Colloid Polym Sci 276:1038–1043 (1998)

SHORT COMMUNICATION

S. Kawaguchi
Y. Hirose
K. Ito
S. Kato
K. Yokota

Aqueous solution behavior of alkali-soluble polyethylene periodic polyelectrolyte, poly(ethylene-*per*-ethylene-*per*-acrylic acid)

Received: 14 April 1998
Accepted: 3 June 1998

S. Kawaguchi (✉) · Y. Hirose · K. Ito
Department of Materials Science
Toyohashi University of Technology
Tempaku-cho
Toyohashi 441-8580
Japan

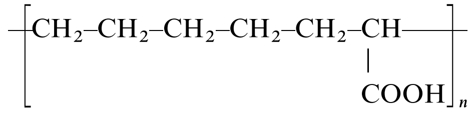
S. Kato · K. Yokota
Department of Materials Science
and Engineering
Nagoya Institute of Technology
Gokiso-cho, Showa-ku
Nagoya 466-0061
Japan

Abstract A sequence-ordered, periodic copolymer of ethylene, ethylene, and acrylic acid, poly (ethylene-*per*-ethylene-*per*-acrylic acid) (PEEA), with $M_w = 1.44 \times 10^5$ has been synthesized by alternating copolymerization of 1,3-butadiene and methyl acrylate, followed by hydrogenation and hydrolysis. Aqueous solution and dissociation properties of the alkali-soluble PEEA were explored by potentiometric titration and intrinsic viscosity at 25 °C. The pH values of PEEA were almost constant (pH $= 6.48 \sim 6.55$) with an increasing degree of dissociation (α) from 0.3 to 0.8 at $C_s = 50$ mN NaCl. Correspondingly, the plots of negative logarithm of apparent dissociation constant (pK_a) against α showed a reversed S-shape curve over the whole α, indicating an extensive precipitation and subsequent transition from compact to coiled conformation. The intrinsic viscosity steeply increased with α above 0.4 up to 9.97 dl/g at $\alpha = 1.0$. Good agreement between the observed electrostatic potential and that calculated from the rod model with a smeared charge density was observed in the region of α higher than 0.9. The dissociation and dissolution processes of PEEA with neutralization in water were described.

Key words Periodic copolymer – ionomer – alkali-soluble polyelectrolyte – poly(ethylene-*per*-ethylene-*per*-acrylic acid) – conformational transition – hydrophobically modified polyelectrolyte

Introduction

Characteristic solution properties of polyelectrolytes are produced by electrostatic interaction and thus strongly depend on their charge density and distribution [1, 2]. During the past decade, we have studied these influences on the electrical properties of polyelectrolyte solutions, especially focusing on the dissociation equilibrium of weak polyacids with a charge density twice as high as a conventional synthetic polyelectrolyte such as poly(acrylic acid). They include poly(maleic acid), its stereoisomer, poly(fumaric acid) [3], poly(itaconic acid) [4], poly(2-methyleneglutaric acid) [5], and alternating copolymer of isobutylene and maleic acid [6]. In the present study in turn, we intend to explore the dissociation behavior of polyelectrolytes with a low charge density, poly(ethylene-*per*-ethylene-*per*-acrylic acid) (PEEA), which has a carboxylic acid group at every sixth carbon atom of the main chain. The molecular structure of PEEA is shown below.



$$\left[\mathrm{CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle COOH}{\underset{|}{CH}}} \right]_n$$

Poly(ethylene-*per*-ethylene-*per*-acrylic acid) (PEEA)

This copolymer is a sequence-ordered, periodic copolymer of ethylene, ethylene, and acrylic acid, which is prepared by alternating copolymerization of 1,3-butadiene and methyl acrylate, followed by hydrogenation and hydrolysis. The effects of the sequence in the copolymers on the physical properties such as glass transition temperature have been intensively investigated by Yokota and his coworkers [7–10]. The present concern is addressed on the dilute solution properties, especially the qualification of electrostatic interaction and the formulation of a dissolution process for the polyelectrolyte with a low charge density in water.

