

# Preparation and Characterization of End-Alkoxysilylated Polystyrene and the Grafting Behaviors onto Inorganic Pigments. I. Utilization of 4-Isopropoxydimethylsilyl- $\alpha$ -methylstyrene

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## SYNOPSIS

Novel end-functional polystyrene having isopropoxydimethylsilyl (IPS) groups at the end part of the chain was prepared. IPS groups were introduced by the reaction between the living polystyryl anion and 4-isopropoxydimethylsilyl- $\alpha$ -methylstyrene (**1**) in THF at 195 K. The resultant polymer was characterized by GPC, <sup>1</sup>H-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. IPS groups in the polymer can be hydrolyzed with strong acid such as mono-*n*-butylphosphate (MBP) but not with weak acid and base. Grafting behaviors of the polymer onto silica and alumina were studied in toluene in the presence of MBP as a catalyst. The polymer was grafted onto silica effectively. However, it cannot be grafted onto alumina because of predominant adsorption of MBP onto alumina having a basic surface. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

End-alkoxysilylated polymers are expected to find applications as macromolecular dispersants for inorganic pigments. This is because silyl ether is hydrolyzed easily and the resulting silanol group can react with a hydroxyl group on a surface of pigment.<sup>1</sup> Furthermore, long graft-chains prevent pigment particles from flocculating in nonpolar media.<sup>2,3</sup> Some end-alkoxysilylated polymers have been prepared by various workers.<sup>4-7</sup> The polymers have, however, only one trialkoxysilyl group at the chain end. Generally, pigments are insoluble in solvents. Hence, a grafting reaction between end-functional polymer and pigment is carried out in a heteroge-

neous solution. To accomplish such a grafting reaction effectively, we need a number of end groups.

The present objective is to prepare a polystyrene having several alkoxysilyl groups at the end part of the chain. We think that the best way is to carry out an anionic polymerization through the sequential addition of styrene and alkoxysilyl-substituted monomers. Hirao et al. reported that the living anionic polymerization of 4-isopropoxydimethylsilylstyrene proceeds successfully at 195 K without side reactions such as cleavage of silyl ether.<sup>8</sup> Incidentally, it is relatively easy to purify monomers of the  $\alpha$ -methylstyrene type because of their low ability to undergo thermal polymerization.<sup>9-11</sup> Taking these facts and speculations into consideration, we have synthesized a new alkoxysilyl-substituted monomer, 4-isopropoxydimethylsilyl- $\alpha$ -methylstyrene (**1**).

This article reports the preparation of end-isopropoxydimethylsilylated polystyrene derived from **1** and styrene and the grafting behaviors of the re-

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sultant polymer onto silica and alumina having well-characterized surfaces.

## EXPERIMENTAL

### 4-Isopropoxydimethylsilyl- $\alpha$ -methylstyrene (1)

Isopropoxydimethylsilyl chloride was prepared from dimethyldichlorosilane and isopropanol in the presence of triethylamine in a similar way to that reported by Hirao et al.<sup>8</sup> 4-Chloro- $\alpha$ -methylstyrene (62.0 g, 0.406 mol) dissolved in tetrahydrofuran (THF, 460 mL) was added dropwise to magnesium turnings (13.8 g, 0.568 mol) under nitrogen gas at 337 K for 2 h and then stirred at the same temperature for 2 h to give the Grignard reagent.

Isopropoxydimethylsilyl chloride (62.0 g, 0.406 mol) dissolved in THF (230 mL) was added dropwise to the Grignard reagent at 313 K for 1 h and then stirred at 316 K for 2 h. Fractional distillation of the product gave 67.5 g (0.288 mol, 71%) of **1** (367–369 K,  $4 \times 10^2$  Pa). From the <sup>1</sup>H-NMR spectrum, the final product was confirmed to be **1**: 360.1 MHz <sup>1</sup>H-NMR (CDCl<sub>3</sub>),  $\delta$  0.3 (s, 6H, CH<sub>3</sub>—Si), 1.1 (d, 6H, CH<sub>3</sub>—CH), 2.1 (s, 3H, CH<sub>3</sub>C=), 3.9 (q, 1H, —CH<), 5.0, 5.3 (t, s, 2H, CH<sub>2</sub>=C), 7.4, 7.5 (2d, 4H, C<sub>6</sub>H<sub>4</sub>). The purification of **1** was carried out in an all-glass apparatus equipped with breakseals under a pressure of  $1 \times 10^{-3}$  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*. Finally, **1** was diluted to about 20 v/v % with purified THF just prior to use.

