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Synthesis of Composite Solid Electrolytes Based on Polyacrylic Acid via Radical Polymerization Initiated from Silica Surface

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Abstract—A procedure has been developed for the synthesis of silica-supported polymerization initiators, which includes chemisorption of (3-aminopropyl)triethoxysilane, hydrolysis of the alkoxy groups, and chemisorption of 4,4′-azobis(4-cyanopentanoic acid). It has been found that the reaction of 4,4′-azobis(4-cyanopentanoic acid) with immobilized amino groups in the presence of *N*,*N*′-dicyclohexylcarbodiimide involves only one functional group in the former. The effect of the solid support porosity on the composition of organosilica obtained by surface-initiated radical polymerization of acrylic acid has been studied. The best yield of grafted polyacrylic acid is obtained on aerosilogel with large mesopores in combinations with developed surface. The dependence of the impedance of polyacrylic acid-modified aerosilogel on the relative air humidity has been studied, and the possibility of using this material in humidity sensors has been shown.

Keywords: polyacrylic acid, silica, radical polymerization, sensor, solid electrolytes

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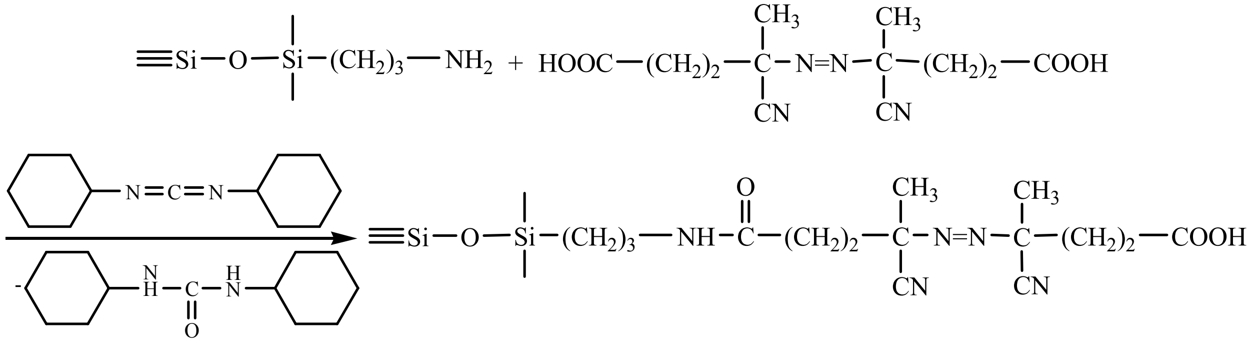
Polymerization on a solid surface may be used to obtain a broad spectrum of functional materials. The formation of a polymer on active centers chemically linked to the surface of solid particles ensures the maximum interaction efficiency between the polymer and filler and uniform distribution of solid particles in the polymer, which could give rise to radically new composites with unique properties. A promising line in the chemical modification of fillers implies activation of their surface with various initiating systems. The subsequent polymerization of monomers on such modified fillers containing active centers leads to a polymer chemically bound to the surface [1, 2]. Cross-linked polymers are frequently used in resistive humidity sensors based on polymer electrolytes. Such polymers are not transferred to solution when condensate is formed under high humidity conditions. However, increase in the degree of cross-linking is accompanied by enhancement of dielectric properties of materials, which impairs the sensitivity. Therefore, it seems reasonable to study the possibility of using for sensing purposes linear polymers chemically grafted to solid surface. One approach to the synthesis of such materials is based on radical polymerization on the surface of an inorganic support containing grafted polymerization initiators.

The goal of the present study was to modify silica surface with radical polymerization initiators with a view to obtain solid electrolytes on the basis of polyacrylic acid. Polymerization initiators were grafted to silica surface by the chemical assembly method [3–7] which includes multistep synthesis of grafted surface compounds and is widely used for chemical modification of solid surfaces. In the first step, chemisorption of (3-aminopropyl)triethoxysilane on silica samples was carried out according to a standard procedure, by treatment of silica with a 10% solution of the reagent in benzene for 3 h at 80°C and subsequent washing with chloroform in a Soxhlet apparatus. The samples thus obtained were subjected to hydrolysis with water vapor to remove alkoxy groups, and 4,4′-azobis(4-cyanopentanoic acid) (radical polymerization initiator) was attached in the presence of *N*,*N*′-dicyclohexylcarbodiimide in dimethylformamide (2 h) (Scheme 1).

It should be noted that covalent bonding of 4,4′-azobis(4-cyanopentanoic acid) to silica surface containing amino groups was confirmed by the diffuse reflectance IR spectra which contained bands at 1564 and 1641 cm^{-1}, typical of amide groups.

Scheme 1.



