ELSEVIER

Biophysical Chemistry 60 (1996) 45–51

Biophysical
Chemistry

Relationship between protonation and ion condensation for branched poly(ethylenimine)

Jiro Nagaya [a], Masahiro Homma [a], Akihiko Tanioka [a], Akira Minakata [b,*]

[a] *Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan*
[b] *Department of Physics, Hamamatsu University School of Medicine, Handa-cho, Hamamatsu 431-31, Japan*

Received 28 August 1995; revised 23 October 1995; accepted 20 November 1995

Abstract

The chloride ion activity, pH and conductance of an aqueous solution of branched poly(ethylenimine) (BPEI) were measured as a function of polymer concentration C_p and degree of protonation α or degree of neutralization β. BPEI is a highly branched polyelectrolyte and has ionizable groups mainly on the main chain. The conductometric titration curve shows a sharp increase before complete protonation, and its starting point, β_c, depends on C_p and does not coincide with the equivalent point determined by potentiometric titration. The chloride ion activity coefficient is very low and decreases with β, but it has a minimum point at about 0.6–0.8, roughly corresponding to β_c. The sharp conductance increase, in the region of $\beta < 1$, is explained in terms of the weakness of the bases in the highly branched spherical polyion. The low values of the counterion activity coefficient is explained in terms of the two-phase model of spherical polyelectrolytes.

Keywords: Poly(ethylenimine), branched; Conductometric titration; Potentiometric titration; Activity coefficient; Polyelectrolyte, spherical

1. Introduction

In the field of aqueous polyelectrolyte solutions, a large number of studies have been carried out in order to understand the relationships between charge density and polyion–counterion interaction [1–17], because the solution properties are greatly influenced by this interaction. The activity coefficient of counterions in a polyelectrolyte solution is lower than that in a simple salt solution at the same concentration, due to quite large interaction between counterions and polyelectrolytes. The higher the charge density of the polyelectrolyte becomes, the larger is the interaction between the polyelectrolyte and counterions. These situations were explained by several authors [13,14]. Also, it has been reported that the ionization behavior depends not only on the charge density but also on polymer configurations [15–17]. For example, the dissociation behavior is different for poly(fumaric acid) and poly(maleic acid), having the same charge density. Most samples used in these studies, however, were anionic rod-like polyelectrolytes which contain charged groups on side chains. There are several studies on cationic polyelectrolytes [18–30], but only a few studies can be found on the polyelectrolytes having charged groups on the main chain [24–30].

Branched poly(ethylenimine) (BPEI) was used in the present study to investigate the counterion activ-

---

[*] Corresponding author.

SSDI 0301-4622(95)00143-3

ity and its effect on the electrical conductivity. BPEI is a weak cationic polyelectrolyte because its ionization is provided by protonation of amine groups. Due to highly branched chain conformation, its overall shape in solution is regarded as a typical example of a spherical polyion [31]. About 50% of the ionizable groups is secondary amine, and about 25% is tertiary amine, which are located on the polymer main chain. Thus, the groups charged by protonation are positioned on the main chain of BPEI. Such overall features and arrangement of the ionized groups are not necessarily common for polyelectrolytes usually studied.

Several experimental and theoretical studies have been proposed to explain potentiometric titration curves and activity coefficients of counterions for BPEI [28,29]. In the work described in the present paper we have measured the activity coefficients of counterions, and carried out conductometric titrations and potentiometric titrations. Considering these results, we finally discuss the distinctive feature of protonation for BPEI.

2. Experimental

2.1. Sample preparation

The polymer sample used was a commercial BPEI (SP-200, Nippon Shokubai Kagaku Kogyou Co., Ltd.), whose MW was 10 000. This BPEI was highly branched and contains primary, secondary and tertiary amine groups in the ratio of approximately 1:2:1 [27]. The sample solutions were prepared by dialysis for two days by cellulose membrane (Spectra/Por® 3 MWCO = 3500 Spectrum Medical Industries, Inc.) and deionized by an ion-exchange resin column (Dowex 1 and Dowex 50, The Dow Chemical Company) before use. The polymer concentration C_p was changed by dilution of this solution.

2.2. Potentiometric titration

The potentiometric titration was carried out with HCl in salt-free or in 2.0 M KCl solution to clarify the ionization behavior as well as to measure C_p accurately with a TOA HM-60V pH meter and a GST-511C pH combination glass electrode. All measurements were carried out in a stirred solution thermostated at 25.0 ± 0.1°C under a nitrogen atmosphere. C_p was varied from 9.10 to 91.0 mM.

