Wormlike Chain Parameters of Cellulose and Cellulose Derivatives

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ABSTRACT: In order to estimate equilibrium chain rigidity, literature data for 12 systems of cellulose and its derivatives and solvents were analyzed on the basis of a wormlike chain model. The persistence length q was calculated by four methods. The q values at the unperturbed state (q^0_{BD}) agreed closely with those derived using the pearl necklace model. The q values evaluated by the Yamakawa–Fujii (YF) theory were smaller than those obtained by the Benoit–Doty equation (q_{BD}); this discrepancy was considered due to the neglect of the partially free draining effect in the YF theory. With increasing solvent polarity, the polymer chain becomes stiffer owing to an increase in solvent–polymer interaction. Most of q^0_{BD} for cellulose derivatives were in the range between 3×10^{-7} and 8×10^{-7} cm, except that for cellulose nitrate. Cellulose and its derivatives may be considered semiflexible.
KEY WORDS Cellulose / Cellulose Derivatives / Wormlike Chain Model / Excluded Volume Effect / Persistence Length / Partially Free Draining Effect /

A number of studies have been carried out on the dilute solution properties of cellulose and its derivatives. In these studies, the molecular parameters of the polymers have been mainly estimated using the pearl necklace model. Kamide and Miyazaki[1] concluded from a systematic analysis of experimental data that the conformation parameter σ for cellulose and its derivatives lies between 2.8—7.5 and that the characteristic ratio C_∞ is in the range 19—115. These unexpectedly large values of σ and C_∞ suggest that the molecules of cellulose and cellulose derivatives behave as a semiflexible or inflexible chain. For extremely inflexible polymers, analysis of dilute solution properties by the pearl necklace model becomes theoretically inadequate. Thus, the applicability of this model to cellulose and its derivatives in solution should be carefully examined.

The wormlike chain was first proposed by Kratky and Porod[2] as a model for chain molecules with large equilibrium rigidity, which is conventionally expressed in terms of the persistence length q. The relationship between q and root mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ of a wormlike chain was derived

by Benoit and Doty (BD),[3] and equations for the limiting viscosity number $[\eta]$ and the sedimentation coefficient s of the same chain were obtained by Hearst,[4] Peterlin,[5] Hearst and Stockmayer (HS),[6] Ullman,[7,8] and Yamakawa and Fujii (YF).[9,10] The q values of many inflexible macromolecules, such as DNA,[7,10] and poly(hexyl isocyanate),[11] were successfully determined by analyzing data for $\langle S^2 \rangle^{1/2}$, $[\eta]$, and s by these theories.

The excluded-volume effect can be incorporated in the BD theory for $\langle S^2 \rangle^{1/2}$, but not easily in the hydrodynamic theories for $[\eta]$ and s.

Another method for estimating q is to use the unperturbed chain dimensions A at the coil limit. Penzel and Schulz[12] estimated q for cellulose nitrate in acetone by this method, but the q value obtained corresponded to infinite molecular weight. Although q is expected to depend on the molecular weight of cellulose derivatives, the q value at finite molecular weight cannot be determined by this method.

In order to compare the equilibrium rigidities of cellulose and its derivatives with those of typical inflexible macromolecules and examine the validity

of the methods based on the pearl necklace model for cellulose and its derivatives, an attempt was made to calculate q, the segment diameter d, and the expansion factor α_s of cellulose and its derivatives in solution.

THEORETICAL BACKGROUND

The persistence length q may be evaluated using any one of the following four methods.

Method Using Light Scattering Data-1 (Benoit-Doty's Method)

Benoit-Doty's expression[3] for the unperturbed radius of gyration $\langle S^2 \rangle_0$ of a monodisperse worm-like chain (Figure 1a) is

$$\langle S^2 \rangle_0 = qM/(3M_L) - q^2 + 2q^3 M_L/M$$
$$- 2\left(\frac{q^4 M_L{}^2}{M^2}\right)[1 - \exp(-M/qM_L)] \quad (1)$$

where

$$M_L = M/L \quad (2)$$

$$L = Nl \quad (3)$$

Here, M is the molecular weight, L, the contour length, N, the number of monomer units, and l, the length of a monomer unit projected on the contour axis of the chain. According to Maeda et al.,[13] L for a wormlike chain may be taken as the total length of an extended chain, in which all repeating units take on the *trans*-conformation with the valence angle fixed constant. In our study, the value of l was taken to be 5.15×10^{-8} cm, which is one half the length of the c axis (parallel to the chain axis) of a unit cell in the cellulose II crystal.[14]

Actual polymers are not monodisperse. Therefore, eq 1 was extended to polymers having Schulz–Zimm type molecular weight distributions. The result is

$$\langle S^2 \rangle_{0,z} = q^2 \left[\frac{M_w(h'+2)}{3qM_L(h'+1)} - 1 + \frac{2qM_L}{M_w} \right.$$
$$\left. - \frac{2q^2 M_L{}^2(h'+1)}{h' M_w{}^2} \left\{ 1 - \left(\frac{qM_L(h'+1)}{qM_L(h'+1)+M_w}\right)^{h'} \right\} \right]$$
$$(4)$$

