332 *Bull. Korean Chem. Soc., Vol. 8, No. 4, 1987*

Chun Hag Jang et al.

Lett., **24**, 1783 (1983).

4. N. Miyaura, T. Yano, A. Suzuki, *Tetrahedron Lett.*, **21**, 2865 (1980).

5. (a) P. M. Maitlis, *The Organic Chemistry of Palladium*, Academic Press, New York, p 210 (1971); (b) J. Tsuji, In *The Chemistry of the Metal-Carbon Bond;* F. R. Hartley, and S. Patai, Ed.: John Wiley & Sons: New York, 1985; p 163; (c) J. P. Collman, L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, p 673 1980; (d) R. F. Heck, *Palladium Reagents in Organic Synthesis;* Academic Press: London, p 117 1985.

6. (a) J. Tsuji, S. Imamura, *Bull. Chem. Soc. Jpn.*, **40**, 197 (1967); Elimination reactions involving -allylic palladium complexes, see reference 5d, p 172.

7. (a) Y. Yamamoto, H. Yatagai, A. Sonoda, S-I. Murahashi, *J. Chem. Soc. Chem. Commun.*, 452 (1976); (b) H. Yatagai, *J. Org. Chem.*, **45**, 1640 (1980); (c) H. C. Brown, J. B. Campbell, *J. Org. Chem.*, **45**, 550 (1980).

8. N. Miyaura, T. Yano, A. Suzuki, *Bull. Chem. Soc. Jpn.*, **53**, 1471 (1980).

9. H. Yatagai, *Bull. Chem. Soc. Jpn.*, **53**, 1670 (1980).

10. L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, p 137 1971.

11. (a) E. R. H. Jones, G. Eglinton, M. C. Whiting, *Org. Synth.*, Coll Vol. 4, 755 (1963). (b) G. Eglinton, M. C. Whiting, *J. Chem. Soc.*, 3654 (1950).

12. Preparation of allylic phenyl ethers, see; D. S. Tarbell, *Org. Reac.*, **2**, 1 (1944).

13. H. C. Brown, *Organic Synthesis via Boranes;* John Wiley: New York, p 54 1975.

14. H. C. Brown, C. G. Scouten, R. Liotta, *J. Am. Chem. Soc.*, **101**, 96 (1979).

15. Preparation of (E)-1-alkenyl-1,3,2-benzodioxaborols, see; (a) reference 13, p 64; (b) reference 2; (c) H. C. Brown, S. K. Gupta, *J. Am. Chem. Soc.*, **94**, 4370 (1972).

16. D. R. Coulson, *Inorg. Synth.*, **13**, 121 (1972).

Non-Newtonian Intrinsic Viscosities of Biopolymeric and Non-biopolymeric Solutions (II)

Chun Hag Jang, Chang Hong Kim, and Taikyue Ree*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131. Received May 7, 1987

This paper is a continuation of our previous paper,[1] and deals with Eq.(1) (see the text), which was theoretically derived in the paper,[1] $[\eta]^f$ and $[\eta]^o$ is the intrinsic viscosity at stress f and f = O, respectively. Equation (1) predicts how $[\eta]^f/[\eta]^o$ changes with stress f, relaxation time β_2 of flow unit 2 and a constant c_2 related with the elasticity of molecular spring of flow unit 2. In this paper, Eq.(1) is applied to a biopolymer, e.g., poly (γ-benzyl L-glutamate), and nonbiopolymers, e.g., polyisobutylene, polystyrene, polydimethylsiloxane and cellulose triacetate. It was found that the c_2 factor is zero for non-biopolymers while $c_2 \neq 0$ for biopolymers as found previously.[1] Because of the non-Newtonian nature of the solutions, the ratio $[\eta]^f/[\eta]^o$ drops from its unity with increasing f. We found that the smaller the β_2, the larger the f_c at which the viscosity ratio drops from the unity, vice versa.

