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Adsorption of Styrene–Butadiene Copolymers on Silica Surface

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ABSTRACT: Adsorption of a series of random copolymers of styrene and butadiene (SB) covering the entire range of chemical composition onto a nonporous silica (Aerosil 130) from their cyclohexane solutions at 35 °C was studied by IR spectroscopy and UV spectroscopy. The fractions of the silanol groups occupied by styrene (θ_S) and by butadiene units (θ_B) and the fractions of styrene (p_S) and butadiene units (p_B) which are directly attached to surface silanol groups could be determined separately from the IR frequency shifts of the silanol groups. Adsorbance was determined by UV spectroscopy. The plateau values of adsorbance, p_S, p_B, θ_S, and θ_B depended on the chemical composition within the SB copolymers. For the same chemical composition these values were constant and independent of molecular weight. Total surface excess, total fraction of silanol groups occupied, and total fraction of directly attached SB copolymer units were estimated. In particular, the chemical composition dependence of total absorbance and total fraction of the adsorbed SB copolymer units was compared with that for adsorption of methyl methacrylate–styrene copolymer. One feature for adsorption of SB copolymer from cyclohexane solution onto silica surface was that the measured quantities depend on the chemical composition.

Several studies on adsorption of copolymers were reported by Howard and co-workers.[1-5] They used in particular styrene–methyl methacrylate copolymers[2-4] and measured not only adsorbance but also the fraction of segments adsorbed on a silica surface as a function of styrene content. The adsorbances of the copolymers were constant and maintained the level of adsorbance exhibited by methyl methacrylate homopolymer over a wide range of composition, and within this range the total fraction of adsorbed segments also stayed constant. They concluded that these experimental results are due to the overwhelming strength of the carbonyl–silanol interaction. Likewise, adsorption experiments with several ethylene–vinyl acetate copolymers on glass spheres demonstrated that the adsorbances are constant and independent of vinyl acetate content since a vinyl acetate comonomer is markedly stronger in the adsorption interaction with the surface than an ethylene comonomer.[6]

However, for copolymers of ethylene oxide and propylene oxide adsorbed onto charcoal[1] the plateau adsorbance increased with increasing ethylene oxide content when the solvent was benzene and with decreasing ethylene oxide when the solvent was water. This chemical composition dependence of adsorbance stemmed from the fact that benzene is a better solvent for propylene oxide than ethylene oxide and water is a better solvent for ethylene oxide than propylene oxide. The stronger interaction between an ethylene oxide unit and the surface than that of a propylene oxide unit was considered as a minor effect.

Adsorption data of polystyrene[7] and of polybutadiene[8] onto the silica surface from their cyclohexane solutions at 35 °C using IR spectroscopy have been reported previously. We showed that the phenyl groups of polystyrene interact with the silanol groups as do also the double bonds of polybutadiene. Hence, we could determine the fractions of the silanol groups occupied by polystyrene and polybutadiene and also the fractions of directly attached styrene and butadiene units to the silica surface. Therefore, it is expected that the respective fractions of attached styrene and butadiene units and the respective fractions of the surface sites occupied by styrene units and by butadiene units can be determined separately by IR spectroscopy for adsorption of styrene–butadiene (SB) copolymer on the silica surface.

The SB copolymer is commonly called SBR and is quite important in industrial applications.[9] In relation to the development of rubber technology, several studies on adsorption of SB copolymers on carbon black or silica particles have been carried out.[10-16] However, comprehensive adsorption data on the copolymers as functions of chemical composition in the copolymer and of molecular weight have been lacking.

The aim of this paper is to offer experimental results for the adsorption of SB copolymers onto a well-characterized Aerosil 130 silica from cyclohexane solutions at 35 °C. Measurements of the copolymer adsorption were carried out with IR and UV spectrometers as functions of sytrene content and molecular weight. The measured values of adsorbance, surface excess, fraction of segments

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Table I
Characteristics of SB Copolymers

		composition, mol %			
			butadiene		
sample	$M_n \times 10^{-3}$	styrene	cis 1,4	trans 1,4	1,2
SB-10-1	184	12.5	19.2	45.4	22.9
SB-10-2	111	12.3	18.1	47.2	22.4
SB-30-1	321	29.6	14.2	41.6	14.6
SB-30-2	234	28.7	14.0	42.4	14.9
SB-30-3	103	27.0	11.3	48.7	13.0
SB-50-1	273	43.3	12.5	35.9	8.3
SB-50-2	196	44.0	11.8	36.0	8.2
SB-50-3	111	45.3	11.7	35.4	7.6
SB-70-1	214	68.4	7.1	20.9	3.6
SB-70-2	160	68.0	7.0	21.3	3.7

adsorbed, and fraction of surface sites occupied are compared with those of styrene and butadiene homopolymers. The characteristics of adsorption of SB copolymer are discussed together with adsorption data for other copolymers.

