

Preparation and Characterization of End-Alkoxysilylated Polystyrene and the Grafting Behaviors onto Inorganic Pigments. II. Utilization of 4-Triethoxysilyl- α -methylstyrene

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SYNOPSIS

Novel polystyrene was prepared with triethoxysilyl (TES) groups at the end of the chain, and the grafting behaviors of the resulting polymer onto silica, alumina, and titania were studied. TES groups were introduced by the reaction between living polystyryl anion and 4-triethoxysilyl- α -methylstyrene (**1**) in THF at 195 K. The end-functional polymer was characterized by GPC, ¹H-NMR, and TLC. It was confirmed that the polymer had several units of **1** at the chain end and a fairly narrow molecular weight distribution. TES groups in the present polymer were found to be hydrolyzed with both acids and bases such as mono-*n*-butylphosphate (MBP) and tetrabutylammonium hydroxide (TBAH), respectively. The polymer was effectively grafted onto silica and alumina in toluene in the presence of MBP and TBAH, respectively. The amount of graft, estimated by thermogravimetry, changed with the selection of substrates and catalysts; about 2 mg/m² at the highest. The change in the amount of graft can be explained by the amount of effective acidic- or basic-hydroxyl groups on the substrate surfaces. However, titania received the largest amount of graft in the absence of catalyst. This may be because the strong acidic sites on the surface of titania act as a hydrolytic catalyst. The present polymer is expected to find wide application as a macromolecular dispersant for various types of inorganic pigments. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the previous paper,¹ we reported that end-functional polystyrene having isopropoxydimethylsilyl (IPS) groups at the end part of the chain can be prepared by living anionic polymerization through the sequential addition of styrene and 4-isopropoxydimethylsilyl- α -methylstyrene. IPS groups in the resultant polymer were hydrolyzed with strong acid such as mono-*n*-butylphosphate (MBP) but not with weak acids and bases. The previous polymer can be grafted onto silica in the presence of MBP. The grafted silica showed excellent dispersibility in toluene solution of polystyrene, indicating usefulness of the end-alkoxysilylated polystyrene as a

macromolecular dispersant for silica. This is because long graft-chains prevent pigment particles from flocculating in nonpolar media.^{2,3} However, the polymer cannot be grafted onto alumina even in the presence of a large amount of MBP. Thus the polymer having IPS end-groups has limited applicability. This unexpected result was due to the predominant adsorption of MBP onto the basic alumina surface.

Surfaces of metal oxide powders are, in general, classified as acidic, basic, or amphoteric, according to their values of isoelectric point.^{4,5} Hence a polymer having end-alkoxysilylated groups which can be hydrolyzed with not only acid but also base is expected to find wide applications as a macromolecular dispersant. However, we must select moderately hydrolyzable alkoxysilyl groups: if an alkoxysilyl group is too hydrolyzable, it will be attacked by a living carbanion during polymerization, resulting in the formation of undesirable products.

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In this work, we adopt the triethoxysilyl (TES) group which is hydrolyzable with base as well as with acid. This is, however, stable against carbanions, because the living anionic polymerization of 4-triethoxysilylstyrene has been reported to proceed favorably with negligible side reactions such as the cleavage of silyl ether.⁶ Incidentally, silane coupling agents bearing triethoxysilyl (TES) groups have been used as surface modifiers for inorganic materials in media acidified with acetic acid.⁷⁻⁹ Hence we synthesized a new monomer, 4-triethoxysilyl- α -methylstyrene (**1**).

The purpose of this work is to prepare the end-triethoxysilylated polystyrene derived from **1** and styrene, and to study the grafting behaviors of the resulting polymer onto silica, alumina, and titania, which have acidic, basic, and amphoteric surfaces, respectively.