where $h'^{-1} = M_w/M_n - 1$, M_w and M_n are the weight- and number-average molecular weights, and $\langle S^2 \rangle_{0,z}$ is the z-average unperturbed radius of
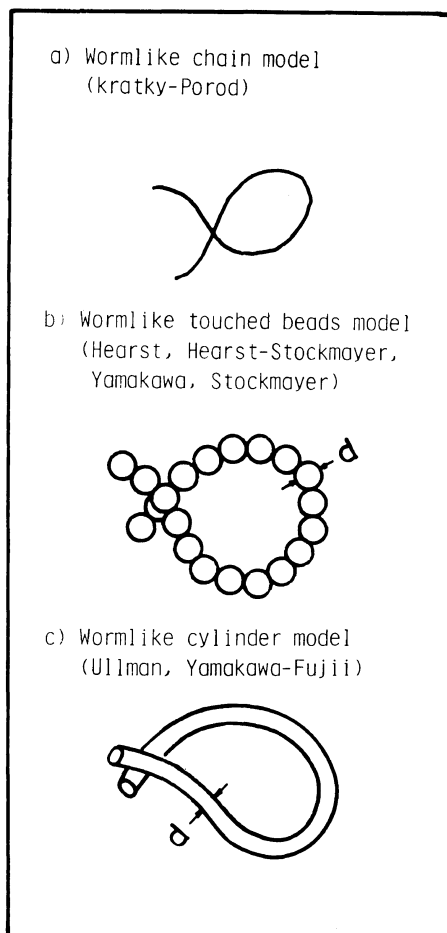
Figure 1. Schematic representation of various worm-like chain models. d is the diameter of a wormlike touched bead (b) or wormlike cylinder (c).

gyration. q can be evaluated by putting data of $\langle S^2 \rangle_z$ and M_w from light scattering measurements and h' into eq 4. We denote this q by q_{BD}.

By incorporating the excluded-volume effect in the wormlike touched-bead chain (see Figure 1b), Yamakawa and Stockmayer (YS)[15] derived the penetration function ψ as a function of the excluded-volume effect parameter z in the form

$$\psi \equiv [A_2 M_w{}^2/(4\pi^{3/2} N_A \langle S^2 \rangle_w{}^{3/2})]$$
$$= (\langle S^2 \rangle_0/\langle S^2 \rangle_{0,\infty})^{-3/2} [\bar{z} h(\bar{z})] \quad (5)$$

with

$$\langle S^2 \rangle_{0,\infty} = qM/(3M_L) \quad (6)$$

$$\bar{z} = z/\alpha_s{}^3 \quad (7)$$

$$h(\bar{z}) = 1 - Q(L, q, d)\bar{z} + \cdots \qquad (8)$$

Here, A_2 is the second virial coefficient, N_A Avogadro's constant, α_s ($\equiv \langle S^2 \rangle^{1/2} / \langle S^2 \rangle_0^{1/2}$) the expansion factor, and $Q(L, q, d)$ a function of L, q, and the diameter d of a bead. Yamakawa and Stockmayer also derived the relation between α_s and z

$$\alpha_s^2 = 1 + (67/70)K(L, q)z + \cdots \qquad (9)$$

where $K(L, q)$ is a function of L and q. For α_s close to unity, Yamakawa and Stockmayer employed a fifth-power law type closed expression.[15] On the other hand, Kamide and his coworkers[1,16-19] evaluated α_s of cellulose and its derivatives using the penetration function of the third-power law type proposed for the pearl necklace model. In order to compare these α_s values with those based on the wormlike touched-bead model, the following closed expression of the Fixman type[20] was derived[21]:

$$\alpha_s^3 - 1 = (3/2)[67K(L, q)/70]z \qquad (10)$$

We derived a closed form of $h(\bar{z})$ as follows[21]:

$$\bar{z}h(\bar{z}) = \frac{1 - [1 + (3.903/2.865)Q\bar{z}]^{-0.478}}{(1.828/2.865)Q} \qquad (11)$$

Equation 11 corresponds to the equation proposed by Kurata–Fukatsu–Sotobayashi–Yamakawa (KFSY-II)[22] for the pearl necklace model. We determined q and α_s numerically from eq 10 and 11. The resulting values are denoted by q_{BD}^0 and $\alpha_{s,3}^w$.

Method Using Light Scattering Data-2 (Gaussian Chain Approximation Method)

For indefinitely large $M/(qM_L)$, an unperturbed polymeric chain can be regarded as Gaussian. For this chain, q is related to the unperturbed chain dimension A_∞ at infinite M_w by

$$q = M_L A_\infty^2 / 2 \qquad (12)$$

The q value estimated by eq 12 is denoted as q_{CL}^0.

We determined A for each cellulose derivative, using method 2B proposed by Kamide and Miyazaki,[1] in which A is given by $(6\langle S^2 \rangle / (\alpha_s^2 M))^{1/2}$ and α_s is evaluated from ψ with the aid of KFSY-II. This value of α_s is designated by $\alpha_{s,3}^p$. The A values of cellulose derivatives often depend significantly on molecular weight in the low molecular weight region. In such cases, we approximated A_∞ by A of the highest molecular weight samples.

Method Using Limiting Viscosity Number (Yamakawa and Fujii's Method)

Neglecting the draining term in the Kirkwood–Riseman integral equation,[23] Yamakawa and Fujii[10] derived an expression of $[\eta]$ for unperturbed wormlike cylinders (Figure 1c), which reads

$$[\eta] = \Phi \cdot (2q/M_L)^{3/2} M^{1/2} \qquad (13)$$

where Φ is a function of q, L, and the diameter of the cylinder d (designated by d_h^w). We determined q, referred to as q_{YF}, for each polymer sample.

