Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 243–245

Mendeleev Communications

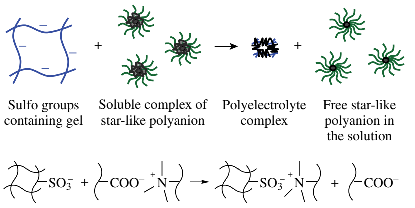
Substitution reaction in the ternary system containing anionic network, star-shaped poly(acrylic acid), and linear polycation

Tatiana V. Panova* and Alexander B. Zezin

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 0174; e-mail: tvk@genebee.msu.ru

DOI: 10.1016/j.mencom.2016.05.007

The possibility of anionic networks to displace star-shaped polyanions from a nonstoichiometric interpolyelectrolyte complex with linear polycations has been revealed.



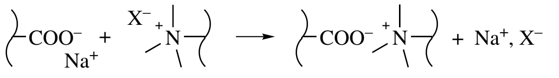
The pairs of oppositely charged linear polyelectrolytes in aqueous solution can form compounds called interpolyelectrolyte complexes (IPC). In an excess of one polyelectrolyte in such a binary system, a nonstoichiometric complex (NIPC) is formed. NIPCs can be soluble in aqueous media due to the presence of free, *i.e.* not involved into interpolyelectrolyte complexation, fragments of polyelectrolyte chains. The processes of NIPC formation and the properties of the resulting compounds have been studied in detail.[1–3] Interactions in the ternary systems consisting of different linear polyions or polyelectrolyte micelles with polyions were also investigated.[4–8] Substitution reactions are observed under certain conditions in such multicomponent systems. Due to these reactions, a linear polyion can be transferred from an oppositely charged polyelectrolyte chain to another having different chemical nature. The substitution reactions in ternary systems containing cross-linked polyelectrolytes have not yet been explored. Such investigations are important considering that polyelectrolyte gels, both on macro and micro scales, and their complexes with oppositely charged species, are useful systems for the creation of various functional and release systems.[9] Here, we present the results of a study of interactions in ternary systems containing cross-linked polyanionic networks of two different types and NIPC of star-shaped poly(acrylic acid) with linear polycations.

Lightly cross-linked polyanionic gels having different types of anionic groups, namely, poly(sodium acrylate) (PANa) and poly(sodium 2-acrylamido-2-methylpropane sulfonate) (PAMPSNa), with approximately one cross-link per fifty and hundred monomer units, respectively, were used. Polyelectrolyte gels were synthesized by the radical copolymerization of acrylic acid or 2-acrylamido-2-methylpropanesulfonic acid with *N*,*N′*-methylenebisacrylamide as a cross-linking agent in aqueous solutions, initiated by potassium persulfate and sodium metabisulfite, as described elsewhere.[10]

The resulting networks were neutralized with an access of NaOH and then washed several times with distilled water; the pH values of surrounding solutions were ~9.5 for PANa, and ~7.0 for PAMPSNa. The equilibrium swelling degrees of the gels, $H = (m_s - m_d)/m_d$ were 750 (PANa) and 460 (PAMPSNa), where m_s and m_d are the weights of swollen and dried to constant weight samples, respectively. The star-shaped poly(acrylic acid) containing 21 arms, $(PAA_{100})_{21}$, where 100 is the arm polymerization degree, was used. The star-shaped polymer was synthesized[11] and kindly provided by Profesor A. H. Muller (Bayreuth University, Germany). Star-shaped poly(acrylic acid) was used as the sodium salt prepared by the neutralization of an aqueous polyacid solution with an equivalent of 1 M NaOH. Linear poly-*N*-ethyl-4-vinylpyridinium bromide (PVPB, $P_n = 600$, Aldrich) and ionene bromide based on 2,2′-bipyridine and 1,5-dibromopentane ($P_n = 35$, synthesized as described[12]) were used as linear polycations.

