Effects of charge density and structure of side-chain branching on the composition of polyanion–polycation complexes

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A combination of methods (turbidimetry and conductometry) was used to study polyanion–polycation complex formation and its stoichiometry. The influence of charge density on the polyelectrolyte complex (PEC) formation and the behaviour of PEC upon addition of salt (sodium chloride) was studied; the specific structure of the individual components was also investigated. As anionic polymer components modified poly(ethylene oxide) ionomers and poly(acrylamide-co-acrylic acid) of various charge densities were used. For the cationic polymer component, cationically modified polyacrylamides, poly(dimethyldiallylammonium chloride) and highly branched poly(ethylenimine) were used. By a variation of chemical structure of the individual polymers and their charge densities, the stoichiometry of the PEC formation could be very strongly influenced, as shown by turbidimetric and conductometric endpoint measurements; a 1:1 stoichiometry is the exception. In contrast to polyacrylamides with various amounts of carboxylate groups (polyacrylate copolymers), carboxylate-containing ethylene oxide comonomers, because of their highly branched structure, have a strong tendency towards immediate gel formation.

(Keywords: polyelectrolyte complexes; phase separation of polymers; structure and properties of polyelectrolytes; polycations; polyanions)

INTRODUCTION

The interaction of ionic groups of acids and bases in copolymers and polymer mixtures have been studied in solution and in the solid state for some time now[1,2]. These interactions are dependent on the type of interacting groups, their spacing and concentration in the polymer chain or (when these groups are in the side chain) on the type and structure of the side chain in general; they also depend on the relative molecular weight between the interacting polymers and the type, length and flexibility of the side chain[3,4]. Such interactions have played an important role in synthetic and, even more importantly, in natural polymers. The products of such interactions may precipitate as polysalts or they may remain in solution as polyanion–polycation aggregates without macroscopic phase separation (soluble PEC). In previous publications[5–7,12–14], one of our laboratories (B.P.) has presented results on the stoichiometry of the precipitation of polysalts and also on the structure of the soluble PEC, the polyanion–polycation aggregates.

When the polysalts were prepared by adding excess of the cationic polymer to a solution of an anionic polymer, the ratio of the cationic to anionic groups was found to be, in many cases, very close to unity—even when the charge densities of the macromolecules were very different. The structure of the soluble PEC, on the other hand, has proved to be very sensitive to the differences in the charge density of the two polyions in solution. Recently we have studied the composition ranges where soluble PEC becomes insoluble and the polysalts precipitate[15]. These investigations were carried out by a combination of techniques: potentiometry, conductometry and turbidimetry. Anionic and cationic polymers of different chemical composition and charge densities were allowed to interact with each other. The endpoint stoichiometry depended substantially on the type of polyelectrolyte, the charge density, and reaction conditions (such as the sequence of addition of the polyelectrolyte components or the concentration of low molecular weight electrolyte, for example, sodium chloride).

The position of the branches and type of branching influence the formation and composition of the PEC, but the actual role of the branches has until now remained unanswered. Some anomalous behaviour has been observed with highly branched poly(ethyleneimine). As a consequence, an investigation was undertaken to elucidate more extensively the composite effect of charge density and branching on the turbidimetric and conductometric endpoint as the PECs are formed. Recently, polymers with well-defined side-chains have become available; these polymers have side-chains whose side-chain lengths are known exactly and the anions are separated from the main chain by an exactly known spacer group. Consequently, we have used these polymers to study their PEC formation and have investigated the reactions between the cationic polymers which had been used in the past with various polymeric anions including those novel poly(ethylene oxide) ionomers which have