2.3. Conductometric titration

The electrical conductivity was measured with a TOA CM-20S conductivity meter and a CG-511B conductivity cell. The frequency was selected to be 80 Hz and 3 kHz, respectively. All measurements were carried out with HCl as titrant in a stirred solution thermostated at 25.0 ± 0.1°C under a nitrogen atmosphere and under salt-free conditions. C_p was varied from 4.55 to 91.0 mM.

2.4. Activity coefficient

The electromotive force (EMF) was measured using a TOA IM-40S ion meter with a CL-125B chloride ion selective glass electrode and an HS-305DS double-junction reference electrode. All measurements were carried out with HCl as titrant in a stirred solution thermostated at 25.0 ± 0.1°C under a nitrogen atmosphere. Calibration was made with a TOA Cl^- standard solution before and after each measurement, and the average value was used for calculation. C_p was varied from 9.10 to 91.0 mM.

3. Results and discussion

The concentration of BPEI solution was measured by potentiometric titration with HCl in the presence of 2.0 M KCl. The end point for this titration is not clear, because BPEI is a weak base. However, to subtract the contribution of free H^+ by a blank titration, the end point of the titration could be determined clearly in order to decide the equivalent concentration [16]. The polymer concentration has to be determined by weighing the polymer sample. The weights of BPEI, however, cannot be found exactly, owing to absorption of atmospheric water vapor during the measurement, because of the hygroscopic nature of the polymer. It is also reported that protonation does not exceed about 70% of the total number of basic nitrogen atoms under fully neutralized conditions [27]. Therefore, we cannot determine the equivalent concentration by weighing the polymer.

For weakly basic or acidic polyelectrolytes the ionization is interfered by the interaction of the neighbour charged groups. Therefore, the degree of ionization and neutralization do not coincide with each other. For cationic polyelectrolytes, the degree of protonation α is related to degree of neutralization β as,

$$\alpha = \beta - [\mathrm{H}^+]/C_p \qquad (1)$$

If the protonation–deprotonation process of an amine group is described in terms of an apparent dissociation constant K_a, we have

$$\mathrm{p}K_a = \mathrm{pH} - \log[(1-\alpha)/\alpha] \qquad (2)$$

Here we disregard the difference in protonation behavior among primary, secondary and tertiary amine groups. The pH of the solution is defined by

$$\mathrm{pH} = \mathrm{p}K_0 + \log[(1-\alpha)/\alpha] - (0.4343/RT)(\mathrm{d}G_{el}/\mathrm{d}\alpha) \qquad (3)$$

where K_0 is the intrinsic dissociation constant, R the gas constant, T the absolute temperature, and G_{el} is the electrostatic free energy for dissociation of an equivalent of protons. From Eqs. 2 and 3, $\mathrm{p}K_a$ is given by

$$\mathrm{p}K_a = \mathrm{p}K_0 - (0.4343/RT)(\mathrm{d}G_{el}/\mathrm{d}\alpha) \qquad (4)$$

In general, $(\mathrm{d}G_{el}/\mathrm{d}\alpha)$ increases with α and $\mathrm{p}K_a$ decreases with α because of repulsion between nearest-neighbour and the other charged groups.

Figs. 1 and 2 show the results of potentiometric titration without salt and $\mathrm{p}K_a$ curves calculated by using Eq. 2 at various polymer concentrations ranging from 9.10 to 91.0 mM. Fig. 2 shows that $\mathrm{p}K_a$ decreases with the degree of protonation α, except for the regions close to $\alpha = 0$ and $\alpha = 1$, where the accuracy of the measurement becomes quite poor. This trend for BPEI is the same as for other polyelectrolytes [14,20], although $\mathrm{p}K_a$ decreases with α, opposite to the cases of polyacids. No significant change in pH value can be found by changing the polymer concentration as can be seen in Fig. 1. More precisely, at first the pH decreases sharply and then slowly, but again decreases a bit sharply at $\beta > 0.5$, and finally slowly. The second sharp decrease in pH, although not clearly observed, may correspond to the release of H^+ and Cl^-, as observed clearly in conductance measurements described below. The pH curves do not show a single step nor multiple steps,

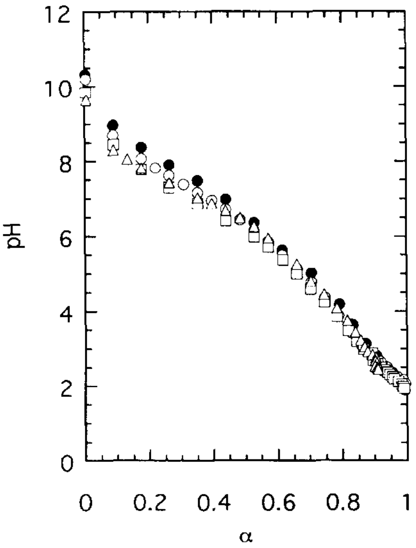

Fig. 1. Potentiometric titration curves for BPEI at various C_p: (●) 91.0, (○) 45.5, (□) 18.2 and (△) 9.10 mM.