Introduction

In a previous paper, [1] we derived the following equation for flow of poly (γ-methyl L-glutamate) (PMLG) solution:

$$\frac{[\eta]^f}{[\eta]^o} = 1 - \frac{A}{[\eta]^o}\left\{1 - \frac{\sinh^{-1}[\beta_2\,(f/\eta_0)\,\exp(-c_2f^2/\eta_0^2kT)]}{\beta_2 f/\eta_0}\right\} \tag{1}$$

where $[\eta]^f$ and $[\eta]^o$ is the intrinsic viscosity at stress f and at f=O, respectively, the latter being given by the following equation:

$$[\eta]^o = \lim_{c\to 0}\frac{1}{C}\left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1 + \frac{x_2\beta_2}{\alpha_2\eta_0}\right) \tag{2}$$

where C is the concentration of PMLG.

In the derivation of Eq.(1), it was assumed that there are three kinds of flow units in the flow system, i.e., solvent flow units (O), Newtonian flow units (1) and non-Newtonian flow units (2) of PMLG. x_0, x_1 and x_2 are the fraction of the shear surface occupied by the respective flow units; β_0, β_1 and β_2

are the respective relxation times; α_0, α_1 and α_2 are the propotional quantities to the shear moduli of the respective units c_2 is a constant related to the elasticity of the non-Newtonian flow unit 2, η_0 is the viscosity constant of the slovent, and

$$A = \lim_{c\to 0}\frac{1}{C}\left(\frac{x_2\beta_2}{\alpha_2\eta_0}\right) \tag{2a}$$

We applied already[1] Eq.(1) to a biopolymeric solution, e.g., PMLG and to non-biopolymeric solutions, e.g., polyisobutylene (PIB) and polystylene (PS) with good results. It was found that $c_2 = O$ for non-biopolymeric solutions, whereas $c_2 \neq O$ for biopolymeric solutions except for the case the helix content F_H in the molecule is zero. In this paper, Eq.(1) is tested further for other cases, and related problems are discussed.

Results and Discussion

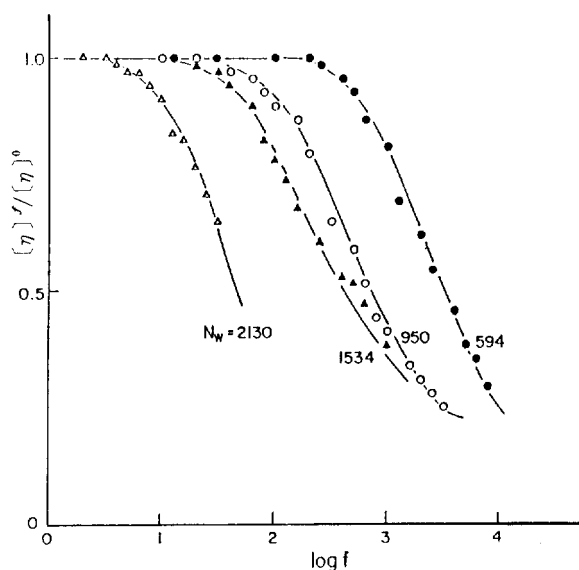### (A) Molecular Weight Effect on the Intrinsic Visco-

Figure 1. Flow curves of poly (γ-benzyl L-glutamate) (PBLG) in metacresol (MC). The chain length ($\overline{N}_w$) of the sample is shown on each curve. The experimental data for $\overline{N}_w = 2130$ at 30°C from ref. 3, and the others at 25°C from ref. 2.

