Interaction of Aluminoxane Particles with Weakly Charged Cationic Polyelectrolytes

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ABSTRACT: In terms of the known concepts about noncovalent bonds in polycomplexes, the unusual case of interaction between positively charged aluminoxane particles (AP) $\sim$ 4.6 nm in size, which comprise the main portion of the dispersed phase in the sols of poly(aluminum hydroxychloride) (PAHC), and weakly charged cationic polyelectrolytes from the Praestol, Organopol, and Zetag series (WCPE) has been examined. Using viscometry, turbidimetry, and elemental analysis, it has been found that interaction between these compounds proceeds if the content of cationic groups in the polyelectrolyte is small and ions of a low-molecular-weight electrolyte occur in solution. Under the given conditions, the electrostatic repulsion of likely charged reagents does not manifest itself but other kinds of noncovalent interactions are realized that lead to formation of water-soluble polymer-colloid complexes (PCCs). Fully charged polyelectrolytes are incapable of such interactions because of a strong electrostatic repulsion of reagents. The scheme illustrating formation of PCC has advanced. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 475–482, 2011

Key words: aluminoxane particles; weak polycationites; polymer-colloid complex; noncovalent interactions

INTRODUCTION

Over the last decade, hybrid nanocomposite materials have assumed great importance in practice due to their new technological applications in micro- and photoelectronics, biomedical devices and sensors, coatings, and catalysts.[1–8] In many cases, such structures form via the self-assembly process in various systems: colloid–colloid,[9–11] polymer–polymer,[12–14] and polymer–colloid.[15–20] Note that nanocomposites may be obtained both in the solid state and in the form of aqueous dispersions and solutions which is of particular importance for the cases of their biomedical application or biocompatible complexes.[21–25] Polymer–colloid complexes (PCCs), which are products of interaction of macromolecules with colloidal objects, belong to this type of hybrid nanomaterials. There is a great number of experimental and theoretical studies[26–34] devoted to the behavior of polymer–colloid complexes in diluted aqueous solutions. It was found that the ability to form stable PCCs between macromolecules and colloidal particles, as well as between complementary macromolecules, accompanied by formation of interpolymer complexes (IPCs)[35–38] is related to manifestation of the fundamental property of macromolecules—a high cooperativity of a system of very weak (per a macromolecule chain) noncovalent interactions (hydrogen bonds, van der Waals interactions, and electrostatic bonds) between macromolecules in IPCs or between a macromolecule and a particle in PCCs.

Polycomplexes may form with participation of not a single but of several types of interactions simultaneously. However, estimation of contribution due to every type of interactions into formation of PCCs presents a problem. It is believed that electrostatic interactions, as the most long-ranging,[39] are primarily realized during formation of PCCs.

Actually, in many papers the formation of polymer–colloid and polyelectrolyte complexes, specifically in the preparation of polyelectrolyte multilayer films, is explained by the action of electrostatic controlling forces.[5,14–17,35,36,40–49] However, the entropy nature of the polycomplexes was assumed in previously published works devoted to polyelectrolyte complexes.[50,51] Recent studies of interacting nanoparticles with a number of block copolymers showed that both enthalpy and entropy factors play an important role during polycomplex formation.[52–56]

Earlier, we have obtained PCCs during mixing of aqueous colloidal solutions of aluminum polyhydroxochloride (APHC) with water-soluble polymers—polyacrylamide and polyethylenimine.[32–34] It is assumed that in the case of polyacrylamide partial hydrolysis may be responsible for occurrence of acidic groups in macromolecules which are involved in electrostatic interactions with positively charged

colloidal aluminoxane particles. As regards poly-ethylenimine, which is cation-active in the proto-nated state, the Coulomb attraction between likely charged particles and macromolecules is excluded.

In this work, we made the attempt to estimate non-electrostatic interactions during formation of PCCs. Therefore, water-soluble polymers containing a small amount of cationic groups—the so-called weakly charged cationic polyelectrolytes (WCPEs), were selected as polymers. In this case, electrostatic inter-actions between the linear polyelectrolyte and alumi-noxane particles (APs) cannot be responsible for formation of polycomplexes and the self-assembly of the latter compounds, if it occurs, is controlled by the loss of the entropy of polymeric chains wrapping colloidal aluminoxane particles.

EXPERIMENTAL

PAHC was prepared as an aqueous solution from the aluminum alloy as described in.[57] The content of aluminum was 12.6 wt %, and the atomic ratio was Cl : Al = 0.46.

