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The Flow Properties of γ-Polyglutamic Acid Solutions in Capillary*[1]

Takeshi Mineshita, Shigeru Matsumura, Hiromi Ono, Takehiko Watanabe
and Sôzaburo Ono

Laboratory of Biophysical Chemistry, College of Agriculture, University of Osaka Prefecture, Sakai, Osaka

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Dependence of the viscosity of the solution of γ-polyglutamic acid in eater at various pH's on the bore-size of the capillary viscometer has been studied at 25°C at various concentrations (0.01—0.05 g/100 m*l*). Measurements were carried out with a Maron-Belner type low shear capillary viscometer with various capillary radii (1.9×10^{-2}—7.6×10^{-2} cm) within the shear stress range 0.2—20 dyn/cm^2 at the capillary wall. The polymer solutions showed a non-Newtonian flow behavior and a capillary bore-size dependence and both of these properties were diminished with the decreasing of pH. This capillary bore-size dependence may be attributed to the geometric hindrance of the capillary wall to the thermal motion of the polymer molecules near the wall. The dissolved state of the polymer molecules in solutions of various pH's has been studied by means of optical rotatory dispersions, flow birefringence and intrinsic viscosity. The dissolved state of the polymer solution as well as the capillary bore-size dependence were sensitive to pH. The polymer molecule in neutral and alkaline media may be in the form of a highly expanded chain and in acid medium in a contracted form having a some ordered chain conformation.

In the previous papers,[1-3] the dependence of the viscosity of polyvinylpyrrolidone solutions on the bore-size of capillary viscometer was reported and the flow of the polymer solution through the capillary was treated by assuming the existence of the double wall layer which is owing to the geometric hindrance of the capillary wall to the thermal motion of the polymer molecules near the wall in the flowing liquid.

In this paper, the similar treatments as stated above, were attempted to the solution of γ-polyglutamic acid, as an example of polyelectrolytes, and also the study on the dissolved state of γ-polyglutamic acid was made concerning the appearance of the capillary bore-size dependence of the viscosity.

Experimental

Materials. γ-Polyglutamic acid, or γ-PGA is a polymer of glutamic acid linked through the γ-carboxyl and α-amino group and was supplied by Dr. Sawao Murao, Laboratory of Fermentational Chemistry of University of Osaka Prefecture. This polymer is produced by the *Bacillus subtlis uar. polyglutamicum* from glucose and urea and composed of about 60% D-glutamic acid and 40% L-anomer. Molecular weight of the polymer is estimated as more than 1000000. More details for the polymer will be presented by Murao in elsewhere.[4]

Measurements. A Maron-Belner type capillary viscometer[5] suitable for the study of the flow of non-Newtonian fluids at the low shear stress of 0.2 to 20 dyn/cm^2 was used. Details on viscosity measurements was the same as described in the previous paper.[1]

Viscometers used for the determination of intrinsic viscosity were the Ubbelohde dilution type having the efflux time of about 180 sec for water at 25°C at which temperature the measurements were made.

The extinction angle, χ, and the birefringence, Δn, were measured with a Rao Flow Birefringence Viscometer Model No. B-23 over the gradient range from 50 to 5000 sec^{-1} at 25 ± 0.01°C.

Optical rotatory dispersion (ORD) measurements were carried out with a Yanagimoto ORD-185. All measurements were made in quartz cells with an optical path of 0.10, 0.20, or 0.50 cm at 25 ± 0.01°C.

Results and Discussion

The plots of viscosity *vs.* rate of shear of γ-PGA solution (0.05%) at pH 2.2 are shown in Fig. 1(a). Non-Newtonian flow behavior and capillary bore-size dependence were observed in all ranges of

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*[1] Partially presented at the 20th Symposium of the Colloid Chemistry, Hokkaido, Aug. 31, 1967.

1) T. Mineshita, T. Watanabe and S. Ono, This Bulletin, **40**, 2217 (1967).

2) T. Mineshita, T. Watanabe and S. Ono, *J. Polymer Sci.* Part C, **23(2)** (1969) in press. (Study on Wall Effect for Flow of Polymer Solution in Capillary).

3) T. Watanabe, T. Mineshita and S. Ono, This Bulletin, **42**, 583 (1969).

4) S. Murao, *Kobunshi* (*High Polymers, Japan*), **16**, 1204 (1967); *Nippon Nogeikagaku Kaishi* (*J. Agri. Chem. Soc. Japan*), in press.

