NOTE

Viscometric and Light Scattering Study on Dilute Solution Properties of Cellulose Acetate with a Degree of Substitution of 1.75

Masatoshi SAITO

Textile Research Laboratory, Asahi Chemical Industry Company, Ltd., Takatsuki, Osaka 569, Japan

A number of the investigations have been made concerning to the dilute solution properties of cellulose acetate (CA), because of the industrial importance of this polymer. However, except for the studies of Kamide and his coworkers,[1-14] the degree of substitution (DS) of CA polymers treated has been restricted only to high values. Using the successive solution fractionation (SSF) method, Kamide *et al.*[4-6,12-14] prepared fractionated CA samples with DS equal to 0.49, 2.46, 2.92 and relatively narrow molecular weight distributions ($1.1 \leq M_w/M_n \leq 1.4$; M_w and M_n are the weight- and number-average molecular weights, respectively). Analysis of light scattering, membrane osmometry, viscosity, and ultracentrifugation data showed that the equilibrium chain rigidity of CA in *N,N*-dimethylacetamide (DMAc) depended on DS and that the unperturbed chain dimension (A) as well as the persistence length (q) become maxima at DS $\simeq 2.5$.[13,15]

In order to clarify the DS dependence of the unperturbed chain dimensions of CA and to evaluate the molecular parameters, we made a study of the dilute solution properties of CA with DS = 1.75 by light scattering, membrane osmometry, and viscosity.

EXPERIMENTAL

A CA sample (DS = 2.46 and $M_w = 1.2 \times 10^5$) synthesized in a previous study[5] was hydrolyzed with hydrochloric acid as a catalyst in a 77% aq

acetic acid for about one week. The hydrolyzed CA was recovered by precipitation with methanol and dried *in vacuo*.

The degree of substitution of this unfractionated CA was determined by back-titration to be 1.75. From its ^{13}C NMR spectra in deuterated dimethylsulfoxide (DMSO-d_6), the average probabilities that the hydroxyl groups attached to the C_2, C_3, and C_6 atoms were substituted by the *O*-acetyl groups, *i.e.*, $\langle\!\langle f_2 \rangle\!\rangle$, $\langle\!\langle f_3 \rangle\!\rangle$, $\langle\!\langle f_6 \rangle\!\rangle$ were estimated to be 0.45, 0.54, and 0.76, respectively. The total degree of substitution determined from $\sum_{i=2,3,6} \langle\!\langle f_i \rangle\!\rangle$ was 1.75, which is in excellent agreement with that evaluated by the neutralizing method.

The CA (DS = 1.75) sample was dissolved in acetone–water (7 : 3, vol/vol) and fractionated by the SSF method with water as the precipitant into 10 almost equal fractions.

The viscosities of the fractions in DMAc were measured by a modified Ubbelohde-type viscometer at 25°C. The limiting viscosity number [η] was determined using the Huggins plot.

The osmotic pressures of the fractions in DMAc at 25°C were determined with a Wescan Osmometer M231 (Wescan Instruments, Inc., USA). The membrane was an Ultracella filter-type SM-11539 (Sartorious GmbH, West Germany).

One wt% stock solutions of the fractions in DMAc were centrifuged at 3.0×10^4 *g* for 1 h in a Hitachi model 55p-7 automatic preparative ultracentrifuge to remove gel-like material. The average

Table I. Results of light scattering, membrane osmometer, and viscosity measurements on CA (DS = 1.75) at 25°C

Sample code	$M_w \times 10^{-4}$	Light scattering			Osmometry		M_w/M_n	Viscosity	$\Phi \times 10^{-23}$	α_s[d]	X[e]
		$\langle S^2 \rangle_z^{1/2}$[a]	$\langle S^2 \rangle_w^{1/2}$	A_2[b]	$M_n \times 10^{-4}$	A_2		$[\eta]$[c]			
KS2-1	—	—	—	—	—	—	—	62	—	—	—
KS2-2	3.75	1.51	1.38	9.8	2.76	9.2	1.36	86	0.94	1.02_8	0.8
KS2-3	4.38	1.67	1.47	9.6	3.43	1.3	1.28	96	1.00	1.02_9	1.0
KS2-4	—	—	—	—	—	—	—	116	—	—	—
KS2-5	5.53	1.96	1.75	9.5	—	—	—	122	1.00	1.02_9	1.0
KS2-6	6.15	2.06	1.84	9.5	4.67	10.9	1.31	132	1.03	1.03_1	1.1
KS2-7	—	—	—	—	—	—	—	144	—	—	—
KS2-8	8.23	2.37	2.12	8.3	—	—	—	157	1.07	1.03_2	1.2
KS2-9	10.0	2.55	2.28	6.8	7.2	9.8	1.39	165	1.10	1.03_1	1.2
KS2-10	13.1	2.95	2.63	6.0	—	—	—	196	1.10	1.03_0	1.3

[a] 10^{-6} cm.
[b] 10^{-4} cm^3 mol g^{-2}.
[c] cm^3 g^{-1}.
[d] Estimated using penetration function ψ.
[e] Estimated by method 1A[17].

of the specific refractive index increments (dn/dc) of three fractions in DMAc was 0.046 (cm^3 g^{-1}) at 25°C.