According to small-angle X-ray scattering, the aqueous dispersion of PAHC is a mixture of colloi-dal particles of two types that significantly differ in size (4.6 and 60 nm). The volume content of particles 60 nm in size does not exceed 1% from the volume of all scattering particles. Particles 4.6 nm is size are dense subunits of the thread-like spatial structure with a fractal dimensionality of $d_f \approx 1.0$.[58]

The samples of acrylamide copolymers from the Praestol, Organopol, and Zetag series were used as WCPE. They differed in the chemical structure, molecular weight, and content of cationic (quaternary ammonium) groups. In contrast to the weakly charged polyelectrolytes, the strong cationic polyelec-trolyte, KF 99 (poly(N,N,N,N-trimethylmethacryloy-loxyethylammonium methyl sulfate), was employed in this study. This selection was associated with a wide application of these copolymers in practice and their high molecular weight. Since the copolymer samples used in this study were commercial and their characteristics were tentative, the quantity of functional groups in the copolymers was measured.

The quantity of cationic groups in WCPE was determined by potentiometric titration with a solution of AgNO₃ with the aid of a silver detector electrode.

The viscosity of WCPE solutions was measured in aqueous and aqueous-saline solutions by means of a Cannon-Ubbelohde-75/008 viscometer with $D_{cap} = 0.54$ mm at 30°C.

The optical density of solutions of the initial reagents and their mixtures was measured at diffe-rent concentrations of NaCl in solution on a Specol-1300 spectrophotometer at a wavelength of $\lambda = 540$ nm and L = 1 ÷ 3 cm.

Table I summarizes characteristics of WCPE. To prepare PCC, the aqueous solutions of WCPE ($c = 0.05$ g/dL) were mixed with a calculated weighted portion of PAHC (for different Al³⁺-to-WCPE unit molar ratios), and the mixture was allowed to stand for one day at room temperature.

To separate the products of interaction of WCPE and AP, the solutions of copolymers with $c = 0.2$ g/dL were prepared. A weighted portion of NaCl ($c_{NaCl} = 4$ mol/L) was added to solution of the product of interaction between PAHC and WCPE. The precipitated PCC was isolated. After drying to a constant weight at 65°C and $p = 10$ mmHg, the content of aluminum in the PCC was determined by chelatometric titration.

RESULTS AND DISCUSSION

Because of the polyelectrolyte effect, the reduced vis-cosity of diluted aqueous solutions of WCPE grows with a decrease in the concentration of polyelectro-lyte, which is typical for all polyelectrolytes.

As is known, the polyelectrolyte effect can be sup-pressed by adding low-molecular-weight salt to solution. To determine the minimal ionic strength, which suppresses the polyelectrolyte effect, the dependence of specific viscosity of aqueous WCPE solutions with a concentration of 0.05 g/dL on the concentration of NaCl has been examined (Fig. 1).

The above results show that for all WCPE the polyelectrolyte effect is completely suppressed when a concentration of NaCl of 0.1 mol/L is achieved.

The complete suppression of the polyelectrolyte effect allows one to determine the intrinsic viscosity of aqueous-saline WCPE solutions and to estimate the concentrations of crossover to study the behavior of WCPE in the region of diluted solutions (Fig. 2).
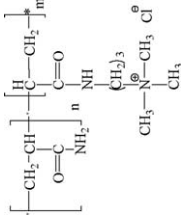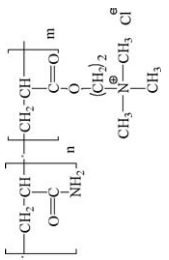
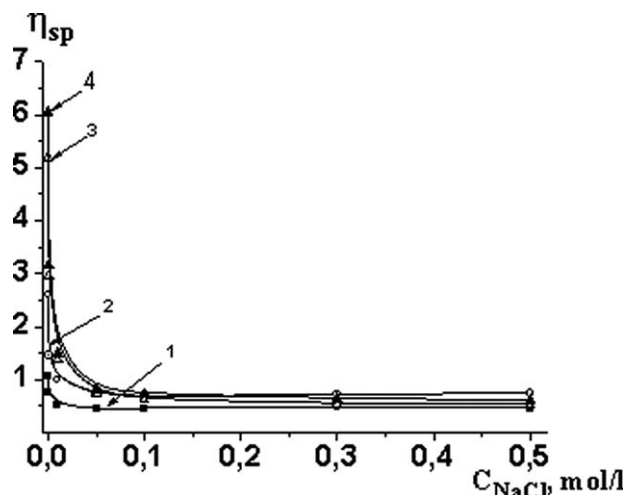The characteristics of the polyelectrolytes are sum-marized in Table I.

Figure 3 illustrates a variation in the specific vis-cosity of the Praestol 611BC aqueous solution with the addition of NaCl and PAHC.

