ureido, -NCO, methacryloxy...
n = *e.g.* 1, 3, 4...

Fig. 1. General formula of an organofunctional silane

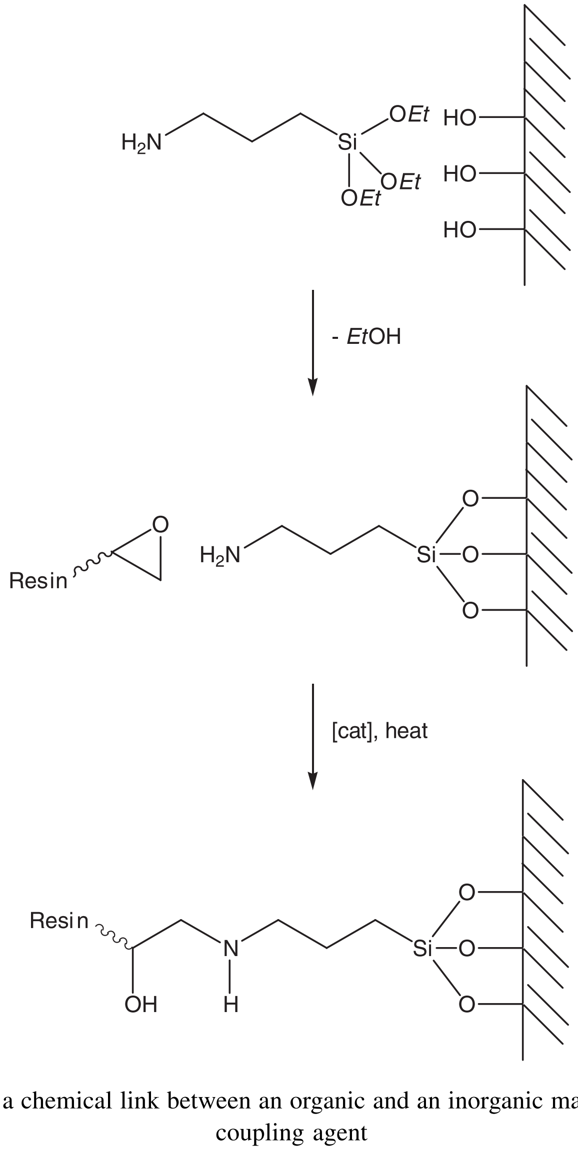


Fig. 2. Formation of a chemical link between an organic and an inorganic matrix engaging a silane coupling agent

- the modification of organic polymers by co-polymerization or grafting (to give moisture curable co-polymers),
- the treatment of inorganic materials like metal surfaces, fillers, or glass fibre to give strong adhesion between organic and inorganic substrates by *e.g.* radical reactions or Michael-type additions.

Despite of the high efficiency of organofunctional silanes for improving *e.g.* the mechanical properties or chemical resistance of organic/inorganic composite materials, several factors governing the reaction behaviour are still not fully understood.

In addition, as environmental requirements become more and more important, new organofunctional silanes have to be developed which are equally efficient in the mentioned application fields but do not show the disadvantages of known organofunctional silanes like liberation of volatile organic or toxic compounds.

In the light of these requirements, we investigated the reactivity of various methacryloyloxyalkylsilanes in comparison to the nowadays most important organofunctional silanes bearing an unsaturated functionality, namely vinyltrimethoxysilane and 3-methacryloyloxypropyltrimethoxysilane.

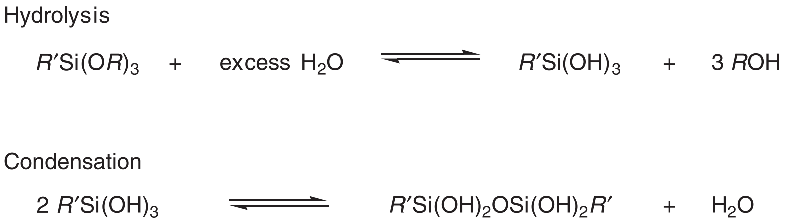
Results and Discussions

Basic Reactivity of Organofunctional Silanes

The reactivity as well as the reaction types possible at the organofunctional terminus of an organofunctional silane strongly depend on the functional group as well as the substrate to be reacted with. On the other hand, commercially important reactions at the organosilicon moiety of these compounds can be mainly divided into two categories, namely *hydrolysis* and *condensation* (Fig. 3) [2]. These reactions are both reversible, many of them being equilibria with substantial concentrations of both products and reactants present under typical conditions unless by-products liberated are removed from the equilibrium or the products separate from the reaction medium, *e.g.* by precipitation. In addition, the reaction scheme is complicated by the fact that both hydrolysis and condensation can occur at the same time with comparable reaction rates.

