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Remarkable Expansion of the Poly(acrylic acid) Chain by Acid-Base Complexation with Low Molecular Weight Amines

Yuki KIMURA and Takahiro SATO†

Department of Macromolecular Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka 560-0043, Japan

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ABSTRACT: The intrinsic viscosity [η] of a poly(acrylic acid) (PAA) sample with a molecular weight of 4×10^6 in aqueous salt solution drastically increased by adding isopropyl amine (A-1). At the infinitely high concentration of the hydrochloric salt of A-1, where the electrostatic interaction is completely screened out, [η] was enlarged by 40 times as the degree of complexation f_c increases from *ca.* zero to 0.6. Here f_c was determined by potentiometric and NMR titrations. Furthermore, [η] at infinite ionic strength for PAA complexed with a bulkier and more hydrophobic amine, (*R*)-(+)-1-(phenyl)ethylamine (A-2), was higher than that for the complex of PAA and A-1 at the same f_c. The drastic expansion of the PAA chain by the complexation with the amines A-1 and A-2 may arise from the chain stiffening and enhanced excluded volume effect. [DOI 10.1295/polymj.38.190]

KEY WORDS Intrinsic Viscosity / Poly(acrylic acid) / Acid-Base Complexation / Titration / Degree of Comlexation / Chain Expansion /

Recent years, supramolecular polymers have attracted much attention in macromolecular science because of their unique properties and functions not exhibited by conventional polymers.[1,2] Components of supramolecular polymers are small molecules and/or macromolecules. Small molecular components can assemble by hydrogen bonding, coordinate bonding, acid-base complexation, or hydrophobic interaction to form supramolecular polymers. An example of macromolecular assemblies in the biological field is tobacco mosaic virus. It consists of a RNA molecule covered with a lot of protein molecules under normal conditions to protect the RNA chain, but dissociates the proteins at multiplication. The association and dissociation of protein molecules are key factors of preservation of their posterity.

The combination of a macromolecule and many small molecules is another type of supramolecular polymers. Yashima *et al.*[3,4] demonstrated that a dynamical helical polymer, poly((4-carboxyphenyl)acetylene) complexed with optically active low-molar-mass amines induced and memorized very strong circular dichroism (CD). The acid-base complexation in this system was much more effective to the CD induction than the normal chiral doping to dynamical helical polymer solutions. Moreover, Ashida *et al.*[5] have recently showed that the complexation with an amine stiffens this helical polymer chain in dimethylsulfoxide, indicating that the complexation affects the internal rotation potential of the polymer chain.

In this study, we have investigated the effect of the acid-base complexation to the chain conformation of a non-helical polymer in aqueous solution. As the simplest example, we have chosen poly(acrylic acid) (PAA) and examined the PAA chain expansion by the complexation with low-molar-mass amines [isopropyl amine (A-1) and (*R*)-(+)-1-(phenyl)-ethylamine (A-2)]. The viscometry has demonstrated a remarkable expansion of the PAA chain by the complexation in aqueous solution. This demonstrates that the polymer-chain conformation can change by altering polymer side chains *supramolecularly*.

In an aqueous solution containing an amine RNH_2, the carboxyl group can take the following three forms, the acid form (–COOH), the complex form (–$COOH_3$-NR), and the free ion (–COO^-) (*cf.* Scheme 1). The fraction of the complex form f_c depends on the concentration of RNH_2 and also *pH*. Along with viscometry, we have undertaken potentiometric and NMR titrations for aqueous solutions containing PAA and amine (A-1 or A-2) to estimate f_c, which is the basic parameter to discuss the mechanism of the PAA chain expansion by the complexation.

EXPERIMENTAL

Preparation of Test Solutions

A commercial PAA sample (Nacalai Tesque, Japan) was dissolved in water and passed through a mixed-bed ion exchanger [Amberlite IR-120 + IRA-900 (1:2)]. The eluted solution was freeze dried to obtain the acid-form PAA sample. The intrinsic viscosity

†To whom correspondence should be addressed (Tel: +81-6-6850-5461, Fax: +81-6-6850-5461, E-mail: tsato@chem.sci.osaka-u.ac.jp).

$$-\mathrm{COOH} + \mathrm{RNH_2} \leftrightarrow -\mathrm{COOH_3NR} \leftrightarrow -\mathrm{COO^-} + \mathrm{RNH_3^+}$$

Scheme 1.