As is seen, the impact of both salts is almost the same. In the case of NaCl, a decrease in the specific viscosity of the aqueous solution of polyelectrolyte is associated with the shielding of charged func-tional groups by counterions of low-molecular-weight salt.[36,37]

As regards the effect of PAHC, such a behavior of WCPE can be explained by two causes. One of them is a change in the ionic strength of polyelectrolyte solution with an increase in the concentration of PAHC. The ionic strength of solution depends not only on the concentration of low-molecular-weight electrolyte but also on the charge of ions contained in the polyelectrolyte.[59] As it was noted above, the dispersion of PAHC in acidic aqueous solutions is

TABLE I
Characteristics of the Copolymers

| Commercial name	Manufacturer	Structural formula	Manufacturer data		Properties of WCPE in aqueous solutions — Experimental data		
			MM	Cationic charge, molar %	$[\eta]$ in 10% NaCl	Content of cationic groups	C_{cros}, g/dL
Praestol 611 BC	JSC Moscow -Stockhausen-Perm′	Copolymer of acrylamide with N-acrylamidopropyl-N,N,N-trimethylammonium chloride (APTMAC)	~ 6 million	3–10	7.54	6.52	0.13
Praestol 851 BC			~ 9 million	3–10	9.76	6.97	0.10
Organopol 6400	Ciba Specialty Chemicals (USA)	Copolymer of acrylamide with acryloxyethyltrimethylammonium chloride	High molecular weight	Weakly cationic	7.69	2.94	0.13
Organopol 6405					11.71	1.65	0.08
Zetag 92			~ 18–20 million	Weakly cationic	–	9.23	–
KF–99	NPP "KF" Volzhsky	Poly(N,N,N-trimethylmethacryloyloxyethylammonium methyl sulfate)	1 million	Strong	–	100	–

Figure 1 The specific viscosity of polyelectrolyte solutions (η_{sp}) vs. the concentration of NaCl. Curves 1, 2, 3, and 4 refer to Organopol 6400, Organopol 6405, Praestol 611BC, and Praestol 851BC, respectively; $C_{WCPE} = 0.05$ g/dL.

composed of positively charged AP surrounded by chloride counterions. Hence, in aqueous solutions, PAHC behaves as an electrolyte. It is impossible to estimate the ionic strength of solution created by PAHC because the amount and charge of potential-determining aluminum ions on the surface of the aluminoxane aggregate, which determine the potential, are unknown. The distribution of chloride counterions between dense and diffuse parts is also unknown. However, taking into consideration that the size of the APHC aggregate is rather high (4.6 nm) and the fact that the aqueous dispersion of PAHC demonstrates an extremely high aggregative and sedimentation stability,[60] it may be suggested that the charge of the APHC colloidal particle will be noticeable.
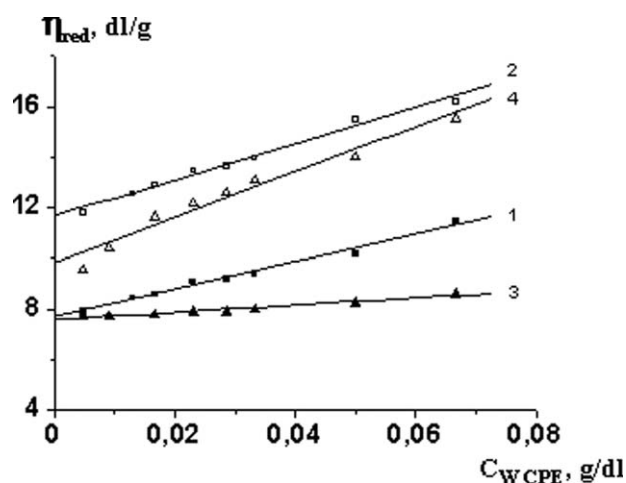
Figure 2 The reduced viscosity of polyelectrolyte solutions (η_{red}) vs. their concentration ($C_{NaCl} = 0.15$ mol/L). Curves 1, 2, 3, and 4 refer to Organopol 6400, Organopol 6405, Praestol 611BC, and Praestol 851BC, respectively.
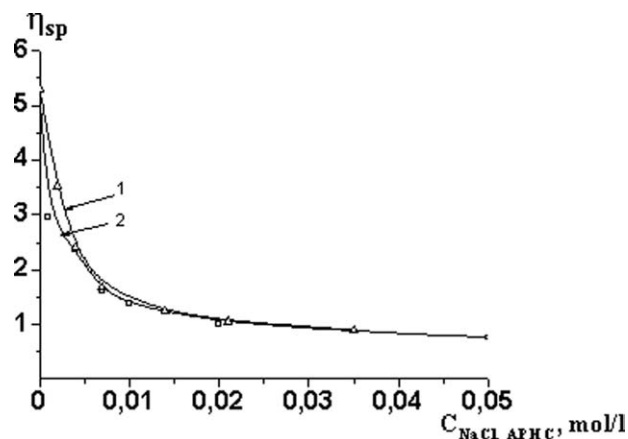
Figure 3 The specific viscosity of the Praestol 611BC solution vs. the nature and concentration of electrolytes. $C_{Praestol} = 0.05$ g/dL. Curve 1 refers to PAHC, and curve 2 refers to NaCl.

