

# Polyelectrolytic Behavior of a Novel Fluorine-Containing Ionomer, PPFNA<sup>†</sup>

Akira Minakata\* and Kuniko Takayama

Department of Physics, Hamamatsu University School of Medicine, 1-20-1 Handayama,  
Hamamatsu 431-3192, Japan

Shin-ichi Yano

Department of Chemistry, Gifu University, Gifu 501-1193, Japan

Yoshito Tanaka, Takayuki Araki, and Tetsuo Shimizu

Daikin Industries Ltd., Osaka 566-8585, Japan

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Solution properties of a novel fluorine-containing ionomer PPFNA were studied by pH titration, conductivity, and viscosity measurements. This polymer is a poly(carboxylic acid) but dissociates strongly, resulting in a low pH value and a high specific conductance at low degrees of neutralization. When the solution was neutralized with NaOH, the conductance decreased sharply at first and then decreased gradually until full neutralization. This conductometric titration profile indicates that this polymer is a fairly strong polyelectrolyte but not a typical strong one such as poly(styrene sulfonic acid) or aliphatic ionenes. The pH measurement showed that this polymer is a strong polyacid, although the titration profile changed slightly upon the addition of salt. The reduced viscosity of the salt-free solution was well fitted to Fuoss' equation, specific to polyelectrolyte solutions. Upon the addition of salt, however, the viscosity–neutralization profile became rather similar to that of weak polyacid, and the concentration dependence of the reduced viscosity shifted gradually to that of nonionic polymer solutions. The corresponding monomer behaves like a completely strong acid, in contrast to the polymer, especially in conductometric titration.

## Introduction

Solution properties of polyelectrolytes are characterized by strong electrostatic interactions between polyion and counterions. There have been a large number of experimental and theoretical studies to clarify the interactions between the polyions and counterions.<sup>1–19</sup> According to the ion condensation theory,<sup>1,2</sup> the charge density parameter,  $\xi$ , defined as

$$\xi = \frac{e^2}{4\pi\epsilon kTb} \quad (1)$$

is regarded as a key parameter in classifying the global features of polyelectrolyte solutions. Equation 1 represents the value when the valence of the ionized group of the polyion and the counterion is unity, and  $b$  is the average linear charge spacing of the polyion. The solution properties are classified into states according to whether condensation occurs for  $\xi > 1$  or not for  $\xi < 1$ . Many experimental results have been interpreted in terms of this concept, and a unified picture was established to understand the characteristics of polyelectrolyte solutions as a whole.

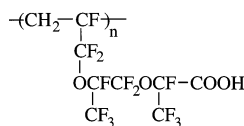
The solution properties are, however, largely different between so-called strong polyelectrolytes, such as poly(styrene sulfonic acid)(PSS) or aliphatic ionenes, and weak polyelectrolytes, such as poly(acrylic acid)(PAA) or poly(ethylenimine).<sup>20–22</sup> This difference is clearly revealed in potentiometric

and conductometric titrations, which is reflected in the electrostatic interaction between a dissociated H<sup>+</sup> or OH<sup>−</sup> and an ionized group on a polymer chain. Also, the limiting viscosity number, a measure of average polymer dimension, is influenced by the electrostatic interaction between ionizable groups and that between ionized groups and low molecular mass ions in solution.

A strong polyelectrolyte solution shows a potentiometric titration profile similar to that of the corresponding monomer. Namely, strong polyacids or polybases exhibit a slight change in pH values until a final abrupt change near the neutralization point. Their conductometric titration curves show a linear decrease with increasing degree of neutralization followed by a linear increase after neutralization, except for a small region near the neutralization point where the conductance changes gradually. The addition of salt has little effect on the potentiometric and conductometric titrations, that is, no appreciable change in titration profiles is observed. However, weak polyacids or polybases exhibit a continuous change in pH in most regions of the degree of neutralization, although a little larger change is observed in the initial region because of the neutralization of the already dissociated H<sup>+</sup> or OH<sup>−</sup>. Their conductometric titration curves show an initial decrease and then a gradual increase until near the neutralization point. The effect of salt on weak polyelectrolytes is more prominent compared to that with strong polyelectrolytes. Such a large difference in the potentiometric and conductometric titration profiles enables us to evaluate the contents of strong and weak charged components when mixed in the same polyelectrolyte molecule.<sup>22</sup>

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\* Corresponding author. E-mail: aminak@nifty.com.