5) S. H. Maron and R. J. Belner, *J. Appl. Phys.*, **26**, 1457 (1955).

rate of shear studied for the solution of higher concentration, while in lower concentration, the flow property approaches to one of Newtonian character and the capillary bore-size dependence becomes slight. The other examples of the plots of viscosity *vs.* rate of shear of γ-PGA solution (0.01%) at pH 7.1 in various capillaries are shown in Fig. 1(b). It is obviously shown that both the non-Newtonian nature and the capillary bore-size dependence of the viscosity were more enhanced in an neutral solution, especially in lower ranges of shear stress.

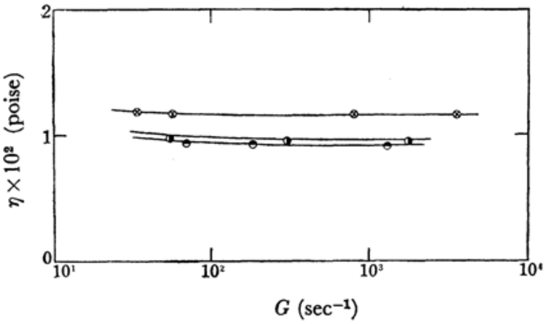

Fig. 1(a). Plots of viscosity *versus* rate of shear for γ-PGA (0.05 g/100 m*l*) aqueous solution (pH=2.2).
⊗ R=0.0761 cm; ◑ R=0.0302cm;
◓ R=0.0228 cm

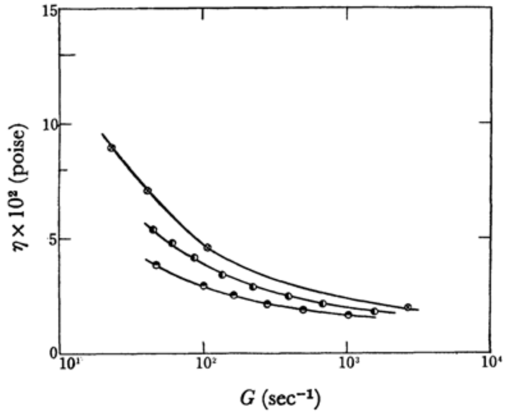

Fig. 1(b). Plots of viscosity *versus* rate of shear for γ-PGA (0.01 g/100 m*l*) aqueous solution (pH=7.1).
⊗ R=0.0761 cm; ◐ R=0.0502 cm;
◓ R=0.0302 cm

The experimental results were expressed by the modified formula of the generalized Ree-Eyring equation[1,6,7] for a flow system containing one Newtonian flow unit and one non-Newtonian unit which includes the additional terms dependent on the capillary bore-size as follows.

$$\eta=\left(\eta_1'-\frac{\sigma_1}{R}\right)+\left(\frac{1}{b_2'}+\frac{\sigma_2}{R}\right)\left(\frac{1}{a_2}\right)\left(\frac{a_2}{G}\right)\sinh^{-1}\left(\frac{G}{a_2}\right) \tag{1}$$

where $\eta_1=\eta_1'-\dfrac{\sigma_1}{R}$ and $\dfrac{1}{b_2}=\dfrac{1}{b_2'}+\dfrac{\sigma_2}{R}$,

$$\sigma_1=-\mathrm{d}\,(\eta_1)\,/\mathrm{d}\left(\frac{1}{R}\right),$$

$$\sigma_2=\mathrm{d}\left(\frac{1}{b_2}\right)\Big/\mathrm{d}\left(\frac{1}{R}\right),\quad \eta_1=x_1\beta_1/\alpha_1,$$

$$a_2=1/\beta_2,\text{ and } b_2=\alpha_2/x_2,$$

and x is the fractional area on a shear surface occupied by the flow unit, β is the relaxation time of the flow unit, and α is the ratio of shear volume to twice the average kinetic energy of the flow unit; the subscripts 1 and 2 of the parameters refer to the Newtonian and non-Newtonian flow units, respectively and R is the radius of the capillary tube.