### Other Chemicals

THF used for the dilution of monomers and the polymerization was purified by the same way as has been reported previously.<sup>12</sup> Styrene, purchased from Nakarai Tesque, Inc., as GR grade, was purified by distillation in the presence of the sodium salt of *n*-octylbenzophenone after the usual purification.<sup>9</sup> The monomer was redistilled finally and diluted to about

10–20 v/v % with purified THF just prior to polymerization. *n*-Butyllithium (*n*-BuLi) was obtained from Nakarai Tesque, Inc., and diluted with purified *n*-hexane.

4-Chloro- $\alpha$ -methylstyrene was obtained from Hokko Chemical Industry Co. Ltd. and distilled over calcium hydride under a reduced pressure. Other reagents were used without further purification.

Silica and alumina were obtained from Nippon Aerosil Co. Ltd. The values of the BET surface area and isoelectric point are listed in Table I. The former values are quoted from catalogs.<sup>13,14</sup>

### Polymerization

Living anionic polymerizations by the sequential addition of **1** and styrene or vice versa were carried out in a sealed-glass apparatus equipped with breakseals under  $1 \times 10^{-3}$  Pa or lower, using essentially the same procedures as have been reported previously.<sup>9–12,15,16</sup> 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 precipitated again for purification. The purified polymers were freeze-dried from the benzene solutions for 24 h.

### Hydrolysis

Hydrolysis of the isopropoxydimethylsilyl (IPS) groups in the present polymer was performed in toluene or THF at room temperature for 0.5 h in the presence of acid or base catalyst. Acid catalysts were hydrochloric acid, *p*-toluenesulfonic acid, mono-*n*-butylphosphate (MBP), and acetic acid. Base catalysts were sodium hydroxide (10% in methanol) and tetrabutylammonium hydroxide (10% in methanol). After being precipitated from toluene or THF solution into an excess of methanol, the polymers were dried *in vacuo* and subjected to IR measurement.

### Grafting

End-alkoxysilylated polymer (2.0 g) dissolved in toluene (40 mL) was added to silica or alumina (3.0 g) dispersed in toluene (40 mL), followed by addition of the necessary amount of catalyst. After being stirred at room temperature for 2 h, the dispersoid was centrifuged at 10,000 rpm for 1 h. After the removal of the supernatant liquid by decantation, the precipitate was dried *in vacuo* at 323 K for 2 h. The

**Table I** Physical Properties of Silica and Alumina

Substrate	BET Surface Area (m <sup>2</sup> /g)	Isoelectric Point (pH)
Silica	130 ± 25	3.5
Alumina	100 ± 15	9.4

**Table II** Preparation of End-alkoxysilylated Polystyrene in THF

No.	<i>n</i> -BuLi (mmol)	Styrene <sup>a</sup> (mol)	<b>1</b> <sup>b</sup> (mmol)	Conv. (%)	GPC		
					10 <sup>-4</sup> <i>M<sub>k</sub></i> <sup>c</sup>	10 <sup>-4</sup> <i>M<sub>n</sub></i>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>
<b>1</b> → Styrene <sup>d</sup>							
1	4.61	0.192	18.9	93	0.53	8.1	2.41
Styrene → <b>1</b> <sup>e</sup>							
2	1.65	0.208	7.87	98	1.4	1.5	1.38
3	1.52	0.203	13.2	93	1.5	1.4	1.26
4	1.58	0.125	22.3	85	0.97	1.1	1.26
5	1.69	0.212	24.6	89	1.5	1.5	1.27

<sup>a</sup> Styrene was polymerized with living anion of poly(**1**) or *n*-BuLi in THF at 195 K for 1 h. Concentration was 5–9%.

<sup>b</sup> **1** was allowed to react with *n*-BuLi or the living polystyryl anion at 195 K for 0.5 h.

