Synthesis and Condensation of 3-(Triethoxysilyl)propyl-Terminated Polystyrene

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ABSTRACT: A well-defined polymeric silane coupling agent, 3-(triethoxysilyl)propyl-terminated polystyrene (TESiP-PS) was synthesized by reaction of polystyryllithium with (3-chloropropyl)triethoxysilane. The reaction is greatly affected by reaction conditions. The yield of TESI-PS was quantitative in a benzene/tetrahydrofuran medium at 0 °C, whereas it was as low as 5% in benzene at room temperature. TESI-PS obtained under the former conditions has 95% functionality and a monodispersity of 1.05. Condensation of TESI-PS proceeds quantitatively in the presence of either base or acid catalyst. This result is different from that for triethoxysilyl-terminated polystyrene (TESi-PS), which undergoes complete cleavage in the presence of base catalysts. This sharp difference indicates that the introduction of a trimethylene group between the trimethoxysilyl group and polystyrene effectively suppressed the cleavage reaction.

KEY WORDS 3-(Triethoxysilyl)propyl-Terminated Polystyrene / Living Polystyrene / Condensation / Spacer / Base Catalyst / Cleavage Reaction /

It is an interesting subject for material technology to improve the performance of a polymer material by hybridizing it with an inorganic substance. The inorganic substance is usually employed as a filler and is often treated with a surface treatment agent to enhance its additional effect on intended properties such as compatibility, strength, or loss factor related to damping property. A variety of silane coupling agents, most of which are relatively low molecular weight compounds,¹ has thus far been developed for these purposes.

Recently, the reaction of alkoxysilyl-functionalized polymers with tetra-alkoxysilyl monomers has been used as the basis for production of hybrid materials. Long *et al.*² reported the successful preparation of the oligomers of phenyltrimethoxysilyl-terminated polystyrene by conventional anionic techniques. They showed that mono-functionalized oligomers are useful as stable precursors for the preparation of soluble star-shaped polymers.

We have studied the synthesis and condensation of the well-defined triethoxysilyl-terminated polystyrene (TESi-PS)^{3–6} as a control for polymeric silane coupling agents. TESI-PS thus prepared was quantitatively condensed by various catalysts.⁶ However, in the presence of strong base catalysts,⁵ we found that optimum yield of condensed TESI-PS was followed by its decomposition with the passage of time to a compound having the same molecular weight as that of TESI-PS.

This sequence was due to a cleavage reaction that involved elimination of polystyrene moieties from condensed TESI-PS; namely, scission of a benzyl-Si bond of TESI-PS. It then becomes apparent that this cleavage reaction would be suppressed by introducing an alkyl group as spacer between a triethoxysilyl group and polystyrene moiety.

In this present study, synthesis and condensation of 3-(triethoxysilyl)propyl-terminated polystyrene (TESiP-PS) was carried out with two aims. One was to develop a well-defined polymeric silane coupling agent that can undergo condensation without side reactions even in the presence of base catalysts. The other was to clarify further the mechanism of the cleavage reaction in the case of base catalysts.

EXPERIMENTAL

Materials

(3-Chloropropyl)triethoxysilane (CPTESi; Shin-Etsu Silicon Chemicals) was dried on a vacuum line over calcium hydride for 24 h, and then distilled. *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) was used after careful filtration and solvent replacement with benzene. Styrene was purified by the method described in the previous paper.⁵ Benzene and tetrahydrofuran (THF) were purified according to the conventional living anionic polymerization technique. TESI-PS

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was prepared by the coupling reaction of PStLi with CTES, as previously reported.³ Catalysts used for condensation, such as methanesulfonic acid, LiOH, NaOH, and KOH, were reagent grade and were used as received.

Methods

Coupling reactions of PStLi with CPTESi were performed by dropwise addition of a benzene solution of PStLi to a solution of CPTESi in benzene or THF. All operations relating to this reaction were carried out under high vacuum in an all-glass apparatus equipped with breakseals. The resulting polymers were recovered by the method described in the previous paper³ for recovering polystyrene.