Evaluation of the Diameter d_h^w

The YF theory requires the value of d_h^w to determine q. Korneeva et al.[24] estimated d_h^w of certain cellulose esters using the Hearst-Stockmayer (HS) theory.[6] As Yamakawa and Fujii pointed out,[9] the HS theory contains a mathematical error when converting the summation type equation to an integral equation and hence yields an inaccurate d_h^w. The hydrodynamic segment diameter estimated from the draining parameter X for the pearl necklace model (designated as d_h^p; the superscript p means the pearl necklace model and the subscript h a hydrodynamic segment) varies markedly with the chosen length of a hydrodynamic segment, a_h^p. If a_h^p is equal to the length of a statistical segment a_s^p in the pearl necklace chain, we obtain $d_h^p \simeq 3.5 \times 10^{-7}$ cm[19] for cellulose acetate (CA) (degree of substitution, DS = 2.46, hereafter the number in parenthesis denotes a DS value) in N,N-dimethylacetamide (DMAc). This d_h^p is too large to be attributed to the solvation alone. Hence, we determine d_h^w on the following assumptions. (1) The hydrodynamic segment lengths (a_h^p and a_h^w) in the pearl necklace and wormlike chain models are proportional to the statistical segment lengths a_s^p and a_s^w in the corresponding models:

$$a_h^p = \lambda a_s^p, \quad \text{and} \quad a_h^w = \lambda a_s^w \qquad (14)$$

$$M_{0h}^p = \lambda M_{0s}^p, \quad \text{and} \quad M_{0h}^w = \lambda M_{0s}^w \qquad (14)'$$

where λ is a proportionality constant, and M_{0h} and M_{0s} are the molecular weights of the hydrodynamic and statistical segments, respectively. (2) d_h^w of the wormlike cylinder is equal to the diameter d_h^p of beads consisting of a pearl necklace chain:

$$d_h^w = d_h^p = d_h \qquad (15)$$

a_s^p and M_{0s}^p are given as functions of A and M_L in

eq 4 and 5 of ref 19.

Now, X is expressed by[25]

$$X = \zeta_p (M/M_{0h}^p)^{1/2}/(6^{1/2}\pi^{3/2}a_h^p\eta_0) \qquad (16)$$

where ζ_p is the friction constant characteristic of the fluid and the segment and η_0 is the viscosity of the solvent. The friction constant ζ_p obeys the Stokes law, i.e.,

$$\zeta_p = 3\pi\eta_0 d_h \qquad (17)$$

With eq 14—17 and eq 4, 5 of ref 19, d_h can be expressed as follows:

$$d_h = \lambda^{3/2}(2\pi/3)^{1/2}(A^3 M_L^2)XM^{-1/2} \qquad (18)$$

The friction constant ζ_w per unit length of the wormlike cylinder is assumed to be equal to ζ_p per unit length of the pearl necklace chain, i.e.,

$$\zeta_w = \zeta_p/a_h^p \qquad (19)$$

Ullman[7] derived a relation between ζ_w and $[\eta]$ for the wormlike cylinder with a finite cross section (see Figure 1c), i.e.,

$$[\eta] = \left(\frac{\sqrt{2}\,\pi N_A q^2 k}{100 M_L}\right)\sum_{i=1}^{n} W_i\phi(x_i, x_i) \qquad (20)$$

with

$$k = \sqrt{2}\,\zeta_w/(12\pi\eta_0) \qquad (21)$$

Here, W_i is the weight associated with variable x_i in the Gaussian quadrature formulas; k is a hydrodynamic interaction parameter corresponding to the draining parameter X for the pearl necklace chain, and $\phi(x_i, x_i)$ is a dimensionless quantity proportional to the torque of the hydrodynamic force acting on a point of the wormlike cylinder. The equations in the Appendix of ref 7 have been corrected for many typographical errors.[26] Using the Gaussian quadrature with n (in eq 20) = 20 and m (in eq R3 of ref 26) = 80 (hereafter referred to as 20—80 GQ), Ullman[7] calculated $[\eta]$ in eq 20 for $M_L = 1.95 \times 10^{10}$ cm^{-1}. In order to check the reliability of our calculation programs, we calculated $[\eta]$ from eq 20 and 20—80 GQ, using the same values of M_L and d_h as chosen by Ullman. The calculated $[\eta]$ agreed with Ullman's within 0.5% relative error for $q = 1.56 \times 10^{-6}$ cm. In general, in the ranges $q \leq 6.25 \times 10^{-6}$ cm, $L \leq 4 \times 10^{-4}$ cm, and $k \geq 1 \times 10^{-2}$, our $[\eta]$ values were in agreement with Ullman's within 2% relative error.

Substitution of eq 17—19 into eq 21 gives

$$k = \sqrt{\pi\lambda/12}\,XAM_L M^{-1/2} \qquad (22)$$

Combination of eq 18 and 22 with eq 20 allows λ to be calculated from data for A, M_L, X, M, $[\eta]$, and q. In actual computations, q_{BD} and M_w were taken to be q and M, respectively. The resulting λ substituted into eq 18 and 22 gives d_h and k.

APPLICATION TO LITERATURE DATA ON CELLULOSE DERIVATIVES

By applying the Benoit–Doty, Yamakawa–Stockmayer coil-limit, and Yamakawa–Fujii methods to the literature data, the wormlike chain parameters q, $\alpha_{s,3}^w$, d_h, and k were determined for cellulose/cadoxen,[27] cellulose/iron sodium tartrate (FeTNa),[28] CA (2.92)/DMAc,[17] CA (2.46)/DMAc,[19] CA (2.46)/acetone,[16] CA (2.46)/tetrahydrofuran (THF),[16] CA (0.49)/DMAc,[18] cellulose nitrate (CN) (2.91)/acetone,[12] CN (2.55)/acetone,[12] hydroxyethyl cellulose (HEC) (1)/water,[29] ethyl hydroxyethyl cellulose (EHEC)/water,[30] sodium carboxymethyl cellulose (NaCMC) (0.88)/aq NaCl (at the limit of infinite ionic strength, i.e., $I \rightarrow \infty$).[31]