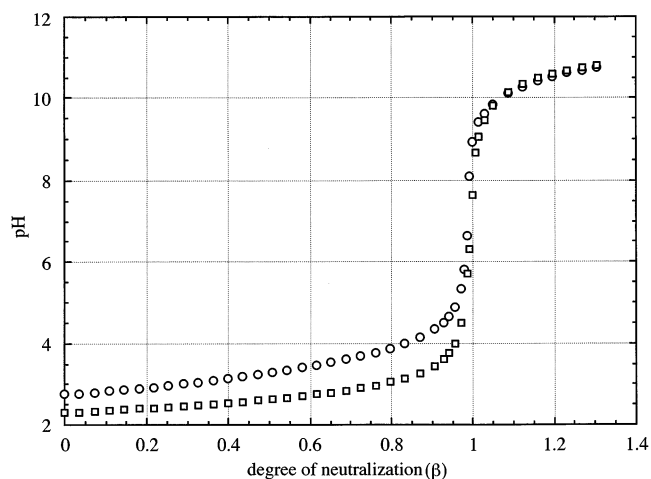
**Figure 1.** Chemical structure of PPFNA, poly(9H,9H-perfluoro-2,5-dimethyl-3,6-dioxa-8-nonenic acid).

Some poly(carboxylic acids) show peculiar titration profiles. In the cases of poly(maleic acid), poly(fumaric acid), and alternating copolymers of maleic acid, a two-step potentiometric titration process was observed because of the strong electrostatic interaction between neighboring groups.<sup>20,23,24</sup> Their strong acidity is understood by this strong interaction, that is, one component of a paired ionizable group is forced to be dissociated at low pH, and the other is left undissociated until near the neutral pH region. The titration profiles cannot be analyzed by the rod model with smeared charge in terms of the Poisson–Boltzmann equation. Anomalous conductance profiles of these polymers are also understood in this manner, although quantitative agreement between the theoretical analysis and experimental results was still insufficient.<sup>23,25</sup> It is interesting to examine poly(carboxylic acids) having strong acidity due to other effects, for example, the polarity of side chains, to understand how the dissociation of carboxyl groups is controlled by other effects as well as how this facilitated dissociation is reflected in the experimental results. The present experiment was carried out to clarify the solution properties of a poly(carboxylic acid), PPFNA (poly(9H,9H-perfluoro-2,5-dimethyl-3,6-dioxa-8-nonenic acid)), a novel ionomer containing a number of fluorine atoms both on the main and side chains. The carboxyl groups are expected to be dissociated at low pH because of the polarity of fluorine atoms. It is important to compare the dissociation behavior of this polymer with that of its monomeric unit, PFNA, because a close analogy holds for a typical strong polyelectrolyte and its monomer. Therefore, we carried out potentiometric and conductometric titrations of the monomeric unit, PFNA, and compared the results with those of the polymer, PPFNA.

## Experimental Section

The sample, PPFNA (poly(9H,9H-perfluoro-2,5-dimethyl-3,6-dioxa-8-nonenic acid)), was prepared in the laboratory of Daikin Industries Ltd. The original substance,  $\text{ICH}_2\text{-CF}_2\text{-[CF}_2\text{-OCF(CF}_3\text{)]}_2\text{-COF}$ , was synthesized by an oligomerization reaction of hexafluoropropylene oxide with 2,2-difluoro-3-iodopropionyl fluoride, and it was esterified with methanol to give  $\text{ICH}_2\text{-CF}_2\text{-[CF}_2\text{OCF(CF}_3\text{)]}_2\text{-COOCH}_3$ . Then the monomer, PFNA,  $\text{CH}_2\text{=CF-[CF}_2\text{OCF(CF}_3\text{)]}_2\text{-COOH}$ , was obtained by the dehalogenation of the above product with Zn in DMF followed by hydrolysis. Finally, polymerization was performed in bulk under a nitrogen atmosphere at room temperature for 24 h to obtain PPFNA with perfluoroalkyleneperoxide as the initiator. PPFNA was thoroughly purified by precipitating with HCFC-225 solution (a mixture of 1,1-dichloropentafluoropropane and 1,3-dichloropentafluoropropane).<sup>26</sup> The limiting viscosity was 0.22 dL/g at 25.0 °C in THF. The number- and weight-average molecular masses of its methyl ester were  $2.2 \times 10^4$  and  $5.8 \times 10^4$ , respectively. Its chemical structure is shown in Figure 1.