The condensation of TESiP-PS or TESi-PS, using methanesulfonic acid as catalyst proceeded throughout in a homogeneous system in THF in a sealed ampoule at 60 °C. In the presence of alkali hydroxide catalysts, the condensation was carried out as follows. Since alkali hydroxides are insoluble in THF, an aqueous solution of hydroxide was added to a THF solution of TESi-PS or TESiP-PS in an ampoule, and the heterogeneous reaction mixture was stirred at 60 °C for the prescribed time. The resulting polymer was recovered by pouring the reaction mixture into a large excess of methanol.

The extent of conversion of TESiP-PS or TESi-PS to the oligomer was determined from the gel permeation chromatography (GPC) curve of the polymer recovered after condensation, *i.e.*, from the ratio of the peak area of condensed compounds to the total response, as obtained using an RI detector.

Characterization

GPC curves were recorded on a Toso HLC-802UR with G2000H and G3000H columns or on a Toso HLC-802A with two GMH columns at a column oven temperature of 40 °C. THF was used as the eluent and the flow rate was 1 mL min⁻¹. The GPC data were calibrated with polystyrene standards (Figure 1). ¹H NMR spectra were obtained with a Varian XL-200 spectrom-

eter. The solvent used was chloroform-*d* containing 1% tetramethylsilane as internal reference.

RESULTS AND DISCUSSION

Synthesis of TESiP-PS

To prepare well-defined TESiP-PS, the coupling reaction of PStLi with CPTESi was carried out under reaction conditions that were focused on the reaction medium, since it has been reported that this type of nucleophilic substitution is highly affected by reaction medium.^{7–10} The functionalities of the prepolymers (TESiP-PS) thus obtained were determined by carrying out their condensation reactions in the presence of sodium hydroxide as catalyst. The results are shown in Table I. The coupling reaction in a benzene/THF medium at 0 °C afforded quantitatively TESiP-PS with more than 94% functionality (*f*) and a monodispersity of $M_w/M_n = 1.05$ (codes 1 and 2, Table I).

In contrast, the coupling reaction in a benzene medium at room temperature gave TESiP-PS in low yield, as shown for codes 3 and 4, Table I, though the reaction of PStLi with CTES afforded TESi-PS³ quan-

Figure 1. GPC calibration curves (elution volume (V_e , counts) vs. molecular weight): polystyrene standards (●) and TESiP-PS polymer (○).

Table I. Preparation of TESiP-PS by coupling PSt-Li with CPTESi

code	PSt-Li soln		CPTESi soln		coupling reaction ^a			TESiP-PS		
	solvent	[LE] ^b (mmol L ⁻¹)	solvent	[CPTESi] (mmol L ⁻¹)	[Cl]/[LE]	temp (°C)	THF (vol %)	$M_n \times 10^{-3}$	M_w/M_n	<i>f</i> ^c
1	benzene	48.6	THF	167.1	3.44	0	26.5	2.20	1.05	96
2	benzene	48.3	THF	169.5	3.51	0	26.9	2.20	1.05	94
3	benzene	29.8	benzene	94.0	3.15	r.t.	0	2.20	1.05	5
4	benzene	19.0	benzene	49.1	2.58	r.t.	0	3.20	1.03	5

^aReaction time, 2 h. ^bMolar concentration of the living end. ^cFunctionality (*f* (the maximum value of *Y*), *Y* (%) = $100 \times [\text{the GPC band area of polymerized TESiP-PS}] / [\text{the total GPC band area of the reacted products}]$) determined from the condensation of coupling reaction product in the presence of NaOH.