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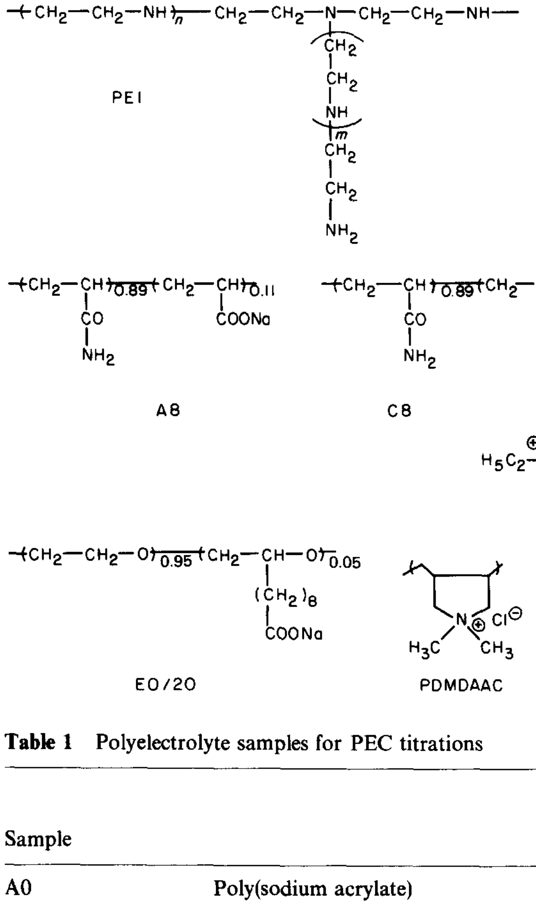
well-defined flexible side chains separating the polymer chain from the anionic functional carboxylate group. Ethylene oxide-based polymers[8–11] of varying charge densities were used for comparing the PEC formation with those of PEC prepared from cationic polymers and a series of acrylamide–acrylic acid copolymers carrying the same ionic group (a carboxylate group) as the ethylene oxide-based polyanions. In the case of the acrylamide–acrylic acid copolymers, the carboxylic acid group or, when neutralized, the carboxylate group was attached directly to the polymer backbone and was not separated from the backbone by a clearly identifiable flexible side-chain.

EXPERIMENTAL

The polymers used in these investigations are described in *Table 1*. Sample designation was based on the molar ratio *n*:*m* according to the formulae of the copolymers; copolymers of acrylic acid were designated by 'A'; cationically modified polyacrylamides by 'C' and the ethylene oxide copolymers by 'EO'. The chemical structure of acrylamide–acrylic acid copolymers or polymers containing *N*-methyl-*N*,*N*-diethylaminoethyl acrylate (MDEEA) is:



They were prepared in one of our laboratories or supplied by VEB Fettchemie, Karl-Marx-Stadt[6]. Poly(dimethyldiallylammonium chloride) (PDMDAAC) was also prepared in the authors' laboratories (B.P.) by radical polymerization of the monomer[17]. The synthesis of ethylene oxide-based ionic polymers has been described previously[8–11]; these polymers were prepared in the laboratory in New York.

Cationic polymers employed in this work included polyelectrolytes which have their cations in the side chain of the polymer and also those which have the cations in the main chain. All anionic polymers had their anionic groups in the side chain and had varying charge densities.

For PEC formation, the polyelectrolytes were used as 1 wt% aqueous solutions. The solutions were prepared by dissolving the polyelectrolytes in water with agitation at room temperature. When some turbidity was observed in ethylene oxide-based anionic polymers due to some impurities (initiator residues) left in spite of repeated precipitation from the polymerization, these slightly turbid solutions were allowed to settle and the clear supernatant solution was used (as much as 2% of insoluble material was removed in some cases, but no significant difference was found in the titration curves of the original turbid and clear solutions).

As a consequence, the original slightly turbid solutions were used and a correction was applied for turbidity. All polyelectrolyte solutions used were of nearly neutral pH (between 6 and 8, except for PEI which had a pH of about 9 to 10; the ethylene oxide-based polymers had a pH of 10 to 11).

For our titration experiments, a thermostable 100 ml glass vessel was used which had a sensor for potentiometric, conductometric or turbidimetric measurements and a mechanical stirring rod. For a better comparison of polymers of different charge densities, the concentrations of the anionic polymers were always adjusted to be 10^{-4} moles of the anionic group in 70 ml of the solution which was placed in the reaction vessel. The dosage of the oppositely charged (cationic) polyelectrolyte was added continuously, using an 'Infucont'[R] (MoD 'B' Type 1051.11) at a dosage rate between 3 and 30 ml/h. The concentration of the polyelectrolyte titrant solution was kept constant in all experiments at about 1 wt%. To examine the influence of the low molecular weight electrolyte on the progress of the titration, sodium chloride was added to the solution of the anionic polyelectrolyte in amounts of 0.1 to 1 mol l^{-1}.