In terms of the chemical nature, "aluminoxane" particles fall into the family of high-basicity aluminum hydroxochlorides. With regard to the term aluminoxanes, it should be noted that earlier it was used to designate polymers with inorganic main chains $\left[Al\text{-}O\right]_n$ similarly to the term "siloxanes"[61] or the products of hydrolysis of organoaluminum compounds used as catalysts for olefin and diene polymerization.[62,63] In the modern literature, the term "aluminoxanes" denotes structures that contain at least one oxo-group bonded to two aluminum atoms $\left[>Al\text{-}O\text{-}Al<\right]_n$ and represent supramolecular clusters with the said structural element.[64–66] Colloidal particles formed in aqueous sols of the high-basicity PAHC possess exactly this structure.

Another cause of the above-mentioned effect is that the viscosity of polymer solutions may decrease due to compaction of macromolecules associated with the formation of PCC similar to the case of PCC of polyacrylamide and PAHC.[32]

Our previous study of the specific viscosity of aqueous WCPE solutions in relation to the concentration of NaCl (Fig. 1) showed that once a certain ionic strength of solution is increased, a further rise in the concentration of low-molecular-weight electrolyte does not lead to a decrease in the specific viscosity of the aqueous solution of polymer. Therefore, if after addition of the aqueous solution of PAHC to the aqueous-saline solution of polyelectrolyte, the specific viscosity will decline, this effect will be evidence for the formation of PCC between the linear polyelectrolyte and the PAHC particles.

Figure 4 plots the relationship between parameter F and the concentration of PAHC in aqueous-saline solution. In all experiments, the concentrations
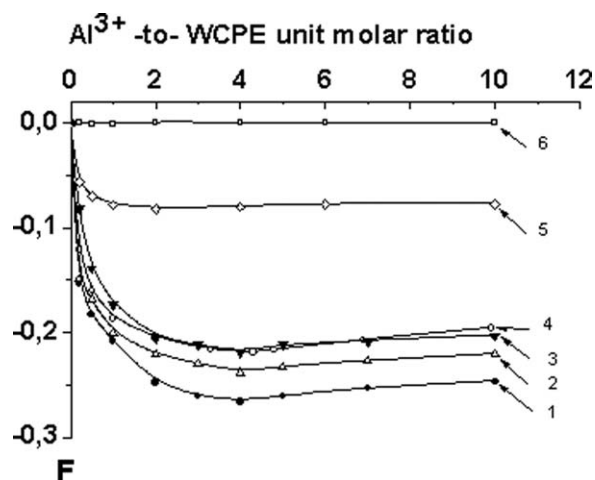
Figure 4 Relationship between parameter F and Al^{3+}-to-WCPE (KF-99) unit molar ratio. The concentrations of WCPE (KF-99) and NaCl are 0.05 g/dL and 0.1 mol/L, respectively. Curves 1, 2, 3, 4, 5, and 6 refer to Praestol 851BC, Organopol 6405, Organopol 6400, Praestol 611BC, Zetag 92, and KF-99, respectively.

of WCPE and NaCl were equal to 0.05 g/dL and 0.10 mol/L, respectively. Parameter F was calculated from equation

$$F = \eta_{exp}/\eta_{calc} - 1,$$

where η_{exp} is the measured specific viscosity of the mixture of WCPE and PAHC solutions and η_{calc} is the sum of specific viscosities of aqueous solutions of WCPE and PAHC measured separately at invariable concentrations of polymers.

