relaxation processes at long channel times. The true value of Q should indeed be positive, but its random variation may extend to the negative domain.

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Appendix. Derivation of Eq 6

For a function $f(x) = b_0 + b_1x + b_2x^2 + \epsilon$, as in eq 1, its matrix representation is

$$\mathbf{F} = \mathbf{xB} + \mathbf{E}$$

where

$$\mathbf{F} = \begin{pmatrix} f_1 \\ f_2 \\ \cdot \\ \cdot \\ \cdot \\ f_n \end{pmatrix} \qquad \mathbf{x} = \begin{pmatrix} 1 & x_1 & x_1^2 \\ 1 & x_2 & x_2^2 \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 1 & x_n & x_n^2 \end{pmatrix} \qquad \beta = \begin{pmatrix} b_0 & b_1 & b_2 \end{pmatrix}$$

and

$$\mathbf{E} = \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \\ \cdot \\ \cdot \\ \cdot \\ \epsilon_n \end{pmatrix}$$

and $\mathbf{x}^{\mathrm{T}}$ is the transpose of the matrix $\mathbf{x}$. The estimated values (β_0, β_1, β_2) for the corresponding parameters (b_0, b_1, b_2) are given by (see eq 2.1.17 of ref 4)

$$\beta = \begin{pmatrix} \beta_0 \\ \beta_1 \\ \beta_2 \end{pmatrix} = (\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}\mathbf{x}^{\mathrm{T}}\mathbf{F}$$

using the relationships Var $(\mathbf{kx}) = \mathbf{k}[\mathrm{Var}\ (\mathbf{x})]\mathbf{k}^{\mathrm{T}}$, and $(\mathbf{AB})^{\mathrm{T}} = \mathbf{B}^{\mathrm{T}}\mathbf{A}^{\mathrm{T}}$

$$\begin{aligned} \mathrm{Var}\ (\beta) &= [(\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}\mathbf{x}^{\mathrm{T}}][\mathrm{Var}\ (\mathbf{F})][(\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}\mathbf{x}^{\mathrm{T}}]^{\mathrm{T}} \\ &= (\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}[\mathbf{x}^{\mathrm{T}}\ \mathrm{Var}\ (\mathbf{F})\mathbf{x}](\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1} \end{aligned}$$

Since Var $(\mathbf{F})$ = Var $(\mathbf{xB})$ + Var $(\mathbf{E})$ = Var $(\mathbf{E}) = \sigma^2$

$$\mathrm{Var}\ (\beta) = \sigma^2(\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1} \qquad \text{(see eq 2.3.1 of ref 4)}$$

Now, if the noise appears in the exponential function

$$f(x) = \exp(b_0 + b_1x + b_2x^2) + \epsilon$$

and a linear least-squares fit is done on $\ln f(x)$

$$\begin{aligned} f'(x) &= \ln\ (e^{b_0+b_1x+b_2x^2+\epsilon}) \\ &= (b_0 + b_1x + b_2x^2) + \epsilon e^{-(b_0+b_1x+b_2x^2)} \end{aligned}$$

the Variance Matrix becomes

$$\mathrm{Var}\ (\beta') = \begin{pmatrix} \beta_0' \\ \beta_1' \\ \beta_2' \end{pmatrix} = (\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}[\mathbf{x}^{\mathrm{T}}\ \mathrm{Var}\ (\mathbf{F}')\mathbf{x}](\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}$$

Since Var $(\mathbf{F}') = \mathbf{W}[\mathrm{Var}\ (\mathbf{E})]\mathbf{W}^{\mathrm{T}} = \sigma^2\mathbf{W}\mathbf{W}^{\mathrm{T}} = \sigma^2\mathbf{W}^2$ where $\mathbf{W}$ is a diagonal matrix with elements

$$W_{ii} = \exp[(b_0 + b_1x_i + b_2x_i^2)]$$

$$\mathrm{Var}\ (\beta') = \sigma^2(\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}(\mathbf{x}^{\mathrm{T}}\mathbf{w}^2\mathbf{x})(\mathbf{x}^{\mathrm{T}}\mathbf{x})^{-1}.$$

Registry No. Polystyrene, 9003-53-6.