The sample was dissolved in pure water at room temperature and dialyzed against distilled water in a refrigerator at about 5 °C for 4 days. Then the sample was filtered and ion exchanged by passing through a Dowex mixed-bed resin column. The ion exchange was carried out just before the preparation of the sample for measurements. The concentration of the polyion,  $C_p$ ,



**Figure 2.** Potentiometric titration of PPFNA.  $C_p = 5.06 \times 10^{-3}$  M.  $C_{\text{NaOH}} = 9.9 \times 10^{-2}$  M.  $\circ$ , salt-free;  $\square$ , 1 M NaCl.

was measured by potentiometric and conductometric titration with NaOH as the titrant in the presence of 1.0 M NaCl. Both measurements gave values that agreed with each other within 0.5%.

The corresponding monomer PFNA, (9H,9H-perfluoro-2,5-dimethyl-3,6-dioxa-8-nonenic acid), was used without further purification. The concentration was determined in the same way, that is, by potentiometric and conductometric titration with NaOH with or without NaCl at  $25.0 \pm 0.1$  °C.

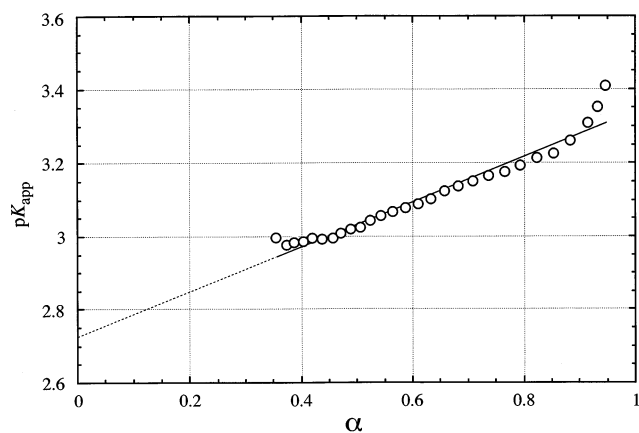
The potentiometric titration was carried out by using a TOA HM-60V ion meter with a GST-5421C electrode for pH measurements. Electrical conductance was measured with a TOA CM-60V conductivity meter with a CT-54101C conductivity cell with a cell constant of  $10.11 \text{ m}^{-1}$  at a frequency of 3 kHz. The polymer concentration ( $C_p$ ) expressed in monomeric units ranged from  $5.06 \times 10^{-3}$  to  $5.0 \times 10^{-5}$  M. The titrant, NaOH or NaCl, was added with a Metrohm 655 Dosimat microburet with a minimum volume of 10  $\mu\text{L}$ . The concentration of NaOH was  $9.9 \times 10^{-2}$  M for polymer solutions with  $C_p > 5.0 \times 10^{-4}$  and  $1.0 \times 10^{-2}$  M for remaining solutions, and the concentration of NaCl was 1.0 M. The initial volume of the polymer solutions both for potentiometric and conductometric titrations ranged from 27.0 mL for the highest  $C_p$  to 50.0 mL for lowest  $C_p$ . The relative dilution (i.e., the relative increase in the sample volume during titration from  $\beta = 0$  to 1) was less than 5.1%, which does not seem to be significant in the precision of the measurements. During the measurements, the solution was stirred and thermostated at  $25.0 \pm 0.1^\circ$  under a  $\text{CO}_2$ -free nitrogen atmosphere.

Viscosity measurements were carried out with a commercial Ostwald-type viscometer with a flow time of 95 s for pure water at 25.0 °C. Each solution for viscometry was prepared prior to the measurement and kept at  $25.0 \pm 0.1$  °C (the same temperature as for the measurement) for 10 min. The polymer concentration was  $1.0 \times 10^{-2}$  to  $2.0 \times 10^{-4}$  M, and the degree of neutralization ( $\beta$ ) was changed from 0 to 1.0 in steps of 0.2.

All chemicals were of guaranteed grade. Water was highly purified with a specific resistance of  $10^8 \Omega \cdot \text{m}$ .

