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Hydrodynamic Studies on Adsorption of Poly(ethylene oxide) in Porous Media. 2.[†] Molecular Weight Dependence of Hydrodynamic Thickness

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ABSTRACT: The hydrodynamic thickness, L_H, of an adsorbed poly(ethylene oxide) (PEO) layer on the pore wall of a Millipore filter was determined by measuring volume flow rates of water (solvent) through the pores as a function of molecular weight. L_H increased with adsorption time and attained its equilibrium value after 1 week for each sample. The time for reaching the equilibrium value was longer with a larger molecular weight sample. The plateau L_H values were half the radius of gyration of an isolated polymer chain in bulk solution. This indicates a flattened conformation of the adsorbed polymer chains. The exponent for the molecular weight dependence of the plateau L_H was obtained to be 0.40, in good agreement with the case of adsorption of polystyrene onto a chrome plate in CCl_4 studied by ellipsometry. The absolute value of the exponent was smaller than that for the molecular weight dependences of the intrinsic viscosity and also the radius of gyration of PEO in water.

The thickness of the adsorbed layer on a solid–liquid interface is one of the most important experimental parameters to describe the conformation of an adsorbed polymer chain. Several experimental methods are now available to measure the thickness of the adsorbed polymer layer: ellipsometry,[1] volume flow,[2] sedimentation,[3] photon correlation spectroscopy,[4] small-angle neutron scattering,[5] and disjoining pressure measurement[6] as well as force–distance measurements[7] between adsorbed polymer layers. It appears that the different methods offer somewhat different measures for the thickness: for example, the thickness measured by photon correlation spectroscopy is larger than that measured by small-angle neutron scattering;[5] both disjoining pressure[6] and force–distance measurements[7] can detect adsorbed chains at a greater distance from the surface compared with other techniques, e.g., ellipsometry. Thus, the absolute values of the thickness of the adsorbed polymer layer depend on the experimental method used.

Nevertheless, the proportionality of the thickness of adsorbed polymer layer with the square root of the molecular weight of polystyrene with a narrow molecular weight distribution under Θ solvent conditions has been obtained by both ellipsometry[1,8,9] and volume flow measurement,[10] and this experimental result is in good agreement with theoretical treatments.[11-15] On the other hand, under good solvent conditions such a consistency has not yet been established since few experiments have been carried out under these conditions, especially with samples with a narrow molecular weight distribution. Available data are described below.

A photon correlation spectroscopic study to measure the adsorbed thickness of poly(ethylene oxide) on polystyrene latex was made by Kato et al.[16] who showed that the thickness is approximately proportional to $M^{0.56}$. Recently, Cosgrove et al.[17] obtained an exponent of 0.8 for a similar system by the same technique.

Kawaguchi and Takahashi[18] extensively accumulated data on the thickness of an adsorbed polystyrene layer on a chrome surface in carbon tetrachloride at 35 °C by ellipsometry. They found the exponent for the molecular weight dependence of the thickness of the adsorbed layer to be 0.4. This small exponent was in good agreement with scaling concepts.[19]

The aim of this paper is to further accumulate experimental data on the hydrodynamic thickness of the adsorbed layer in good solvent conditions and to clarify the molecular weight dependence of the thickness by using homodisperse poly(ethylene oxides). Volume flow rate measurements of water through the pore coated by poly(ethylene oxide) were carried out as a function of molecular weight at 35 °C. Measurements were performed by repeating at least five runs to check the reproducibility. The exponent of the molecular weight dependence of the hydrodynamic thickness is discussed by comparison with the molecular weight dependences of the dimensions of free PEO chains in water.

Table I
Characteristics of Poly(ethylene oxides)

sample	$M_w \times 10^{-3}$	M_w/M_n	$[\eta]$, 100 mL/g
PEO-1	40	1.03	0.580
PEO-2	73	1.02	0.894
PEO-3	150	1.04	1.44
PEO-4	660	1.10	4.00
PEO-5	1200	1.12	6.32

Experimental Section

Materials. Five poly(ethylene oxides) (PEO) with a narrow molecular weight distribution were purchased from Toyo Soda Co. Intrinsic viscosity measurements of PEO in water at 35 °C were carried out with an Ubbelohde-type viscometer. Characteristics of PEO are listed in Table I.

