# Adsorption of Polystyrene at the Θ Temperature[†]

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ABSTRACT: Adsorption of polystyrene having molecular weights from 10 000 to 13 000 000 onto a chrome plate from cyclohexane at the Θ temperature was studied by ellipsometry. Comparisons were made at different quantitative levels, using the theories of Hoeve, Silberberg, and Scheutjens and Fleer. Poor agreement between Hoeve's theory and our adsorption isotherms was observed, and the two parameters $\sigma$ and $c$ which appeared in his theory were not constant at all. The molecular-weight dependence of the adsorbed amount $\Gamma$ was in excellent agreement with Silberberg's loop-train model but the average loop size was too small to predict the observed large root-mean-square extension of the adsorbed layer. A model of Scheutjens and Fleer, in which the predominant contribution of tails to the extension of the adsorbed layer was taken into account, appeared to predict not only the observed extension but also its molecular-weight dependence and the adsorbed amount $\Gamma$.

During the past 3 decades a large amount of theoretical and experimental effort has been devoted to clarification of the conformation of polymers adsorbed onto a flat solid surface. The unique characteristic of polymer adsorption compared with the adsorption of small molecules is the large number of conformations the adsorbed polymer may adopt at the solid–solution interface. Since the beginning of polymer-adsorption studies, the importance of these configurational problems has been well recognized since the amounts of the adsorbed polymer correspond to many layers if all segments of the polymer are in contact with the solid surface. It is now widely accepted that a part of adsorbed polymer chains makes direct contact with the surface as trains, while remaining segments extend into solution as loops and tails leading to a thick adsorbed layer.[1-20]

The model accounts qualitatively for two experimental observations of polymer adsorption, namely, high adsorbance and high extension of adsorbed polymer. Statistical thermodynamic approaches of polymer adsorption have been developed; however, no single theory exists which has been widely accepted because different theoretical treatments are qualitatively similar and are in agreement with some experimental data. In most of the theories, some of the parameters used in the treatments cannot be directly related to the experimentally measurable quantities and experimental work has not kept pace with theoretical work.

Experimentally, it appears that ellipsometry[21,22] is, among various experimental techniques,[21-29] a very suitable technique for measuring two important quantities simultaneously, as in the case of adsorbance and extension. Stromberg, Tutas, and Passaglia[21] have pioneered in the measurement of the adsorption of polystyrene onto a chrome plate from cyclohexane solutions by ellipsometry; the molecular weights of samples studied ranged from $7.6 \times 10^4$ to $3.3 \times 10^6$. It was found that the extension of the adsorbed layer was approximately proportional to the square root of the molecular weight, except for the highest molecular weight sample. However, the relationship between the adsorbance and molecular weight was not reported in detail. Subsequently, the adsorption of polystyrene onto various metal surfaces from the Θ solvents was measured by Gebhard and Killmann[22] by ellipsometry covering molecular weights from $7.6 \times 10^4$ to $34 \times 10^4$. Proportionality between the extension of the adsorbed layer and the square root of the molecular weight was also observed and adsorbance increased with increasing molecular weight.

Table I
Characteristics of Polystyrenes

| samples[a] | $10^{-4}M_w$ | $M_w/M_n$ |
|---|---|---|
| P-1 | 1 | 1.06 |
| P-2 | 3.7 | 1.06 |
| P-3 | 11 | 1.06 |
| P-4 | 20 | 1.06 |
| P-5 | 49.8 | 1.06 |
| P-6 | 67 | 1.15 |
| FF-33 | 242 | 1.07 |
| FF-34 | 459 | 1.08 |
| FF-35 | 762 | 1.05 |
| FF-36 | 970 | 1.06 |
| FF-37 | 1340 | 1.05 |

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

To compare experimental with theoretical work, it is desirable to accumulate comprehensive data covering a wide range of molecular weight in adsorption experiments. Thus samples having molecular weights ranging from $1 \times 10^4$ to $13 \times 10^6$ were used in this study and the adsorption of polystyrene onto a chrome plate from cyclohexane solutions was studied by ellipsometry. The data will be compared with the theoretical predictions made by Hoeve,[8] Silberberg,[3] and Scheutjens and Fleer.[20] Comparisons will be made at different quantitative levels, depending on the theory considered. The set of equations containing two parameters put forward by Hoeve[8] have been calculated analytically. Published results of Silberberg[3] and Scheutjens and Fleer[20] have been used for comparison of their theories. It is expected that these comparisons will provide facts for further theoretical developments.

## Experimental Section

**Materials.** Linear polystyrene samples having a narrow molecular weight distribution supplied by Pressure Chemical Co. (P Series) and Toyo Soda Co. (FF Series) were used. The characteristics of the eleven polystyrene samples are given in Table I. First-grade cyclohexane was distilled, passed through a silica gel column to remove aromatic impurities, refluxed over sodium metal, and then distilled fractionally just before use. All polystyrene–cyclohexane solutions were filtered through a Millipore HA filter prior to measurement.