The rate with which the respective equilibrium is reached strongly depends on various parameters, *e.g. pH*, temperature, *etc.* In general, the following simplified statements can be made, with exceptions depending on the specific structure of the silane investigated:

- In neutral medium, the hydrolysis rate of alkoxysilanes displays a minimum.
- Under basic conditions below *pH* 10, hydrolysis of the first alkoxy group is the rate determining step and data obtained suggests a S_N2^{**}–Si mechanism (above *pH* 10, ionization of the SiOH group has major influence on the mechanism).



Hydrolysis

$$R'Si(OR)_3 + \text{excess } H_2O \rightleftharpoons R'Si(OH)_3 + 3\,ROH$$

Condensation

$$2\,R'Si(OH)_3 \rightleftharpoons R'Si(OH)_2OSi(OH)_2R' + H_2O$$

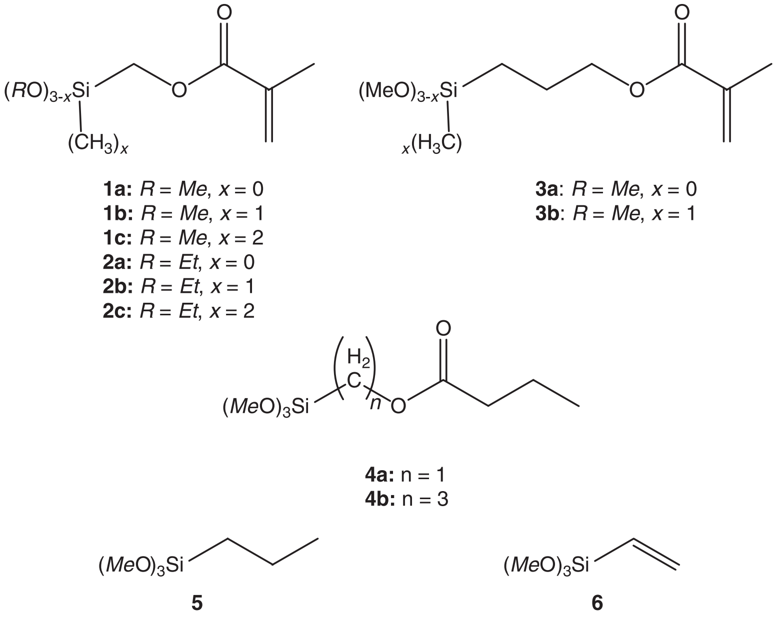
Fig. 3. Key reactions of alkoxysilanes (in the condensation the two silanols are not necessarily identical, one may, *e.g.*, be a surface-SiOH group)

- In acidic medium, hydrolysis of the first alkoxy group is fast compared to hydrolysis of further alkoxy groups present in the molecule. The hydrolysis rate strongly depends on the kind of leaving group with the hydrolysis rate decreasing in the order *Me*O → *Et*O → *Me*OCH$_2$CH$_2$O–. Data obtained implies a S$_N$2 mechanism on a protonated alkoxysilane.
- The rate of condensation of silanols strongly depends on the substitution pattern at silicon: Trisilanols show a condensation rate minimum at about *pH* 4, whereas disilanols are most stable at about *pH* 6. Finally, monosilanols show a rate minimum at about *pH* 6.5–7.
- Under acidic conditions, hydrolysis in most cases is faster than condensation. In contrast, in basic medium condensation of partially hydrolyzed alkoxysilanes may occur prior to complete hydrolysis.

For industrial applications of organofunctional silanes, both the hydrolysis (as a prerequisite for condensation) as well as the condensation reaction are of fundamental importance.

In the present study, hydrolysis was investigated by ^{1}H NMR, whereas ^{29}Si NMR was used to observe and analyze the condensation behaviour of various methacryloyloxyalkylfunctional alkoxysilanes which are depicted in Fig. 4. In addition, vinyltrimethoxysilane **6** as well as the saturated analogues **4a**, **4b**, and **5** were investigated as model substances for silane modified co-polymers.