EXPERIMENTAL

4-Triethoxysilyl- α -Methylstyrene (**1**)

4-Chloro- α -methylstyrene (76.3 g, 0.500 mol) dissolved in THF (400 mL) was added dropwise to magnesium turnings (13.4 g, 0.551 mol) under nitrogen gas at 337 K for 2 h and then stirred at the same temperature for 2 h to produce the Grignard reagent. The Grignard reagent was added dropwise to tetraethoxysilane (208.3 g, 1.00 mol) dissolved in THF (100 mL) at 303 K for 2 h, then stirred at the same temperature for 1 h and at 333 K for 2 h.⁶ After being filtered off, the crude product was fractionally distilled to give 60.3 g (0.215 mol, 43%) of **1** (377 K/ 1×10^2 Pa). From the ¹H-NMR spectrum, the final product was confirmed to be **1**: 360.1 MHz ¹H-NMR (CDCl₃), δ 1.2 (t, 9H, CH₃—CH₂—), 2.1 (s, 3H, α —CH₃), 3.9 (q, 6H, —CH₂—O—), 5.1, 5.4 (t, s, 2H, CH₂=), 7.4, 7.6 (2d, 4H, C₆H₄). The purification of **1** was carried out in an all-glass apparatus equipped with break seals under a pressure of 1×10^{-3} Pa or lower. After being dried over calcium hydride, **1** was transferred into a vacuum apparatus and purified with *sec*-butylmagnesium bromide in three stages by distillation *in vacuo*.^{1,10} Finally **1** was redistilled and diluted to about 10–20 vol/vol % with purified THF just prior to use.

Other Chemicals

Other chemicals were the same as used in the preceding paper.¹

Silica (Aerosil 130) and alumina (Aluminum oxide C) were the same as used in the preceding paper.¹

Titania (Titanium oxide P-25) was obtained from Nippon Aerosil Co. Ltd. (Japan). The values of their BET surface areas were 130, 100, and 50 m²/g, respectively, as quoted in the catalogues.^{13,14} The powders were dried at 323 K for 2 h *in vacuo* just prior to the grafting reaction.

Polymerization

Living anionic polymerizations of styrene were carried out in THF with *n*-butyl lithium (*n*-BuLi) at 195 K for 1 h in a sealed-glass apparatus equipped with break seals under 1×10^{-3} Pa or lower, using essentially the same procedures as have been reported previously.^{1,10-12,15,16} The resulting polystyryl anions were further allowed to react with **1** at the same temperature for 0.5 h. After being quenched with methanol, polymers were precipitated from THF solution into an excess of methanol. After being dried *in vacuo*, the samples dissolved in benzene were reprecipitated for purification. The purified polymers were freeze-dried from the benzene solutions for 24 h.

Hydrolysis

Hydrolysis of the TES groups in the present polymer was carried out in toluene at room temperature for 0.5 h in the presence of MBP or TBAH (10% in methanol). After being precipitated from toluene solution into an excess of methanol, the polymers were dried *in vacuo* and subjected to IR measurement.

Grafting

Grafting reactions of the end-triethoxysilylated polystyrene onto silica, alumina, and titania were performed as reported in the preceding paper.¹ The present polymer (2.0 g) dissolved in toluene (40 mL) was added to the substrates (3.0 g) dispersed in toluene (40 mL), followed by addition of a catalyst (0.2–0.3 g), and then stirred at room temperature for 2 h. After the dispersoid was centrifuged at 10,000 rpm. for 1 h, supernatant liquid was removed by decantation and subjected to IR measurement to confirm the hydrolysis of TES groups. After being dried at 323 K for 2 h *in vacuo*, part of the precipitate was subjected to thermogravimetric analysis (TGA). The remaining powder was further washed with toluene (80 mL), followed by centrifugation, decantation, and vacuum drying at 323 K. The procedures were repeated until a constant thermogravimetric loss was attained.