From the structural point of view, PEEA is very unique as a polyelectrolyte in water in that it has a very low charge density and successive five-methylenes per one carboxylic acid on the main chain. This implies that for a fully neutralized PEEA chain the average intercharge distance is calculated to be 0.756 nm, by assuming the main chain conformation as a trans zigzag. The dimensionless parameter, charge density parameter, ξ, defined as

$$\xi = \frac{e^2}{DkTb} , \quad (1)$$

is always less than 1 during the neutralization, where e is the elementary electric charge, D the dielectric constant of solvent, k the Boltzmann constant, T the absolute temperature, and b the average intercharge distance on a polyion. Therefore, in the PEEA polyelectrolyte, no counterion condensation should occur during the neutralization [11, 12].

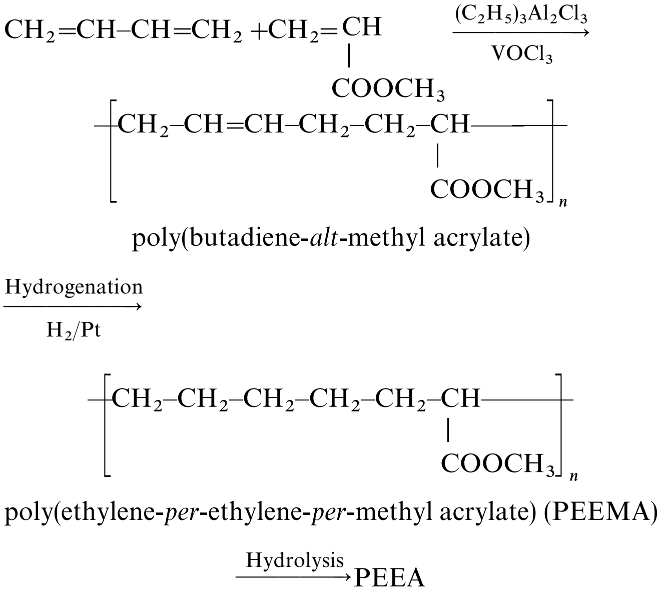
On the other hand, since the hexylene chain per carboxylic acid on the main chain is moderately hydrophobic, PEEA does not dissolve in water before the neutralization, but does dissolve after the neutralization. Thus, it is one of the "alkali-soluble" polymers of recent concern. An interesting observation in industry is that when ionomers, polyethylene copolymer with, say, less than 10 mol% methacrylic acid in the content, are neutralized with potassium hydroxide, they are fairly water-swellable to form a dispersion at room temperature and even apparently dissolved into water at higher temperature. The PEEA is considered as a model material for the understanding of the aqueous solution behavior of the neutralized ionomers, including dissociation, dissolution process, and formation of microparticles.

In the present study, we synthesized PEEA and investigated the dissociation behavior and dissolution process of the main chain-hydrophobically modified low charge density polyelectrolytes in water, by measuring potentiometric titration and intrinsic viscosity.

Experimental

Materials

PEEA was synthesized according to a following reaction scheme [7, 8].



$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}\underset{\displaystyle COOCH_3}{\underset{|}{CH}} \xrightarrow[VOCl_3]{(C_2H_5)_3Al_2Cl_3} \left[CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle COOCH_3}{\underset{|}{CH}}\right]_n$$

poly(butadiene-*alt*-methyl acrylate)

$$\xrightarrow[H_2/Pt]{Hydrogenation} \left[CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle COOCH_3}{\underset{|}{CH}}\right]_n$$

poly(ethylene-*per*-ethylene-*per*-methyl acrylate) (PEEMA)

$$\xrightarrow{Hydrolysis} PEEA$$

First, alternating copolymer of 1,3-butadiene with methyl acrylate (MA) was synthesized by radical copolymerization at 0 °C for 24 h, in the presence of ethylaluminium sesquichloride, $(C_2H_5)_3Al_2Cl_3$ and vanadyl chloride, $VOCl_3$ [7–9]. ^1H and ^{13}C NMR spectra showed that the copolymer contains equimolar amounts of butadiene and MA units, that successive butadiene and MA units are absent, and that the butadiene units are of 95%, 1,4-trans and 5% 1,2-structure. Second, the alternating copolymer, poly(butadiene-*alt*-methyl acrylate) was hydrogenated. The copolymer was dissolved in tetrahydrofuran and magnetically stirred with a platinum black catalyst. Tiny hydrogen bubbles were passed into the suspension from a capillary for 4 days. The catalyst was precipitated and methanol was added to the supernatant. The hydrogenated copolymer (PEEMA) was quantitatively recovered and was freeze-dried from benzene. Third, the copolymer (1.115 g) was further hydrolyzed by refluxing for 21 h in a mixed solution of 30 ml dioxane, 16 ml MeOH, and 4 ml H_2O containing 1N NaOH, followed by refluxing for another 50 h in a mixed solvent of 46 ml MeOH and 4 ml H_2O. The PEEA was purified by three times reprecipitation from MeOH to H_2O (yield 83.3%). The sample was kept under nitrogen atmosphere. ^1H NMR spectrum of PEEA is shown in Fig. 1 and the degree of hydrolysis is determined to be 99.9%. The