Table 1 Polyelectrolyte samples for PEC titrations

Sample		Average distance between charge centres (nm)	Notes
A0	Poly(sodium acrylate)	0.25	M wt ~ 5×10^6
A4	Copolymer of sodium acrylate and acrylamide	1.26	M wt ~ 2×10^6
A8	Copolymer of sodium acrylate and acrylamide	2.27	M wt ~ 2×10^6
EO/0	Poly(sodium carboxyoctylethylene oxide)	0.35	
EO/5	Copolymer of sodium carboxyoctylethylene oxide and ethylene oxide	2.10	
EO/20	Copolymer of sodium carboxyoctylethylene oxide and ethylene oxide	7.35	
C0	Poly(*N*-methyl-*N*,*N*-diethylaminoethyl acrylate)	0.25	M wt ~ 1×10^6
C4	Copolymer of *N*-methyl-*N*,*N*-diethylaminoethyl acrylate and acrylamide	1.26	M wt ~ 3×10^6
C8	Copolymer of *N*-methyl-*N*,*N*-diethylaminoethyl acrylate and acrylamide	2.27	M wt ~ 1×10^6
PEI	Poly(ethyleneimine) 'Polymin P'	0.36	M wt ~ 7×10^5
PEI–HCl	Poly(ethyleneimine) neutralized with HCl	0.36	Highly branched
PDMDAAC	Poly(dimethyldiallyl) ammonium chloride	0.38	M wt ~ 4×10^4

The conductometric and turbidimetric measurements of the systems were registered continuously during the course of titration; the curves were used for a graphic endpoint determination. Under the conditions chosen, the titration curves at the endpoints showed good reproducibility; the deviation between two sets of experiments was generally less than 4% of the titrant consumption up to the endpoint.

RESULTS

The endpoint stoichiometry (moles of cationic groups per mole anionic groups) obtained by combining the acrylamide-based 'C'- and 'A'-samples is summarized in *Table 2*. Generally, a good agreement between the turbidimetric and the conductometric end-point determination was observed; with the 'low charge density combinations' A4/C8 and A8/C8, no sharp break could be seen in the conductometric curve; the conductometric endpoint was therefore omitted from the Table. With decreasing charge density of one or both components, we found a general tendency towards a higher titrant consumption, i.e. a higher ratio of cationic groups per anionic groups at the maximum of the turbidity curve and the break in the conductivity curves, respectively (*Figure 1*). This tendency was most pronounced in samples C0, C4 and C8, and also between A0, A4 and A8; no clear-cut order could be recognized between A4 and A8.

The behaviour of poly-DMDAAC as a high-charge-density polyelectrolyte on the borderline between the types where the ion was directly attached to the main chain or was present as a pendant group, as in the case of the neutralized PEI (PEI–HCl), fitted well into the general concept (*Table 3*). The free PEI-base, on the other hand, behaved quite differently as far as the stoichiometry of the end-point was concerned (*Table 3*). Titrant consumption far exceeded that of all the other cationic PEC components, and the break in the conductivity curve was found at a much smaller titrant consumption than the point where maximal turbidity was observed. The course of the turbidity as a function of titrant consumption (*Figure 2*) depended on the specific polyelectrolyte involved, but general trends could be observed. With most systems, a distinct turbidity maximum indicated the beginning of flocculation after a gradual or sharp increase in the turbidity. The increase in turbidity was sharpest and consequently most pronounced in systems in which both components had a high charge density, as, for example, in A0/C0 or A0/poly-DMDAAC. With decreasing charge density of the components, the turbidity maximum became flatter and less distinct, and with some systems like A0/C8, only a smooth flat maximum without an onset of macroscopic flocculation was observed.

Our experiments with EO-based anionic polymers of decreasing charge density EO/0, EO/5 and EO/20 resulted in endpoint stoichiometries which are presented in *Tables 4* and *5*. The C-series of cationic polyelectrolytes (*Table 4*) showed that endpoints could be obtained only with samples of highest charge density (C0). In the case of samples C4 and C8, gelation was observed upon addition of the titrants EO/0 and EO/5 and began immediately as soon as C8 was added, or, with sample C4, after consumption of about 50% of the 'theoretical' amount of titrant needed for a 1:1 stoichiometry. With the anionic polymer EO/20 as the reactant, which had a very low charge, no visible interaction was observed and no break in the course of conductance was obtained.

