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Synthesis of Polyelectrolyte Gels with Embedded Voids Having Charged Walls

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Introduction. The idea of matrix synthesis of polymers originally came from molecular biology. The discovery of a matrix mechanism of the synthesis of DNA and RNA on DNA templates initiated the attempts to develop simple macromolecular systems modeling these complicated biological processes. Shwarz was the first who proposed to use simple synthetic macromolecules as templates for synthesis of complementary polymer chains.[1] Later Kargin, Kabanov, and Kargina have experimentally demonstrated the matrix mechanism of polymerization of protonated 4-vinylpyridine on anionic matrices of polyacids.[2,3] The cooperative formation of hydrogen bonds between growing macroradicals of poly(acrylic acid) (or poly(methacrylic acid)) and poly(ethylene glycol) determines the matrix mechanism of the formation of polyacids.[4,5] The main features of matrix polymerization and arising problems are discussed in the reviews.[5−10] Matrix polymerization can be considered as a particular case of a more general case of polymerization in organized media.[10] For instance, radical copolymerization of hydrophilic and hydrophobic monomers in nanostructured media, e.g., containing micelles or microemulsions, leads to copolymers with well-defined quasi-block structure.[11]

In the present work we will apply the ideas of matrix synthesis of polymers and of the copolymerization in organized media for synthesis of microporous polyelectrolyte gels with the charged units localized near the surfaces of the micropores. The synthesis of the polymers is based on the effect of concentrating of the counterions near the surface of micelles or the drops of emulsions, stabilized with ionic surfactants. As monomers for the gel synthesis we have chosen acrylamide and cationic monomer (3-acrylamidopropyl)trimethylammonium chloride.

Experimental Section. (3-Acrylamidopropyl)trimethylammonium chloride (APTAC), acrylamide (AAm), *N*,*N*′-methylenebisacrylamide (BAA), ammonium persulfate (PS), sodium dodecyl sulfate (SDS), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich Fine Chemicals. Sodium dodecyl benzoate (SDBS) was obtained from Fluka Chemical Co. Benzene and cyclohexyl bromide were of fine chemical grade (>99.5 wt %). Water was of Millipore quality. Three solutions for polymerization were prepared. Solution 1 contained AAm-6.09; BAA-0.17; APTAC (75 wt % solution in water)-2.74 wt %; the rest water. Solution 2 was prepared by dissolving 0.195 g of SDS in 10 mL of solution 1. Solution 3 was prepared by mixing of the “oil” and solution 2 in the ratio 1:3 by volume. The “oil” was a mixture of benzene and cyclohexyl bromide.

The emulsion containing monomers, “oil”, and surfactant was prepared by intensive mixing of solution 3 on a magnetic stirrer in a closed flask for 1 h. Then the emulsion was sonicated using a “high-intensity Ultrasonic processor 50 W model”.

Copolymerization was performed as described elsewhere.[12] During polymerization solution 3 remained white turbid, and transparent solution 2 became strongly opaque, while solution 1 remained transparent. Washing of gel 1 was performed in water; gels 2 and 3 were washed in a water−ethanol mixture (1:1 by volume) containing sodium chloride with concentration ca. 2 M. Immediately after polymerization before washing several different pieces of gel 3 were studied by optical microscopy using an Axiolab Pol microscope (Zeiss). The size of the droplets in electronic images was measured using Adobe Photoshop.

Polyelectrolyte gel−surfactant complexes were prepared as previously described.[12] The composition of the complexes of the gels with surfactants was characterized by the ratio ($[\mathrm{SDBS}]_g/[\mathrm{APTAC}]$) between the total number of surfactant ions in the gel phase, $[\mathrm{SDBS}]_g$, and the number of APTAC cations, [APTAC], contained in the gel sample. The amount of surfactant absorbed by the gels was determined by spectrophotometry after extraction of the surfactant from the gel by a 2 M solution of sodium chloride in a water−ethanol mixture.

Results and Discussion. A schematic representation of the copolymerization of cationic and neutral monomers in the absence of the surfactant and oil is shown in Figure 1a,b. Monomers are randomly distributed in the solution (a). Because of close reactivity of the monomers in the radical copolymerization,[11] the sequence of the monomer units along the chains of the network is also random (b). Both the initial monomer solution and the final gel are transparent.

