NOTE

Comment on the Applicability of the Plot $M^{1/2}/[\eta]$ vs. $M^{-1/2}$ to Cellulose, Amylose, and Their Derivatives

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Tanner and Berry[1] have derived the following equation for expressing the molecular weight M dependence of the limiting viscosity number $[\eta]$ for polymers having a non-negligible free draining effect in solutions:

$$M^{1/2}/[\eta]=[K'(6\langle S^2\rangle/M)^{3/2}]^{-1}(1+A' M^{-1/2}) \quad (1)$$

where K' and A' are parameters depending on the models used and $\langle S^2\rangle$ is the mean-square radius of gyration. This eq 1, which corresponds to eq 31 in their paper, has been derived by postulating $a_2 [\equiv \mathrm{d} \log (\langle S^2\rangle_0/M)/\mathrm{d} \log M]\neq 0$ and $a_\Phi(\equiv \mathrm{d} \log \Phi/\mathrm{d} \log M)\neq 0$. Here $\langle S^2\rangle_0$ is $\langle S^2\rangle$ at unperturbed state and Φ is the Flory viscosity parameter. Using eq 1 and appropriate values for the draining parameter X, and assuming that $a_1 (\equiv \mathrm{d} \log \alpha_\mathrm{s}/\mathrm{d} \log M)=0$ (where α_s is the linear expansion factor), Tanner and Berry estimated $\langle S^2\rangle_0/M$ from the intercept of a plot of $M^{1/2}/[\eta]$ vs. $M^{-1/2}$ (Tanner—Berry plot) for some cellulose derivatives. Hereafter this method is briefly designated as method 2H.

Kamide and Miyazaki[2] have demostrated that $a_2\leq 0$, $a_\Phi>0$, and $a_1\gtrsim 0$ for cellulose, amylose, and their derivatives in solvents. In this note, we examine the applicability of method 2H to the above polymers. Kamide and Miyazaki[2] have established some methods for estimating the unperturbed chain dimensions A $[\equiv 6^{1/2} (\langle S^2\rangle_0/M)^{1/2}]$ in the general case of $a_2\neq 0$, $a_\Phi\neq 0$, and $a_1\neq 0$, and evaluated the values of A $(A_{(\mathrm{m})})$ for cellulose, amylose and their derivatives with confience. Here, $A_{(\mathrm{m})}$ is defined as the average of the A values obtained by method 2A, 2B, 2C, 2D, and 2G. Since the details of these methods are given in ref 2, they are not described here. Figure 8 in ref 2 shows that the magnitude $a_\Phi+1.5a_2$ in-

fluences the A value, as determined by the viscosity plot (method 2E in ref 2), especially in the vicinity of $a_\Phi+1.5a_2\simeq 0$. Therefore, it can also be expected that the intercept of the Tanner—Berry plot will be sensitively influenced by $1.5a_2+a_2$, which is completely neglected in eq 1. When $a_1\neq 0$, $a_2\neq 0$, eq 1 should be rearranged into eq 2:

$$M^{a_1+1.5a_2+0.5}/[\eta]=(K'6^{3/2}K_0^{3/2}K_\alpha)(1+A'M^{-1/2})$$
$$(2)$$

where

$$K_0=(\langle S^2\rangle_0/M)/M^{a_2} \quad (3)$$

and

$$K_\alpha=\alpha_\mathrm{s}{}^3/M^{a_1} \quad (4)$$

The plot of $M^{a_1+1.5a_2+0.5}/[\eta]$ vs. $M^{-1/2}$ should be linear and K_0 can be evaluated from it's intercept at $M^{-1/2}=0$, provided that K_α is given in advance. Unfortunately, the experimental determination of a_1, a_2, and K_α (especially of a_1 and K_α) is not accurate enough to employ eq 2 for estimating K_0.