Table 2 PEC formation between A- and C-samples (molar ratio of cationic to anionic groups at the endpoint)

Anionic component	Endpoint	Molar ratio at endpoint		
		C0	C4	C8
A0	Turbidimetric	0.58	0.72	1.11
	Conductometric	0.58	0.74	1.11
A4	Turbidimetric	1.29	1.19	2.14
	Conductometric	1.29	1.15	–[a]
A8	Turbidimetric	0.95	1.60	2.11
	Conductometric	0.95	1.60	–[a]

[a] Endpoint unmeasurable

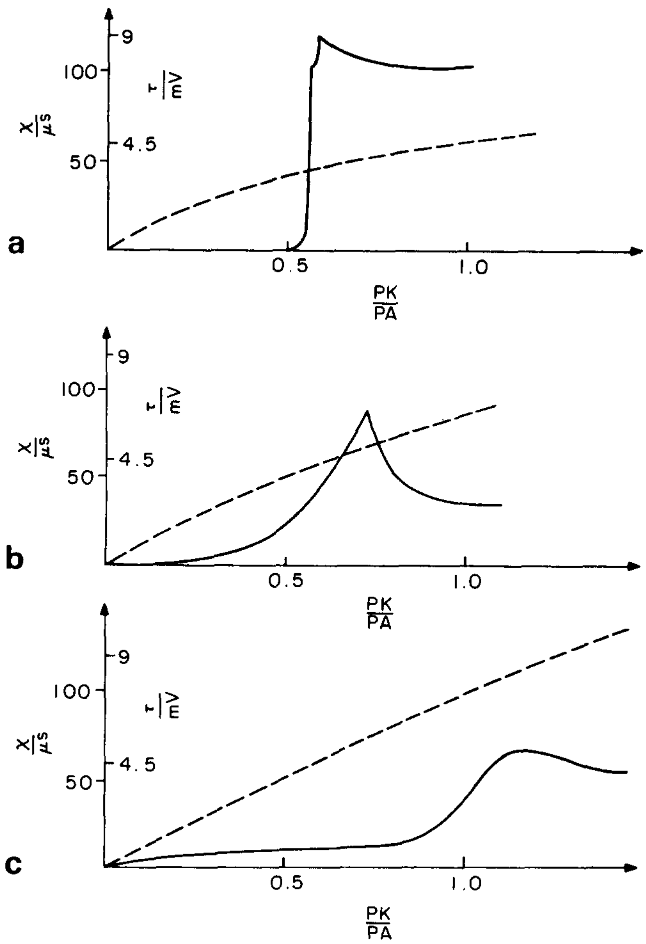


Figure 1 Influence of charge density of the cationic component on the turbidimetric (——) and conductometric (– – –) curves: (a) A0+C0; (b) A0+C4; (c) A0+C8

Table 3 PEC formation between A-samples and various cationic polyelectrolytes (molar ratio of cationic to anionic groups at the endpoint)

Anionic component	Endpoint	Molar ratio at endpoint		
		Poly DMDAAC	PEI–HCl	PEI
A0	Turbidimetric	0.43	0.57	2.21
	Conductometric	0.41	0.57	1.09
A4	Turbidimetric	1.19	0.77	11.57
	Conductometric	1.23	0.77	5.47
A8	Turbidimetric	0.78	1.08	26.62
	Conductometric	0.78	1.08	4.30

