*Macromolecules* 1983, *16*, 1465–1469

# Molecular Weight Dependence of the Thickness of the Polystyrene Layer Adsorbed onto a Metal Surface in Good Solvent Conditions

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ABSTRACT: To determine the exponent of the molecular weight dependence of the thickness of the adsorbed layer in good solvent conditions, we measured the adsorption of polystyrene onto a chrome plate in cyclohexane at 40 and 45 °C and in carbon tetrachloride at 35 °C as a function of the molecular weight by ellipsometry. We examined at least duplicate runs for each sample covering molecular weights from $11 \times 10^4$ to $13 \times 10^6$. Their reproducibilities in the measurements of adsorbance and thickness of the adsorbed layer were very good, with the error being less than 10%. It was found that the molecular weight dependence of the thickness of the adsorbed layer in three good solvents is definitely smaller than that in the Θ solvent. The exponent of the molecular weight dependence is obtained to be 0.4 ± 0.02 for the respective solvents. This value is in good agreement with that predicted by the polymer adsorption theory of de Gennes based on scaling concepts.

## Introduction

It is now generally accepted both theoretically and experimentally that in the Θ solvent condition the molecular weight dependence of the thickness of the adsorbed polymer layer on a solid surface is proportional to the square root of the molecular weight.[1-9] While in good solvent conditions various theoretical works[3,4,10-16] have been devoted to clarifying the adsorption behavior of polymer chains near a solid wall, the general concept on the molecular weight dependence of the thickness of the adsorbed polymer layer has not yet been reached.

In our previous papers[17,18] we measured the thickness of the polystyrene layer adsorbed on a chrome plate using ellipsometry in cyclohexane at 40 and 45 °C,[17] in carbon tetrachloride at 35 °C, and in toluene at 35 °C[18] for a wide range of molecular weight. From comparison with theories based on mean field theory, a conclusion was reached that the larger thickness than that in the Θ solvent condition is predominantly determined by tails. The measured thickness of the adsorbed layer in these four good solvents was *approximately* proportional to the square root of the molecular weight. However, in the previous paper, we hesitated to stress the difference in the slopes between the good solvent condition and the Θ solvent condition due to the lack of data on the thickness in cyclohexane at 40 and 45 °C for the lower range of molecular weight. A closer inspection of the data[18] of thickness of the adsorbed polystyrene layer from carbon tetrachloride and toluene reveals that the slope of the molecular weight dependence of the thickness is smaller than 0.5.

The aim of this paper is to determine exactly the exponent of the molecular weight dependence of the thickness of the adsorbed layer in the good solvent condition experimentally. Measurements of adsorption of polystyrene onto chrome plates were carried out by ellipsometry using the same narrow molecular weight distribution samples reported previously.[17,18] Special attention was exercised to repeat at least duplicate runs to check the reproducibility of adsorption measurements. The dependence of the molecular weight on the thickness of the adsorbed polystyrene layer measured in cyclohexane and in carbon tetrachloride at 35 °C is examined and discussed in light of the theories with some reasonable assumptions, and particularly the exponent of the molecular weight dependency is quantitatively compared with the theoretical treatment of de Gennes based on scaling concepts.

## Experimental Section

**Samples.** Ten polystyrene samples with a narrow molecular weight distribution were purchased from Pressure Chemical Co. and from Toyo Soda Co. Their characteristics quoted from the manufacturers are given in Table I.

The cyclohexane and carbon tetrachloride solvents were purified by the procedure described in the previous papers.[7,18] Solvents and their polystyrene solutions were filtered through a Millipore FH-type filter.

Viscosity measurements of polystyrenes in cyclohexane at 40 and 45 °C and in carbon tetrachloride at 35 °C were carried out by using a Ubbelohde viscometer.

Electrodeposited chrome plates were used as substrates. They were cleaned by the method described previously.[7,17-19]

**Ellipsometry.** A Shimadzu horizontal ellipsometer was used. The details of the ellipsometric measurement and the analysis of the ellipsometric data were described in the previous papers.[7,17,19,20] All adsorption measurements were carried out at a polystyrene concentration where the plateau region in the adsorption isotherms is well established: in cyclohexane solutions at a polystyrene concentration of 0.3 g/100 mL and in carbon tetrachloride solutions at a polystyrene concentration of 0.1 g/100 mL. The measuring temperature was 40 and 45 °C in cyclohexane and 35 °C in carbon tetrachloride.