The above results demonstrate that, except strong polyelectrolyte KF-99, all copolymers form complexes with PAHC particles. It is typical that the greater the
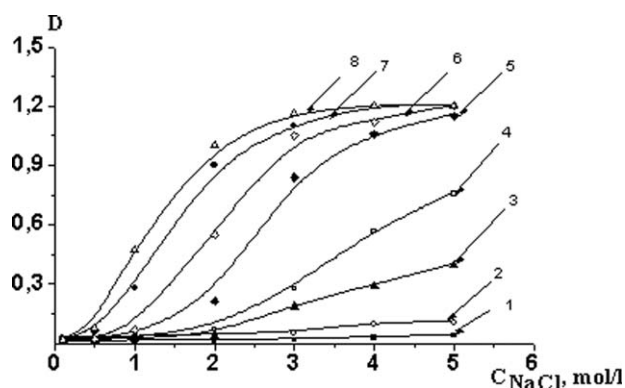
Figure 5 Optical density (D) of Organopol 6405, PAHC, and their mixtures at different Al^{3+}-to-WCPE unit ratios vs. the concentration of NaCl. In all experiments, the concentration of the polymer is 0.05 g/dL. Curves 1 and 2 refer to Organopol 6405 and PAHC, respectively; curves 3, 4, 5, 6, 7, and 8 refer to mixtures at Al^{3+}-to-Organopol 6405 unit molar ratios of 0.5 : 1, 1 : 1, 2 : 1, 4 : 1, 6 : 1, and 10 : 1, respectively.
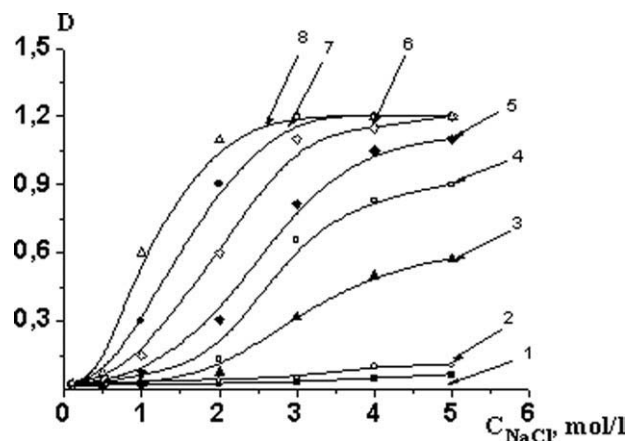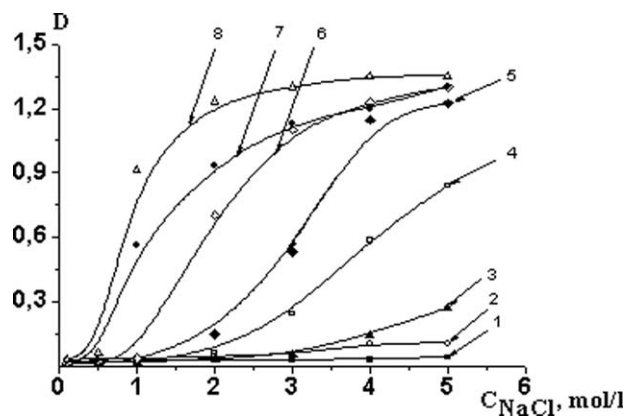

Figure 6 Optical density (D) of Praestol 611BC, APHC, and their mixtures at different Al^{3+}-to-Praestol 611BC unit ratios vs. the concentration of NaCl. In all experiments, the concentration of the polymer is 0.05 g/dL. Curves 1 and 2 refer Praestol 611BC and (2) APHC, respectively; curves 3, 4, 5, 6, 7, and 8 refer to mixtures at Al^{3+} : Organopol 6405 unit molar ratios of 0.5 : 1, 1 : 1, 2 : 1, 4 : 1, 6 : 1, and 10 : 1, respectively.

cationic charge of the polyelectrolyte, the smaller the compaction of macromolecules during formation of PCC. Parameter F declines to an Al^{3+}-to-WCPE unit molar ratio of 2 : 1 for Organopol 6405 and Organopol 6400 and to 3 : 1 for Praestol 611BC and Praestol 851BC and then remains invariable. This behavior may be explained by the fact that WCPE and PAHC form the complex of a certain composition, and, when PAHC is in deficiency, the excess linear polymer occurs in solution along with PCC.

It is noteworthy that the mixing of WCPE solutions with PAHC sols proceeds without any visible changes in light transmittance, that is, PCC, if they form, are soluble within the entire range of reagent ratios.

To unambiguously confirm the formation of PCC and characterize their composition, it was necessary to precipitate them from solution into the separate phase and to analyze precipitates by elemental analysis. For this purpose, it was necessary to select a component, the addition of which to the aqueous WCPE solution could bring about polymer isolation to the separate phase. At the same time, the addition of this component to the aqueous PAHC solution should not lead to its separation from solution. Our attempts to select such a component failed. However, as was shown in,[32,33] PCC formed through the mixing of aqueous solutions of PAHC and polyacrylamide (PAA) precipitates from solution with an increase in its ionic strength.

Figures 5, 6, and 7 display the optical densities of aqueous solutions of the initial WCPE and PAHC and their mixtures measured at different reagent ratios as a function of the concentration of NaCl in solution.

Figure 7 Optical density (*D*) of Zetag 92, PAHC, and their mixtures at different Al^{3+} : Zetag 92 unit molar ratios vs. the concentration of NaCl. In all experiments, the concentration of the polymer is 0.05 g/dL. Curves 1 and 2 refer to Zetag 92 and PAHC, respectively; curves 3, 4, 5, 6, 7, and 8 refer to mixtures at Al^{3+} : Organopol 6405 unit molar ratios of 0.5 : 1, 1 : 1, 2 : 1, 4 : 1, 6 : 1, and 10 : 1, respectively.