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Static and Dynamic Solution Properties of Pullulan in a Dilute Solution

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ABSTRACT: Pullulan, an extracellular polysaccharide, has been studied in the dilute region by both static and dynamic light scattering techniques. The samples used are fractions with narrow molecular weight distribution over the range of molecular weight from 5×10^3 to 2.4×10^6. The radii of gyration (R_G) have been estimated from the scattered light intensity with the usual Zimm plot. The hydrodynamic radii (R_H) have been obtained from the translational diffusion coefficient (D_0) at infinite dilution. The characteristic exponents for the molecular weight dependence of polymer chain dimensions in good solvents are determined as ν_G for the R_G values and ν_H for the R_H values, respectively. The ν_G value ($\nu_G = 0.58$) falls close to the asymptotic value predicted theoretically. The ν_H value ($\nu_H = 0.52$) is, however, smaller than the ν_G value obtained. The ratios ($\rho = R_G/R_H$) estimated from the experimental results for each fraction used are discussed. The concentration dependence coefficients (k_D) of the diffusion coefficient are also discussed in terms of the hydrodynamic theories. It is confirmed that pullulan aqueous solutions behave as typical solutions of linear polysaccharides in good solvents.

Introduction

Polymer chain dimensions in dilute solutions have been determined conventionally by both static and dynamic light scattering experiments. For samples having sufficiently high molecular weight, the dimensions extrapolated to the infinite dilution limit depend on the molecular weight, M, at a constant temperature as a simple power law:

$$R_G \sim M^{\nu_G} \qquad (1)$$

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$$R_H \sim M^{\nu_H} \quad (2)$$

where R_G is the radius of gyration obtained by static light scattering measurements and R_H is the hydrodynamic radius estimated through the translational diffusion coefficient using dynamic light scattering measurements. The characteristic exponents, ν_G and ν_H, have been of interest both experimentally and theoretically. The consistency between the values of ν_G and ν_H was predicted by Flory[1] in terms of nondraining chain concepts and also in terms of recent arguments proposed by de Gennes.[2,3] The theoretical values in the asymptotic limit of excluded volume effect are $\nu = 0.6$ in Flory's theory and $\nu = 0.588$ in the renormalization calculation.[4] However, many experimental examples for discrepancies between static and dynamic characteristic exponents were reported for polystyrene in various good solvents[5-7] and polyacrylamide in water.[8] Moreover, interpretations of these discrepancies were successfully discussed using the blob models.[9-11]

On the contrary, experimental results for polystyrene in toluene at 20 °C obtained by Appelt and Meyerhoff[12] and those for poly(α-methylstyrene) in toluene at 25 °C and in benzene at 30 °C obtained by Selser[13] seemed to support the consistency of the exponents even in the molecular weight range used in experiments.

Consequently, at the present stage of the discussions, it is very important to accumulate experimental results for various kinds of polymers and also to investigate whether the molecular architecture of a polymer sample affects its dilute solution behavior in good solvents.

For these purposes, pullulan, an extracellular polysaccharide of the fungus *Aureobasidium pullulans*, was chosen as a polymer sample for systematic investigation. Pullulan is a flexible, amorphous, and water-soluble polymer. The molecular architecture is a linear polysaccharide polymerized from maltotriose as the repeating unit through the α-1,6-glucosidic linkage. Recently, studies of the basic molecular characteristics of pullulan have been reported elsewhere.[14-16]

In this study, both static and dynamic light scattering measurements were carried out in water at 25 °C using samples with narrow molecular weight distribution over a range of molecular weight. Finally, with the experimental results obtained, the dilute solution behavior of pullulan is discussed in the terms of both static and dynamic properties.

Experimental Section

Materials. Pullulan samples F81, F83, and F85 (F series) were the same samples reported elsewhere.[14,15] These samples were refractionated from PF801, PF803, and PF805 (PF series in the previous studies) using water as solvent and isopropyl alcohol as precipitant for the present purpose. The molecular weight distribution of the F series became narrower than that of the PF series after refractionation.

Eight samples coded from P5 to P800 were made by Hayashibara Biochemical Laboratories (Japan) and were purchased from Showa Denko (Japan) as the standard samples for aqueous gel chromatography with narrow molecular weight distribution. Detailed descriptions for purification and successive precipitation fractionation concerning these standard samples were reported by Kawahara et al.[16] Samples of P2000A and P2000B were also prepared by using the same procedure as the standard sample series. The procedures are outlined as follows: Original, unfractionated samples of pullulan were produced from sugar and partially hydrolyzed starch. The average molecular weights were controlled by varying the cultivating condition of the fungus *Aureobasidium pullulans*. Some samples of low molecular weight were also prepared by partial degradation with pullulanase or dilute hydrochloric acid. Each original sample was dissolved in water and precipitated into concentrated gel to remove impurities by addition of methanol. The gel was dissolved again in water and fractionation was carried out in the usual way with methanol as precipitant at 30 °C. After successive fractionation, all samples were purified by precipitation into methanol and dried in a desiccator at room temperature.