The ellipsometric data on the refractive index $n_f$ and the thickness $t$ of the uniform adsorbed layer give the adsorbance $A$ by using the equation

$$A = t(n_f - n_0)(\partial n/\partial C) = tC_f \qquad (1)$$

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. The same values as in the previous papers[17,18] for $n_0$ and $\partial n/\partial C$ for the respective solvents were employed.

## Results

Typical results for the thickness of the adsorbed layer $t$ as a function of adsorption time are shown in Figure 1 for P-3 and P-6 in cyclohexane at 40 °C, FF-35 and FF-36 in cyclohexane at 45 °C, and FF-33 in carbon tetrachloride at 35 °C. The open, half-closed, and closed points represent separate runs. The thickness values increase with adsorption time until a final equilibrium plateau is reached. The time required to attain the equilibrium plateau was about 500 min for all of the samples. The results for the different runs are represented by one curve for the respective molecular weights and show that the reproducibility of the measured thickness of the adsorbed polystyrene layer onto the chrome plate is very good for even triplicate runs.

Typical results for the adsorbance, $A$, are given in Figure 2. In a manner similar to the behavior of the thickness, the values of $A$ increase with time and finally reach constant values after 500 min. As seen from both Figures 1 and 2 we regard the data determined after 1 day as the

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Table I
Characteristics of Polystyrene

| sample[a] | $M_w \times 10^{-3}$ | $M_w/M_n$ | $[\eta]_{\text{cyclohexane}}$ at 40 °C | $[\eta]_{\text{cyclohexane}}$ at 45 °C | $[\eta]_{CCl_4}$ at 35 °C |
|---|---|---|---|---|---|
| P-3 | 110 | 1.06 | 0.258 | 0.275 | 0.500 |
| P-4 | 200 | 1.06 | | | 0.660 |
| P-5 | 498 | 1.06 | | | 1.05 |
| P-6[b] | 670 | 1.15 | 0.703 | 0.777 | |
| FF-32 | 775 | 1.04 | | | 1.82 |
| FF-33 | 2420 | 1.07 | 1.43 | 1.63 | 3.78 |
| FF-34 | 4590 | 1.08 | 2.04 | 2.35 | 5.10 |
| FF-35 | 7620 | 1.05 | 2.70 | 3.14 | 7.65 |
| FF-36 | 9700 | 1.06 | 3.09 | 3.61 | 9.30 |
| FF-37 | 13400 | 1.05 | 3.69 | 4.35 | |

[a] The P series was purchased from Pressure Chemical Co. and the FF series was purchased from Toyo Soda Co.
[b] Sample code P-1 in ref 17 corresponds to P-6 in this paper.

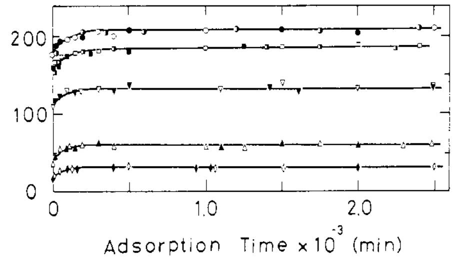

**Figure 1.** Thickness, $t$, of the adsorbed layer as a function of adsorption time: (◇,◆) $M_w = 110 \times 10^3$ in cyclohexane at 40 °C; (△,▲) $M_w = 670 \times 10^3$ in cyclohexane at 40 °C; (▽,▼) $M_w = 2420 \times 10^3$ in carbon tetrachloride at 35 °C; (□, ◧, ■) $M_w = 7620 \times 10^3$ in cyclohexane at 45 °C; (○,◑,●) $M_w = 9700 \times 10^3$ in cyclohexane at 45 °C. The open, half-closed, and closed points represent separate measurements made on the same chrome plate.