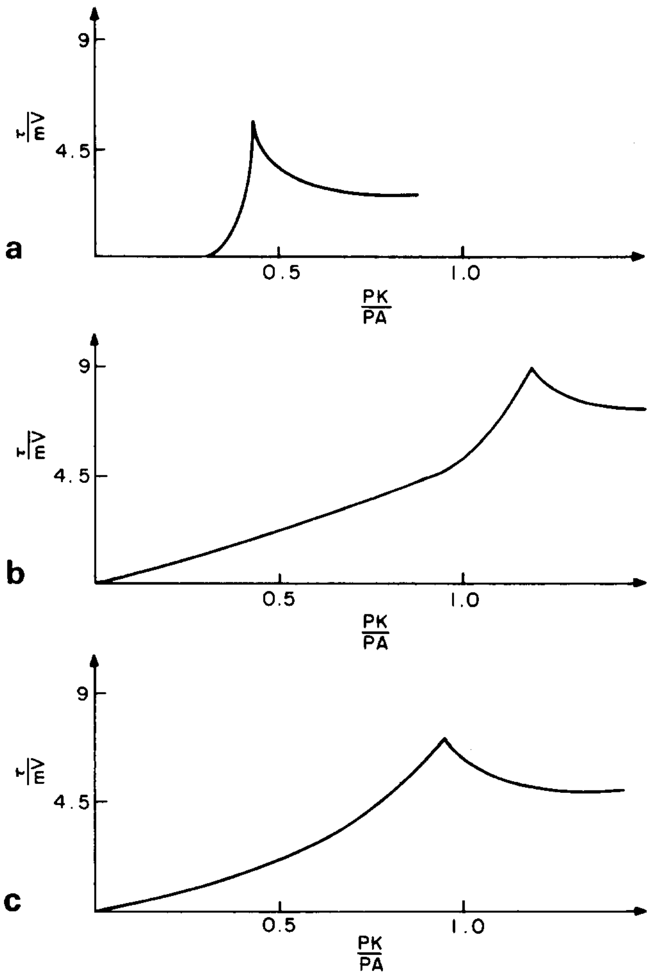


Figure 2 Influence of charge density of the anionic component on the turbidimetric curves: (a) A0+poly-DMDAAC; (b) A4+poly-DMDAAC; (c) A8+poly-DMDAAC

Table 4 PEC formation between EO- and C-samples (molar ratio of cationic to anionic groups at the endpoint)

Anionic component	Endpoint	Molar ratio at endpoint		
		C0	C4	C8
EO/0	Turbidimetric	0.81	–^{b}	–^{b}
	Conductometric	0.79	–^{a}	–^{a}
EO/5	Turbidimetric	0.94	–^{b}	–^{b}
	Conductometric	0.76	–^{a}	–^{a}
EO/20	Turbidimetric	0.42	–^{c}	–^{c}
	Conductometric	1.67	–^{a}	–^{a}

^{a} Endpoint not measurable
^{b} Gelation
^{c} No turbidity

Table 5 PEC formation between EO- and various cationic polyelectrolytes (molar ratio of cationic to anionic groups at the endpoint)

Anionic component	Endpoint	Molar ratio at endpoint		
		Poly-DMDAAC	PEI–HCl	PEI
EO/0	Turbidimetric	0.55	0.65	4.37
	Conductometric	0.55	0.65	1.83
EO/5	Turbidimetric	1.46	1.29	13.3
	Conductometric	1.22	1.17	3.1
EO/20	Turbidimetric	0.86	–	7.92
	Conductometric	1.73	–	5.66

Linear cationic polymers of high charge density, i.e. C0 and poly-DMDAAC, exhibited a similar behaviour in PEC formation with the EO-samples. Titrant consumption increased in both cases from EO/0 to EO/5 with low charge density. When EO/20 of low charge density was used as the titrant, its consumption increased at the *conductometric* endpoint but decreased clearly at the *turbidimetric* endpoint. In the EO-series, PEC formation with PEI–HCl closely resembled that of the PEC formation of poly-DMDAAC. With the free PEI-base as titrant, consumption of free PEI-base found to be several times higher. As in the case of the A-series, the turbidimetric endpoints occurred at a much higher titrant consumption than that observed by conductometric titration, but with EO/20 this difference was less pronounced than with other anionic polymers.

The turbidity behaviour as a function of titrant consumption in the case of EO/0 and EO/5 in combination with cationic polymers of high charge density was similar to that of the A-series, the maximum of turbidity becoming less pronounced with decreasing charge density (*Figure 3*). In contrast to this normal behaviour, as represented by the turbidimetric curves, turbidity increased sharply from the very beginning when EO/20 was the anionic titrant component, but remained almost constant after a small amount of titrant consumption. The break between the initial sharp rise and the constant plateau of turbidity was taken as the 'endpoint'.