TABLE II
The Content of Aluminum in PCC in Relation to the Molar Ratio of Reagents in the Mixtures of PAHC and WCPE

No	Molar ratio of Al^{3+} : WCPE unit	Al^{3+} (wt %)		
		Praestol 611 BC	Organopol 6405	Zetag 92
1	0.2 : 1	–	–	1.9
2	0.5 : 1	3.5	5.9	2.5
3	1 : 1	4.6	6.3	7.5
4	2 : 1	7.6	11.1	12.3
5	4 : 1	12.8	12.1	12.7
6	6 : 1	12.7	12.2	12.7
7	10 : 1	12.7	12.2	12.7

As follows from our data, the introduction of NaCl into solution does not affect the solubility of initial WCPE and PAHC. A quite different behavior is observed in the case of their mixtures. An increase in the ionic strength of solution brings about isolation of the PCC into the separate phase. Note that an increase in the Al^{3+}-to-WCPE unit molar ratio in the initial solution causes a shift in turbidimetric curves toward smaller ionic strengths. Also note that for different WCPE up to 2 : 1 ÷ 4 : 1*M* ratios, an increase in the concentration of PAHC brings about an increase in the maximal optical density of solution. The reason behind such a behavior of the mixtures under investigation is quite understandable. As was mentioned above, the compaction of polyelectrolyte macromolecules takes place during formation of PAHC complexes with WCPE. Upon introduction of a strong electrolyte (NaCl), this process is enhanced due to an increase in the ionic strength of solution. As a result, the thermodynamic affinity of bound polymeric chains for water decreases and water becomes a poor solvent for polymer coils that separate in the form of concentrated microphase. This phenomenon was employed to isolate PCC from solutions and their subsequent analysis. Table II gives the results of chelatometric analysis for Al^{3+} in precipitated PCC.

The results of this study demonstrate the formation of polycomplexes during the cooperative interaction of polyelectrolyte macromolecules with a sequence of functional groups on the surface of aluminoxane particles. The content of aluminum in the polycomplexes formed by various copolymers increases with an increase in its amount in the mixture up to a certain molar ratio (relative to the amount of macromolecules) from 2 : 1 to 4 : 1. This is associated with different contents of cationic groups in the macromolecules and different molecular weights of the copolymers.

On the basis of the above-described data, the formation of PCCs of weakly charged cationic polyelectrolytes with aluminoxane particles may be described by the scheme depicted in Figure 8.
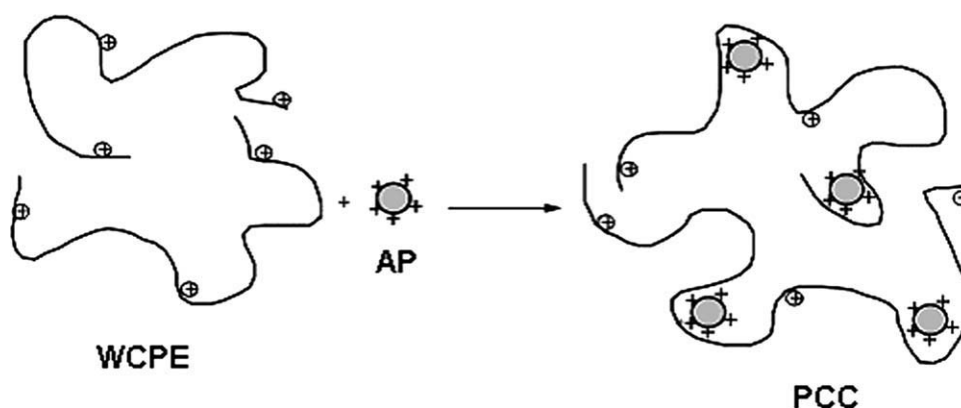
Figure 8 Schematic representation of formation of PCC of weakly charged polyelectrolytes with aluminoxane particles.

Figure 8 shows Scheme illustrating formation of PCCs of weakly charged cationic polyelectrolytes with aluminoxane particles.

At a high molecular weight ($6–20 \cdot 10^6$), there should be a wide conformational set of unfolded macromolecules for the considered flexible-chain acrylamide copolymers in diluted aqueous solutions. If cationic groups are located far apart in polymer chains, the amount of lengthy uncharged segmental portions should always be considerable. As was shown in,[67] flexible- and semiflexible-chain polyelectrolytes partially or wholly wrap a sphere during interaction with spherical particles and eventually form a solenoid depending on the degree of shielding with a low-molecular-weight polyelectrolyte. A similar situation is also possible for small (~ 4.6 nm) aluminoxane particles in APHC sols. The nature of bonds formed between wrapping segmental portions of polyelectrolyte macromolecules and surface of aluminum particles may be different, as was noted above for noncovalent interactions.

The cooperative stabilization of polycomplexes in the case under consideration is of the entropy nature. When cationic groups are widely spaced in chains of weakly charged polyelectrolytes, the forces of electrostatic repulsion do not appear with respect to positively charged aluminoxane particles and do not hinder the said stabilization. This mechanism is confirmed by the fact that a strong polyelectrolyte KF-99 does not form polymer–colloid complexes with aluminoxane particles, as evidenced by an almost zero value of parameter F (Fig. 4) at any reagent ratios and by the absence of precipitation of the product of their interaction in the reagent mixture upon its treatment with the saturated aqueous solution of NaCl.