Figure 1 illustrates the typical Tanner—Berry plots for cellulose, amylose, and their derivatives. The literature data used in ref 2 were also employed in Figure 1. The plots can be reasonably approximated with straight lines, giving $[K'(6\langle S^2\rangle/M)^{3/2}]^{-1}$ as the intercepts. Since for these polymers $X\lesssim 2$ has been confirmed extensively by Kamide and Miyazaki,[2] K' can be taken as $2.87/1.259\times 10^{23}$, using Table VIII of ref 1. Table I summarizes the A values thus determined, $(A_{(2\mathrm{H})})$, together with $A_{(\mathrm{m})}$. The values $A_{(2\mathrm{H})}$ do not always coincide with $A_{(\mathrm{m})}$. The ratio $A_{(2\mathrm{H})}/A_{(\mathrm{m})}$ increases significantly with increase in $a_1+1.5a_2$, as shown in Figure 2, where the full line is a regression curve
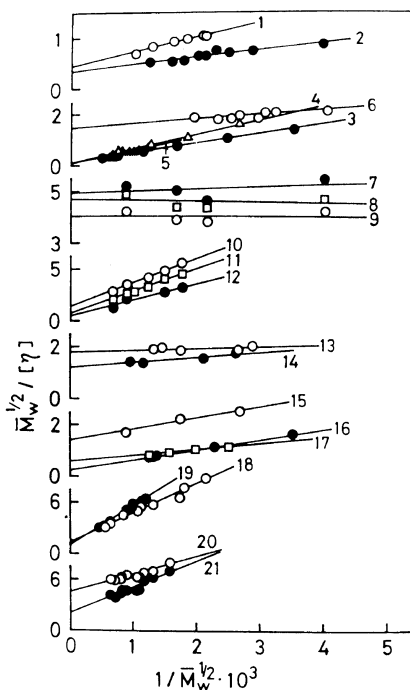
Figure 1. Plot of $M_w^{1/2}/[\eta]$ against $M_w^{-1/2}$: 1, cellulose in cadoxen; 2, cellulose in FeTNa; 3, cellulose trinitrate (CTN) in acetone; 4, cellulose nitrate (CN) (N=12.9%) in acetone; 5, cellulose acetate (CA) in acetone; 6, cellulose tricaproate (CTCp) in 1-chloronaphthalene; 7, CTCp in dioxane—water; 8, CTCp in dimethylformamide (DMF); 9, cellulose tricarbanilate (CTC) in cyclohexanone; 10, CTC in acetone; 11, CTC in dioxane; 12, methylcellulose (MC) in water; 13, sodium carboxymethyl cellulose (NaCMC) in aq. NaCl solution; 14, sodium cellulose xanthate (NaCX) in 1-M NaOH; 15, hydroxyethyl cellulose (HEC) in water; 16, ethylhydroxyethyl cellulose (EHEC) in water; 17, amylose in DMF; 18, amylose triacetate (ATA) in nitromethane; 19, amylose tricarbanilate (ATC) in pyridine—water; 20, ATC in pyridine.

Table I. Unperturbed chain dimensions A estimated by eq 1, as compared with $A_{(m)}$

Polymer[a]	Solvent	$A_{(2H)} \times 10^8$, cm	$A_{(m)} \times 10^8$, cm	$\dfrac{A_{(2H)}}{A_{(m)}}$
Cellulose	Cadoxen[b]	2.15	1.71	1.26
	FeTNa[c]	2.34	2.39	0.98
CTN (N=13.9%)	Acetone	3.32	2.43	1.37
(N=13.6%)	Acetone	3.80	2.08	1.83
(N=12.9%)	Acetone	3.32	1.86	1.78
CA (AC=55.6%)	Acetone	1.44	1.79	0.80
CTCp	DMF	1.03	2.02	0.51
	1-Chloronaphalene	0.96²	1.91	0.50
	Dioxane—water	0.97⁷	1.90	0.51
CTC	Acetone	1.99	1.37	1.45
	Cyclohexanone	1.50	1.35	1.11
	Dioxane	2.35	1.85	1.27
MC (DS=2)	Water	1.34	2.32	0.58
NaCMC (DS=0.88)	NaCl (I→∞)	1.55	1.46	1.06
HEC (DS=1)	Water	2.63	2.25	1.17
EHEC (DS=2)	Water	2.06	2.30	0.90
NaCX (DS=0.78)	1-M NaOH	1.47	3.79	0.39
Amylose	DMSO	1.52	1.55	0.98
ATA	Nitromethane	1.73	0.99⁵	1.74
ATC	Pyridine—water	1.00	1.07	0.93
	Pyridine	1.38	1.08	1.28