Hydrolysis of the various unsaturated silanes was studied in the presence of a 30-fold excess of water with acetone as co-solvent at *pH* 4 (0.001 *M* HCl) as well as at *pH* 9 (buffer solution boric acid/potassium chloride/sodium hydroxide). Due to the high reactivity of the investigated methacryloyloxymethylsilanes,



1a: *R* = *Me*, *x* = 0
1b: *R* = *Me*, *x* = 1
1c: *R* = *Me*, *x* = 2
2a: *R* = *Et*, *x* = 0
2b: *R* = *Et*, *x* = 1
2c: *R* = *Et*, *x* = 2

3a: *R* = *Me*, *x* = 0
3b: *R* = *Me*, *x* = 1

4a: n = 1
4b: n = 3

5

6

Fig. 4. Molecules investigated in the present study

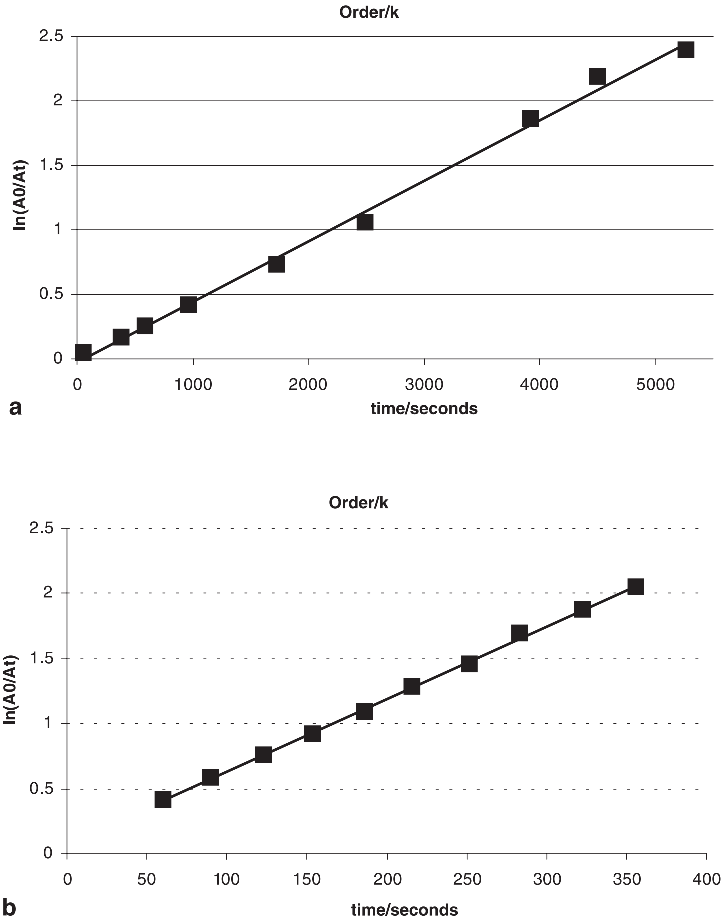


Fig. 5. Comparison of hydrolysis rates of **3a** (a) $k = 1.59\,h^{-1}$ and **1a** (b) $k = 21.8\,h^{-1}$ under acidic conditions ($pH = 4$, 30-fold excess water)

condensation observed by ^{29}Si NMR was performed at *pH* 6.5 in order to slow down the condensation relative to the time required to obtain the NMR spectra.

Surprisingly, all methacryloyloxyfunctional silanes bearing a methylene spacer connecting the methacrylic functionality and the silane moiety were found to exhibit exceptionally high hydrolysis rates under the experimental conditions. As an example, the plots for the acidic hydrolysis of the first methoxy group of 3-methacryloyloxypropyltrimethoxysilane **3a** and methacryloyloxymethyltrimethoxysilane **1a** are depicted in Figs. 5a and 5b. The reactions were found to proceed according to the expected pseudo first order rate law in the silane [3], but compared to **3a**, the hydrolysis of **1a** is faster by a factor of 13.6. In Table 1 the rate constants obtained for all investigated substances are summarized.

In summary, four conclusions can be drawn from the data obtained:

1. Hydrolysis of the methylene spacer bearing methacryloyloxyfunctional silanes is up to 60 times faster than that of 3-methacryloyloxypropyltrimethoxysilane both in case of methoxy and ethoxy derivatives under acidic or basic conditions.

Table 1. Summarized rate constants for the hydrolysis of the first alkoxy group found for the investigated compounds **1–6** under acidic and basic conditions

Compound	Hydrolysis rate at *pH* 4 h^{-1}	Hydrolysis rate at *pH* 9 h^{-1}
1a	21.8	24.0
1b	14.4	67.9
1c	[a]	17.5
2a	[b]	1.2
2b	27.2	9.5
2c	[a]	2.2
3a	1.6	1.2
3b	[c]	0.5
4a	31.5	27.7
4b	4.9	1.6
5	5.2	0.6
6	13.7	6.4

[a] Hydrolysis of compounds **1c** and **2c**, respectively, was extremely fast; after 60 seconds, only the silanol could be observed besides liberated methanol; [b] The rate constant for the first hydrolysis step of compound **2a** could not be determined due to excessive overlap of the signals under the chosen conditions; [c] Hydrolysis of compound **3b** was found to be extremely slow under acidic conditions; almost no reaction was found to proceed within 1 h

Under basic conditions the ethoxy silanes **2a** and **2c** hydrolyze at rates comparable to **3a** (except the difunctional **2b**), whereas the methoxy compounds **1a**–**1c** still exhibit an extremely high rate of hydrolysis.