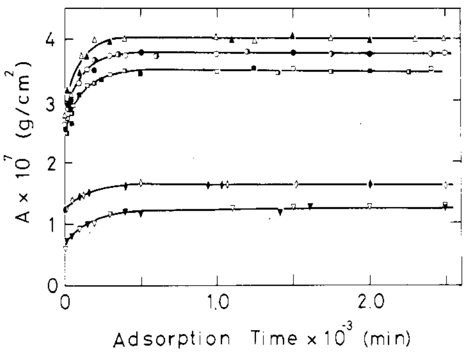

**Figure 2.** Adsorbance, $A$, as a function of adsorption time. Symbols are the same as in Figure 1.

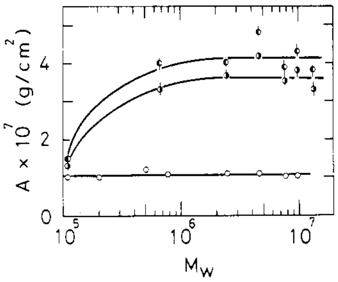

**Figure 3.** Adsorbance, $A$, vs. the molecular weight: (◐) cyclohexane at 40 °C; (◑) cyclohexane at 45 °C; (○) carbon tetrachloride at 35 °C.

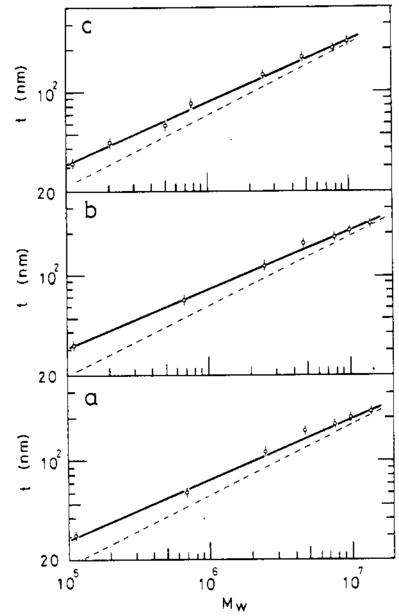

**Figure 4.** Thickness, $t$, of the adsorbed layer vs. molecular weight: (a) cyclohexane at 40 °C; (b) cyclohexane at 45 °C; (c) carbon tetrachloride at 35 °C.

equilibrium value. For other samples similar behaviors for plots of $t$ and $A$ as a function of adsorption time were observed.

In Table II, average values of $A$, $t$, and $C_f$ obtained from duplicate and triplicate runs are summarized for all of the samples used and the errors in the data are also included. For the respective samples adsorbances decrease in the order of solvent power, i.e., cyclohexane at 40 °C, cyclohexane at 45 °C, and carbon tetrachloride at 35 °C while the thickness of the adsorbed layer increases with increasing solvent power.

The adsorbances listed in Table II are plotted semilogarithmically against the molecular weight in Figure 3. The values of $A$ in cyclohexane increase until $M_w \sim 10^6$ and then become independent of the molecular weight, while the value of $A$ in carbon tetrachloride remains constant for all of the samples examined.

Figure 4 shows the double-logarithmic plot of the thickness of the adsorbed layer vs. the molecular weight. The vertical line for each point represents the range of the error in thickness measurements. The solid straight lines in the figure are drawn according to the best fitted line method for the respective solvents. For comparison the straight line with slope 0.5 is drawn (dashed line). The slopes of the solid lines are 0.4 ± 0.02 within experimental reproducibility and definitely smaller than 0.5.

## Discussion

Various theories[1-4] based on the mean field approach have been presented to explain the molecular weight dependence of the thickness of the adsorbed layer. It is generally predicted that the thickness of the adsorbed layer in the Θ solvent condition is proportional to the square root

Table II
Adsorption Data of Polystyrene onto a Chrome Plate and Critical Polymer Concentration $C^*$