Table I Preparation of End-Triethoxysilylated Polystyrene in THF at 195 K

No.	<i>n</i> -BuLi (mmol)	Styrene ^a (mol)	1 ^b (mmol)	Conv. (%)	10 ⁻⁴ M _k ^c	GPC		N ^d	
						10 ⁻⁴ M _n	M _w /M _n	Theoretical ^e	Found ^f
1	1.58	0.151	15.7	84	1.1	1.1	1.28	9.9	3.4
2	2.54	0.349	31.5	88	1.6	1.7	1.28	12.4	6.6
3	2.23	0.341	14.7	93	1.7	1.7	1.27	6.6	3.3
4	0.0650	0.160	1.28	98	26	27	1.17	19.7	6

^a Styrene was polymerized with *n*-BuLi in THF at 195 K for 1 h. Concentration was 5–9%.

^b 1 was allowed to react with living polystyryl anion at 195 K for 0.5 h.

^c Kinetic molecular weight, calculated from the ratio of amounts of styrene to *n*-BuLi, and average number of 1 units per molecule.

^d Average number of 1 units per molecule.

^e Calculated from the molar ratio of 1 to *n*-BuLi.

^f Determined by ¹H-NMR (see text).

Characterization

Number average molecular weight, M_n , and molecular weight distribution, M_w/M_n , were measured by gel permeation chromatography (GPC) at 298 K using an HLC-803D instrument (Tosoh Ltd., Japan) with refractive index (RI) detector. The columns were G4000H8 or G3000H8 (Tosoh Ltd.) calibrated with standard polystyrenes. THF was used as an eluent.

¹H-NMR spectra were obtained at room temperature in CDCl₃ with a Bruker AM-360 spectrometer (360.1 MHz). Chemical shift was referred to chloroform (7.25 ppm) in CDCl₃. IR spectra of the end-functional polymer and grafted substrates were obtained by the solution method in toluene with a JASCO IR-80 and by the diffuse reflectance method with a Nicolet 60 SX infrared spectrophotometers, respectively.

Thin-layer chromatography (TLC) was performed using silica gel plates. The developing solvent was a mixture of *n*-hexane/benzene = 1/4 vol/vol %. Two standard polystyrenes ($M_n = 9.1 \times 10^3$, $M_w/M_n = 1.02$ and $M_n = 1.9 \times 10^5$, $M_w/M_n = 1.04$) were used as references. Ultraviolet absorption at 254 nm of the resulting chromatoplates was measured by a Dual Wavelength Flying-Spot Chromatoscanner (Shimadzu Co., Japan).

Thermogravimetric analysis of the grafted powders was carried out with SSC-5200 instruments (Seiko Instrument Inc., Japan). The temperature was raised from 293 to 773 K at a rate of 5 K/min and maintained at 773 K for 50 min. Under these conditions, the weight losses of the end-functional polymer, TBAH, and MBP were found to be almost 100%, 100%, and 62 ± 3%, respectively. These TGA measurements agree with gravimetric analysis measurements from the preceding paper,¹ within experimental error.

The amounts of acidic and basic sites on the surface of the maiden powders were estimated by potentiometric titration, using an electrometer (HIR-ANUMA COMTITE-8) with glass and Ag-AgCl electrodes, according to the method of Kobayashi and co-workers.¹⁷ For example, 0.5 g of alumina (corresponding to 50 m² of surface area) was sonicated in 0.02N methylisobutylketone solution (30 mL) of acetic acid. After the dispersoid was centrifuged at 10,000 rpm. for 1 h, the supernatant liquid was titrated with a 0.01N methylisobutylketone solution of potassium methoxide, from which we obtained the amount of basic site on the alumina surface. In measuring for acidic site, triethylamine and perchloric acid were used instead of acetic acid and potassium methoxide, respectively.

The ultraviolet-visible spectrum of silica dispersed in toluene was obtained at room temperature with a Simadzu UV-2100 spectrophotometer. Every sample was sonicated for 10 min just prior to measurement. Trimethylsilylated silica (Aerosil R812; BET surface area = 260 m²/g) was used as a standard.