Experimental Section

Materials. Four series of SB copolymers with different sytrene contents of SB-10, SB-30, SB-50, and SB-70 prepared by emulsion polymerization at Japan Synthetic Rubber Co. (Yokkaich, Japan) were used. They were dissolved in benzene, filtered through a 3G-2 sintered glass filter, and precipitated by dropwise addition of benzene solutions to a large volume of vigorously stirred acetone to remove nonpolymeric impurities. The resulting precipitates were soaked in acetone and finally dried in a vacuum oven at room temperature. This procedure was repeated until the IR absorption band of C=O at 1730 cm^{-1} disappeared; this band originates from the surfactant used in emulsion polymerization of the SB copolymer. The purified SB copolymers were dissolved in benzene and fractionated into several fractions, using methanol as precipitant at 25 °C. Each fraction was freeze-dried from benzene solution. Their number-average molecular weights were determined by a 502 high-speed membrane osmometer (Hewlett-Packard) in toluene at 30 °C. The contents of styrene and butadiene, including cis-1,4, trans-1,4, and 1,2 units in the fractionated samples, were determined from the IR spectra of films cast from benzene solutions onto a glass plate. The IR instrument used was a Nippon Bunko Jasco IR-G spectrometer. The bands of particular interest were located at 967 (trans-1,4 of butadiene), 911 (1,2 unit of butadiene), 724 (cis-1,4 unit of butadiene), and 699 (styrene) cm^{-1}, respectively. Extinction coefficients for the four important bands determined by Hampton[17] were employed for the quantitative determination of styrene and butadiene contents in the SB copolymers.

For the present measurements, two fractions of the SB-10 and SB-70 series and three fractions of the SB-30 and SB-50 series were selected. Their characteristics are given in Table I.

Cyclohexane was distilled, passed through a silica gel column to remove aromatic impurities, refluxed over sodium metal, and distilled fractionally just before use.

The nonporous Aerosil 130 silica supplied by Degussa AG (West Germany) was used as the adsorbent after being cleaned by the procedure described in previous papers.[7,8] The concentration of surface silanol groups was determined by the method of Boehm and Schneider[18] to be three silanol groups per 100 Å^2. According to the manufacturer, the particle diameter is 160 Å with a surface area of 141 m^2/g.

Adsorption of SB Copolymer onto the Silica. Twenty milliliters of a SB copolymer solution in cyclohexane of known concentration was mixed with the silica (0.16 g) in a stoppered centrifuge tube, and the mixture was gently stirred by a magnetic chip for 20 h at 35 °C. The silica suspensions were centrifuged at 5000*g* for 10 min to sediment the silica, and the supernatant was carefully removed.

The equilibrium concentration of the SB copolymer, C_p, in the supernatant was determined at λ = 263 nm by a UV spectrometer (Union Giken System 77-1). The relevant concentration of the SB copolymer was determined from a calibration curve. Adsorbance (g/cm^2), A, was determined by the difference between the amount of the SB copolymer initially added and that in the supernatant and also from the amount of silica added.

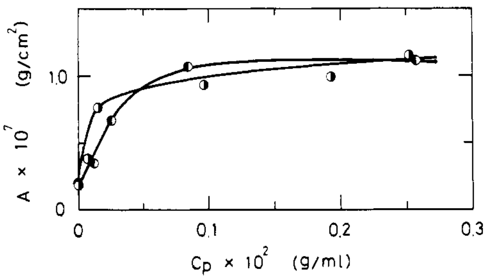

Figure 1. Adsorption isotherms of series SB-10: (◑) SB-10-1; (◐) SB-10-2.