## Results

Figure 2 shows the pH values of PPFNA as function of the degree of neutralization ( $\beta$ ) in the absence of and in 1.0 M NaCl, respectively. The data are averaged for three measurements, and the reproducibility is expressed within the symbols in this Figure. The titration profile is similar to those of strong polyelectrolytes



**Figure 3.** Plot of  $pK_{app}$  vs degree of dissociation  $\alpha$  for salt-free PPFNA.  $C_P = 5.06 \times 10^{-3}$  M.

such as PSS or aliphatic ionenes, but an appreciable shift in pH values is observed in the presence of salt, in contrast to the case of strong polyelectrolytes.<sup>27–29</sup>

The negative logarithm of the apparent dissociation constant  $pK_{app}$  is defined as

$$pK_{app} = pH - \log_{10} \frac{\alpha}{1-\alpha} = pK_0 + \frac{0.434}{RT} \frac{\partial G_{el}}{\partial \alpha} \quad (2)$$

where  $\alpha$  is the degree of dissociation and is related to the degree of neutralization  $\beta$  as

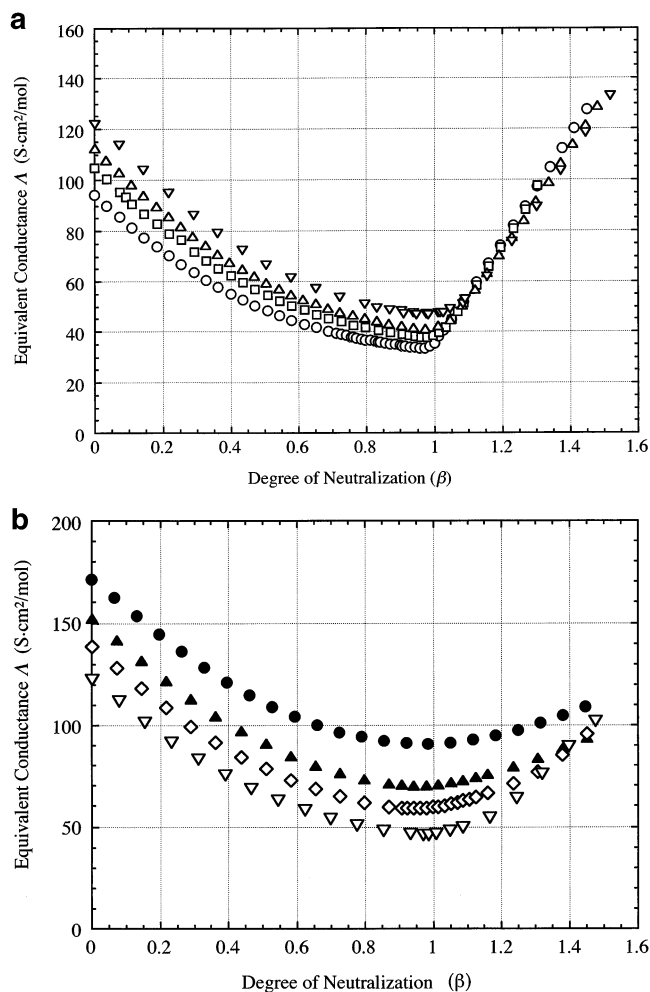
$$\alpha = \beta + \left( [H^+] - \frac{[OH^-]}{C_P} \right) \quad (3)$$

$pK_0$  is the negative logarithm of the intrinsic dissociation constant, and  $G_{el}$  is the electrostatic Gibbs free energy of the dissociation.

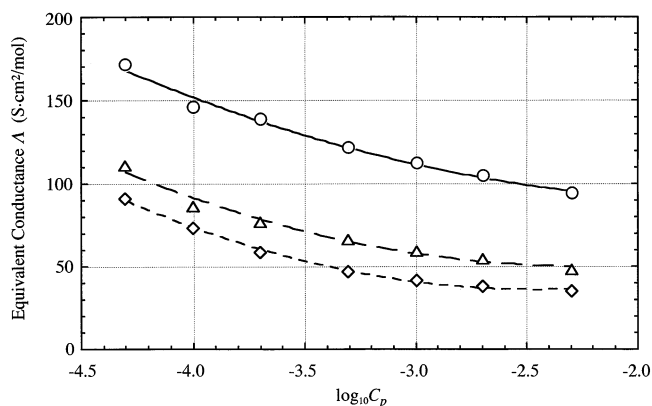
The value of  $pK_{app}$  increases almost linearly with  $\alpha$  as shown in Figure 3. From this plot, we can obtain the value of  $pK_0$  to be 2.73 for the salt-free solution, which is much lower than that of ordinary poly(carboxylic acids). Likewise, the value of  $pK_0$  was 2.62 for the 1 M NaCl solution.