RESULTS

Preparation and Characterization of End-triethoxysilylated Polystyrene

Table I shows the results of anionic polymerization through the sequential addition of styrene and 1. When 1 was added to a solution of living polystyrene which had been prepared in THF with *n*-BuLi at 195 K, the color of the solution immediately changed from yellowish red to dark brownish red and remained unchanged. All the polymers showed single and fairly narrow GPC peaks. The value of M_n for

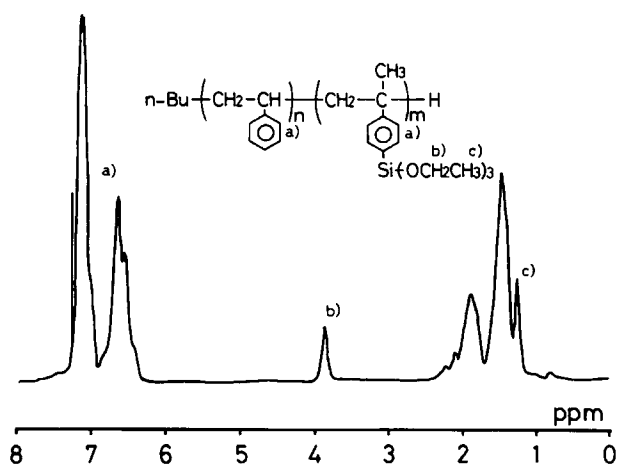


Figure 1 $^1\text{H-NMR}$ spectrum of end-functional polymer (sample no. 2 in Table I). Solvent was CDCl_3 .

each polymer was close to that of the kinetic molecular weight, M_k , which is calculated from the polymer yield, the molar ratio of styrene to $n\text{-BuLi}$, and the average number of **1** units per molecule, as will be discussed later.

TLC was taken for both the end-functional polymers and standard polystyrenes. The present polymers, nos. 1–3 in Table I, showed no developing spot whereas a polystyrene ($M_n = 9.1 \times 10^3$) showed a single developing spot. Under the same conditions as above, sample no. 4 showed one developing spot. This may not be due to the absence of end-functional group, but due to the high molecular weight which is 15–20 times as high as those of the other samples (nos. 1–3). Sample no. 4 can be distinguished from a polystyrene ($M_n = 1.9 \times 10^5$) in benzene containing a small amount of acetic acid. The former showed no developing spot, but the latter still showed a developing spot. These facts suggest that the end-functional polymers were pure and contained no homopolystyrene.

The $^1\text{H-NMR}$ spectrum of sample no. 3 is shown in Figure 1. Other samples also showed similar spectra. The signal at around 7 ppm is assigned to phenyl protons; signals at 1.2 and 3.8 ppm were assigned to the methyl and methylene protons in the TES group, respectively. The average number of **1** units per molecule, N , can be estimated from the signal intensity ratio of the methylene to phenyl protons and the value of M_n . The values estimated for all the samples, listed in Table I, are smaller than those calculated from the molar ratio of **1** to $n\text{-BuLi}$. The discrepancy between the found and the theoretical values may be due to the very low propagation rate of monomer **1**, which is similar to 4-isopropoxydimethylsilyl- α -methylstyrene.¹

Figure 2 shows IR spectra of sample no. 2 before (broken curve) and after (solid curve) hydrolysis in the presence of MBP. The peak at 960 cm^{-1} assigned to the ethoxysilyl group¹⁸ disappeared after the reaction, indicating that TES group in the present polymer was completely hydrolyzed with MBP. Similar results were obtained in the presence of either acetic acid or TBAH. All the results clearly show that the desired end-alkoxysilylated polystyrene was successfully prepared and the end-silyl ether can be hydrolyzed with not only acid but also base.

Grafting

Grafting reactions of the end-triethoxysilylated polystyrene (sample no. 2 in Table I) onto silica, alumina, and titania were carried out in toluene. The reactions were tested in both the presence and absence of catalyst, MBP, or TBAH. Similar operations with only the catalyst were performed as a control.

