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# Treatment of alkyltriethoxysilanes with Amberlyst 15 cation-exchange resin in the presence of hexamethyldisiloxane

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## Abstract

Methyltriethoxysilane and ethyltriethoxysilane were treated with Amberlyst 15 cation-exchange resin in the presence of hexamethyldisiloxane at 40 °C. The reaction involves partial or full replacement of the ethoxyl group by trimethylsiloxyl to give $RSi(OEt)_n(OSiMe_3)_{3-n}$ ($n = 0$, 1, 2). The degree of substitution depends mainly on the ratio in which hexamethyldisiloxane and alkyltriethoxysilane are mixed. The nature of alkyl group in an alkyltriethoxysilane had little effect on the degree of substitution at a given mixing ratio.

## Introduction

Polymerization of tetraalkoxysilanes (TAOS) after hydrolysis occurs at random, not only in aqueous solutions containing sodium ions [1], but also in alcoholic solutions with a small amount of water containing hydrochloric acid as catalyst [2]. A method to control the reactions of TAOS is to change the functionality of TAOS. From this point of view, partial substitution of the alkoxyl groups by trimethylsiloxyl by treating TAOS in the presence of hexamethyldisiloxane ($(CH_3)_3SiOSi(CH_3)_3$) with Amberlyst 15 cation-exchange resin was performed and it was found that the molar ratio of hexamethyldisiloxane to TAOS substantially affected the degree of trimethylsiloxylation undergone by TAOS [3].

Alkyltrialkoxysilanes have been used as sources for the synthesis of polyhedral and ladder-like alkylsilsesquioxanes [4,5]. Recently these compounds as well as TAOS are important new starting materials in sol-gel processing for the synthesis of organic-inorganic hybrid materials [6,7] or precursors for ceramics [8]. Therefore, it is desirable that the reactivity of alkyltrialkoxysilanes is controlled to avoid the random polymerization.

This study was aimed so as to produce partially trimethylsiloxylated derivatives from alkyltriethoxysilanes (ATEOS) in order to change their functionality by

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substituting the trimethylsiloxyl group for the ethoxyl group. Methyltriethoxysilane (MTEOS, $CH_3Si(OC_2H_5)_3$) and ethyltriethoxysilane (ETEOS, $C_2H_5Si(OC_2H_5)_3$) were used as ATEOS in this study. They were treated with Amberlyst 15 cation-exchange resin in the presence of hexamethyldisiloxane (HMDS) in an oven at 40 °C. The products obtained by the treatment were analysed by gas-liquid chromatography and were identified by combined gas chromatography-mass spectrometry. The effects of the molar ratio of HMDS to ATEOS (abbreviated to the HMDS/ATEOS ratio) and treatment time were investigated.

$$RSi(OEt)_3 + (3-n)\,Me_3SiOSiMe_3 \rightarrow RSi(OEt)_n(OSiMe_3)_{3-n} + (3-n)\,Me_3SiOEt$$

## Experimental

### *Materials*

The methyltriethoxysilane and ethyltriethoxysilane used were of reagent grade. Hexamethyldisiloxane was used after a single distillation (b.p. 100–100.5 °C). Before use, Amberlyst 15 cation-exchange resin was heated in an oven at 80 °C for 4 h, and then cooled in a desiccator for standardization, as was suggested by Garzó et al. [9].

### *Preparation of solutions*

Solutions with an HMDS/ATEOS ratio from 0.5 to 15.0 were prepared by mixing given amounts of ATEOS and HMDS. After the reaction mixture was stirred for 5 min to ensure uniformity of the solutions, ca. 0.5 g of Amberlyst 15 cation-exchange resin was added to the mixture and the vessel was sealed up. After the samples had been kept in an oven at 40 °C for 85 h, they were analysed by gas-liquid chromatography. The effect of treatment time experiment was carried out after various intervals on the solution with an HMDS/MTEOS ratio of 0.5.