$[\eta]$ of the PAA sample was measured in 1.5 M aqueous NaBr at 15 °C, after the PAA solution was neutralized with aqueous NaOH. The viscosity average molecular weight of the acid (Na salt) form of the PAA sample was estimated to be 3.67×10^6 (4.79×10^6), using the Mark–Houwink–Sakurada equation for the Na salt form of PAA in that solvent condition (the θ state) reported by Takahashi and Nagasawa.[6]

Isopropyl amine (A-1) and (*R*)-(+)-1-(phenyl)-ethylamine (A-2) purchased (Wako chemicals, Japan) were used without purification. Water used was purified by Milli-Q SP.

The dried PAA sample was dissolved in aqueous solutions of A-1 with different amine concentrations, and *pH* of the PAA solutions and also solvents (aqueous amine solutions) were adjusted to 3, 4, 5, 7, and 10 by using 0.1–1 N HCl. Aqueous PAA solutions containing A-2 with different amine concentrations and $pH = 7$ were also prepared in a similar way. The addition of aqueous HCl was taken into account to calculate the mass concentration c of PAA in the solution and the molar concentration C_A° of total amine in the solvent. Our solvent is a ternary system consisting of an amine, hydrochrolic salt of the amine, and water. The molar concentrations of amine (C_A) and its HCl salt (C_s) in the solvent can be calculated by $C_A = C_A^\circ - C_{HCl}$ and $C_s = C_{HCl}$, respectively, where C_{HCl} is the molar concentration of added HCl in the solvent. In what follows, the solvent condition is specified either in terms of C_A° and *pH* or of C_A and C_s.

Viscometry

Viscosities of the above aqueous solution containing PAA, amine, and its HCl salt were measured at 25 °C using a Ubbelohde-type capillary viscometer. For solutions with $pH = 10$, the shear rate dependence of the viscosity was examined using a low-shear-rate four bulb capillary viscometer.[7,8] After measured the viscosity, the original solution was diluted with the solvent with the same C_A°, and *pH* in the viscometer, and the viscosity measurement was made again to obtain the PAA concentration dependence of the solution viscosity at the constant C_A° and *pH*. The intrinsic viscosity $[\eta]$ at each C_A° and *pH* was determined from the common intercept of the following Huggins and Mead–Fuoss plots:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c^2 + \cdots \quad (1)$$

and

$$(\ln \eta_r)/c = [\eta] - \left(\frac{1}{2} - k'\right)[\eta]^2 c^2 + \cdots \quad (2)$$

where η_{sp} and η_r are the specific and relative viscosities, respectively, and k' is the Huggins coefficient.

Potentiometric Titration

Potentiometric titration measurements were made using a *pH* meter (Horiba, F-23) for aqueous NaCl solutions of PAA with $c = 1.4 \times 10^{-4}$ g/cm^3 or the molar concentration of the carboxyl group $C_C = 0.002$ M (before titration) and different ionic strength I using 0.05 N aqueous NaOH as the titrant. The degree of ionization f_- of the carboxyl group was estimated by

$$f_- = \frac{C_{NaOH} + [OH^-] - [H^+]}{C_C} \quad (3)$$

where C_{NaOH} is the molar concentrations of NaOH titrated. The molar concentrations of the hydrogen ion $[H^+]$ and the hydroxyl ion $[OH^-]$ were calculated from *pH* of the solution. The dilution of the test solution during titration was taken into account to calculate C_{NaOH} and C_C in eq 3. The dissociation constant K_C of the carboxyl group was estimated by

$$K_C = [H^+] f_-/(1 - f_-) \quad (4)$$

as a function of f_- and ionic strength I.