Curve a in Figure 3 shows the IR spectrum of the alumina powder which was treated with end-triethoxysilylated polystyrene in the presence of TBAH. Curves b and c in Figure 3 are IR spectra of maiden alumina and the end-triethoxysilylated polystyrene, respectively. In Figure 4, curves a and b are IR spectra of the titania powders treated and untreated, respectively.

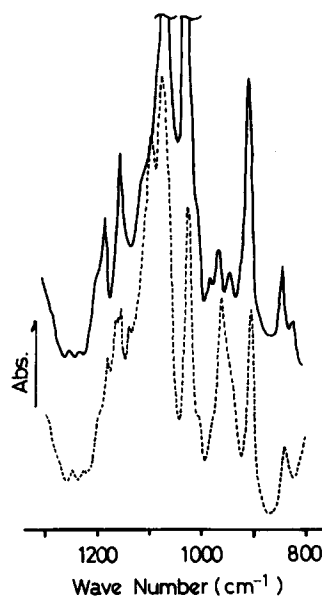


Figure 2 IR spectra of end-functional polymer (sample no. 2 in Table I) before (broken curve) and after (solid curve) hydrolysis.

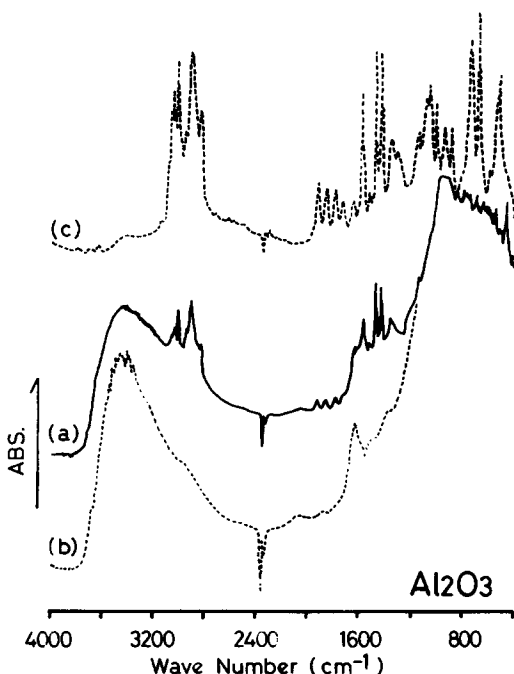


Figure 3 IR spectra of alumina (a) treated with end-functional polymer (sample no. 2 in Table I) in the presence of TBAH, (b) untreated, and (c) end-functional polymer (sample no. 2 in Table I). Spectra a and b were obtained by the diffuse reflectance method.

The peaks assigned to the polystyrene segment were observed at 1450, 1490, and around 1800 cm^{-1} in both curves a of Figures 3 and 4, showing the existence of the end-functional polymer on the surfaces of both the treated alumina and titania.

The IR spectrum of the silica powder treated in a way similar to the above excepting the difference in catalyst, MBP in this case, clearly showed the existence of the end-functional polystyrene. It is well known that polystyrene never adsorbs onto silica in a nonpolar, organic solvent such as benzene or ethylbenzene.^{19,20} Hence it is clear that the present polymer can be grafted onto the substrates, silica, alumina, and titania, in the presence of the appropriate catalyst.

The results of thermogravimetry are shown in Figures 5–8. Curve a in Figure 5 shows the thermogravimetric loss of the present polymer. Curves b and c in Figure 5 are the thermogravimetric loss of silica mixed with MBP and TBAH, respectively. Maiden silica exhibited little weight loss, as shown in curve d. The weight loss of the end-functional polymer was observed above 573 K, whereas those of TBAH and MBP were observed mainly below 573 K. In curves a, b, and c, however, the weight losses were not observed at 773 K for at least 50 min.