The conductometric titration curves are shown in Figure 4a for  $C_P$  from  $5.06 \times 10^{-3}$  to  $5.0 \times 10^{-4}$  M and in Figure 4b for  $C_P$  from  $5.0 \times 10^{-4}$  to  $5.0 \times 10^{-5}$  M, where the abscissa is the degree of neutralization ( $\beta$ ) and the ordinate is the equivalent conductance ( $\Lambda$ ) in  $S \cdot cm^2/mol$ . A continuous increase in the equivalent conductance was observed with decreasing  $C_P$ . The titration curves became broader as  $C_P$  decreased, as seen in Figure 4b, possibly because of a lack of precision at low  $C_P$ . The curves exhibit an initial decrease due to the combination of the already dissociated protons with hydroxyl ions added. The slope deviates gradually from linearity and is concave upward, and this tendency continues with increasing  $\beta$  until  $\beta = 1$ . The change in the slope means that the released protons are partially trapped in the neighborhood of a dissociated carboxyl group, and the trapped fraction increases gradually as the dissociation proceeds. Such a gradual change in the slope was not observed in ordinary strong polyelectrolytes (e.g., PSS<sup>22</sup>).

Figure 5 shows the equivalent conductance plotted against  $\log C_P$  for  $\beta = 0, 0.5$ , and  $1.0$ . All curves exhibit a gradual increase as  $C_P$  decreases with no tendency of saturation in the concentration range studied. Measurement in the concentration region lower than  $5.0 \times 10^{-5}$  M seems necessary to clarify whether the saturation of the equivalent conductance appears,



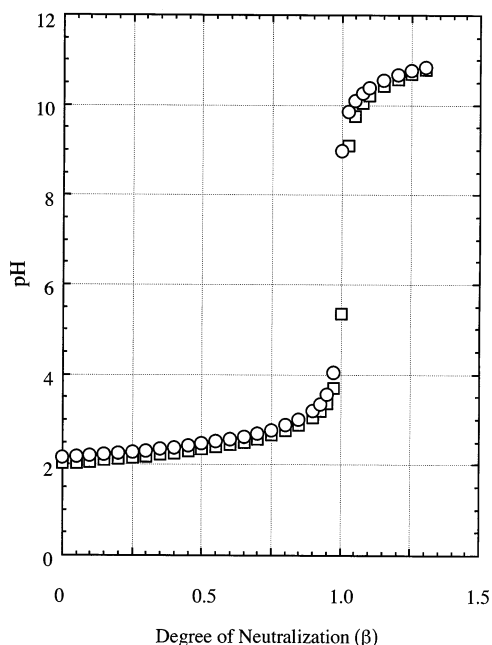
**Figure 4.** (a) Conductometric titration of PPFNA. Equivalent conductance  $\Lambda$  vs degree of neutralization  $\beta$ .  $C_P = (5.06$  (O),  $2.02$  (□),  $1.01$  (△), and  $0.50$  (▽))  $\times 10^{-3}$  M. (b) Conductometric titration of PPFNA.  $C_P = (5.0$  (▽),  $2.0$  (◇),  $1.0$  (△), and  $0.5$  (●))  $\times 10^{-4}$  M.