References

1. Laine, R. M.; Sanchez, C.; Brinker, C. J.; Giannelis, E., Eds. Organic/Jnorganic Hybrid Materials—2000; Materials Research, Society: Warrendale, PA, 2000; Vol. 628.
2. Erashad-Langrondi, A.; Mai, C.; Vigier, G.; Vassoille, R. J Appl Polym Sci 1997, 65, 2387.
3. Balazs, A. C.; Emrick, T.; Russell, T. P. Science 2006, 314, 1107.
4. Schmidt, A. M. Colloid Polym Sci 2007, 285, 953.
5. Lin, H.; Zhu, G.; Xing, J.; Gao, B.; Qiu, S. Langmuir 2009, 24, 10159.
6. Gann, J. P.; Yan, M. Langmuir 2008, 24, 5319.
7. Roman-Leshkov, Y.; Moliner, M.; Davis, M. E. Chem Mater 2010, 22, 2646.
8. Zafiropoulou, J.; Paragelis, K.; Boukos, N.; Siokou, A.; Niarchos, D.; Tzizios, V. J Phys Chem C 2010, 114, 7582.
9. Huo, Z.; Tsung, C.-K.; Huang, W.; Fardy, M.; Yan, R.; Zhang, X.; Li, Y.; Yang, P. Nano Lett 2009, 3, 1260.
10. Kontos, A. J.; Likodimos, V.; Stergiopoulos, T.; Tsouhleris, D. S.; Falaras, P. Chem Mater 2009, 21, 662.
11. Portehault, D.; Giordano, C.; Sanchez, C.; Antonietti, M. Chem Mater 2010, 22, 2125.
12. Hockel, J. C.; Kisley, L. M.; Mannion, J. M.; Chumanov, G. Langmuir 2009, 25, 9671.
13. Smith, G.; Bedrov, D. Langmuir 2009, 25, 11239.
14. Sedlak, M.; Konak, C. Macromolecules 2009, 42, 7430.
15. Mori, H.; Muller, A. H.; Klee, J. E. J Am Chem Soc 2003, 125, 3712.
16. Bucur, C. B.; Sui, Z.; Schlenoff, J. J Am Chem Soc 2006, 128, 13690.
17. Alves de Rezende, C.; Lee, L-T.; Galembeck, F. Langmuir 2008, 24, 7346.
18. Chakraborty, S.; Bishnoi, S. W.; Perez-Luna, V. H. J Phys Chem C 2010, 114, 5947.
19. Colver, P. J.; Colard, C.; Bon, S. J Am Chem Soc 2008, 130, 16850.
20. Unger, E. L.; Ripaud, E.; Lerichc, P.; Cravino, A.; Roncali, J.; Johansson, E.; Hagfeldt, A.; Boshloo, G. J Phys Chem C 2010, 114, 11659.
21. Sotiropoulou, M.; Bokias, G.; Staikos, G. Macromolecules 2003, 36, 1348.
22. Sotiropolou, M.; Oberdisse, J.; Staikos, G. Macromolecules 2006, 39, 3065.
23. Roselt, E.; Fischer, S.; Foerster, S.; Weller, M. Langmuir. 2009, 25, 13906.
24. Akagi, T.; Watanabe, K.; Kim, H.; Akashi, M. Langmuir 2010, 26, 2406.
25. Hong, J.; Stavis, S. W.; DePaoli Lacerda, S. H.; Locascio, L. E.; Raghavan, S. R.; Gaitan, M. Langmuir 2010, 26, 11581.
26. Papisov, I. M.; Litmanovich, A. A. Coll Surf 1999, 151, 399.
27. Buchhammer, H.-M.; Petzold, G.; Lunkwitz, K. Langmuir, 1999, 15, 4306.
28. Papisov, I. M.; Bolyachevskaya, K. I.; Litmanovich, A. A.; Matveenko, V. N.; Volochkova, L. L. Eur Polym J 1999, 35, 2087.
29. Yu, Y. Y.; Chen, W. C. Mater Chem Phys 2003, 82, 388.
30. Radhakrichnan, B.; Ranjan, R.; Brittain, W. J. Soft Matter 2006, 2, 386.
31. Baglioni, P.; Giorgi, R. Soft Matter 2006, 2, 293.
32. Novakov, I. A.; Radchenko, F. S.; Papisov I. M. Vysokomol Soedin Ser A 2003, 45, 1340.
33. Novakov, I. A.; Radchenko, F. S.; Pastukhov, A. S.; Papisov, I. M. Vysokomol Soedin Ser A 2005, 47, 73.
34. Novakov, I. A.; Radchenko, S. S.; Radchenko, F. S. Zh Prikl Khim (St. Petersburg) 2004, 77, 1699.
35. Pergushov, D. V.; Remizova, E. V.; Feldthuzen, Y.; Zezin, A. B.; Miller, A. M.; Kabanov, V. A. J Phys Chem 2003, 107, 8043.
36. Kabanov, V.A. Usp Khim 2005, 74, 5.
37. Sui, Z.; Schlenott, J. B. Macromolecules 2006, 39, 8145.
38. Chelushkin, P. J.; Lysenko, E.A.; Bronich, T. K.; Kabanov, V.A.; Kabanov, A. V. J Phys Chem 2007, 111, 8419.
39. Holmberg, K.; Jonsson, B. L. Surfactans and Polymers in Aqueous Solution; Wiley: England, 2005.
40. Sotiropoulou, M.; Oberdisse, J.; Staikos, G. Macromolecules 2006, 39, 3065.
41. Berret, J.–F.; Vigolo, B.; Eng, R.; Herve, P. Macromolecules 2004, 37, 4922.
42. Vasilevskaya, V. V.; Leclerreq, L.; Boustta, M.; Vert, M.; Khokhlov, A. R. Macromolecules 2007, 40, 5934.
43. Buron, C. C.; Callegari, V.; Nyston, B.; Jonas, A. M. Langmuir 2007, 23, 9667.
44. Munoz–Banilla, A.; Ibarboure, E.; Papon, E.; Radriguez–Hernandez, J. Langmuir 2009, 25, 6493.
45. Liu, D.; Wang, T.; Keddie, L. Langmuir 2009, 25, 4526.
46. Yockell–Lelievre, H.; Gingras, D.; Vallee, R.; Ritcey, F. V. J Phys Chem 2009, 113, 212963.
47. Jayaraman, A.; Schweizer, K. S. Macromolecules 2009, 42, 8423.
48. Aulin, C.; Johansson, E.; Wagberg, L.; Lindstrom, T. Biomacromolecules 2010, 11, 872.
49. Ke, B. B.; Wan, L. S.; Xu, Z.–K. Langmuir 2010, 26, 8946.
50. Michaels, A. S. J. Ind Eng Chem 1965, 57, 32.
51. Kabanov, V. A.; Papisov, I. M. Vysokomol Soedin Ser A 1979, 21, 243.