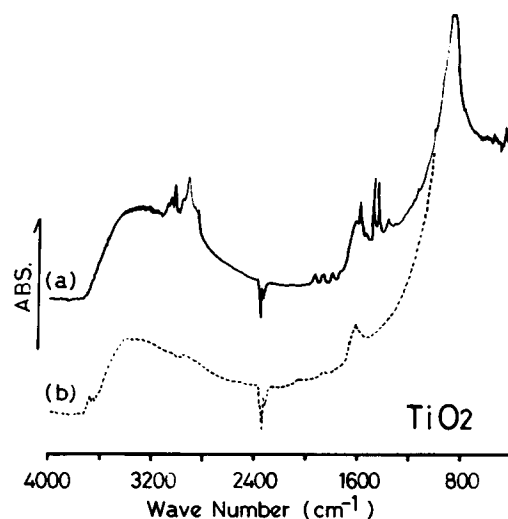


Figure 4 IR spectra of titania (a) treated with end-functional polymer (sample no. 2 in Table I) in the presence of TBAH and (b) untreated. Spectra were obtained by the diffuse reflectance method.

Hence we can distinguish the end-functional polymer, catalysts, and substrates by TGA measurement. In Figure 6, curves a and b show the TGA profiles of the grafted silica with the catalysts MBP and TBAH, respectively. Curves c and d show the profiles of silica adsorbing only MBP and only TBAH, respectively. Both curves c and d show single-step weight losses, whereas curves a and b show multiple-step weight losses. In all curves in Figure 6, the weight losses at the first step ended below 573 K. Furthermore, the change of curve b at the first step is almost the same as observed in curve d. The pair of curves a and c also show similar features. Other

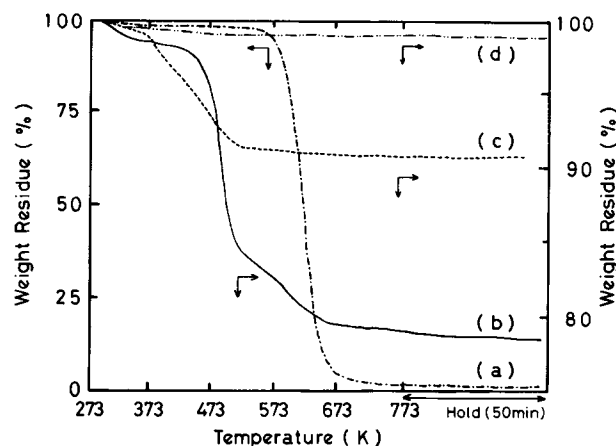


Figure 5 Thermogravimetric analysis profiles: (a) end-functional polymer (sample no. 2 in Table I), (b) silica mixed with TBAH, (c) silica mixed with MBP, and (d) maiden silica.

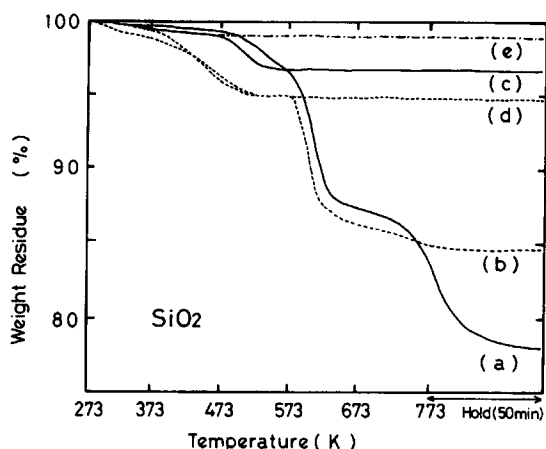


Figure 6 Thermogravimetric analysis profiles for silica (a) treated with end-functional polymer in the presence of MBP, (b) treated with end-functional polymer in the presence of TBAH, (c) treated with MBP only, (d) treated with TBAH only, and (e) untreated (duplicate of d in Fig. 5). End-functional polymer used was sample no. 2 in Table I.

substrates, alumina and titania, also exhibited similar features as shown in Figures 7 and 8, respectively. The changes below 573 K were found to be due to catalysts (Fig. 5).