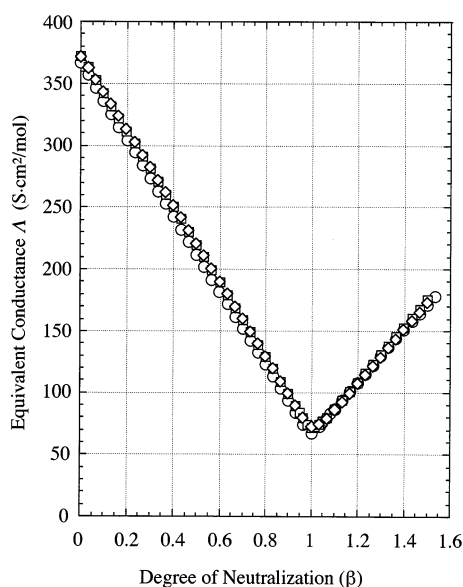
**Figure 5.** Concentration dependence of the equivalent conductance of PPFNA  $\Lambda$  vs  $\log C_P$ . Degree of neutralization  $\beta = 0$  (O),  $0.5$  (△), and  $1.0$  (◇).

as reported in the concentration region of  $10^{-5}$  to  $10^{-6}$  M.<sup>15,30–32</sup> It is quite difficult, however, to extend the  $C_P$  region owing to the decrease in the accuracy of conductance measurements for the lower-concentration region.

Figure 6 shows the potentiometric titration curve of the monomer, PFNA, in the absence and presence of 1.0 M NaCl. The curve is similar to that of a typical strong acid, and the



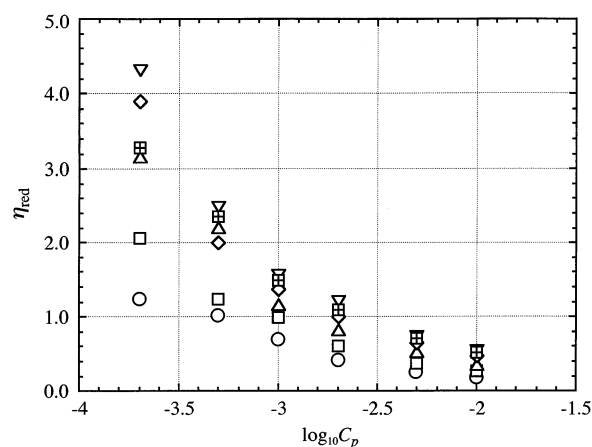
**Figure 6.** Potentiometric titration of the monomer PFNA.  $C = 5.0 \times 10^{-3}$  M.  $\circ$ , salt-free;  $\square$ , 1 M NaCl.



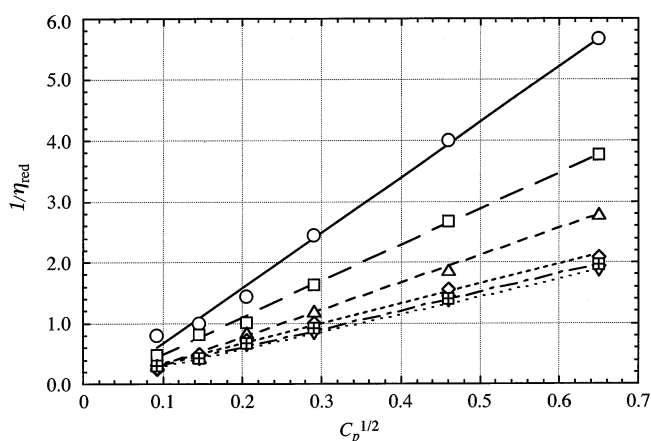
**Figure 7.** Conductometric titration of PFNA.  $C = (5.0 (\circ), 2.0 (\square), 1.0 (\diamond)) \times 10^{-3}$  M.

effect of the salt is much less pronounced as compared with that seen in the curve of the polymer, PPFNA. The observed  $pK_0$  values were 2.34 and 2.46 with and without 1 M NaCl, respectively. The conductometric titration of salt-free PFNA is shown in Figure 7 for concentrations  $C = 5.0 \times 10^{-3}$ ,  $2.0 \times 10^{-3}$ , and  $1.0 \times 10^{-3}$  M. The curves consist of a linear decrease for  $\beta < 1$  and a linear increase for  $\beta > 1$  with no appreciable curved region. The concentration dependence was found to be quite small. These data indicate that the monomer PFNA, a carboxylic acid, is a typical strong acid, in contrast with the polymer PPFNA.