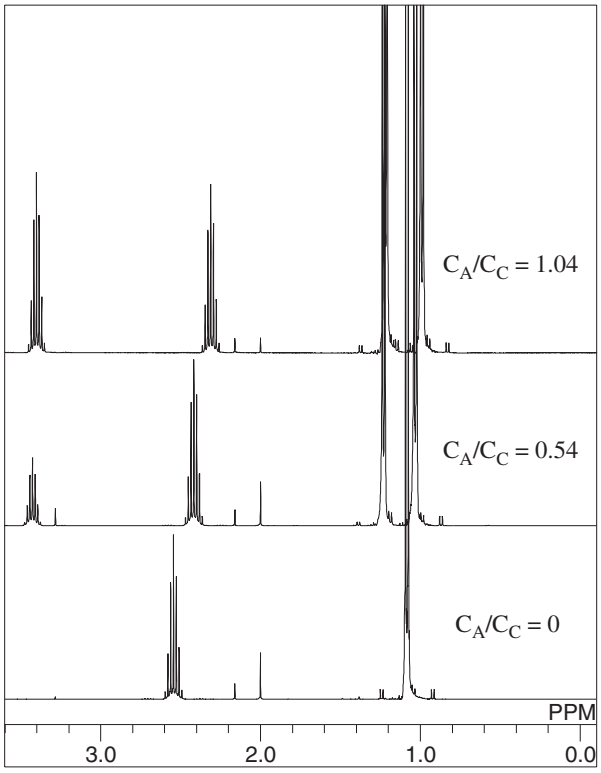
It is known that the dissociation constant of the low-molar-mass acid and the protonation constant of low-molar-mass amine are independent of f_- and I. From *pH* measurements, the dissociation constant K_C' of isobutylic acid (a model compound for PAA; see below) was determined to be 1.59×10^{-5} M, while protonation constants K_A for A-1 and A-2 were determined to be 1.45×10^{11} and 4.57×10^9 M^{-1}, respectively.

NMR Titration

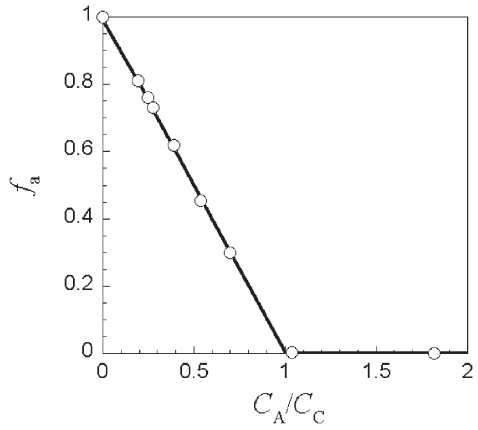
NMR measurements were made at 25 °C for D_2O solutions of isobutylic acid and amine A-1 with the molar concentrations C_C (= 0.11 M) and C_A (= 0–0.2 M), respectively using an Excallibur 400 NMR spectrometer. Here isobutylic acid was used as the model compound for PAA, and a trace amount of acetonitrile was added to the solutions as the standard material.

Figure 1a shows NMR spectra of D_2O solutions of isobutylic acid and A-1 with three different ratios C_A/C_C. From the chemical shift δ for the central peak of the isobutylic acid methyne signal around 2.3–2.5 ppm, the mole fraction f_a of the acid form of isobutylic acid in the solution was estimated by

$$f_a = \frac{\delta - \delta_0}{\delta_1 - \delta_0} \quad (5)$$



(a)



(b)

Figure 1. (a) NMR spectra of D_2O solutions containing isobutylic acid (a model compound of PAA) and amine A-1 with three different ratios C_A/C_C; (b) the mole fraction f_a of the acid form of isobutylic acid in aqueous A-1 solution as a function of C_A/C_C, where the solid line indicates theoretical values calculated by eq 6 with $K'_C = 1.59 \times 10^{-5}$ M, $K_A = 1.45 \times 10^{11}\,M^{-1}$, and $K = 4.7 \times 10^6\,M^{-1}$.

where δ_0 (= 2.544 ppm) and δ_1 (= 2.311 ppm) are the chemical shifts at $C_A/C_C = 0$ and in the saturated state, respectively.