The electrodeposited chrome plates were used as the substrates. Prior to the adsorption measurements, the chrome plates were cleaned by warm toluene in a Soxhlet apparatus, immersed in warm 18% aqueous sodium hydroxide solution for 1 h, washed in distilled water, dried, and finally passed several times through the flame of an ethyl alcohol lamp.

**Ellipsometry.** A Shimadzu ellipsometer was used. The chrome plate was immersed in a trapezoid glass cell[30] containing cyclohexane. Both the relative phase difference Δ and the amplitude ratio tan $\psi$ for the chrome plate in cyclohexane solvent

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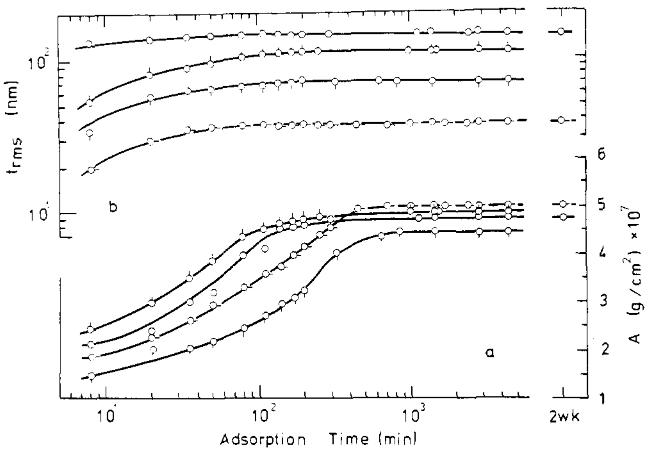

**Figure 1.** (a) Adsorbance of polystyrene at a constant bulk polymer concentration of 0.3 g/100 mL as a function of adsorption time. (b) Root-mean-square extension of the adsorbed polymer layer at a constant bulk polymer concentration of 0.3 g/100 mL as a function of adsorption time: (○-) $M_w = 67 \times 10^4$; (ϙ) $M_w = 242 \times 10^4$; (ȯ) $M_w = 762 \times 10^4$; (○) $M_w = 1340 \times 10^4$.

were first determined at λ 546 nm. Then the cyclohexane was removed and a cyclohexane solution of polystyrene was introduced into the cell by means of a hypodermic syringe. Changes of both Δ and ψ were measured as a function of time. Usually measurements were continued for 3 days or more. All adsorption measurements were carried out at 35 °C, which is the Θ temperature of polystyrene in cyclohexane.

The refractive index $n_f$ of the adsorbed layer and the extension $t$ of the uniform adsorbed layer normal to the surface were calculated by a FACOM 270-20 computer and an NBS computer program[31] from the values of Δ and ψ. The adsorbance $A$ (g/cm$^2$) was calculated by eq 1, where $n_0$ (=1.4203) is the refractive index

$$A = t(n_f - n_0)/(\mathrm{d}n/\mathrm{d}c) = tC_f \qquad (1)$$

of cyclohexane at λ 546 nm, d$n$/d$c$ is the refractive index increment of polystyrene in cyclohexane (determined as 0.172 cm$^3$/g with a Wood differential refractometer), and $C_f$ is the average polymer concentration in the adsorbed polymer layer. The decrease of polymer concentration in a bulk solution due to the adsorption was negligible.

The root-mean-square extension, $t_{rms}$, depends on the segment distribution function normal to the surface.[32] The procedure proposed by Stromberg, Tutas, and Passaglia[21] was employed to estimate the root-mean-square extension, assuming an exponential distribution of segments normal to the surface. Thus $t_{rms}$ is given as $t/1.5$.

## Results

**Adsorption Kinetics.** As shown in Figure 1, both adsorbance and root-mean-square extension of adsorbed polymer increase with adsorption time. The adsorbance increases rather slowly whereas the extension of the adsorbed polymer layer increases rapidly.

The equilibrium extension was reached within several hours, but the equilibrium adsorbance was attained after 1 day. After the attainment of the equilibrium both the adsorbance and extension did not change for 2 weeks. Therefore adsorbance determined after 3 days was taken as the equilibrium value in this investigation. This observation is in accordance with what has been reported by Stromberg, Tutas, and Passaglia[21] and Grant, Smith, and Stromberg.[29]

