ELSEVIER

European Polymer Journal 37 (2001) 1571–1575

EUROPEAN
POLYMER
JOURNAL

www.elsevier.nl/locate/europolj

Influence of low-molecular-weight salts on the formation of polyelectrolyte complexes based on polycations with quaternary ammonium salt groups in the main chain and poly(sodium acrylate)

Stela Dragan *, Mariana Cristea

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda nr. 41-A, 6600 Iasi, Romania

Received 23 October 2000; received in revised form 20 December 2000; accepted 5 February 2001

Abstract

The effects of NaCl, NaI and Na_2SO_4 on the formation of polyelectrolyte complex (PEC) between a polycation with *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the main chain (PCA_5) and poly(sodium acrylate) (NaPA) were studied. The NaCl concentration in the polyelectrolyte solutions ranged from 0 to 2 M. Viscometric and turbidimetric measurements were used to follow the effect of the salt concentration and of the counterion nature on the PEC formation. The influence of counterions was different depending on both the radius of the hydrated ion and its valence. At the same concentration of the low-molecular-weight salt, the following order of the PEC separation in dependence on the counterion was evidenced: $R_{sep}(SO_4^{2-}) < R_{sep}(I^-) < R_{sep}(Cl^-)$. The critical concentration of NaCl for this system was established. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte; Polyelectrolyte complex; Counterion binding; Critical ionic strength

1. Introduction

The interactions between complementary polymers (electrostatic interactions, hydrogen bonding, hydrophobic interactions) have received considerable attention due to their potential for many applications [1,2]. So far, the high interactions between oppositely charged polyelectrolytes which give rise to polyelectrolyte complexes (PEC) have been used in a number of applications like biotechnology (protein purification and separation) [3,4], medicine (antithrombogenic agents, artificial immunogens and vaccines) [5,6], environmental control by flocculation [7], self-assembled multilayer membranes [8], etc.

Many papers have delt with the factors that influence the process of PEC formation such as the nature of polyelectrolytes and the reaction medium [9–12]. With regard to the later much cautioness must be paid to the ionic strength, and this one is considered in two situations: the formation of PECs in the presence of low-molecular-weight salts (LMWS) [4,13,14] and the effect of LMWS on the stability of PEC already formed [15,16]. The critical ionic strength is defined as the ionic strength value which impedes the formation of PEC or the ionic strength value when the PEC is broken up in the starting polyelectrolytes. Kabanov and Zezin [17] have settled that the presence of LMWS, in the concentration range of 0.002–0.1 mol/l, is one of the necessary conditions for the preparation of water soluble nonstoichiometric PEC from oppositely charged macromolecules taken in nonequivalent ionic ratios. Trinh and Schnabel [18] have obtained water soluble PEC at unit molar ratios between the oppositely polyelectrolyte

---

* Corresponding author. Fax: +40-3221-1299.
E-mail address: sdragan@ichpp.tuiasi.ro (S. Dragan).

PII: S0014-3057(01)00025-8

higher than 1:1, but at an ionic strength close to the critical value. The above considerations show that the potential applications of the PECs in the presence of LMWS need further studies of the PEC formation in aqueous solutions of different salts.

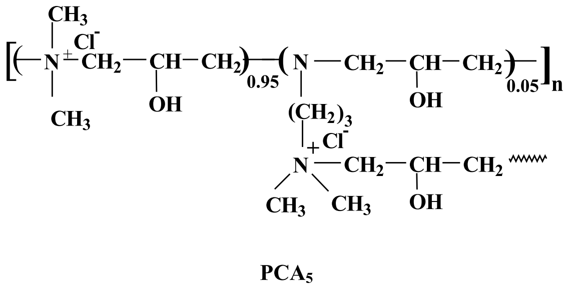
In previous articles we reported on the formation of PECs using polycations with different contents of *N*,*N*-dimethyl-2-hydroxypropylene ammonium chloride units in the main chain and three different polyanions, poly(sodium acrylate) (NaPA) [19], poly(sodium 2-acrylamido-2-methylpropanesulfonate) (NaPAMPS) [20] and poly(sodium styrenesulfonate) [16], in saltless aqueous solutions. The stability of the PECs formed with poly(sodium styrenesulfonate) as anionic component, at the subsequent addition of NaCl up to an ionic strength of 3.5 M on the reaction mixture, in dependence on the polycation structure, was also investigated [16]. Contrary our earlier investigations, in the present study we followed the formation of the PECs between a polycation with 95 mol% *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the main chain (PCA_5) and NaPA in aqueous solutions of different LMWS (NaCl, NaI and Na_2SO_4).