Light scattering measurements were made at 25°C with a FICA model 42000 photogoniometer, using unpolarized light (wavelength $\lambda_0 = 436$ nm) in a scattering angle range from 30° to 150°.

RESULTS AND DISCUSSION

The results from light scattering, osmotic pressure, and viscosity measurements on CA (DS = 1.75) fractions in DMAc at 25°C are summarized in Table I. The polydispersity parameter M_w/M_n averaged for all fractions was 1.34. The measured z-average radii of gyration ($\langle S^2 \rangle_z^{1/2}$) were converted to weight-average radii of gyration ($\langle S^2 \rangle_w^{1/2}$), assuming the Schulz–Zimm molecular weight distribution function with $M_w/M_n = 1.34$. The tenth and eleventh columns of Table I show the Flory viscosity parameter Φ and the linear expansion factor α_s ($\equiv \langle S^2 \rangle^{1/2}/\langle S^2 \rangle_0^{1/2}$; the subscript 0 denotes the unperturbed state). The latter was estimated from the data for M_w, A_2, and $\langle S^2 \rangle_z^{1/2}$ in DMAc, using the expression of Kurata–Fukatsu–Sotobayashi–Yamakawa[16] (KFSY) for the penetration function ψ. The draining parameter X in the twelveth column of Table I was determined by method 1A described

previously.[17]

Figures 1a—1c depict the molecular weight dependence of $[\eta]$, $\langle S^2 \rangle_z^{1/2}$, and Φ for the CA (DS = 1.75) fractions (filled circles) in DMAc. In these figures the literature data on CA (DS = 0.49)[12] (open circles), CA (DS = 2.46)[13] (triangles), and CA (DS = 2.92)[6] (rectangles) in DMAc at 25°C are shown for comparison. The following Mark–Houwink–Sakurada (MHS) equation was derived for the CA (DS = 1.75) fractions in DMAc by the least-squares method:

$$[\eta] = 9.58 \times 10^{-2} M_w^{0.65} \quad (\text{cm}^3 \text{ g}^{-1}) \quad (1)$$

The exponent a in the MHS equation

$$[\eta] = K_m M^a \quad (2)$$

(K_m and a are the parameters characteristic of a given polymer/solvent system at a given temperature) decreases in the order: CA (DS = 2.46) $\gg$ CA (DS = 2.92) > CA (DS = 1.75) > CA (DS = 0.49). The relation between $\langle S^2 \rangle_z^{1/2}$ and M_w for the CA (DS = 1.75) fractions in DMAc is represented by

$$\langle S^2 \rangle_z^{1/2} = 0.38 \times 10^{-8} M_w^{0.52} \quad (\text{cm}) \quad (3)$$

Compared at the same M_w, the $\langle S^2 \rangle_z^{1/2}$ value for the CA (DS = 2.46)/DMAc system is larger than those of other CA/DMAc systems in the range of $M_w \leq 10^6$, suggesting that the CA molecule in
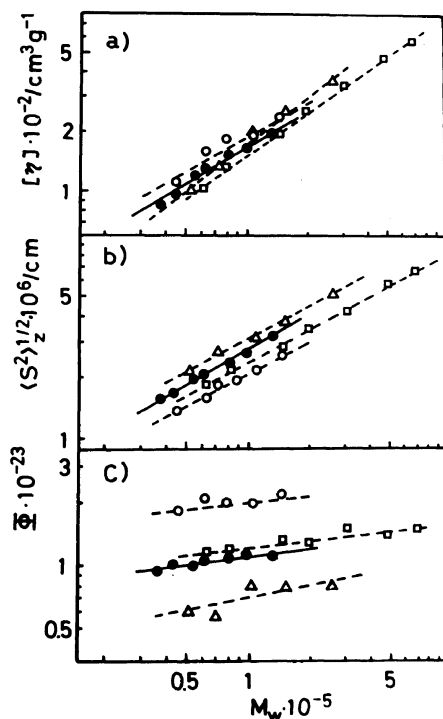
Figure 1. a) Molecular weight dependence of limiting viscosity number $[\eta]$; b) z-average radius of gyration $\langle S^2 \rangle_z^{1/2}$, and c) Flory's viscosity parameter Φ of CA with various DS in DMAc at 25°C. Closed circles, CA (DS = 1.75); open circles, CA (DS = 0.49); triangles, CA (DS = 2.46); rectangles, CA (DS = 2.92). Full line represents data for CA (DS = 1.75) and broken lines, those for CA (DS = 0.49), CA (DS = 2.46), and CA (DS = 2.92).