Table 1. ^{a} **Dependence of β_2 and c_2 on the Chain Length of PBLG in Metacresol Solvent**

F_H	$\overline{N}_w$	$[\eta]^o$ (dl/g)	A (dl/g)	$\beta_2 \cdot 10^4$ (sec)	$c_2 \cdot 10^{22}$ (erg. sec^2)
1	594	1.3	0.99	2.13	0.27
1	950	2.9	2.24	10.7	2.91
1	1534	6.7	4.82	23.1	10.3
1	2130	7.41	8.47	79.1	70.6

^{a} $[\eta]^o$ and $\overline{N}_w$ are experimental data.^{2,3} A, β_2 and c_2 are determined by a non-linear regression method. ^{b} $\eta_0(MC) = 0.1233$ poise at 25°C = 0.1087 poise at 30°C.

sities In Figure 1, the flow curves, $[\eta]^f/[\eta]^o$ vs. log f, for poly (γ-benzyl L-glutamate) (PBLG) in metacresol (MC) solvent are shown. The chain length of the solute molecules $\overline{N}_w$ (= the number of monomer units) is given on each curve. The flow curves of $\overline{N}_w = 594,950$ and 1530 were obtained at 25°C by Yang^2 whereas the curve for $\overline{N}_w = 2130$ at 30°C by Byerley *et al.*^{3}

We applied Eq.(1) to the flow curves, and obtained the parametric values of A, β_2 and c_2 appearing in Eq.(1) by a non-linear regression method,^{4} the results are summerized in Table 1. The full cruves were calculated from Eq.(1) by using the parametric values in Table 1. One notes that the agreement between theory and experiment is satisfactory.

We note from Table 1 that when the molecular weight (or $\overline{N}_w$) is small β_2 is small, and vice versa. This is natural because small molecules are easy to flow, i.e., β_2 is small.

We also note from Fig. 1 that all the flow curves fall off from the unity line of $[\eta]^f/[\eta]^o$ at some stress f_c as stress f increases. And it is also noted that the smaller relaxation time β_2 of the flow unit (see Table 1), the larger f_c, vice versa. See for example, the curve of $\overline{N}_w = 594$ in Fig. 1, the β_2 of the flow unit is $2.13 \cdot 10^{-4}$ sec (Table 1) and the f_c of the curve $1.38 \cdot 10^2$ dyn/cm^2 (Figure 1), whereas for the curve of $\overline{N}_w = 950$, $\beta_2 = 10.7 \cdot 10^{-4}$ sec (Table 1), and $f_c = 20.2$ dyn/cm^2

(Figure 1). This fact is explained from Eq.(1) in the following way:

$$\lim_{f \to 0} \frac{[\eta]^f}{[\eta]^o} = \lim_{f \to 0} \left(1 - \frac{A}{[\eta]^o} \left\{ 1 - \frac{\sinh^{-1}[\beta_2 (f/\eta_0) \exp(-c_2 f^2/\eta_0^2 kT)]}{\beta_2 f/\eta_0} \right\} \right)$$

$$\approx 1 - \frac{A}{[\eta]^o} \left(1 - \frac{\sinh^{-1}\beta_2 f/\eta_0}{\beta_2 f/\eta_0} \right)$$

$$\approx 1 - \frac{A}{[\eta]^o} \left(1 - \frac{\beta_2 f/\eta_0}{\beta_2 f/\eta_0} \right) \approx 1 \qquad (3)$$

That is at f→0, $[\eta]^f/[\eta]^o \to 1$. The relation,

$$\sinh^{-1}(\beta_2 f/\eta_0) \approx \beta_2 f/\eta_0 \qquad (3a)$$

in the second equality of Eq.(3), however, fails to hold if f becomes larger than f_c. Thus the flow curve drops from the unity line of $[\eta]^f/[\eta]^o$ at f_c. Let β_2' and f_c' be the corresponding β_2 and f_c values for the flow curve of $\overline{N}_w = 594$ in Figure 1, and let β_2'' and f_c'' be the quantities for curve of $\overline{N}_w = 950$. At each f_c point, the relation (3a) holds. From the series,

$$\sinh^{-1} u = u - \frac{1}{2}\frac{u^3}{3} + \frac{1}{2}\frac{3}{4}\frac{u^5}{5} - \cdots \qquad (4)$$