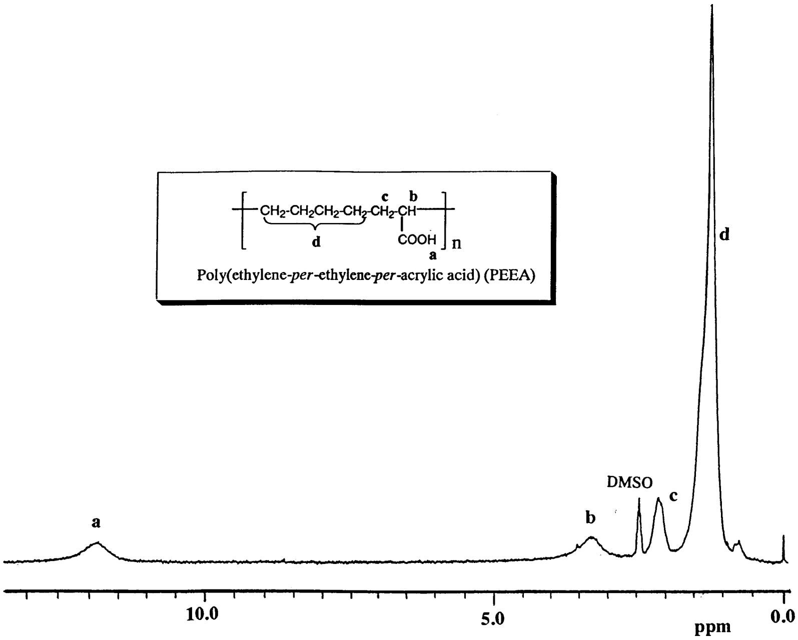


Fig. 1 ^{1}H NMR spectrum of PEEA in d_6-DMSO. HMDS is used as an internal standard

weight-averaged molecular weight (M_w) and distribution (M_w/M_n) of PEEMA before hydrolysis was determined to be $M_w = 1.6 \times 10^5$, $M_w/M_n = 2.5$ by SEC measurement. A small amount of PEEA was again converted to the methyl ester by reacting with diazomethane. The M_w and M_w/M_n of the PEEMA were determined to be 1.7×10^5 and 2.3, respectively, implying that no chain scission occurs during the hydrolysis.

Measurements

Size exclusion chromatography (SEC) of PEEMA was measured using a Tosoh HLC 803D with GMX-, G1000-, G2000-, and G4000-HXL columns in series. The eluent was THF and its flow rate was 1 ml/min at 40 °C. The retention time was taken as a measure of molecular weight with reference to polystyrene standards. ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Varian XL-200 spectrometer. The spectra were determined for 5–10 wt% polymer concentration at 25 °C under with tetramethylsilane or hexamethyldisilazane (HMDS) as an internal standard. The potentiometric titration was carried out with an Iwaki Glass M-225 Digital pH meter with an IW051 complex electrode at 25 °C under argon atmosphere [3, 4]. Polymer (C_p) and salt (NaCl) (C_s) concentrations were C_p = 2–3 mN and 5–50 mN, respectively. Since the acid form of PEEA does not dissolve in water, an equivalent amount of NaOH to carboxylic acid was added and titrated with HCL solution. Viscometry measurements were carried out using a capillary viscometer of the modified Ubbelohde at 25 °C [3, 4]. The Huggins plot [13] and the Fuoss–Mead plot [14] were combined to determine [η]. Some examples are given in Fig. 2.

