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Time-dependent conformational changes of polyelectrolyte complexes in solution

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Abstract

Changes in the conformation of the polyelectrolytes when contacted with oppositely charged polyelectrolytes or when subjected to shifts in solution conditions (pH), have been studied in this work along with reversibility of the changes using fluorescence spectroscopy. While changes due to both of the above are marked, they are measurably different from each other. Thus, the extent of coiling of the complexes formed between the anionic polyelectrolyte, maleicacid anhydride–propene and the cationic polyelectrolytes was much higher than that achieved by the change in pH alone. Also, while the changes due to pH shifts were fast and reversible, that due to complexation between oppositely charged ones involved first a rapid uncoiling followed by slow recoiling to a new structure. Interestingly, shifting the coiled conformation to an even more coiled one resulted in a new *reversible* state, but shifting to a stretched state by complexation led to a somewhat *irreversible* structure. Also maximum interaction obtained between the anionic and one cationic polyelectrolyte was markedly higher than that between the former and another cationic polymer. These observations using fluorescence spectroscopy was consistent with that obtained by the potentiometric titration. The study clearly shows the importance of the manner in which the polyelectrolytes are equilibrated to desired solution conditions. These results are interpreted here in terms of deprotonation/protonation of the polyelectroytes upon pH change and complexation with oppositely charged ones resulting in screening of charges as well as stiffening.

Keywords: Polyelectrolyte; Time-dependent; Fluorescence spectroscopy

1. Introduction

Synthetic polyelectrolytes are used in a wide range of technical applications to modify surfaces of particles and thereby to flocculate, disperse, bind or deposit them. Their properties in solutions and at solid/liquid interfaces have been studied in the past, but since a combination of reagents are often used in many applications, it is also important to understand interactions of polyelectrolytes with other charged and uncharged species [1–3]. Attempts have been made recently to determine stoichiometry, stability, exchange and phase behavior of various polyelectrolyte complexes (PEC) that can result from such interactions [4–9].

Fluorescence spectroscopy has proved useful for the investigation of conformation of polymers in solution and at the surface of particles. By using an appropriate label it is possible to monitor polymer association even in relatively short periods of time but making sure that only small amounts of label are used lest the behavior of the polyelectrolyte is altered by the label [10–15]. In this paper, conformational changes of a polyelectrolyte due to the addition of a second one are studied under static and shifting pH changing conditions. A major aim was also to identify irreversible processes involved in the formation as well as reconformation of the complexes and to monitor the effect of experimental conditions on their structure. Owing to the important role played by conformation in determining the efficiency of various interfacial processes, a knowledge of the changes in the structural features of the complexes

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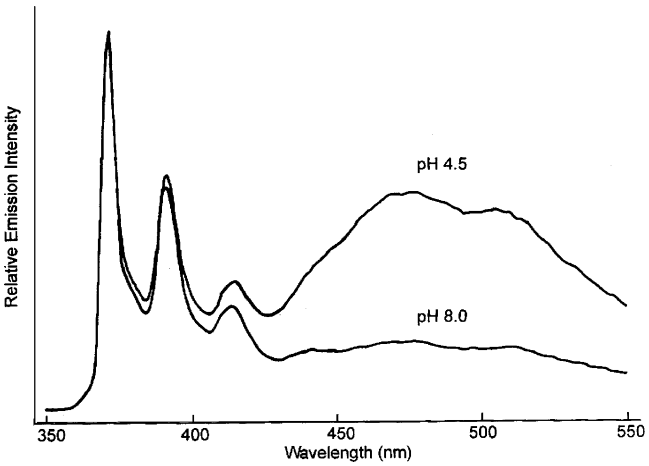

Fig. 1. Flourescence spectra of pyrene-labelled aqueous maleic acid–propene-copolymer solution at different pH-values.

can prove helpful to optimize the performance of such processes.