2. Dialkoxymethyl silanes bearing the methacryloyloxymethyl group hydrolyze at a rate comparable to the corresponding trialkoxy silanes under acidic conditions (and at a somewhat higher rate under basic conditions). This is in contrast to the behaviour of 3-methacryloyloxypropyl(dimethoxy)methylsilane, the hydrolysis of which is much slower than that of its trimethoxy counterpart.
3. Under acidic conditions ethoxy substituted methacryloyloxymethylsilanes hydrolyze at rates comparable to those of the corresponding methoxy silanes. This again is in contrast to the propylene spacer bearing analogues: 3-methacryloyloxypropyltriethoxysilane is known to hydrolyze extremely slow compared to the methoxy derivative [4], making it attractive for *e.g.* dental applications which require relatively long shelf-lifes.
4. The saturated butanoic acid derivatives **4a** and **4b** of the silicon containing methacrylic acids esters **1a** and **3a** hydrolyze at rates comparable to the unsaturated compounds under both acidic and basic conditions. This indicates that incorporation of these substances into co-polymers with standard unsaturated monomers (*e.g.* styrene, acrylic acid, methyl methacrylate, *etc.*) does not slow down the hydrolysis rate. In contrast, the saturated analog of vinyltrimethoxysilane **6** (which shows a hydrolysis reactivity comparable to the methacryloyloxymethylsilanes), namely propyltrimethoxysilane **5**, shows a much lower reaction rate.

The surprisingly high reactivity of the methacryloyloxymethylsilanes **1a**–**1c** and **2a**–**2c** may be explained in terms of an electronic influence of the ester group on the electron density at the silicon atom. In principle, three different possibilities may be assumed, namely

- intermolecular interactions between the silicon atom of a first molecule with the ester group of a second molecule (Fig. 6a),
- intramolecular activation of the silicon atom by interaction with the carbonyl group by forming a silatrane analog five-membered ring (Fig. 6b), and
- intramolecular activation of the silicon moiety by electron transfer from the ester group via the methylene group either through space, via the σ-bonds, or by hyperconjugation (Fig. 6c).

The first possibility is unlikely, because this effect should also play a significant role in case of methacryloyloxyalkylsilanes bearing a propylene spacer. Evidence for one of the latter two models can be drawn from the comparison of the ^{29}Si NMR data of compounds **1a**, **1b**, **2a**, and **2b** with **3a** and **3b** (Table 2).

This data reveals that all methacryloyloxyalkylsilanes bearing a methylene spacer show a high-field shift of 8–14 ppm compared to their counterparts bearing a propylene spacer. This indicates a partial electron transfer from one of the oxygen

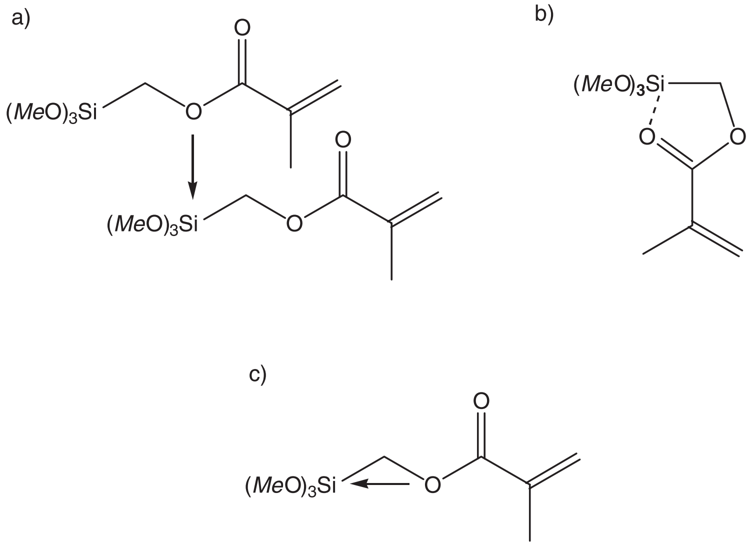


Fig. 6. Possible electronic influence explaining the high reactivity of the methacryloyloxymethylalkoxysilanes