4,4′-Azobis(4-cyanopentanoic acid) is a difunctional reagent. To ensure immobilization of such reagents on a solid surface through only one functional group it is necessary to use fairly high concentration and large excess of the modifier. Therefore, we carried out the reaction with 5 equiv of both 4,4′-azobis(4-cyanopentanoic acid) and *N*,*N*′-dicyclohexylcarbodiimide with respect to the surface aminopropyl groups. The progress of the reaction was monitored by determining the concentration of free amino groups by the adsorption of Acid Bright Orange Zh, as well as by the Pregl–Dumas technique. The absence of free amino groups on the sample surface indicated quantitative acylation. According to the elemental analysis data, the concentration of grafted 4,4′-azobis(4-cyanopentanoic acid) in all samples was consistent with the concentration of amino groups on the silica surface before acylation (0.09–0.25 mmol/g). These findings lead us to conclude that 4,4′-azobis(4-cyanopentanoic acid) was linked to the aminated silica surface through only one carboxy group in each molecule. It should be noted that the mode of addition of 4,4′-azobis(4-cyanopentanoic acid) to a solid surface is important for subsequent graft polymerization. If 4,4′-azobis(4-cyanopentanoic acid) is linked to a surface via both functional groups, the initiation efficiency is reduced since radicals generated by homolytic dissociation of the initiator molecule appear in proximity to each other, and the probability for their recombination increases (cage effect) [1].

Silica-supported 4,4′-azobis(4-cyanopentanoic acid) was then used to initiate radical polymerization of acrylic acid at 60°C (1 h) with a view to obtain grafted poly(acrylic acid). The formation of grafted polymer was observed with all samples, and its amount was determined after removal of poly(acrylic acid) not linked to the silica surface. Different porous silica samples were tested: aerosilogel [8], MPS-2000 porous glass, S-80 silochrom, and commercial wide-pore KSK and ShSK silicas. The data in table show that the concentration of grafted polymer per sample weight unit depends on both specific surface area and pore diameter.

An important parameter characterizing graft polymerization on an inorganic support is the yield of grafted polymer. From this viewpoint, the best support turned out to be aerosilogel which possesses large mesopores in combination with high specific surface area and is a nanostructured silica with globular structure and open-end pore system (Fig. 1). Therefore, just aerosilogel-supported poly(acrylic acid) was examined as promising proton conductivity material for the design of resistive humidity sensors. Samples were prepared as follows: an aqueous suspension of aerosilogel with grafted poly(acrylic acid) was dropped onto a dielectric glass fiber laminate equipped with gold electrodes (standard assembly produced by N-Texno), and the sample was then dried at room temperature.

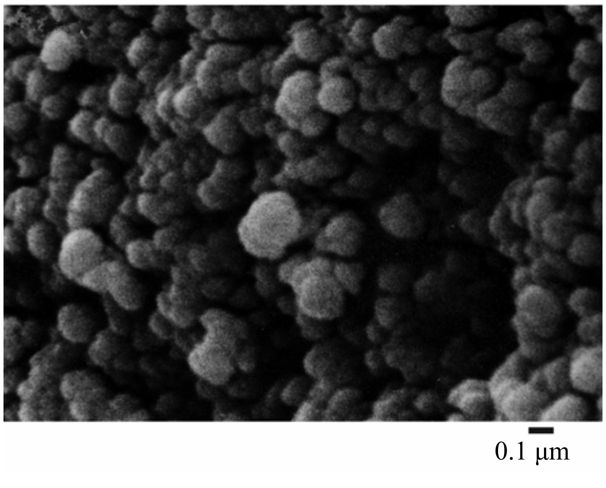


Fig. 1. SEM image of aerosilogel.

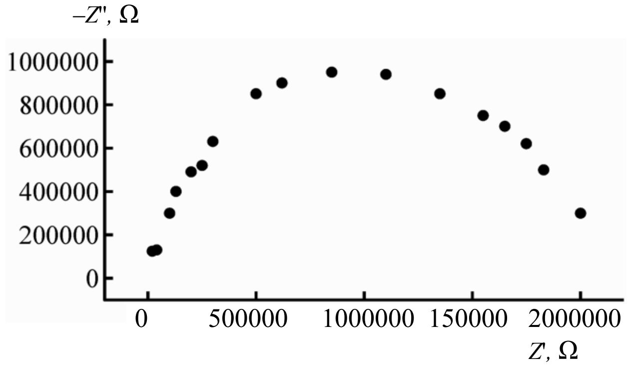


Fig. 2. Impedance of aerosilogel-supported poly(acrylic acid) at a relative air humidity of 32%.

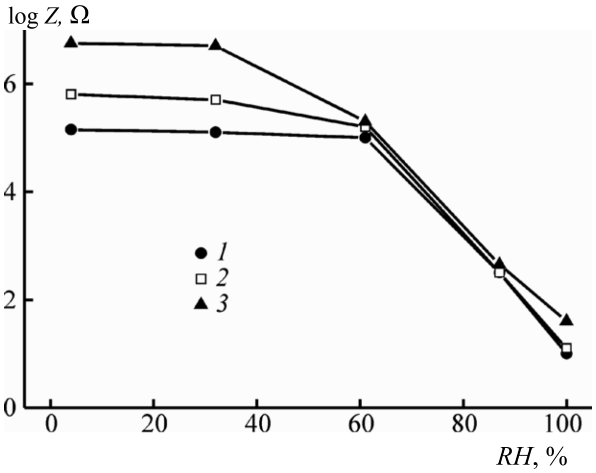


Fig. 3. Effect of the relative air humidity on the total resistance of aerosilogel-supported poly(acrylic acid) at a frequency of (*1*) 500, (*2*) 100, and (*3*) 10 kHz.