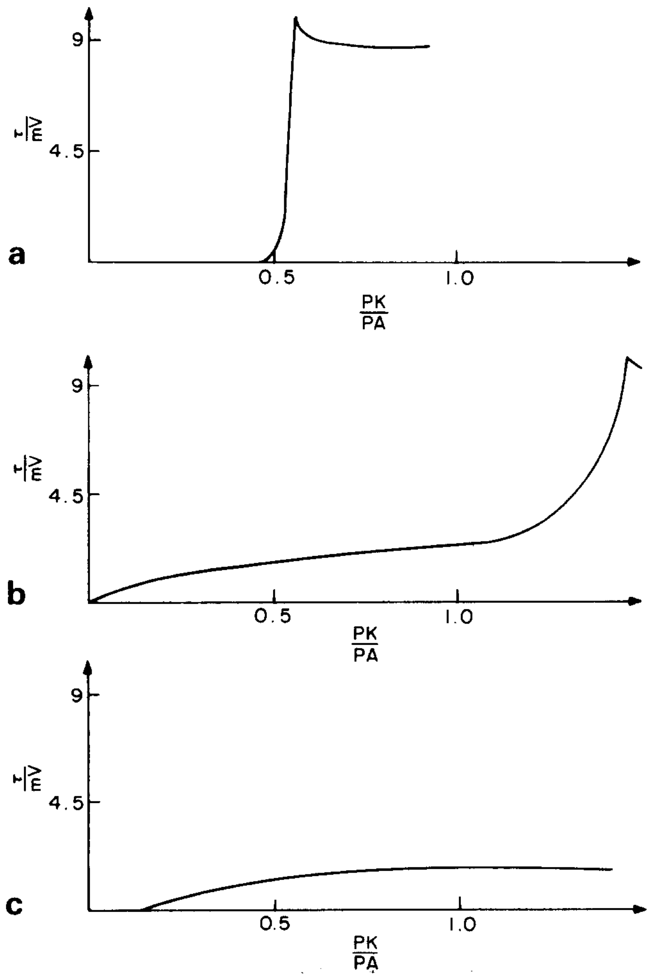


Figure 3 Influence of charge density of the anionic component on the turbidimetric curves: (a) EO/0+poly-DMDAAC; (b) EO/5+poly-DMDAAC; (c) EO/20+poly-DMDAAC

The influence of a low molecular electrolyte on the course of PEC titration was investigated by adding 0.1 (or 1.0) mol l^{-1} sodium chloride to the aqueous solution of the anionic polymer. Due to the drastic increase in ionic conductance of the system, only the turbidimetric titration technique could be used. The results are presented in *Table 6* and *Figure 4*.

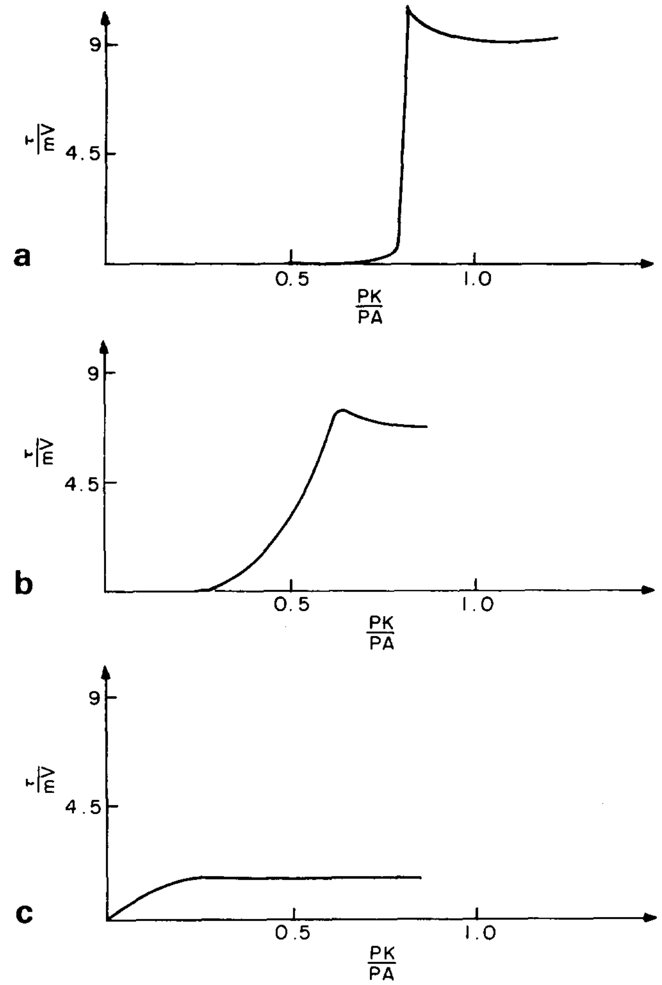


Figure 4 Influence of NaCl on the turbidimetric curves: (a) EO/0+C0 in water; (b) EO/0+C0 in 0.1 M sodium chloride; (c) EO/0+C0 in 1 M sodium chloride

Considering first the A-series of anionic polymers, the addition of a 0.1 molar sodium chloride solution led to a decrease in titrant consumption in the system consisting of A0 and one of the cationic polyelectrolytes. When A4 or A8, with their lower polymer charge density, was the anionic electrolyte, no clear-cut order could be established. A decrease as well as an increase in the titrant consumption was observed; the turbidity curves exhibited a 'normal shape' in all cases. At high sodium chloride concentration (1 molar), neither turbidity nor flocculation was observed. For this case, C-samples or poly-DMDAAC were added as the cationic component; a similar behaviour was observed as in our previous work with other systems[15]. A peculiar behaviour was found only with the system PEI–HCl; a normal titration curve was observed in this case; the titrant consumption increased in the order A0→A4→A8.