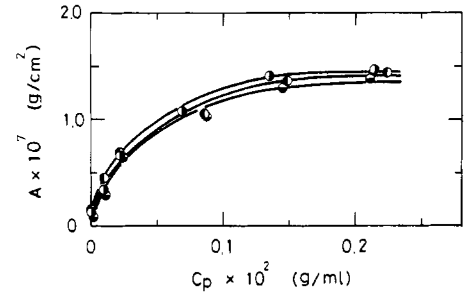

Figure 2. Adsorption isotherms of series SB-30: (◑) SB-30-1; (◐) SB-30-2; (◒) SB-30-3.

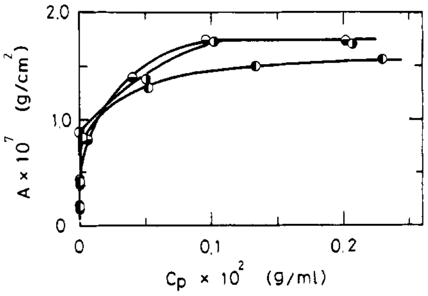

Figure 3. Adsorption isotherms of series SB-50: (◑) SB-50-1; (◐) SB-50-2; (◒) SB-50-3.

IR measurements on the sedimented silica were carried out according to a method similar to that described previously.[7,8]

Results and Discussion

Adsorbance. Adsorption isotherms of the SB-10, SB-30, SB-50, and SB-70 series are shown in Figures 1–4, respectively. The adsorption isotherms generally consist of an initial steep rise in adsorbance followed by a plateau region where adsorbance is almost constant. For the same

Table II
Adsorption Data of SB Copolymers on Aerosil 130 at the Highest Equilibrium Polymer Concentration

sample	$C_p \times 10^2$/ (g mL^{-1})	$A \times 10^7$/ (g cm^{-2})	$A_S \times 10^7$/ (g cm^{-2})	$A_B \times 10^7$/ (g cm^{-2})	θ_S	θ_B	p_S	p_B	Γ_S	Γ_B
SB-10-1	0.246	1.16	0.25_0	0.91_0	0.20_8	0.21_0	0.25_3	0.051_6	0.48_2	3.3_8
SB-10-2	0.266	1.11	0.23_6	0.87_4	0.20_2	0.20_0	0.23_3	0.051_4	0.46_0	3.2_4
SB-30-1	0.213	1.46	0.65_3	0.80_7	0.28_7	0.19_5	0.17_8	0.052_1	1.2_6	2.9_9
SB-30-2	0.224	1.42	0.61_9	0.80_1	0.29_3	0.19_1	0.17_3	0.056_3	1.1_9	2.9_7
SB-30-3	0.213	1.38	0.57_3	0.80_7	0.28_8	0.19_4	0.16_8	0.057_8	1.1_1	2.9_9
SB-50-1	0.206	1.72	1.02_3	0.69_7	0.37_8	0.15_0	0.15_4	0.058_9	1.9_7	2.5_9
SB-50-2	0.230	1.53	0.92_1	0.60_9	0.38_3	0.14_2	0.15_3	0.060_2	1.7_8	2.2_6
SB-50-3	0.201	1.75	1.07_5	0.67_5	0.38_0	0.14_4	0.15_4	0.057_1	2.0_8	2.5_1
SB-70-1	0.184	1.92	1.55_8	0.36_2	0.47_7	0.10_1	0.14_4	0.072_9	3.0_1	1.3_4
SB-70-2	0.184	1.91	1.53_4	0.37_6	0.48_3	0.12_3	0.14_7	0.079_3	2.9_6	1.3_9

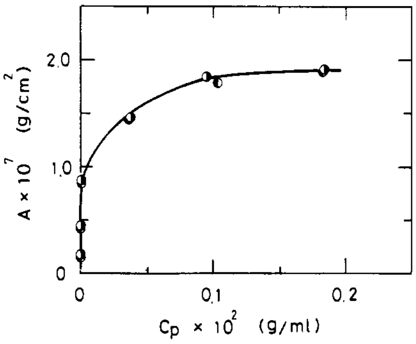

Figure 4. Adsorption isotherms of series SB-70: (◑) SB-70-1; (◐) SB-70-2.