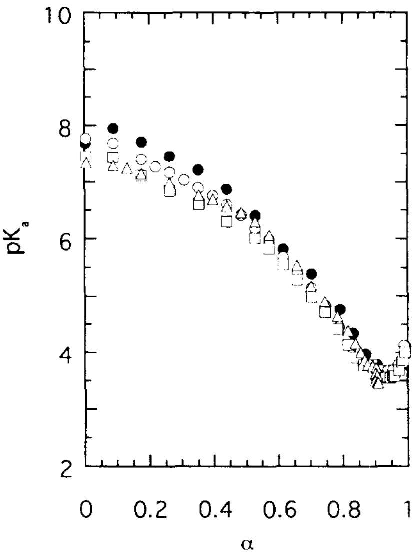

Fig. 2. Plot of $\mathrm{p}K_a$ vs. α for BPEI at various C_p. Symbols are the same as those in Fig. 1.

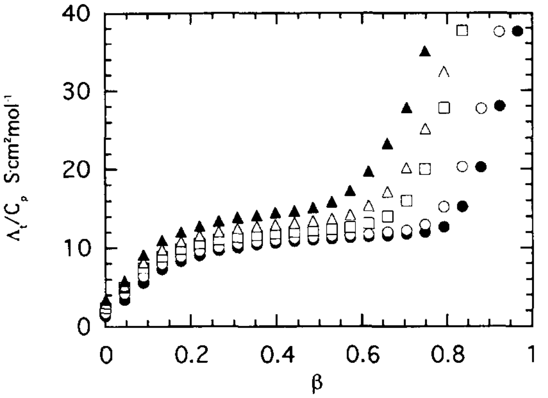

Fig. 3. Conductometric titration curves for BPEI at various C_p: (●) 91.0, (○) 45.5, (□) 18.2, (△) 9.10 and (▲) 4.55 mM.

although BPEI has three kinds of charged groups. Precise discussion is not attempted here, although there are some studies to explain the quantitative evaluation of this curve [29].

Fig. 3 shows the conductometric titration curves for various C_p values without salt. The polymer concentrations are 91.0, 45.5, 18.2, 9.10 and 4.55 mM, respectively. For all polymer concentrations studied, the larger the polymer concentrations are, the smaller are the equivalent conductance and the gradient of increase with increasing β. The conductance increases sharply with β in the region of β less than 0.2. This increase corresponds to a large pH drop in the corresponding region of α, which is shown in Fig. 1. The conductance increases slightly in the region of $\beta > 0.2$. In general, protonation of an amine group with increasing β is influenced by the interaction between counterions and the other charged groups in weakly basic polyelectrolytes. Therefore, the increase in conductance is largely interfered. Finally, a sharp increase in conductance is observed with β larger than about 0.6. These trends are the same for all polymer concentrations. In an ordinary conductometric titration, the starting point of the sharp increase in the conductance, due mainly to the increase in free acid, can be determined as an equivalent point, namely, this point should be unity for most polyelectrolyte studies. Fig. 3 shows, however, that the starting point of the sharp increase in the conductance β_c is less than unity and increases with polymer concentration C_p.

The conductance of the solution Λ_t is defined by the following equation

$$\Lambda_t = \Lambda_p + \Lambda_{Cl} + \Lambda_H + \Lambda_{OH} \tag{5}$$

where Λ_p, Λ_{Cl}, Λ_H and Λ_{OH} are the contributions of the conductance of the polyelectrolyte, Cl^-, H^+ and OH^- to the total conductance, respectively. Here, the values of Λ_p were determined by subtracting other contributions from Λ_t.