The mole fraction f_a may be calculated from the complexation constant K (*cf.* eq A·4 in Appendix), the dissociation constant K'_C of isobutylic acid, and the protonation constant K_A of the amine by solving the following simultaneous equations:

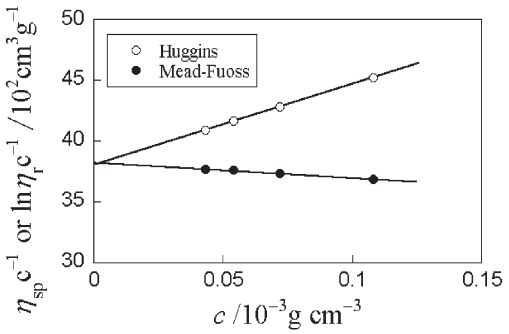
$$\begin{cases} f_a = (1 + K'_C/[H^+] + K[RNH_2])^{-1} \\ [RNH_2] = \dfrac{C_A}{1 + K_A[H^+] + KC_C f_a} \\ [H^+] = \sqrt{\dfrac{10^{-14} + K'_C C_C f_a}{1 + K_A[RNH_2]}} \end{cases} \quad (6)$$

When K is chosen to be $4.7 \times 10^6\,M^{-1}$, and K'_C and K_A determined by potentiometric titration (see above) were used in the above equations, theoretical f_a values indicated by the solid line in Figure 1b fit the experimental data points. This value of K was confirmed by potential titration, and was taken to be identical with that for PAA and the amine in what follows. In a similar way, K between isobutylic acid and A-2 was determined to be $1.4 \times 10^5\,M^{-1}$.

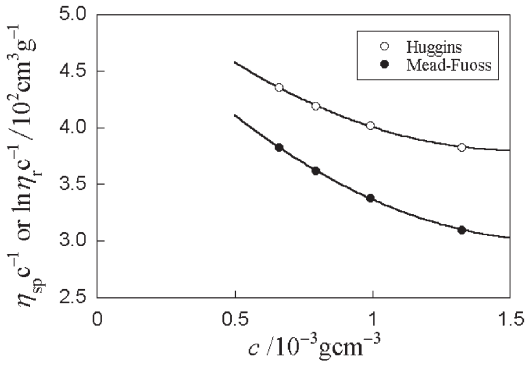
RESULTS AND DISCUSSION

Intrinsic Viscosities

Figure 2 compares the Huggins and Mead–Fuoss plots for PAA–A1 solutions with $C^\circ_A = 0.05$ M and $pH = 7$ prepared in the way mentioned in Experimental Section (Panel a) with the plots for PAA directly



(a)



(b)

Figure 2. Huggins and Mead–Fuoss plots for PAA–A1 solutions with $C^\circ_A = 0.05$ M and $pH = 7$; (a) PAA solution prepared in the way mentioned in Experimental Section with adjusting *pH*; (b) PAA directly dissolved in A-1 solution without adjusting *pH*.

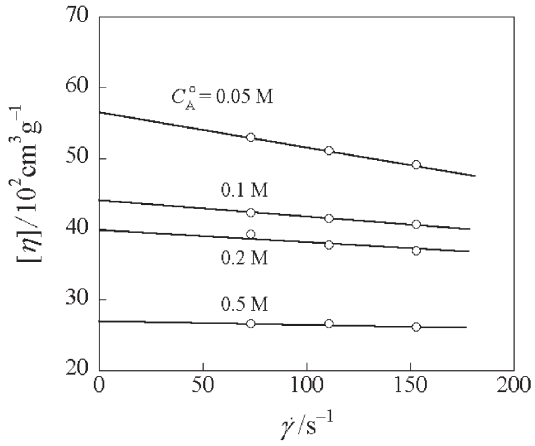


Figure 3. Shear rate dependencies of the intrinsic viscosity at $pH = 10$ and different C_A° of A-1.

dissolved in an A-1 solution with $C_A^\circ = 0.05\,\mathrm{M}$ and $pH = 7$ (Panel b). Since *pH* of the solution in Panel b was not adjusted after dissolution of PAA, *pH* increased with decreasing *c*. As the result, the plots showed strongly upswing *c* dependencies, and it was difficult to determine the intrinsic viscosity $[\eta]$. On the other hand, *pH* of the PAA–A1 solution in Panel a was adjusted to 7, and $[\eta]$ was estimated from the plots with the normal *c* dependencies without any difficulty.

Apparent shear rate $\dot{\gamma}$ dependencies of $[\eta]$ for PAA–A1 solutions with $pH = 10$ and different C_A° are shown in Figure 3. With decreasing C_A° (or ionic strength), the absolute value of $[\eta]$ increases and its shear rate dependence becomes stronger. We have determined $[\eta]$ at $\dot{\gamma} = 0$ by extrapolation at $pH = 10$.