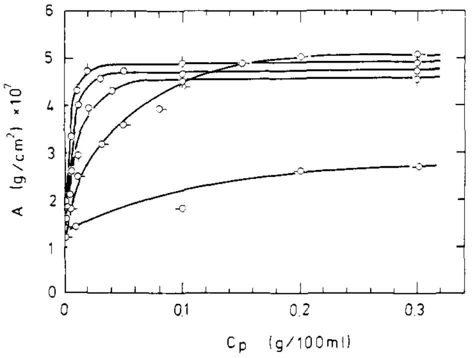

**Figure 2.** Adsorption isotherms of polystyrene: (-○) $M_w = 11 \times 10^4$; other symbols as in Figure 1.

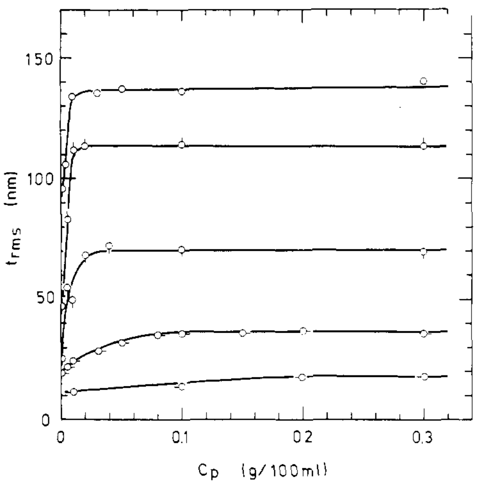

**Figure 3.** Root-mean-square extension of the adsorbed polymer layer vs. polymer concentration. Symbols as in Figure 2.

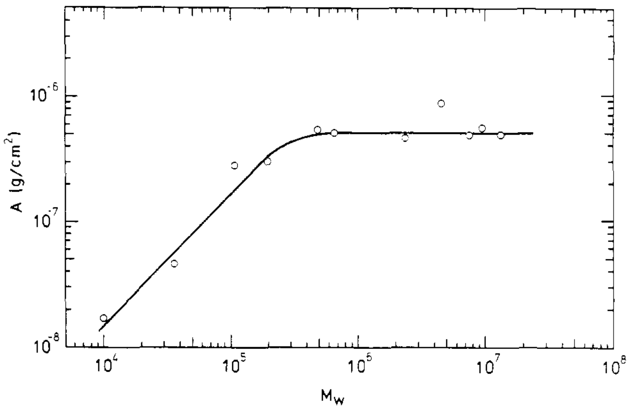

**Figure 4.** Adsorbance at a constant bulk polymer concentration of 0.3 g/100 mL vs. the molecular weight.

**Adsorption Isotherms.** Adsorption isotherms are shown in Figure 2 and the data of adsorption are summarized in Table II. Initially adsorption isotherms rise steeply with increasing polymer concentration and then reach a long plateau region. Adsorption isotherms are of the high-affinity type, showing that the adsorbance at a bulk polymer concentration of 0.3 g/100 mL is in the plateau region irrespective of the molecular weight. The rather gradual rise of the adsorption isotherm of the sample with molecular weight 67 × 10$^4$ is considered due to broad molecular weight distribution of the sample, as shown in Table I.

**Concentration Dependence of the Extension of the Adsorbed Layer.** The plots of the extension of the adsorbed layer against bulk polymer concentration are shown in Figure 3 and the data are listed in Table II. The extension of the adsorbed layer also rises quite steeply with increasing bulk polymer concentration and then reaches a constant value. Moreover, the initial slope of extension vs. the concentration plot increases with increasing molecular weight. The extension of the adsorbed layer at a bulk polymer concentration of 0.3 g/100 mL is well in the plateau region for all samples.

Table II
Adsorption Data of Polystyrenes onto Chrome Plates

| $10^{-4}M_w$ | $C_p$, g/100 mL | $t_{rms}$ nm | $10^7 A$, g/cm$^2$ | $C_f$, g/100 mL |
|---|---|---|---|---|
| 1 | 0.300 | 2.$_5$ | 0.17$_0$ | 4.4$_7$ |
| 3.7 | 0.300 | 5.$_3$ | 0.45$_0$ | 5.6$_3$ |
| 11 | 0.010 | 11.$_1$ | 1.4$_2$ | 8.5$_3$ |
|  | 0.100 | 13.$_7$ | 1.7$_6$ | 8.5$_3$ |
|  | 0.200 | 17.$_3$ | 2.5$_9$ | 9.9$_8$ |
|  | 0.300 | 17.$_8$ | 2.6$_6$ | 9.9$_8$ |
| 20 | 0.300 | 19.$_5$ | 2.9$_2$ | 9.9$_8$ |
| 49.8 | 0.300 | 32.$_4$ | 5.3$_9$ | 11.$_1$ |
| 67 | 0.001 | 18.$_9$ | 1.3$_1$ | 4.6$_4$ |
|  | 0.005 | 22.$_0$ | 1.8$_0$ | 5.4$_6$ |
|  | 0.010 | 24.$_1$ | 2.5$_5$ | 7.0$_8$ |
|  | 0.030 | 28.$_1$ | 3.1$_8$ | 7.5$_5$ |
|  | 0.050 | 32.$_4$ | 3.5$_8$ | 7.3$_7$ |
|  | 0.080 | 35.$_4$ | 3.9$_4$ | 7.4$_3$ |
|  | 0.100 | 35.$_8$ | 4.6$_5$ | 8.6$_5$ |
|  | 0.150 | 35.$_8$ | 4.8$_9$ | 9.1$_0$ |
|  | 0.200 | 37.$_6$ | 5.0$_2$ | 8.8$_8$ |
|  | 0.300 | 35.$_7$ | 5.0$_7$ | 9.4$_6$ |
| 242 | 0.001 | 25.$_3$ | 1.5$_8$ | 4.1$_2$ |
|  | 0.005 | 55.$_1$ | 2.6$_3$ | 3.1$_9$ |
|  | 0.010 | 49.$_2$ | 2.9$_5$ | 4.0$_0$ |
|  | 0.020 | 68.$_0$ | 3.9$_6$ | 3.8$_9$ |
|  | 0.040 | 72.$_0$ | 4.3$_1$ | 4.0$_0$ |
|  | 0.100 | 70.$_7$ | 4.4$_9$ | 4.2$_4$ |
|  | 0.300 | 68.$_7$ | 4.5$_1$ | 4.3$_8$ |
| 459 | 0.300 | 104 | 8.5$_9$ | 5.5$_1$ |
| 762 | 0.001 | 47.$_1$ | 1.8$_8$ | 2.6$_7$ |
|  | 0.005 | 83.$_3$ | 3.3$_4$ | 2.6$_7$ |
|  | 0.010 | 112 | 4.2$_8$ | 2.5$_5$ |
|  | 0.020 | 113 | 4.7$_3$ | 2.7$_8$ |
|  | 0.100 | 114 | 4.8$_5$ | 2.8$_4$ |
|  | 0.300 | 113 | 4.8$_3$ | 2.8$_4$ |
| 970 | 0.300 | 128 | 5.5$_6$ | 2.9$_0$ |
| 1340 | 0.001 | 96.$_7$ | 1.9$_3$ | 1.3$_3$ |
|  | 0.003 | 107 | 2.1$_3$ | 1.3$_3$ |
|  | 0.010 | 135 | 4.0$_8$ | 2.0$_2$ |
|  | 0.030 | 135 | 4.5$_9$ | 2.2$_6$ |
|  | 0.050 | 139 | 4.7$_0$ | 2.2$_6$ |
|  | 0.100 | 137 | 4.6$_3$ | 2.2$_6$ |
|  | 0.300 | 141 | 4.6$_6$ | 2.2$_0$ |