Table 2. Comparison of the ^{29}Si NMR data of the investigated compounds

Compound	Chemical shift	Chemical shift	Compound
1a	– 53.3	– 42.8	**3a**
2a	– 56.6		
1b	– 11.4	– 3.1	**3b**
2b	– 14.9		
6	– 56.0	– 41.5	**5**

atoms to silicon. This is also true for vinyltrimethoxysilane **6**, which exhibits a high-field shift of 14.5 ppm compared to propyltrimethoxysilane **5**. A comparable effect was found, for example, for substituted diphenylsilanes: The chemical shift of diphenylmethylchlorosilane was found to be 10.6 ppm. Introduction of a methoxymethyl substituent at the ortho-position of the phenyl group was accompanied by a high-field shift of about 7 ppm to 3.4 ppm by intramolecular coordination [5]. A decision, whether the influence on the electronic structure of silicon is due to intramolecular ring formation (Fig. 6b) or hyperconjugation (Fig. 6c) cannot be made based on the present data. The data obtained for the rate constants may be explained by the following mechanistic assumptions:

a) Acidic conditions: Protonation of an alkoxy oxygen is the first reaction step under acidic conditions and is becoming slower from mono- to di- to trialkoxysilanes. This trend is enhanced by intramolecular coordination of the ester group. Steric crowding should play only a minor role in this state of the reaction. After protonation nucleophilic displacement of the protonated alkoxy group by a water molecule occurs. This step is fast for trialkoxysilanes and becomes slower for di- and monoalkoxysilanes due to the electron-withdrawing effect of the alkoxy groups (which is in accordance with the slow hydrolysis of **3b** compared to **3a**). Intramolecular coordination should slow down the rate of this reaction step in all three cases. On the other hand, due to steric reasons, attack on the protonated monoalkoxysilanes might be accelerated relative to the di- and trialkoxysilane analogues. The balance between these two competiting effects might be an explanation for the rate constants observed for the first hydrolysis step under acidic conditions.
b) Basic conditions: Under basic conditions, formation of a pentacoordinate intermediate is presumed to be the rate determining step. Due to electronic reasons (electron withdrawing influence of alkoxy groups), this reaction step is faster for trialkoxysilanes than for di- and monoalkoxysilanes. Due to coordination of the ester oxygen, the electron density at silicon is enhanced, slowing down the formation of the pentacoordinate intermediate. On the other hand, steric crowding might lower the reaction rate from mono- to di- to trialkoxysilanes. These competiting effects might explain the reactivity maximum observed for the dialkoxysilanes **1b** and **2b** in the row tri-, di-, and monofunctional.

Condensation of the silanols resulting from the hydrolysis of the silanes **1**–**6** has been investigated in a qualitative manner by ^{29}Si NMR spectroscopy under neutral conditions (*pH* 6.5). No products resulting from hydrolysis or condensation were observed in case of the methacryloyloxymethylsilanes **2a**–**2c**, as well as in case of **3a**, **3b**, **4b**, **5**, and **6** within 12 hours at room temperature. In contrast, a dramatic reactivity enhancement was found for the methacryloyloxymethylsilanes **1a**–**1c** and the saturated counterpart **4a**. In case of **1a** and **4a**, complete consumption of the starting compound was observed within 90 minutes leading to T-structures without the observation of silanol intermediates.

In case of **1b**, the monosilanol and the disilanol could be observed along with the formation of M- and D-structures. After 12 hours, approximately 50% of the starting compound have been consumed. In case of **1c**, about 90% of the starting compounds remained unchanged after 12 hours, with the monosilanol and the dimer being present in a molar ratio of approximately 1:1.

This decrease in reactivity is in accordance with the well-known differences in stability of mono-, di-, and trisilanols depending on the *pH* of the solvent. The lack of reactivity of compounds **2a**–**2c**, **3a**, **3b**, **4b**, **5**, and **6** under the choosen conditions can presumably be explained by the slow hydrolysis of the compounds under neutral conditions.

Conclusions

The performed analysis of the hydrolysis/condensation behaviour of several methacryloyloxymethylalkoxysilanes has revealed a significant reactivity enhancement changing from a propylene to a methylene spacer group. This change in reactivity is most likely due to an intramolecular electronic influence of the ester group on the silicon moiety via the methylene spacer. The high reactivity observed makes the methacryloyloxymethylalkoxysilanes promising candidates for applications which require highly reactive alkoxysilyl groups.