The flow represented by Eq. (1) becomes Newtonian under the condition of $(G/a_2)\rightarrow\infty$, and $(G/a_2)\rightarrow0$, and the values of viscosity, η_∞ (at $G/a_2\rightarrow\infty$) and η_0 (at $G/a_2\rightarrow0$) are reduced to

$$\eta_\infty=\eta_1=\eta_1'-\frac{\sigma_1}{R} \tag{2}$$

and

$$\eta_0=\eta_1+\frac{1}{a_2b_2}=\left(\eta_1'-\frac{\sigma_1}{R}\right)+\left(\frac{1}{a_2}\right)\left(\frac{1}{b_2'}+\frac{\sigma_2}{R}\right)$$
$$=\left(\eta_1'+\frac{1}{a_2b_2'}\right)-\left(\frac{\sigma_1-\dfrac{\sigma_2}{a_2}}{R}\right)=\eta_0'-\frac{\left(\sigma_1-\dfrac{\sigma_2}{a_2}\right)}{R} \tag{3}$$

The values of η_1, a_2, b_2 and $\eta_0\left(=\eta_1+\dfrac{1}{a_2b_2}\right)$ obtained with Eq. (1) are shown in Table 1.

The relationships between $\eta_1(=\eta_\infty)$ and $1/R$ for γ-PGA solutions at various pHs are shown in Fig. 2. For comparing this relation for γ-PGA with that for PVP solution, one of the typical one obtained with PVP (K-90 0.5%) 0.25M $MgCl_2$ aqueous solution, is also shown in Fig. 2

Plots of η_1 *vs.* $1/R$ show approximately linear relation with negative slope of σ_1 in all examples. Therefore, also in the case of γ-PGA solutions, this dependence of η_1 of the polymer solution on R may be treated as the similar dependence as presented in preceding paper[1] for PVP in various

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[6] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Process," McGraw-Hill, New York (1941), p. 477.

[7] T. Ree and H. Eyring, *Rheology* (ed. Eirich), **2**, Chap. 3, p. 83 (1958).

Table 1. Parameters of viscosity equation (at 25°C)

$R\times10^2$ (cm)	$\eta_1\times10^3$ (poise)	b_2	$(\eta_1+(1/a_2b_2))$ $\times10^3$ (poise)
γ-PGA (0.05%) in water (pH=2.2) where $a_2=5.0$			
7.61	11.6	200	12.6
3.02	9.3	200	10.3
2.28	9.0	200	10.0
γ-PGA (0.01%) in water (pH=7.1) where $a_2=5.0$			
7.61	16.8	1.3	170.6
5.02	15.7	1.6	140.7
3.02	14.8	2.5	94.8

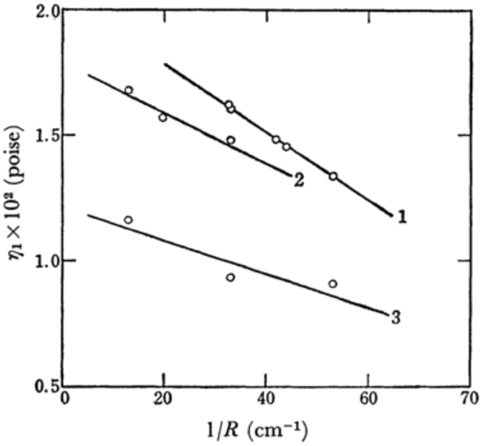

Fig. 2. Plots of η_1 *versus* $1/R$ for γ-PGA and PVP solutions.
(1) K-90 (0.5%) in 0.25 M $MgCl_2$ aqueous solution
(2) γ-PGA (0.01%) aqueous solution (pH=7.1)
(3) γ-PGA (0.05%) aqueous solution (pH=2.2)

solvents. This dependence will be due to the decrease in relaxation time of the solvent molecules near the wall compared with that of the bulk, because of the geometric hindrance of the capillary wall to the thermal motion of the polymer molecules oriented in the preferred direction under the streamline of the flow near the wall. And the resistance of the polymer molecules against the flow of the solvent molecules under the shear stress will become weaker near the wall than that in the bulk; this wall effect on the orientation of the polymer molecules will extend a certain distance from the wall into the central part of the solution in a capillary. Thus, as shown in preceding paper,[1)] the viscosity of the solution in the narrower capillary will decrease compared with that in the wider one.