<sup>c</sup> *M<sub>k</sub>*, calculated from the ratio of amounts of styrene to *n*-BuLi and average number of **1** units per molecule. In the case of no. 1, *M<sub>k</sub>* was calculated from the ratio of amount of styrene to *n*-BuLi.

<sup>d</sup> **1** was allowed to react with *n*-BuLi before the polymerization of styrene.

<sup>e</sup> **1** was allowed to react with the living polystyryl anion.

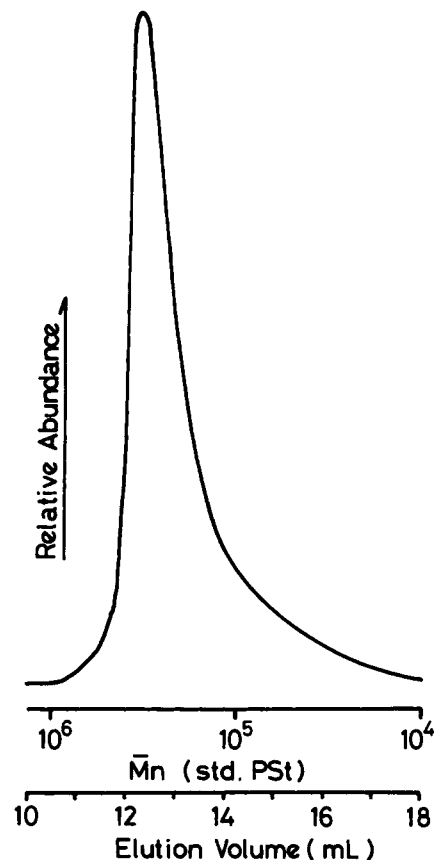
supernatant liquid was subjected to IR measurement to confirm hydrolysis of IPS groups in the present polymer. The resulting powder was washed with toluene (80 mL), followed by centrifugation and vacuum drying at 323 K. Such procedures were repeated until a constant weight was attained.

### Characterization

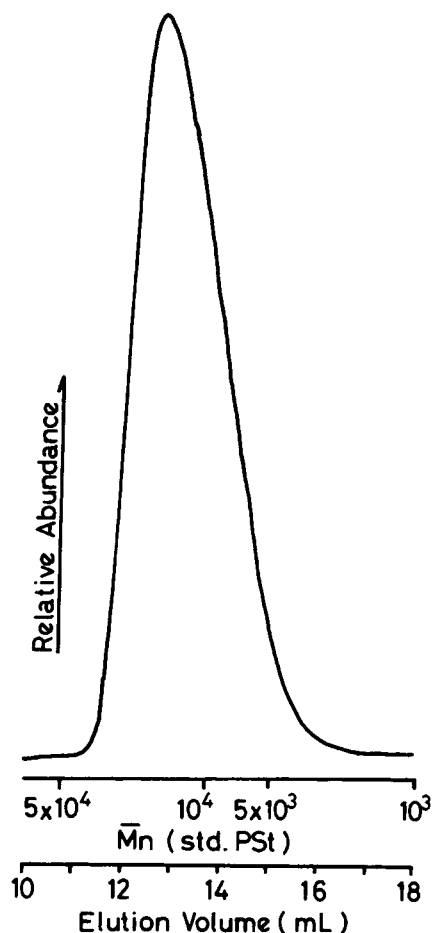
Number-average molecular weight, *M<sub>n</sub>*, and molecular weight distribution, *M<sub>w</sub>*/*M<sub>n</sub>*, were measured by gel permeation chromatography (GPC) at 298 K using an HLC-803D instrument (Tosoh Ltd.) with refractive index (RI) detector. The columns were G4000H8 or G3000H8 (Tosoh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

<sup>1</sup>H-NMR spectra were obtained at room temperature in CDCl<sub>3</sub> with a Bruker AM-360 spectrometer (360.1 MHz). The chemical shift was referred to chloroform (7.25 ppm) in CDCl<sub>3</sub>. IR spectra of the end-functionalized polymers and grafted substrates were obtained in toluene, with a JASCO IR-80 and by the pellet method with a Nicolet 60 SX infrared spectrophotometer, respectively.