Applications like glass fibre sizing, utilization as adhesion promoter for inorganic substrates, *e.g.* glass, metals like iron, aluminum or steel, fillers like korundum, silica, quarz, mica, *etc.* should be mentioned.

In addition, copolymerization with unsaturated acrylic monomers (acrylic or methacrylic acid or their derivatives) or other unsaturated monomers like vinyl acetate, styrene, or combinations thereof to give moisture curable compounds is a highly promising application field for the investigated monomers. Thus, the obtained materials can be used as basic materials for elastomers, coatings, adhesives, sealants, or foams (*e.g.* in the automotive industry, wood coating applications, scratch resistant coatings, *e.g.* for automotive polycarbonate windshields, food package material, wall paints, *etc.*), avoiding tin-based condensation catalysts or avoiding liberation of toxic methanol by using ethoxysilanes.

Furthermore, incorporation of methacryloyloxymethylsilanes in polyolefins like *LDPE*, *LLDPE*, *HDPE*, and *PP* as well as in olefin copolymers, *e.g.* *EVAc* and *EMA*, by copolymerization or grafting gives moisture curable thermoplastics which are very versatile for the manufacture of silane crosslinkable polyolefin compositions for use in electric cables and wires as well as for the manufacture of tubes and pipes. Economic advantage is provided especially by the high crosslinking speed due to the high hydrolysis/condensation rate of the methacryloyloxymethylsilanes compared to the established vinyl- and 3-methacryloyloxypropylsilanes, **3a** and **6**, respectively.

Due to the high reactivity of the methacryloyloxymethylsilanes, even the production of fast-curing adhesives can be envisioned, replacing the established, toxic cyanacrylate adhesives.

Experimental

All chemicals were used as purchased, compounds **1**–**4** were synthesized. ^{1}H NMR spectra of the pure silanes were recorded on a Bruker AVANCE DPX 360 (360.13 MHz) or DPX 400 (400.13 MHz). ^{29}Si NMR spectra were measured on a Bruker AVANCE 300 (59.63 MHz) or DPX 360 (71.54 MHz) with chromium(III) acetylacetonate as relaxation accelerator under ^{1}H inverse gated decoupling. The ^{1}H NMR measurements for studying the hydrolysis behaviour of the silanes were performed on a Bruker AVANCE DPX 400 spectrometer, the ^{29}Si NMR spectroscopic analysis was carried out on a Bruker AVANCE 300.

General Procedure for the Synthesis of **1–4**

1 Mol 50% aqueous KOH solution and 300 g of toluene were placed into a 1 dm^3 four-necked vessel equipped with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser. From the dropping funnel, 1 mol of methacrylic acid was slowly added while stirring the reaction mixture. After addition was complete, the water was removed by azeotropic distillation, followed by removal of 270 g of toluene by distillation. To the thus obtained potassium methacrylate, a solution of 10 mmol of tetra-*n*-butylphosphoniumchloride and 5 mmol of 4,4′-bismethylene(2,6-di-*tert*-butylphenol) in a mixture of 50 g of toluene, 17 g of ethyl methyl ketone, and 1 mol of the corresponding chloroalkylalkoxysilane was added. The suspension was heated for four hours to 110°C under stirring, the potassium chloride formed was filtered off and washed with toluene, and the products were isolated by column distillation under reduced pressure. Yields were between 92 and 96% based on the chloroalkylalkoxysilane employed.

(Methacryloyloxymethyl)trimethoxysilane (**1a**, $C_8H_{15}O_5Si$)

^{1}H NMR (C_6D_6, 360.13 MHz): $\delta = 1.70$ (s, 3H, CH_3), 3.30 (s, 9H, $3OCH_3$), 3.85 (s, 2H, $SiCH_2O$), 5.09 (s, 1H, $\underline{H}(H)C{=}$), 5.98 (s, 1H, $H(\underline{H})C{=}$); ^{29}Si NMR (C_6D_6, 71.54 MHz): $\delta = -53.28$.

(Methacryloyloxymethyl)dimethoxymethylsilane (**1b**, $C_8H_{15}O_4Si$)

^{1}H NMR (C_6D_6, 360.13 MHz): $\delta = 0.23$ (s, 3H, $SiCH_3$), 1.93 (s, 3H, CH_3), 3.44 (s, 6H, $2OCH_3$), 4.01 (s, 2H, $SiCH_2O$), 5.31 (s, 1H, $\underline{H}(H)C{=}$), 6.21 (s, 1H, $H(\underline{H})C{=}$); ^{29}Si NMR (C_6D_6, 59.63 MHz): $\delta = -11.42$.