The solvent water was doubly distilled by using a Pyrex apparatus.

The porous media used as an adsorbent were Millipore filters, Type HA, made from a mixture of cellulose esters. According to the manufacturer the diameter is 2.5 cm, the thickness is 1.5 × 10^{-2} cm, the average pore diameter is 0.45 μm, and the porosity is 79%. The Millipore filters were soaked and washed thoroughly with water and then were treated under vacuum to remove trapped air.

Measurement of Water Permeability. Volume flow rate was measured by weighing the amount of water through the filter as a function of time under a constant hydrostatic head, h, of 15 cm of H_2O, which was maintained by using a glass apparatus equipped with two water reservoirs with a volume of 500 mL connected by glass tubes as shown in Figure 1. The pressure change during the measurements is negligible owing to the large volume of the reservoirs. The Millipore filter was mounted in a Millipore filter holder Type Swinnex 25 made from polypropylene. The apparatus was placed in an air box controlled at 35 ± 0.1 °C.

After the volume flow rate of water through a soaked filter was measured, the filter was placed in a closed vessel containing 20 mL of aqueous PEO solution with known concentration, and the vessel was put in an air box controlled at 35 ± 0.1 °C and left for determined time intervals. After a predetermined time, the filter was removed and washed with water, and the volume flow

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[†] Part 1 is ref 18.

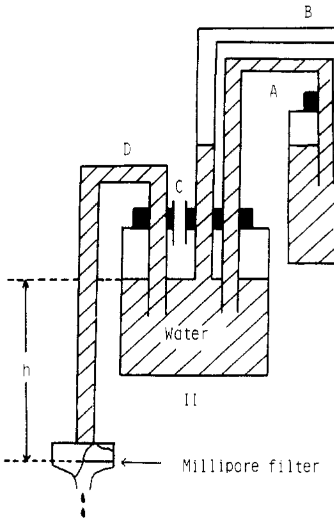

Figure 1. Schematic illustration of flow rate apparatus. I and II are water reservoirs; A, B, C, and D are glass tubes.

rate of water through the adsorbed filter was measured. The volume flow rate of water was taken as an average value over all water permeability measurements.

The volume flow rates, Q_0 and Q, of water before and after adsorption are expressed in units of $cm^3\ s^{-1}$, respectively. According to Poiseuille's law the hydrodynamic thickness, L_H, of an adsorbed polymer layer is expressed in terms of Q_0, Q, and the pore radius, r.

$$L_H = r[1 - (Q/Q_0)^{0.25}] \quad (1)$$

Here, we employed the manufacturer's value of 0.225 μm for r. At a given concentration five sheet filters were used and five runs of the measurement of water permeability were performed for each sheet. Average L_H values contain experimental errors within 10%.

Results and Discussion

The hydrodynamic thickness, L_H, corresponds to the reduction of the pore size from r to $r - L_H$ due to adsorption. Varoqui and Dejardin[20] first showed that L_H can be theoretically related to the average loop length, b, of the adsorbed polymer chains for an exponential distribution of segment density in the adsorbed layer as a function of the pore radius by taking into account hydrodynamic interaction. They showed that L_H can be written as the product of r and a function F of r/b and the dimensionless "shielding ratio" parameter, b/l, as follows:

$$L_H = rF(r/b;b/l) \quad (2)$$

Here l is defined as

$$l = (\eta/fn_0)^{1/2} \quad (3)$$

where η is the viscosity of the liquid, f is the friction coefficient between polymer and liquid, and n_0 is the polymer density in the adsorbed layer. Since the direct experimental determination of n_0 is difficult at the present time, we cannot easily convert L_H into a suitable value using eq 2. Therefore, we will employ the L_H calculated from eq 1 for the discussion below.