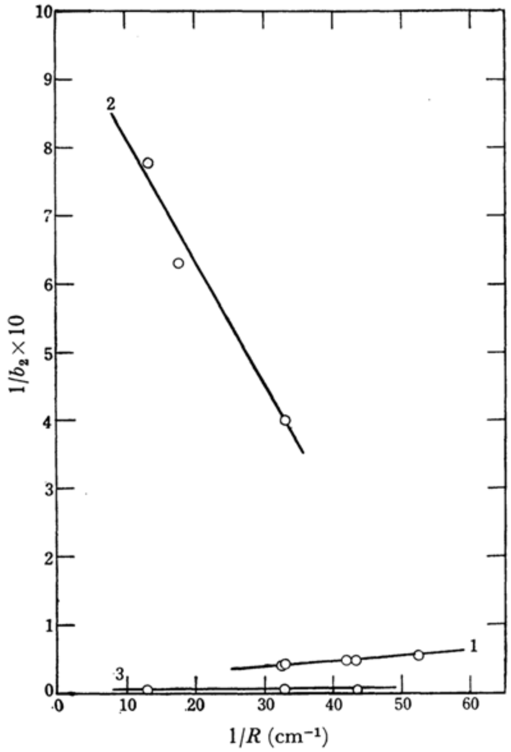

Fig. 3. Plots of $1/b_2$ *versus* $1/R$ for γ-PGA and PVP solutions.
(1) K-90 (1.5%) in *n*-propanol
(2) γ-PGA (0.01%) aqueous solution (pH=7.1)
(3) γ-PGA (0.05%) aqueous solution (pH=2.2)

The relationships between $1/b_2$ and $1/R$ for γ-PGA solutions at various pHs are shown in Fig. 3. A typical plot of PVP obtained with K-90 (1.5%) *n*-propanol solution is compared with that of γ-PGA solution. Plots of $1/b_2$ *vs.* $1/R$ for PVP solution in *n*-propanol show the linear relation, of which slope σ_2 takes a positive value, while the one for γ-PGA solution at pH 7.1 shows a negative one, and $1/b_2$ decreases with the increase of $1/R$.

When no additional effect of the wall on the flow of the polymer solution will occur with the decrease of rate of shear except the one considered in the case of η_∞ (G/a_2 or $G\to\infty$), the following relationship must be held between σ_1 and σ_2.

$$-\frac{\sigma_1}{\eta_1'}=\left(\frac{\sigma_2}{a_2}\right)\Big/\left(\frac{1}{a_2b_2'}\right)$$

or

$$\sigma_2=-\sigma_1\left(\frac{1}{b_2'}\right)\Big/\eta_1' \qquad (4)$$

The experimental value of σ_2 obtained with γ-PGA solutions at pH 7.1 is more negative than the calculated one by Eq.(4). This result suggests the occurence of the slippage of the γ-PGA molecules at the wall because of the existence of the repulsive force between the negatively charged glass surface and negatively charged γ-PGA molecules owing to the ionization of the carboxyl group of the polymer.

According to the flow equation based on the double wall layer model presented in the previous paper³⁾ experimental value of viscosity(η_{exp}) is represented as follows;

$$\eta_{exp}=\frac{(\eta_w+C)(\eta_w+A)(\eta_c+B)}{(\eta_w+C)\ (\eta_w+A)\ +\ (A-C)\ (\eta_c+B)D_o\ +\ (\eta_c-\eta_w)\ (\eta_w+C)D_i\ +\ (B-A)\ (\eta_w+C)D_i} \tag{5}$$

where $D_i=4(d_i/R)-6(d_i/R)^2+4(d_i/R)^3-(d_i/R)^4$ and
$D_0=4(d_o/R)-6(d_o/R)^2+4(d_o/R)^3-(d_o/R)^4$

Where $(G/a_2)\rightarrow\infty$, the values of A, B, C in above flow equation are zero, *i. e.*, A, B, $C=0$. Therefore, the flow model will reduced to simpler one composing of the wall layer (thickness: d_i) having the viscosity of η_w and the bulk liquid of viscosity η_c, and under the conditions of $(G/a_2)\rightarrow 0$, where $\eta_0\geq\eta_\infty$, the relations, A, B, $C\geq 0$ and $d_o\leq d_i$ are held.

Combining Eq. (1) with Eq. (5) as the same manner as stated in the previous paper,³⁾ the values of d_o and d_i corresponding to each R were calculated as shown in Fig. 4.

With the solution at pH 2.2, the following relationship holds among the viscosity of the each layer $\eta_c+B>\eta_w+C>\eta_w+A$ as in the case of PVP in n-propanol and this fact suggests the some structural formation at the wall in the flowing liquid in capillary tube. On the contrary, with the solution at pH 7.1, where $\eta_c+B>\eta_w+A>\eta_w+C$, the slippage of the polymer molecules will occur at the wall surface.