Figure 4 shows C_A° and *pH* dependencies of $[\eta]$ and the Huggins coefficient k' for PAA–amine solutions. In Panel a, $[\eta]$ decreases with increasing C_A° and decreasing *pH* in A-1 solution, and the *pH* dependence is drastic. At $pH = 7$, $[\eta]$ in A-2 solution is lower than that in A-1 solution within the C_A° range examined, and its C_A° dependence is weaker than that in A-1 solution. At $pH = 10$, the zero-shear-rate $[\eta]$ (filled circles) are larger than those at a $\dot{\gamma}$ of *ca.* $10^3\,\mathrm{s^{-1}}$ (unfilled circles). In Panel b, k' are mostly within a range of 0.3–0.55, indicating normal dissolution of PAA in the amine solutions. Only at $C_A^\circ = 0.42\,\mathrm{M}$ and $pH = 3$, k' is exceptionally large. The degree of ionization of PAA is low while the ionic strength is high in that solvent condition, and thus the solubility of PAA to this amine solution is quite low. The large k' may reflect this poor solubility.

In Figure 5, $[\eta]$ of PAA in aqueous amine and its hydrochloric salt solutions are plotted against the reciprocal of the square root of the hydrochloric salt concentration C_s. The C_s dependence of $[\eta]$ is more pronounced at higher *pH*. Using the lines shown in Figure 5, we have extrapolated $[\eta]$ to the infinite C_s

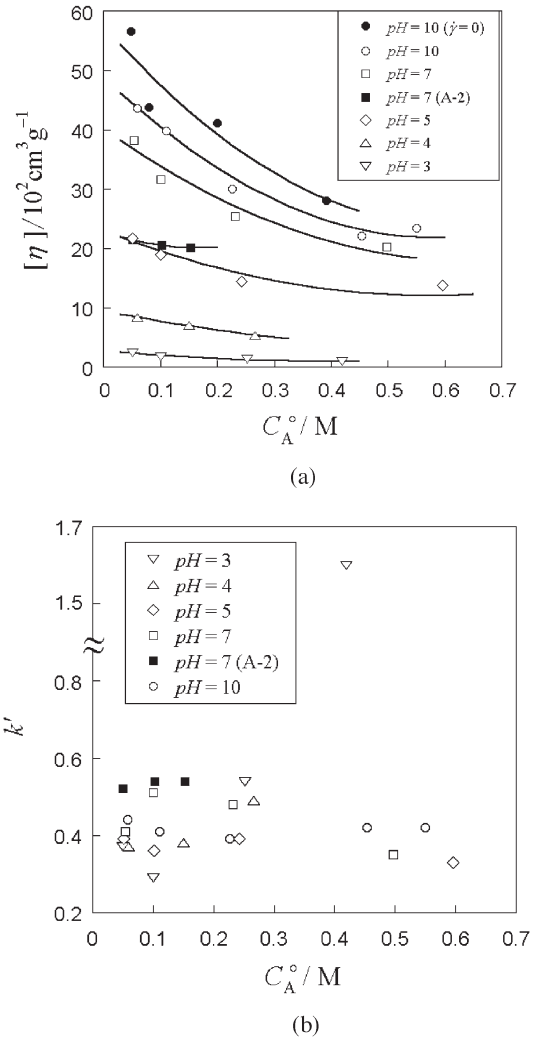


Figure 4. C_A° and *pH* dependencies of (a) the intrinsic viscosity $[\eta]$ and of (b) the Huggins coefficient k'. Data points except for filled squares are for PAA–A1 solutions.