Thin-layer chromatograms (TLC) were obtained with a silica gel plate. The developing solvent was a mixture of *n*-hexane/benzene = 1/4 v/v %. Standard polystyrene (*M<sub>n</sub>* = 9.1 × 10<sup>3</sup>, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.02) was used as a reference. Ultraviolet absorption at 254 nm of the resulting chromatoplates was mea-



**Figure 1** GPC chromatogram of sample no. 1 in Table II. Column was G4000H8. Carrier was THF at 298 K. Flow rate, 1 mL/min; concentration, 0.1 g/dL; detector, RI detector.



**Figure 2** GPC chromatograms of sample no. 4 in Table II. Column was G3000H8. Other measurement conditions were the same as in Figure 1.

sured by a Dual Wavelength Flying-Spot Chromatoscanner (Shimadzu).

The isoelectric point of maiden powders was estimated by the measurement of the colloid-vibrational potential as a function of pH in the aqueous solution of 0.01*N* potassium nitrate with an Acoustophoretic Titrator System 7000 (Penkem).<sup>17</sup> The pH of the solution was adjusted with the aqueous solutions of 1*N* potassium hydroxide and 1*N* nitric acid.

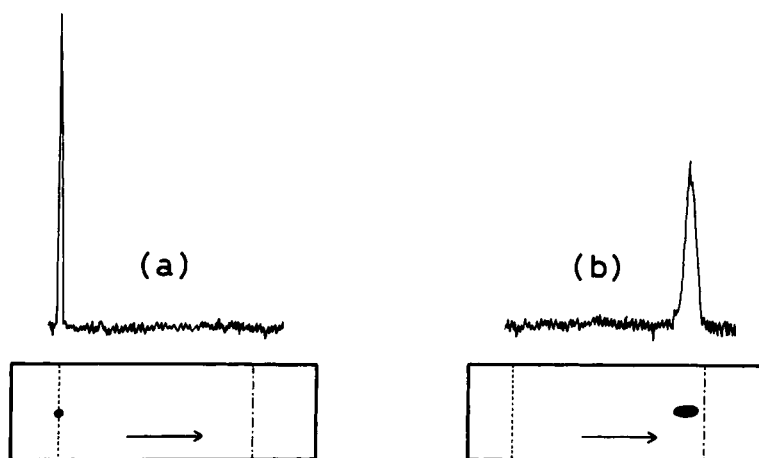
The viscosity and the yield value of the dispersed system of grafted silica in a toluene solution of polystyrene ( $M_n = 2.6 \times 10^4$ ) was measured by a rotational viscometer equipped with cone-and-plate geometry (Type E, Tokyo Keiki) at 298 K.

## RESULTS AND DISCUSSION

### Preparation of End-Isopropoxydimethylsilylated Polystyrene

There are two ways to prepare the desired end-functional polymer: the addition of styrene to the previously polymerized **1** (preintroduction of IPS groups) and vice versa (postintroduction of IPS groups).

The first row in Table II (no. 1) shows the result by the "preintroduction" method. Figure 1 shows the GPC chromatogram of the sample. When **1** was added to *n*-BuLi dissolved in THF at 195 K, the solution showed a dark, brownish red color, which remained unchanged. On addition of styrene, the



**Figure 3** Thin-layer chromatograms and ultraviolet absorption curves at 254 nm of the chromatoplates: (a) sample no. 4 in Table II and (b) standard polystyrene ( $M_n = 9.1 \times 10^3$ ,  $M_w/M_n = 1.02$ ). Developing solvent was a mixture of benzene/*n*-hexane (4/1 in volume ratio). The ultraviolet absorption curves were obtained by a chromatoscanner.

