*Pure Appl. Chem.*, Vol. 81, No. 12, pp. 2417–2424, 2009. doi:10.1351/PAC-CON-08-11-20 © 2009 IUPAC, Publication date (Web): 29 November 2009

# Study of the sulfonation of expanded polystyrene waste and of properties of the products obtained\*

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*Abstract*: Waste-expanded polystyrene (EPS) and virgin polystyrene (VPS) were converted into ion exchangers by chemical modification. For this purpose, we used silica sulfuric acid as the sulfonating agent and conducted sulfonation under heterogeneous conditions. For VPS, the influence of the quantity of the sulfonating agent, the temperature, and the reaction time on the product properties were studied. As it appeared, silica sulfuric acid simplifies the reaction in comparison with the conventional sulfonation methods. Fourier transform-infrared (FT-IR) spectra and elemental analysis revealed that products were cross-linked and the content of sulfonate groups in a polymer chain varied. Some of the yielded polymers exhibited good water absorption and cation-exchange properties. The ion-exchange capacity (IEC) for chosen products was also determined, and it turned out to be similar to the commercial resin. The batch method was used to study the purification of solutions of Zn<sup>2+</sup> and Cu<sup>2+</sup> by the obtained resins. The performed study proved the usefulness of waste PS derivatives for the water treatment process.

*Keywords*: FT-IR; polystyrene waste; sulfonation processes; silica sulfuric acid; treatment processes.

# INTRODUCTION

Chemical recycling of polystyrene (PS) waste is of crucial importance to the environment. Sulfonation is one of the ways to change the original chemical and physical properties of waste PS. It is possible to receive a water-soluble PS derivative which can be used as a flocculent agent or as a concrete plasticizer through sulfonation from polymer insoluble in water. The products with low sulfonation degree can be used as membranes which separate electrodes and conduct protons in fuel cells—the modern

<sup>\*</sup>Paper based on a presentation at the International Symposium on Novel Materials and their Synthesis (NMS-IV) and the 18<sup>th</sup> International Symposium on Fine Chemistry and Functional Polymers (FCFP-XVIII), 15–18 October 2008, Zhenjiang, China. Other presentations are published in this issue, pp. 2253–2424.

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source of energy. Sulfonation can also lead to obtaining cross-linked and water-absorbing polymers, which can be used as ion-exchange resins [1].

The current intense research and the general interest in heterogeneous sulfonation is the result of the opportunities such systems present for basic research and of the undisputable importance such systems have for industry and the developing technologies. Therefore, we have applied the Neihoff method of sulfonation to convert PS into a polymeric water-soluble flocculant [2]. These sulfonated derivatives usually find application in industrial water treatment due to the several times lower consumption of the coagulants used, short flocculation time, and improved sedimentation properties of suspensions [3–5].

Unfortunately, the Neihof method of sulfonation poses problems caused by the reaction of desulfonation. Moreover, this method, as many sulfonation methods, requires a large excess of sulfonation agent since the water by-product slows the reaction down by diluting the acid. In this case, a large amount of "used acid" is obtained which in batch reactions is usually neutralized and disposed of, while in continuous processes it has to be recycled by complex techniques. Also, the separation of the products from the sulfonation agent is a difficult and energy-consuming process that habitually implies a basic aqueous work-up. Moreover, many sulfonation agents are corrosive and dangerous to transport and handle. Consequently, any reduction in the amount of the sulfonation agent required and/or any simplification in the handling procedures would be highly desirable in terms of risk reduction, economic advantages, and environment protection.

In order to decrease the environmental hazard of the reaction and to increase its economy, we decided to study the usefulness of the silica sulfuric acid in the PS sulfonation reaction. Up until now, this solid sulfonating agent was mainly used in the sulfonation reaction of small aromatic compounds [6].

### EXPERIMENTAL

Samples consisting of 5 g of virgin polystyrene (VPS) were dissolved in 100 ml of 1,2-dichloroethane each. These substrates were then mixed with an appropriate amount of silica sulfuric acid in a thermostatted reaction vessel. Since 1.5–4 mol of  $ClSO_3H$  was used per 1 monomeric unit of PS to synthesize silica sulfuric acid, the PS to sulfonating agent ratio was  $1:1.5 \div 1:4$ . The experiments were performed for the duration from 60 to 720 min and in the temperature range from 30 to 60 °C. The suspension of poly(styrenesulfuric acid) in 1,2-dichloroethane was decanted over silica sulfuric acid granules deposit. Granules were twice washed with pure solvent. After a second washing, particles of poly(styrenesulfuric acid) were not observed in the solvent. PS derivative was then flushed using water and dried to get rid of the possible presence of  $H_2SO_4$ , the by-product of sulfone formation. The experiment was also performed for expanded polystyrene waste (EPS) under conditions:  $1EPS:2ClSO_3H$  [mol], 420 min, 60 °C. The PS sulfonation with the use of silica sulfuric acid probably proceeds as follows:



Preparation of silica sulfuric acid: a 500-ml suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting the HCl gas over the adsorbing solution (i.e., water) was used. It was filled with silica gel dried at 160 °C (2–7 mm particle size, from POCh). Chlorosulfonic acid from Sigma-Aldrich was added dropwise over a period of 30 min at room temperature. The substrates were mixed with a constant quantity of silica gel: 4.5 g to 1 ml of chlorosulfonic acid [6]. Thus, the HCl gas was immediately released from the reaction vessel. After completing the addition of the silica gel, the mixture was shaken for at least 3 h. The chlorosulfonic acid probably reacts with silanol  $\equiv$  SI–OH and silanodiol = Si(OH)<sub>2</sub> groups from the silica gel surface and in consequence silica sulfuric acid is formed as follows:

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$$= si \langle OH \\ OH \\ = si \langle OH \\ OH \\ \end{pmatrix}^{H} \qquad = si \langle O-SO_{3}H \\ = si \langle O-SO_{3}H \\ = si \langle O-SO_{3}H \\ \end{pmatrix}^{H} \qquad (2)$$

The Fourier transform-infrared (FT-IR) spectra for the selected products were obtained on the Perkin-Elmer Spectrum One FT-IR spectrometer. Samples were prepared in the form of KBr discs.

The contents of sulfur and carbon in products of PS sulfonation were determined by using a Perkin-Elmer CHNS/O elemental analyzer. The contents of sulfur and carbon were then used for calculations of the number of sulfonic groups per monomer unit (*n.sulf*).

Water absorption of sulfonated products was determined by weight from mass differences between wet and dry polymers. This parameter indicates the increase of polymer weight after 24 h contact with water.

The ion-exchange capacity (IEC, with unit of mmol  $g^{-1}$  of dry polymer) of sulfonated virgin polystyrene (VPSS) and expanded polystyrene (EPSS) was determined by measuring the concentration of H<sup>+</sup> that was exchanged with sodium cation in 24 h at constant temperature of 25 °C while acid-form resin (about 0.2 g of dry resin) samples were equilibrated with 100 ml 0.2 mol  $1^{-1}$  NaCl solution.

Solutions of heavy metals (Zn, Cu as nitrate; reagent grade; POCh) were prepared in distilled water without adjusting the pH. In order to estimate the adsorption capacity, stock solutions of 1000 mg l<sup>-1</sup> of each metal were diluted to obtain standard solutions containing 25–400 mg l<sup>-1</sup> of metal ions. Under these experimental conditions, it was confirmed that no chemical precipitation had occurred. The solutions (in conversion to 100 ml per 0.14 g of dry resin) were shaken (180 rpm) in 150-ml flasks with appropriate amounts of resins in an incubator at 25 °C for a period of 24 h. Thermo E.C. Solaar M AAS spectrometer was used to determine initial and final metal concentrations in solutions. In each case, the final concentration of each metal ion was determined after 24 h.

The percent of *metal adsorption* and distribution ratio  $K_d$  were calculated using the following equations:

metal adsorption = 
$$(c_i - c_f) 100/c_i$$
 (%) (3)

where  $c_i$  and  $c_f$  are the concentrations of the metal ion in initial and final solutions, respectively

$$K_{d} \frac{\text{amount of metal in adsorbent}}{\text{amount of metal in solution}} \cdot \frac{V}{m} \left( \text{ml g}^{-1} \right)$$
(4)

where V is the volume of the solution (ml) and m is the weight of the adsorbent (g).

 $K_d$  is defined as the ratio of metal ion concentration in the resin to that in the aqueous solution.

# **RESULTS AND DISCUSSION**

Products (VPSS, EPSS) non-soluble in water were obtained by using silica sulfuric acid as the sulfonation agent for PS sulfonation. The great advantage of the method was that sulfonated derivatives of PS were easily separated from silica sulfuric acid by decantation of their suspension in 1,2-dichloroethane. Then, sulfonated polymer suspension was decantated (the residual amount of solvent is evaporated from the product) under optimal conditions.

FT-IR spectroscopy was applied to study the course of the sulfonation (Fig. 1). To normalize the intensities of the absorption bands, we used the stretching vibration band of the benzene ring at 1601 cm<sup>-1</sup>, which is insensitive to structural changes during substitution. The appearance of a band at 1175 cm<sup>-1</sup> during the stretching vibration of SO<sub>2</sub> was used to confirm the sulfonation of PS. Further evidence of sulfonation could be seen by observing the peaks at 1097 and 1128 cm<sup>-1</sup>. These bands have been attributed to the in-plane skeletal vibrations of the disubstituted benzene rings [7].



**Fig. 1** FT-IR spectra of VPSS and EPSS from sulfonation using silica sulfuric acid under the following conditions: T = 60 °C, t = 420 min; *IEC* [mmol g<sup>-1</sup>].