Cellulose

Figure 2a and 2b illustrate q_{BD}, q_{BD}^0, q_{CL}^0, and q_{YF} for cellulose/cadoxen and cellulose/FeTNa. For the former system, all these q are practically independent of M_w and the following relation holds: $q_{BD} > q_{BD}^0 \simeq q_{CL}^0 \simeq q_{YF}$. This figure contains no data of q_{BD}^0
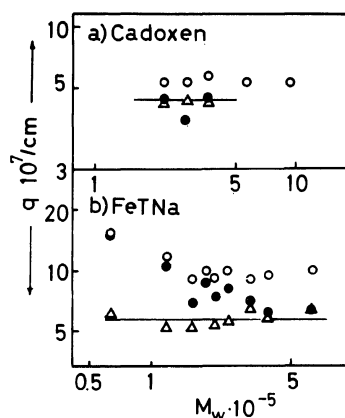
Figure 2. Various persistence lengths q as a function of the weight-average molecular weight M_w for cellulose/cadoxen (a) and cellulose/FeTNa (b), $\bigcirc$, q_{BD}; $\bullet$, q_{BD}^0; $\triangle$, q_{YF}; solid line, q_{CL}^0.

and q_{YF} for two high molecular weight samples, because these samples did not allow d_h to be determined owing to $X = \infty$. For the latter system, q_{BD} and q_{BD}^0 decrease with M_w, approaching an asymptotic value (9.4×10^{-7} cm for q_{BD}) at M_w of 2×10^5—4×10^5, and q_{YF} is constant, being smaller by *ca.* 3.5×10^{-7} cm than q_{BD} in the same solvent.

The significant difference between q_{BD} and q_{BD}^0 for cellulose/cadoxen and that at high M_w for cellulose/FeTNa reflect appreciable excluded-volume effects.

q_{CL}^0 is approximately equivalent to q_{BD}^0 over the whole range of M_w in cadoxen or at high M_w in FeTNa. At least, in these ranges of M_w the Gaussian approximation is reasonable.

The q values determined by the same method were found to be larger in FeTNa than in cadoxen. However, it would be unreasonable to regard this difference as significant, because cellulose is expected to form complexes with solvent,[32] though no detailed structure of the complexes is as yet known. Thus, it is hazardous to conclude that cellulose is more rigid in FeTNa than in cadoxen.

Cellulose Acetate

Figure 3 depicts various q plotted against M_w for CA (2.92)/DMAc. q_{BD}, q_{BD}^0, and q_{YF} are practically independent of M_w. q_{BD} is 10% larger than q_{BD}^0, indicating that the excluded-volume effect ($\alpha_{s,3}^w \simeq 1.1$) on q cannot be neglected. q_{YF} is smaller than q_{BD}, as is the case of cellulose/cadoxen and FeTNa.

Assuming that the deviation from the linear relation between $[\eta]/M_w^{1/2}$ and $M_w^{1/2}$ reflects the semiflexible nature of CA, Dondos *et al.*[33] estimated for CA (2.92)/DMAc to be 4.1×10^{-7} cm which is much smaller than those ($\geq 6.0 \times 10^{-7}$ cm) obtained in this paper. As Kamide *et al.*[1,16-19,34-36] pointed out, the Stockmayer–Fixman method underestimates the unperturbed chain dimensions if the draining effect is not negligible, as is the case for the systems examined here.

Figures 4a-4c show plots of q_{BD}, q_{BD}^0, q_{CL}^0, and q_{YF} as a function of M_w for CA (2.46) in DMAc (a), acetone (b), and THF (c). In DMAc and THF, any q is independent of M_w and $q_{BD} > q_{BD}^0 \geq q_{CL}^0$ (in both solvents) $\gg q_{YF}$ (in DMAc). In contrast, in acetone, q_{BD} and q_{BD}^0 decrease significantly with M_w. Kamide *et al.*[16,19] indicated that CA (2.46) is non-Gaussian in acetone (*i.e.*, a_2 ($\equiv$ d ln ($\langle S^2 \rangle_0/M$)/d ln M) < 0)
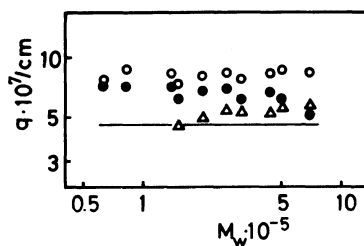

Figure 3. Various persistence lengths q as a function of the weight-average molecular weight M_w for CA (2.92)/DMAc. $\bigcirc$, q_{BD}; $\bullet$, q_{BD}^0; $\triangle$, q_{YF}; solid line, q_{CL}^0.
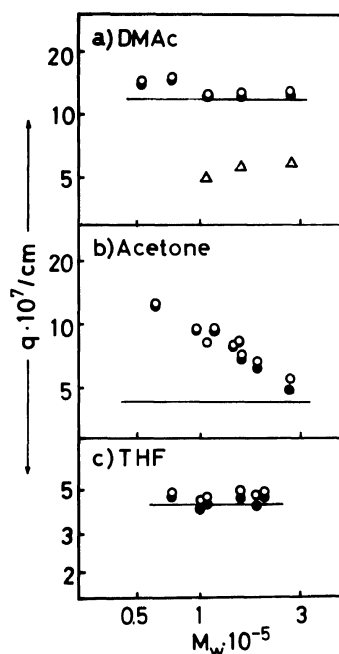

Figure 4. Various persistence lengths q as a function of the weight-average molecular weight M_w for CA (2.46)/DMAc (a), acetone (b), and THF (c). $\bigcirc$, q_{BD}; $\bullet$, q_{BD}^0; $\triangle$, q_{YF}; solid line, q_{CL}^0.