one finds that when u = 0.23,

$$\sinh^{-1} 0.23 = 0.23 - 2.028 \cdot 10^{-3} + 0.4827 \cdot 10^{-4} \cdots$$

i.e.,

$$\sinh^{-1} 0.23 = 0.23 \qquad (4a)$$

We assume that Eq.(4a) can be applied to (3a), i.e.,

$$\sinh^{-1}(\beta_2 f/\eta_0) = \beta_2 f/\eta_0 = 0.23 \qquad (4b)$$

By applying Eq.(5b) to the points of f'_c and f''_c of the flow curves of $\overline{N}_w = 594$ and 950, we obtain the following relations:

$$\frac{f'_c \beta'_2}{\eta_0} = 0.23$$

$$\frac{f''_c \beta''_2}{\eta_0} = 0.23 \qquad (4c)$$

where $\eta_0 = 0.1233$ poise is the viscosity of solvent MC at 25°C, $\beta'_2 = 2.13 \cdot 10^{-4}$ sec and $\beta''_2 = 10.7 \cdot 10^{-4}$ sec as mentioned above. By using these data, f'_c and f''_c are calculated and compared with observed values in the following:

$f'_c = 1.33 \cdot 10^2$ dyn/cm^2 when $\beta_2 = 2.13 \cdot 10^{-4}$ sec

     $= 1.38 \cdot 10^2$ dyn/cm^2 (obs.)

$f''_c = 26.5$ dyn/cm^2 when $\beta_2 = 10.7 \cdot 10^{-4}$

     $= 20.2$ dyn/cm^2 (obs.)

The results are satisfactory, i.e., we were able to explain the fact that the smaller β_2, the larger f_c, vice versa. The similar fact, i.e., the smaller β_2, the larger f_c, was found also for PMLG [poly (γ-methyl L-glutamate)] solutions in a previous paper,^{1} although precise comments were not given thereupon.

A PBLG molecule has a polypeptide chain (-CO-NH-CHR-)$_n$ which makes a helix, the intramolecular hydrogen bonds formed in the peptide chain help the helix formation.^{5}
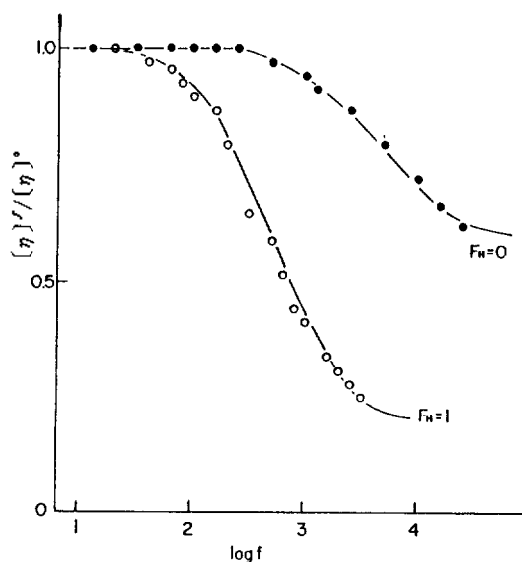
Figure 2. Flow curves of PBLG at 25°C from ref. 2. The solvent of the curve of $F_H=0$ is dichloroacetic acid, and that of the curve of $F_H=1$ is MC. The molecular weight of PBLG is 208,000 ($\bar{N}_w=950$).

Table 2. ^a **Intrinsic Viscosities of PBLG Solutions and flow Parameters at 25°C for Samples of $F_H=0$ and 1**

F_H	$[\eta]^o$ (dl/g)	A (dl/g)	$\beta_2 \cdot 10^4$ (sec)	c_2 (erg/sec)	β_2/η_0
0(in DCA)	1.2	0.51	0.647	0	$1.05 \cdot 10^{-3}$
1(in MC)	2.9	2.24	10.7	$2.91 \cdot 10^{-22}$	$8.68 \cdot 10^{-3}$