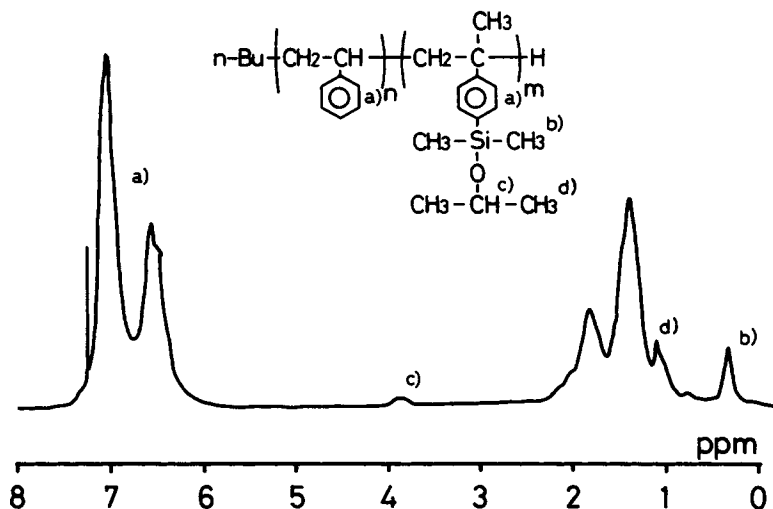


Figure 4  $^1\text{H-NMR}$  spectrum of sample no. 4 in Table II. Solvent was  $\text{CDCl}_3$ .

color immediately changed to a yellowish red, which is a characteristic color of a carbanion of living polystyrene, but returned to the former dark, brownish red a few minutes later. The changes in color of the solution indicate that the propagation reactions proceeded at least in three stages, i.e., the propagation of monomer **1** at first, then styrene, and, finally, **1** again. This may be due to the very low rate of propagation of **1** in an anionic mechanism in comparison with that of styrene. The residual **1** caused a broad molecular weight distribution of sample no. **1**. Sample no. **1** may have the units of **1** at both chain ends and/or in the chain. Hence, the "preintroduction" method is not appropriate for the present purpose.

The results by the "postintroduction" method are summarized in Table II (nos. 2–5). When styrene was added to *n*-BuLi dissolved in THF at 195 K, the solution showed a yellowish red color that remained unchanged, but changed immediately to a dark, brownish red upon addition of **1**. In every

sample of nos. 2–5, the value of  $M_n$  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*-BuLi, and the average number of **1** units per molecule, as will be mentioned later. The GPC chromatogram of sample no. 4 is shown in Figure 2. The GPC peak was single and fairly narrow. Other samples also showed similar peaks. Figure 3(a) and (b) show the TLC chromatograms of sample no. 4 and standard polystyrene ( $M_n = 9.1 \times 10^3$ ,  $M_w/M_n = 1.02$ ), respectively. Sample no. 4 showed no developing spot, whereas polystyrene did show a single one. Samples nos. 2, 3, and 5 also showed no development. Hence, it is clear that samples 2–5 were pure and contained no homopolystyrene.

Figure 4 shows the  $^1\text{H-NMR}$  spectrum of sample no. 4. Samples nos. 2, 3, and 5 showed similar spectra. The signal at 0.3 ppm is assigned to  $\text{CH}_3\text{—Si}$  protons, and the ones at 1.1 and 3.9 ppm, to primary and tertiary protons in the IPS group, respectively. Signals assigned to  $\alpha$ -methyl protons of isotactic, heterotactic, and syndiotactic triads in poly( $\alpha$ -methylstyrene) have been known to appear at 0.18, 0.43, and 0.92 ppm, respectively.<sup>18</sup> In this study, however, small signals due to triads of **1** units cannot be distinguished. The average number of **1** units per molecule,  $N$ , can be estimated from the signal intensity ratio, i.e., the intensity ratio of  $\text{CH}_3\text{—Si}$  to phenyl protons or that of primary protons in isopropyl groups to the phenyl protons, and the value of  $M_n$ . The values estimated are listed in Table III. The values of  $N$  by the two methods are in fairly good agreement for all the samples, though the values by NMR are smaller than those calculated from the ratio of the amounts of **1** to *n*-BuLi. The dis-

Table III Average No. of **1** Units per Molecule,  $N$

No.	Kinetic Value of $N^a$	$N^b$	
		Silyl	Isopropyl
2	4.8	4.9	5.3
3	8.7	5.9	6.3
4	14.1	6.7	7.1
5	14.5	6.8	7.3

<sup>a</sup> Calculated from the ratio of the amounts of **1** to *n*-BuLi.

<sup>b</sup> Determined by  $^1\text{H-NMR}$  (see text).

crepancies between the observed and kinetic values of  $N$  may be due to a very low rate of propagation of the monomer **1**. It is, however, clear from the results of GPC, TLC, and NMR measurements that the samples prepared by the "postintroduction" method have several units of **1** at one end of the chain, as expected.