2. Methods, materials and procedures

2.1. Fluorescence

The fluorescence spectrum of pyrene, used as label here, is characterized by a peak assigned to the monomer fluorescence and to the excimer fluorescence (Fig. 1). The emission spectra between 350 and 550 nm were recorded using a Photon Technology International LS-100 fluorescence spectrophotometer with an excitation wavelength of 335 nm. The ratio of intensity of the excimer fluorescence to that of the monomer fluorescence ($I_{excimer}/I_{monomer}$), called as "coiling index" (CI), is a measure of the coiling of the polymer. High coiling index values represent a coiled polymer chain and low values an expanded or stretched polyelectrolyte. Typical emission spectra of pyrene-labeled maleic acid–propene-copolymer given in Fig. 1 shows the differences in the excimer peaks at different pH values.

2.1.1. Pyrene-system

Monomer fluorescence

$$P + h\nu \rightarrow P^* \rightarrow P + h\nu, \quad \lambda_1 = 373\,\text{nm},\ \lambda_2 = 383\,\text{nm}$$

Excimer fluorescence

$$P + P \rightarrow (PP)^*_{excimer} \rightarrow P + P + h\nu, \quad \lambda_{excimer} \cong 480\,\text{nm}$$

2.1.2. Potentiometric titration

A combination of Brinkmann 665 dosimat, Orion 701a digital ionalyzer and Orion 8103 Ross combination electrode was employed for determining the charge distribution on the polyion as a function of pH.

Cationic polyelectrolytes used (Fig. 2) were branched Polymin G 100 of 4000 g/mol molecular weight and poly(diallyldimethylammonium) chloride (PDADMAC) of 78,000 g/mol of molecular weight and the anionic was a maleic acid anhydride–propene-copolymer of 23,000 g/mol molecular weight. Polymin G 100 is a BASF poly(ethyleneimine) type polymer [16] This is a weak polycation with the protonation of its primary, secondary and tertiary amine groups increasing with decreasing pH. The theoretical charge density of the fully charged polyethyleneimine is 23.3 meq/g and almost four times that of PDADMAC. PDADMAC provided by the Berlin Institute of Chemical Technology had a charge density of 6.2 meq/g. Owing to the quaternary ammonium groups, the degree of dissociation of the ionic groups is independent of pH within a wide range. The anhydride anionic copolymer, obtained from Leuna AG in Germany, was dissolved in water by heating to 55 °C overnight. The degree of dissociation of the hydrolyzed, water-soluble polymer (MS-P) is pH dependent and was adjusted as required using sodium hydroxide.

The maleic acid anhydride–propene-copolymer was pyrene labeled by reaction with aminopyrene purchased from Aldrich Chemicals (Fig. 3). The pyrene label is covalently attached to the polymer via a cyclic imid-bond and the amount of label in the polymer (MS-P*) was approximately 2% [17].

Enhanced excimer formation was observed above 200 ppm and above 0.1M NaCl. The increase in $I_{excimer}$ at higher polymer concentrations is brought about by interpoly-

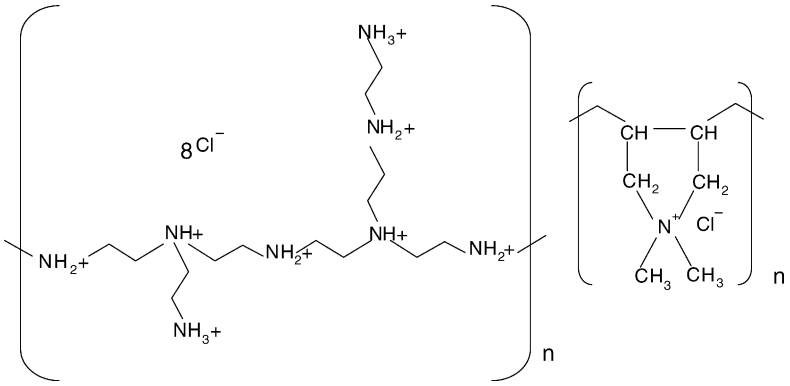

Fig. 2. Polyethyleneimine Polymin G 100 (protonated state) and poly(diallyldimethylammonium chloride), PDADMAC.