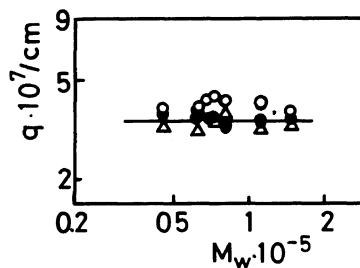**Figure 5.** Various persistence lengths q as a function of the weight-average molecular weight M_w for CA (0.49)/DMAc. $\bigcirc$, q_{BD}; $\bullet$, q_{BD}^0; $\triangle$, q_{YF}; solid line, q_{CL}^0.

and Gaussian in DMAc and THF. In these three solvents, the excluded-volume effect on q is only minor and, in fact, $\alpha_{s,3}^{w}$ are less than 1.06 (see Figure 9).

Figure 5 shows plots of q_{BD}, q_{BD}^{0}, q_{CL}^{0}, and q_{YF} vs. M_w for CA (0.49) in DMAc. All these q are more or less independent of M_w, being smaller than 5×10^{-7} cm and, the order: $q_{BD} > q_{BD}^{0} \simeq q_{YF} \simeq q_{CL}^{0}$. The equality of q_{BD}^{0} and q_{CL}^{0} suggests that the CA (0.49) chain in DMAc can be regarded as Gaussian.

Cellulose Nitrate

Figures 6a and 6b show the plots of various q vs. M_w for CN (2.91) and CN (2.55)/acetone, respectively. Except for the lowest molecular weight fraction of CN (2.91), q_{BD} and q_{BD}^{0} are nearly independent of M_w. In contrast, for $M_w > 7 \times 10^6$, q_{YF} increases remarkably with M_w. This unexpected increase in q_{YF} cannot be explained by the excluded-volume effect alone. Throughout the entire range of M_w, the following relation was obtained: $q_{BD} \geq q_{BD}^{0} \geq q_{CL}^{0} \geq q_{YF}$. In particular, $q_{BD} \simeq q_{BD}^{0}$ at low M_w and $q_{BD}^{0} \simeq q_{CL}^{0}$ at high M_w. For relatively large molecular weights ($M_w \geq 7 \times 10^6$), q_{YF} tends to agree with other kinds of q.

The q values of CN are smaller for lower DS, as was found in the case for σ and C_∞ in ref 1.

Miscellanea

Figures 7a—7c illustrate the molecular weight dependence of q for HEC/water, EHEC/water, and NaCMC/aq NaCl ($I \to \infty$), respectively. In the first two systems, q_{BD} and q_{BD}^{0} agree well with each other. Interestingly, for HEC/water, both q_{BD} and q_{BD}^{0} decrease significantly with increasing M_w. Kamide and Miyazaki[1] pointed out that these two systems have negative a_2 (i.e., $a_2 = -0.128$ for HEC/water and -0.256 for EHEC/water). A negative a_2 is considered due to a molecular weight dependence of the solvation of HEC or EHEC with water as a result of the large polarity of water. q_{YF} of HEC/water and EHEC/water are smaller than other kinds of q and increase gradually with M_w, approaching q_{BD} or q_{BD}^{0} at high molecular weight.

Aq NaCl ($I \to \infty$) is a Flory theta solvent for NaCMC[31] (i.e., $q_{BD} = q_{BD}^{0}$). The q values of NaCMC in this solvent are about 5.0×10^{-7} cm, indicating that NaCMC in aq NaCl ($I \to \infty$) is flexible.
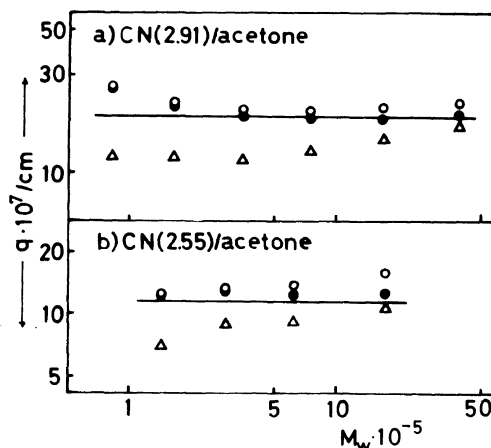

Figure 6. Various persistence lengths q as a function of the weight-average molecular weight M_w for CN (2.91)/ acetone (a) and CN (2.55)/acetone (b). ○, q_{BD}; ●, q_{BD}^{0}; △, q_{YF}; solid line, q_{CL}^{0}.
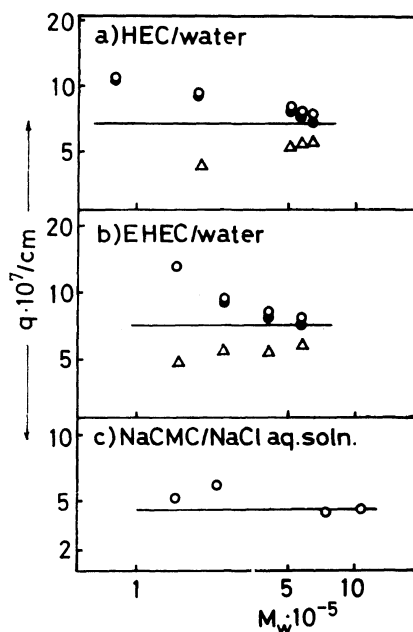

Figure 7. Various persistence lengths q as a function of the weight-average molecular weight M_w for HEC/water (a), EHEC/water (b), and NaCMC/NaCl aq soln. (c). ○, q_{BD}; ●, q_{BD}^{0}; △, q_{YF}; solid line, q_{CL}^{0}.

