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Novel Polysiloxane Formation Process from Dimethyldiethoxysilane in the Presence of Oxalic Acid

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Abstract. Polysiloxane formation in dimethyldiethoxysilane (DMDES)-ethyl alcohol (EtOH(D))-oxalic acid (OA) (DMDES:EtOH(D):OA = 1:2:0.5) and DMDES-dimethylsulfoxide (DMSO)–OA (DMDES:DMSO:OA = 1:2:0.5) systems was investigated by gas chromatography-mass spectrometry and ^{29}Si-nuclear magnetic resonance. While the DMDES–EtOH(D)–OA system was homogeneous, the DMDES–DMSO–OA system consisted of two immiscible phases. In both systems, ethoxy-terminated linear oligomers ($(EtO)Me_2SiO(Me_2SiO)_nSiMe_2(OEt)$; $n = 0$–4, $Et = C_2H_5$, $Me = CH_3$) and cyclic tetramer ($(Me_2SiO)_4$) were identified. The reaction mechanism for polysiloxane formation is discussed.

Keywords: dimethyldiethoxysilane, oxalic acids, polydimethylsiloxane, reaction mechanism, non-aqueous system

1. Introduction

Sol-gel processing has attracted much attention, and for most of the processes of SiO_2-based materials, tetraalkoxysilanes are used as starting materials [1]. These processes are usually conducted in homogeneous alkoxysilane-alcohol-water-catalyst (acids or bases) systems. These processes consist of two steps; 1) hydrolysis of alkoxysilane and 2) subsequent polycondensation between two silanol groups (SiOH) or between one silanol group and one alkoxy group. Hence, water is a necessary component for sol-gel processing because of the necessity of silanol formation.

1) Hydrolysis reaction:

$$\equiv\text{Si–OR} + H_2O \xrightarrow{H^+/OH^-} \equiv\text{Si–OH} + \text{ROH}$$

2) Polycondensation reaction:

$$\equiv\text{Si–OH} + \text{HO–Si}\equiv \xrightarrow{H^+/OH^-} \equiv\text{Si–O–Si}\equiv + H_2O$$

$$\equiv\text{Si–OH} + \text{RO–Si}\equiv \xrightarrow{H^+/OH^-} \equiv\text{Si–O–Si}\equiv + \text{ROH}$$

In usual sol-gel processing of alkoxysilanes, both of the aforementioned two steps affect the structures of final products considerably. Hence, if polysiloxane bonds form directly from alkoxysilanes, the control of the reactions can become simplified. Non-aqueous systems can offer unique media for such polycondensation reactions. Actually, Corriu et al. very recently have proposed new non-hydrolytic sol-gel processing of oxides via the reactions between tetraalkoxysilanes and organic oxygen-containing compounds (alcohol, aldehyde and ether) [2] or between metal alkoxides and metal halides [3, 4].

We have reported siloxane formation in a tetraethoxysilane (TEOS)-ethyl alcohol-oxalic acid system without the addition of water [5]. The resulting oligomers were mainly ethoxy-terminated species, implying possible reaction mechanism without hydrolysis reactions. The formed oligomers could be used as starting materials for sol-gel processing, since new routes from ordered alkoxy-terminated oligomers (cubic octamer [6] and cyclic tetramer [7]) have been proposed. Thus, the condensation reactions in alkoxysilane-oxalic acid systems are of interest for both possible non-hydrolytic reaction mechanism and processing of alkoxy-terminated oligomeric species.

In our previous work [5], possible water-formation by esterification reaction between ethyl alcohol and oxalic acid made the discussion of the reaction mechanism difficult. Also, oligomeric species with variable structures could be formed from TEOS. In this

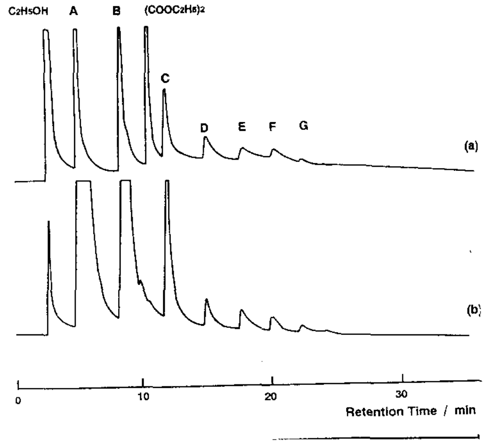

Fig. 1. Gas chromatogram of (a) the solution allowed to react for three days in the DMDES–EtOH–OA system (DMDES:EtOH:OA = 1:2:0.5) and (b) the solution allowed to react for seven days in the DMDES–DMSO–OA system (DMDES:DMSO:OA = 1:2:0.5).

