

SHORT COMMUNICATIONS

**Hydrolysis of Condensed Triethoxysilyl-Terminated Polystyrene with Acid Catalyst**

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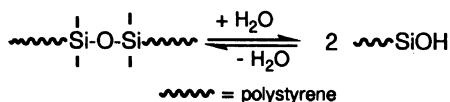
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In composite technology, combinations of polymers (matrix) and inorganic substances (filler) have received much interest in obtaining materials with superior physical properties. Some of the inorganic substances such as glass fiber, talc, and mica often have been used, particularly, to elevate mechanical properties to a higher level. To enhance the efficiency of inorganic fillers, a number of silane coupling agents have been developed for the surface modification of the fillers. Generally, most silane coupling agents are low molecular weight compounds. In recent years, polymeric silane coupling agents have become of interest in obtaining a higher efficiency and/or other functionalities and attractive results have been reported.<sup>1-3</sup>

In the reaction of polymeric silane coupling agents, the concentration of functional groups must be extremely low compared with conventional silane coupling agents. This fact and that the silanol coupling is equilibrium reaction<sup>4</sup> led us to study the condensation of triethoxysilyl-terminated polystyrene (TESi-PS), as a fundamental study of the reaction of polymeric silane coupling agents.<sup>5</sup> In the reaction, the extent of conversion of TESI-PS was largely dependent on its concentration, suggesting that the condensation was an

equilibrium reaction. Also, the condensation products were found to be dimeric and trimeric polymers of TESI-PS, and there is no detectable amount of polymer having higher molecular weight than trimeric polymer, although the precursor has three functional groups.

In the present work, we examined the hydrolysis of condensed TESI-PS (*i.e.*, reverse reaction of the condensation of TESI-PS), to

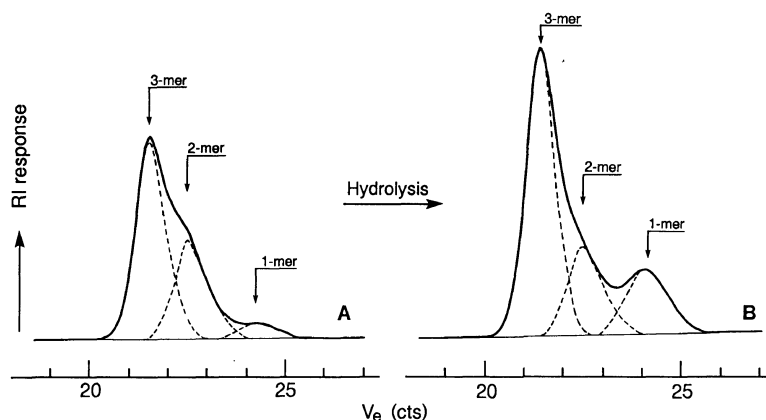


obtain further information on the condensation. As a result, characteristic data of the hydrolysis were obtained in connection with the condensation.

TESi-PS and condensed TESI-PS polymers used are listed in Table I. As a condensation or hydrolysis catalyst hydrochloric acid was used, and it sufficiently served in tetrahydrofuran (THF). The reaction procedures and conditions were the same as in the previous paper<sup>5</sup> unless otherwise noted. The determination of the extent of conversion and the analysis of products became possible by gel permeation chromatography (GPC), owing to an excellent monodispersity and high functionality of TESI-PS. GPC was performed at a column-

**Table I.** Preparation of condensed TESi-PS<sup>a</sup>

Code	TESi-PS		[HCl] mol kg <sup>-1</sup>	Temp. °C	Time h	Condensed TESi-PS, components/%		
	$M_n$ × 10 <sup>-3</sup>	[Si] /mmol kg <sup>-1</sup>				1-mer	2-mer	3-mer
C-1	3.0 <sup>b</sup>	21.5	0.520	60	24	25	42	33
C-2	3.0 <sup>b</sup>	31.8	0.535	60	24	7	38	55
C-3	3.0 <sup>b</sup>	31.9	0.115	60	24	5	33	62
C-4	6.8 <sup>c</sup>	46.5	0.532	40	24	5	62	33
C-5	6.8 <sup>c</sup>	95.0	0.518	60	48	1	5	94

<sup>a</sup> Solvent, THF.<sup>b</sup>  $M_w/M_n=1.04$ ; functionality, 0.95.<sup>c</sup>  $M_w/M_n=1.07$ ; functionality, 0.99.**Figure 1.** GPC traces of condensed TESi-PS polymers before (A) and after (B) hydrolysis (C-3 in Table II).

oven temperature of 38°C on a Tosoh HLC-802UR equipped with G2000H<sub>8</sub> and G3000H<sub>8</sub> columns or on a Tosoh HLC-802A equipped with two GMH<sub>6</sub> columns. Vapor pressure osmometry (VPO) measurements were carried out on a Corona 117 osmometer using benzene as the solvent at 40°C.