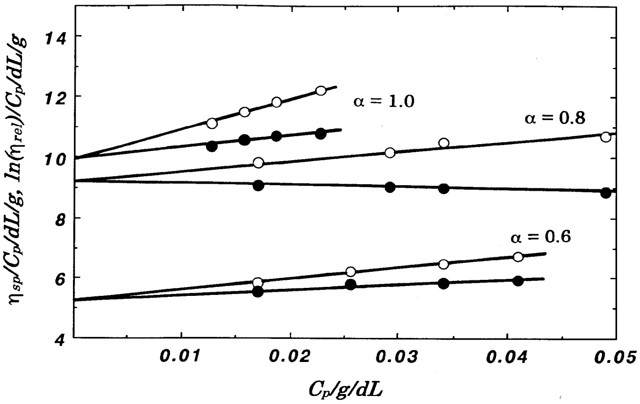
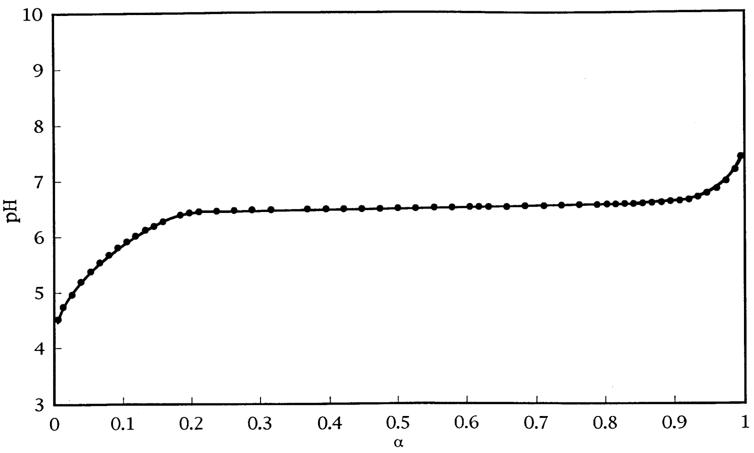


Fig. 2 Viscosity–concentration profiles of PEEA at α = 0.6, 0.8, and 1.0 in 10 mN NaCl aqueous solution at 25 °C

Results and discussion

An example of potentiometric titration curve of PEEA at C_s = 50 mN NaCl is given in Fig. 3, where pH values are plotted against the degree of dissociation (α). The value of pH steeply increased with α up to 0.2 but then became

Fig. 3 Potentiometric titration of PEEA (C_p = 2.02 mN) in NaCl (C_s = 50 mN)



almost constant (pH = 6.48 ~ 6.55) for $0.3 < \alpha < 0.8$. The very small change (ΔpH = 0.07) in pH over the wide range of α is likely due to the inter- and intramolecular association in water, as will be discussed later. In fact, the solution began to produce a turbidity below $\alpha \approx 0.3$ and the extent of the cloudiness increased with the decrease of α and to develop extensive precipitation below $\alpha = 0.05$.

The potentiometric titration curves in the polyelectrolyte solutions are usually expressed by a negative logarithm of the apparent dissociation constant, pK_a, defined by [3]

$$\mathrm{p}K_a = \mathrm{p}H + \log\frac{1-\alpha}{\alpha} . \tag{2}$$

The pK_a can then be expressed by a sum of two terms as

$$\mathrm{p}K_a = \mathrm{p}K_0 + \frac{0.434}{RT}\frac{\partial G_{ex}}{\partial \alpha} , \tag{3}$$

where K_0 is the intrinsic dissociation constant independent of α, R the gas constant, G_{ex} the excess free energy of dissociation of 1 mol of protons. The plots of pK_a vs α at different C_s's are shown in Fig. 4. There are two features to be noted. First, there is an evident C_s-dependence of pK_a, implying that electrostatic interaction affects the dissociation of proton also in such a low charge density polyelectrolyte. Second, the pK_a value increases very sharply with α up to 0.03, increases somewhat gradually with α to 0.2 to reach a maximum, then decreases linearly with α up to 0.9 until finally it tends to level off with α. The reversed S-shape curve has been frequently observed for the hydrophobically modified polyelectrolytes including alternating copolymers of maleic acid with hydrophobic monomers, styrene [15] and alkylvinyl ether [16]. These polyelectrolytes exhibit a conformational transition from compact globule (high carboxyl density, i.e. high slope in pK_a vs. α) to coil-like forms (low carboxyl density, i.e. low slope) in water with increasing neutralization. The pK_a values decrease with increasing α in the intermediate region between them. The titration result in Fig. 4 is, therefore, thought to be quite reasonable because the PEEA chain may also experience the conformational transition, intermolecular association, and precipitation. The very high slope in pK_a vs. α below 0.05 is partly likely due to the significant precipitation. The value of pK_0 was determined to be 4.7 ± 0.1 by extrapolating pK_a to α = 0, which is very close to that (4.63) of corresponding low-molecular weight analogue, isobutylic acid [17].