study, in order to discuss the reaction mechanism of oxalic acid-containing systems further, we used dimethyldiethoxysilane (DMDES) instead of TEOS for simplifying the reactions by reducing the number of possible oligomers. In addition, as solvents, we used dimethylsulfoxide (DMSO), as well as ethyl alcohol, in order to suppress water-formation during the reactions. Reaction products in DMDES-solvent -oxalic acid systems without the addition of water were analyzed by gas-chromatography (GC), GC-mass spectrometry (MS), and ^{29}Si-nuclear magnetic resonance (NMR).

2. Experimental

DMDES, C_2H_5OH (EtOH), C_2H_5OD (EtOD), DMSO ($(CH_3)_2SO$), and oxalic acid ($(COOH)_2$; OA) were used without further purification. For NMR measurements, EtOD was used to obtain a NMR-lock signal, and a trace of chromium(III)tris(acetylacetonate) ($Cr(acac)_3$) was also added to shorten relaxation time of Si–species.

Reaction was conducted in two systems; DMDES–EtOH(D)–OA and DMDES–DMSO–OA. $Cr(acac)_3$ (for NMR samples of DMDES–EtOD–OA system only) and OA were dissolved in the solvents (EtOH(D) and DMSO), and DMDES was added to the mixture dropwise. Until the analyses, the mixture was allowed to react in a closed system with stirring (for NMR measurements of DMDES–EtOD–OA system, the sample was kept in the NMR tube without stirring, because several spectra were recorded with intervals).

Table 1. The assignments of labeled GC peaks in Fig. 1.

Peak	m/e $[M\text{-}15]^{+}$¶	Formula (Relative Molecular Mass)
A	133	$(CH_3)_2Si(OC_2H_5)_2$ (148)
B	207	$(CH_3)_4Si_2O(OC_2H_5)_2$ (222)
C§	281	$(CH_3)_6Si_3O_2(OC_2H_5)_2$ (296)
D§	281	$(CH_3)_8Si_4O_4$ (296)
E	355	$(CH_3)_8Si_4O_3(OC_2H_5)_2$ (370)
F	429	$(CH_3)_{10}Si_5O_4(OC_2H_5)_2$ (444)
G	503	$(CH_3)_{12}Si_6O_5(OC_2H_5)_2$ (518)

¶ No parent peaks were observed under the present experimental conditions.

§ Assignments of peak C and peak D were based on the isotope effect.

The GC analysis was performed with a Shimadzu GC-8A gas-liquid chromatograph equipped with a hydrogen flame ionization detector (FID) and 6-m column packed with OV-17 (3 m) and SE-30 (3 m). Column temperature was programmed from 80 to 270°C with the heating rate of 8°C/min. The injection port was maintained at 300°C. GC-MS studies were conducted using a Shimadzu GC-MS-QP 1100 EX equipped with 2.1-m column packed with OV-17 (50 mass%) and SE-30 (50 mass%). Column temperature was programmed from 80 to 270°C with the heating rate of 5°C/min, and the temperature of the injection port was 300°C. Mass spectra were obtained with ionizing energy of 20 eV.

Silicon-29–$\{^1H\}$–NMR spectra were obtained with a JEOL NM-GSX-400 at 79.4 MHz at ambient temperature. For DMDES–DMSO–OA system, the analyzed solution mainly consisted of Si-species; hence a ^{29}Si–NMR spectrum was recorded without applying a lock signal. Details of NMR measurements were described elsewhere [8].

3. Results and Discussion

3.1. DMDES-EtOH(D)-OA System (DMDES: EtOH/EtOD:OA = 1:2:0.5)

Fig. 1(a) shows the gas chromatogram of the solution allowed to react for three days. On the basis of the GC-MS results, labeled signals are assigned (Table 1). For DMDES and siloxanes, no parent peaks were detected, and the most structurally-informative peaks correspond to $[\mathrm{M}\text{-}15]^+$ions. In addition to EtOH and $(\mathrm{COOEt})_2$, ethoxy-terminated linear oligomers $((\mathrm{EtO})\mathrm{Me_2SiO}(\mathrm{Me_2SiO})_n\mathrm{SiMe_2}(\mathrm{OEt})$, $n = 0$–4) and cyclic tetramer $((\mathrm{Me_2SiO})_4)$ were detected. It should be noted that no hydroxyl-containing linear species were detected.