These contributions are assumed to be written by

$$\Lambda_p = \beta C_p \lambda_p$$

$$\Lambda_{Cl} = \beta C_p \gamma_{Cl} \lambda_{Cl}$$

$$\Lambda_H = 10^{-pH} \lambda_H$$

$$\Lambda_{OH} = 10^{-(14-pH)} \lambda_{OH} \tag{6}$$

where λ_p, λ_{Cl}, λ_H and λ_{OH} are the equivalent conductance of the polyelectrolyte, Cl^-, H^+ and OH^-, respectively. The value of λ_{Cl} is the equivalent conductivity of Cl^- in a KCl solution at the same concentration, calculated from the literature [32]. The value of pH and γ_{Cl} are given by the results of the present study. Here the above expressions are written on the basis of the formulation of Huizenga et al. [33], because the contribution of counterions to the conductance is primarily approximated by that of free counterions for any size and shape of polyions in solution, although an expression with a slightly different numerical factor was proposed for a rod-like polyion [34]. It is also assumed that the equivalent conductance of the polyelectrolyte exhibits no serious change in the region where the acid was added, more than at the starting point of the sharp increase in the conductance. Strictly speaking, Λ_p is proportional to α, instead of β. In most regions of β, however, the difference between α and β is quite small, and γ_{Cl} is given as a function of β, so that α is replaced by β in Eq. 6.

Fig. 4 shows each contribution to equivalent conductances at $C_p = 45.5$ mM. Above the point of β_c, $\Lambda_H + \Lambda_{OH}$ and Λ_{Cl} increases sharply. The sharp increase in conductance may be due mainly to the increase in free HCl at $\beta > \beta_c$.

Fig. 5 shows the dependence of the values of β_c on the polymer concentration, plotted as a function of C_p^{-1}. The values of β_c tend to 1.0 as the polymer

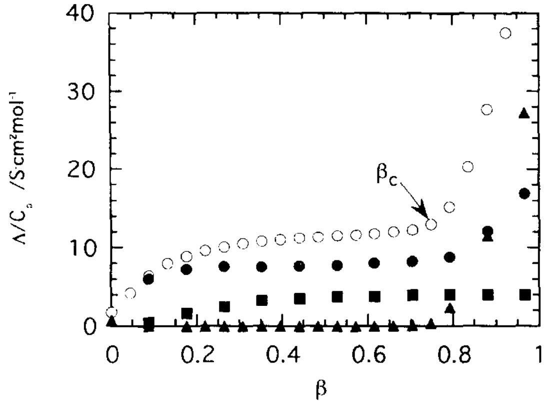

Fig. 4. Contribution of each ionic species to the equivalent conductance at $C_p = 45.5$ mM: (○) Λ_t/C_p, (●) Λ_{Cl}/C_p, (■) Λ_p/C_p and (▲) $\Lambda_{(H+OH)}/C_p$.

concentration increases, but its dependence is not well known quantitatively.

BPEI has three kinds of charged groups as described before. Fig. 2 tells us, however, that there is no large difference in the apparent dissociation constant among these charged groups, because no stepwise changes are observed. Thus, it is assumed that BPEI is composed of one kind of charged groups. In this system, BPEI can be charged by protonation as shown in Eq. 7.

$$H^+ + Cl^- + R-NH \rightleftarrows R\text{-}NH_2^+ + Cl^- \rightleftarrows R\text{-}NH_2^+Cl^- \quad (7)$$

Fig. 6 shows the conductance of BPEI solution, diminished by the contribution of the blank titration, as a function of β larger than 1 at $C_p = 9.10$ mM. This figure indicates that the apparent contribution to the conductance from the polyion decreases and finally becomes constant by adding HCl when β is greater than unity. It is also understood from Fig. 4 that BPEI is not protonated perfectly at $\beta = 1$. The more $[H^+]$ increases, the more the protonation advances, and the difference in the conductance, $\Lambda_t - \Lambda_b$ decreases with β at $\beta > 1$, as suggested by Eq. 7. The difference in the conductance expresses the extent of incomplete protonation and anion condensation, which occurs at high concentrations of acids. The data indicate that the protonation occurs quite gradually. This final constant value corresponds to the sum of the conductance of the polyelectrolytes and counterions. The value at $\beta = 1$ is the sum of the conductance of polyelectrolytes, counterions and the acid added which cannot protonate the polyelectrolytes. If C_p increases, the protonation increases and the starting point of the sharp increase in the conductance shifts to higher values. The sharp increase in Λ_t in Fig. 3 at $\beta > \beta_c$ is considered to be due to the free acid. The protonation becomes incomplete as C_p decreases, due mainly to the nature of the amine groups, as well as the repulsion from other protonated groups in case of a highly branched spherical polyion [31].