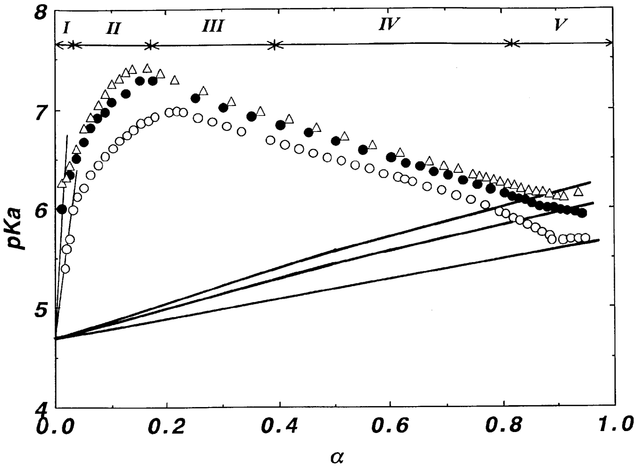


Fig. 4 Plot of pK_a of PEEA (C_p = 2.02 mN) against α in NaCl solutions at C_s = 5, 10, and 50 mN from top to bottom, respectively. The thick solid lines are calculated for the rod model with the parameters given in the text

Figure 5 shows the results of viscometry plotting [η] vs. α at C_s = 10 mN NaCl. The value of [η] was found to steeply increase with α higher than 0.4. This behavior is

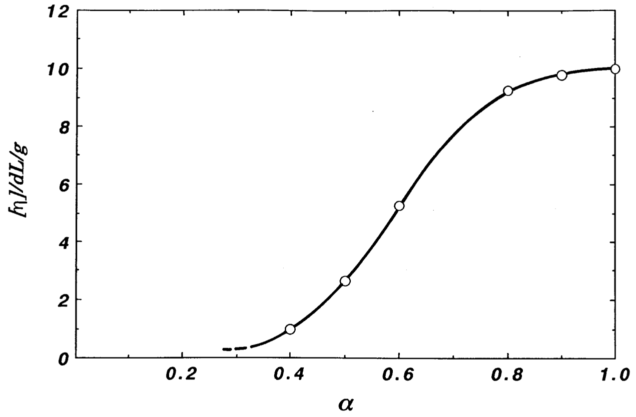


Fig. 5 Dependence of $[\eta]$ of PEEA of α in C_s = 10 mN NaCl at 25°C

also characteristic of hydrophobic polyelectrolytes. The value of $[\eta]$ at $\alpha = 1.0$ in $C_s = 10$ mN solution is 9.97 dl/g, which can be comparable to that (8–9 dl/g) of poly(sodium acrylate) (PNaA) with the same contour length as PEEA [18]. Therefore, the PEEA chain above $\alpha \approx 0.8$ in water appears to assume a coil-like conformation similar to PNaA.

When G_{ex} is the free energy only form the electrostatic interaction, it is related to the electrostatic potential (ψ) on the surface of the polyelectrolyte chain given by [3]

$$\partial G_{ex}/\partial\alpha = \partial G_{el}/\partial\alpha = N_A e\psi , \tag{4}$$

where N_A is Avogadro's constant. The electrostatic potential ψ was calculated by solving Poisson–Boltzmann equation, where the PEEA chain was treated as an infinite rod. The solid lines in Fig. 4 represent the theoretical ones determined by use of computer, assuming the apparent diameter of a rod as 0.55 nm, dielectric constant of water as 78, the temperature as 298.15 K, and intercharge distance at $\alpha = 1$ as 0.756 nm. It is seen that the theoretical lines are in good agreement with the experimental electrostatic potential of the PEEA in the region of α higher than 0.9. This is in contrast with the results of other low charge density polyelectrolytes, such as hyaluronic acid [19] and xanthan [20], to which the rod model with a smeared charge density was found to be inapplicable. For these polyelectrolytes with a large rod diameter the rod model with a smeared charge density may overestimate the electrostatic potential.