^a $[\eta]^o$ and F_H are expreimental data.[2] A, β_2 and c_2 are determined by a non-linear regression method. ^b $\eta_0=0.1233$ poise (MC), $\eta_0=0.06164$ poise (DCA). The molecular weight of PBLG is 208,000 $\bar{N}_w=950$).
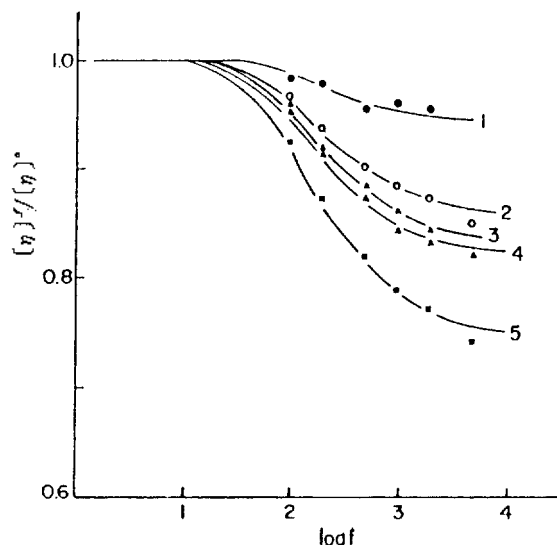

Figure 3. Flow curves of polyisobutylene in various solvents at 25°C.[6] The curve numbers give also the sample numbers in Table 3, and also the solvents shown in Table 3. The order of curve numbers, 1,2,--5 accords with the order of the solubilities of the solvents from poor to the best.

The c_2 factor is related to the elasticity constant of the helix chain.[1] One easily understands that the chain of large $\bar{N}_w$ has a longer chain with larger number of hydrogen bonds, as a

Table 3. ^a **Intrinsic Viscosities and flow Parameters of Polyisobutylene in Various Solvents at 25°C**

sample	$\bar{M}_w \cdot 10^{-6}$	$[\eta]^o$	α_f	A	β_1/η_1	c_2	solvent
1^b	1.59	1.50	1.94	0.093	0.017	0	Benzene
2	1.59	2.90	2.50	0.42	0.021	0	Decalin
3	1.59	3.87	2.74	0.65	0.023	0	$C_6H_5C_2H_5$
4	1.59	4.40	2.88	0.79	0.025	0	Isooctene
5	4.85	6.35	3.22	1.61	0.026	0	C_6H_{12}

^a $[\eta]^o$, $\bar{M}_w$ and α_f (extension factor) are experimental data of Passaglia *et al.* ^b A, β_2/η_0 and c_2 are those determined by a nonlinear regression method. ^b The sample numbers 1 to 5 indicate also the order of solubility power of the solvents from the poor to the best. The order accords also with that of the α_f.

result, the elasticity constant increases rapidly with $\bar{N}_w$ (see Table 1).

(B) Effect of F_H on Intrinsic Viscosities When PBLG ($\bar{M}_w=208,000$) was dissolved in dichloroacetic acid (DCA) the helix content in it becomes $F_H=0$, i.e., the PBLG takes a random coil form, whereas in metacresol the helix content becomes $F_H=1$, i.e., rigid rod.[2] The flow curves[2] of PBLG for $F_H=0$ and $F_H=1$ are shown in Figure 2. We applied Eq. (1) to the flow curves of $F_H=0$ and $F_H=1$ in Figure 2, and obtained the parametric values shown in Table 2. One notes that the sample of $F_H=0$ has $c_2=0$ as was found in a previous paper.[1] The full curves in Figure 2 were calculated from Eq.(1) by using the parametric values in Table 2. The agreement between experiment and theory is satisfactory. We also note that the flow curve with low β_2 falls off from the unity line of $[\eta]'/[\eta]^o$ line at higher f_c, vice versa, in agreement with our findings mentioned above as well as in a previous paper.[1]