Table II. Condensation of the prepolymers (codes 3 and 4 in Table I) using acid or base catalyst using various conditions^a

run	prepolymer code	(mmol kg ⁻¹)	catalyst (mol kg ⁻¹)	time (h)	condensate yield (%)
1	3	19.8	CH ₃ SO ₃ H	0.10	72
2	4	40.1	CH ₃ SO ₃ H	0.10	48
3	3	19.8	NaOH	0.95	72
4	4	19.0	NaOH	0.99	72

^aTemperature, 60 °C; solvent, THF. **Figure 2.** ¹H NMR spectra of the coupling products of PSt-Li with CPTESi in benzene/THF and benzene: spectra I and II are of those in codes 1 and 3 in Table I, respectively.

titatively under similar conditions. In order to clarify the reason for the very low yield of TESiP-PS, an alternative method was employed to determine the functionalities of reaction products in the benzene medium; *i.e.*, the condensation of prepolymers (codes 3 and 4) were carried out using methanesulfonic acid as catalyst instead of sodium hydroxide. As shown in Table II, yields of condensates of prepolymers under acidic conditions were about 80%, indicating that at least 80% of the polystyrene molecules have functional groups susceptible to condensation by the acid catalyst.

The sharp contrast between the extent of condensation by acid catalysts and that by base catalysts may result from the structure of the functional groups. Possible functional groups, which are formed in the coupling reaction of PStLi with CPTESi, are a 3-(triethoxysilyl)propyl group and a (3-chloropropyl)diethoxysilyl group. To confirm the functional group, ¹H NMR measurements were taken for representative prepolymers (codes 1 and 3, Table I). Figure 2 shows the NMR spectra of the prepolymers. In spectrum I (code 1), the signal of the methylene protons (a) of the ethoxy group is observed from 3.62 to 3.77 ppm, and the methyl protons (b) of the initiator fragment (*sec*-butyl) can be seen from 0.58 to 0.80 ppm. The peak area ratio of the methylene protons to the methyl protons (*i.e.*, a : b) was evaluated as 5.91 (theor, 6) : 6. This value shows that the functionality of the

Scheme 1. Reactions of PStLi with CPTESi in benzene/THF and benzene.

code 1 prepolymer is 98%. In spectrum II, the peak c around 3.35 ppm comes from the chloromethylene signal of the code 3 prepolymer. The ratio of the peak areas of the chloromethylene protons to methyl protons b' was estimated to be 1.77 : 6, showing that (3-chloropropyl)diethoxysilyl groups were introduced at the end of polystyrene giving 89% functionality to the code 3 prepolymer. These ¹H NMR functionality values are somewhat higher than those obtained after condensation in the presence of acid catalyst. The difference may be due to the incompleteness of the condensation process and / or to the precision of ¹H NMR analyses.

In conclusion, results for the synthesis of TESiP-PS under two different reaction conditions are summarized in Scheme 1. With benzene/THF as the medium and a temperature of 0 °C, the reaction of PStLi with CPTESi affords quantitatively well-defined TESiP-PS. With benzene as medium and at room temperature, the yield of TESiP-PS is as low as 5%, while (3-chloropropyl)diethoxysilyl-terminated polystyrene is obtained as a major product in a yield of 75% (89% by ¹H NMR).

Condensation of TESiP-PS.

TESiP-PS and TESi-PS (for purposes of comparison) were subjected to condensation using base catalysts. Characteristics of TESiP-PS and TESi-PS were as follows. TESiP-PS: $M_n = 2.10 \times 10^3$, $M_w/M_n = 1.05$, $f = 96\%$. TESi-PS: $M_n = 7.60 \times 10^3$, $M_w/M_n = 1.06$, $f =$

Table III. Condensations of TESiP-PS and TESi-PS in the presence of base catalysts^a

run	prepolymer (mmol kg ⁻¹)	catalyst		time (h)	condensate		
		(mol kg ⁻¹)			yield ^b (%)	DP ^c	M_w/M_n
TESiP-PS							
1	20.0	LiOH	0.99	1	94	5	1.07
2	20.1	LiOH	0.98	2	93	5	1.06
3	20.0	LiOH	1.00	168	94	5	1.07
4	19.7	NaOH	1.00	1	91	5	1.08
5	20.0	NaOH	0.99	2	95	5	1.07
6	19.8	NaOH	0.96	168	94	5	1.09
7	20.0	KOH	1.00	1	84	5	1.03
8	20.0	KOH	1.00	2	91	5	1.04
9	20.0	KOH	0.99	168	92	5	1.05
TESi-PS							
10	19.9	LiOH	1.01	1	92	4	1.06
11	20.0	LiOH	1.00	168	0	—	—
12	20.0	NaOH	1.09	4	62	5	1.08
13	20.0	NaOH	1.01	168	0	—	—