Organic solvents were used after distillation. Water was doubly distilled in an all-Pyrex distillation apparatus. Sodium azide was added to the water (0.2% (w/w)).

Intrinsic Viscosity. Intrinsic viscosities, $[\eta]$, of all samples used in this study were measured in water at 25 °C in an Ubbelohde-type viscometer. The flow time of solvent was 133 s and the kinetic energy correction was always negligible. Solution concentrations were determined by dry weight measurement. The water content of the sample stocked in a desiccator was around 6% (w/w).

Aqueous Gel Chromatography. The aqueous gel chromatographic system was an analytical type, TSK-HLC802A (Toyo Soda (Japan)), with two TSK-gel G5000 PW columns and one TSK-gel G3000PW column. The chromatographic solvent was water with 0.2% (w/w) sodium azide. A 0.1-mL sample solution with a concentration of 0.3 mg/mL was injected and the elution rate was 1.0 mL/min. The concentration detector was a differential refractometer. A series of poly(ethylene oxide) standards purchased from Toyo Soda was used to obtain a universal calibration curve. The molecular weight distribution was estimated at 25 °C using the calibration curve, as reported previously.[15]

Light Scattering Measurement. In the region of dilute solution, the translational diffusion coefficient, D_0, of an isolated polymer chain in solution at infinite dilution can be estimated from the reduced first cumulant, Γ/q^2, of the scattering intensity autocorrelation function measured directly by dynamic light scattering using the following equations:

$$\Gamma = -[\mathrm{d} \ln S(q,t)/\mathrm{d}t]_{t=0} \quad (3)$$

$$\Gamma/q^2 = D_z(c,q) = D_z(c)(1 + BR_G{}^2q^2 - ...) \quad (4)$$

$$D_z(c) = D_0(1 + k_Dc + ...) \quad (5)$$

where Γ is the first cumulant, $S(q,t)$ the dynamic structure factor related to the scattering intensity autocorrelation function, q the scattering vector, R_G the radius of gyration ($R_G = \langle S^2\rangle_z{}^{1/2}$), $D_z(c)$ the diffusion coefficient at the limit $q \rightarrow 0$, B the coefficient in the q^2 dependence of the reduced first cumulant, and k_D the concentration dependence coefficient of $D_z(c)$. As the reduced first cumulant is a function of the particle scattering factor, $P_z(q)$,[18,20] the optical alignment of the spectrometer should be achieved so that the $P_z(q)$ factor can be estimated precisely from the angular dependence of the scattered light intensity observed by the dynamic light scattering spectrometer. For this purpose, Bantle, Schmidt, and Burchard[21] recommended an instrument capable of simultaneous measurement of both static and dynamic light scattering.

In this study, we used a Union Giken LS601A automatic light scattering analyzer (Union Giken, Japan) for both measurements. The receiving optics for scattered light were made up by two sets of diaphragm systems. One consisted of a pair of pinhole apertures (0.2-mm diameter) for dynamic light scattering measurements and the other consisted of a pair of narrow metal slit apertures with sharp edges (0.5 × 4 mm) for static light scattering measurements. The apertures were attached to the central position on both ends of metal cylindrical pipes (20-mm diameter and 12 cm long) with an adjustable mounting. As the two diaphragm systems could be interchanged without disturbing the metal cylinders and without distortion of the optical alignment, we could perform an alternating measurement of static and dynamic properties of the polymer solution in a measuring glass cell that was placed in a thermostated toluene bath at 25 ± 0.1 °C. The light source was an argon ion laser with the 488-nm line of vertically polarized light. Optical clarification of the sample solutions was done by direct filtration through a 0.45-μm Millipore filter into the cell. The solution concentration was chosen to be lower than the overlap concentration of the polymer chain in solution. The scattering light intensity was observed over an angular range from 10° to 150° at appropriate intervals.

