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polymerizations will be published in the near future.

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Adsorption of Polystyrene onto a Metal Surface in Good Solvent Conditions

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ABSTRACT: The adsorption of linear polystyrene from carbon tetrachloride and toluene solutions onto a chrome plate at 35 °C was studied by ellipsometry. The adsorbance is lower than that in the Θ solvent (cyclohexane, 35 °C) and the thickness of the adsorbed layer is larger than that in the Θ solvent. In particular, the dependence of molecular weight on the measured quantities of both adsorbance and thickness of the adsorbed layer in the plateau region was studied. In both solvents, the adsorbance is almost independent of the molecular weight and the thickness is approximately proportional to the square root of the molecular weight. As a result, the average polymer concentration in the adsorbed polymer layer varies in inverse proportion to the square root of the molecular weight. The results are compared with the theories of Silberberg and Scheutjens and Fleer. The molecular weight dependence of the adsorbance is in agreement with both theories but the molecular weight dependence of the thickness of the adsorbed layer is interpreted supposing that the dangling tails in adsorbed chains predominantly determine the thickness of the adsorbed layer as predicted by Scheutjens and Fleer. It is concluded that the thickness of the adsorbed polystyrene layer onto the chrome surface is governed by tails.

Adsorption of polymers on an interface plays an essential role in a diversity of practical problems in industry, technology, and biology, including adhesion, flocculation and stabilization of colloid particles, chromatography, reinforcement, and artificial organs in medicine. In these cases not only the adsorbance but also the conformation of adsorbed polymer on an interface is of considerable importance. Various efforts have been devoted to clarify the conformation of adsorbed polymer chains.[1-24] For the conformation of flexible polymer chain adsorbed on an interface, it is now widely accepted that some portions of the polymer chain come into direct contact with the interface as trains, with remaining portions extending into the bulk solution as loops and/or tails, which lead to a thick adsorbed layer.

In a previous paper,[22] adsorption of polystyrene onto a chrome plate from cyclohexane at the Θ temperature was studied by ellipsometry. It was shown that the conformation of polystyrene is the loop–train–tail, and predominant contribution of tails to the thickness of the adsorbed layer was indicated.

In good solvent conditions, one intuitively expects the thickness of the adsorbed layer to be greater than that in Θ solvents due to interactions between loops or tails caused by the excluded-volume effect. The adsorbance should be smaller than that in Θ solvents since the occupied area per polymer chain on the interface will increase with solvent power.

In another paper,[23] we studied the adsorption of polystyrene on a chrome plate from cyclohexane solution at 40 and 45 °C by ellipsometry and showed that the adsorbance slightly decreases and the thickness of the adsorbed layer slightly increases with increasing temperature. The adsorbance was nearly constant, independent of the molecular weight, and the thickness of the adsorbed layer was approximately proportional to the square root of the molecular weight at both temperatures.

Several theoretical studies of the effect of solvent power on polymer adsorption have been reported.[2,3,10,14,16-20] Although theories predicted that the adsorbance decreases with increasing solvent power, in some theoretical predictions[2,10] particularly based on the loop–train model, it was concluded that the thickness due to loops in good solvents is smaller than that in Θ solvents, since in good solvents more segments are forced to contact the surface.

To clarify the solvent power dependence of the adsorbed polymer layer, we use in this study toluene and carbon tetrachloride as solvents. Since they are better solvents than cyclohexane at 40 and 45 °C for polystyrene, we may expect in these good solvents more pronounced differences in the thickness of the adsorbed layer and the adsorbance compared with the data in cyclohexane.[23] The aim of this paper is to offer experimental results for the adsorption of homodisperse polystyrene onto chrome plates from toluene and carbon tetrachloride since data for such well-defined systems are rare but are needed to compare with theoretical predictions. Measurements of polystyrene adsorption were carried out by ellipsometry at 35 °C. The dependences of molecular weight and solvent power on the thickness of the adsorbed layer, the adsorbance, and the average polymer concentration in the adsorbed layer are examined and discussed in light of relevant theories.