2. Experimental

2.1. Materials

The polycation PCA_5 was synthesized by the condensation polymerization of epichlorohydrin with dimethylamine and the polyfunctional amine *N*,*N*-dimethyl-1,3-diaminopropane (A) according to Ref. [21]. The structure of the polycation PCA_5 is presented in Scheme 1. The index, in the short name of the polycation, indicates mol% of the polyfunctional amine A.

The polycation was carefully purified by dialysis against distilled water until the absence of Cl^- ions in the external water was achieved. The dilute aqueous solution of polycation was concentrated by gentle heating in vacuum and then the polymer was precipitated with acetone and purified again by reprecipitation in methanol/acetone. The polycation was kept for days in vacuum on P_2O_5, at room temperature. The intrinsic viscosity in 1 M NaCl aqueous solution at 25°C was 0.432 dl/g.



PCA_5

Scheme 1.

Poly(sodium acrylate) (NaPA) with $M_v = 217\,600$ g/mol, determined in NaOH 2N at 25°C, was used as polyanion. The LMWS (NaCl, NaI, Na_2SO_4) reagent grade were used without further purification.

2.2. Methods

Polyelectrolyte solutions of each component were prepared one day before their using with bidistilled water or aqueous solutions of different LMWS as solvents. The complex formation was carried out into 100 ml glass vessels, at room temperature, by adding the NaPA (10^{-2} mol/l) dropwise into 50 ml PCA_5 (10^{-3} mol/l) until a certain mixing molar ratio *R* was achieved. This one is defined as the ratio between the anionic groups of NaPA to the oppositely charged groups of PCA_5: $R = [\mathrm{NaPA}]/[\mathrm{PCA}_5]$ (mol/mol). The concentration of NaPA was ten times higher than that of PCA_5 to minimize the effect of dilution. The solutions were stirred continuously during the titration and 2 h after that. The same concentration of LMWS was used in both polyelectrolyte solutions.

The complex formation in salt aqueous solution was studied by viscometric and turbidimetric methods. The viscometric measurements were made using an Ubbelohde viscometer with internal dilution, at 25°C. The turbidimetric measurements were performed at the wavelength of 420 nm using a FEK-M LMWS photocolorimeter.

3. Results and discussion

The formation of PECs in the presence of LMWS usually reveals some peculiarities which arise from the specific interaction of different small ions with macroions. The electrostatic repulsion between the ionic groups with the same charge is gradually diminished with the increase of the LMWS concentration. Therefore, the extended polyelectrolyte conformation turns first into a flexible one and then into a compact macromolecular coil.

Fig. 1 shows the turbidity variation in dependence on the mixing molar ratio *R* for the system NaPA/PCA_5, at different concentrations of NaCl in the starting solutions.

In saltless aqueous solution the turbidity advanced slowly until close to the end-point (the point when the phase separation took place and which corresponds about to the equivalence between the complementary ionic groups only in saltless aqueous solution) and increased abruptly then. The PECs started to form just