Previously, it was shown that star-shaped poly(sodium acrylate) can form water-soluble NIPCs containing an excess of a polyanion with PVPB or ionene bromide in aqueous salt solutions.[13,14] NIPCs of a star-shaped polyanion and linear polycations were prepared by the step-by-step addition of an aqueous solution of linear PVPB (0.1 base-mol dm^{-3}) or an aqueous solution of ionene bromide (0.003 base-mol dm^{-3}) to the $(PAA_{100})_{21}$ solution (0.01 base-mol dm^{-3}) in the presence of NaCl with vigorous stirring. The concentration of NaCl in the final mixture was 0.05 M in the case of PVPB or 0.01 M in the case of ionene bromide; the concentration of $(PAA_{100})_{21}$ in the resulting NIPC solution was 0.005 base-mol dm^{-3}.

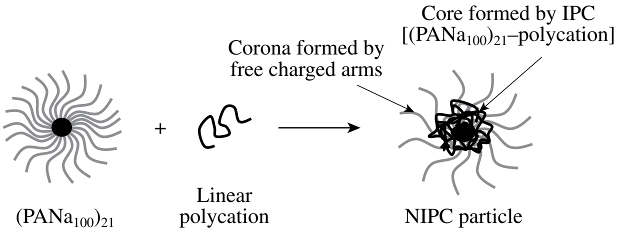
The ratio of oppositely charged groups in the NIPCs formed is $\varphi = n_{N^+}/n_{COO^-}$, where n_{N^+} is the mole amount of polycation amino groups, and n_{COO^-} is the mole amount of carboxylate groups of the polyanionic star in the resulting NIPC; $\varphi = 0.3$ for NIPCs containing both PVPB and ionene bromide. The driving force of the NIPC formation is the free energy of an addition reaction between carboxylic groups of the star-shaped polyanion and amino groups of the linear polycation (Scheme 1).



$$\mathrm{-COO^-\,Na^+} + \mathrm{X^-\,{}^+N} \longrightarrow \mathrm{-COO^-\,{}^+N} + \mathrm{Na^+, X^-}$$

Scheme 1

It was shown earlier that linear polycations in NIPC particles are located in the central region of the star-shaped polyanion.[15,16] Thus, a core-corona structure is formed in the NIPC particle in



Scheme 2

such a way that the relatively hydrophobic stoichiometric complex (star-shaped polyanion–linear polycation) is surrounded with negatively charged star arms not involved into interactions with the polycationic groups, which provide the solubility of NIPC in aqueous media (Scheme 2). According to theoretical predictions, some of the star arms are fully collapsed and incorporated into the NIPC core, while others are free forming a charged hydrophilic corona.[17]

Here, we studied the interactions of the NIPC [(PAA$_{100}$)$_{21}$–polycation] with two polyanionic gels having carboxylic groups (PANa) or sulfo groups (PAMPSNa). A polyanionic gel sample of about 1–1.5 g was immersed in 8–10 ml of the NIPC solution; then, the appearance and the mass of the gel sample and the concentration of linear polycations in the surrounding solution were determined. In order to avoid the evaporation of solution and CO$_2$ absorption from the environment, the experiments were carried out in well-isolated vials.

The concentration of the linear PVPB and ionene bromide in aqueous solutions was measured spectrophotometrically based on absorption band intensities at $\lambda = 265$ and 260 nm, respectively.

Let us first consider the interactions of NIPC with PAMPSNa gel. After several days, the initially transparent gel sample became covered with an opalescent film, and the size and mass of the gel sample significantly decreased. At the same time, the concentration of linear polycations in the solution also decreased. Figure 1 shows the kinetic curves of sorption of linear ionene bromide (curve *1*) and PVPB (curve *3*) from aqueous solutions of their NIPCs with (PAA$_{100}$)$_{21}$ by PAMPSNa network. Here, the degree of sorption, *F*, represents the molar ratio of the amount of cationic groups in the linear polycation sorbed to the amount of negatively charged groups of the network. One can see that linear polycations are gradually sorbed by the PAMPSNa network from NIPC aqueous solutions. The concentration of a star-shaped polyanion in the aqueous solution surrounded the gel sample can be determined by turbidimetric titration with a corresponding linear polycation.[14] The turbidimetric titration data showed that all star-shaped polyanions remained in the surrounding media.