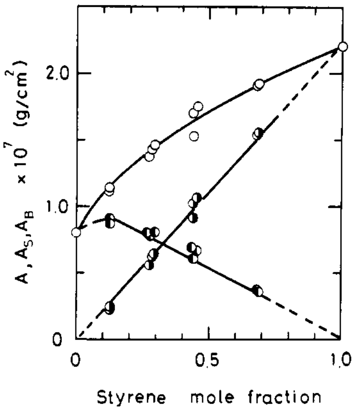

Figure 5. Plots of A, A_S, and A_B vs. styrene mole fraction: (○) A; (◑) A_S; (◐) A_B.

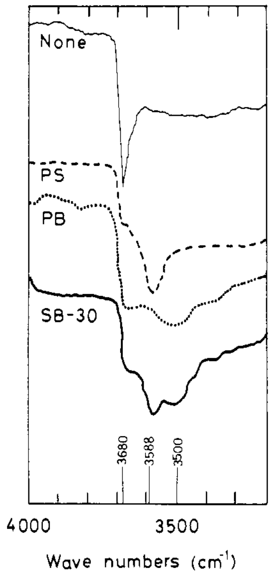

Figure 6. IR spectra of Aerosil 130 in cyclohexane: (—) none; (**—**) in the presence of SB-30-1; (---) in the presence of polystyrene (PS) with M_w = 498 × 10^3; (···) in the presence of polybutadiene (PB) with M_w = 173 × 10^3.

series the adsorbances in the plateau region were almost constant and independent of molecular weight. The measured values of adsorbance A at the highest equilibrium concentration are summarized in Table II for all the samples used. Increasing styrene content appears to increase the plateau adsorbance. The amount of styrene units A_S adsorbed on the silica and that of butadiene units A_B adsorbed can be calculated by the product of A and the weight fractions of styrene and butadiene, respectively. The values of A_S and A_B calculated by this procedure are listed in Table II.

The plateau adsorbances of the SB copolymers are plotted against styrene mole fraction in Figure 5. For comparison, the plateau data for polybutadiene with molecular weight 314 × 10^3 and for polystyrene with the molecular weight 498 × 10^3 are also displayed in Figure 5. These data are quoted from our previous papers.[7,8] Total adsorbances A for the SB copolymers depend on chemical composition, increase with increasing styrene mole fraction, and do not exceed the adsorbance of the styrene homopolymer but exceed the adsorbance of the butadiene homopolymer. These results may derive from two effects. First, the interaction between a styrene unit and the silica surface is considered to be stronger than that of a butadiene unit by taking into account preferential polystyrene adsorption in perchloroethylene solutions of polystyrene–polybutadiene mixtures.[16] Second, with a decrease of styrene content the solubility of SB copolymer in cyclohexane will increase and the adsorbance will decrease since the solvent is a Θ solvent for polystyrene and a good solvent for polybutadiene.[8] If the first factor were dominant, the adsorbance would perhaps become independent of copolymer composition as in the case of adsorption of styrene–methyl methacrylate copolymer[2] and that of ethylene–vinyl acetate copolymer.[6] As a result, the observed data are mainly governed by the second factor.

In the figure, plateau adsorbances of styrene units A_S and butadiene units A_B are plotted against styrene mole fraction. The A_S values increase linearly with styrene mole fraction and a linear extrapolation of A_S to 100% styrene mole fraction agrees well with the adsorbance of the styrene homopolymer. Above 10% styrene mole fraction A_B decreases linearly with an increase in styrene mole fraction, and the values of A_B for the series of SB-10 are almost equal to the adsorbance of the butadiene homopolymer.

Fraction of Surface Sites Occupied, *θ*. The differential infrared spectrum between the supernatant SB-30-1 and the silica on which SB-30-1 was adsorbed shows three characteristic bands in Figure 6: a band located at 3680 cm^{-1} due to the isolated silanol groups, a band at 3588 cm^{-1}