Experimental Section

Materials. Linear polystyrene samples having a narrow molecular weight distribution were supplied from Pressure Chemical

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Table I
Characteristics of Polystyrenes

sample[a]	$M_w \times 10^{-3}$	M_w/M_n	$[\eta]$, dL/g CCl$_4$	$[\eta]$, dL/g toluene
P-3	110	1.06		
P-4	200	1.06	0.560	0.650
P-5	498	1.06	1.05	1.34
FF-32	775	1.04		
FF-33	2420	1.07	3.78	4.92
FF-34	4590	1.08		
FF-35	7620	1.05		
FF-36	9700	1.06		

[a] The P series was supplied by Pressure Chemical Co. and the FF series was supplied by Toyo Soda Co.

Co. and from Toyo Soda Co. Characteristics of the eight samples are given in Table I. Except for FF-32, all samples were those used in our previous studies.[22,23] Cyclohexane was purified by the procedure described previously.[22,23] Carbon tetrachloride and toluene were Merck spectrograde and distilled fractionally just before use. All polystyrene solutions were filtered through a Millipore FH filter prior to measurement.

Intrinsic viscosities of polystyrenes in carbon tetrachloride and in toluene at 35 °C were measured with a Ubbelohde viscometer.

Electrodeposited chrome plates were used as substrates. They were cleaned by the method described previously.[22,23,25]

Ellipsometry. A Shimadzu horizontal ellipsometer was used. The details of the ellipsometric measurement and the analysis of the ellipsometric data were reported previously.[22-25] All adsorption measurements were carried out at 35 °C.

The basic data derived from the ellipsometric measurements, namely, the refractive index n_f of the adsorbed layer and the thickness t of the uniform adsorbed layer, give the adsorbance A (g/cm^2), using the equation

$$A = t(n_f - n_0)/(\partial n/\partial c) = tC_f \tag{1}$$

where n_0 is the refractive index of a solvent, $\partial n/\partial c$ is the refractive index increment of polymer in the solvent, and C_f is the average polymer concentration in the adsorbed layer: For carbon tetrachloride the values of n_0 and $\partial n/\partial c$ are 1.4540 and 0.149 mL/g, and for toluene, the values of n_0 and $\partial n/\partial c$ are 1.4921 and 0.117 mL/g.

Results

Adsorption Kinetics. The adsorption process was followed by measuring the time dependence of both A and t. Values measured at a bulk polymer concentration C_p of 0.1 g/100 mL are plotted against the adsorption time in Figure 1. It is found that the equilibrium A and t are attained after several hours, independent of the molecular weight and the solvent used. A similar dependence was observed in the other experiments. Therefore, both A and t determined after 1 day were taken as the equilibrium values.

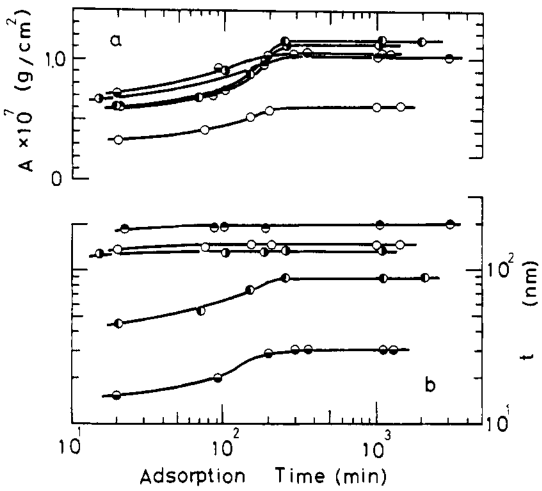

Figure 1. (a) Adsorbance A of polystyrene as a function of adsorption time. (b) Thickness t of the adsorbed layer as a function of adsorption time: (⊖) M_w = 110 × 10^3 in carbon tetrachloride; (◐) M_w = 775 × 10^3 in carbon tetrachloride; (◑) M_w = 2420 × 10^3 in carbon tetrachloride; (●) M_w = 7620 × 10^3 in carbon tetrachloride; (○) M_w = 2420 × 10^3 in toluene.