Silicon-29 NMR measurement also revealed the presence of D^1 $(\mathrm{Me_2SiO_{(0.5)}(OEt)})$ (with ethoxy group only) and D^2 $(\mathrm{Me_2SiO_{(0.5)}}_2)$ circumstances of silicon atoms, indicating the formation of siloxane bonds. Only one signal due to DMDES was observed in the D^0 region; no hydrolyzed monomeric species were detected. In the D^1 and D^2 regions, six signals were observed. On the basis of the behavior of signal intensities (for up to one day), these signals are assigned to ethoxy-terminated dimer, linear trimer, and linear tetramer, consistent with GC-MS results. Cyclic tetramer was not detected by NMR, possibly because the reactions further proceeded at the injection port of GC and GC-MS to form cyclic tetramer.

The present results for the DMDES–EtOH(D)–OA system are similar to those for the TEOS–EtOH(D)–OA system, where ethoxy-terminated species were dominantly observed. As discussed in the previous report [5], the water-formation by the esterification reaction [9] should be considered for these systems. If the alcohol-producing polycondensation reaction proceeded much faster than the hydrolysis reaction, the silanol groups were consumed immediately to give ethoxy-terminated species only. Hence, we have conducted the reactions in the DMDES–DMSO–OA system, where DMSO was not involved in the esterification reaction.

3.2. DMDES–DMSO–OA System (DMDES: DMSO:OA = 1:2:0.5

DMDES and DMSO were immiscible even after the reaction for one day. Thus, after the reaction for seven days, the upper part containing alkoxides was separated and analyzed by GC and GC–MS (Fig. 1(b)). Ethyl alcohol, linear oligomers (up to hexamer) and cyclic tetramer were detected. The GC and GC-MS analysis of the lower part (not shown) revealed that the lower part mainly consisted of DMSO, and ethyl alcohol was also detected. Since OA is well dissolved in DMSO, OA should also be present in the lower part (OA cannot be detected by FID-equipped GC and GC-MS instruments.) The GC and GC-MS studies also showed that only small amounts of $(\mathrm{COOEt})_2$ were present in both the upper and the lower parts.

Silicon-29 NMR revealed that the presence of D^1 and D^2 signals and a signal due to cyclic tetramer, indicating the formation of siloxane bonds. No hydrolyzed monomeric species were detected in the D^0 region. Detailed discussion on the D^1 and D^2 signals, however, cannot be possible, since the resolution of the spectrum was not high enough (the spectrum was obtained without NMR-lock).

In both DMDES–EtOH(D)–OA and DMDES–DMSO–OA systems, oligomeric species formed. Thus, in spite of the phase separation, similar reactions appeared to occur in the DMDES–DMSO–OA system. The comparison of the reaction rates between two systems, however, cannot be possible because of the immiscibility of DMDES and DMSO.

Although ethyl alcohol formed during the reactions, the amount of $(\mathrm{COOEt})_2$ was much smaller than that in the DMDES–EtOH(D)–OA system. Hence, possible water-formation via esterification should successfully be suppressed in the DMDES–DMSO–OA system. One alternative reaction mechanism could be considered on the basis of the previous work on the catalytic behavior of acetic acid ($\mathrm{CH_3COOH}$; AcOH) [10];

$$\mathrm{Si(OEt)_4} \xrightarrow[\text{-ROH}]{\text{AcOH}} \mathrm{Si(OEt)_3(OAc)}$$

$$\xrightarrow{\text{ROH}} \mathrm{Si(OEt)_3(OH)} + \mathrm{EtOAc}$$

Hence, in the present system, a postulated mechanism is that the ethoxy group is replaced with the oxalate group, which is further reacted with ethyl alcohol to form the silanol group and $(\mathrm{COOEt})_2$. Actually, we have identified $\mathrm{Me_2Si(OEt)(OAc)}$ in a DMDES–AcOH system by GC-MS, consistent with the substitution of the acetate group of TEOS for ethoxy one [5, 10–12]. Under the present experimental conditions, however, no intermediates for this mechanism (oxalate- and silanol-containing species) were detected. Hence, another reaction mechanism should be required to interpret the present observation.

Although there have been a few reports for the effect of counter anions on the acid-catalyzed sol-gel processes [10, 13] and for acetate-substituted alkoxysilanes [11, 12], the interaction between counter anions and soluble Si-containing species have not been clarified completely. Since polysiloxane formation in the present system should involve novel interaction between DMDES (and ethoxy-terminated polydimethylsiloxane) and OA, the reaction mechanism is of interest, and further work is now under investigation.

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