Hence the difference between the value of the weight loss at 573 K and the final value at 773 K may correspond to the amount of grafted polymer. From the difference, we can estimate the amount of graft per unit surface area of the substrate, ΔW . As mentioned in the Experimental section, 38% of

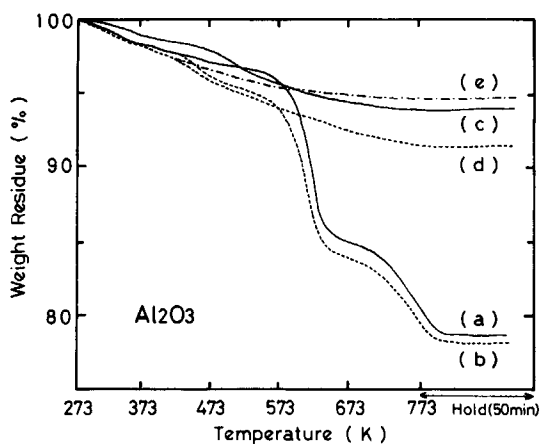


Figure 7 Thermogravimetric analysis profiles for alumina (a) treated with end-functional polymer in the presence of MBP, (b) treated with end-functional polymer in the presence of TBAH, (c) treated with MBP only, (d) treated with TBAH only, and (e) untreated. End-functional polymer used was sample no. 2 in Table I.

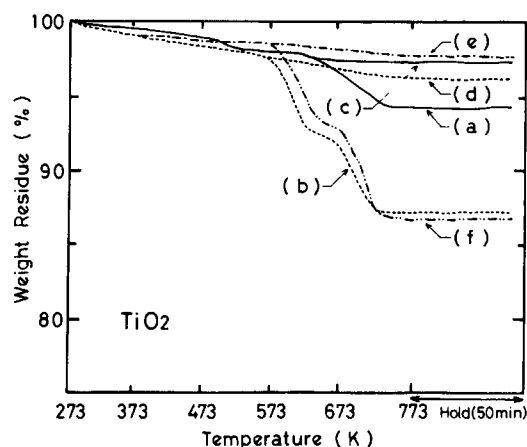


Figure 8 Thermogravimetric analysis profiles for titania (a) treated with end-functional polymer in the presence of MBP, (b) treated with end-functional polymer in the presence of TBAH, (c) treated with MBP only, (d) treated with TBAH only, (e) untreated, and (f) treated with end-functional polymer in the absence of catalyst. End-functional polymer used was sample no. 2 in Table I.

MBP still remained as ash under our heating condition. The same behavior is expected to appear in the grafted substrates. Hence the values of ΔW with MBP were estimated from the values of the weight losses and the amount of the ash.

The ΔW values estimated, summarized in Table II, depend on the kinds of catalysts. However, ΔW attained the value of around 2 mg/m² (at most) regardless of the kinds of substrates. It is known that 1–2 mg/m² of adsorbed resin is enough to cover the surface of a pigment particle as an adsorption layer.²¹ Hence the highest value obtained in this work, about 2 mg/m², implies that the grafted polymer chains

Table II Grafting Reaction of End-Triethoxysilylated Polystyrene onto Silica, Alumina, and Titania^a

Substrate	Amount of Graft, ΔW (mg/m ²) in the Presence of		
	MBP ^b	TBAH ^c	No Catalyst
Silica	1.9	0.91	0.70
Alumina	2.1	1.9	0.65
Titania	0.67	2.1	2.4

^a Grafting reactions were carried out in toluene at room temperature for 2 h. Recipe: substrate, 3.0 g; end-triethoxysilylated poly(styrene), 2.0 g; catalyst, 0.2–0.3 g; toluene, 80 mL.

^b Mono-*n*-butylphosphate.

^c Tetrabutylammonium hydroxide.