^aTemperature, 60 °C; heterogeneous system (TESiP-PS in THF, catalyst in H₂O).^bDetermined by the GPC method. ^cDegree of polymerization that was determined from the peak-top count of the GPC curve with calibration using polystyrene standards. **Figure 3.** Time courses of condensate yields for the condensations of TESiP-PS catalyzed by LiOH (▲), NaOH (●), and KOH (■) and for the condensation of TESi-PS catalyzed by NaOH (○). Reaction conditions: solvent, THF; temperature, 60 °C; [prepolymer] ≈ 20 mmol kg⁻¹; [cat.] ≈ 1 mol kg⁻¹.

97%. The results are summarized in Table III. TESiP-PS was condensed almost quantitatively by LiOH, NaOH, or KOH catalyst within 1 h. It was found that the degree of polymerization (DP) of the condensates was 5 (based on PSt standards calibration (Figure 1)) and that the molecular weight distribution was very narrow ($M_w/M_n = 1.03$ –1.09). We confirmed that these DP values did not vary with reaction time or temperature. Conversely, in the case of TESi-PS which does not possess the spacer (trimethylene group), no condensate was detected after a long reaction time, although some condensate was obtained after a relatively short reac-

Figure 4. GPC curves of condensation products of TESiP-PS and TESi-PS. Curves a, b, c, and d are the condensation products of TESiP-PS (runs 4 and 6 in Table III) and of TESi-PS (runs 12 and 13 in Table III), respectively.

tion time. The time-dependence of condensate yield can be seen more clearly in Figure 3. In the condensations of TESiP-PS by alkali hydroxides, the curves of condensate yield–time were found to saturate at values of *ca.* 90% yield within 1 h, and these values did not vary with reaction time. However, in the case of TESi-PS, it was found that the condensate yield–time curve reaches a maximum point at a reaction time of 5 h, and then the yield decreases with time. After 20 h no condensate was obtained.

The condensation products for TESiP-PS and TESi-PS were traced with GPC. The results are shown in Figure 4. We found that the GPC profiles of products found in condensations of TESiP-PS after either a short or long reaction time are almost the same, implying that

Figure 5. ^1H NMR spectra of the condensation products of TESiP-PS and TESI-PS: spectra I_B and II_B are of those obtained for the products from runs 6 and 13 in Table III, respectively; comparative spectra I_A and II_A are for original TESiP-PS and TESI-PS, respectively.

there is no decomposition of oligomers of TESiP-PS, once formed, even after a long reaction time. In contrast, it was confirmed by GPC profiles that oligomers of TESI-PS, once formed, decomposes completely after a long reaction time to a polymer whose molecular weight is virtually the same as that of TESi-PS.

The cause of this curious result was examined using ^1H NMR. ^1H NMR spectra of the products, which were obtained after condensation of TESiP-PS and TESI-PS, catalyzed by NaOH for 168 h, I_B and II_B , respectively, together with comparative spectra of the original TESiP-PS (I_A) and TESI-PS (II_A), are shown in Figure 5.

Comparison of spectra I_B and I_A reveals that their

resonance peaks are almost identical except for the resonance peaks of the ethoxy methyl protons (b and e, 1.14 ppm) and ethoxy methylene protons (a and d, 3.71 ppm). However, comparison of spectra II_B and II_A shows that spectrum II_B furnishes a new signal, (g), at 2.25 ppm due to the benzyl protons and that the peaks due to the ethoxy protons (methyl protons, (e), 1.05 ppm; methylene protons, (d), 3.71 ppm) disappear. The intensity ratio of the new signal (g) to that for the methyl protons (h) of the initiator fragment was 2.1 (theor, 2) : 6. These findings indicate the quantitative scission of the Si-CHPh single bond of TESI-PS.