(Methacryloyloxymethyl)dimethylmethoxysilane (**1c**, $C_8H_{15}O_3Si$)

^{1}H NMR (C_6D_6, 360.13 MHz): $\delta = 0.00$ (s, 6H, $Si(CH_3)_2$), 1.77 (s, 3H, CH_3), 3.18 (s, 3H, OCH_3), 3.80 (s, 2H, $SiCH_2O$), 5.13 (s, 1H, $\underline{H}(H)C{=}$), 6.05 (s, 1H, $H(\underline{H})C{=}$); ^{29}Si NMR (C_6D_6, 71.54 MHz): $\delta = 12.71$.

(Methacryloyloxymethyl)triethoxysilane (**2a**, $C_{11}H_{22}O_5Si$)

^{1}H NMR (C_6D_6, 360.13 MHz): $\delta = 1.24$ (t, $J = 7.04$ Hz, 9H, $3CH_2C\underline{H_3}$), 1.96 (s, 3H, CH_3), 3.92 (q, $J = 7.04$ Hz, 6H, $3OC\underline{H_2}CH_3$), 4.16 (s, 2H, $SiCH_2O$), 5.33 (s, 1H, $C{=}C(\underline{H})H$), 6.27 (s, 1H, $C{=}C(H)\underline{H}$); ^{29}Si NMR (C_6D_6, 71.54 MHz): $\delta = -56.59$.

(Methacryloyloxymethyl)diethoxymethylsilane (**2b**, $C_{10}H_{20}O_4Si$)

^{1}H NMR (C_6D_6, 360.13 MHz): $\delta = 0.05$ (s, 3H, $SiCH_3$), 0.96 (t, $J = 7.04$ Hz, 6H, $2CH_2C\underline{H_3}$), 1.71 (s, 3H, CH_3), 3.54 (q, $J = 7.04$ Hz, 4H, $2OC\underline{H_2}CH_3$), 3.81 (s, 2H, $SiCH_2O$), 5.11 (s, 1H, $C{=}C(\underline{H})H$), 5.99 (s, 1H, $C{=}C(H)\underline{H}$); ^{29}Si NMR (C_6D_6, 71.54 MHz): $\delta = -14.95$.

(Methacryloyloxymethyl)dimethylethoxysilane (**2c**, $C_9H_{18}O_3Si$)

^{1}H NMR (C_6D_6, 360.13 MHz): $\delta = 0.01$ (s, 6H, $2SiCH_3$), 0.98 (t, $J = 6.85$ Hz, 3H, $CH_2C\underline{H_3}$), 1.71 (s, 3H, CH_3), 3.46 (q, $J = 6.85$ Hz, 2H, $OC\underline{H_2}CH_3$), 3.72 (s, 2H, $SiCH_2O$), 5.15 (s, 1H, $C{=}C(\underline{H})H$), 6.02 (s, 1H, $C{=}C(H)\underline{H}$); ^{29}Si NMR (C_6D_6, 71.54 MHz): $\delta = 10.3$.

[3-(Methacryloyloxy)propyl]trimethoxysilane (**3a**, $C_{10}H_{20}O_5Si$)

^1H NMR ($CDCl_3$, 400.13 MHz): $\delta = 0.66$ (t, $J = 8.43$ Hz, 2H, $SiCH_2$), 1.76 (qui, $J = 7.66$ Hz, 2H, CH_2), 1.91 (s, 3H, CH_3), 3.55 (s, 9H, $3OCH_3$), 4.09 (t, $J = 6.72$ Hz, 2H, CH_2O), 5.52 (s, 1H, $\underline{H}(H)C=$), 6.07 (s, 1H, $H(\underline{H})C=$); ^{29}Si NMR (C_6D_6, 59.62 MHz): $\delta = -42.71$.

[3-(Methacryloyloxy)propyl]dimethoxymethylsilane (**3b**, $C_{10}H_{20}O_4Si$)

^1H NMR (C_6D_6, 360.13 MHz): $\delta = 0.00$ (s, 3H, $SiCH_3$), 0.51 (t, $J = 8.4$ Hz, 2H, $SiCH_2$), 1.64 (qui, $J = 7.66$ Hz, 2H, CH_2), 1.83 (s, 3H, CH_3), 3.30 (s, 6H, $2OCH_3$), 4.03 (t, $J = 6.93$ Hz, 2H, CH_2O), 5.22 (s, 1H, $\underline{H}(H)C=$), 6.11 (s, 1H, $H(\underline{H})C=$); ^{29}Si NMR (C_6D_6, 71.54 MHz): $\delta = 3.00$.