52. Schultz, A. J.; Hall, C. K.; Gen, J. Macromolecules 2005, 38, 3007.

53. Warren, S. C.; Disalvo, F. J.; Wiesner, U. Nat Mater 2007, 6, 156.

54. Chui, J. J.; Kim, B. J.; Kramer, E. J.; Pinc, D. J. J Am Chem Soc 2005, 127, 5036.

55. Bucur, C.; Sui, Z.; Schlenoff, J. J Am Chem Soc 2006, 128, 13690.

56. Oren, R.; Liang, Z.; Bamard, J. S.; Warren, S. C.; Wiesner, U.; Huck, W. T. J Am Chem Soc 2009, 1317, 1670.

57. Novakov, I. A.; Bykadorov, N. U.; Radchenko, S. S.; Kargin, Y. N.; Mokhov, V. F.; Zhokhova, O. K.; Parkhomenko, A. I.; Otchenashev, P. I. RF Pat. 2083495; Byull. Izobret., 1997, 19.

58. Ozerin, A. S.; Radchenko, F. S.; Timofeeva, G. I.; Novakov, I. A. Ross Nanotekhnol 2009, 4, 145.

59. Concise Chemical Encyclopedia, Vol.2; Knunyants, I. L., Ed.; "Sovetskaya Encyclopedia". Moskwa. 1963, 307.

60. Zakharchenko, S. O.; Litmanovich, E. A.; Radchenko, F. S.; Pastukhov, A. S.; Zezin, A. B.; Novakov, I. A.; Kabanov, V.A. Kolloidn Zh 2006, 68, 467.

61. Andrianov, K. A. Polymers with Inorganic Main Chains; Akad. Nauk SSSR: Moscow, 1962; p 237.

62. Sakharovskaya, G. B.; Korneev, N. N.; Popov, A. F.; Larikov, E. S.; Zhigach, A. F. Zh Obshch Khim 1964, 34, 3455.

63. Rozuvaev, G. L.; Sangalov, Y. A.; Nenkel'baum, Y. Y.; Minsker, K. S. Izv Akad Nauk SSSR, Ser Khim 1975, 11, 2547.

64. Mason, M. R.; Smith, F. M.; Bott, S. G.; Barron, A. R. J Am Chem Soc 1993, 115, 4971.

65. Laundry, C. C.; Davis, J. A.; Apblett, A. W.; Barron, A. R. J Mater Chem 1993, 3, 597.

66. Stephen, O. Y.; Barron, A. R. U. S. Pat. 6 322 890 JPC B32 B5/ 16, 2001.

67. Netz, R. R.; Joanny, J.-F. Macromolecules 1999, 32, 9026.