Accordingly, the condensation reactions of TESiP-PS and TESI-PS are represented in Scheme 2. We may postulate the mechanism of the cleavage reaction from the difference in behavior of the condensation reactions of TESiP-PS and TESI-PS. In nucleophilic substitution, the Si-CHPh benzyl group of TESI-PS is assumed to be a much more superior leaving group than is the trimethylene group of TESiP-PS. That is, first, a bimolecular substitution between PS moiety and OH^- , which arises from the nucleophilic attack of OH^- at the ^1Si atom, occurs (process (a)), or second, the base draws out the H^+ ion from the silanol to form the silanolate and, as a consequence, the cleavage of the ^1Si -CHPh bond of the silanolate, through formation of a silanone and benzyl anion-terminated polystyrene as intermediate, may occur (process (b)). The first assumption may be similar to the so-called $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$ concerted process. Furthermore, the high stability of the benzyl anion probably reduces the activation energy of this elimination reaction. The second assumption is supported by the reports^{11–13} showing that nucleophilic substitution of a Si-leaving group proceeds *via* silanone formation. Eaborn *et al.*^{11,12} and Stanczyk *et al.*¹³ found that cleavage of R-Si bonds occurs rapidly in solutions of RSiMe_2OMe ($\text{R} = m\text{-ClC}_6\text{H}_4\text{CH}_2$ or $\text{PhC}\equiv\text{C}$) in 5 vol% H_2O -MeOH containing relatively small concentrations of NaOMe. They suggested that unimolecular dissociation of $^-\text{O}(\text{X})\text{Si}<$ species to give X^- and $\text{O}=\text{Si}<$ (which immediately reacts with the solvent) accounts for features of the base-catalyzed cleavage of R-Si bonds.

In the case of TESI-PS, the increase in hyperconjugative electron release into the benzene ring from the CH- ^1Si bond probably occurs,¹⁴ promoting the cleavage reaction of the ^1Si -CHPh single bond. However, for TESiP-PS, the $(\text{CH}_2)_3$ group may reduce such hyperconjugative effect. The reduction of this effect probably inhibits the cleavage of the Si-CH $_2$ single bond of the $\text{Si}(\text{CH}_2)_3\text{CHPh}$ group. Thus, in the TESiP-PS related silane-coupling agents containing the $\text{Si}(\text{CH}_2)_n\text{CHPh}$ group ($n > 3$), such a cleavage reaction probably does

TESiP-PS

TESi-PS

Scheme 2. Proposed reaction scheme of TESI-PS and TESI-P-PS catalyzed by alkali hydroxides.

not occur, even under the strongly basic condition.

From the time-independence of the DP values for the TESI-P-PS condensates, we may propose the presence of possible cyclic molecular structures for the condensates (to be reported separately). Further work (for example, a ^{29}Si CP MAS NMR study¹⁵) is highly desirable, in order to determine which cyclic structure is predominantly stabilized in solution and in the solid state. Recently, Izawa *et al.*¹⁶ successfully used SAXS spectra to detect the aggregates of alkyl-alkoxysilane in ethanol. They also used 2D correlation GPC¹⁷ to confirm the correlation between the silane-coupling monomer-polymer aggregates, thus confirming the presence of the aggregates.

Thus, in the case of the TESI-P-PS condensates, the presence of aggregates brought about by the hydrophobic polystyrene portions is possible. Moreover, steric hindrance by the bulky polystyrene moiety isolates the SiOH groups, thus preventing further reaction.

CONCLUSIONS

A polymeric silane coupling agent, TESI-P-PS, which

can be condensed by each of base and acid catalysts, has been developed. Synthesized TESI-P-PS possesses a high functionality and a narrow molecular weight distribution, and its molecular weight is easily controlled, since the polymeric moiety is prepared by living anionic polymerization.

The condensation of TESI-P-PS proceeds quantitatively in the presence of either base or acid catalysts and affords oligomers (TESi-P-PS)_a with a degree of polymerization of 5.0 and a narrow molecular weight distribution. In the condensation, the oligomers of TESI-P-PS do not undergo cleavage in the presence of base catalyst, although the oligomers of TESI-PS are cleaved completely. This difference verifies that the trimethylene spacer group is effective for perfect suppression of the cleavage reaction.

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