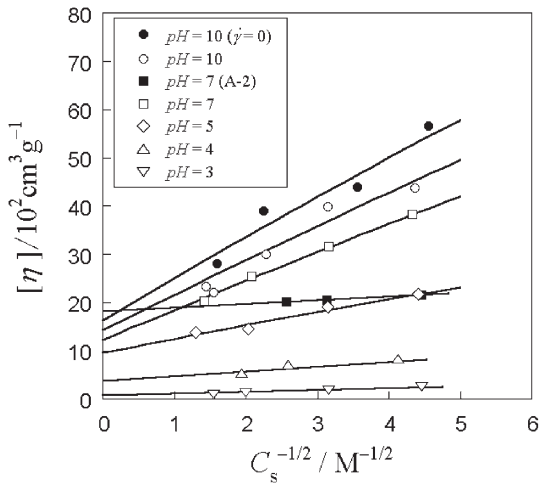


Figure 5. Plots of $[\eta]$ against $C_s^{-1/2}$ for aqueous amine solutions of PAA at different *pH*; filled squares, data for PAA–A2 solutions; other symbols, data for PAA–A1 solutions.

where the electrostatic interaction is fully screened out. At $pH = 10$, the zero-shear rate $[\eta]$ are extrapolated to infinite C_s, and the result is slightly larger than that without the shear rate correction. Although we did not examine the shear rate dependence of $[\eta]$ at *pH* other than 10, we may expect that the non-Newtonian effect is not so important at the infinite C_s for our PAA sample at all *pH* examined.

Figure 5 contains also the results of PAA complexed with amine A-2 at $pH = 7$. The C_s dependence of $[\eta]$ for this complex is much weaker and its extrapolated $[\eta]$ is larger than that for the complex with A-1 at the same *pH*. The amine A-2 is more hydrophobic than A-1 and thus the affinity of the PAA chain complexed with A-2 to water may be poorer than the PAA–A1 complex. Since the increase of C_s (or the concentration of the hydrochrolic salt of A-2) makes the solvent quality better, the excluded volume effect of the PAA–A2 complex should be enhanced with increasing C_s. This effect may compensate the reduction of the electrostatic excluded volume effect.

The intrinsic viscosity $[\eta]_\infty$ extrapolated to infinite C_s is plotted against *pH* in Figure 6. In general, both degrees of ionization and complexation increase with increasing *pH*, and both contribute to the increase in $[\eta]$. However, we can expect only the contribution of the acid-amine complexation to $[\eta]_\infty$, because the electrostatic interaction is not important at $C_s = \infty$. At $pH = 7$, $[\eta]_\infty$ for the PAA–A2 complex (filled circle in Figure 6) is larger than that for the PAA–A1 complex. The complexation of the bulkier and more hydrophobic amine A-2 expands more the PAA chain.

Degrees of Complexation and Ionization

As shown in Scheme 1, the carboxyl group attaching to PAA chain can take one of the three states, the acid, complex, and free ion forms. Both complexation and ionization change the PAA chain conformation through the chain stiffening and intramolecular excluded volume effect. The degrees of complexation f_c and of ionization f_- at given C_A° and *pH* can be calculated by eqs A·5 and A·6 in Appendix from the complexation constant K and the dissociation constant K_c.

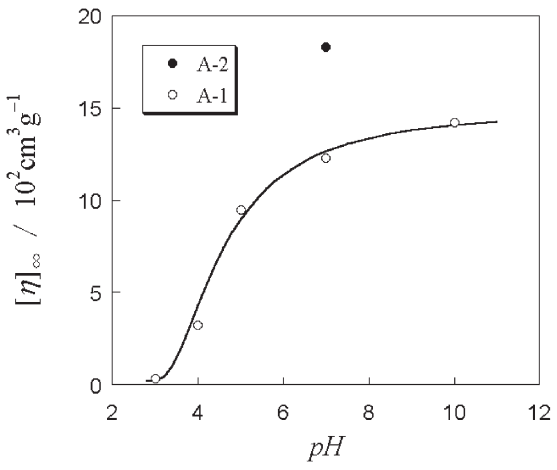


Figure 6. $[\eta]_\infty$ plotted against *pH* for PAA complexed with A-1 (unfilled circles) and A-2 (filled circle).

Figure 7a shows K_c of PAA in aqueous NaCl solutions, determined by potentiometric titration. In general, K_c for polyelectrolytes depends on the polymer degree of ionization f_- and ionic strength I. Using these results of K_c as well as K from the NMR titration (*cf.* Experimental Section), we have calculated f_c and f_- for PAA (at infinitely dilution) in aqueous solutions of amine and its hydrochloric salt. (Since K_c depends on f_-, the calculated f_- must be consistent with K_c at that f_-, and we made iterative calculations to obtain f_c and f_-). The results of f_c and f_- are shown in Figure 7b. Both f_c and f_- increase with *pH* and almost saturate above $pH = 7$. The C_s dependencies of f_c and f_- are strong at $pH = 4$ and 5, but rather weak at other *pH*. Using the curves indicated, we have estimated the degree of complexation $f_{c,\infty}$ at infinite ionic strength I.