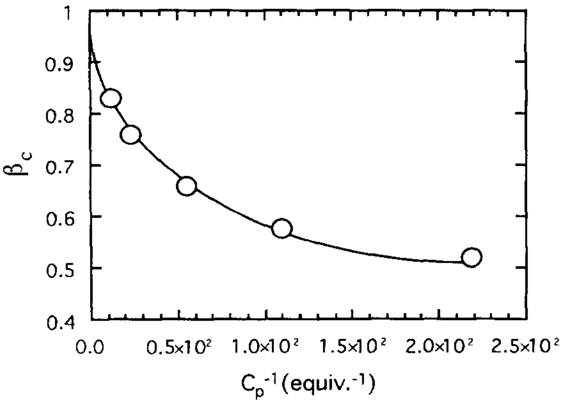

Fig. 5. Plot of the values of the sharp increase in the conductance β_c vs. C_p^{-1}, to indicate that β_c tends to 1.0 as C_p increases.

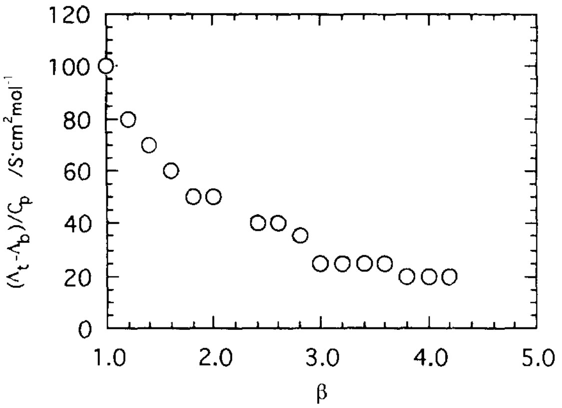

Fig. 6. Difference in equivalent conductances between BPEI and those of the blank titration at $C_p = 9.10$ mM.

Activity coefficients of Cl^- (γ^-) for various C_p are plotted as a function of degree of neutralization β in Fig. 7. Usually the higher the charge density of the polyelectrolyte becomes, the lower the activity coefficient should be as discussed above. Fig. 7

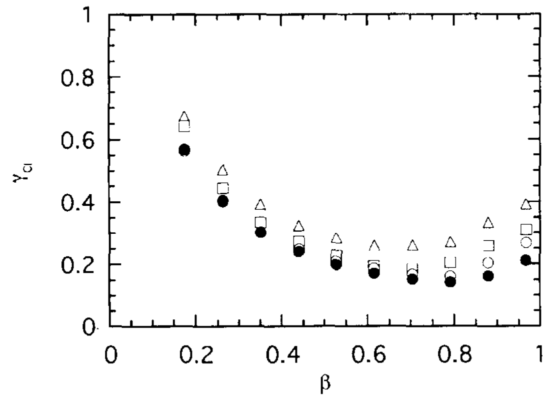

Fig. 7. Plots of activity coefficients of Cl^- for BPEI at various C_p: (●) 91.0, (○) 45.5, (□) 18.2 and (△) 9.10 mM.

indicates that γ^- decreases with β at low β values and has a minimum at β values between 0.6 and 0.8 and then increases with β at higher β values. The values of β at the minimum points of γ^- shift toward higher ones with C_p, which corresponds to the starting point of the sharp increase of the conductance at the same C_p. Therefore, the increase in γ^- is due to the contribution of added HCl which cannot protonate BPEI.

There are two anomalous characteristics of BPEI in the present results; increase in the conductance before complete neutralization, e.g., 0.6 to 0.8, and quite low values of γ^-. The former is ascribed to be the weakness of the bases, that is, the protonation is limited to some extent, leading to the release of protons for further titration. On the other hand, the latter means that the counterions are bound strongly, irrespective of the weakness of the bases. The reason for the low values of γ^- may be due to the overall conformation of BPEI. Since BPEI is highly branched, the overall shape is more or less spherical with a large number of ionizable groups inside in the spherical region. The two-phase model for the spherical polyions in solution can be applied to this case, as follows [31].

According to this model (p. 15 of Ref. [31]), the activity coefficients of the counterions are calculated to be 0.125, assuming the radius of the polyion to be 25 Å [35]. The radius can also be estimated by a computer simulation of the polymer growth based on the attachment of a monomer with one of the three kinds of amine groups, which gives the value of the radius to be 17 Å, leading to a value of $\gamma^- = 0.1$ (M. Higa et al., to be published). These values are reasonable to explain the present results.