Figure 2 displays the hydrodynamic thickness, L_H, as a function of adsorption time for various molecular weights at dosed PEO concentrations, C_p, around 2.0×10^{-2} g/100 mL. L_H gradually increases with adsorption time and attains a constant value. The time required to reach the constant value is longer for larger molecular weight. After 1 week the final equilibrium is established for all samples. Therefore, L_H values determined after 1 week were taken as equilibrium values. The time to reach an equilibrium value is much longer than in the case of ellipsometric measurement.[1,8,9,18,21] The slow attainment of the equilibrium agrees with the adsorption of poly(vinyl acetates)[22] and polyacrylamides[23] onto the same type of filter. The long time required for attainment of the equilibrium may be attributed to the enhanced slower diffusion process of a larger molecular weight sample caused by the increase of surface population of polymers. For other concentrations similar results were obtained.

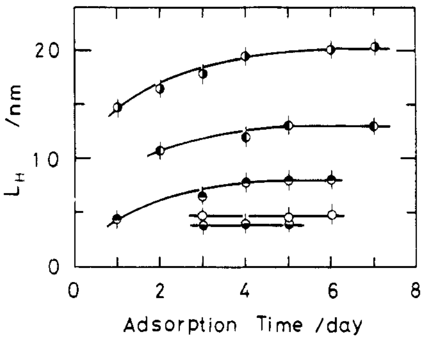

Figure 2. Plots of L_H as a function of adsorption time. PEO concentration, C_p, expressed by g/100 mL. (◒) PEO-1, $C_p = 0.02$; (○) PEO-2, $C_p = 0.02$; (⊖) PEO-3, $C_p = 0.019$; (◐) PEO-4, $C_p = 0.021$; (◑) PEO-5, $C_p = 0.019$.

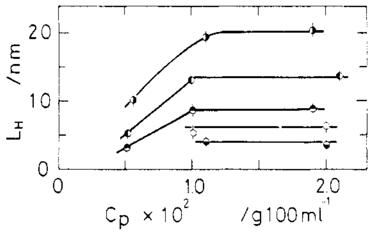

Figure 3. Plots of L_H vs. PEO concentration. Symbols are the same as in Figure 2.

Table II
Hydrodynamic Thickness (L_H), Radius of Gyration ($\langle S^2 \rangle^{1/2}$), and Photon Correlation Spectroscopy Thickness (t_{pcs})

sample	L_H	$\langle S^2 \rangle^{1/2}$, nm	t_{pcs},[a] nm
PEO-1	4.5_5	9.2_3	20
PEO-2	6.2_7	$13._1$	29
PEO-3	8.7_6	$19._4$	44
PEO-4	$13._6$	$44._9$	99
PEO-5	$20._3$	$63._7$	156

[a] Data quoted from ref 16.

Plots of the equilibrium value of L_H against dosed PEO concentration, C_p, are shown in Figure 3 for various molecular weights. The value of L_H increases at lower C_p and then reaches a constant value above $C_p = 1.0 \times 10^{-2}$ g/100 mL, irrespective of molecular weight. The plateau values of L_H measured at the highest dosed PEO concentration (around 2.0×10^{-2} g/100 mL) are well into the plateau region for all samples and they are listed in Table II.

Figure 4 shows a double-logarithmic plot of L_H measured at the highest dosed PEO concentration against the molecular weight of PEO. The solid straight line with the slope of 0.4 is drawn in the figure. This exponent agrees with the case for adsorption of polystyrene from carbon tetrachloride onto a metal surface.[18]

In the past, comparison between L_H and the intrinsic viscosity, $[\eta]$, has been made, leading to linear relationships between L_H and $[\eta]$.[2,10,22] As a result, it has often been concluded that the molecular weight dependence of L_H is quite the same as that of $[\eta]$. However, in this case, the molecular weight dependence of L_H is weaker than the exponent 0.69 for the molecular weight dependence of $[\eta]$ as seen from Figure 4. This experimental finding may