When the EO-systems were studied, the addition of 0.1 molar aqueous sodium chloride solution prevented gelation which had been observed with C4 and C8, and 'normal' turbidimetric curves were obtained in all cases (*Figure 4*). The addition of 0.1 molar aqueous sodium chloride led to a decrease in titrant consumption for combinations of EO with C0 or poly-DMDAAC, respectively, but an increase was observed with systems having a lower charge density such as EO/5 when it was titrated with the same polycations.

At higher ionic strength (1 molar sodium chloride solutions), the turbidity and flocculation did not occur in most of the EO-based systems, as was the case in the A-series. Exceptions were again the systems with PEI–HCl or C0 as the cationic component. The C0 system showed a relatively small titrant consumption and an anomalous titration curve with a sharp rise and a subsequent plateau.

DISCUSSION AND CONCLUSIONS

Based on the experimental results presented here, conclusions can be drawn with regard to three problems of PEC formation and PEC structure: (i) The general features of turbidity and conductance during PEC formation and their changes depend on the charge density. (ii) In the A- and EO-series of the anionic polymers: both contain carboxylic functions but of

Table 6 Influence of NaCl on the turbidimetric endpoint in PEC titrations

Anionic component	NaCl (mol l^{-1})	Molar ratio at endpoint				
		C0	C4	C8	Poly-DMDAAC	PEI–HCl
A/0	0.0	0.58	0.72	1.11	0.43	0.57
	0.1	0.49	0.43	0.86	0.36	0.52
	1.0	–[a]	–[a]	–[a]	–[a]	0.41
A/4	0.0	1.29	1.19	2.14	1.19	0.77
	0.1	1.17	0.64	1.63	1.23	1.20
	1.0	–[a]	–[a]	–[a]	–[a]	5.52
A/8	0.0	0.95	1.60	2.11	0.78	1.08
	0.1	1.81	1.53	1.04	1.89	2.19
	1.0	–[a]	–[a]	–[a]	–[a]	12.68
EO/0	0.0	0.81	–[b]	–[b]	0.55	0.65
	0.1	0.62	0.20	0.56	0.45	0.51
	1.0	0.23	–[a]	–[a]	–[a]	0.35
EO/5	0.0	0.94	–[b]	–[b]	1.46	1.29
	0.1	1.04	0.77	0.91	0.96	1.70
	1.0	0.42	–[a]	–[a]	–[a]	–

[a] No turbidity
[b] Gelation

different charge densities but behave differently when allowed to interact with cationic polymers. In the A-series, the anion is attached directly to a relatively stiff hydrophobic polymer backbone. In the EO-series the anion is attached by a long, flexible, hydrophobic side chain (spacer group) with a flexible hydrophilic polymer backbone chain. (iii) The development of turbidity is affected by the ionic strength of the polymer when it is gradually decreased by addition of sodium chloride.

We have investigated a number of systems and found that turbidimetric and conductometric endpoints were in good agreement, which implies that the beginning of flocculation coincided with the end of the interaction which corresponded to PEC formation. When both (or at least one) of the two polyelectrolytes had high charge densities, the turbidity exhibited a sharp and distinct maximum; a definite break between the two linear branches of the conductometric curves could be determined exactly. At lower charge density, the increase of the turbidity was much less pronounced. At very low charge density, the turbidity maximum became less distinct and flattened out; no sharp break could be detected in the conductance as a function of titrant consumption. On the basis of our conductometric results for polymers of high charge density which show two linear sections in the titration curves, we believe that the best explanation for this behaviour is a gradual liberation of low molecular weight ions during the titration.

This explanation is different from previous interpretations[16], which considered the onset of flocculation as an instantaneous diffusion of molecular ions from the sites of reaction. At low charge density, the liberation of small ions could very well be shown at the end of the reaction, which resulted in a smoother conductance curve.