(C) Solvent Effect for Polyisobutylene Viscosities The flow curves of polyisobutylene (PIB) at 25°C are shown in Figure 3,[6] more details on the curves are given in Table 3. We applied Eq. (1) to the flow curves, and the parametric values shown in Table 3 were obtained. One notes from Table 3 that in this case the c_2 factor is zero (i.e., $F_H=0$) for all the flow curves.(Refer to our paper.[1]) The full curves were calculated from Eq.(1) with $c_2=0$ by using the parametric values in Table 3. The agreement between experiment and theory is very good. The curve numbers, 1,2,···,5 (which accord with the sample number in Table 3) show also the order of solubilities of PIB in the solvents, i.e., benzene is the poorest solvent and cyclohexane the best (see Table 3). It is well known that a solute molecule occupies a small volume in poor solvent whereas the contrary is true in a better solvent, i.e., the solute molecule extends more in a good solvent. Thus, the extension factor α_f parallels the solubility (see Table 3). One also notes in Table 3 that β_2/η_0 parallels the solubility power since the relaxation time β_2 increases in good solvents. [Note: The increase in β_2 in good solvents exceeds the increase in η_0, thus β_2/η_0 increases according to the order of 1 to 5 in Table 3. It is also noted that the fall-off point (f_c) from the unity-line of $[\eta]'/[\eta]^o$ accords with our previous findings, i.e., the smaller β_2, the larger f_c.

Next we note in Figure 3 that all the flow curves approach limiting values of $[\eta]'/[\eta]^o$ as $f \to \infty$. From Eq. (1) with $c_2=0$, we obtain

$$\lim_{f \to \infty} \frac{[\eta]'}{[\eta]^o} = \lim_{f \to \infty} \left\{ 1 - \frac{A}{[\eta]^o} [1 - \frac{\ln(2\beta_1 f/\eta_0)}{\beta_1 f/\eta_0}] \right\} = 1 - \frac{A}{[\eta]^o} \equiv L \quad (4)$$

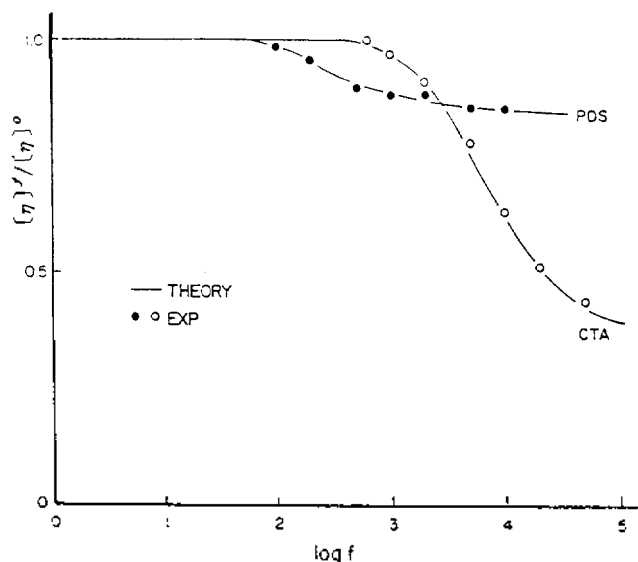**Figure 4.** Flow curves[6] of polydimethylsiloxane (PDS) and cellulose triacetate (CTA) in toluene and metacresol, respectively, at 25°C. $\overline{M}_w$ of PDS and CTA are shown in Table 4.

Table 4. [a] **Intrinsic Viscosities and flow Parameters of Polydimethylsiloxane (PDS) and Cellulose Triacetate (CTA) solutions at 25°C**

sample	$\overline{M}_w \cdot 10^{-6}$	$[\eta]^o$	α_f	A	β_2/η_0	c_2	solvent
PDS	8.20	1.94	2.20	0.31	$1.03 \cdot 10^{-2}$	0	Toluene
CTA	0.61	1.80	3.45	1.20	$5.612 \cdot 10^{-4}$	0	Metacresol

[a] $\overline{M}_w$, $[\eta]^o$ and α_f are experimental data of Passaglia *et al.*[6] A, β_2/η_0 and c_2 are those determined by a non-linear regression method.

we calculate the limiting value L ($= 1 \cdot A/[\eta]^o$) by using the data of A and $[\eta]^o$ in Table 3, and obtain the following values of L:

Sample:	1	2	3	4	5
L :	0.938	0.852	0.832	0.820	0.746

These L values agree well with the respective asymptotic values of the curves (see Figure 3).