The concentration dependence of the reduced viscosity ( $\eta_{\text{red}}$ ) of salt-free solutions is plotted against  $\log C_P$  for  $\beta = 0$  to 1.0, as seen in Figure 8. The reduced viscosity increased as concentration decreased, and no maximum values were observed. The values of  $\eta_{\text{red}}$  increase with increasing  $\beta$  up to  $\beta = 0.8$ , suggesting the expansion of overall dimension of the



**Figure 8.** Concentration dependence of reduced viscosity,  $\eta_{\text{red}} (= \eta_{\text{sp}}/C_P)$  vs  $\log_{10} C_P$  of salt-free PPFNA;  $\eta_{\text{red}}$  is given in dL/g. Degree of neutralization  $\beta = 0 (\circ), 0.2 (\square), 0.4 (\triangle), 0.6 (\diamond), 0.8 (\nabla)$ , and 1.0 (subdivided square).



**Figure 9.** Fuoss plot ( $\eta_{\text{red}}^{-1}$  vs  $C_P^{1/2}$ ) of salt-free PPFNA. Symbols are the same as in Figure 8.

polyion with neutralization. This tendency is the same as that observed in weak polyelectrolytes such as PAA. The experimental results suggest that PPFNA may expand with neutralization by accumulating counterions and by increasing hydration layers. However, conductometric titration shows that neutralization induces the loss of the free protons that are already dissociated in the unneutralized state, which may induce the shrinkage of the polyion, as discussed in the next section.

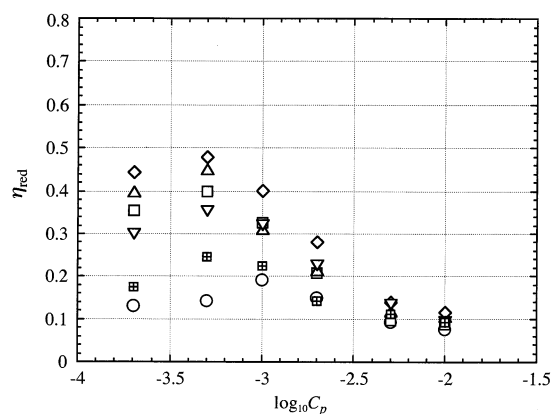
Figure 9 is the Fuoss plot ( $\eta_{\text{red}}^{-1}$  vs  $C_P^{1/2}$ ) of the data in Figure 8. The data are well fitted to the Fuoss equation,<sup>33</sup>

$$\eta_{\text{red}} = \frac{A}{1 + B\sqrt{C_P}} \quad (4)$$

Usually, this equation holds for typical salt-free polyelectrolyte solutions, although the physical meaning of this equation is still unknown. It simply means that the concentration dependence is roughly expressed by eq 4, with no maxima of  $\eta_{\text{red}}$ . The data might deviate from eq 4 for the more dilute region because the maximum of  $\eta_{\text{red}}$  has already been reported in another case.<sup>34</sup>

Figure 10 is the concentration dependence of reduced viscosity in 0.1 M NaCl solutions. The reduced viscosity decreased significantly as compared with that of salt-free solutions. This decrease means that the salt effect is remarkable on the overall dimensions of the polymer chain, as observed in most polyelectrolytes. The curves exhibited a maximum at  $C_P = (4.0 \text{ to } 5.0) \times 10^{-4}$  M. The overall profiles shifted to those





**Figure 10.** Concentration dependence of the reduced viscosity of PPFNA in the presence of 0.1 M NaCl. Symbols are the same as in Figure 8.

**TABLE 1: List of Intrinsic Dissociation Constants of Carboxylic Acids**

acids and polyacids	$C_{\text{NaCl}}$ (mol/L)	$pK_0$	ref
PPFNA	0	2.73	
	1.0	2.62	
poly(maleic acid)	0.1	3.40	20
poly(fumaric acid)	0.1	3.45	20
PAA	0.1	4.13	20
PFNA(monomer)	0	2.46	
	1.0	2.34	
monofluoroacetic acid	0	2.59	35
monochloroacetic acid	0	2.87	35
hydrofluoric acid	0	3.45	35

of nonionic polymers, that is, the reduced viscosity decreased as the concentration decreased in the low-concentration region. Consequently, the Fuoss equation was inapplicable to this case. Also, the values of  $\eta_{\text{red}}$  increase with increasing  $\beta$ , but peaks were found at about 0.6, as usually found in ordinary poly(carboxylic acids).

