During the *second stage* additional unsymmetrical disiloxane is formed by reaction of $(Me_3Si)_2O$ with Et_3SiOH

$$Me_3SiOSiMe_3 + Et_3SiOH \rightarrow Et_3SiOSiMe_3 + Me_3SiOH \quad (4)$$

Again the Me_3SiOH that forms is removed rapidly by the reactions shown in eq 2 and 3. The net result of reactions 3 and 4 is to convert 1 mol of $(Me_3Si)_2O$ and 2 mol of Et_3SiOH to 2 mol of $Et_3SiOSiMe_3$ and 1 mol of HOH. This stage takes 2–3 h and accounts for the observed simultaneous disappearance of $(Me_3Si)_2O$ and Et_3SiOH.

The much slower *third stage* begins after most of the Et_3SiOH is gone and is the redistribution (linearization) reaction of the symmetrical disiloxanes that gives the unsymmetrical disiloxane as the product

$$(Me_3Si)_2O + (Et_3Si)_2O \rightarrow 2Et_3SiOSiMe_3 \quad (5)$$

Catalysts are not necessary for the first stage reaction but they may speed up the second and third stage reactions.

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Chemistry of Silane Coupling Reactions. 2. Reaction of Dimethylmethoxysilanated Poly(butadiene) with Triethylsilanol and with Glass

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ABSTRACT: Poly(butadiene) having a dimethylmethoxysilane end group has been found to react with a model silanol, triethylsilanol, in the same way as a simple silane does, yielding the addition product, methanol, and dimers of the two starting materials. This reaction takes place readily at room temperature in benzene solution. A corresponding addition reaction between silanated poly(butadiene) and the OH groups present on the surface of glass has therefore been inferred. This is corroborated by a greater degree of retention of silanated poly(butadiene) compared to unsilanated poly(butadiene) on glass slides subjected to thorough washing, and by direct observation of polymer particles, about 0.3 μm in size, adhering to the glass treated with silanated poly(butadiene).

In studying the effect of chemical bonding on the adhesion of elastomers to various substrates, it is important to separate the effects of two reactions: chemical bonding to the substrate, and cross-linking the elastomer to form a coherent solid. The first reaction can in principle be achieved by silane coupling[1-5] and the second by free-radical processes, so that it seems possible, at least in principle, to carry them out independently. In order to study the first reaction, a poly(butadiene) sample with a silane end group has been prepared. The reactions of this material with triethylsilanol, a model substance containing OH groups comparable to those on glass, and with glass itself, are reported here. To avoid cross-linking the poly(butadiene) these reactions have been carried out under mild conditions, at room temperature and in the presence of a stabilizer.

Experimental Section

(a) Materials. Sample I of silanated poly(butadiene) was prepared by anionic polymerization of butadiene in benzene using *sec*-butyllithium as initiator[6] and then terminating the reactive chain end by adding an excess of dimethyldichlorosilane. The resulting dimethylchlorosilanated poly(butadiene) was then converted to the corresponding methoxysilane $(PB)Me_2SiOMe$ by adding excess methanol. The polymer was isolated by precipitation in methanol. The product was purified by dissolving in benzene and reprecipitating again with methanol. Gel permeation chromatography (GPC) tracings indicated a bimodal molecular weight distribution with approximately half the product having a number-average molecular weight $\overline{M}_n$ of 1.5×10^5 and the other half having $\overline{M}_n = 3.0 \times 10^5$, Figure 1. We surmise that about half the poly(butadiene) had combined by end linking to form the disiloxane $(PB)Me_2SiOSiMe_2(PB)$. On this basis the silicon content of the polymer is computed to be $\sim 6.7 \times 10^{-6}$ mol of silicon per g of polymer.

Sample II of silanated poly(butadiene) was similarly prepared except that the reactive chain end was terminated by adding dimethylmethoxychlorosilane, which gave $(PB)Me_2SiOMe$ without further addition of methanol. This polymer had a unimodal molecular weight distribution with $\overline{M}_n \simeq 1.8 \times 10^5$.