When the copolymerization is performed in the presence of SDS, the surfactant forms micelles. The high charge density on the surface of the anionic micelles results in concentration and condensation of the cations near and on the surface of micelles (Figure 1c). Thus, the local concentration of the cations of APTAC is strongly enhanced near the surface of the SDS micelles, and one can expect inhomogeneous structure of the formed copolymer chains (Figure 1d). Moreover, the formation of the chain fragments enriched with cationic monomer units should result in the formation of strong polyelectrolyte gel−surfactant complexes (PESC) between the surfactant aggregates and cationic chains. The appearance of turbidity of the reaction media during copolymerization and gel formation shows that PESC segregates from the low charged regions of the gel and that the size of the segregated regions are at least of the order of hundreds of nanometers. This result gives rise for the assumption that the formation of PESC occurs with some positive feedback effects. In other words, the first small segregated particles of PESC are the centers of concentrating of the new portions of the surfactant and APTAC. Thus, it can be expected that in this case the polyelectrolyte network contains large regions enriched with the cationic monomer units.

Figure 1e shows a schematic representation of the surface of the oil droplet covered with surfactant anions. As in the case of micelles, the cations of APTAC are

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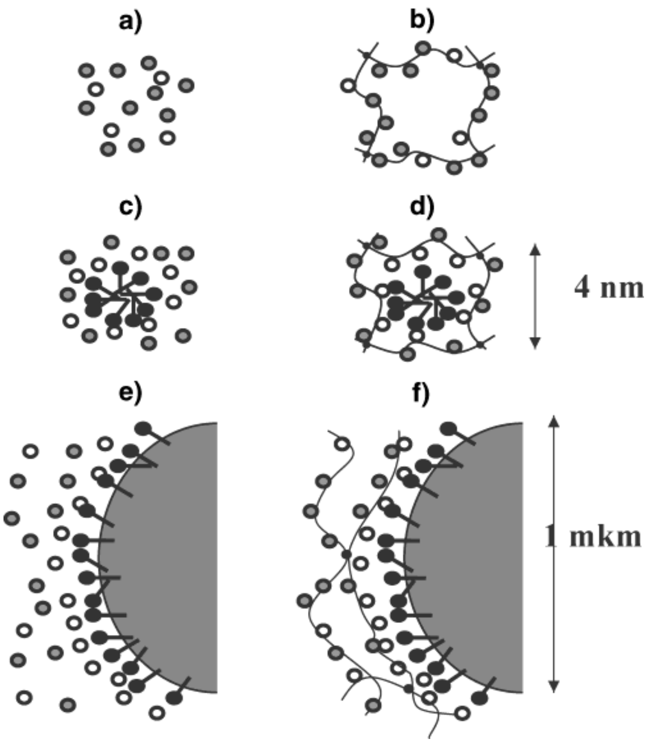
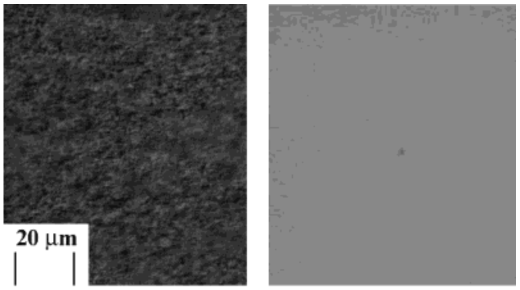


Figure 1. Schematic representation of the copolymerization of the cationic (gray) and neutral (white) monomers in aqueous solution. Monomers are randomly distributed in the solution (a). The sequence of the monomer units along the chains of the network is also random (b). (c) Concentration and condensation of the cations near and on the surface of micelle should take place. (d) Inhomogeneous structure of the formed copolymer chains. (e) Schematic representation of the surface of the oil droplet covered with surfactant anions. After polymerization the layer of polymer chains with a high local concentration of cationic monomer units surrounding the droplet should be formed (f).



a) b)

Figure 2. Micrographs obtained for gels 3 (a) and 1 (b) after polymerization.

concentrating near the negatively charged surface. After polymerization the layer of polymer chains with a high local concentration of cationic monomer units surrounds the droplet (Figure 1f). After the removal of the oil from the gel, the latter represents a continuous phase incorporating voids with the “walls” enriched with cationic monomer units.

Figure 2 shows one of the micrographs obtained for gel 3 after polymerization. One can see a lot of small spherical particles that fill the entire visible field. These particles are absent in the micrographs obtained for gels 1 and 2, and their presence can be attributed to the oil particles of emulsion. Figure 3 shows the histogram of the size distribution of the oil droplets in the gel. The mean value of the droplets diameter d is 1.12 μm.

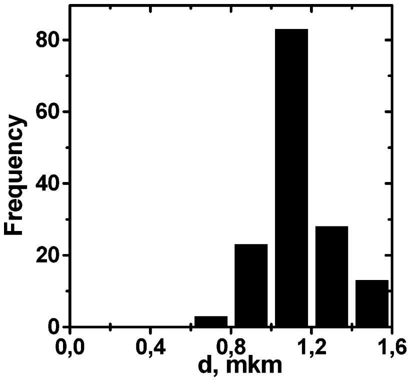


Figure 3. Histogram of size distribution of the oil droplets in the gel.