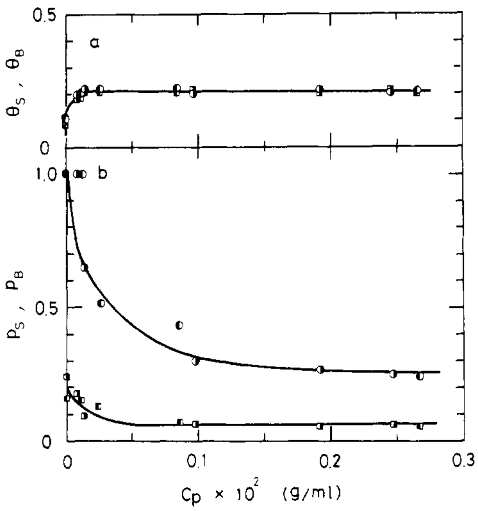

Figure 7. (a) Plots of θ_S and θ_B vs. equilibrium polymer concentration for series SB-10: (◑) θ_S for SB-10-1; (◐) θ_S for SB-10-2; (◨) θ_B for SB-10-1; (◧) θ_B for SB-10-2. (b) Plots of p_S and p_B vs. equilibrium polymer concentration for the same series: (◑) p_S for SB-10-1; (◐) p_S for SB-10-2; (◨) p_B for SB-10-1; (◧) p_B for SB-10-2.

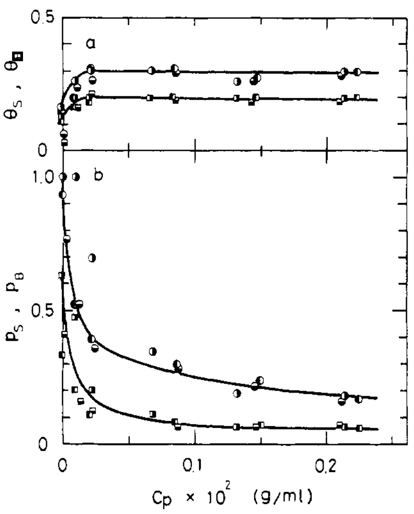

Figure 8. (a) Plots of θ_S and θ_B vs. equilibrium polymer concentration for series SB-30: (◑) θ_S for SB-30-1; (◐) θ_S for SB-30-2; (◒) θ_S for SB-30-3; (◨) θ_B for SB-30-1; (◧) θ_B for SB-30-2; (⬒) θ_B for SB-30-3. (b) Plots of p_S and p_B vs. equilibrium polymer concentration for the same series: (◑) p_S for SB-30-1; (◐) p_S for SB-30-2; (◒) p_S for SB-30-3; (◨) p_B for SB-30-1; (◧) p_B for SB-30-2; (⬒) p_B for SB-30-3.

due to the interaction between the silanol groups and the phenyl groups of styrene units[7] in the adsorbed SB copolymer, and a band at 3500 cm^{-1} due to the interaction between the silanol groups and the double bonds of butadiene units[8] in the adsorbed copolymer. For comparison, the differential spectra of Aerosil 130 in cyclohexane in the presence of styrene and butadiene homopolymers are also illustrated in Figure 6. It is clear that the observed frequency shifts of silanol groups attached by phenyl groups and double bonds in the present experiment are consistent with those in the previous experiments.[7,8]

Thus we can determine the number of the free silanol groups (S_{3680}), that of the silanol groups occupied by phenyl groups (S_{3588}), and that of the silanol groups occupied by double bonds (S_{3500}) since the extinction coefficients ϵ of the respective bands were determined previously:[7,8] $\epsilon_{3680} = 55.6$, $\epsilon_{3588} = 115.1$, and $\epsilon_{3500} = 134.0$ L mol^{-1} cm^{-1}. The fraction of surface sites occupied by styrene units θ_S and that by butadiene units θ_B can be obtained from the equations

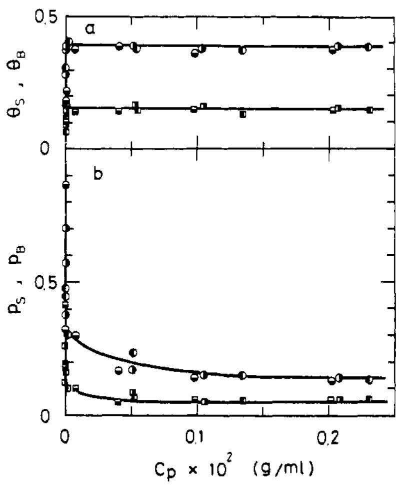

Figure 9. (a) Plots of θ_S and θ_B vs. equilibrium polymer concentration for series SB-50; (◑) θ_S for SB-50-1; (◐) θ_S for SB-50-2; (◒) θ_S for SB-50-3; (◨) θ_B for SB-50-1; (◧) θ_B for SB-50-2; (⬒) θ_B for SB-50-3. (b) Plots of p_S and p_B vs. equilibrium polymer concentration for the same series: (◑) p_S for SB-50-1; (◐) p_S for SB-50-2; (◒) p_S for SB-50-3; (◨) p_B for SB-50-1; (◧) p_B for SB-50-2; (⬒) p_B for SB-50-3.