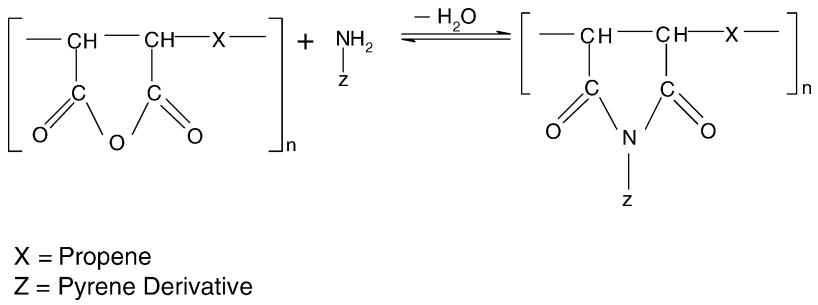

Fig. 3. Polymer analogous reaction of maleic acid anhydride–propene-copolymer with aminopyrene.

mer excimer formation while the screening of charges at high ionic strengths results in reduction of the charged nature of the polyelectrolyte. All experiments were therefore performed below 50 ppm MS-P* and below 1 mM ionic strength. The pH of the solutions was adjusted with 0.1N HCl or NaOH and the ionic strength was kept constant with NaCl solutions as desired.

2.2. Preparation of the polyelectrolyte complexes

Solutions of 10 ml MS-P*, PDADMAC and Polymin G 100 in 1 mM NaCl were equilibrated at the desired pH for 1 h and then for the complexation experiments, the polycation sample was added using a syringe pump at a constant speed of 1 ml/min to the stirred polyanion sample for a final concentration of 25 ppm of each polymer. The coiling index reached a constant value after stirring for approximately 2 h but all the samples were stirred for 20 h and then spectra measured. The pH was then shifted as required to the desired value and the change in the coiling index monitored. It may be noted that in no case was flocculation or precipitation observed.

3. Results and discussion

The degree of dissociation of maleic acid–propene-copolymer and the degree of protonation of Polymin G 100 is shown in Fig. 4 as a function of pH. Even though no distinct p*K*-value could be identified for Polymin G 100, it is highly charged at low pH and uncharged above pH 10. Two p*K*s are detected for maleic acid–propene-copolymer, the position of p*K*s being depended on the solution properties and the titration procedure [17]. The first p*K* is at approximately pH 4 while the second p*K* is between 8 and 10. While nearly uncharged at low pH values, the maleic acid–propene-copolymer becomes increasingly charged with increase in pH with two anionic charges per monomer unit around pH 11.

Coiling index of maleic acid–propene-copolymer in solution, illustrated in Fig. 5 as a function of pH, shows the polymer to be coiled due to the protonation of the carboxylic groups. Excimer formation is minimal at higher pH values as the polymer uncoils due to electrostatic repulsion. The conformational motion in solution was found to be reversible and the same value was obtained for the index at a given pH whether the experiments were started at acidic or basic pH value and then the pH shifted to the desired value.

The coiling indices of maleic acid–propene-copolymer complex with Polymin G 100 and PDADMAC are shown in Fig. 6 along with that for MS-P* alone. As already shown above, mixing oppositely charged polyions (MS-P/Polymin G 100) leads to strong interactions resulting in the formation of the polyelectrolyte complex. This interaction results in the screening of the charges on the polyanion, which in turn leads to an increase in the degree of dissociation of the maleic

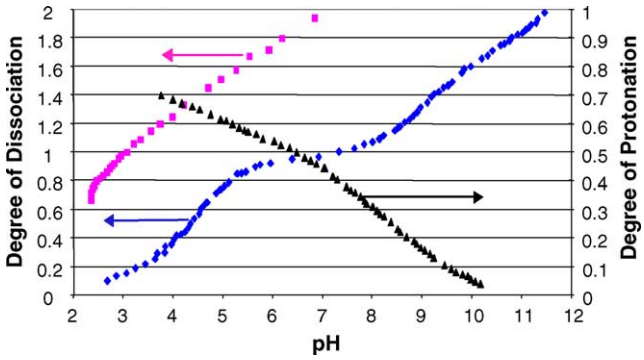

Fig. 4. Variation of the degree of dissociation of maleic acid–propene-copolymer (♦) and degree of protonation of Polymin G 100 (▲) with pH. The curve (■) represents the shift in the degree for dissociation of the maleic acid–propene-copolymer due to interaction with Polymin G 100.