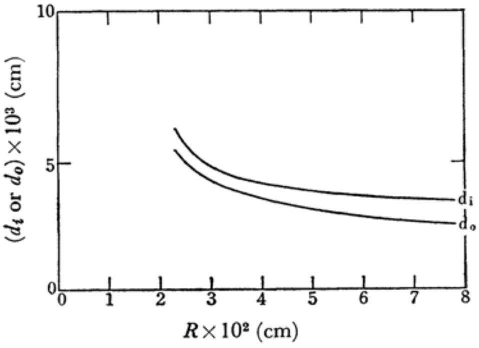

Fig. 4(a). Plots of d_i or d_o *versus* R for γ-PGA (0.05%) aqueous solution (pH=2.2), where $\eta_w=8.0\times10^{-3}$ (poise), $\eta_c=12.5\times10^{-3}$ (poise), $A=0.64\times10^{-3}$ (poise), $B=1.0\times10^{-3}$ (poise), $C=1.0\times10^{-3}$ (poise).

The structural formation at the wall was ascertained by the measurement of the concentration change of the solution between the one before and after the filtration through the glass filter as the same manner as stated in the previous paper.³⁾ With neutral solution no appreciable change in concentration was observed in spite of the very high

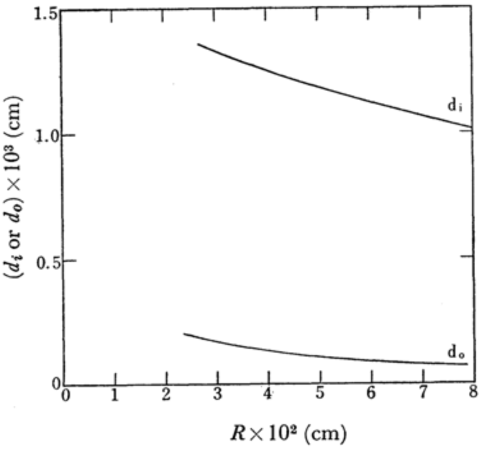

Fig. 4(b). Plots of d_i or d_o *versus* R for γ-PGA (0.01%) aqueous solution (pH=7.1), where $\eta_w=12.0\times10^{-3}$ (poise), $\eta_c=18.0\times10^{-3}$ (poise), $A=125\times10^{-3}$ (poise), $B=187\times10^{-3}$ (poise), and $C=0$.

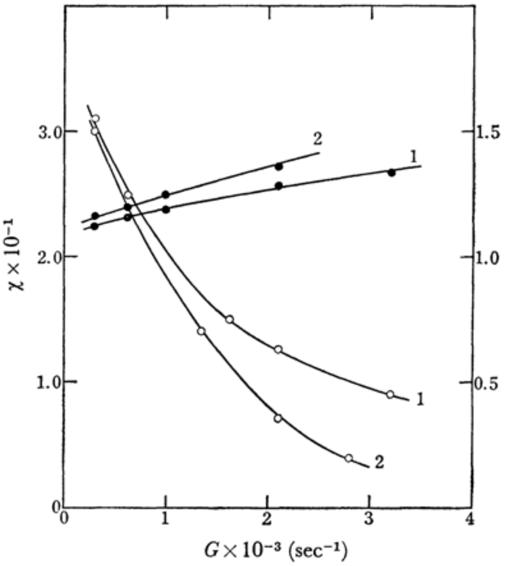

Fig. 5. Relationship between χ and Δn for γ-PGA solutions (○) extinction angle (χ); (●) birefringence (Δn), 1, γ-PGA (0.01%) in water (pH=7.0); 2, γ-PGA (0.01%) in water (pH=11.2).

value of intrinsic viscosity as stated below. Whereas in acid solution the decrease in concentration of γ-PGA by the filtration was observed and this fact will support the above assumption of the some structural formation at the wall in acid medium.

For the interpretation on the cause of the marked difference in flow of the two kinds of solutions (at low pH and neutral or higher pH) the experiments have been made as follows. The plots of extinction angle and the birefringence of the polymer solution against the rate of shear are shown in Fig. 5. The lower extinction angle and higher flow birefringence was observed with the increase of rate of shear for the polymer solution of neutral or higher pH and it obviously shows that the polymer molecules would orient remarkably. However, at lower pH, the position of the arms of the cross of isocline could not be detected in all rates of shear, and the orientation under the streamline of the flow could not be observed. It may be assumed that the γ-PGA molecules in acid medium will actually orient under the streamline of the flow because if the molecules did not show the tendency to orient, the capillary bore-size dependence of the viscosity must disappear as the case of the PVP aqueous solution with cosolute as stated in the previous paper.[3] The change in the degree of the orientation of the polymer molecules at each pH may be due to the change in the dissolved states of the polymer in each solvents.