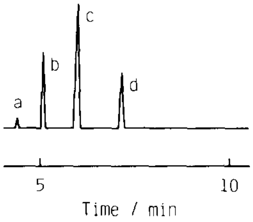
### *Analytical procedure*

The analysis of the solutions by gas-liquid chromatography was carried out under the same conditions as those described previously [3]. The results are expressed in terms of percentages of total peak area since standard substances could not be prepared. Although it is impossible to elucidate the distribution of the products quantitatively, the main product in the system can be estimated from the peak area ratio.

The peaks on the gas chromatograms were identified by combined gas chromatography-mass spectrometry with a JEOL JMS-DX 300 gas chromatograph-mass spectrometer and an ionizing energy of 20 eV. The ion source block was maintained at 100 °C and the molecular separator at 100 °C. The column consisted in 2 m coiled glass packed with 20% SF-96. The column was operated isothermally. The carrier gas was He at a flow rate of 15 $cm^3$ $min^{-1}$.

## Results and discussion

Figures 1 and 2 show the gas chromatograms of the solutions, which have been treated with Amberlyst 15 at 40 °C for 85 h, at a HMDS/MTEOS ratio of 3.0 and a



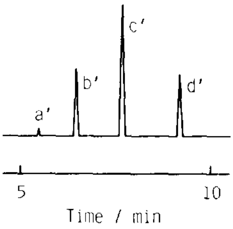


Fig. 1. Gas chromatogram of the solution (HMDS/MTEOS ratio of 3.0) which has been treated with Amberlyst 15 at 40 °C for 85 h.

Fig. 2. Gas chromatogram of the solution (HMDS/ETEOS ratio of 3.0) which has been treated with Amberlyst 15 at 40 °C for 85 h.

HMDS/ETEOS ratio of 3.0, respectively. Four peaks labelled a, b, c and d in Fig. 1, and a′, b′, c′ and d′ in Fig. 2, appear on each of the gas chromatograms of the MTEOS- and ETEOS-HMDS systems.

These peaks were identified by combined gas chromatography-mass spectrometry. In the mass spectra of trimethylsilylated derivatives of silicates, the molecular ion is either of very low abundance or not detectable and the major structurally significant ion is that corresponding to the loss of a methyl radical from the molecular ion, $[M-15]^+$ [10]. These characteristics are applicable to the mass spectra of trimethylsilylated derivatives of hydrolyzed and polycondensed products of MTEOS [11]. Substitution of a trimethylsiloxyl group for an alkoxyl group is indicated by the difference in the mass numbers of $[M-15]^+$ in regard to neighbouring peaks on the gas chromatogram [12,13]. In this study, the mass numbers of $[M-15]^+$ differ by 44, which corresponds to the difference between $Si(CH_3)_3$ (73) and $C_2H_5$ (29) in the ethoxyl group of ATEOS.

By conducting combined gas chromatography-mass spectrometry, the characteristics of the mass spectra described above could be confirmed to agree with each peak shown in Fig. 1 and 2. The identification of each peak by gas chromatography-mass spectrometry is listed in Tables 1 and 2. From these results, it is seen that ATEOS is partially or fully trimethylsiloxylated by treating with Amberlyst 15 in HMDS.

The effect of the HMDS/ATEOS ratio on the distribution of the derivatives is shown in Fig. 3 for the MTEOS-HMDS system and Fig. 4 for the ETEOS-HMDS system. The main product in the systems varies with the HMDS/ATEOS ratio. In

Table 1

Combined gas chromatography–mass spectrometric data and the chemical formula of the compound corresponding to each peak in Fig. 1

| Peak | *m/e* $[M-15]^+$ | Formula | Mol. wt. |
|---|---|---|---|
| a | 163 | $CH_3SiO_3(C_2H_5)_3$ | 178 |
| b | 207 | $CH_3SiO_3(C_2H_5)_2[Si(CH_3)_3]$ | 222 |
| c | 251 | $CH_3SiO_3(C_2H_5)[Si(CH_3)_3]_2$ | 266 |
| d | 295 | $CH_3SiO_3[Si(CH_3)_3]_3$ | 310 |