DISCUSSION

Table I summarizes the averages and standard deviations of d_h, λ, and k for cellulose and its

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Table I. Averages and standard deviations of the hydrodynamic diameter d_h, the proportionality constant λ, and the hydrodynamic interaction parameters k of cellulose and its derivatives/solvent systems

Polymer (DS)[a]	Solvent	Sample No.	$\dfrac{d_h}{10^{-7}\,cm}$	λ	k
Cellulose (0)	Cadoxen	3	$1.6\ (0.4_5)^b$	$0.50\ (0.1_4)^b$	$0.15\ (0.0_3)^b$
	FeTNa[c]	9	$2.8\ (0.8_4)$	$0.71\ (0.2_0)$	$0.08\ (0.0_2)$
CA (2.92)	DMAc[d]	10	$3.4\ (0.4_8)$	$0.72\ (0.1_1)$	$0.16\ (0.0_3)$
	DMAc	5	$2.8\ (0.5_4)$	$0.50\ (0.0_0)$	$0.07\ (0.0_1)$
CA (2.46)	Acetone	9	$3.6\ (0.3_5)$	$0.72\ (0.0_9)$	$0.13\ (0.0_4)$
	THF[e]	6	$3.9\ (0.5_0)$	$0.43\ (0.0_5)$	$0.38\ (0.0_4)$
CA (0.49)	DMAc	10	$2.4\ (0.5_0)$	$0.40\ (0.1_1)$	$0.35\ (0.0_5)$
CN (2.91)	Acetone	6	$2.6\ (1.2_9)$	$0.50\ (0.0_0)$	$0.11\ (0.0_2)$
CN (2.55)	Acetone	4	$2.1\ (0.3_1)$	$0.35\ (0.0_5)$	$0.10\ (0.0_1)$
HEC (1)	Water	5	$2.9\ (0.7_6)$	$0.76\ (0.0_5)$	$0.10\ (0.0_3)$
EHEC (2)	Water	4	$2.9\ (0.2_7)$	$0.63\ (0.1_1)$	$0.10\ (0.0_4)$
NaCMC (0.88)	Aq sodium chloride $(I^f\!\to\!\infty)$	4	$3.0\ (1.2_0)$	$0.25\ (0.1_5)$	$0.53\ (0.2_5)$

[a] Degree of substitution.
[b] Standard deviation.
[c] Iron sodium tartrate.
[d] N,N-Dimethylacetamide.
[e] Tetrahydrofuran.
[f] Ionic strength.

derivatives analyzed above. The average d_h lies between 1.6×10^{-7} and 3.9×10^{-7} cm. These values are apparently larger than those estimated from crystallographic data, which are 9.0×10^{-8} cm and 8.2×10^{-7} cm, respectively, when the a and b axes of a cellulose II unit cell are taken for the diameters.[14] The solvent layer formed around pyranose rings should increase the radius of a hydrodynamic segment. However, there is available no direct estimation of d_h for solvated cellulose molecules. Most of the average λ are smaller than 0.8, indicating that the hydrodynamic segment length is smaller than the statistical segment length. The average values of k for all cellulose derivatives examined are significantly smaller than the value at the nondraining limit ($k \geq 10$),[7] so that the hydrodynamic interaction should be relatively weak in cellulose and its derivatives in solution.

Figure 8 shows the relation between $\alpha_{s,3}^w$ and d_h for a CA (2.46) sample (EF3-15) in DMAc.[19] In the range $d_h \geq 5 \times 10^{-8}$ cm, $\alpha_{s,3}^w$ is almost independent of d_h. As shown in Table I, the d_h values of cellulose derivatives are larger than 5×10^{-8} cm. Even if these d_h values are not very accurate, it may be
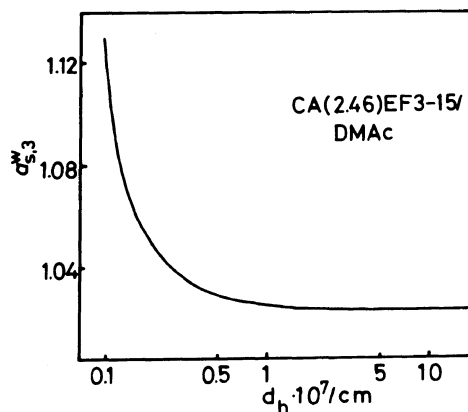

Figure 8. Relation between the expansion factor $\alpha_{s,3}^w$ and the hydrodynamic diameter d_h for a CA (2.46) sample (code EF3—15[19]) in DMAc.

concluded that $\alpha_{s,3}^w$ is insensitive to d_h.

Figure 9 shows $\alpha_{s,3}^w$ plotted against $\alpha_{s,3}^p$, with the solid line representing the relation $\alpha_{s,3}^w = \alpha_{s,3}^p$. For all the polymer samples investigated, the relation $\alpha_{s,3}^w < \alpha_{s,3}^p$ holds. In other words, the analysis in terms of the wormlike chain model results in a
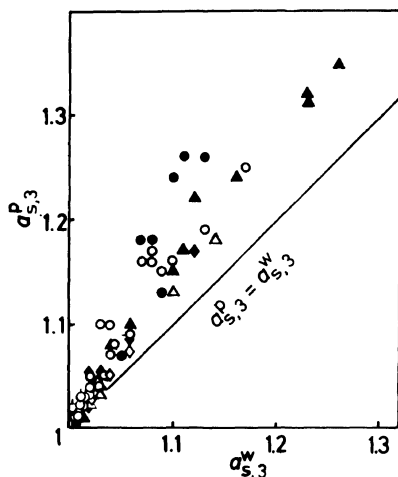
Figure 9. The plot of $\alpha_{s,3}^w$ and $\alpha_{s,3}^p$. $\triangle$, cellulose/cadoxen; $\blacktriangle$, cellulose/FeTNa; $\bigcirc$, CA (2.92)/DMAc; $\dot{\bigcirc}$, CA (2.46)/DMAc; $-\bigcirc$, CA (2.46)/acetone; $\bigcirc-$, CA (2.46)/THF; $\bullet$, CA (0.49)/DMAc; $\diamondsuit$, CN (2.91)/acetone; $\blacklozenge$, CN (2.55)/acetone; $\square$, HEC/water; $\blacksquare$, EHEC/water; $\triangledown$, NaCMC/aq NaCl. The solid line represents the relation $\alpha_{s,3}^w = \alpha_{s,3}^p$.
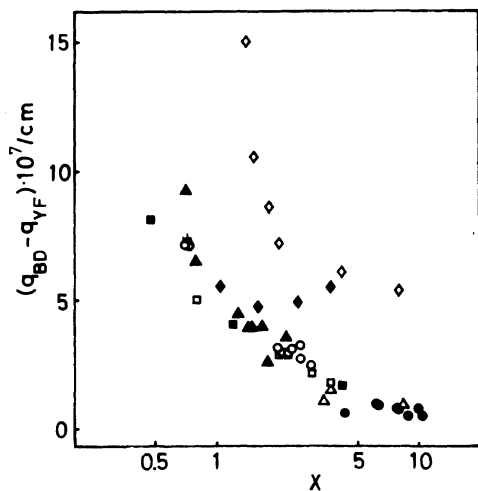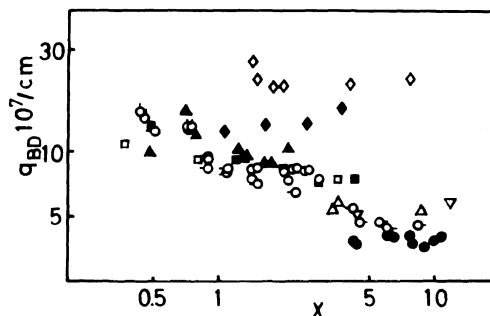