| | $A \times 10^7$, g/cm$^2$ | | | $t$, nm | | | $C_f$, g/100 mL | | | $C^*$, g/100 mL | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | cyclohexane | | | cyclohexane | | | cyclohexane | | | cyclohexane | | CCl$_4$ |
| sample | at 40 °C | at 45 °C | CCl$_4$ at 35 °C | at 40 °C | at 45 °C | CCl$_4$ at 35 °C | at 40 °C | at 45 °C | CCl$_4$ at 35 °C | at 40 °C | at 45 °C | at 35 °C |
| P-3 | 1.5 ± 0.1 | 1.3 ± 0.1 | 1.0 ± 0.05 | 30 ± 2 | 32 ± 2 | 32 ± 2 | 5.0 ± 0.1 | 4.0 ± 0.1 | 3.3 ± 0.1 | $4.5_2$ | $4.2_3$ | $2.3_4$ |
| P-4 | | | 1.0 ± 0.05 | | | 44 ± 4 | | | 2.3 ± 0.1 | | | $1.7_7$ |
| P-5 | | | 1.2 ± 0.05 | | | 58 ± 4 | | | 2.0 ± 0.1 | | | $1.1_1$ |
| P-6 | 4.0 ± 0.2 | 3.4 ± 0.2 | | 60 ± 5 | 66 ± 5 | | 6.6 ± 0.1 | 5.1 ± 0.1 | | $1.6_6$ | $1.4_9$ | |
| FF-32 | | | 1.1 ± 0.05 | | | 83 ± 6 | | | 1.3 ± 0.05 | | | $0.64_8$ |
| FF-33 | 4.0 ± 0.2 | 3.7 ± 0.2 | 1.1 ± 0.05 | 112 ± 6 | 119 ± 6 | 130 ± 6 | 3.6 ± 0.1 | 3.1 ± 0.1 | 0.82 ± 0.05 | $0.81_6$ | $0.71_5$ | $0.30_9$ |
| FF-34 | 4.8 ± 0.2 | 4.2 ± 0.2 | 1.1 ± 0.05 | 162 ± 7 | 170 ± 7 | 175 ± 8 | 3.0 ± 0.1 | 2.5 ± 0.1 | 0.59 ± 0.04 | $0.57_1$ | $0.49_6$ | $0.22_9$ |
| FF-35 | 3.9 ± 0.2 | 3.5 ± 0.2 | 1.0 ± 0.05 | 178 ± 7 | 185 ± 7 | 202 ± 8 | 2.2 ± 0.1 | 1.9 ± 0.1 | 0.50 ± 0.03 | $0.43_3$ | $0.37_2$ | $0.15_1$ |
| FF-36 | 4.3 ± 0.2 | 3.8 ± 0.2 | 1.0 ± 0.05 | 203 ± 8 | 209 ± 8 | 222 ± 10 | 2.1 ± 0.1 | 1.8 ± 0.1 | 0.45 ± 0.03 | $0.37_3$ | $0.32_3$ | $0.12_6$ |
| FF-37 | 3.8 ± 0.2 | 3.3 ± 0.2 | | 221 ± 10 | 232 ± 10 | | 1.7 ± 0.1 | 1.4 ± 0.05 | | $0.31_3$ | $0.26_6$ | |

of the molecular weight irrespective of the different conformational models for the adsorbed polymer chains.

We reported that the thickness of the adsorbed polystyrene layer onto a chrome plate in $\Theta$ solvent (cyclohexane at 35 °C) is proportional to the square root of the molecular weight for molecular weight ranging from $110 \times 10^3$ and $13.4 \times 10^6$.[7] Similar experimental results were reported by Stromberg, Tutas, and Passaglia[5] and by Gebhard and Killmann[6] using ellipsometry as well as by Dejardin and Varoqui[8] using a hydrodynamic method.

Some theories predict that the thickness of the adsorbed layer in good solvent conditions is smaller than that in the $\Theta$ condition,[3,4,12] while others suggest that the thickness of the adsorbed layer is larger than that in the $\Theta$ solvent condition.[10,14,15] Also, the molecular weight dependence of the thickness of the adsorbed layer in good solvent conditions has not yet been established.

In particular, the theories of Silberberg[3] and Scheutjens and Fleer[4] deal with the thickness of the adsorbed layer as a function of molecular weight by using the lattice model. With a loop–train conformation, Silberberg suggested that the thickness corresponding to the average loop length becomes smaller with increasing solvent power, and the molecular weight dependence of the loop size in good solvent conditions is less than that in the $\Theta$ solvent condition. While Scheutjens and Fleer employed the loop–train–tail conformation for the adsorbed chains and concluded that not only the molecular weight dependence of the thickness of tails and loops but also that of the overall thickness consisting of an average of the loop and tail thickness values are proportional to the square root of the molecular weight in any solvent conditions. Hence, both theories do not interpret quantitatively the measured molecular weight dependence of the thickness of the adsorbed polystyrene layer onto a chrome plate in good solvent conditions.