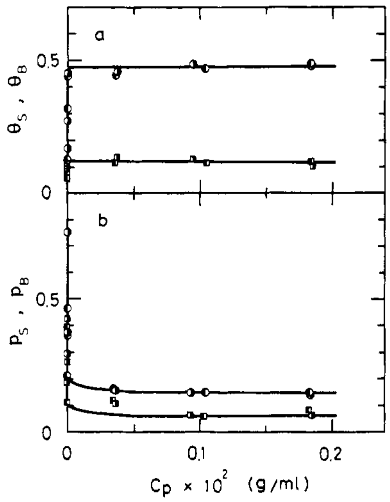

Figure 10. (a) Plots of θ_S and θ_B vs. equilibrium polymer concentration for series SB-70: (◑) θ_S for SB-70-1; (◐) θ_S for SB-70-2; (◨) θ_B for SB-70-1; (◧) θ_B for SB-70-2. (b) Plots of p_S and p_B vs. equilibrium polymer concentration for the same series: (◑) p_S for SB-70-1; (◐) p_S for SB-70-2; (◨) p_B for SB-70-1; (◧) p_B for SB-70-2.

$$\theta_S = S_{3588}/(S_{3680} + S_{3588} + S_{3500}) \qquad (1)$$

and

$$\theta_B = S_{3500}/(S_{3680} + S_{3588} + S_{3500}) \qquad (2)$$

The values of θ_S and θ_B calculated from eq 1 and 2 are plotted against the equilibrium SB copolymer concentration in Figures 7a, 8a, 9a, and 10a for series SB-10, SB-30, SB-50, and SB-70, respectively. In all cases, both θ_S and θ_B steeply increase at lower equilibrium polymer concentration and then become constant around $C_p = 0.02$ g/100 mL. For the same series of SB copolymers, the values of θ_S and θ_B fall nearly on the same master curve independent of the molecular weight.

For series SB-10 the values of θ_S are almost equal to those of θ_B. In the other series, the values of θ_S are larger than those of θ_B and the difference in the magnitude be-

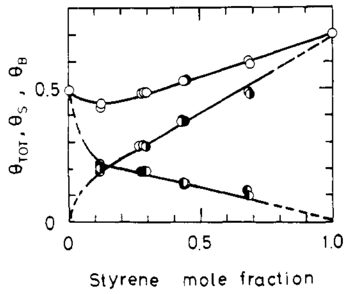

Figure 11. Plots of θ_{tot}, θ_S, and θ_B vs. styrene mole fraction: (○) θ_{tot}; (◑) θ_S; (◐) θ_B.

tween θ_S and θ_B increases with increasing styrene content. The θ_S and θ_B at the highest equilibrium concentration are listed in Table II.

In Figure 11, the plateau values of θ_S and θ_B are plotted against styrene mole fraction, and, for comparison, the plateau values of θ for the styrene[7] and butadiene[8] homopolymers are also illustrated. The θ_S linearly increases whereas the θ_B linearly decreases with increasing styrene mole fraction. The values of θ_S and θ_B are smaller than those of θ for styrene and butadiene homopolymers, respectively. Above 30% styrene mole fraction the values of θ_S are larger than those of θ_B.

The total fraction of the surface sites occupied by the copolymers, θ_{tot}, is defined by the sum of θ_S and θ_B. The values of θ_{tot} displayed in Figure 11 increase with increasing sytrene mole fraction and do not exceed the value of θ for the styrene homopolymer.