Figure 10. The difference between the Benoit–Doty persistence length q_{BD} and the Yamakawa–Fujii persistence length q_{YF}, $q_{BD} - q_{YF}$, plotted against the draining parameter X for cellulose and its derivatives in solution. The symbols in the figure are the same as in Figure 9.

smaller expansion factor than does that in terms of the pearl necklace model. The $\alpha_{s,3}^w$ values for cellulose derivatives are smaller than 1.14, except the
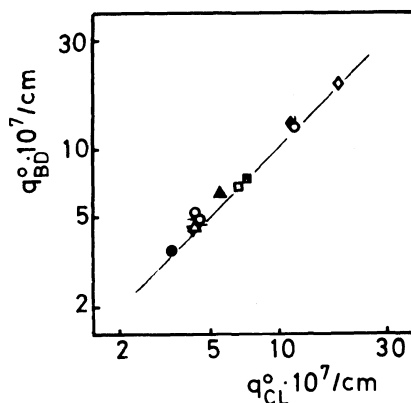
Figure 11. Correlation between the unperturbed Benoit–Doty persistence length q_{BD}^0 and the persistence length at the coil limit q_{CL}^0. The symbols are the same as in Figure 9.

Figure 12. The dependence of the Benoit–Doty persistence length q_{BD} on the draining parameter X. The symbols are the same as in Figure 9.

high molecular weight samples in cellulose/FeTNa, CA (2.92)/DMAc, and CA (0.49)/DMAc. Thus, the solvents may be considered to be poor. Therefore, the conclusions on the thermodynamic properties of cellulose derivative solutions deduced by Kamide and his coworkers[1,16–19] from the pearl necklace model are acceptable.

As shown in the previous section, q_{BD} does not agree closely with q_{YF} for any cellulose drivatives examined. Figure 10 shows the difference $q_{BD} - q_{YF}$ plotted against the draining parameter X estimated by method 1A.[1] Evidently, for any of these cellulose derivatives $q_{BD} > q_{YF}$ holds and $q_{BD} - q_{YF}$ has a negative correlation with X (correlation coefficient $r = -0.60$). Considering that q_{YF} is less dependent on d_h for $d_h > 5 \times 10^{-8}$ cm,[10] we can conclude that the relation $q_{BD} > q_{YF}$ is due neither to a relatively

Table II. Persistence length of stiff and flexible polymers
estimated by various methods

Polymer	Solvent	$q \times 10^8$ cm	Method	ref
Poly(vinylpyridiniumbutylbromide)	5×10^{-4} M Aq sodium chloride	704	V	7
Polymethylacrylic acid	5×10^{-4} M Aq sodium chloride	625	V	7
DNA[b]	0.79 M Aq sodium chloride	520	V	7
	0.2 M Aq sodium chloride	565	V	10
Poly(hexyl isocyanate)	n-Hexane	420	LS, V, s	11
Poly(n-butylisocyanate)	Tetrachloromethane	375	V	10
Polymethylmethacrylate	Benzene	14	SAXS	38
Polyethylene	Bis-2-ethylhexyl adipate	9.6[a]	LS	39
Polyvinylacetate	Heptane/3-methyl-2-butanone	16[a]	LS	40
Polystyrene	Cyclohexane	9—10	SAXS	41

[a] Estimated from unperturbed chain dimensions reported in the literature.
[b] DNA, deoxyribonucleic acid.

inaccurate d_h value nor to the polydispersity of the samples, but to a significant role played by the free draining effect. This is because the correction of $[\eta]$ in the YF theory for this effect should raise the value of q_{YF}.

Yamakawa and Fujii[10] found that the draining term does not appear in the integral equation for the flow rate of fluid, provided that the fluid does not slip on the surface of the wormlike cylinder, and concluded that the draining effect does not exist in the wormlike cylinder model. As has often been mentioned, in cellulose derivative solutions, a solvated solvent layer is formed around the naked cellulose chain. Obviously, since these systems have not distinct boundary between the solvent as a continuous medium and the solute molecule, the boundary condition employed by Yamakawa and Fujii seems to be too oversimplified to explain the dilute solution properties of cellulose derivatives.