Recently, de Gennes[16] suggested that the molecular weight dependence of the thickness of the adsorbed layer can be derived from the concentration profile for a polymer solution near an adsorbing wall constructed by using scaling concepts. Since the polymer concentration $\phi(z)$ in the adsorbed layer at a distance $z$ from the wall assumes a moderate value, the local correlation length $\xi$ in the adsorbed layer is expressed as a function of $\phi(z)$. In good solvent conditions $\xi$ is given by[21]

$$\xi = a\phi(z)^{-3/4} \tag{2}$$

where $a$ is the length of a monomer. If we could know the concentration profile $\phi(z)$ and stand at a given distance from the wall, we can construct a value of $\xi[\phi(z)]$. Therefore, the only possible function $\xi$ is a function $z$ as follows:

$$\xi[\phi(z)] \sim z \tag{3}$$

Thus, we arrive at the following result by imposing the conditions of eq 2 and 3.

$$\phi(z) = (a/z)^{4/3} \sim z^{-4/3} \tag{4}$$

The resulting profile is universal and independent of the polymer concentration in the bulk solution and, moreover, is different from the profile calculated by Jones and Richmond[15] based on mean field theory. Since eq 4 holds until $z = \xi_b$,[16a] which is the correlation length of the bulk solution, we calculate the average thickness of the adsorbed layer from the wall by using eq 4

$$\bar{z} = \int_0^{\xi_b} z\phi(z)\,dz \sim \xi_b^{2/3} \tag{5}$$

The upper limit $\xi_b$ of the integration range depends on the polymer concentration in the bulk polymer solution.

The thickness of the adsorbed layer determined by ellipsometry corresponds to an average thickness of the uniform adsorbed layer and ellipsometry gives no information about the concentration profile in the adsorbed polymer layer. We presume that $t$ is proportional to $\bar{z}$, and we qualitatively compare the measured thickness $t$ with the value of $\bar{z}$ calculated from eq 5. Therefore, we do not convert $t$ into the root-mean-square thickness $t_{\mathrm{rms}}$ as proposed by Stromberg, Tutas, and Passaglia.[5]

The correlation length of $\xi$ depends on the polymer concentration.[21] The value of $\xi$ is considered to be equal to the Flory radius $R_{\mathrm{F}} = \langle S^2\rangle^{1/2}$ below the critical polymer concentration $C^*$, where polymer coils begin to overlap. The value of $C^*$ is defined by

$$C^* = M/(4/3)\pi\langle S^2\rangle^{3/2}N_{\mathrm{A}} \tag{6}$$

where $M$ is the molecular weight of the polymer and $N_{\mathrm{A}}$ is Avogadro's number. The value of $\langle S^2\rangle^{1/2}$ is related to the intrinsic viscosity $[\eta]$ as follows:[22]

$$[\eta] = 6^{3/2}\phi\frac{\langle S^2\rangle^{3/2}}{M} \tag{7}$$

where $\phi$ is Flory's universal constant. Since data on $\langle S^2\rangle^{1/2}$ for polystyrene in the three solvents used are unavailable, we estimated $\langle S^2\rangle^{1/2}$ from eq 7 by using the intrinsic viscosity listed in Table I. In the calculation we assumed $\phi = 2.0 \times 10^{21}$ for the respective solvents. The values of $C^*$ calculated from such a procedure are summarized in Table II. As seen from the calculated value of $C^*$, the measuring bulk polystyrene concentration corresponds to the dilute region. Therefore, the correlation length in the bulk polymer solution is equivalent to the Flory radius $R_{\mathrm{F}}$. This fact means that the upper limit of integration in eq 5 corresponds to $R_{\mathrm{F}}$, and that the average polymer concentration $C_{\mathrm{f}}$ in the adsorbed layer is larger than the $C^*$ value. Since the Flory radius is given by $R_{\mathrm{F}} = aN^{3/5}$[21] in good solvent, where $N$ is the degree of polymerization, the molecular weight dependence of $\bar{z}$ is calculated by substituting $R_{\mathrm{F}}$ into $\xi_{\mathrm{b}}$ in eq 5. We obtain

$$t \sim \bar{z} = \int_0^{R_{\mathrm{F}}} z\phi(z)\,\mathrm{d}z \sim R_{\mathrm{F}}^{2/3} \sim N^{2/5} \tag{8}$$

Note that the thickness of the adsorbed layer is proportional to $N^{0.4}$, *whereas mean field theory*[15,21] *in good solvent, where* $\phi(z) \sim z^{-2}$, *leads to an even weaker* $t \sim \ln N$ *molecular weight dependence.*