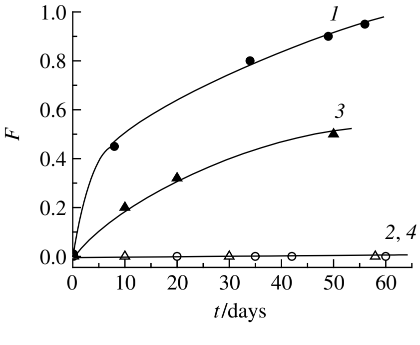
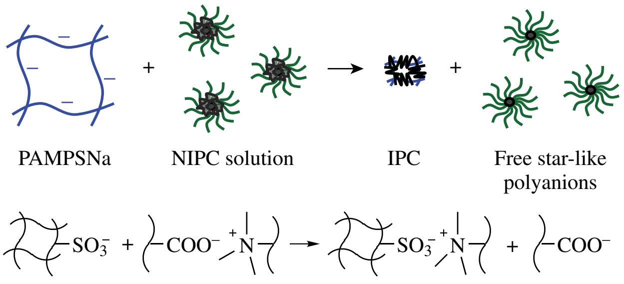


Figure 1 Kinetic curves of sorption of (*1*) linear ionene bromide and (*3*) PVPB from aqueous solution of [(PAA$_{100}$)$_{21}$–polycation] NIPEC by PAMPSNa gel, and (*2*) linear ionene bromide and (*4*) PVPB by PANa gel; [(PAA$_{100}$)$_{21}$] = 0.005 mol dm^{-3}, $\varphi = 0.3$. Here, *F* corresponds to the molar ratio of the amount of cationic groups in the linear polycation sorbed to the amount of negatively charged network groups.

Taking into account all of the above results, we can conclude that, in the test system, the linear polycations from NIPC with star-shaped polyanions are sorbed by the negatively charged network with the formation of the new IPC between the gel and liner polyamine, while the free star-shaped polyanion remains in the surrounding solution. Note that the sorption process is very slow, and in the case of NIPC [(PAA$_{100}$)$_{21}$–ionene bromide] the sorption completes in approximately 60 days. During this time, the PAMPSNa gel sample sorbs an amount of linear polycations equivalent to the amount of negatively charged groups of a network (*F* = 1), and the swelling degree of the gel sample drastically drops (from *H* ~ 460 for PAMPSNa to *H* ~ 1 for IPC). In the case of NIPC [(PAA$_{100}$)$_{21}$–PVPB], the sorption process is even slower, and the full transformation of PAMPSNa into IPC (*F* = 1) could be achieved in approximately 100 days.

Thus, the formation of new IPC in the whole gel volume and the displacement of star-shaped poly(acrylic acid)–linear polycation contacts with polyanionic network–linear polycation contacts are observed. The substitution reaction in the test system is shown in Scheme 3.



Scheme 3

Quite the opposite, in the case of PANa immersed into the aqueous solution of NIPC [(PAA$_{100}$)$_{21}$–polycation], the concentration of a linear polycation in the surrounding solution remains almost constant, as is evident from Figure 1 (curves *2* and *4* for ionene bromide and PVPB, respectively), and the appearance of the gel sample does not change for 60 days and more. This indicates that the linear polycation is not sorbed from NIPC particles by the PANa network.

Note that the substitution reaction with PAMPSNa gel does not proceed in the absence of a low-molecular-weight salt (NaCl) in the surrounding solution. Thus, the necessary condition for the substitution reaction occurrence is the presence of low molecular ions in the NIPC solution. It was shown earlier that the presence of a low-molecular-weight electrolyte in a reaction system results in a significant rise of the rate of interpolyelectrolyte reactions since it facilitates intramolecular rearrangements.[1,6]

The substitution reaction observed in the test system is in a good agreement with published data. Previously, it was shown that linear polysulfonates are capable to substitute linear polyacrylate anions in their NIPCs with linear polyamines, which could be explained by higher affinity of poly(sulfonic acids) to PVPB compared to polycarbonic ones.[4–6]

Thus, we found that the sulfo-containing network can effectively displace carboxyl polyanions from their NIPCs with linear polycation. Here, the chemical nature of the network charged groups determines the substitution reaction equilibrium and the possibility of linear polycation transfer from the NIPC solution into the gel volume. At the same time, the change of the gel swelling ability represents clear evidence of the occurrence of substitution reaction. The data can be used for the understanding of physico-chemical mechanisms of interactions in multicomponent polyelectrolyte mixtures and for the design of functional polyelectrolyte systems based on cross-linked charged gels.