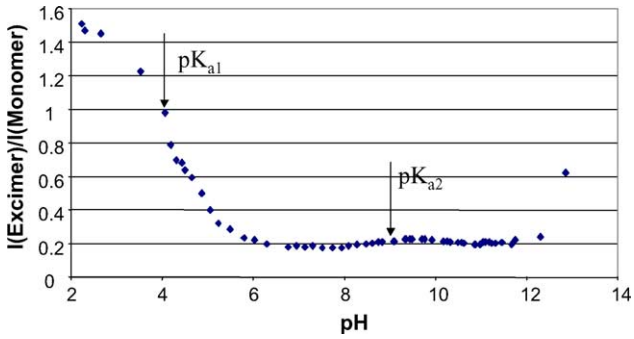

Fig. 5. Variation of coiling index of maleic acid–propene-copolymer in aqueous solution with pH. The position of the two p*K*s, measured by potentiometric titration, is indicated.

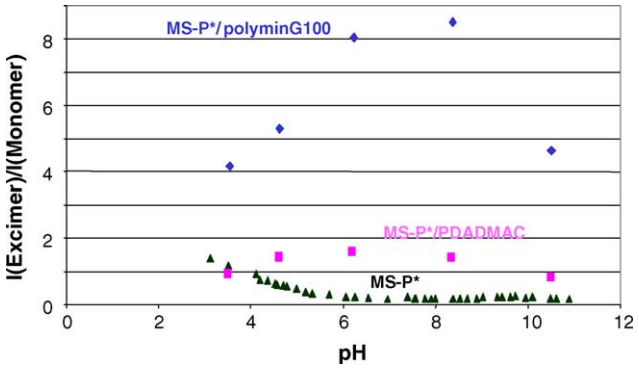

Fig. 6. Variation of coiling index of polyelectrolyte complexes of maleic acid–propene-copolymer with Polymin G 100 and PDADMAC in aqueous solution with pH. The pH-dependence of the coiling index of maleic acid–propene-copolymer is also given for comparison.

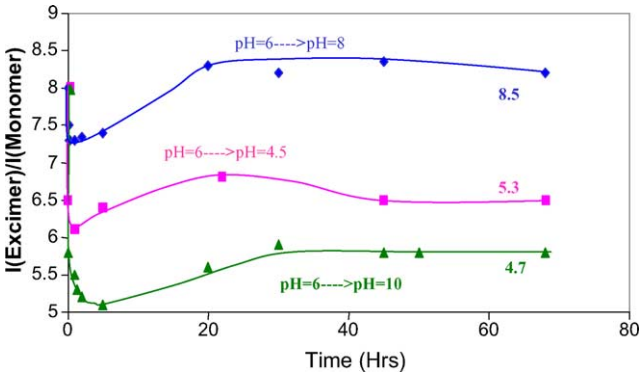

Fig. 7. Time-dependent changes of the coiling index of polyelectrolyte complexes of maleic acid–propene-copolymer and Polymin G 100 due to pH shifts: (■) pH from 6 to 4.5; (▲) pH from 6 to 10; (♦) pH from 6 to 8. The values in the boxes are those obtained under fixed pH conditions at the final pH obtained by shifting.

acid–propene-copolymer with a corresponding shift in the potentiometric curve from that of the free MS-P. This shift can also be used as a measure of the stability of the polyelectrolyte complex. The coiling index estimated from the fluorescence spectral measurements also shows a strong interaction of the oppositely charged polyelectrolytes with each other. In the case of MS-P*/Polymin G 100, the coiling index increases when pH is raised from low pH, due to the increase in charge on the MS-P* and a rather high maximum is obtained between pH 6 and 8. This is consistent with the observed increase in the degree of dissociation of the MS-P* in the PEC with increase in pH and thus the large number of interacting sites on it. The decrease in the coiling index observed around pH10 is attributed to the decrease in the amount of charge on the Polymin G 100. Comparison of the $I_{excimer}/I_{monomer}$ values suggests that the polyelectrolyte complexation leads to an increased degree of coiling of MS-P* in solution at any certain pH. The values of the coiling index obtained are much smaller for the MS-P*/PDADMAC system than those for MS-P*/Polymin G 100 but there is a similar maximum, even though slight, around neutral pH. This difference is attributed to the rather stiff nature of Polymin G 100 as well as the difference between the charge density of the two polymers.