Fraction of the Segments Adsorbed, *p*. The fraction of styrene units directly attached to the silica p_S and that of attached butadiene units p_B can be calculated from the equation derived by Fontana and Thomas[19]

$$p_S = \frac{\text{wt of attached styrene units}}{\text{wt of total adsorbed styrene units}} \tag{3}$$

$$p_B = \frac{\text{wt of attached butadiene units}}{\text{wt of total adsorbed butadiene units}} \tag{4}$$

The numerators in eq 3 and 4 are obtained from the product of the number of silanol groups occupied by the phenyl groups (S_{3588}) and the molecular weight of a styrene unit and that of the number of silanol groups occupied by the double bonds (S_{3500}) and the molecular weight of a butadiene unit, respectively. The denominators in eq 3 and 4 correspond to the values of A_S and A_B, respectively.

The values of p_S and p_B calculated from eq 3 and 4 for series SB-10, SB-30, SB-50, and SB-70 are plotted against the equilibrium polymer concentration in Figures 7b, 8b, 9b, and 10b, respectively. In all cases, at lower equilibrium concentrations both p_S and p_B have large values near 1, indicating a flattened adsorbed conformation; they then decrease and become constant above $C_p = 0.1$ g/100 mL, showing formation of loops and tails. For the same series of the SB copolymers both p_S and p_B fall nearly on the same master curve and are independent of molecular weight. The measured values of p_S and p_B at the highest equilibrium concentration are listed in Table II.

In Figure 12, the plateau values of p_S and p_B are plotted against the sytrene mole fraction, and, for comparison, the plateau values of p for polystyrene[7] and polybutadiene[8] are also displayed. It can be seen that the values of p_S are always larger than those of p_B, though the difference in the magnitude between p_S and p_B decreases as the styrene content increases. The values of p_S decrease with increasing styrene mole fraction and are somewhat smaller than the value of p for the styrene homopolymer except for series SB-10. The values of p_B increase with increasing styrene mole fraction, i.e., p_B decreases with increasing butadiene content and is much smaller than p for the butadiene homopolymer.

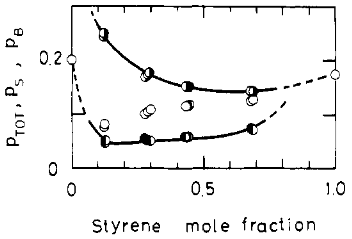

Figure 12. Plots of p_{tot}, p_S, and p_B vs. styrene mole fraction: (○) p_{tot}; (◑) p_S; (◐) p_B.

Table III
Total Fraction of Surface Site Occupied, Total Fraction of Adsorbed SB Copolymers, and Total Surface Excess

sample	θ_{tot}	p_{tot}	Γ_{SB}	$\theta_{\text{tot}}/p_{\text{tot}}$
SB-10-1	0.41_8	0.094_5	3.8_6	4.4_2
SB-10-2	0.40_2	0.089_9	3.7_0	4.4_7
SB-30-1	0.48_2	0.10_8	4.2_5	4.4_6
SB-30-2	0.48_4	0.10_7	4.1_6	4.5_2
SB-30-3	0.48_2	0.10_3	4.1_0	4.6_8
SB-50-1	0.52_8	0.11_5	4.5_6	4.5_9
SB-50-2	0.52_5	0.11_6	4.0_4	4.5_2
SB-50-3	0.52_4	0.11_7	4.5_9	4.4_8
SB-70-1	0.57_7	0.13_0	4.3_5	4.4_4
SB-70-2	0.60_6	0.13_3	4.3_6	4.5_6
PS[a]	0.70_7	0.18_2	4.0_5	4.0_9
PBR[b]	0.51_5	0.19_2	2.7_6	2.6_1

[a] Data from ref 7. [b] Data from ref 8.

Herd et al.[2] reported that the adsorbed fraction of methyl methacrylate units interacting with the silanol groups decreases with increasing methyl methacrylate content in styrene–methyl methacrylate copolymers and is much larger than the adsorbed fraction for methyl methacrylate homopolymer. However, the fraction of adsorbed styrene units in the copolymer is almost zero until the styrene content becomes high. These results are in contrast to our data.