Figure 2. Molecular weight dependence of the draining parameter X of CA with various DS in DMAc. The symbols have the same meaning as in Figure 1. Full lines represent the relation between X and M_w determined by the least-squares method from the data for CA with various DS.
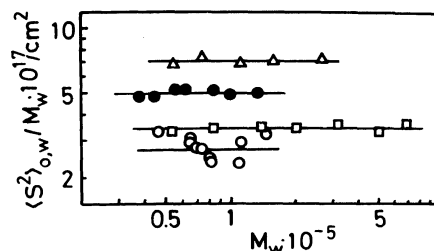
Figure 3. Molecular weight dependence of the mean-square weight-average radius of gyration in the unperturbed state relative to M_w ($\langle S^2 \rangle_{0,w}/M_w$) for CA with various DS in DMAc. The symbols have the same meaning as in Figure 1. Full lines represent the relation between $\langle S^2 \rangle_{0,w}/M_w$ and M_w determined by the least-squares method from the data for CA with various DS.
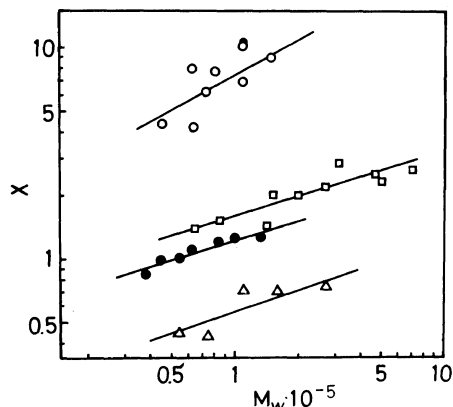
DMAc becomes most rigid at DS = 2.46.

The value of Φ for the CA (DS = 1.75) fractions in DMAc depends on molecular weight as follows:

$$\Phi = 0.26 \times 10^{23} \, M_w^{0.12} \qquad (4)$$

A similar significant molecular weight dependence of Φ was found for other CA in the same solvent. It is noted that even for the highest molecular weight fraction of CA (DS = 1.75), the Φ value is about 60% smaller than the theoretical limiting value 2.87×10^{23} for non-draining and unperturbed linear polymers and hence the draining effect is not negligible for CA (DS = 1.75) in DMAc.

The α_s values of the CA (DS = 1.75) fractions in DMAc are smaller than 1.03, so that the excluded-volume effect on CA (DS = 1.75) in DMAc is as small as that on CA with other DS in DMAc.[6,12,13]

The X values of the CA (DS = 1.75) fractions in DMAc range from 0.8 to 1.3. The draining effect on CA/DMAc systems decreases in the order: CA (DS = 2.46) $\gg$ CA (DS = 1.75) $\geq$ CA (DS = 2.92) $\gg$ CA (DS = 0.49) (see Figure 2).

Figure 3 shows the log-log plot of the mean-square weight-average radius of gyration in the unperturbed state relative to M_w, i.e., $\langle S^2 \rangle_{0,w}/M_w$ vs. M_w. Here, $\langle S^2 \rangle_{0,w}$ was calculated from the values of α_s (method 2B[17]). For CA (DS = 1.75) in DMAc, the ratio $\langle S^2 \rangle_{0,w}/M_w$ can be regarded, within experimental error, as independent of M_w (i.e., a_2 ($\equiv$ d ln ($\langle S^2 \rangle_{0,w}/M_w$)/d ln M_w) = 0). In

Table II. Unperturbed chain dimensions A, conformation parameter σ, and characteristic ratio C_∞ of cellulose acetate with various DS in DMAc at 25°C, estimated by thermodynamic and hydrodynamic methods

Methods	$A \times 10^8$/cm			
	DS = 0.49	DS = 1.75	DS = 2.46	DS = 2.92
2B (α_s from ψ)	1.28	1.73	2.05	1.43
2C ($a_2 = 0$)	1.38	1.73	1.98	1.49
2E ($a_2 = a_\Phi = 0$)	1.12	1.12	0.79	0.89
2F ($a_2 = a_\Phi = 0$)	1.14	1.16	0.92	1.00
2G ($a_2 \neq 0$, $a_\Phi \neq 0$)	1.40	1.79	1.90	1.47
2K ($a_2 \neq 0$, $a_\Phi \neq 0$)	1.45	1.73	1.85	1.46
Most probable A	1.38	1.75	1.95	1.46
Conformation parameter σ	2.46	3.47	4.10	3.14
Characteristic ratio C_∞	11.6	24.1	33.7	20.3

other words, CA (DS = 1.75) as well as CA with other DS behave as Gaussian chains in DMAc.