The weight-average molecular weight, $(M_w)^{LS}$, the z-average mean square radius of gyration, $\langle S^2\rangle_z$, and the second virial coefficient, A_2, were estimated from the static light scattering

Table I
Results of Light Scattering, Intrinsic Viscosity, and GPC for Pullulan Samples

sample	$(M_w)^{LS}/10^4$	$(M_w)^{SE}/10^4$	$\langle S^2\rangle_z^{1/2}$, nm	$A_2/10^{-4}$, cm^3 mol g^{-2}	$[\eta]/10^2$, cm^3 g^{-1}	M_w/M_n
P2000A	236		75.2	1.46	3.38	1.27
F81	210		66.0	1.20	3.10	1.28
P2000B	149		56.0	1.50	2.50	1.21
F83	105		45.0	1.35	2.25	1.25
P800	81.1	75.8	37.5	1.38	1.75	1.19
F85	57.2		31.5	1.60	1.45	1.20
P400	38.4	33.8	25.1	1.60	1.02_1	1.11
P200	18.8	18.6	17.0	2.20	0.70_0	1.11
P100	10.7	10.0_2	(15.0)	2.50	0.44_2	1.09
P50		4.80			0.27_5	1.08
P20		2.08			0.16_0	1.04
P10		1.20			0.12_0	1.05
P5		0.53			0.07_3	1.04

measurements using the procedure described elsewhere.[14]

Data processing of dynamic light scattering was made by a time-interval digitizer and a microcomputer SORD M223 Mark III (SORD, Japan), which was a computer-controlled software correlator, as reported by Matsumoto et al.[22] The scattering intensity autocorrelation function, $G_n(\tau)$, was plotted against delay time, τ (channel number), and we could estimate the reduced first cumulant, $\Gamma/q^2 = D_z(c,q)$, as a function of both scattering angle and concentration of sample solution.

Results

Molecular Characteristics. The values of $(M_w)^{LS}$, A_2, and the z-average radius of gyration, $\langle S^2\rangle_z^{1/2}$ ($=R_G$), measured by static light scattering are summarized in Table I. The light scattering measurements for the samples with molecular weights lower than 10^5 could not be carried out with reliable accuracy because of the extraordinary scattered light intensity at scattering angles lower than 30°. The $(M_w)^{SE}$ values obtained from sedimentation equilibrium by Kawahara et al.[16] are also shown in the third column of Table I as compared with $(M_w)^{LS}$. The $(M_w)^{LS}$ values are in good agreement with the $(M_w)^{SE}$ values. Hence, the $(M_w)^{SE}$ values in the range of molecular weight from 5.3×10^3 (P5) to 48×10^3 g mol^{-1} (P50) were used to evaluate the molecular weight distribution (MWD) from the chromatograms. Since the universal calibration procedure was supported experimentally for the poly(ethylene oxide) standards and pullulan, as reported previously,[14,15] the MWD indexes, M_w/M_n, were estimated with the universal calibration curve. The values thus obtained are presented in the last column of Table I. The MWD for pullulan fractions is reasonably narrow. Intrinsic viscosity data are also shown in Table I. The Mark–Houwink–Sakurada viscosity equation was obtained by double-logarithmic plots of $[\eta]$ against M_w for samples having molecular weights greater than 10^5 as

$$[\eta] = 2.21 \times 10^{-2} M^{0.66} \quad (\text{cm}^3\ \text{g}^{-1}) \qquad (6)$$

This equation is in agreement within experimental error with both viscosity equations reported by Kawahara et al.[16] and the previous study.[14] Furthermore, the molecular weight dependence of A_2 agrees the equation reported:[14]

$$A_2 = 5.42 \times 10^{-3} M_w^{-0.26} \quad (\text{cm}^3\ \text{mol g}^{-2}) \qquad (7)$$

The molecular weight dependence of R_G is shown in Figure 1, and the following equation was obtained in the molecular weight range from 10^5 to 2.4×10^6:

$$R_G = 1.47 \times 10^{-2} M^{0.58} \quad (\text{nm}) \qquad (8)$$

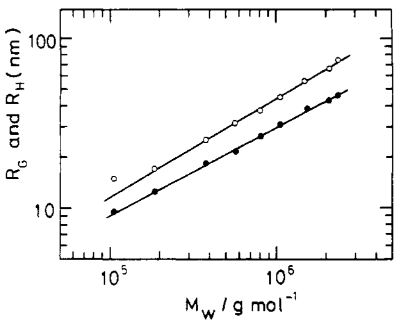

Figure 1. Double-logarithmic plots of the polymer chain dimensions against M_w for pullulan in water at 25 °C. Open circles denote the data of the radii of gyration (R_G) and filled circles denote the data of the hydrodynamic radii (R_H).