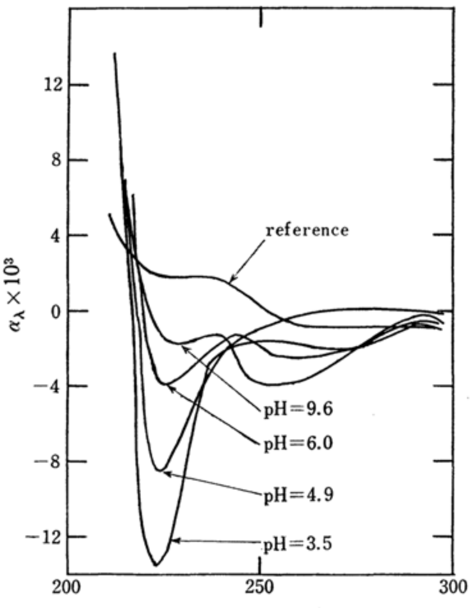

Fig. 6. Optical rotatory dispersion curves for γ-PGA (0.012%) in water.

The change in the conformation of the polymer molecules at various pH's, will be reflected in ORD curves in ultraviolet zone. The curves are shown in Fig. 6. The curves, at the lower pH show a negative Cotton effect with a trough at 225 mμ and the depth of the trough becomes deeper with decreasing in pH. Dependence of the ORD curves on pH values shows obviously the conformation change of the polymer molecules, from the disordered conformation at higher pH to the more ordered one with the decrease of the pH values.

The change in the hydrodynamic volume of the polymer molecules in solution may be estimated by the change in the value of the intrinsic viscosity between the solutions at pH 2.7 and 6.5. The results are shown in Fig. 7. The intrinsic viscosity at higher pH is very larger compared with that of the lower one: at pH 6.5 about 150 (100 ml/g) and at pH 2.7 about 7.0 (100 ml/g). This fact shows that the polymer molecules in higher pH solution will be dissolved as the more expanded form than that in the lower one.

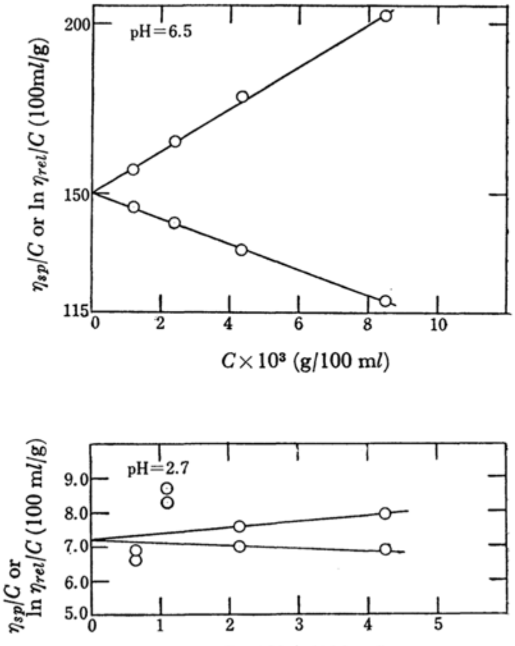

Fig. 7. Plots of η_{sp}/C or $\ln \eta_{rel}/C$ *versus* C for γ-PGA solutions.

Thus, from the results of flow birefringence, optical rotatory dispersion, and intrinsic viscosity, the polymer molecule in neutral and alkaline media will be in highly expanded chain conformation while that in the acid medium in contracted form having a some ordered conformation. Therefore, the polymer molecule in neutral and alkaline media will be as the form readily to orient under the streamline of the flow, while that in the acid medium will be in the contracted form of which the tendency to orient under the streamline of the flow could not be obviously observed by the flow birefringence measurement because the length of the dissolved molecules becomes shorter than the minimum length necessary for the observation with the apparatus. Therefore, it may be said that the measurement of the capillary bore-size dependence of the polymer solution is a sensitive method for the estimation of the anisotropy of the shape of the dissolved polymer molecules.