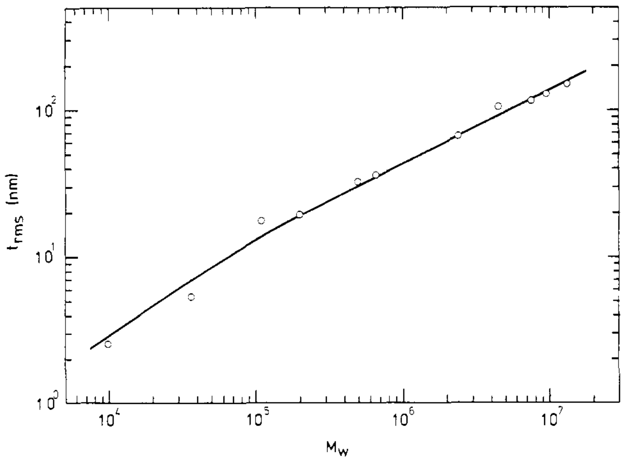

**Figure 5.** Root-mean-square extension of the adsorbed polymer layer at a constant bulk polymer concentration of 0.3 g/100 mL vs. the molecular weight.

**Molecular-Weight Dependence of Adsorbance and Extension of the Adsorbed Layer.** In Figure 4, adsorbance obtained at a constant bulk polymer concentration of 0.3 g/100 mL is plotted against the molecular weight. At first, adsorbance increases linearly with molecular weight up to $M_w$ = 50 × $10^4$ but above this adsorbance becomes independent of the molecular weight.

In Figure 5, the root-mean-square extension of the adsorbed layer determined at a bulk polymer concentration of 0.3 g/100 mL is plotted against the molecular weight on a logarithmic scale. Above the molecular weight of 20 × $10^4$, the line has a slope of 0.5, showing that $t_{rms}$ is linearly proportional to the square root of the molecular weight up to the rather high molecular weight of 13 × $10^6$. These results show that this molecular-weight dependence of the extension of the adsorbed layer is in good agreement with the experimental results of Stromberg, Tutas, and Passaglia[21] and Gebhard and Killmann.[22] However, the magnitude of the extension of the adsorbed layer is somewhat different in various experiments. The differences may be attributed to the differences of the surface roughness of the chrome plates used. Stromberg et al. used a commercial chrome ferro-type plate, while Gebhard and Killmann used a chrome plate prepared by evaporation of chromium metal on a glass plate. We used an electrodeposited chrome plate.

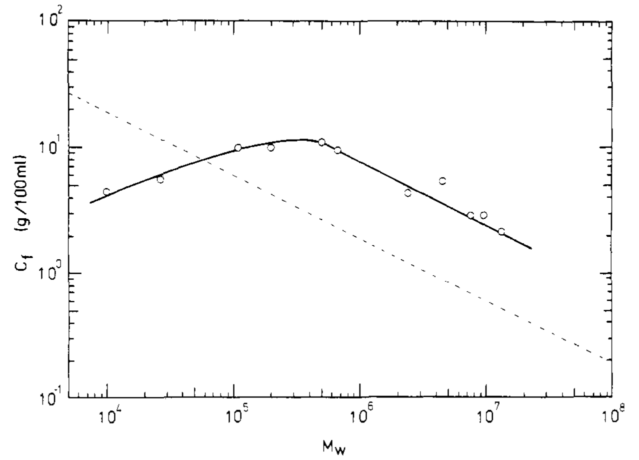

**Figure 6.** Average polymer concentration in the adsorbed layer at a constant bulk polymer concentration of 0.3 g/100 mL vs. the molecular weight. The dotted line denotes the average segment density of a free random coil in polystyrene–cyclohexane solution at the Θ temperature.