Figure 8 plots $[\eta]_\infty$ against $f_{c,\infty}$, obtained in Figures 5 and 7b, respectively. For the complex with amine A-1 (unfilled circles), $[\eta]_\infty$ enlarges by *ca.* 40 times as $f_{c,\infty}$ increases from *ca.* zero to 0.6. Although the degree of ionization $f_{-,\infty}$ at infinite I increases along with $f_{c,\infty}$ (*cf.* Figure 7b), the ionization may not contribute to $[\eta]_\infty$ because the electrostatic interaction is completely screened out at C_s or $I = \infty$. Therefore, we can say that the complexation with amine A-1 remarkably increases the PAA chain dimension. Furthermore, the complexation with bulkier and more hydrophobic amine A-2 increases the PAA chain dimension more at the same $f_{c,\infty} \sim 0.6$.

The complexation with amine may restrict the internal rotation of the PAA main chain, which can stiffen the PAA main chain. This is one of reasons for the chain expansion by the complexation. Recently, Ashida *et al.*[5] reported that the persistence length of a stiff helical polymer, poly((4-carboxyphenyl)acetylene), increased twice (from 4.2 to 8.6 nm) by complexation with an optically active amine [(*R*)-(+)-1-(1-naphtyl)ethylamine] in dimethylsulfoxide, and attributed the stiffening to the reduction of the torsional fluctuation by the steric hindrance among amines complexed with the polymer. On the other hand, the complexation with amine makes the affinity of the chain to the solvent with infinite C_s of the hydrochloric salt of the amine better, which enhances the excluded volume effect. Since PAA is a flexible chain, the excluded volume effect may be also an important factor of the chain expansion by complexation with amine.