The effect of relative air humidity on the resistance of samples prepared in such a way was studied by impedance spectroscopy. Figure 2 shows a typical impedance spectrum for aerosilogel-supported poly(acrylic acid). The dependence of its total resistance on the relative air humidity (*RH*) is presented in Fig. 3; the total resistance was calculated from the impedance spectra at 10, 100, and 500 kHz. It is seen that the total resistance of the sample considerably changes over a fairly wide relative humidity range (30–100%). The most significant variation in the resistance within the given *RH* range is observed at a frequency of 10 kHz, which determines the possibility for practical application of the examined moisture-sensitive material.

Characteristics of samples with grafted polyacrylic acid and porous structure of support materials

Sample	Grafted polymer concentration, g per g of the product	Polymer yield, % (calculated on the filler)	Pore size, nm	Specific surface area, m^2/g
Aerosilogel	0.45	82	24	180
KSK silica	0.41	70	12	220
Silochrom S-80	0.36	56	50	76
Porous glass MPS-2000	0.17	57	200	28
ShSK silica	0.20	25	9	250

Thus, our results show that chemical bonding of radical initiators to solid surface makes it possible to synthesize polymers grafted on solid supports with various porous structures. Taking into account this fact, as well as the possibility of using monomers with various functional groups, the developed procedure for modification of silica surface with radical polymerization initiators may be regarded as a fairly simple but general method for obtaining various functional materials, including composite solid polyelectrolytes which are widely used at present for the design of sensors and hydrogen energy materials [9].

EXPERIMENTAL

The following reagents were used in this work: (3-aminopropyl)triethoxysilane (98%, Fluka), 4,4′-azobis-(4-cyanopentanoic acid) (98%, Alfa Aesar), *N*,*N*′-dicyclohexylcarbodiimide (chemically pure, *Vekton*), acrylic acid (chemically pure, *Vekton*). Acrylic acid was additionally purified from stabilizer by vacuum distillation before use.

The specific surface area was determined according to Brunauer–Emmett–Teller by low-temperature adsorption of nitrogen. The pore structure of silicas was studied by the Barrett–Joyner–Halenda method using a Micromeritics ASAP 2020 MP analyzer. The porous structure of silochrom and aerosilogel was examined with the aid of a PA-3M1 mercury porometer. The concentration of grafted polymer was determined by titration. The surface morphology of aerosilogel was analyzed using a JSM JEOL scanning electron microscope. The IR spectra were recorded on a Perkin Elmer 1760x instrument with a resolution of 4 cm^{-1} (scan number 20).

The total alternating current resistance was measured by impedance spectroscopy in the frequency range from 500 kHz do 5 Hz using an Autolab PGSTAT302 instrument. All measurements were carried out in a specially designed cell maintained at a constant temperature. The required relative humidity in the cell was maintained using sulfuric acid solutions with different concentrations.

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REFERENCES

1. *Reaktsii v polimernykh sistemakh* (Reactions in Polymer Systems), Ivanchev, S.S., Ed., Leningrad: Khimiya, 1987.
2. Ivanchev, S.S., *Radikal'naya polimerizatsiya* (Radica Polymerization), Leningrad: Khimiya, 1985.
3. Aleskovskii, V.B., *Stekhiometriya i sintez tverdykh soedinenii* (Stoichiometry and Synthesis of Solids), Leningrad: Nauka, 1976.
4. Gimanova, I.M. and Postnov, V.N., *Zh. Prikl. Khim.*, 1985, vol. 58, no. 8, p. 1911.
5. Postnov, V.N., Novikov, A.G., and Vakhrutdinov, A.G., *Russ. J. Gen. Chem.*, 1996, vol. 66, no. 9, p. 1535.
6. Postnov, V.N., Makarov, K.A., Aleskovskii, V.B., and Kol'tsov, S.I., *Dokl. Akad. Nauk SSSR*, 1977, vol. 235, no. 3, p.599.
7. Postnov, V.N. and Bogomolova, N.G., *Dokl. Akad. Nauk SSSR*, 1986, vol. 291, no. 1, p. 119.
8. *Modifitsirovannye kremnezemy v sorbtsii, katalize i khromatografii* (Modified Silicas in Sorption, Catalysis, and Chromatogrpahy), Lisichkin, G.V., Ed., Moscow: Khimiya, 1986.
9. Ivanov-Shits, A.K. and Murin, I.V., *Ionika tverdogo tela* (Solid State Ionics), St. Petersburg: Sankt-Peterb. Gos. Univ., 2010, vol. 2.