**Molecular-Weight Dependence of Average Polymer Concentration in the Adsorbed Layer.** The average polymer concentration expressed as $C_f$ (g/100 mL) in the adsorbed layer at a constant bulk polymer concentration of 0.3 g/100 mL is plotted against the molecular weight in Figure 6. The dotted line shown in the figure is the average segment concentration of a single isolated random coil of polystyrene in cyclohexane at the Θ temperature. The slope of this dotted line is naturally −0.5. As is clear from Figure 6, $C_f$ increases with molecular weight up to $M_w$ = 50 × $10^4$, reaches a maximum, and ultimately decreases linearly with increasing molecular weight, having a slope of −0.5. Moreover, $C_f$ is about 4 times larger than the average polymer concentration in a single isolated random coil.

## Discussion

**Adsorption Kinetics.** The extension of the adsorbed layer increases with the adsorption time fairly rapidly. This is explained in terms of conformational rearrangement, in which the early arrivals adopt a flatter conformation on the sparsely populated surface. Later arrivals must occupy a small number of vacant sites and therefore must adopt a much more extended conformation normal to the surface. Since the average conformation is determined by the total surface population of the polymer, continuous conformational rearrangements must occur on the surface to reach the equilibrium adsorbance.

**Adsorption Isotherms.** The adsorption isotherms shown in Figure 2 display the typical high-affinity-type isotherm with a long plateau region which is common to polymer adsorption.[24] Many adsorption isotherms, most of them based on statistical thermodynamics, have been proposed by many authors to account for the adsorption of nonionic polymers onto solid surfaces. Comparisons between theories and experiments have seldom been achieved.

Hoeve[8] derived an adsorption isotherm based on a loop-train model, which is based on infinite molecular weight approximation since tails are neglected. His adsorption isotherm is expressed as

$$N_p/\delta = N_f \exp(-\lambda_{ad} n) \tag{2}$$

where $N_p$ is the number of adsorbed polymers per unit area, $\delta$ is the thickness of the first adsorbed layer, $N_f$ is the number of polymer molecules per unit volume in the solution, $n$ is the degree of polymerization, and $-\lambda_{ad}$ is equal to the free energy of adsorption per segment divided by $kT$, where $k$ is the Boltzmann constant and $T$ is the absolute temperature. The $-\lambda_{ad}$ is given as

$$-\lambda_{ad} = \ln \sigma + \ln (1 + 2.162c) + \ln (1 - v_2{}^0) + 2\chi_1 v_2{}^0 \tag{3}$$

where $\sigma$ is a parameter and is defined as the ratio of partition function of an adsorbed unit to that of a unit in the bulk solution, $c$ is the flexibility parameter, $v_2{}^0$ is the volume fraction of segments in the first layer, and $\chi_1$ is Flory's interaction parameter. Assuming $\delta = v_1{}^{1/3}$, where $v_1$ is the volume of a solvent molecule, and taking $v_1 = 0.185$ nm$^3$, the free energy of adsorption $-\lambda_{ad}kT$ can easily be calculated from the adsorbance data.

The two parameters, namely, $\sigma$ and the flexibility parameter $c$, can be estimated from $-\lambda_{ad}$ as follows. Assuming that both $c$ and $\sigma$ are constant on a series of molecular weight fractions, we can eliminate $\ln \sigma$ from eq 3 for the molecular weight fractions 1 and 2:

$$-\lambda_1 - -\lambda_2 = [\ln \{1 - v_2{}^0(1)\} + 2\chi_1 v_2{}^0(1)] - [\ln \{1 - v_2{}^0(2)\} + 2\chi_1 v_2{}^0(2)] \tag{4}$$

According to Hoeve,[8] $v_2{}^0(i)$ is given as

$$v_2{}^0(i) = \frac{1 + 2.612c}{1 + 2.612c + \{\pi/-\lambda_i\}^{1/2}} \, \frac{n_i (N_p)_i v_1}{\delta} \tag{5}$$

for $i = 1$ and 2.

Assuming $\chi_1 = 0.5$ and regarding $c$ as an adjustable parameter, eq 4 and 5 can be solved for the pair of $-\lambda_1 - -\lambda_2$ at given $n$ and $N_p$. For the pair of low molecular weight fractions, namely, P-1 and P-2, the procedure resulted in $c = 0.11$ and $\sigma = 0.86$, which are in reasonable agreement with Hoeve's estimation.[8] However, for other pairs, $c$ was never constant; usually it had a very large positive value but sometimes $c$ became very negative. The reason for this failure to estimate $c$ and $\sigma$ is not clear. Hoeve[33] pointed out that in the estimation of $c$ and $\sigma$ the adsorption isotherms for lower molecular weights in the region should be used.