(D) Stiff and Flexible Polymers Generally, stiff polymers present larger non-Newtonian effects.[7] Figure 4 show the flow curves of polydimethylsiloxane (PDS),[6] which is known to be one of the most flexible polymers, and cellulose triacetate (CTA)[6] which has stiff chain[8] and very extended configuration. One notes from Figure 4 that CTA has larger non-Newtonian effect. It will be interesting to test whether CTA behaves like biopolymers, i.e., $c_2 = 0$ or not.

We applied Eq.(1) to the flow curves in Figure 4, and obtained the parametric values shown in Table 4. From Table 4, one notices that the c_2 factor is zero in both cases, i.e.,

CTA behaves like a nonbiopolymer although it has a stiff chain, and cellulose is generally treated as one of biopolymers.

As one notes from Figure 4, the curves of PDS and CTA cross with each other. The crossing occurs by the interrelation between the parameters β_2/η_0, $[\eta]^o$ and $A/[\eta]^o$ of the curves as mentioned in our previous paper.[1] For β_2/η_0, cruve PDS>curve CTA, which is caused by the molecular-weight effect (Table 4), and the former drops from the line of $[\eta]^f/[\eta]^o = 1$ at the lower value of f_c while the reverse is ture, i.e., the curve CTA drops at a larger values of f_c (see Figure 4). This fact accords with our previous findings.

Next we consider the limiting value L of $[\eta]^f/[\eta]^o$ at $f \to \infty$ for curves PDS and CTA. From Eq.(4) and by using the data of A and $[\eta]^o$ in Table 4, we obtain the following values of L:

$$L(PDS) = 1-(0.31/1.94) = 0.840$$
$$L(CTA) = 1-(1.20/1.80) = 0.333$$

These, L values agree with the asymptotic values of the curves at $f \to \infty$ (see Figure 4). Since curve PDS starts at a lower f_c and approaches a higher value of L whereas the reverse is true for curve CTA [i.e., starts at a large f_c and approaching a lower L] curve PDS crosses curve CTA at a point (log f = 3.4) as shown in Figure 4.

(E) On the c_2 Factor Some comments have been made already about the c_2 factor, which is included in the $\sinh^{-1}$ term in the braces on the right of Eq.(1). We found that $c_2 = 0$ for non-biopolymeric solutions while $c_2 \neq 0$ for biopolymeric solutions, this is due to the presence of helix chains in the latter, whereas the non-biopolymers in solution have random coil forms.

References

1. C. H. Jang, J. R. Kim, and T. Ree, *Bull. Korean Chem. Soc.*, **8**(4), 318 (1987).
2. J. T. Yang, *J. Am. Chem. Soc.*, **80**, 1783 (1958); **81**, 3902 (1959).
3. A. J. Byerley, B. R. Jennings and H. G. Jerrard. *J. Chem. Phys.*, **48**, 5526 (1968).
4. J. L. Kuester and J. H. Mize, "Optimization Techniques with Fortran," MeGraw-Hill, New York, 1973, pp. 240-250.
5. H. Morawetz, "Macromolecules in Solutions," John Wiley, New York, 1975, p. 143.
6. E. Passaglia, J. T. Yang and N. J. Wegemer, *J. Polym. Sci.*, **47**, 333 (1960).
7. J. A. Subirana, *J. Chem. Phys.*, **41**, 3852 (1964).
8. A. L. Lehninger, "Principles of Biochemistry," Worth Publishers, Inc., New York, 1982, pp. 289-293.