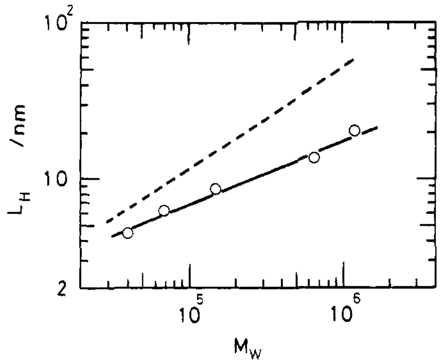

Figure 4. Double-logarithmic plot of L_H vs. molecular weight of PEO. The dashed line denotes an exponent of 0.69 for the molecular weight dependence of the intrinsic viscosity of PEO in water 35 °C.

show that PEO chains are adsorbed with much distortion in comparison with a random coil; i.e., the conformation of adsorbed PEO chains is considered to be a flattened one.

The L_H values can be compared with the thickness data, t_{pcs}, for the adsorption of PEO on polystyrene latices using photon correlation spectroscopy in Table II. The L_H values are considerably smaller than t_{pcs} values for the same molecular weight. The different magnitudes for L_H and t_{pcs} can be attributed to the different surface characters of the adsorbents rather than the difference in experimental techniques: cellulose ester is more polar than polystyrene. Thus, PEO molecules adsorb more strongly on cellulose ester filters than on polystyrene latices. Therefore, strong adsorption may lead to a flattened conformation for adsorbed PEO.

Recently, de Gennes[19] proposed a concentration profile from an adsorbing wall for good solvent conditions in terms of scaling concepts. The concentration profile is quite different from that derived by Jones and Richmond[24] based on the mean field theory.

Eisenriegler, Kremer, and Binder[25] have pointed out that the concentration profile close to the adsorbing wall (proximal region) proposed by de Gennes is not valid and showed the correct form for the proximal region. de Gennes and Pincus[26] then revised the earlier paper and reached the same results as Eisenriegler et al. Eisenriegler[27] carried out a detailed analysis of the earlier paper[19] of de Gennes, but his concentration profile for the central and distal regions was the same as that of de Gennes.[19]

In ref 19 de Gennes particularly referred to an effective hydrodynamic thickness, L_H, of the adsorbed polymer layer by considering a weak shear flow near the adsorbing wall in the limit $\phi_b \rightarrow 0$ (flows of the pure solvent), where ϕ_b is the concentration of the bulk solution. Such a limit ($\phi_b = 0$) corresponds to this experimental condition. de Gennes constructed the concentration profile inside the adsorbed layer to determine L_H using dynamical scaling arguments.[19] The resulting concentration profile is different from the exponential concentration profile. Thus he was led to a conclusion that L_H scales like the Flory radius, $\langle S^2 \rangle^{1/2}$.

For comparison the $\langle S^2 \rangle^{1/2}$ values of PEO in water are listed in Table II. The values of $\langle S^2 \rangle^{1/2}$ are calculated from the equation

$$[\eta] = 6^{3/2}\Phi \frac{\langle S^2 \rangle^{3/2}}{M_w} \qquad (4)$$

We employ Flory's universal constant Φ as 2.0×10^{21}. The orders of magnitude for L_H and $\langle S^2 \rangle^{1/2}$ are in good agreement, but the L_H is about half of $\langle S^2 \rangle^{1/2}$. The molecular weight dependence of $\langle S^2 \rangle^{1/2}$ is obtained to be 0.56 and this exponent is larger than the exponent of L_H. This difference is difficult to interpret and may be attributed to the fact that PEO chains are adsorbed strongly on the polar concave surface of the cellulose ester filter. Such a discrepancy of the exponents between the hydrodynamic thickness and the radius of gyration was also obtained by Cosgrove et al.[17] However, in our previous paper[16] both exponents agree well. Clearly, further theoretical work and accumulation of extensive experimental data are necessary to interpret the exponents.

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