**Molecular-Weight Dependence of Adsorbance.** Silberberg[3] defined the adsorbed amount $\Gamma$ which is related to the adsorbance. The adsorbed amount $\Gamma$ is expressed as the ratio of the average polymer concentration in the adsorbed polymer layer $C_f$ to that of an isolated random coil $C_0$ (eq 6). Equation 6 can be rewritten as eq 7 by using

$$\Gamma = C_f/C_0 \tag{6}$$

$$\Gamma = A/tC_0 \tag{7}$$

adsorbance and the extension of the adsorbed polymer layer. If $\Gamma = 1$, 1 equiv of monolayer is adsorbed. In Figure 7, the adsorbed amount $\Gamma$ at a constant bulk polymer concentration of 0.3 g/100 mL or a volume fraction of $\phi^* \simeq 3 \times 10^{-3}$ is plotted as a function of the molecular weight. The adsorbed amount $\Gamma$ increases with increasing molecular weight up to $M_w = 50 \times 10^4$ and then reaches a constant value of 4 above $M_w = 50 \times 10^4$. The loop-train model of Silberberg was used to calculate theoretical $\Gamma$; the result with the conformational parameter $\gamma_B\gamma_S = 0.1$, the segment–substrate interaction parameter $\chi_S = \infty$, $\chi_1 = 0.5$, and $\phi^* = 3 \times 10^{-3}$ is shown in Figure 7. The agreement between Silberberg's theory and experiment is excellent above molecular weight $50 \times 10^4$; however one should not draw conclusions too hastily about the validity of selecting the theoretical parameters $\gamma_B\gamma_S$ and $\chi_S$ as this might be only fortuitous. We shall only maintain that the shape of the molecular-weight dependence of $\Gamma$ conforms to the predictions put forth by Silberberg's model.

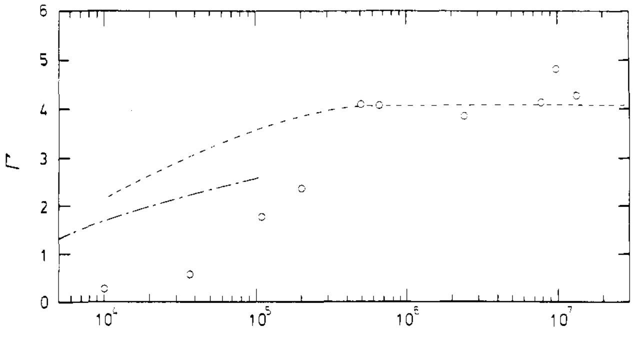

**Figure 7.** Adsorbed amount $\Gamma$ as a function of the molecular weight. Theoretical dependence predicted for the Θ solvent ($\chi_1 = 0.5$): (– – –) by the theory of Silberberg for $\gamma_B\gamma_S = 0.1$, $\chi_S = \infty$, and $\phi^* = 3 \times 10^{-3}$; (–·–) by the theory of Scheutjens and Fleer for $\chi_S = 5$ and $\phi^* = 10^{-3}$.

The adsorbed amount $\Gamma$ proposed by the theory of Scheutjens and Fleer for $\chi_S = 5$, $\chi_1 = 0.5$, and $\phi^* = 10^{-3}$ is also shown in Figure 7. Their adsorbed amount $\Gamma$ is lower than that from the theory of Silberberg and is closer to the observed $\Gamma$. Above molecular weights of $10^5$ the adsorbed amount $\Gamma$ cannot be estimated since their calculations are limited to degrees of polymerization of $10^3$. However, it should be noted that Scheutjens and Fleer's model involves the loop-train-tail model and the presence of 15% of segments in one tail per adsorbed molecule except for the fraction of segments present in loops and trains.

**Molecular-Weight Dependence of Extension of the Adsorbed Layer.** The root-mean-square extension $t_{rms}$ at a constant polymer concentration of 0.3 g/100 mL is plotted against the square root of the molecular weight in Figure 8. It is clear that the root-mean-square extension is a linear function of the square root of the molecular weight up to $M_w = 13 \times 10^6$. An increase in the root-mean-square extension from the surface proportional to the square root of the molecular weight has been predicted for adsorbed polymers by Simha, Frisch, and Eirich,[1] by Hoeve,[8] by Silberberg,[3] and recently by Scheutjens and Fleer.[20] In the theories of Hoeve and Silberberg the molecular-weight dependence of the extension of the adsorbed polymer layer is predicted by the loop size. On the contrary Scheutjens and Fleer claim that the contribution of segments in the tails to $t_{rms}$ dominates over that of loops and that there are not too many segments in the loops compared to the number of segments in the tails.