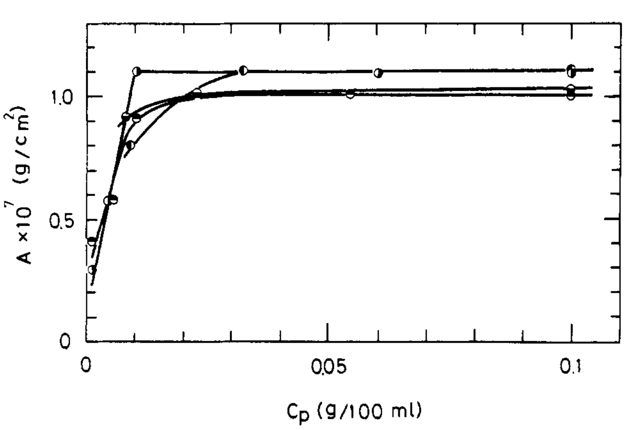

Figure 2. Adsorption isotherms of polystyrene from carbon tetrachloride solutions. Symbols are the same as in Figure 1.

Adsorption Isotherms. Adsorption isotherms in carbon tetrachloride are shown in Figure 2 for P-3, FF-32, FF-33, and FF-35. The values of A initially rise sharply with increasing C_p and reach a wide plateau region. This indicates that adsorption isotherms are of the high-affinity type. The A data obtained at the polymer concentration in the plateau region, i.e., C_p = 0.1 g/100 mL, are summarized in Table II. The values of A in toluene at C_p = 0.1 g/100 mL are also listed in Table II. Except for FF-32, the A data in cyclohexane at C_p = 0.3 g/100 mL were quoted from our previous paper.[22]

Concentration Dependence of the Thickness of the Adsorbed Layer. Figure 3 shows plots of t in carbon tetrachloride against C_p. The t value rises sharply with increasing C_p and reaches a constant value. The values of t measured at C_p = 0.1 g/100 mL are well into the

Table II
Adsorption of Polystyrene onto a Chrome Plate at a Constant Bulk Polymer Concentration of 0.1 g/100 mL

sample	$A \times 10^7$, g/cm^2 CCl$_4$	$A \times 10^7$, g/cm^2 toluene	$A \times 10^7$, g/cm^2 cyclohexane[a]	t, nm CCl$_4$	t, nm toluene	t, nm cyclohexane[a]	C_f, g/100 mL CCl$_4$	C_f, g/100 mL toluene	C_f, g/100 mL cyclohexane[a]
P-3	1.0_5		2.6_6	$32._0$		$26._7$	3.2_7		9.9_8
P-4	1.0_3		2.9_2	$44._0$		$29._3$	2.3_4		9.9_8
P-5	1.1_7		5.3_9	$57._9$		$48._6$	2.0_1		$11._1$
FF-32	1.1_5		5.1_6	$89._9$		$71._0$	1.2_8		7.2_7
FF-33	1.1_1	0.60_9	4.5_1	$134._8$	$142._4$	$103._0$	0.82_3	0.42_7	4.3_8
FF-34	1.0_8	0.64_8	8.5_9	$182._6$	$189._4$	$156._0$	0.59_1	0.34_2	5.5_1
FF-35	1.0_2	0.64_8	4.8_3	$201._5$	$210._0$	$170._0$	0.50_4	0.30_8	2.8_4
FF-36	1.0_0	0.62_8	5.5_6	$222._4$	$223._4$	$192._0$	0.45_0	0.28_1	2.9_0

[a] Except for FF-32, the adsorption data in cyclohexane are for a bulk polymer concentration of 0.3 g/100 mL.