References

1 V. A. Kabanov, *Russ. Chem. Rev.*, 2005, **74**, 3 (*Usp. Khim.*, 2005, **74**, 5).

2 V. Kabanov and A. Zezin, *Pure Appl. Chem*., 1984, **56**, 343.

3 O. Yu. Milyaeva, B. A. Noskov, A. V. Akentiev and S.-Y. Lin, *Mendeleev Commun*., 2014, **24**, 264.

4 V. A. Izumrudov, T. K. Bronich, M. B. Novikova, A. B. Zezin and V. A. Kabanov, *Polymer Sci. (Engl. Transl.)*, 1982, **24**, 367 (*Vysokomol. Soedin.*, 1982, **24**, 339).

5 V. A. Izumrudov, A. B. Zezin and V. A. Kabanov, *Russ. Chem. Rev.*, 1991, **60**, 792 (*Usp. Khim.*, 1991, **60**, 1570).

6 V. A. Izumrudov, T. K. Bronich, A. B. Zezin and V. A. Kabanov, *J. Polym. Sci. B*, 1985, **23**, 439.

7 V. A. Kabanov, A. B. Zezin, V. A. Izumrudov, T. K. Bronich and K. N. Bakeev, *Macromol. Chem. Phys*., 1985, **13**, Issue Suppl. 13, 137.

8 E. A. Lysenko, A. N. Trusov, P. S. Chelushkin, T. K. Bronich, A. V. Kabanov and A. B. Zezin, *Polym. Sci., Ser. A (Engl. Transl.)*, 2009, **51**, 606 (*Vysokomol. Soedin., Ser. A*, 2009, **51**, 929).

9 *Biomedical Applications of Hydrogels*, eds. R. M. Ottenbrite, K. Park and T. Okano, Springer, New York, 2010.

10 V. A. Kabanov, A. B. Zezin, V. B. Rogacheva, T. V. Panova, E. V. Bykova, J. G. Joosten and J. Brackman, *Faraday Discuss.*, 2005, **128**, 341.

11 F. A. Plamper, H. Becker, M. Lanzendörfer, M. Patel, A. Wittemann, M. Ballauff and A. H. E. Müller, *Macromol. Chem. Phys*., 2005, **206**, 1813.

12 Zh. G. Gulyayeva, A. B. Zezin, E. F. Razvodovskii and T. Z. Berestetskaya, *Polym. Sci. USSR (Engl. Transl.)*, 1974, **16**, 2145 (*Vysokomol. Soedin.*, 1974, **16**, 1852).

13 D. V. Pergushov, I. A. Babin, F. A. Plamper, A. B. Zezin and A. H. E. Müller, *Langmuir*, 2008, **24**, 6414.

14 T. V. Panova, M. F. Zansokhova, V. B. Rogacheva and A. B. Zezin, *Dokl. Phys. Chem. (Engl. Transl.)*, 2015, **461**, 84 (*Dokl. Akad. Nauk*, 2015, **461**, 537).

15 D. V. Pergushov, I. A. Babin, A. B. Zezin and A. H. Müller, *Polym. Int.*, 2013, **62**, 13.

16 D. V. Pergushov, O. V. Borisov, A. B. Zezin and A. H. Müller, *Adv. Polym. Sci*., 2011, **241**, 131.

17 S. V. Larin, A. A. Darinskii, E. B. Zhulina and O. V. Borisov, *Langmuir*, 2009, **25**, 1915.

Received: 2nd November 2015; Com. 15/4765