In addition to the behavior under fixed pH conditions, the conformational changes of the polyelectrolyte complexes due to pH shifts were also investigated. In many processes, combinations of oppositely charged polyelectrolytes are used and dynamics of conformational changes due to perturbations in system properties such as pH can have important implications.

Fig. 7 provides an insight into the time dependence of conformational changes of the PEC of the maleic acid–propene-copolymer and Polymin G 100. As mentioned earlier, both polyelectrolytes are of weak character and the pH shifts modify the charge distribution on the polycation as well as that on the polyanion. In these experiments, the initial pH was 6 and after mixing for 20 h, it was shifted to pH 4.5, 8 or 10 and the changes in coiling index were monitored. The coiling index of the polyelectrolyte prepared and equilibrated at fixed pH of 8, 4.5, and 10 are displayed in the boxes on the right-hand side of Fig. 7 so that direct comparison may be made easily with those for pH shift curves. Starting at an $I_{excimer}/I_{monomer}$ value of 8 at pH 6, in all cases immediately after the pH shift, the coiling decreased sharply reaching a minimum within 3–4 h. Surprisingly, the complexes in solutions undergo further coiling for more than 24 h. The initial uncoiling upon the pH shift from 6 to 8 is attributed to the simultaneous decrease in the charge of the polycation and the increase in that of the polyanion and possible delinking of some bonds between the two polyelectrolytes.

This suggests that the whole polyelectrolyte complex structure undergoes reconformation before adopting a new stable state. While the first step of decoiling is related to the rather rapid dissociation of carboxylic groups or protonation of the amine groups, the reconformation of the complex due to the pH shift to a minimum energy structure takes days. Interestingly, the results show that the final reconfirmation obtained due to perturbations can be different from that attained under static conditions. In the case of the pH shift from 6 to 8, the coiling index changes from 8 to 8.5, consistent with the value obtained in the static experiment. Clearly, the complex is able to move from an already coiled state to an even more coiled conformation without significant hindrance.

If pH 6 is shifted to 4.5 or 10, a noticeable difference is seen between the coiling indexes under static and shifted conditions. Both $I_{excimer}/I_{polymer}$ values of the static experiments (5.3 and 4.7) are well below those obtained under the shifted conditions. Thus, a significant irreversibility of the changes involved is revealed. The nature of the structure obtained under dynamic conditions may be very different from that under static pH conditions.

4. Conclusions

The polyanion considered behaves like a weak polyelectrolyte in solution and stretching of the polyanion takes place

at high pH, due to deprotonation and interpolymer charge repulsion. At low pH, the polymer is most protonated and highly coiled. The change between the above two states in solution is relatively fast and reversible.

Polyelectrolyte complexes are formed with oppositely charged polyelectrolytes and the screening of the charged groups causes coiling of the polymer. The extent of the coiling of the complexes is even higher than those of the polyelectrolyte in solutions at low pHs. The maximum coiling index obtained for the system of cationic Polymin G 100 and the anionic MS-P* is consistent with the potentiometric results. Furthermore, a measurable difference between the coiling index values of PDADMAC and Polymin G 100 systems has been observed and this is attributed to the higher charge density of the Polymin G 100 and/or the rigid shape of the polyethyleneimine.

Equilibration of the solutions of complexes at different pH leads to coiling indices, which is very different from those obtained when the final pH is obtained by shifting from a lower or higher pH. The combination of the fast polyelectrolyte dissociation process with the reconfirmation process leads the polyelectrolyte to a new structure, which is different from that obtained under fixed pH conditions. Also some irreversibility has been observed when shifting from a coiled to a less coiled structure. This irreversibility of the conformation suggests the non-equilibrium nature of the polyelectrolyte, which has practical applications as well.

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