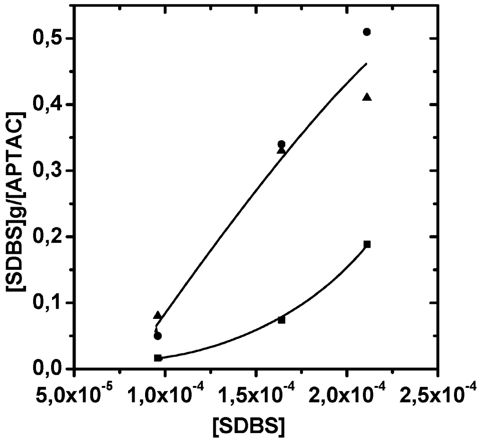


Figure 4. Dependences of the ratio $[SDBS]_g/[APTAC]$ on the concentration of SDBS in the solution [SDBS] containing 0.3 M sodium chloride for gels 1 (squares), 2 (triangles), and 3 (circles).

To find the difference between cationic gels 2 and 3 having the areas with high local charge density and gel 1 having the same network composition but randomly distributed charges, we compared the ability of these gels to absorb anionic surfactants. It is known that the increase of the ionic strength of the solution leads to dissociation of polyelectrolyte gel−surfactant complexes. This effect depends strongly on the charge density of the networks. The lower is the charge density the easier is to induce the dissociation of complexes by the addition of salts.[13,14] For example, in the case of swollen cationic network 1 having 10 mol % of charged groups at high enough concentration of inorganic salt the absorption of anionic surfactants is suppressed. Figure 4 demonstrates that at the same conditions gels 2 and 3 (with the same average charge density) having the areas enriched with cationic monomer units form stable complexes with the surfactant.

Indeed, Figure 4 shows the dependences of the composition of the complexes (the ratio $[SDBS]_g/[APTAC]$) between the number of the surfactant ions, $[SDBS]_g$, and the number of APTAC cations, [APTAC], containing in the gel sample) for the gels on the concentration of anionic surfactant SDBS in the solution. The dependence is obtained for the solutions containing 0.3 M sodium chloride. Gels 2 and 3 synthesized in the presence of anionic surfactant or surfactant and oil emulsion absorb much more SDBS than gel 1 with randomly distributed charges. This difference can be attributed to the existence of the regions enriched with cationic groups in these gels and the formation of a much stronger complex with anionic surfactant, SDBS, due to this fact.

Conclusion. This paper demonstrates the possibility to use the principles of matrix polymerization and polymerization in organized media for design of polymer gels containing embedded voids having the walls enriched with ionic monomer units. The principle of concentrating of the charged monomers near oppositely charged surfaces of micelles or "oil" drops of emulsions stabilized with ionic surfactants allows to obtain polyelectrolyte gels with much better ability to absorb oppositely charged surfactants in comparison with the gels having random distribution of the charged monomer units.

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References and Notes

(1) Shwarz, M. *J. Polym. Sci.* **1954**, *13*, 887.

(2) Kargin, V. A.; Kabanov, V. A.; Kargina, O. V. *Dokl. Akad. Nauk USSR* **1965**, *161*, 6, 1131.

(3) Kabanov, V. A. *Pure Appl. Chem.* **1971**, *4*, 425.

(4) Osada, Y.; Antipina, A. D.; Papisov, I. M.; Kabanov, V. A. *Dokl. Akad. Nauk USSR* **1970**, *191*, 2, 399.

(5) Papisov, I. M.; Litmanovich, A. A. *Adv. Polym. Sci.* **1989**, *90*, 140.

(6) Kabanov, V. A.; Papisov, I. M. *Vysokomol. Soedin.* **1979**, *A21*, 243.

(7) Challa, G.; Tan, Y. Y. *Pure Appl. Chem.* **1981**, *53*, 627.

(8) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 4.

(9) Bamford, C. H. *Chem. Aust.* **1982**, *49*, 341.

(10) Kabanov, V. A. *Polymerization in Organized Media*; Gordon & Breach Sci. Publ.: Langhorne, PA, 1992; Chapter 7, p 369.

(11) Candau, F.; Braun, O.; Essler, F.; Stähler, K.; Selb, J. *Macromol. Symp.* **2002**, *179*, 13.

(12) Mironov, A. V.; Starodoubtsev, S. G.; Khokhlov, A. R.; Dembo, A. T.; Yakunin, A. T. *Macromolecules* **1998**, *31*, 7698.

(13) Khokhlov, A. R.; Starodubtzev, S. G.; Vasilevskaya, V. V. *Adv. Polym. Sci.* **1993**, *109*, 128.

(14) Khokhlov, A. R.; Kramarenko, E. Yu.; Makhaeva, E. E.; Starodubtzev, S. G. *Macromolecules* **1992**, *25*, 4779.

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