Table 2

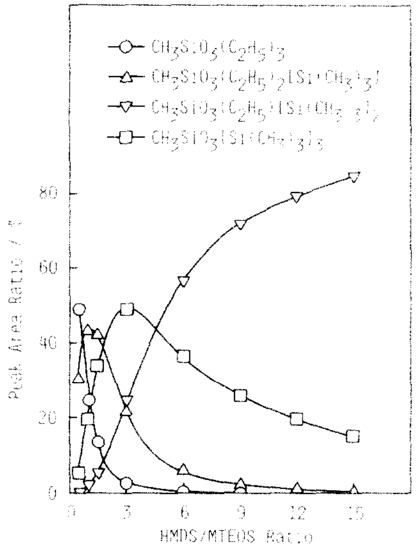
Combined gas chromatography–mass spectrometric data and the chemical formula of the compound corresponding to each peak in Fig. 2

| Peak | $m/e$ $[M-15]^+$ | Formula | Mol. wt. |
|---|---|---|---|
| a′ | 177 | $C_2H_5SiO_3(C_2H_5)_3$ | 192 |
| b′ | 221 | $C_2H_5SiO_3(C_2H_5)_2[Si(CH_3)_3]$ | 236 |
| c′ | 265 | $C_2H_5SiO_3(C_2H_5)[Si(CH_3)_3]_2$ | 280 |
| d′ | 309 | $C_2H_5SiO_3[Si(CH_3)_3]_3$ | 324 |

other words, the degree of trimethylsiloxylation of ATEOS by Amberlyst 15 treatment in HMDS varies with the molar ratio of HMDS to ATEOS.

The pattern of variation in the distribution of each derivative is almost the same in both the MTEOS/HMDS and ETEOS/HMDS systems. This fact suggests that the identity of an alkyl group of ATEOS, which is bonded directly to a silicon atom, has little effect on the partial or full trimethylsiloxylation of ATEOS by Amberlyst treatment in HMDS. Moreover, it was found that irrespective of the type of ATEOS, the most favourable conditions are: for monosubstitution a HMDS/ATEOS ratio of 1.0, for disubstitution a HMDS/ATEOS ratio of 3.0.

Figure 5 shows the gas chromatogram of the solution at the HMDS/MTEOS ratio of 0.5, which has been treated with Amberlyst 15 for 817 h at 40 °C. Five new peaks, labelled e, f, g, h and i, not present seen in Fig. 1 appear. On the basis of the characteristics of the mass spectra of the trimethylsilylated derivatives of silicates



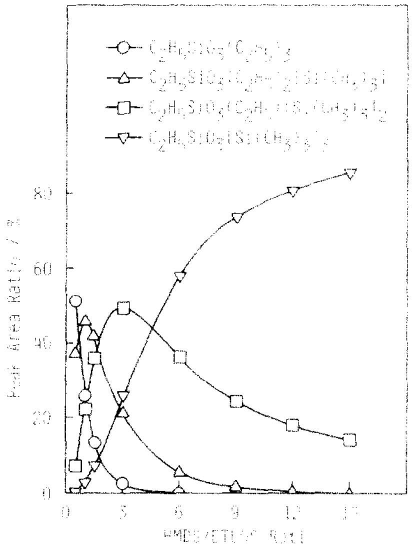


Fig. 3. Effect of HMDS/MTEOS ratio on the peak area ratios of the derivatives from MTEOS($CH_3SiO_3(C_2H_5)_3$) under Amberlyst 15 treatment at 40 °C for 85 h.

Fig. 4. Effect of HMDS/ETEOS ratio on the peak area ratios of the derivatives from ETEOS($C_2H_5SiO_3(C_2H_5)_3$) under Amberlyst 15 treatment at 40 °C for 85 h.