A sample of poly(butadiene) of similar microstructure, but with unreactive end groups (Diene 35NFA), was obtained from the Firestone Tire and Rubber Co. It was dissolved in benzene and

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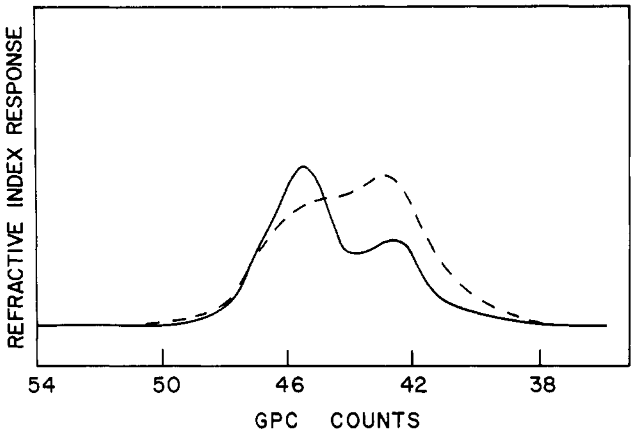

Figure 1. GPC tracing of (PB)Me_2SiOMe before and after reaction with Et_3SiOH: —, - - -, after.

Table I
Quantities Used for Gas Chromatography Studies

expt no.	Et_3-SiOH,[a] μL	Et_4Si, μL	(PB)Me_2-SiOMe,[b] g	octane, μL	benzene, mL	PBNA, g
1	96		0.05	35	1.2	0.1
2		113	0.05	35	1.2	0.1

[a] 96 μL $Et_3SiOH = 6.0 \times 10^{-4}$ mol assuming pure Et_3-SiOH. See the preceding paper[7] for a discussion of the purity of this compound. [b] 0.05 g is equivalent to 6.7×10^{-7} mol of silicon. Even this low concentration gave a very viscous solution that was difficult to sample with a 100-μL syringe.

precipitated into methanol twice before use.

Monomers and solvents were the same as described in the preceding paper.[7]

(b) Reactions with Et_3SiOH and Et_4Si. Reactions for examination by gas-liquid chromatography (GLC) were carried out in 2-dram vials with polyethylene snap caps. Two solutions, A and B, were prepared first. Solution A consisted of (PB)-Me_2SiOMe dissolved in 83% of the total amount of benzene. Solution B contained benzene, octane, stabilizer PBNA, and Et_3SiOH or Et_4Si. At the beginning of the GLC experiment, solution B was added to solution A. The amounts of reactants used in each experiment are given in Table I.

For the GPC study sample I of (PB)Me_2SiOMe (0.49 g) was dissolved in benzene (50 mL) before acetic acid (0.1 mL) and Et_3SiOH (0.1 mL) were added. After standing for 68 h, the polymer was precipitated into methanol and dried in a vacuum oven.

(c) Reactions with glass. A solution of poly(butadiene) (2.5 g) and stabilizer Neozon A (0.05 g) in dry benzene (300 mL) was prepared by shaking overnight. Fisherbrand precleaned Microscope Slides (Cat. No. 12-550A) were used as substrates for reaction with the silanated polymer. They were washed successively with boiling 2% Micro Solution, freshly redistilled water, boiling 1% H_3PO_4, and freshly redistilled water before drying at 150 °C for 1.5 h and storing in a desiccator over P_2O_5. Similar results were obtained, however, with slides which were used without further cleaning. All glassware, dishes, and racks were washed before use with hot 2% Micro Solution (International Products Corp.), water, distilled water, and acetone and then dried at 150 °C for 1.5 h.

Six slides in a stainless steel rack were weighed and immersed in the poly(butadiene) solution for 2.25 h with stirring every 15 min. The slides and rack were then transferred into three successive baths of fresh dry benzene (300 mL each) at 2-h intervals. Each bath was stirred every 15 min. The purpose of this benzene washing was to remove unreacted poly(butadiene) from the glass slides. Each solution was later evaporated to dryness and all dishes, slides, and racks were dried to constant weight in vacuo at room temperature. The slides were then examined by optical and scanning electronmicroscopy.