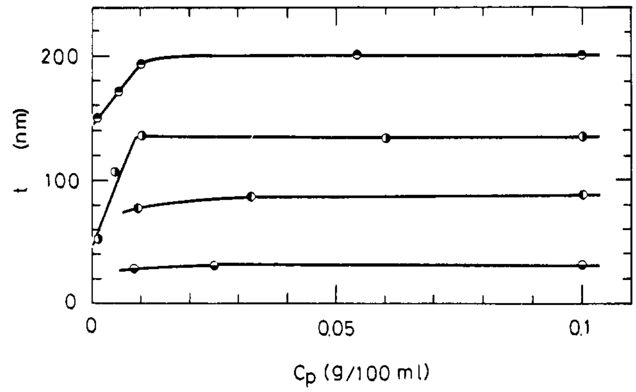

Figure 3. Thickness t of the adsorbed layer vs. polymer concentration. Symbols are the same as in Figure 1.

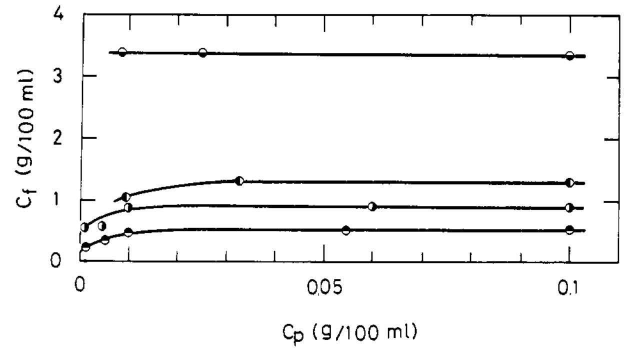

Figure 4. Average polymer concentration C_f in the adsorbed layer vs. polymer concentration. Symbols are the same as in Figure 1.

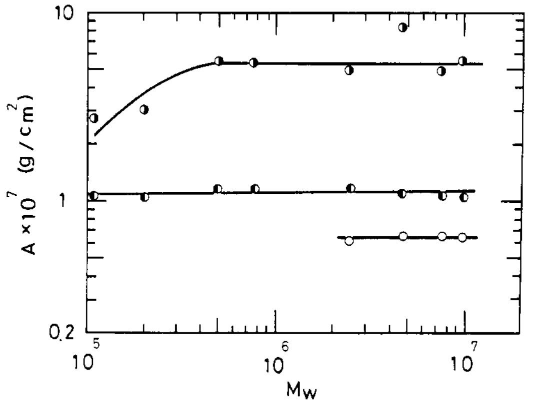

Figure 5. Adsorbance A at C_p = 0.1 g/100 mL vs. the molecular weight: (◐) carbon tetrachloride; (○) toluene; (◑) cyclohexane.

plateau region for all samples and they are listed in Table II together with those measured in toluene and in cyclohexane.

Concentration Dependence of the Average Polymer Concentration in the Adsorbed Layer. The value of C_f in carbon tetrachloride is plotted against C_p in Figure 4. The C_f value also rises sharply at low C_p and then levels off to a constant value; its plateau value at C_p = 0.1 g/100 mL is listed in Table II.

Molecular Weight Dependence of Adsorbance, Thickness of the Adsorbed Layer, and Average Polymer Concentration in the Adsorbed Layer. In Figure 5, the A value at C_p = 0.1 g/100 mL is plotted against the molecular weight on a double-logarithmic scale. It is apparent that the values of A in good solvents are lower than that in the Θ solvent and are almost independent of the molecular weight. The A value in carbon tetrachloride is larger than that in toluene. This difference stems from the fact that toluene is a better solvent for polystyrene than carbon tetrachloride.

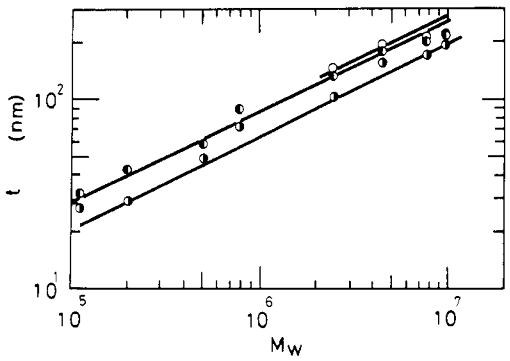

Figure 6. Thickness t of the adsorbed layer at C_p = 0.1 g/100 mL vs. the molecular weight. Symbols are the same as in Figure 5.