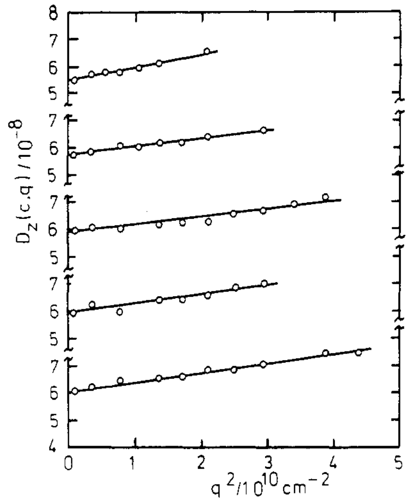

Figure 2. Plots of the reduced first cumulant, $\Gamma/q^2 = D_z(c,q)$, against q^2 for sample P2000A. Sample concentration (from the top): 2.772×10^{-4}, 5.418×10^{-4}, 8.209×10^{-4}, 1.095×10^{-3}, and 1.367×10^{-3} g mL^{-1}.

Translational Diffusion Coefficient and Hydrodynamic Radius. As the $S(q,t)$ data for the samples with low molecular weight were obtained in the small-q region characterized by $qR_G \ll 1$ over the whole range of the scattering angles, the first cumulant can be determined experimentally as the initial slope of the plots of the ln $S(q,t)$ against the time, t. With increasing molecular weight, the qR_G value becomes comparable to unity or larger than unity. Therefore, ln $S(q,t)$ data were fitted as $-\Gamma t(1 + At + A't^2 + ...)$ by linear regression analysis to determine a reliable value of the first cumulant, where A and A' are the coefficients related to the architecture and shape of polymer and also to the polydispersity of the sample. The reduced first cumulants, Γ/q^2, for P2000A at various polymer concentrations are plotted against q^2 in Figure 2 according to eq 4. The data were extrapolated linearly to the limit $q^2 \to 0$ at the same polymer concentration and the $D_z(c)$ value was estimated as the value of the intercept at $q^2 = 0$. The coefficients, B, in the q^2 dependence of $D_z(c)$ in eq 4 were around 0.15. The value is slightly smaller than the value ($B = 0.173$) estimated from the nonpreaveraged hydrodynamic interactions.[18,21] Figure 3 shows plots of $D_z(c)$ thus estimated against the polymer concentration c for the various samples. It is evident that the concentration dependences of $D_z(c)$ can be approximated by a linear relation over the entire concentration range investigated. Linear extrapolations were performed to determine the translational diffusion coefficients at infinite dilution, D_0, from the intercept and the k_D values from the slope. The k_D values are positive for high molecular weight samples and decrease gradually to become negative with decreasing molecular weight. The

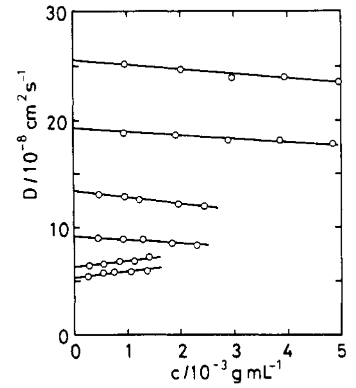

Figure 3. Plots of $D_z(c)$ against polymer concentration, c, for the various pullulan samples. Samples (from the top): P100, P200, P400, P800, P2000B, and P2000A.

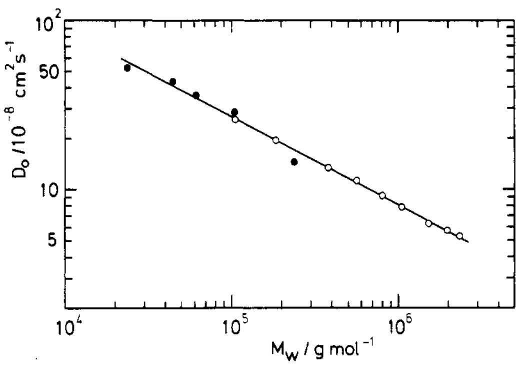

Figure 4. Double-logarithmic plots of the translational diffusion coefficients, D_0, against M_w for pullulan in water at 25 °C. Open circles denote the data in this study and filled circles denote the data of Wallenfels et al.[23] using the classical boundary formation technique.