### Hydrolysis of the Isopropoxysilyl Group

Figure 5 shows IR spectra of sample no. 4 before (broken curve) and after (solid curve) hydrolysis in the presence of MBP. There was no change in the absorption peak at  $1250\text{ cm}^{-1}$  assigned to the symmetrical bending vibration in  $\text{CH}_3\text{—Si—CH}_3$ , whereas the peaks at  $880$ ,  $1020$ , and  $1120\text{ cm}^{-1}$  assigned to  $\text{Si—O—CH}(\text{CH}_3)_2$  (Ref. 19) disappeared after the reaction. Hence, the silyl ether is certainly hydrolyzed. However, the broad peak appeared at  $1000\text{--}1100\text{ cm}^{-1}$ . This is assigned to the stretching vibration in  $\text{Si—O—Si}$ . This shows that some of the resulting silanol groups were consumed through condensation.

The results of the hydrolysis of IPS group with various catalysts are summarized in Table IV. Strong acids such as MBP and *p*-toluenesulfonic acid are available, whereas weak acid such as acetic acid and bases are not.

### Grafting

Run no. 1 in Table V shows the result of the graft reaction of the end-functional polymer no. 4 onto

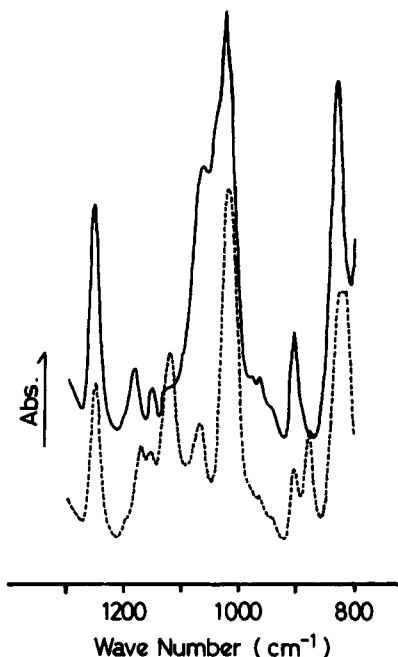


Figure 5 IR spectra of sample no. 4 in Table II before (broken curve) and after (solid curve) hydrolysis.

silica in the presence of MBP. The supernatant liquid taken after centrifugation of the reaction mixture showed an IR spectrum similar to the solid curve in Figure 5, indicating complete hydrolysis of IPS groups in the present polymer. After the processes of washing, centrifugation, and vacuum drying of the resultant powder, the weight increment per unit weight of silica ( $\Delta W\text{ g/g}$ ) was  $0.19 \pm 0.01$ . Run no.

Table IV Hydrolysis of Isopropoxysilyl Groups in End-functional Polymer<sup>a</sup>

Catalyst			
Name	(mmol)	Solvent	Hydrolysis <sup>b</sup>
Mono- <i>n</i> -butylphosphate	0.36	THF	○
	0.036	THF	○
	0.036	Toluene	○
<i>p</i> -Toluenesulfonic acid	0.29	THF	○
	0.48	THF	○
Hydrochloric acid (35%)	0.048	Toluene	○
	0.83	THF	X
Acetic acid			
Sodium hydroxide (10% in methanol)	0.13	THF	X
Tetrabutylammonium hydroxide (10% in methanol)	0.19	THF	X

<sup>a</sup> Sample no. 4 in Table II, 0.1 g, was dissolved in 10 mL of solvent; temp: room temperature; time: 30 min.

<sup>b</sup> ○: Hydrolyzed, X: unhydrolyzed.

**Table V** Grafting of End-alkoxysilylated polystyrene onto Silica and Alumina in Toluene

No.	Substrate (g)		Polymer <sup>a</sup>		MBP <sup>b</sup> (g)	$\Delta W^c$ (g/g)
	Silica	Alumina	Name	(g)		
1	3.0	—	Si-PSt	2.0	0.2	0.19 ± 0.01
2	3.0	—	Si-PSt	2.0	—	0.06 ± 0.01
3	3.0	—	PSt	2.0	—	0.00
4	3.0	—	—	—	0.2	0.01
5	3.0	—	—	—	—	0.00
6	—	3.0	Si-PSt	2.0	2.0	0.28 ± 0.02
7	—	3.0	—	—	2.0	0.28

<sup>a</sup> Si-PSt: sample no. 4 in Table II; PSt: polystyrene,  $M_n = 9.1 \times 10^3$ ,  $M_w/M_n = 1.02$ .