Since cyclohexane at 40 °C and cyclohexane at 45 °C are less good solvents than carbon tetrachloride for polystyrene, they should be regarded to be in the vicinity of the Θ solvent condition. In analogy to de Gennes' calculation described above, we can derive the concentration profile for an adsorbed polymer chain in the vicinity of the Θ condition by using the following relations of $\xi$ and $R_{\mathrm{F}}$ derived by Daoud and Jannink[23] as a function of the reduced temperature $\tau = T/\Theta - 1$ with the theta temperature, Θ.

$$\xi \sim \phi^{\nu/(1-\nu d)}\tau^{(\nu-\nu_{\mathrm{t}})/\psi_{\mathrm{t}}(1-\nu d)} \tag{9}$$

$$R_{\mathrm{F}} \sim aN^{\nu}\tau^{(\nu-\nu_{\mathrm{t}})/\psi_{\mathrm{t}}} \tag{10}$$

where $\nu$ is the critical exponent of the excluded volume, $\nu_{\mathrm{t}}$ and $\psi_{\mathrm{t}}$ are the tricritical exponents of the excluded volume and crossover, respectively, and $d$ is the space dimensionality. For $d = 3$, eq 9 and 10 can be rewritten by introducing $\nu = 0.6$, $\nu_{\mathrm{t}} = 0.5$, and $\psi_{\mathrm{t}} = 0.5$.

$$\xi \sim \phi^{-3/4}\tau^{-1/4} \tag{11}$$

$$R_{\mathrm{F}} \sim N^{3/5}\tau^{1/5} \tag{12}$$

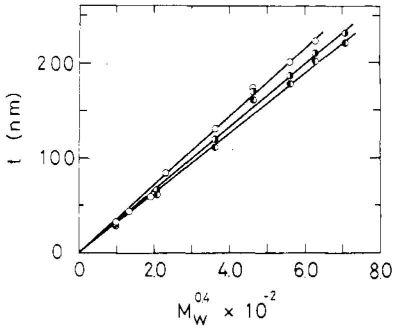

**Figure 5.** Plots of thickness, $t$, of the adsorbed layer against $M^{0.4}$. Symbols are the same as in Figure 3.

We obtain the concentration profile $\phi'(z)$ in the vicinity of the Θ solvent condition as follows:

$$\phi'(z) = (a/z)^{4/3}\tau^{-1/3} \tag{13}$$

Thus, $\phi'(z)$ shows the same function of $z$ as eq 4. The thickness of the adsorbed layer is calculated from

$$t \sim \bar{z} = \int_0^{R_{\mathrm{F}}} z\phi'(z)\,\mathrm{d}z \sim \tau^{-1/3}R_{\mathrm{F}}^{2/3} \sim \tau^{-1/5}N^{2/5} \tag{14}$$

Note that eq 14 still shows that *even in the vicinity of the Θ solvent condition* the thickness of the adsorbed layer is also proportional to $N^{0.4}$. Since the good solvent condition corresponds to $\tau$ approaching unity, we obtain the relation of $\xi \sim \phi^{-3/4}$ and $R_{\mathrm{F}} \sim aN^{3/5}$.

Figure 5 demonstrates the plot of the measured values of $t$ in three solvents against $M^{0.4}$. Thus, aside from the absolute values of thickness, it is clear from the figure that the thickness of the adsorbed layer is well fitted on the respective straight lines as predicted by de Gennes' approach for polymer adsorption based on scaling concepts.

Incidentally, de Gennes' approach will lead to the molecular weight dependence of the thickness of the adsorbed layer in the Θ solvent condition by using a method similar to that employed in the good solvent condition. In the Θ solvent condition, by substituting $\nu = \nu_{\mathrm{t}} = 0.5$, $\psi_{\mathrm{t}} = 0.5$, and $d = 3$ into eq 9 and 10, we obtain $R_{\mathrm{F}\Theta} = aN^{1/2}$ and $\xi_{\Theta} \sim \phi^{-1}$. Using these relationships, we can derive the concentration profile $\phi_{\Theta}(z)$ of the adsorbed polymer in the Θ solvent condition as follows:

$$\phi_{\Theta}(z) = a/z \tag{15}$$

The concentration profile is proportional to the inverse of the distance $z$ and its dependence is different from that in good solvent conditions. The thickness of the adsorbed layer in the Θ solvent condition is calculated as

$$t_{\Theta} \sim \bar{z} = \int_0^{R_{\mathrm{F}\Theta}} z\phi_{\Theta}(z)\,\mathrm{d}z \sim R_{\mathrm{F}\Theta} \sim N^{1/2} \tag{16}$$