Table II
Results of Dynamic Light Scattering for Pullulan Samples

sample	$D_0/10^{-8}$, cm^2 s^{-1}	R_H, nm	$(k_D)^{obsd}$	$(k_D)^Y$	$k_f/[\eta]$	k_{f0}	ρ
P2000A	5.30	46.0	$114._8$	176.4	1.69	5.81	1.66
F81	5.67	43.0	30.2	106.8	1.52	5.03	1.54
P2000B	6.30	38.7	76.2	80.1	1.48	3.77	1.45
P83	7.87	31.0	−35.0	41.3	1.42	4.44	1.45
P800	9.20	26.5	−36.4	31.0	1.48	4.50	1.42
F85	11.2	21.8	−40.2	26.9	1.54	4.87	1.44
P400	13.4	18.2	−30.5	9.0	1.50	3.87	1.38
P200	19.4	12.6	−22.7	5.7	1.51	3.76	1.40
P100	25.6	9.5	−20.1	0.6	1.59	3.64	(1.58)

Table III
Characteristic Exponents of $[\eta]$, s_0, and D_0 for Pullulan Samples in Water and Comparison with Theoretically Predicted Values

exponent	characteristic exponents		
		theor value	
	obsd	$\nu_G = \nu_H$	blob theory
a	0.66	0.74	0.68
b	0.445	0.42	0.48
c	−0.52	−0.58	−0.52

hydrodynamic radius, R_H, can be obtained from the D_0 value according to the Stokes–Einstein relation:

$$D_0 = k_B T / 6\pi\eta_0 R_H \tag{9}$$

where k_B is Boltzmann's constant, T the absolute temperature, and η_0 the viscosity of the solvent. The experimental results of dynamic light scattering are listed in Table II. Double-logarithmic plots of D_0 against M_w are shown in Figure 4 and the following equation was obtained:

$$D_0 = 1.07 \times 10^{-4} M^{-0.52} \quad (\text{cm}^2\ \text{s}^{-1}) \tag{10}$$

The filled circles in the figure denote data obtained by Wallenfels et al.[23] using the classical boundary formation technique. These data seem to be in good agreement with the data in this study, although the samples of Wallenfels et al. were of very broad distribution due to the degradation with hydrochloric acid and their molecular weights were estimated from sedimentation and diffusion measurements. The molecular weight dependence of R_H is shown in Figure 1 in the same molecular weight range as that used for the molecular weight dependence of R_G. The following equation was obtained:

$$R_H = 2.25 \times 10^{-2} M^{0.52} \quad (\text{nm}) \tag{11}$$

Discussion

On the assumption that a is the exponent in the Mark–Houwink–Sakurada equation, $[\eta] = K_\eta M^a$, and b and c are the corresponding exponents for the molecular weight dependences of the sedimentation coefficient at infinite dilution, s_0, and the diffusion coefficient, D_0, i.e., $s_0 = K_s M^b$ and $D_0 = K_D M^c$, respectively, the following relations among the exponents are predicted by Flory:[1]

$$b = (2 - a)/3 \tag{12}$$

$$c = (1 + a)/3 \tag{13}$$

where K_η, K_s, and K_D are the coefficients. In the second column of Table III are listed the exponents determined from eq 6 and 10, using the equation for s_0 determined by Kawahara et al., $s_0 = 2.86 \times 10^{-15} M_w^{0.445}$ (in s).[16] The theoretical exponents can be related to the characteristic exponents, ν, as the following equations on the basis of the consistency of $\nu = \nu_G = \nu_H$:[9]

$$a = 3\nu - 1; \qquad b = 1 - \nu; \qquad c = -\nu \tag{14}$$

If the observed value ($\nu = 0.58$) is assumed, the values of a, b, and c may be calculated by using eq 14, as listed in the third column of Table III. The disagreements between the observed values and the values thus calculated become apparent. Therefore, to modify the theory, Weill and des Cloizeaux[9] deduced the relation $[\eta] \sim R_G{}^2 R_H / M$ for the intrinsic viscosity using the blob concept. Substituting the observed values of ν_G and ν_H in this relationship, one can calculate the theoretical exponents listed in the fourth column of Table III. These calculated values are in good agreement with the observed exponents, as compared with the values listed in the third column. It seems, therefore, possible to explain the discrepancies between ν_G and ν_H with the blob concept, including other newer blob theories[10,11,24] which successively improve the original one.[9] However, the relation $[\eta] \sim R_G{}^2 R_H / M$ in the good solvent region was recently criticized by Tanaka,[25] based on the conflicts of the deduction of $[\eta] \sim R_G{}^2 R_H / M$ with experiment. For a more detailed discussion concerning the blob theory, the expansion factors for both static and dynamic dimensions should be directly estimated from the experimental results; however, the Θ condition for pullulan is not yet known. Therefore, we must discuss another viewpoint to study the relation between both dimensions.