When the conformational transition takes place with neutralization, the term, G_{ex} can be expressed by a sum of two terms as

$$\partial G_{ex}/\partial\alpha = \partial G_{conf}/\partial\alpha + N_A e\psi , \tag{5}$$

where G_{conf} is the free energy change due to the conformational transition. The G_{conf} was estimated to be 1.3 ± 0.1 Kcal mono-mol^{-1} from the result in Fig. 4 with the equation,

$$G_{conf} = 2.303\,RT\oint(\mathrm{p}K_a - \mathrm{p}K_o)\,\partial\alpha - \oint N_A e\psi\partial\alpha . \tag{6}$$

This value obtained is larger than 0.4_2 Kcal mono-mol^{-1} for poly(styrene-*alt*-maleic acid) [15] and 0.31 Kcal mono-mol^{-1} for poly(*n*-butylvinly ether-*alt*-maleic acid) [16] but comparable to 1.2 Kcal mono-mol^{-1} for poly(indene-*alt*-maleic acid) [21, 22] and 1.13 Kcal monomol^{-1} for poly(*n*-hexylvinyl ether-*alt*-maleic acid) [23].

A schematic dissolution process of PEEA in water with neutralization is shown in Fig. 6. There appears to be at least five stages in the neutralization of PEEA in water, corresponding to the pK_a-α profiles as indicated in Fig. 4. In region I, inter- and intramolecular association extensively occurs to produce precipitation. In region II, the titratable carboxylic acid groups located on the surface of the precipitates were neutralized to swell the surface region by water. In region III, water-swellable microparticles (micelles) are formed to afford a dispersion or a milky system. The extent of swelling increases with increasing α and intermolecular association begins to become loose to separate swollen microparticles to unimolecularly dissolved PEEA chains. In this region, the value of pH was almost constant, as shown in Fig. 3, which is consistent with the titration of acid soap [24]. The theoretical and experimental studies of the titration curves for the associating system have been reported by Maeda [25].

At the beginning of the region IV, the solution becomes clear and unimolecularly dissolved PEEA chain may exist, while a PEEA chain still assumes a compact conformation by intramolecular hydrophobic interaction. Whereas the boundary between III and IV is not so clear in this study, we suppose the region IV begins at $\alpha \approx 0.4$. In this region, the intrinsic viscosity steeply increases with α, most likely corresponding to conformational transition from the unimolecular micelle to the coil-like one [26, 27]. In the final region V, all the PEEA chains assume a coil-like conformation. The electrostatic potential calculated from the rod model with a smeared charge density quantitatively predicts the experimental pK_a of the PEEA in this region.

Conclusions

The preparation and solution properties of sequence-ordered, periodic copolymer, PEEA, were presented in this paper. PEEA is soluble in water above pH = 6.5. The plots of pK_a against α showed a reversed S-shape curve