Equation 16 shows that the molecular weight dependence of the thickness of the adsorbed layer derived from the scaling concepts is quite the same as derived by the mean field approach.[1-4]

## Conclusions

We have extensively and rigorously accumulated data on the thickness of an adsorbed polystyrene layer onto a chrome surface in the vicinity of the Θ solvent condition and good solvent condition by using ellipsometry in order to check the reproducibility in the adsorption experiments. We found that the molecular weight dependence of the adsorbed layer in three good solvents is clearly less than that in the Θ solvent condition. Though ellipsometry yields no information about the concentration profile in the adsorbed layer, we compared the exponent in the molecular

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weight dependence of the measured thickness of the adsorbed polystyrene layer with that of the average thickness of the adsorbed layer calculated from the concentration profile in the adsorbed polymer chain derived by de Gennes. We found the exponent to be in good agreement with the theoretical calculation of de Gennes.

**Acknowledgment.** M.K. is pleased to express his thanks to Professor P.-G. de Gennes for his encouragement and useful discussion.

**Registry No.** Polystyrene, 9003-53-6.

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# Viscoelastic Behavior of Atactic Polypropylene

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ABSTRACT: The shear creep and recovery behavior of completely amorphous polypropylene was determined at 14 temperatures between −19 and +71 °C. The resulting compliance curves were reduced to 25 °C with apparent success, indicating thermorheological simplicity, but extensive viscosity measurements indicated a different temperature dependence from that of the recoverable compliance in the softening transition, which precludes such simplicity. The retardation spectrum and other viscoelastic functions have been calculated from the creep and recovery response. The glass temperature was ascertained to be −14 °C, and the molecular weight per entangled unit was found to be 4650. The form of the viscoelastic response in the softening transition was found to be semiquantitatively the same as that of polystyrene and poly(vinyl acetate).

## Introduction

Isotactic polypropylene, PP, is an important commercial polymer and as such its physical properties have been investigated extensively. Since it cannot be quenched to the completely amorphous state, only the mechanical response of the partially crystalline material has been measured.[1-8] Most of the measurements were made with a continuously varying temperature and a constant frequency or a slowly varying natural frequency of free oscillation or vibration. A few bona fide viscoeleastic studies have been made on partially crystalline polypropylene which was predominantly isotactic. Maxwell and Heider[9] measured the complex dynamic elongational modulus over 5 decades of frequency ($10^{-3}$–$10^{2}$ Hz) at 11 temperatures between 30 and 110 °C. The results showed the polycrystalline material to be thermorheologically complex; at least three different groups of loss mechanisms were observed.

Earlier, Faucher reported[10] elongational stress relaxation moduli ($E(t)$) measured at times from 10 to 2000 s on highly crystalline isotactic PP at 18 temperatures from −67 to +140 °C. His relaxation spectrum obtained from a reduced modulus curve also indicated three sets of viscoelastic mechanisms. He also presented $E(t)$ curves measured at 14 different temperatures from −67 to +50 °C on a sample of "amorphous" polypropylene. This sample was an ethyl ether extract of a polypropylene of low-crystallinity content. This predominantly amorphous material was estimated from its density of 0.856 g/cm$^3$ to be about 8% crystalline. The density $\rho$ (25 °C) for completely amorphous PP is 0.850 g/cm$^3$.[11] The softening dispersion peak of the amorphous component dominates the relaxation spectrum $H$ of this material. However, the crystalline fraction prevents viscous relaxation, corresponding to the flow or permanent deformation that one would observe in a creep experiment. Hence, $H$ does not drop off rapidly toward zero at long times as it does for viscoelastic fluids. Instead relaxation mechanisms are found over the entire measured reduced time-scale range.

Creep measurements have also been made on samples of PP with high and low degrees of crystallinity by Hideshima,[12] but, unfortunately, only the time-scale shift factors were reported. The principal goal in his report was to explain the wide range of glass temperature ($T_g$) values (−35 to +7 °C) that have been reported in the literature.[2-8,13-17] Natta et al.[13] interpreted the volume–temperature curves of a number of polypropylenes with varying tacticities to all show a $T_g$ break at −35 °C. Hideshima concurred that such breaks are present but that alternate approximately linear portions of the volume–temperature