The ρ ratio, a dimensionless quantity defined by

$$\rho \equiv R_G / R_H \tag{15}$$

is a very useful parameter for discussing the discrepancy between the static and dynamic radius.[26-28] The ρ ratio for a monodisperse linear chain in the unperturbed state has been discussed.[27,29] For linear chains in good solvents, the ratio has been deduced on the basis of the blob model.[3,9,11] Akcasu et al.[11] predicted ρ values in the range from $\rho = 1.506$ (at the Θ condition) to $\rho = 1.862$ (in good solvents). The values estimated from the observed R_G and R_H values are listed in the last column of Table II. These estimated ρ values seem to be molecular weight independent and are in agreement with the values reported by Bantle et al.[21] for linear polystyrenes in toluene. However, the estimated values are much smaller than any values predicted by the blob concepts. Taking into consideration an increase of the ρ value due to the sample polydispersity, the disagreement becomes more pronounced. These disagreements between the observed and theoretical ρ values have been reported even at Θ conditions[28] and some efforts at interpretation have also been reported.[30] Therefore, inspection of the theoretical treatment for hydrodynamic interaction between the chain segments in an isolated polymer chain is of interest.

The theoretical expressions for the k_D coefficient in good solvents are described by the Yamakawa theory as[29,31]

$$k_D = 0.8A_2M - V_h - \bar{v} \tag{16}$$

and for the Pyun and Fixman theory:[32]

$$k_D = 2A_2M - k_f - \bar{v} \tag{17}$$

$$k_f = k_{f0}V_h \tag{18}$$

$$V_h = 4\pi R_H{}^3 N_A / 3M \tag{19}$$

where V_h is the specific hydrodynamic volume, $\bar{v}$ the partial specific volume of the polymer, k_{f0} the coefficient predicted by the theory, which falls in the range from $k_{f0} = 2.23$ for the soft-sphere model at the Θ condition to $k_{f0} = 7.16$ for the hard-sphere model in the asymptotic limit of the excluded volume effect, and N_A Avogadro's number. If the partial specific volume of pullulan in aqueous solution at 25 °C is $\bar{v} = 0.602$ mL g^{-1}, as reported by Kawahara et al.,[16] the k_D values predicted by the Yamakawa theory for the sample fractions can be estimated by using the experimental results in Tables I and II. In the fifth column of Table II are listed values of $(k_D)^Y$, the k_D values calculated by the Yamakawa theory.[31] The calculated values decrease with decreasing molecular weight. The values are, however, positive, in contrast to the negative values observed in the low molecular weight range. Using eq 17–19, one can obtain the k_f and k_{f0} values on the basis of the Pyun and Fixman theory.[32] The values of $k_f/[\eta]$ are listed in the sixth column of Table II and are independent of molecular weight. The average value of $k_f/[\eta] = 1.53$ is in good agreement with the old findings of Wales and Van Holde[33] for flexible polymers. The average value ($k_f/[\eta] = 1.4$) directly obtained by sedimentation velocity is slightly smaller than the value of 1.53.[16] But taking into account the experimental errors in k_D and A_2, this discrepancy is not significant. The k_{f0} values are listed in the seventh column of Table II. The values are intermediate between the value for soft spheres and that for hard spheres. It may be concluded that the Pyun and Fixman theory predicts reasonable k_D values for pullulan in aqueous solution, contrary to the conclusion of Selser for poly(α-methylstyrene) in toluene and in benzene.[13]

In summary, despite the rather voluminous and complicated molecular structure of pullulan, both the static solution behavior and the dynamic solution behavior are very similar to the solution behavior of polystyrene in good solvents. The discrepancy of the molecular weight dependence for the static and dynamic chain dimensions is apparent. The ρ ratio is smaller than the theoretical value of ρ (=1.504) predicted for monodisperse linear polymer at the Θ condition. The k_D values are predicted by Pyun and Fixman theory.

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