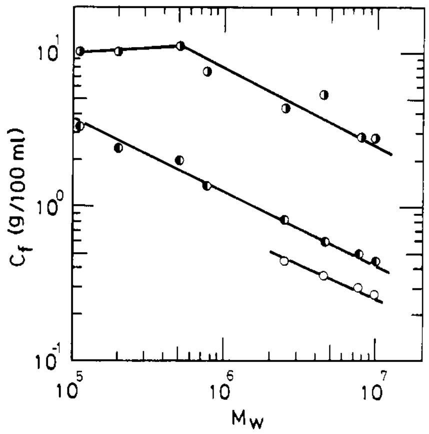

Figure 7. Average polymer concentration C_f in the adsorbed layer at C_p = 0.1 g/100 mL vs. the molecular weight. Symbols are the same as in Figure 5.

In Figure 6, the t value at C_p = 0.1 g/100 mL is plotted against the molecular weight. The values of t in good solvents are larger than that in the Θ solvent. The t in toluene is larger than that in carbon tetrachloride. The slopes of the solid lines drawn in Figure 6 are 0.5. Although the data points are somewhat scattered, the thickness of the adsorbed polystyrene layer is within experimental error proportional to the square root of the molecular weight in the good solvents used except for higher molecular weight.

The value of C_f at C_p = 0.1 g/100 mL is plotted against the molecular weight in Figure 7. The C_f in good solvents is smaller than that in the Θ solvent and the value in carbon tetrachloride is larger than that in toluene. The slopes of the solid lines drawn for the double-logarithmic plot of the C_f vs. the molecular weight are −0.5.

Discussion

In good solvents low adsorbance and large thickness compared with the case of the Θ solvent are considered to be due to the excluded-volume effect between loop and/or tail segments. Hoeve[10] and Jones and Richmond[18] attempted to incorporate the excluded-volume effect into the expansion factor of the thickness of the adsorbed layer. In the theories of Hoeve and Jones and Richmond an expansion factor α_t is defined by $t_{rms}/t_{rms,\Theta}$, where t_{rms} and $t_{rms,\Theta}$ are the root-mean-square thicknesses of the adsorbed layer in good and Θ solvents, respectively. In the theory of Hoeve,[10] based on the loop–train conformation, it is assumed that the segment density distribution in any loop is uniformly and one-dimensionally expanded by a factor α_t as a result of loop–loop interactions. In the theory of Jones and Richmond[18] no particular conformation of adsorbed polymer chain is assumed. They solved a diffusion equation for polymer chains adsorbed on a flat adsorbing interface by using the self-consistent mean-field approach for the excluded-volume effect.

The equations for α_t derived by Hoeve (eq 19 of Hoeve's paper[10b]) and Jones and Richmond (eq 41 of Jones and Richmond's paper[18]) are analytical in form. However, in both theories, expressions are given for α_t and thereby imply taking the thicknesses of the adsorbed layer in good and Θ solvents *at the same adsorbance*. Hence, we cannot compare the measured value of α_t with the theoretical predictions for α_t of Hoeve and Jones and Richmond due to the dependence of the measured adsorbance on the solvent power as seen from Figure 5.

In an attempt to explain the dependences of molecular weight and solvent power on the experimental data of the thickness of the adsorbed layer and the adsorbance and also to propose a possible conformation in the plateau region, namely, at $C_p = 0.1$ g/100 mL, with relevant theories. Besides the theories of Hoeve and Jones and Richmond several theories for polymer adsorption in good solvents are available. In particular, the theories of Silberberg[2] and Scheutjens and Fleer[19,20] specify particular conformations for adsorbed polymer chains: a loop–train conformation in Silberberg's theory and a loop–train–tail conformation in Scheutjens and Fleer's theory. Both theories are based on a lattice model taking into account interactions between adsorbed polymer chains but the published results of these authors deal with only the cases for Θ ($\chi = 0.5$) and athermal ($\chi = 0$) conditions.