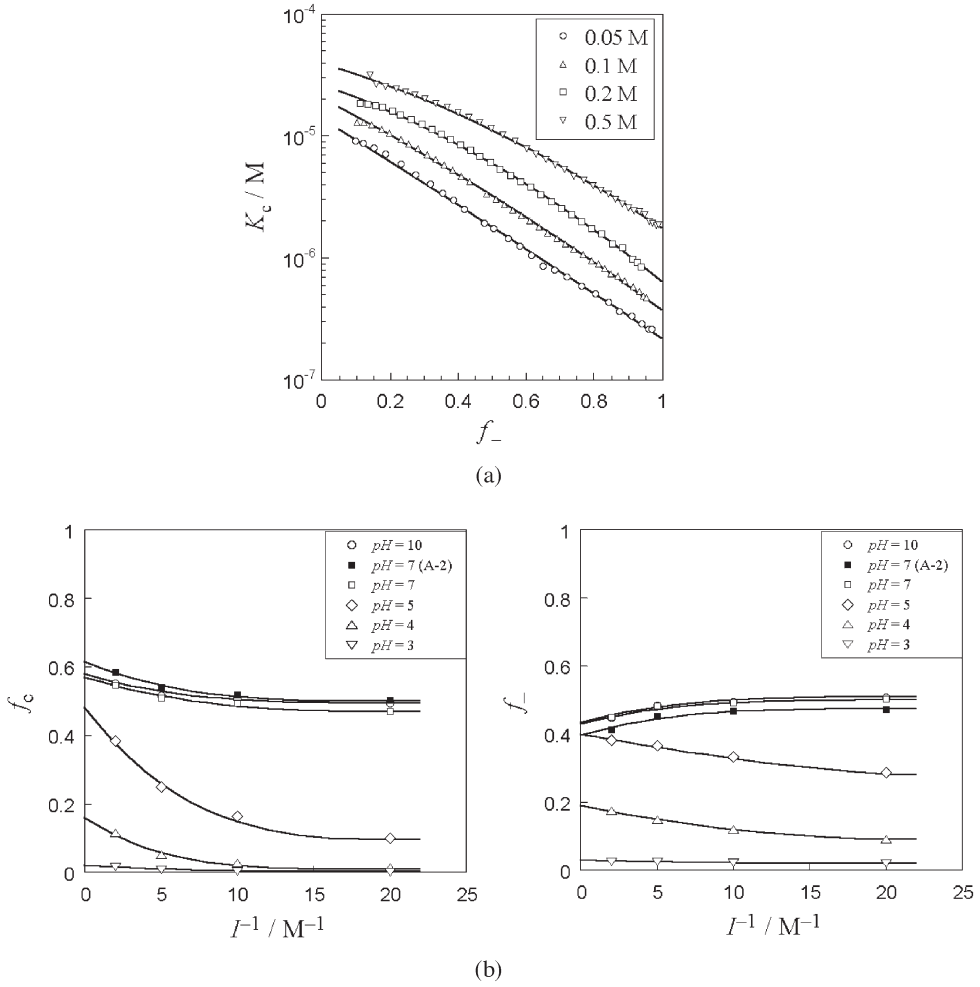


Figure 7. (a) Dissociation constant K_C of PAA in aqueous NaCl solution at different f_- and I, and (b) f_c and f_- of PAA in amine solutions at different pH and I; data points other than filled squares, for PAA in A-1 solutions.

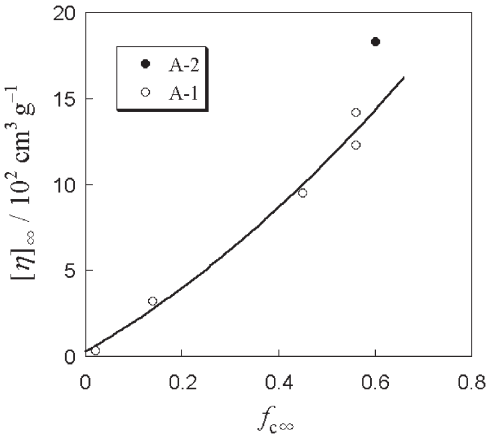


Figure 8. Plots of $[\eta]_\infty$ against $f_{c,\infty}$ for PAA complexed with amines A-1 (unfilled circles) and A-2 (filled circle).

APPENDIX: DEGREES OF COMPLEXATION AND IONIZATION

Let us consider an aqueous solution containing an amine RNH_2 and its hydrochloric salt RNH_3Cl. The salt RNH_3Cl is assumed to be perfectly dissociated into RNH_3^+ and Cl^- in the aqueous solution. The molar concentrations $[RNH_3^+]$ and $[RNH_2]$ are calculated from the electro-neutral condition and mass conservation rule, respectively, by

$$[RNH_3^+] = C_{HCl} + [OH^-] - [H^+] \qquad (A{\cdot}1)$$

and

$$[RNH_2] = C_A^\circ - [RNH_3^+] \qquad (A{\cdot}2)$$

Here C_{HCl} is the concentration of hydrochloric acid added to adjust pH, C_A° is the total amine concentration in the solution, and the molar concentrations of the hydrogen ion $[H^+]$ and hydroxyl ion $[OH^-]$ are calculated from pH of the solution.

When a carboxylic acid is added to the above aqueous solution of RNH_2 and RNH_3Cl, it can take one of the three forms: the acid form –COOH, the complex form $–COOH_3NR$, and the free ion $–COO^-$ (*cf.* Scheme 1). Under the equilibrium condition, the molar concentrations of the three forms are related to each other by

$$K_C = [\text{–COO}^-]\cdot[\text{H}^+]/[\text{–COOH}] \qquad (A\cdot3)$$

and

$$K = [\text{–COONH}_3\text{R}]/([\text{–COOH}]\cdot[\text{RNH}_2]) \qquad (A\cdot4)$$

where K_C and K are the equilibrium constants of dissociation and complexation, respectively. If the acid concentration is infinitely dilute, we can calculate the degrees of complexation f_c and of ionization f_- from the above relations by

$$f_c = \frac{K[\text{RNH}_2]}{1 + (K_c/[\text{H}^+]) + K[\text{RNH}_2]} \qquad (A\cdot5)$$

and

$$f_- = \frac{[\text{H}^+]/K_c}{1 + (K_c/[\text{H}^+]) + K[\text{RNH}_2]} \qquad (A\cdot6)$$

where $[\text{RNH}_2]$ can be estimated from eqs A·1 and A·2.

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