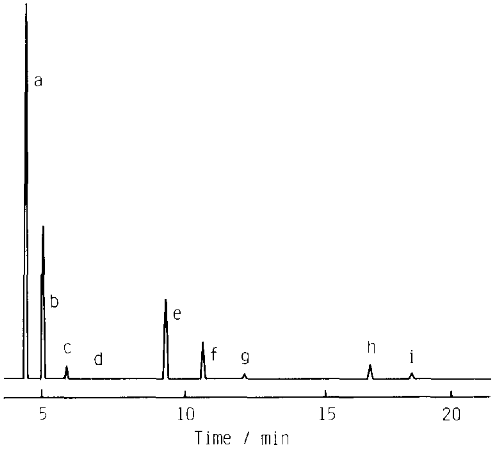


Fig. 5. Gas chromatogram of the solution (HMDS/MTEOS ratio of 0.5) after 817 h of Amberlyst 15 treatment at 40 ° C.

described above, these peaks were identified as is shown in Table 3. From this Table it can be seen that the compounds corresponding to peaks e, f and g have the dimeric structures in their skeletons of methylsilsesquioxane and those corresponding to peaks h and i have linear trimeric structures. It is thought that the occurrence of dimers and trimers is caused by the higher concentration of MTEOS in the solution because of the lower HMDS/MTEOS ratio along with a prolonged treatment time.

In order to elucidate the effect of treatment time with Amberlyst 15 on the peak area ratios of the derivatives from MTEOS in solution at a HMDS/MTEOS ratio of 0.5 was investigated and the result is shown in Fig. 6. The number of monomeric species decreases, and that of the dimeric and trimeric species increases with increased treatment time. This fact indicates that the polycondensation is time dependent. The distribution, however, scarcely changes after ca. 400 h of treatment, suggesting that equilibrium in the system has been achieved.

In conclusion, MTEOS and ETEOS are partially or fully trimethylsiloxylated by treatment with Amberlyst 15 cation-exchange resin in the presence of HMDS at 40 ° C. Regardless of the type of alkyl group on ATEOS, the degree of trimethyl-

Table 3

Combined gas chromatography–mass spectrometric data and the chemical formula of the compound corresponding to each peak in Fig. 5

| Peak | $m/e$ $[M-15]^+$ | Formula | Mol. wt. |
|---|---|---|---|
| e | 267 | $(CH_3)_2Si_2O_5(C_2H_5)_4$ | 282 |
| f | 311 | $(CH_3)_2Si_2O_5(C_2H_5)_3[Si(CH_3)_3]$ | 326 |
| g | 355 | $(CH_3)_2Si_2O_5(C_2H_5)_2[Si(CH_3)_3]_2$ | 370 |
| h | 371 | $(CH_3)_3Si_3O_7(C_2H_5)_5$ | 386 |
| i | 415 | $(CH_3)_3Si_3O_7(C_2H_5)_4[Si(CH_3)_3]$ | 430 |

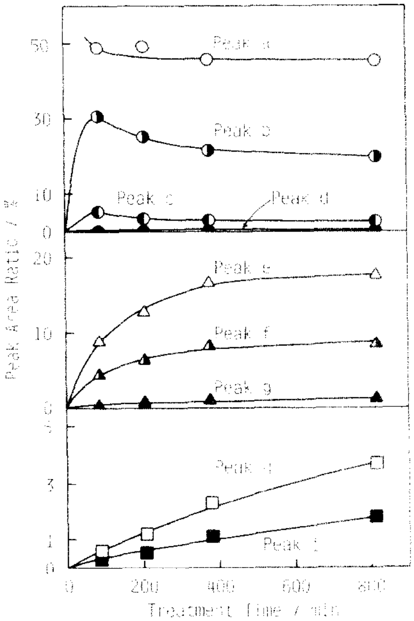


Fig. 6. Effect of time of Amberlyst 15 treatment on the peak area ratio of each derivative from MTEOS in the solution (HMDS/MTEOS ratio of 0.5) at 40 °C.

siloxylation of ATEOS, and hence functionality of ATEOS depends mainly on the HMDS/ATEOS ratio. In the solutions at lower HMDS/ATEOS ratios, ATEOS polycondenses into dimers and trimers, which is probably caused by the high ATEOS concentration in solution and long treatment time.

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