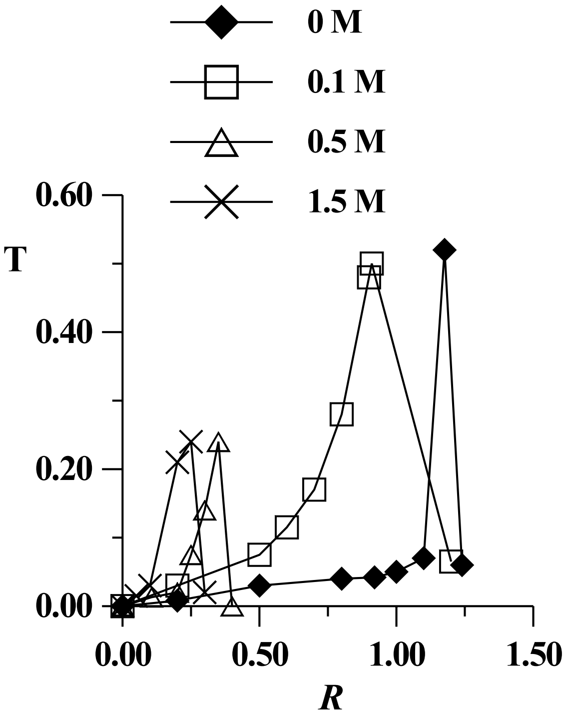


Fig. 1. Variation of turbidity vs the mixing molar ratio R in the formation of PEC in NaCl aqueous solutions with different concentrations.

when the first drops of the NaPA solution came into contact with PCA_5 solution in NaCl aqueous solutions, as follows from the rise of turbidity right from the start. A progressive and uniform growth in turbidity was monitored for 0.1 M NaCl concentration, associated with the shift of the end-point to lower values of R. The fast turbidity rise took place at a lower mixing molar ratio R when the NaCl concentration was further increased. Due to the screening effect of the counterions in excess, the ionic sites available for electrostatic interactions decreased gradually with the increase of the NaCl concentration. Consequently, the higher the salt concentration was, the lower the mixing molar ratio R corresponding to the end-point and hence the lower amount of polyanion included in the PEC. The PEC separation took place in that moment and was accompanied by the vanishing of the turbidity. In addition, Fig. 1 indicates that the maximum turbidity was diminished at higher NaCl concentrations (0.5 M, 1 M). One can notice that the PEC particles were much smaller at higher NaCl concentrations, comparative with those obtained at lower NaCl concentrations, since a lower amount of PEC is formed and separated at the end-point.

In Table 1 are listed the specific viscosities (η_{sp}) of the reaction mixture, before the end-point, and of the supernatant solution, after the end-point, as a function of the mixing molar ratio R, at the specified NaCl concentration.

Conformational changes of the polyelectrolyte chains during the PEC formation, for the same NaCl concentration, are evidenced by the decrease of the specific viscosity. This is a direct consequence of reducing the free polycation concentration by interaction with the polyanion. Because the packing density of the PEC particles is high enough they have not perceptibly influenced the value of η_{sp}. The minimum value of η_{sp}, very close to zero, was reached at the end-point (R_{sep}). Further polyanion solution added after the minimum η_{sp} induced the increase of the specific viscosity. After the end-point the supernatant solution should contain only NaPA in excess, because the PEC has settled down. As the NaCl concentration has been risen, at the same R, η_{sp} values decreased since the NaPA backbone coiled up as more as the medium contained more NaCl. Some specific aspects can be noticed when the concentration of NaCl in solution was 2 M. The reaction mixture remained clear irrespective of the mixing molar ratio R. Moreover, the flow time for each sample was situated under the flow time of the solvent. Therefore, we could infer that the critical NaCl concentration for this system is close to 2 M.

Table 1
Variation of the specific viscosities of the reaction mixture in dependence on the mixing molar ratio R and the NaCl concentration in the PEC formation between PCA_5 and NaPA

R	η_{sp}				
	$C_{NaCl} = 0$	$C_{NaCl} = 10^{-1}$ M	$C_{NaCl} = 0.5$ M	$C_{NaCl} = 1$ M	$C_{NaCl} = 1.5$ M
0	0.03320	0.02490	0.00673	0.00380	0.00440
0.2	0.03080	0.02330	0.00420	0.00046	0.00095
0.5	0.01550	0.01445	0.00375	0.00060	0.00155
1	0.00168	0.00853	0.00458	0.00080	0.00490
1.5	0.0389	0.01340	0.00662	0.00253	<0
R_{sep}	1.12	0.92	0.4	0.32	0.27