(Butyryloxymethyl)trimethoxysilane (**4a**, $C_8H_{18}O_5Si$)

^1H NMR (C_6D_6, 360.13 MHz): $\delta = 0.80$ (t, 3H, $J = 7.1$ Hz, $CH_2–C\underline{H}_3$), 1.48 (quin, 2H, $J = 7.1$ Hz, $CH_2C\underline{H}_2CH_3$), 2.18 (t, 2H, $J = 7.1$ Hz, $CH_2C=O$), 3.30 (s, 9H, $3OCH_3$), 4.15 (s, 2H, $SiCH_2$), 5.09 (s, 1H, $\underline{H}(H)C=$), 5.98 (s, 1H, $H(\underline{H})C=$); ^{29}Si NMR (C_6D_6, 71.54 MHz): $\delta = -53.02$.

[3-(Butyryloxy)propyl]trimethoxysilane (**4b**, $C_{10}H_{22}O_5Si$)

^1H NMR ($CDCl_3$, 400.13 MHz): $\delta = 0.66$ (t, $J = 8.43$ Hz, 2H, $SiCH_2$), 1.03 (t, 3H, $J = 7.1$ Hz, $CH_2–C\underline{H}_3$), 1.70 (quin, 2H, $J = 7.1$ Hz, $CH_2C\underline{H}_2CH_3$), 1.80 (quin, $J = 7.66$ Hz, 2H, CH_2), 2.41 (t, 2H, $J = 7.1$ Hz, $CH_2C=O$), 3.77 (s, 9H, $3OCH_3$), 4.15 (t, $J = 6.72$ Hz, 2H, CH_2O); ^{29}Si NMR (C_6D_6, 59.62 MHz): $\delta = -42.2$.

Procedure for Hydrolysis Study by ^1H NMR

100 mm^3 of buffer (or 0.001 *N* HCl, respectively) were added to 600 mm^3 of acetone-d6 (Merck, 99.8%) in a 5 mm NMR sample tube. After tuning and matching the probehead to this solvent mixture the spectrometer was also shimmed to achieve good resolution and sensivity in the following aquisitions. During this procedure the sample tube with the solvent mixture was preequilibrated to 303 K. The NMR sample tube was ejected again and 50 mm^3 of silane were added with a syringe and mixed. 60 s after the addition of the silane the first time dependent ^1H NMR measurement of the locked sample was started using an aquisiton time of 4.09 s and a sweep width of 8012 Hz. Only one scan per spectrum was recorded with a 90° pulse width. By choosing suitable delays the time difference between the beginning of two following measurements was adjusted to 32 and 96 s, respectively. In cases of slow reaction times, 16 scans had been accumulated at greater time intervals with a 30° pulse width and a delay D1 of 4 s.

Procedure for Hydrolysis Study by ^{29}Si NMR

Spectroscopic analysis was carried out after addition of 900 mm^3 of silane to 0.3 cm^3 of water (*pH* 7) in 1.8 cm^3 of acetone-d6 with 3% chromium(III) acetylacetonate as relaxation accelerator in a 10 mm NMR sample tube. During the first 12 hours every hour a spectrum was accumulated under inverse gated decoupling (1280 scans; time domain: 64 k; sweep width 11905 Hz; 30° pulse width; relaxation delay D1 0.1 s [6]). Afterwards, ^{29}Si measurements were carried out with an relaxation delay of 4 s accumulating 2048 scans.

References

[1] a) Plueddemann EP (1991) Silane Coupling Agents, 2^{nd} ed Plenum Press, New York; b) Mittal KL (ed) (1992) Silanes and other Coupling Agents. VSP, Utrecht

[2] a) Brinker CJ, Scherer GW (1990) Sol–Gel Science. Academic Press, London; b) Osterholtz FD, Pohl ER (1992) J Adhesion Sci Technol **6**: 127

[3] Brand M, Frings A, Jenkner P, Lehnert R, Metternich HJ, Monkiewicz J, Schram J (1999) Chem Sciences **54**: 155

[4] Altmann S, Pfeiffer J, unpublished results

[5] Berlekamp UH, Mix A, Jutzi P, Stammler HG, Neumann B (2000) Oxygen, Phosphorus or Sulfur Donor Ligands in Higher-Coordinated Organosilyl Chlorides and Triflates. In: Auner N, Weis J (eds) Organosilicon Chemistry IV. Wiley-VCH, Weinheim, p 489

[6] D1 of 0.1 s was chosen in analogy to Rodríguez SA, Colón LA (2001) Applied Spectroscopy **55**: 472