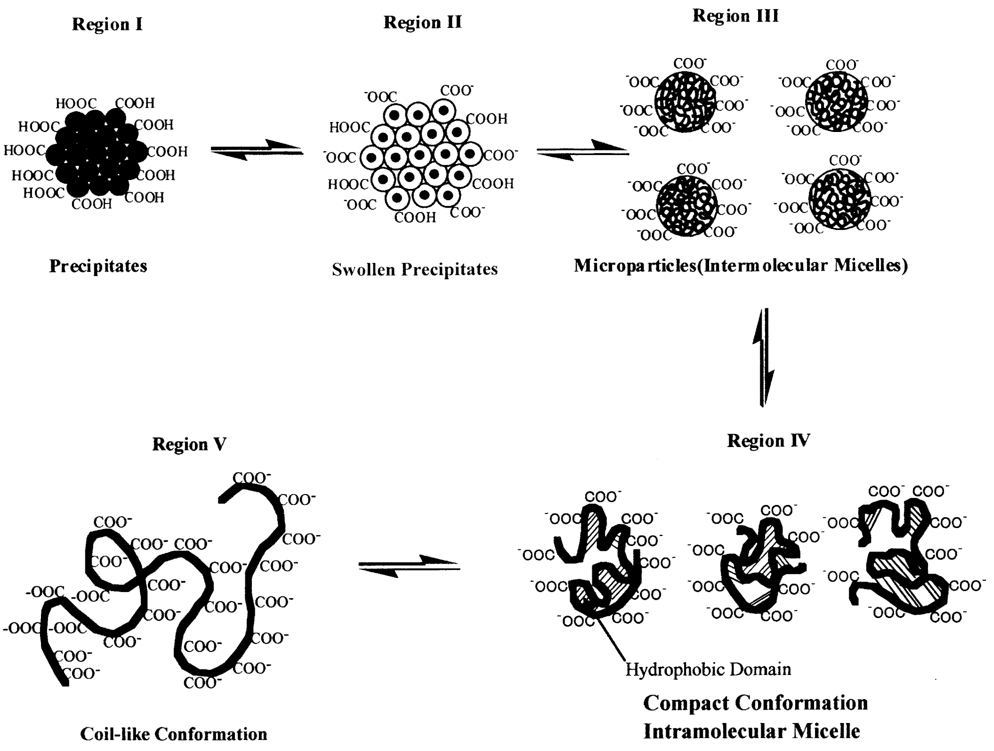


Fig. 6 Schematic dissociation and dissolution processes of PEEA in water as a function of α, with the corresponding regions as indicated in Fig. 4

over the whole α. The intrinsic viscosity steeply increased with α above 0.4 and attained up to 9.97 dl/g at $\alpha = 1.0$. The observed electrostatic potential of PEEA in the region of α higher than 0.85 was in good agreement with that calculated from the rod model with a smeared charge density. The dissolution process of an alkali-soluble main-chain hydrophobic polyelectrolyte in water with neutralization was presented.

References

1. Rice SA, Nagasawa M (1961) Polyelectrolyte Solutions. Academic Press, New York
2. Crescenzi V (1968) Adv Polymer Sci 5:358
3. Kitano T, Kawaguchi S, Ito K, Minakata A (1987) Macromolecules 20:1598
4. Kawaguchi S, Nishikawa Y, Kitano T, Ito K, Minakata A (1990) Macromolecules 23:2710
5. Hirose Y, Sakamoto Y, Tajima H, Kawaguchi S, Ito K (1996) J Phys Chem 100:4612
6. Kitano T, Kawaguchi S, Anazawa N, Minakata A (1987) Macromolecules 20:2498
7. Yokota K, Miwa M, Hirabayashi T, Inai Y (1992) Macromolecules 25:5821
8. Hirabayashi T, Kawasaki T, Yokota K (1990) Polym J 22:287
9. Mori Y, Sumi H, Hirabayashi T, Inai Y, Yokota K (1994) Macromolecules 27:1051
10. Yokota K (1995) Kobunshi Kako 44:29
11. Oosawa F (1971) Polyelectrolytes. Marcel Dekker
12. Manning GS (1972) J Phys Chem 51:924
13. Huggins ML (1942) J Am Chem Soc 64:2716
14. Mead DJ, Fuoss RM (1942) J Am Chem Soc 64:277
15. Ohno N, Sugai S (1984) Macromolecules 17:634
16. Dubin PL, Strauss UP (1976) J Phys Chem 71:2757; (1970) 74:2842
17. Kortüm G, Vogel W, Wandrussov K (eds) (1961) Dissociation constants of organic acids in aqueous solution. Butterworths, London
18. Noda I, Tsuge T, Nagasawa M (1970) J Phys Chem 74:710
19. Cleland RL (1984) Macromolecules 17: 634
20. Zhang L, Takemitsu T, Norisuye T (1987) Macromolecules 20:2882
21. Sasaki S, Minakata A (1976) Rept Progr Polym Phys Jpn 19:65
22. Ohno N, Sugai S (1990) J Macromol Sci Chem A27(7):861
23. Schleschinger UP, Strauss UP (1978) J Phys Chem 82:571
24. Feinstein ME, Rosano HL (1969) J Phys Chem 73:601
25. Maeda H (1988) J Phys Chem 92:4490
26. Dubin PL, Strauss UP (1970) J Am Chem Soc 74:2842
27. Morishima Y, Itoh Y, Nozakura S (1981) Makromol Chem 182:3135