## Discussion

Concerning the acidity of PPFNA, the values of  $pK_0$  obtained by potentiometric titration were 2.73 for salt-free and 2.62 for 1 M NaCl solutions, and those of the corresponding monomer PFNA were 2.46 for salt-free and 2.34 for 1 M NaCl solutions, respectively, as mentioned before. As listed in Table 1, these values indicate that PPFNA and its monomer are strong acids. The values for PPFNA are comparable to and those for PFNA are lower than that of monofluoroacetic acid.<sup>35</sup> Other poly(carboxylic acids) with strong acidity show higher values of  $pK_0$ . Therefore, PPFNA is supposed to assume a stretched conformation in solution as a strong polyelectrolyte molecule.

The present experiments revealed, however, that PPFNA is not a typical strong polyacids in many respects. The most remarkable feature is the change in the slope of the equivalent conductance versus neutralization plot. The strong acidity is reflected in high values of the equivalent conductance because of the high mobility of the dissociated protons. The addition of alkali removes these protons, resulting in a decrease of the equivalent conductance for all ranges of  $0 \leq \beta \leq 1$ . The decrement of the equivalent conductance with  $\beta$  (i.e., the absolute value of the slope) is, however, slightly decreased over the whole range of  $\beta$  in this case. Ordinary strong polyelectrolytes such as PSS and aliphatic ionene do not exhibit such a gradual change in the slope.<sup>20,27–29</sup> The change in the slope means that the released protons are mostly combined with

hydroxyl ions added but partially trapped in the neighborhood of a dissociated carboxyl group, and the trapped fraction increases gradually as the dissociation proceeds in most of the region of the neutralization. The fluorine-rich side chain may also facilitate the trapping.

The change in the slope with neutralization may be primarily due to the conformational change of the PPFNA molecule. This polymer has a large polar side chain that may provide side chain–side chain interaction, resulting in the coiled or wormlike conformation rather the rodlike conformation as is found in most strong polyions. The mobility of the PPFNA molecule may be controlled by the conformation as well as the net charge. The dissociation of protons implies an increase in the net charge, leading to the expansion of the polyion, but it provides an increase in hydrodynamic resistance.

The polymer concentration studied is in the semidilute to dilute region and was determined by estimating the Debye length and contour length. The Debye length under salt-free conditions ranged from 11 nm for the highest  $C_P$  to 110 nm for the lowest  $C_P$ , and the estimated contour length was 12 to 32 nm, corresponding to number- and weight-average molecular masses. This polymer has long side chains of about 0.9 nm so that the overall shape is an ellipsoid rather than a thin rod. However, the large value of the polydispersity, given by  $M_w/M_n = 2.6$ , affects further quantitative evaluation. This is why such a slight and continuous change in the equivalent conductance is difficult to understand. In cases of ordinary strong polyelectrolytes with relatively small side chains, the overall conformation may be regarded as a rod or a fairly extended semiflexible chain, which makes the interpretation simpler. Most theoretical analyses of the potentiometric and conductance behavior of polyelectrolytes are inapplicable to this case because these are based on the rodlike model as a first approximation. This tendency is not due to a neighboring interaction between ionizable groups on a polyion because if it were the slope would be a two step because of the facilitated release of a proton by other nonionized groups in the initial stage followed by a depressed release by other ionized groups when more than half of the ionizable groups are dissociated, as is found in poly(maleic acid) and copolymers of maleic acid.

In cases of ordinary poly(carboxylic acids), the dissociation enhances the interaction between carboxylate groups, the association of counterions, and the expansion of hydration layers around the charged group, resulting in the expansion of the polymer chain. In this case, however, the carboxyl groups of PPFNA are mostly dissociated even in the unneutralized state, and the neutralization induces the loss of the free protons, which may cause the reverse effects. The present data suggest that the factors determining the conformation of PPFNA molecule are not only the electrostatic interaction between charged groups but the interaction between side chains, although the latter is of secondary importance. Actually, in cases of polymers and copolymers of maleic acid and similar substances, viscosity decreased with increasing  $\beta$  for  $\beta > 0.5$ .<sup>20,23,24</sup> At present, it is difficult to give a simplified interpretation in such a viscosity–neutralization profile. Although the overall dimensions may have a primary effect on the reduced viscosity, other factors such as electroviscous effect might be considered in this case. More data on the conformation of this polymer may be needed in the future to understand the present experimental results more concretely.

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