[a] Meanings of notations are given in the legend of Figure 1.
[b] Triethylenediamine zinc hydroxide.
[c] Iron-sodium-tartrate.

and the broken lines are the 95-% confidence limits. In this case $a_1 + 1.5a_2$ was calculated from the sixth and last columns of Table III in ref 2. The correlation coefficient r is estimated to be 0.75 between $A_{(2H)}/A_{(m)}$ and $a_1 + 1.5a_2$. Considering the large experimental uncertainty in $a_1 + 1.5a_2$, we can conclude that $A_{(2H)}$ is approximately equal to $A_{(m)}$ only at $a_1 + 1.5a_2 \simeq 0$, as our theory predicts (see eq 2).

Table II. Average and standard deviation of the difference $A_{(2i)} - A_{(m)}$ for cellulose, amylose, and their derivatives

Analytical method	Average $(A_{(2i)} - A_{(m)})$ $\times 10^8$, cm $i = \mathrm{B}, \mathrm{C} \cdots \mathrm{H}$	Standard deviation σ
2B eq 3 of ref 2	-0.057	0.18_1
2C eq 32 of ref 2[a]	0.090	0.15_9
2D eq 33 of ref 2[b]	0.033	0.07_7
2E eq 40 of ref 2[c]	-1.001	0.54_4
2F eq 43 of ref 2[d]	-0.982	0.53_5
2G eq 46 of ref 2[e]	-0.042	0.15_8
2H eq 1[f]	0.018	0.91_8

[a] Baumann plot. [b] BKM plot. [c] Stockmayer—Fixman plot. [d] Kamide, *et al.*, plot. [e] Kamide—Miyazaki plot. [f] Tanner—Berry plot.

Table II compiles the average and standard deviation of the difference $A_{(2H)} - A_{(m)}$ for cellulose, amylose, and their derivatives as given in Table I. Table II contains also the corresponding values obtained by the other methods (2B, $\cdots$, 2G) employed in ref 2. As was pointed out by Kamide and Miyazaki,[2] methods 2E and 2F apparently underestimate the A value and their standard deviations are significantly large, due to the ignoring of the draining effect and the non-
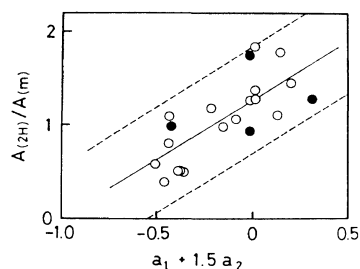

Figure 2. Dependence of the ratio $A_{(2H)}/A_{(m)}$ on $a_1 + 1.5a_2$: $\bigcirc$, cellulose and its derivatives; $\bullet$, amylose and its derivatives.

Gaussian nature. The average A value obtained by method 2H is accidentally in agreement with an averaged $A_{(m)}$, because the values of $a_1 + 1.5a_2$ for cellulose, amylose, and their derivatives scatter equally around zero (Figure 2). But the standard deviation of $A_{(H)} - A_{(m)}$ is five to ten times larger than those obtained by methods 2B, 2C, 2D, and 2G, indicating that method 2H is less accurate and the conclusions drawn by using eq 1 are seriously questionable.

In conclusion, eq 1 is not applicable to cellulose, amylose, and their derivatives, in which the non-Gaussian nature of a chain ($a_2 \neq 0$) and the excluded volume effect ($a_1 \neq 0$) cannot be completely neglected. In the region $a_1 + 1.5a_2 > 0$, the Tanner—Berry plot overestimates the A value; in the region of $a_1 + 1.5a_2 < 0$, the Tanner—Berry plot underestimates the A value.

REFERENCES

1. D. W. Tanner and G. C. Berry, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 941 (1974).
2. K. Kamide and Y. Miyazaki, *Polym. J.*, **10**, 409 (1978).