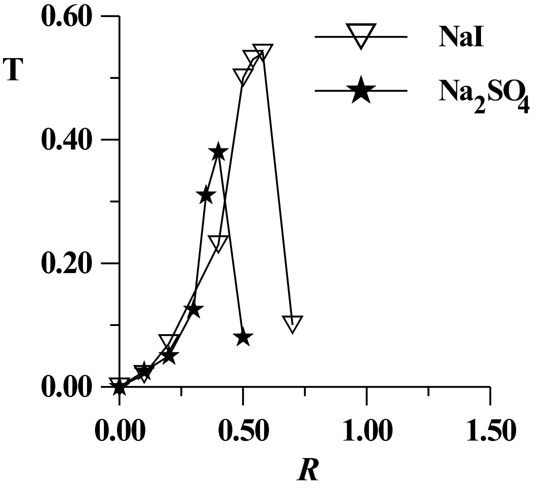


Fig. 2. Variation of turbidity vs the mixing molar ratio R in the formation of PEC in 0.1 M NaI and 0.1 M Na_2SO_4 aqueous solutions.

Fig. 2 illustrates the variation of turbidity when the complex NaPA/PCA_5 was formed in the presence of other two salts with the same concentration: 0.1 M NaI and 0.1 M Na_2SO_4. These salts were used in order to evidence the influence of the specific interaction between PCA_5 and different counterions on the PEC formation, the coion being constant (Na^+).

Taking into account the results collected in Fig. 2 and also the behavior of the system in 0.1 M NaCl (Fig. 1), one can see that the screening effect of different counterions for positive charges of PCA_5 decreases in the following order:

$$SO_4^{2-} > I^- > Cl^-,$$

which corresponds to the following order of the PEC separation in these systems:

$$R_{sep}(SO_4^{2-}) < R_{sep}(I^-) < R_{sep}(Cl^-).$$

The above series confirm our previous results obtained in the study of the interaction between the polycations with different contents of *N*,*N*-dimethyl-2-hydroxypropyleneammonium chloride units in the main chain and different monovalent counterions which showed that a halogen ion with a lower hydrated ionic radius interacted more strongly than one with a higher hydrated ionic radius [22]. I^- counterion interacts more strongly with the positive sites of the PCA_5 than Cl^- counterion due to the weaker hydration of I^- comparative with Cl^-, which determines an increase in the extent of the counterion binding. Similarly, the counterions with higher valence (in the present case SO_4^{2-} ions) are preferred instead of the monovalent ions (I^-, Cl^-). The above results show also that the PEC formation between PCA_5 and NaPA, in LMWS aqueous solutions, takes place in accordance to the counterion binding to the polycations with quaternary ammonium salt groups in the main chain. The influence of the specific interaction between monovalent counterions and other polycations on the formation of the nonstoichiometric PECs [23,24] and in the polyelectrolyte multilayer formation [12] was also mentioned.

4. Conclusions

By the results presented in this paper we brought new evidences on the importance of the LMWS in the PECs formation. The specific interaction between the positive charges of the polycation of integral type PCA_5 and different counterions (I^-, Cl^- and SO_4^{2-}) can determine the formation of PECs with different ratios between the complementary polyelectrolytes. The stronger the counterion binding is, the lower mixing molar ratio corresponding to the phase separation. The PEC formation in salt aqueous solutions with different concentrations of NaCl showed the decrease of the mixing molar ratio corresponding to the end-point with the increase of the salt concentration until close to 2 M NaCl when the complex formation was impeded. Hence, the mixing molar ratio corresponding to the PEC separation in the system PCA_5/NaPA decreased as more salt was present in the system and with decreasing of the hydrated counterion radius.

References

[1] Tsuchida E, Abe K. Interactions between macromolecules in solution and intermacromolecular complexes. Adv Polym Sci 1982;45(1):1–119.

[2] Philipp B, Dautzenberg H, Linow KJ, Koetz J, Dawydoff W. Polyelectrolyte complexes – recent developments and open problems. Prog Polym Sci 1989;14(1):91–172.

[3] Yu J, Liu H, Chen J. Flocculation and characterization of protein by anionic copolymer containing reactive functional groups. Colloid Surfaces A: Physicochem Engng Aspects 2000;163(2–3):225–32.

[4] Trinh CK, Schnabel W. Ionic strength dependence of the stability of polyelectrolyte complexes. Its importance for the isolation of multiply charged polymers. Angew Makromol Chem 1993;212(3718):175–82.