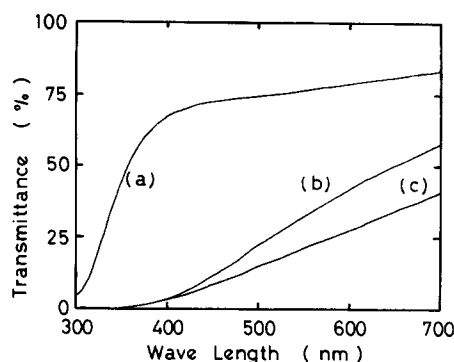


Figure 9 Ultraviolet-visible spectra of dispersion of (a) grafted, (b) trimethylsilylated, and (c) maiden silica in toluene at room temperature.

shield the surface of the substrate from further grafting.

For titania, the value of ΔW with no catalyst was the highest one. It is known that titania has strong acidic sites on the surface.⁴ Consequently, these sites may act as a hydrolytic catalyst for the grafting reaction.

Figure 9 shows ultraviolet-visible spectra of grafted, trimethylsilylated, and maiden silica dispersed in toluene. The grafted silica dispersed in toluene has fairly high transmittance through shorter wave length in comparison with the other dispersions. This means that the grafted silica is finely dispersed in toluene. It is confirmed that the long graft chains on the silica surface are effective for high dispersibility.

DISCUSSION

The grafting reaction occurs between silanol groups in the end-functional polymer and acidic- and/or basic-hydroxyl groups on the surface of the metal oxide powders.⁴ In all the grafting reactions, there

are enough silanol groups to attain the highest value of ΔW because of easy hydrolysis of the present triethoxysilyl ether. However, ΔW changed depending on the combination of substrate and catalyst. This suggests that the amount of hydroxyl groups on the substrate surface depends on the kinds of catalysts.

Acidic and basic catalysts are adsorbed by substrate at the basic and acidic sites, respectively. The hydroxyl groups on which catalyst has been adsorbed may not work in the grafting reaction. Only the free hydroxyl groups may be active. The amounts of the effective site can be estimated by acid-base titration. The values estimated are listed in Table III, together with the molar amounts of graft. From the amounts of graft, it is clear that, stoichiometrically, we need at least $0.12 \mu\text{mol}/\text{m}^2$ of effective sites to obtain the highest value of ΔW . For silica, there exist enough acidic sites but too few basic sites. Alumina was found to have enough of both acidic and basic sites. Titania has a large number of basic sites, which are consistent with the observed values of ΔW for the combinations of substrate catalyst. For titania with MBP, however, ΔW was less than the expected value. Titania is known to adsorb phosphate ion strongly,²² which may be one reason for the unexpected results. It may be concluded that the existence of enough effective sites on the substrate surface is necessary to get a high value of ΔW .

CONCLUSION

Novel end-functional polystyrene having triethoxysilyl groups at the chain end was successfully prepared by the reaction between living polystyryl anion and 4-triethoxysilyl- α -methylstyrene (**1**). Triethoxysilyl groups in the present polymer can be hydrolyzed with both acids and bases such as mono-*n*-butylphosphate and tetrabutylammonium hydroxide, respectively. The resulting polymer was

Table III Properties of the Substrates and Molar Amounts of Graft

Substrate	Acidic Site ($\mu\text{mol}/\text{m}^2$)	Basic Site ($\mu\text{mol}/\text{m}^2$)	Amounts of Graft in the Presence of	
			MBP ^a ($\mu\text{mol}/\text{m}^2$)	TBAH ^b ($\mu\text{mol}/\text{m}^2$)
Silica	3.6	0.06	0.11	0.05
Alumina	1.7	4.1	0.12	0.11
Titania	1.0	3.4	0.04	0.12

^a Mono-*n*-butylphosphate.

^b Tetrabutylammonium hydroxide.

grafted onto silica, alumina, and titania in the presence of the catalyst. The amount of graft per unit surface area of the substrate (ΔW) was, at most, 2 mg/m² regardless of the kinds of substrates. The existence of enough effective sites on the substrate surface is necessary to obtain a high ΔW value.

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