The molar ratio of cationic to anionic groups at the endpoint of titration in systems near the neutral point (pH ~ 7) was much less than unity at high charge density, but considerably exceeded unity in systems of low charge density. We have found in the polycation–polyanion systems investigated by us, under the conditions under which the two types of polyelectrolytes were added, that a molar ratio of polycation charge to polyanion charge of 1, i.e. the formation of a 1:1 PEC, is the exception rather than the rule in contrast to results obtained by elemental analysis of precipitated polysalts prepared with a large excess of one of the components (for comparison see refs. 5–7). In addition to the charge density of the polymer itself, the difference in charge densities between the individual polyelectrolytes played a part in determining the PEC stoichiometry at the endpoint of the titration. While the PEC systems with PEI–HCl as the polymer cation component fitted rather well in spite of the branched structure of the polycation, systems in which the free PEI-base was the starting polymer for the preparation of the PEC system showed a peculiar behaviour. The PEC formed had a very high molar ratio of cationic to anionic groups and flocculation did not occur until the conductometric endpoint was far exceeded. The high titrant consumption can be explained by an inactivation of basic groups due to deprotonization in the basic medium; the delayed flocculation may be caused by a post-aggregation of primary PEC particles by hydrogen bond formation involving additional PEI-molecules.

While the explanations presented so far seem to agree in principle in both series of anionic polymers (the A- *and* the EO-samples), some peculiarities surrounding the EO-samples must be emphasized: The tendency toward gelation of EO/0 as well as of EO/5 during the addition of the oppositely charged C4 and C8 polyelectrolytes. With highly charged polycations, normal titration curves could be obtained. On the other hand, when the sample of EO/20 of low charge density was titrated with polycations, also of low charge density, no detectable interaction was found. It should be emphasized that the solutions of the polymeric anions had equal amounts of anionic groups, irrespective of their chemical structure (A- or EO-series) and their charge density.

In our opinion, the gelation tendency of the EO-based systems is caused mainly by the flexibility of the side chains which permits some free movement of the anionic groups attached at the end of the side chains but which still keeps them covalently bound to the polymer backbone. The formation of a continuous gel network on addition of even a small amount of polycations of low charge density is favoured, while the formation of a structure of discrete PEC particles does not occur. These results dramatically demonstrate the effect of flexible and well-defined groups separating the anion from the polymer main chain.

When highly charged polycations are bound to a 'hard' PEC then tendency to form discrete PEC structures predominates. With very low charge density of polymer EO/20, the interaction with polycations of low charge density is too weak to form a permanent gel network, and neither gelation nor flocculation occurs. With an oppositely charged polyion of high charge density, however, the interaction is strong enough for PEC aggregation to occur which falls between the normal development of turbidity with subsequent flocculation and the 'anomalous' gelation. The binding forces of the EO-base PEC gels may be of a predominantly coulombic nature. Finally, it must be stressed that the model considerations outlined here are still in the state of a 'working hypothesis' which still has to be confirmed by additional experiments.

The influence of increasing ionic strength of the systems by stepwise addition of sodium chloride to the solution of the anionic polymer can also be better understood. Two effects are counteracting each other, i.e. the salting out favours precipitation and tends to shield the charges by influencing the strong electrolyte sodium chloride near the macroion resulting in a weaker interaction, which means a higher titrant consumption, which delays the onset of flocculation. In these cases, turbidity did not occur on addition of the polycations. This interpretation is in agreement with our previous results and the conclusions drawn therefrom[15]. We conclude that in the presence of 0.1 molar sodium chloride solution, titrant consumption is lower, especially when highly charged polymers are used for the titration, while the shielding effect appears to be more evident when the turbidimetric titration curves are analysed. Instead of the sharp rise in turbidity observed in the salt-free system, a continuous increase of τ is observed, as might be seen in systems of relatively low charge density. In 1N sodium chloride solutions, the shielding effect clearly predominates, and a development of turbidity with subsequent flocculation was observed. Only when PEI–HCl was present, which was then combined with the A- and EO-samples and when C0 was combined with EO/0 or EO/5, did these systems have an additional strong non-coulombic interaction; this seems to be facilitated by hydrogen bonds which assist in the complex formation of the polyelectrolytes.

The results discussed here and the model proposed seem to agree with the conclusion that the PEC formation in the range between 'soluble PEC' and 'polysalt precipitation' is predominantly determined by the charge density of the components. The general structure of the polyions, i.e. the mobility of the charge centres with respect to the main chain, plays a major part.

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This paper is also paper number XV in Professor Otto Vogl's series on poly(alkylene oxide) ionomers.

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