In some experiments with sample II of silanated poly(butadiene) the unreacted poly(butadiene) from the immersion solution was isolated by precipitation into methanol and then examined by GPC.

(d) Chromatography. All gas-liquid chromatography was carried out using the Hewlett Packard 5750 chromatogram described in the preceding paper.[7]

Gel permeation chromatograms of dilute polymer solutions in tetrahydrofuran at 37 °C were obtained on a Waters Associates Ana-Prep chromatogram. Details of the GPC analysis have been described elsewhere.[8]

(e) Microscopy. Glass slides were examined at ×45 to ×100 using a Leitz Orthoplan Microscope fitted with a Polaroid Land Camera. In experiments with water droplets, drops of 0.05 to 0.1 μL were placed on the slide using a microliter syringe. Slides were also examined with a JSM-U3 scanning electron microscope, after staining with osmium tetroxide and/or coating with gold.

Results and Discussion

(a) Reactions with Model Compounds. Silanated poly(butadiene) was mixed with either Et_3SiOH or Et_4Si (experiments 1 and 2 in Table I). In the former case methanol was formed in a few seconds indicating a rapid reaction between the end groups of the silanated poly(butadiene) and the OH groups of triethylsilanol. This reaction is presumably the same as that found before between a small-molecule silane and triethylsilanol.[7] It resulted then in rapid formation of the addition product and also in a significant degree of dimerization of the silane. Although in the present case the adduct was not detected directly (it can be inferred, however, from the rapid evolution of methanol), clear indications of an enhanced "dimerization" of the poly(butadiene) were obtained from GPC results, Figure 1. A greater portion of the poly(butadiene) was found to have doubled in molecular weight as a result of the silanol reaction. As before, $Et_3SiOSiEt_3$ was identified by gas-liquid chromatography among the reaction products. Thus, the polysiloxane appears to react with silanols in exactly the same way as the simple siloxane studied previously, with rapid formation of an adduct and some dimerization of the reagents.

Control experiments with Et_4Si gave no indication of reaction. Also, addition of Et_3SiOH to the unfunctionalized poly(butadiene) led to no formation of methanol or increase in molecular weight.

(b) Reaction with Glass. The amount of silanol groups present on the surface of glass is too small to permit direct observation of methanol as before. Evidence for the formation of a reaction product between the silanated poly(butadiene) and glass was therefore sought by examining the degree of retention of the polymer on the glass surface after applying it in dilute solution, in comparison with the unfunctionalized poly(butadiene), by GPC study of the poly(butadiene) isolated, and by microscopic examination of the slides.

In both cases most of the polymer adhering to the glass slides could be removed by repeated washing with benzene. Of the total amount washed off (~0.04 and ~0.02 g for the silanated and unsilanated poly(butadiene), respectively) 81, 12, and 7% of the silanated poly(butadiene) was removed in three successive washings, compared to 98, 2, and 0% of the unsilanated material. The total amounts of poly(butadiene) recovered from the washings and original solutions were 93 and 99.2% of the original weights used for the silanated and unsilanated poly(butadiene), respectively. Thus, the silanated materials adhered more strongly and resisted removal to a greater degree than the unfunctionalized polymer, which was almost completely removed in the first washing.[9]

Number average molecular weights $\overline{M}_n$ of silanated

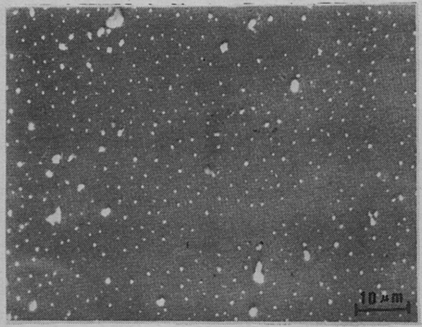

Figure 2. Electronmicrograph of glass slide treated with (PB)Me_2SiOMe (×1400).