The observation that p_S is larger than p_B at all styrene mole fractions indicates that styrene units are more strongly adsorbed than butadiene units. Adsorption enthalpy, which is a measure of the strength of adsorption of monomer units on surface sites, has been related to the infrared frequency shift[20–22] of silanol groups. The observed frequency shifts of silanol groups show that the adsorption enthalpy of a butadiene unit should be larger than that of a styrene unit. However, the experimental values of p_S and p_B do not coincide with the magnitude of the adsorption enthalpies. It may be concluded that the adsorption enthalpy itself cannot be directly related to the fraction of adsorbed segments p. The steric effect related to the manner in which the segments can be sterically accommodated on the surface sites is also very important. As shown in Table I, butadiene units in the present SB copolymers have complicated structures consisting of cis-1,4, trans-1,4, and 1,2-units. This structural complexity perhaps causes a steric hindrance to the occupation of surface sites, resulting in p_B being smaller than p_S.

The total fraction p_{tot} of adsorbed SB copolymer segments can be calculated with values of p_S and p_B as follows:

$$p_{\text{tot}} = w_S p_S + (1 - w_S) p_B \tag{5}$$

where w_S is the weight fraction of styrene units in the copolymers. The plateau values of p_{tot} calculated from eq 5 are plotted as a function of styrene mole fraction in Figure 12 and are listed in Table III. The values of p_{tot} increase with increasing styrene mole fraction and do not exceed the values of p for both homopolymers. p_{tot} depends on the chemical composition of the SB copolymers and this dependence is quite different from that of the adsorption of styrene–methyl methacrylate copolymers from trichloroethylene, where the total fraction of adsorbed segments of copolymers is constant and independent of styrene content.[2]

Surface Excess Γ. The surface excess Γ, the total number of segments adsorbed per lattice site is defined as

$$\Gamma = AN_{\mathrm{A}}/n_{\mathrm{OH}}M_{\mathrm{u}} \tag{6}$$

where A is the adsorbance expressed in weight per unit area, N_{A} is Avogadro's number, n_{OH} is the number of sites per unit area, corresponding to the number of the silanol groups in the present experiment and being 3×10^{14}, and M_{u} is the molecular weight of the monomer unit.

In analogy to eq 6, the surface excesses Γ_{S} and Γ_{B} of styrene and butadiene units for the SB copolymers are expressed by

$$\Gamma_{\mathrm{S}} = A_{\mathrm{S}}N_{\mathrm{A}}/n_{\mathrm{OH}}M_{\mathrm{u,S}} \tag{7}$$

$$\Gamma_{\mathrm{B}} = A_{\mathrm{B}}N_{\mathrm{A}}/n_{\mathrm{OH}}M_{\mathrm{u,B}} \tag{8}$$

where the values of A_{S} and A_{B} are adsorbances of styrene and butadiene units and the values of $M_{\mathrm{u,S}}$ and $M_{\mathrm{u,B}}$ are the molecular weights of styrene and butadiene monomers, respectively. In Table II are shown the plateau values of Γ_{S} and Γ_{B} calculated from eq 7 and 8 using the adsorbances A_{S} and A_{B} at the highest equilibrium concentration. For the same series, Γ_{S} is almost constant and independent of molecular weight but *increases* with increasing styrene content. Also for the same series, Γ_{B} is constant and independent of molecular weight but *decreases* with increasing styrene content.

Total surface excesses Γ_{SB} for SB copolymers may be given as the sum of Γ_{S} and Γ_{B}. The values of Γ_{SB} are listed in Table III. For the same series, although the values of Γ_{SB} in the plateau region are somewhat scattered, they are nearly constant within experimental error and independent of molecular weight.

The surface excess Γ value is also defined as

$$\Gamma = \theta/p \tag{9}$$

The total surface excesses Γ_{SB} are compared with $\theta_{\mathrm{tot}}/p_{\mathrm{tot}}$ in Table III. We find that the values of total surface excess determined by the two methods are consistent. Therefore, it is important to observe that good agreement between eq 6 and 9 is obtained for adsorption of the SB copolymer.

Conclusion

The IR frequency shifts of the silanol groups caused both by interactions between the phenyl groups in styrene units and the silanol groups and by interaction, between the double bonds in butadiene units and the silanol groups were observed separately. The fraction of adsorbed units (p) and the fraction of occupied surface sites (θ) could be determined as functions of chemical composition and molecular weight. The values of θ and p and adsorbance A depend on chemical composition within the SB copolymers.

Acknowledgment. We are indebted to Dr. T. Honma and Mr. N. Tagata of Japan Synthetic Rubber Co. for supplying the styrene–butadiene copolymer samples.

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