As previously reported,<sup>5</sup> TESi-PS condenses in the presence of HCl in THF. The condensation products was found to be monomeric polymer (1-mer), dimeric polymer (2-mer), and trimeric polymer (3-mer)\* of TESi-PS, although Long *et al.*<sup>6</sup> reported that the condensation of trimethoxysilyl-terminated

polystyrene gave the tetrameric polymer. The ratio of the components are largely dependent on reaction conditions, particularly the concentration of TESi-PS. GPC curve of A in Figure 1 is of C-3 polymer (in Table I) prepared by the condensation at a TESi-PS concentration of 31.9 mmol kg<sup>-1</sup>. Curve B is of polymer recovered after hydrolysis of the polymer. The hydrolysis conditions were the same as in the condensation, except that the concentration of TESi-PS was as low as 1.99 mmol kg<sup>-1</sup>. In the comparison between curves A and B, it is apparent that when the condensed TESi-PS is hydrolyzed in its dilute solution, the peak of

\* The confirmation of trimer was made by VPO measurements: Sample, trimer of TESi-PS ( $M_n$  of monomeric TESi-PS =  $6.8 \times 10^3$ ) purified by the fractional precipitation to a level of >98%;  $M_n$  by VPO,  $20.5 \times 10^3$ ;  $M_n$  by GPC,  $21.3 \times 10^3$ .

**Table II.** Change in components of condensed TESI-PS before and after the hydrolysis

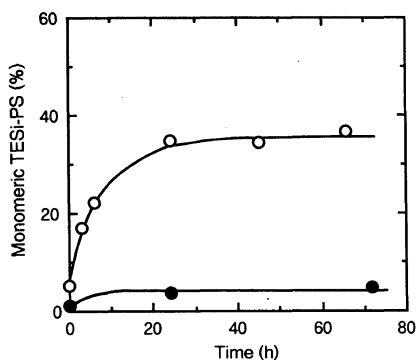
Run	Sample code <sup>a</sup>	Before/% <sup>b</sup>			After/% <sup>b</sup>		
		1-mer	2-mer	3-mer	1-mer	2-mer	3-mer
1 <sup>c</sup>	C-1	25	42	33	31	23	46
2 <sup>d</sup>	C-2	7	38	55	9	23	68
3 <sup>c</sup>	C-3	5	33	62	13	23	64

<sup>a</sup> Corresponds to the code number in Table I.

<sup>b</sup> Determined by the GPC method.

<sup>c</sup> Hydrolysis conditions:  $[\text{Si}] \approx 2.0 \text{ mmol kg}^{-1}$ ;  $[\text{HCl}] \approx 0.12 \text{ mol kg}^{-1}$ ; solvent, THF; time, 24 h; temperature, 60°C.

<sup>d</sup> Hydrolysis conditions:  $[\text{Si}] = 8.33 \text{ mmol kg}^{-1}$ ;  $[\text{HCl}] = 0.116 \text{ mol kg}^{-1}$ ; the other conditions are the same as in runs 1 and 3.



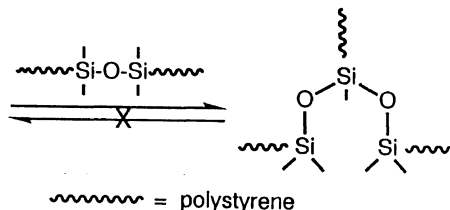
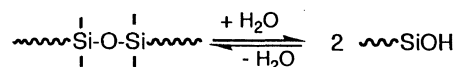
**Figure 2.** Plots of amounts of monomeric TESI-PS formed by hydrolyses of condensed TESI-PS polymers, C-4 (○) and C-5 (●) (see Table I) as a function of time. Hydrolysis conditions:  $[\text{Si}] \approx 2.0 \text{ mol kg}^{-1}$ ;  $[\text{HCl}] \approx 0.12 \text{ mol kg}^{-1}$ ; solvent, THF; temperature, 60°C.

2-mer decreases while those of 1- and 3-mer increase. Although 3-mer increased, polymer with higher molecular weight than 3-mer did not form. The quantitative relation of the equilibrated components are shown as run 3 in Table II, in which results of other runs also are shown. Table II indicates that dimerically condensed TESI-PS is subjected to hydrolysis to yield 1- and 3-mers in the dilute solution but trimerically condensed TESI-PS is hardly hydrolyzed.

In order to confirm the above findings, we carried out the hydrolysis experiments on two type of polymers. One is the polymer of code C-4 (in Table I) of which main component is 2-mer. The other is C-5 polymer (in Table I)

which consists of almost all 3-mer. The hydrolysis results are demonstrated in Figure 2. In the case of 2-mer rich polymer (C-4), a relatively large amount of monomeric TESI-PS forms through the hydrolysis. However, in the case of C-5 polymer, the yield of monomeric TESI-PS is only a several percent per the feed amount of the precursor. Considering the amount of 2-mer included in C-5 polymer, it can be claimed that the trimerically condensed TESI-PS hardly undergoes the hydrolysis under the reaction conditions.

In conclusion, 2-mer is reversibly hydrolyzed to give monomeric TESI-PS, which can condense with 2-mer to yield 3-mer. In the reaction forming 3-mer, the equilibrium lies so far to the right. These results are summarized as in the following equation. In spite of the



above equation, equilibrated monomeric TESI-PS and 2-mer remain in the reaction system. This may be due to very low concentration of

silyl groups and to the existence of equilibrium concentrations of TESI-PS and 2-mer. The reason for the extremely low reactivity of 3-mer is not clear, but our speculations are steric hindrance by three arms of polystyrene and/or transformation of silanol groups.

More detailed investigations are in progress and development of a novel method for synthesis of star-shaped polymers by the trimer forming reaction will be the subject of forthcoming papers.

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