<sup>b</sup> Mono-*n*-butylphosphate.

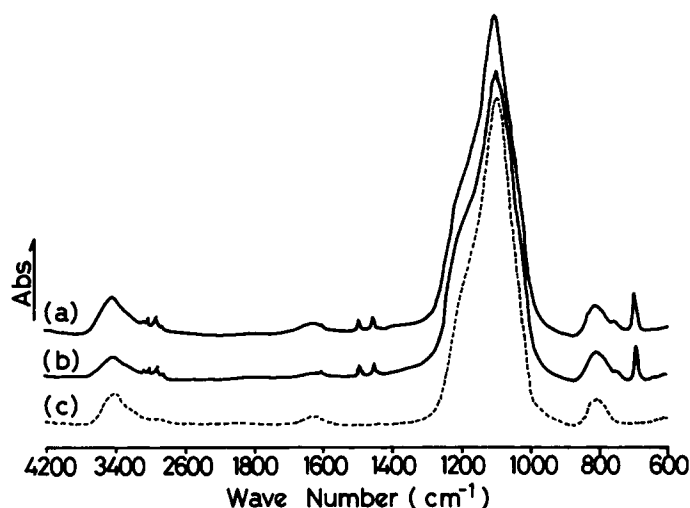
<sup>c</sup> Weight increment per gram of substrate.

2, whose conditions for operation were the same as in run no. 1, except for the lack of MBP, showed  $\Delta W = 0.06 \pm 0.01$ , which is fairly small in comparison with the value in no. 1. However, similar operations onto silica with only polystyrene (no. 3), only MBP (no. 4), and no additives (no. 5) showed zero or negligibly small value of  $\Delta W$ . These observations indicate that silanol and also IPS groups in the present polymer can interact with the silica surface but polystyrene, MBP, and solvent (toluene) cannot do so.

Curve a in Figure 6 shows the IR spectrum of the powder obtained (run no. 1 in Table V). Curves b and c in Figure 6 are IR spectra of a mixture of 0.19 g of the end-alkoxysilylated polymer and unit gram of maiden silica powder and maiden silica powder,

respectively. Absorption peaks assigned to the styrene unit are observed at 700, 1450, and 1490  $\text{cm}^{-1}$  in both curves a and b, but are not in curve c. The relative absorbancy of these peaks in curve a to the large peak at 1000–1300  $\text{cm}^{-1}$  assigned to Si—O—Si is almost the same as that in curve b. These results confirm that the weight increment observed in no. 1 is due to the end-functional polymer.

As shown in Figure 5, self-condensation of the present polymer was observed after hydrolysis. Hence, a part of the silanol groups may be consumed through the self-condensation during deprotection and workup. As listed in Table VI, however, the grafted amount of the present polymer onto silica is much more than the reported values of other end-alkoxysilylated polymers.<sup>2,3</sup> Furthermore, our ob-



**Figure 6** IR spectra of silica: (a) treated with sample no. 4 in Table II in the presence of MBP (no. 1 in Table V); (b) mixture of sample no. 4 and maiden silica (the weight ratio of sample no. 4 to silica was adjusted to  $\Delta W$  of no. 1 in Table V); (c) untreated.

**Table VI** The Amount of Added and Grafted End-alkoxysilylated Polymers onto Silica

Polymer	Amount of Added Polymer (Wt %)	Amount of Grafted Polymer		Ref. in Text
		(Wt %)	(mg/m <sup>2</sup> )	
End-trimethoxysilylated polyoxazoline	49	9.7	<sup>a</sup>	2
End-triethoxysilylated poly( <i>tert</i> -butylaziridine)	50	7	0.24	3
	100	12	0.45	
Present polymer	67	16	1.5	This work