[5] Kataoka K, Tsuruta T, Akaike T, Sakurai Y. Biomedical behavior of synthetic polyion complexes toward blood platelets. Makromol Chem 1980;181(7):1363–73.

[6] Kabanov VA. Synthetic membrane active polyelectrolytes in design of artificial immunogens and vaccines. Makromol Chem, Macromol Symp 1986;1:101–24.

[7] Yu X, Somasundaran P. Enhanced flocculation with double flocculants. Colloid Surfaces A: Physicochem Engng Aspects 1993;81(1–3):17–23.

[8] Krasemann L, Tieke B. Selective ion transport across self-assembled alternating multilayers of cationic and anionic polyelectrolytes. Langmuir 2000;16(2):287–90.

[9] Vishalakshi B, Ghosh S, Kalpagam V. The effects of charge density and concentration on the composition of polyelectrolyte complexes. Polymer 1993;34(15):3270–5.

[10] Koetz J, Koepke H, Schmidt-Naake G, Zarras P, Vogl O. Polyanion-polycation complex formation as a function of the position of the functional groups. Polymer 1996;37 (13):2775–81.

[11] Izumrudov VA, Ortega Ortiz H, Zezin AB, Kabanov VA. Temperature controllable interpolyelectrolyte substitution reactions. Macromol Chem Phys 1998;199(6): 1057–62.

[12] Dubas ST, Schlenoff JB. Factors controlling the growth of polyelectrolyte multilayers. Macromolecules 1999;32(24): 8153–60.

[13] Dautzenberg H. Polyelectrolyte complex formation in highly aggregating systems. 1. Effect of salt: polyelectrolyte complex formation in the presence of NaCl. Macromolecules 1997;30(25):7810–5.

[14] Willett JL. Complexes of oppositely charged ionic starches. Starch 1995;47(1):29–32.

[15] Dautzenberg H, Karibyants N. Polyelectrolyte complex formation in highly aggregating systems. Effect of salt: response to subsequent addition of NaCl. Macromol Chem Phys 1999;200(1):118–25.

[16] Dragan S, Cristea M. Polyelectrolyte complexes. IV. Formation and stability of interpolyelectrolyte complexes between polycations with *N*,*N*′-dimethyl-2-hydroxypropylene ammonium chloride units in the chain backbone and poly(sodium styrenesulfonate) in dilute aqueous solution. J Colloid Interface Sci, submitted for publication.

[17] Kabanov VA, Zezin AB. Soluble interpolymeric complexes as a new class of synthetic polyelectrolytes. Pure Appl Chem 1984;56(3):343–54.

[18] Trinh CK, Schnabel W. Polyelectrolyte complexes from poly(N-ethyl-4-vinylpyridinium bromide) and poly(sodium methacrylate). A stopped-flow/light scattering investigation. Macromol Chem Phys 1997;198(5):1319–29.

[19] Dragan S, Cristea M, Luca C, Simionescu BC. Polyelectrolyte complexes. I. Synthesis and characterization of some insoluble polyanion-polycation complexes. J Polym Sci: Part A: Polym Chem 1996;34(17):3485–94.

[20] Cristea M, Dragan S, Dragan D, Simionescu BC. Interpolyelectrolyte complexes formation in dependence on the nature of polyelectrolytes. Macromol Symp 1997;126:143–55.

[21] Dragan S, Ghimici L. Cationic polyelectrolytes XI. Polymers with quaternary N-atoms in the main chain obtained by condensation polymerization of epichlorohydrin with amines. Angew Makromol Chem 1991;192(3317):199–211.

[22] Ghimici L, Dragan S, Popescu F. Interaction of the low-molecular weight salts with cationic polyelectrolytes. J Polym Sci: Part B: Polym Phys 1997;35(16):2571–81.

[23] Pergushov D, Izumrudov VA, Zezin AB, Kabanov VA. Effect of low molecular weight salts on the behavior of water-soluble nonstoichiometric polyelectrolyte complexes. Visokomol Soedin: Ser A 1993;35(7):844–9.

[24] Nordmeier E. Phenomena of counterion binding, polyion complexation and polyion condensation. Macromol Symp 1999;145:21–37.