Sorption and Ion Exchange Processes

Sulfoethylated Polyaminostyrene: Synthesis in a Gel and Selectivity of Sorption of Silver(I) and Copper(II) Ions

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Abstract—A procedure was developed for preparing a new chelating ampholytic polymer, poly\{N-(2-sulfoethyl)aminostyrene\}, by synthesis in a gel via treatment of polyaminostyrene with sodium 2-bromoethanesulfonate. The procedure allows preparation of the polymer with the degree of substitution of up to 0.7. Sulfoethylated polyaminostyrene with the degree of modification of 0.5 selectively takes up silver(I) and copper(II) ions from multicomponent solutions.

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Chemical transformation of polymers is an important route to expanding the range of practically significant properties of known and available polymeric materials and hence the fields of their application. The only obstacle is either limited commercial availability of the polymer or low reactivity of polymers produced on the large-tonnage scale. In the latter case, it becomes necessary to additionally functionalize the polymer to obtain a useful derivative. Polystyrene is a widely used and efficient polymer matrix for preparing various sorption materials based on it [1, 2], including sorbents of metal ions [3, 4]. Lipophilic nature of polystyrene facilitates its reactions with organic compounds [5]. On the other hand, introduction of functional groups allows preparation of both high-capacity [6, 7] and selective [8] sorbents of metal and nonmetal ions. The presence of the amino group not only enhances the reactivity of polystyrene toward various ions [9–11], but also allows modification of the polymer using a wider range of organic reactions [12]. Sulfoethylolation of polyaminostyrene has not been performed previously, but sorbents with such functional groups [13] proved to be highly selective in sorption of silver(I) and copper(II) ions from multicomponent solutions [14].

This study was aimed at developing a procedure for preparing a new polymer, poly\{N-(2-sulfoethyl)aminostyrene\}, and at evaluating its ability to selectively take up transition and alkaline earth metal ions.

EXPERIMENTAL

Linear polystyrene (MM = 400 kDa) was purchased from Alfa Aesar. Sodium ethenesulfonate and sodium 2-bromoethanesulfonate (98.0%) were purchased from Sigma–Aldrich and were used without additional purification. The degrees of nitration, reduction, and sulfoethylation were calculated from the results of the C,H,N,S analysis performed with a Perkin Elmer automatic analyzer. The diffuse reflectance IR spectra were taken with a Spectrum-One spectrometer (Perkin Elmer). Synchronous thermal gravimetric and differential thermal analysis was performed with a TGA/DSC 1 thermal analyzer (Mettler Toledo) at a heating rate of 10 deg min\(^{-1}\) in an argon stream (60 mL min\(^{-1}\)). The IR spectra of the
Sulfoethylation of polymers is usually performed either with sodium 2-chloroethanesulfonate or with sodium ethenesulfonate [18] in a strongly alkaline medium. Both reagents efficiently functionalize both hydroxy and amino groups. To prepare a sulfoethyl polyaminostyrene derivative, we initially used treatment with sodium ethenesulfonate under the conditions of polymer-analogous transformations (“synthesis in a gel”). Such procedure was successfully used previously in carboxy- and hydroxyalkylation reactions [7, 8, 19]. The reaction can be described by the following Scheme 1.

The data obtained (Table 1) show that functionalization of the polymer with sodium ethenesulfonate does not occur to a noticeable extent, probably because of low nucleophilicity of PAS and low activity of sodium ethenesulfonate. The use of sodium 2-bromoethanesul-