Figure 11 shows the relation between q_{BD}^0 and q_{CL}^0 for the highest molecular weight sample of each cellulose derivative. q_{BD}^0 agrees well with q_{CL}^0 for any of the cellulose derivatives investigated, implying that A in the pearl necklace model varies with q in the wormlike chain model at these highest molecular weight samples.

Figure 12 shows the relationship between q_{BD} and X. Except for cellulose nitrate (2.91 and 2.55)/acetone, q_{BD} decreases significantly with an increase in X, indicating that the cellulose derivative chain becomes less flexible as the draining effect plays an

important role. Recently, Tsvetkov and Andreeva[37] stated that the hydrodynamic interaction is weaker for rigid chain coils than flexible chain coils and that the draining effect should be taken into the hydrodynamic parameters. However, they did not investigate quantitatively the role of the draining effect.

Since, as shown above, the excluded-volume effect is small, though not negligible, and the draining effect plays an important role in solution of cellulose derivatives, q_{BD}^0 obtained from the light scattering data should be a more reliable measure of polymer chain rigidity than the hydrodynamic persistence length including q_{YF}. The q_{BD}^0 values of cellulose derivatives vary from 3.0×10^{-7} to 2.5×10^{-6} cm, with most found between 3.0×10^{-7} cm and 8.0×10^{-7} cm (see Figures 2—7). In Table II, the literature q values obtained by analyzing light scattering (LS), viscosity (V), sedimentation (s), and small-angle X ray scattering (SAXS) data are given. Although the q values of typical stiff chains, such as DNA and poly(hexyl isocyanate), are not corrected for the polydispersity or excluded-volume effects, these q values are five to ten times larger than those of cellulose derivatives. For flexible polymers like polystyrene, q is always less than about 2.0×10^{-7} cm. Thus, it is clear that the chains of cellulose derivatives may be classified as semiflexible.

In Figure 13, q_{BD}^0 is plotted against the chemical shifts of O-acetyl methyl and hydroxyl groups (δ_{CH_3} and δ_{OH})[42] and the number of grams (n)[43] of solvent
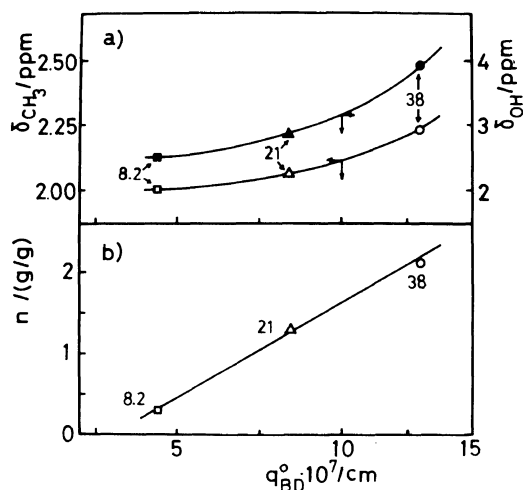
Figure 13. a) Plot of the chemical shifts of methyl and hydroxyl protons, δ_{CH_3} (open marks) and δ_{OH} (closed marks) against the unperturbed Benoit–Doty persistence length q_{BD}^0 for a CA (2.46) sample (code EF3—13[16,19]) in DMAc (circle), acetone (triangle), and THF (rectangle). b) Plot of the number grams n of solvated molecules per 1 g of polymer molecules against q_{BD}^0 for CA (2.46) in three solvents.

molecules per 1 g of polymer in CA (2.46)/DMAc, acetone, and THF. The figures appearing on the curves indicate the dielectric constant of the solvents. It can be seen that q_{BD}^0 is correlated closely with the degree of solvation, being larger in a more polar solvent. In a polar solvent, probably there is a strong interaction between the O-acetyl methyl and hydroxyl groups and the solvent and the solvent molecules about the polymer chain interfere with the internal rotation of the cellulose acetate chain. These should lead to an expanded conformation of the chain. The solvation was also observed for other cellulose derivatives,[44] and we conclude that it contributes greatly to the rigidity of the cellulose chain.

CONCLUSIONS

(1) Cellulose and its derivatives belong to the category of semiflexible polymers and not to the family of inflexible polymers.

(2) Cellulose and its derivatives in solution can be reasonably well modeled either by the pearl necklace chain or the wormlike chain, and the conclusions deduced on the basis of the pearl

necklace model are definitely acceptable.

(3) The excluded-volume effect is relatively small in solutions of cellulose and its derivatives, but cannot be ignored when estimating the unperturbed persistence length.

(4) The draining effect cannot be neglected even in the wormlike chain model. This effect is real, not the apparent one found by applying the experimental data for cellulose and its derivatives beyond the applicability limit of the pearl necklace model.

(5) The unperturbed persistence length (q_{BD}^0), evaluated by the BD theory, is the most reliable among q estimated by various methods.

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26. For example, eq B3 and B4 in ref 7 should be read as eq R1 and R2, respectively.

$$A_{ij} = \frac{kLW_j}{2q} K\left(\frac{L}{2q}|x_j - x_i|\right) \qquad (i \neq j) \qquad \text{(R1)}$$

and

$$A_{ii} = 1 + \frac{W_i kL}{q(x_{i+1} - x_{i-1})} \int_{(x_{i-1}+x_i)/2}^{(x_{i+1}+x_{i-1})/2}$$

$$\times K\left(\frac{L}{2q}|x - x_i|\right) dx \qquad (i = j) \qquad \text{(R2)}$$

Equation R2 can be rearranged to eq R3 using the *m*-th Gaussian Quadrature (see text).

$$A_{ii} = 1 + \frac{W_i kL}{4q} \sum_{j=1}^{m} W_j K$$

$$\times \left[\left(\frac{qL}{8}\right)|(x_{i+1} - x_{i-1})x_j + (x_{i+1} - 2x_i + x_{i-1})|\right]$$

$$\text{(R3)}$$

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