The values of χ are evaluated as 0.452 in carbon tetrachloride and 0.440 in toluene, respectively, from the Stockmayer–Fixman plot[26] of intrinsic viscosities listed in Table I. The χ values herein obtained are in good agreement with those determined from the osmotic pressure measurements.[27,28] Hence, we are unable to quantitatively compare our results with the theories of Silberberg and Scheutjens and Fleer. Moreover, the adsorption energy parameter χ_s that applies to the chrome surface used is not known.

For the thickness of the adsorbed layer, Stromberg, Tutas, and Passaglia[21] proposed to convert the thickness t determined by ellipsometry into the root-mean-square thickness t_{rms}, defined by $t_{\mathrm{rms}} = t/1.5$, assuming that the segment distribution in the adsorbed layer is an exponential distribution, which is the case for the loop–train conformation.[7,11] However, if tails are present, we do not employ their procedure. Hence, we qualitatively compare the measured t in good solvents with theoretical predictions of Silberberg and Scheutjens and Fleer at $\chi = 0$.

Silberberg[2] predicted that for the cooperative factor, representative of the case in which the chain introduces an additional train–loop pair into the conformation, $\gamma_s\gamma_B = 0.1$, $\chi_s = \infty$, and volume fraction of polymer $\phi^* = 10^{-3}$, the adsorbed amount of polymer decreases with increasing solvent power. In good solvent, the adsorbed amount of polymer becomes almost independent of molecular weight, in accordance with our experimental results. Adopting $\chi_s = \infty$ and $\gamma_s\gamma_B = 0.1$, we find that the thickness of the adsorbed layer, which corresponds to the average loop size, decreases with increasing solvent power and that the molecular weight dependence of the average loop size in good solvent is weaker than that in the Θ solvent. The dependence of the solvent power on the thickness of the adsorbed layer in the theory of Silberberg is different from our experimental finding.

In the theory of Scheutjens and Fleer[19] the amount of adsorbed polymer in good solvent is lower than that in the Θ solvent and adsorption isotherms are of the high-affinity type. The amount of adsorbed polymer in good solvent levels off above a degree of polymerization 10^2 for $\chi_s = 1.0$ and $\phi^* = 10^{-2}$. These features are in good agreement with the theoretical predictions of Silberberg and also with our experimental results. Unless otherwise noted, we use the calculated data for $\chi_s = 1.0$ and $\phi^* = 10^{-2}$ in the theory of Scheutjens and Fleer for the present discussion.

Scheutjens and Fleer[20] further calculated the thicknesses of the adsorbed layer due to loop and tail segments separately and also the overall thickness as some average of loop and tail thicknesses. They showed that the loop thickness in good solvent is smaller than that in the Θ solvent while the tail thickness in good solvent is larger than that in the Θ solvent and moreover that the tail thickness is considerably larger than the loop thickness under the same conditions. However, the overall thickness in good solvent is somewhat smaller than that in the Θ solvent. Moreover, Scheutjens and Fleer predicted that not only the thicknesses due to loop and tail segments but also the overall thickness of the adsorbed layer in good solvent are approximately proportional to the square root of the molecular weight.

As seen from Figure 6 the measured thickness of the polystyrene layer adsorbed on the chrome surface increases with increasing solvent power. This experimental result is opposite to the solvent effect on the overall thickness but is similar to that on the thickness due to tail segments. In conclusion, the comparison between theories and experiments for the dependence of solvent power and molecular weight on the measured thickness of the adsorbed polystyrene in good solvents leads us to propose that the tail portions in the adsorbed polystyrene chains predominantly determine the thickness of the adsorbed polystyrene layer.

Conclusions

We studied the adsorption of polystyrenes covering a wide range of molecular weight from 11×10^4 to 970×10^4 onto a chrome surface in the good solvents carbon tetrachloride and toluene by ellipsometry. The molecular weight dependence of the adsorbance and the thickness of the adsorbed layer measured in the plateau region are qualitatively compared with the theoretical predictions of Silberberg and Scheutjens and Fleer for athermal condition. From the comparisons it is concluded that the thickness of the adsorbed polystyrene layer on the chrome surface is predominantly determined by tails.

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Registry No. Polystyrene, 9003-53-6; chromium, 7440-47-3.

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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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