poly(butadiene) (II) isolated by precipitation after treating slides were determined by GPC. The $\overline{M}_n$ of the polymer was found to be increased from about 1.8×10^5 to 2.5×10^5 and 3.0×10^5 in two typical experiments whereas the number average molecular weight of the unsilanated poly(butadiene) did not change significantly. An increase in $\overline{M}_n$ and a shift toward doubled $\overline{M}_n$ would be expected if the silanated poly(butadiene) dimerized under reaction conditions in the same way that trimethylmethoxysilane did.[7]

Examination of the slides by optical microscopy (×45) did not reveal any adhering polymer. Significantly different wetting behavior by water was found, however. Drops of water spread uniformly on clean slides, formed regular circular droplets on the slides treated with unsilanated poly(butadiene), and formed irregularly shaped drops on the slides treated with silanated poly(butadienes). Because of the irregular shape of the drops no attempt was made to measure contact angles.

Examination by SEM gave no evidence of adhering polymer on slides treated with the unfunctionalized polybutadiene. On the other hand slides treated with silanated polybutadiene were found to have widely separated discrete particles, about 300 nm in diameter, adhering to them, as shown in Figure 2. The dimensions of these particles are rather larger than those expected for isolated polybutadiene molecules of 150 000–300 000 molecular weight (with a root-mean-square molecular end-to-end distance $(\overline{R^2})^{1/2}$ of about 40–60 nm) and therefore they probably represent aggregates of several polymer molecules. It seems probable that polybutadiene is quite incompatible with glass and does not spread over the surface even when it is chemically bonded by end linking.

Conclusions

Silanated poly(butadiene) having a number-average molecular weight of 150 000 appears to react with triethylsilanol in exactly the same way as the simple silane Me_3SiOMe. The overall reaction can be written:

$$\mathrm{(PB)Me_2SiOMe + Et_3SiOH \rightarrow (PB)Me_2SiOSiMe_2(PB) + Et_3SiOSiEt_3 + MeOH + (PB)Me_2SiOSiEt_3}$$

Three of these reaction products have been identified directly, and the fourth, the addition product, can therefore be inferred with some confidence.

Similar reactions of silanated poly(butadiene) with OH groups on the surface of glass slides have been inferred from the greater retention of the silanated poly(butadiene) compared to unsilanated poly(butadiene) against washing and the direct observation of microscopic particles, presumably of poly(butadiene), adhering to the glass at widely separated points. These results suggest that poly(butadiene) with a silane end group can be used as a coupling agent to form primary chemical bonds between poly(butadiene) and glass surfaces. An experimental investigation of this system will be reported elsewhere.

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(9) In these initial experiments we were overly concerned about the stability of any polysiloxane bonds that formed and chose the mild washing procedure described above. In later work to be published in connection with adhesion studies, we have washed the slides more vigorously with hot benzene for 24 h in a Soxhlet extractor without destroying the bonds formed with silanated poly(butadiene).

A Procedure for Preparing Aryl Esters of Polyacids. The Conversion of Poly(methacrylic acid) to Poly(phenyl methacrylate)

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ABSTRACT: Poly(methacrylic acid) reacts with excess phenol and phosphoryl chloride to form a copolymer of phenyl methacrylate and methacrylic anhydride. Reaction of this copolymer with sodium phenoxide in phenol yields a phenyl methacrylate–methacrylic acid copolymer that can be converted into essentially pure poly(phenyl methacrylate) by subsequent reaction with phenol and phosphoryl chloride. This process retains the stereochemical integrity of the polymer backbone and can be used to prepare stereoregular poly(aryl methacrylates) from the corresponding poly(methacrylic acids).

One of the most useful polymer analogous reactions known is the alkylation of acidic groups on polymers with diazoalkanes.[1] This reaction has been used extensively in studies on polymer microstructure and reactivity.[2–5] Other

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