One should find poor agreement between the theory of Hoeve and the experimental adsorption isotherms. That is, the two parameters $\sigma$ and $c$ which appeared in his theory are not constant, as seen in the previous section. Therefore, it seems judicious not to use the theory of Hoeve in

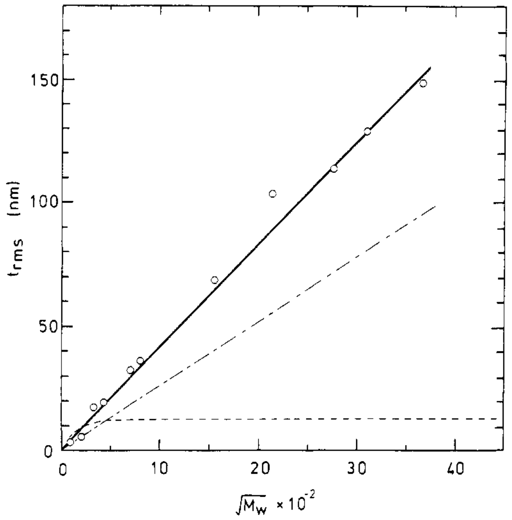

**Figure 8.** Root-mean-square extension as a function of the square root of the molecular weight: (---) by the theory of Silberberg for $\gamma_B\gamma_S = 0.1$, $\chi_S = \infty$, and $\phi^* = 3 \times 10^{-3}$; (--–) by the theory of Scheutjens and Fleer.

any comparison with the observed root-mean-square extension.

Comparing the observed root-mean-square extension of the adsorbed layer and the average loop size $P_B$ predicted by Silberberg, it seems reasonable that $(P_B/2)b$ should be employed as an extension of the adsorbed layer consisting of loops, where $b$ is the effective bond length. One should remember that the $(P_B/2)b$ is the fully stretched extension of a loop. The calculated extension $(P_B/2)b$, using $\gamma_B\gamma_S = 0.1$, $\chi_S = \infty$, $\chi_1 = 0.5$, and Berry's light scattering data[34] of $b = 0.69$ nm, is shown in Figure 8. It is clear that the calculated extension $(P_B/2)b$ is proportional to the square root of the molecular weight up to $M_w = 10^5$ and then levels off, while the calculated extension nearly coincides with the observed extension in the lower molecular weight region. Above $M_w = 50 \times 10^4$ the calculated extension is nearly a constant 12 nm. This constant value seems too small to predict the observed extension since the observed extension in the higher molecular weight region ranges from 20 to 150 nm. The small loop size and its independence of molecular weight as compared with the observed extension in the higher molecular weight region may be due to the loop-train model used in the theory of Silberberg in which uniform loop size is assumed and the presence of tails is neglected.

Provided the conformation parameter $\gamma_B\gamma_S$, whose physical meaning is obscure, is adopted as 0.0316, the average loop size $(P_B/2)b$ becomes large, but quantitative agreement between the observed extension and the loop size is still limited to the low molecular weight region. Moreover, at $\gamma_B\gamma_S = 0.0316$ the adsorbed amount $\Gamma$ predicted by Silberberg's theory considerably exceeds the observed one. Furthermore, large loop formation is unfavorable, since the form of the partition function of a loop of size $i$ is proportional to $i^{-3/2}$,[8,14] whereas that of a tail of the same size is proportional to $i^{-1/2}$.[16] It is unlikely that the observed extension of the adsorbed layer is predictable by the loop size alone.

Roe,[10,11] Motomura and Matsuura,[35] Hesselink,[16] Clark and Lal,[36] and, more recently, Scheutjens and Fleer[20] and Feigin and Napper[37] have pointed out that tails make predominant contribution to the root-mean-square extension. Scheutjens and Fleer in particular showed that 15% of segments in a polymer chain exist as one tail per adsorbed molecule and the tails strongly contribute to the extension of the adsorbed layer. Furthermore, they showed that the root-mean-square extension increases proportionally with the square root of the molecular weight. Therefore, the root-mean-square extension $t_{rms}$ is given as

$$t_{rms} = k\langle i\rangle_t^{1/2} b \tag{8}$$

where $k$ is a constant, $\langle i\rangle_t$ is the average tail size, and $b$ is the effective bond length (=0.69 nm). $k$ is given as 1.08 for the set of tails by Hesselink,[16] while Feigin and Napper[37] proposed that $k$ is 1.33 for an isolated tail. Thus, the value of $k$ is not yet settled. We employed unity for $k$ and $\langle i\rangle_t$ is regarded as $15/100n$, according to Scheutjens and Fleer, where $n$ is the degree of polymerization. Although the model of Scheutjens and Fleer is only confirmed to be valid for $n$ lower than $10^3$ due to limited computation time, the root-mean-square extension of tails may be calculated from eq 8, assuming that eq 8 is valid up to a molecular weight of $13 \times 10^6$, and is plotted in Figure 8. The calculated root-mean-square extension of tails is nearer to the observed extension of the adsorbed layer than that calculated by the loop-train model of Silberberg. However, the ratio of the observed extension to the calculated one is 1.57 (on the average). Therefore, the contribution of tails to the extension of the adsorbed layer seems to account for the observed large extension of the adsorbed layer.