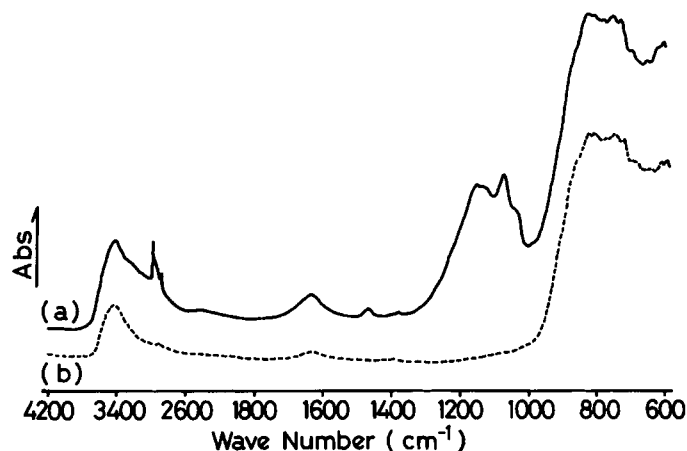
<sup>a</sup> The surface area of silica was not mentioned.

tained value, 1.5 mg/m<sup>2</sup>, reaches the necessary value (1–2 mg/m<sup>2</sup>) to form an effective steric barrier that prevents the particles from flocculating.<sup>20</sup> Hence, we may conclude that the present polymer can be grafted effectively onto the silica surface in the presence of MBP.

Table VII shows the viscosity and the yield values of grafted and untreated silica dispersed in the toluene solution of polystyrene, together with those of the unloaded solution. Both values for the grafted silica were much smaller than those for untreated silica. This result suggests that the grafted silica was finely dispersed in the toluene solution of polystyrene.

A grafting reaction of the end-alkoxysilylated polymer onto alumina was also performed. Under conditions similar to those in run no. 1—3.0 g of alumina, 2.0 g of the present polymer, and 0.2 g of MBP—no IPS groups in the end-functional polymer

were hydrolyzed. When a tenfold amount of MBP was used, as shown in run no. 6, the IPS groups were hydrolyzed and the value of  $\Delta W$  was  $0.28 \pm 0.02$ . A similar operation onto alumina with only MBP (no. 7) gave the same value of  $\Delta W$  as that in run no. 6. The curves a and b in Figure 7 show the IR spectra of the powder obtained in no. 6 and maiden alumina powder, respectively. In curve a, no peak was observed at 700, 1450, or 1490 cm<sup>-1</sup>, but two peaks were observed at 1075 and around 1150 cm<sup>-1</sup>, which are assigned to stretching vibrations of P—OH and P=O, respectively. Hence, MBP exists on the alumina surface, but the present polymer does not. As judged from the value of the isoelectric point listed in Table I, silica has an acidic surface, whereas alumina has a basic one. Hence, MBP is easily adsorbed onto alumina. It may be considered that no end-alkoxysilylated polymer was grafted onto the alumina surface because of predominant adsorption of MBP onto the surface.



**Figure 7** IR spectra of alumina: (a) treated with sample no. 4 in Table II in the presence of MBP (no. 6 in Table V); (b) untreated.



**Table VII Viscosity and Yield Value of Dispersed System of Silica in Toluene Solution of Polystyrene<sup>a</sup> at 298 K**

Silica	Viscosity (Pa-s)		Yield Value (Pa)
	19.2 s <sup>-1</sup>	192 s <sup>-1</sup>	
Grafted silica	0.65	0.50	0.21
Untreated silica	35	64	230
Unloaded	0.31	0.29	0.0

<sup>a</sup> Recipe of dispersion: silica 0.5 g; polystyrene ( $M_n = 2.6 \times 10^4$ , 26 wt % of toluene solution) 2.6 g.

## CONCLUSION

Novel end-functional polystyrene, having isopropoxydimethylsilyl groups at the chain end, was successfully prepared by the reaction between the living polystyryl anion and 4-isopropoxydimethylsilyl- $\alpha$ -methylstyrene (**1**). The isopropoxydimethylsilyl group was hydrolyzed with a strong acid such as mono-*n*-butylphosphate (MBP) but not with acetic acid and bases. End-isopropoxydimethylsilylated polystyrene was grafted onto silica by  $0.19 \pm 0.01$  g per g of silica in the presence of MBP. However, it cannot be grafted onto alumina because the catalyst, MBP, is predominantly adsorbed onto alumina which has a basic surface.

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