Table II presents the unperturbed chain dimension A ($\equiv (6\langle S^2 \rangle_0 / M)^{1/2}$) estimated by various methods (2B—2K).[17-19] This table includes the A values determined for CA with different DS[6,12,13,18] for comparison. The A values of CA (DS = 1.75) estimated by methods 2E and 2F which neglect the draining effect ($a_\Phi (\equiv d \ln \Phi / d \ln M_w) = 0$), are smaller than those estimated by other methods, as was found for other cellulose derivatives, including CA having different DS in DMAc.[17-19] The most probable A, obtained as the average of the values by methods other than 2E and 2F is 1.75×10^{-8} (cm) for CA (DS = 1.75) in DMAc. The conformation parameter σ ($\equiv A / A_f$; A_f is the A for a hypothetical freely rotating chain) and the characteristic ratio C_∞ corresponding to the most probable A are also included in Table II. Here we used 0.504×10^{-8} (cm) for A_f.[13] These values of σ and C_∞ indicated that CA (DS = 1.75) is stiffer than CA (DS = 0.49) and CA (DS = 2.92), but more flexible than CA (DS = 2.46), on making a comparison of all these polymers in DMAc. We found by NMR and ultrasonic interferometer measurements that solvation occurs in DMAc solutions of CA (DS = 0.49), CA (DS = 2.46), and CA (DS = 2.92) and that this solvation contributes mainly to the chain rigidity of cellulose acetate in DMAc.[13] Therefore, it may be concluded that the difference in equilibrium chain rigidity among CA with different DS is a reflection of the difference in degree of solvation.

REFERENCES

1. K. Kamide, S. Manabe, and E. Osafune, *Makromol. Chem.*, **168**, 173 (1973).
2. K. Kamide, T. Terakawa, and S. Manabe, *Sen'i Gakkaishi*, **30**, T-464 (1974).
3. K. Kamide, T. Terakawa, S. Manabe, and Y. Miyazaki, *Sen'i Gakkaishi*, **31**, T-401 (1975).
4. S. Ishida, H. Komatsu, T. Terakawa, Y. Miyazaki, and K. Kamide, *Mem. Fac. Eng., Kanazawa Univ.*, **12**, 103 (1979).
5. K. Kamide, T. Terakawa, and Y. Miyazaki, *Polym. J.*, **11**, 285 (1979).
6. K. Kamide, Y. Miyazaki, and T. Abe, *Polym. J.*, **11**, 523 (1979).
7. K. Kamide, Y. Miyazaki, and T. Abe, *Makromol. Chem.*, **180**, 2801 (1979).
8. H. Suzuki, Y. Miyazaki, and K. Kamide, *Netsusokutei*, **7**, 37 (1980).
9. H. Suzuki, Y. Miyazaki, and K. Kamide, *Eur. Polym. J.*, **16**, 703 (1980).
10. K. Kamide, K. Okajima, and M. Saito, *Polym. J.*, **13**, 115 (1981).

11. K. Kamide and K. Okajima, *Polym. J.*, **13**, 127 (1981).

12. K. Kamide, M. Saito, and T. Abe, *Polym. J.*, **13**, 421 (1981).

13. K. Kamide and M. Saito, *Polym. J.*, **14**, 517 (1982).

14. S. Ishida, H. Komatsu, H. Katoh, M. Saito, Y. Miyazaki, and K. Kamide, *Makromol. Chem.*, **183**, 3075 (1982).

15. M. Saito, *Polym. J.*, **15**, 213 (1983).

16. M. Kurata, M. Fukatsu, H. Sotobayashi, and H. Yamakawa, *J. Chem., Phys.*, **41**, 139 (1964).

17. K. Kamide and Y. Miyazaki, *Polym. J.*, **10**, 409 (1978).

18. K. Kamide and M. Saito, *Eur. Polym. J.*, **17**, 1049 (1981).

19. K. Kamide and M. Saito, *Eur. Polym. J.*, **18**, 661 (1982).

20. K. Kamide and M. Saito, unpublished results.