## Conclusion

Our data are spread over an extended range of molecular weight when compared with previously reported work. Attempted comparison at a quantitative level with the theories of Hoeve, Silberberg, and Scheutjens and Fleer was made. The adsorbed amount $\Gamma$ is in excellent agreement with the theoretical calculation of Silberberg, but the loop size was too small to predict the observed root-mean-square extension and, moreover, the molecular-weight dependence of extension is not qualitatively explained in the higher molecular weight region. The model of Scheutjens and Fleer, in which the contribution of the tail to the root-mean-square extension is dominant, was compared with experiments. It is concluded that about 15 to 20% of segments should be present in one tail per adsorbed molecule.

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# Ultrasonic Relaxation in Aqueous Solutions of Dextran

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ABSTRACT: The ultrasonic absorption coefficients of aqueous solutions of dextran and some saccharides have been measured in a frequency range from 0.8 to 130 MHz and over a temperature range from 10 to 35 °C. In all solutions of dextran two relaxation processes are observed within the frequency range examined, which have relaxation frequencies at about 1 and 12–15 MHz. They are likely independent of molecular weight and temperature. However, the aqueous solutions of saccharides do not exhibit any relaxation. The relaxation processes observed in aqueous solutions of dextran are considered to be volume relaxations due to the segmental motion of the polymer chain. The most likely origin of the volume relaxations is the exchange process of the hydrated water molecules in the hydration sphere of the polymer.

The solution properties of dextran have been investigated by a variety of methods, including viscosity, light scattering, and sedimentation.[1-3] However, the information obtained by these methods cannot reveal the "dynamical" properties of aqueous solutions of dextran.

The ultrasonic relaxation method has proved to be a powerful and efficient tool for investigating the dynamics of molecular processes such as conformational changes associated with polymer chains in the time range of $10^{-5}$–$10^{-10}$ s.[4,5]

The ultrasonic relaxation in aqueous solutions of dextran was first reported by Hawley and Dunn about 10 years ago.[6] Their study was very suggestive for the understanding of the relaxation mechanism of aqueous solutions of dextran. However, their measurement was carried out at 20 °C only, and the volume of data in the frequency range below 10 MHz was not sufficient for detailed discussion of the relaxation mechanism.

As was mentioned in our previous paper,[7] the data below 10 MHz are particularly important for discussion of the chain dynamics of stiff polymers such as cellulose acetate and dextran, and the ultrasonic absorption should be measured accurately as a function of temperature over a wide frequency range.

In this paper, we report accurate measurements of ultrasonic absorption of aqueous solutions of dextran at different temperatures, together with those of some saccharides. We discuss the possible mechanisms of the relaxation process in aqueous solutions of dextran with reference to the results on aqueous solutions of some saccharides.

## Experimental Section

**Materials.** The dextran samples (1,6-poly(anhydroglucose)) used were supplied by Pharmacia Fine Chemical Co., Ltd. Molecular weight and the ratio of $M_w/M_n$ of the samples are summarized in Table I. The samples of saccharides, glucose, maltose, and raffinose used were commercial extrapure grade reagents.

**Table I**
**Molecular Weights and Intrinsic Viscosities of Dextran Samples**

| sample | $M_w$ | $M_n$ | $M_w/M_n$ | $[\eta]^a$ |
|---|---|---|---|---|
| T-10 | $9.4 \times 10^3$ | $5.3 \times 10^3$ | 1.71 | 0.096 |
| T-40 | $4.0 \times 10^4$ | $3.0 \times 10^4$ | 1.33 | 0.21 |
| T-110 | $1.1 \times 10^5$ | $7.6 \times 10^4$ | 1.44 | 0.32 |
| T-2000 | $2.0 \times 10^6$ | | | 0.70 |

[a] At 20 °C.

**Ultrasonic Absorption Measurements.** The ultrasonic absorption coefficient, $\alpha$ (neper cm$^{-1}$), was measured by using a standard-pulse apparatus in the frequency range of 15–130 MHz. In the low-frequency range, 0.8–8 MHz, $\alpha$ was measured by a cylindrical resonator method. Two types of resonators were used in this work: one had a 1.65-mm path length and paired 2-MHz *x*-cut crystals having a 50-mm diameter, and the other had a 0.83-mm path length and 5-MHz *x*-cut crystals having a 30-mm diameter. A more detailed description of the apparatus and the experimental procedures have been published elsewhere.[7]

Distilled water was used as the reference material for the resonator method.

**Sound Velocity and Density Measurements.** The ultrasonic velocity was mainly measured with an interferometer working at a fixed 4.000-MHz frequency and occasionally with the cylindrical resonators. The density was measured with an Ostwald-type pycnometer of 20-mL capacity.

All measurements were carried out on freshly prepared solutions to avoid the aging effect. According to Hawley and Dunn,[6] the ultrasonic absorption of aqueous solutions of dextran varies linearly with concentration up to 10% throughout the molecular weight and frequency ranges. Therefore all the measurements were carried out at a constant concentration of 5.00 g/100 mL.

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