In this study, we considered only a single protonation process of amine groups. Actually there are three kinds of amine groups in BPEI, and the effect of the distribution of these charged groups on a polymer chain is neglected. More detailed study may be needed for further refined analysis.

References

[1] H. Vink, J. Chem. Soc. Faraday Trans. 1, 77 (1981) 2439.
[2] G.S. Manning, J. Phys. Chem., 79 (1975) 262.
[3] S. Lifson, J. Chem. Phys., 26 (1957) 727.
[4] Ming-H. Hao and S.C. Harvey, Macromolecules, 25 (1992) 2200.
[5] J.J. Hermans and J.Th.G. Overbeek, Recl. Trav. Chim. Pays-Bas, 67 (1948) 761.
[6] M. Nagasawa, M. Izumi and I. Kagawa, J. Polym. Sci., 37 (1959) 375.
[7] M. Nagasawa and I. Kagawa, J. Polym. Sci., 25 (1957) 61.
[8] S. Sugai and K. Nitta, Biopolymers, 12 (1973) 1363.
[9] L. Kotin and M. Nagasawa, J. Chem. Phys., 36 (1962) 873.
[10] M. Hara, A.H. Lee and J. Wu, J. Polym. Sci. Polym. Phys. Ed., 25 (1987) 1407.
[11] H.P. Gregor and M. Frederick, J. Polym. Sci., 23 (1957) 451.
[12] L.M. Penafiel and T.A. Litovitz, J. Chem. Phys., 96 (1992) 3033.
[13] G.S. Manning, J. Chem. Phys., 51 (1969) 924.
[14] A. Katchalsky, Z. Alexandrowicz and O. Kedem, in B.E. Conway and R.G. Barradas (Eds.), Chemical Physics of Ionic Solutions, Wiley, New York, 1966, p. 295.
[15] T. Kitano, S. Kawaguchi, K. Ito and A. Minakata, Macromolecules, 20 (1987) 1598.
[16] S. Kawaguchi, Y. Nishikawa, T. Kitano, K. Ito and A. Minakata, Macromolecules, 23 (1990) 2710.
[17] S. Kawaguchi, T. Kitano, K. Ito and A. Minakata, Macromolecules, 24 (1991) 6335.
[18] H.E. Ríos, L.N. Sepúlveda and C.I. Gamboa, J. Polym. Sci. Polym. Phys. Ed. , 28 (1990) 505.
[19] J.W. Klein and B.R. Ware, J. Chem. Phys., 80 (1984) 1334.
[20] H. Ochiai, Y. Anabuki, O. Kojima, K. Tominaga and I. Murakami, J. Polym. Sci. Polym. Phys. Ed., 28 (1990) 233.
[21] T. Itaya and H. Ochiai, Polym. Commun., 32 (1991) 564.
[22] L. Zhuomei, Z. Xuexin, C. Yuanpei and Z. Yuanzhen, Macromolecules, 25 (1992) 450.
[23] H. Ochiai, M. Handa, H. Matsumoto, T. Moriga and I. Murakami, Makromol. Chem., 186 (1985) 2547.
[24] K.F. Weyts and E.J. Goethals, Makromol. Chem. Rapid Commun., 10 (1989) 299.
[25] R.G. Smits, M.E. Kuil and M. Mandel, Macromolecules, 26 (1993) 6808.

[26] R.G. Smits, G.J.M. Koper and M. Mandel, J. Phys. Chem., 97 (1993) 5745.

[27] C.R. Dick and G.E. Ham, J. Macromol. Sci.-Chem., A4(6) (1970) 1301.

[28] E.J. Shepherd and J.A. Kitchener, J. Chem. Soc., 4 (1956) 2448.

[29] C.J. Bloys van Treslong et al., Recl. Trav. Chim. Pays-Bas, 93 (1974) 171; 97 (1978) 13, 22.

[30] D.R. Chang, S. Harden and N. Loverro, J. Macromol. Sci.-Chem., A23(6) (1986) 801.

[31] F. Oosawa, Polyelectrolytes, Marcel Dekker, New York, 1971.

[32] V.M.M. Lobo, Physical Sciences Data, Vol. 41, Elsevier, Amsterdam, 1989, p. 799.

[33] J.R. Huizenga, P.F. Grieger and F.T. Wall, J. Am. Chem. Soc., 72 (1950) 2636.

[34] G.S. Manning, Biopolymers, 9 (1970) 1543.

[35] G.M. Lindquist and R.A. Stratton, J. Colloid Interface Sci., 55 (1976) 45.