Changes in the intensities of the band at 698 and 756 cm<sup>-1</sup> were also observed. These two bands are characteristic for out-of-plane skeleton binding vibrations of the benzene ring and the out-of-plane binding vibration of the five -C(H)- groups in the benzene ring characteristic of the monosubstituted benzene ring, i.e., without the sulfo group [8]. Depending on the sulfonation conditions, the formation of sulfone and the cross-linking of the product are possible. The IR spectra of different polysulfones [9] have characteristic bands for the C–S(O)<sub>2</sub>–C group. We observed a band at 770 cm<sup>-1</sup>, which corresponds to the symmetric stretching of C–S–C. However, at low sulfonation this band is obscured due to the vicinity of the intensive band at 756 cm<sup>-1</sup>. The OH (probably from  $-S(=O)_2(OH)$  groups) stretching vibration at frequency 34XX cm<sup>-1</sup> and its scissor vibration at 16XX cm<sup>-1</sup> were observed in VPSS and EPSS FT-IR spectra [10].

With increase of the sulfonating agent content, the increase of the relative intensities of bands from sulfo groups and from disubstituted phenyl groups after electrophilic substitution is observed (Fig. 2). Simultaneously, the decrease of relative intensities of bands, which are characteristic for the monosubstituted benzene ring, confirms the presence of the sulfonation product. It is noteworthy that the relative intensity of the band from C-S-C (sulfone group) decreases with the increase of the content of silica sulfuric acid VPS:CISO<sub>3</sub>H from 1:1.5 to 1:4. This suggests that in the applied conditions, the increase of the quantity of the sulfonating agent induces the decrease of product cross-linking. An ion-exchange resin that is highly cross-linked is resistant to the diffusion of various ions via the resin and less useful for water purification. The correlation between the intensity of O=S=O group band and the water absorption was also observed. Water absorption is one of the parameters used to characterize ion-exchange resins. Products of the reaction of sulfonation conducted at 60 °C for a period longer than 300 min and with the molar ratio of the VPS:CISO<sub>3</sub>H from 1:2 to 1:4 had high and very high water absorption properties. Products of VPS sulfonation yielded under optimal conditions (60 °C, 420 min and VPS:ClSO<sub>3</sub>H 1.5  $\div$  3) had IEC between 2.2 and 2.7 mmol g<sup>-1</sup>. At temperature below 60 °C, the sulfonation of the obtained products dropped drastically although the same amount of silica sulfuric acid was used.



**Fig. 2** Dependence of the mole content of chlorosulfonic acid used for the preparation of the sulfonation agent (silica sulfuric acid) per mole of PS monomeric unit on relative FT-IR bands intensities and on water absorption of VPSS.

Elemental analysis showed that products yielded at these conditions had approximately 0.5 to even 0.9 sulfonic group per monomer unit (*n.sulf*). The increase of time and temperature of the sulfonation reaction and content of the sulfonating agent influence the increase of the relative intensities of the band from sulfo group and *n.sulf*. The problem arises when sulfonation is conducted at *T* higher than 60 °C and above VPS:CISO<sub>3</sub>H 1:3, the sulfonated PS separation from constant sulfonating agent becomes difficult. However, the increase of the sulfonation level (*n.sulf*) can be achieved by extending the reaction time (Fig. 3).



**Fig. 3** Dependence of the reaction time on *n.sulf* parameter of PS sulfonation products conducted under conditions: 1VPS:2CISO<sub>3</sub>H, 60 °C.

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The IEC of the obtained resins was determined by measuring the concentration of hydrogen cations that were exchanged with sodium cations when acid-form resin samples were equilibrated with sodium chloride solution. The cation exchange capacity of resins from VPS was 2.6 and from EPS  $3.1 \text{ mmol g}^{-1}$  (both 1PS:2ClSO<sub>3</sub>H, 60 °C, 420 min), which is similar to the commercial Amberlite IR:  $3-5 \text{ mmol g}^{-1}$ .

Batch uptake studies allow for the measurement of the quantity of metal ions absorbed from a solution onto the absorbent after maintaining contact for long enough to reach equilibrium. Data from the batch uptake tests were used to calculate the distribution ratio  $K_d$  and the metal adsorption.

The adsorption of  $Zn^{2+}$  and  $Cu^{2+}$  by modified waste PS as a function of their initial concentrations at 25 °C are shown in Fig. 4. The maximal exchange attained for the smallest concentrations was at least 94 % for both metal ions and with virgin (VPSS) and expanded (EPSS) derivatives. Adsorption of metal ions decreases with increasing metal concentration in aqueous solutions. During the ion exchange, metal ions had to pass through the cross-linked resin lattice and then replace the exchangeable ions.



**Fig. 4** Adsorption of metal ions by VPSS and EPSS sample as a function of initial concentration; m = 0.14 g, V = 100 ml, t = 24 h; sulfonation conditions: 1V/E PS:2CISO<sub>3</sub>H, T = 60 °C, t = 420 min.

Figure 5 illustrates  $K_d$  as a function of metal ion concentrations. The  $K_d$  values increase with the decreasing concentration of metal ions. In other words, the  $K_d$  values increase with the dilution of metal ions in the solution. These results indicate that with increasing metal concentration in the aqueous solution energetically less favorable sites become involved. The Zn and Cu metal cations are present as hexaaqua complex ions with six surrounding water molecules in the solution and they probably pass through resin in this form [11]. Since the adsorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important. The charges of the metal cation are the same, therefore,  $Zn^{2+}$  ions (with a bigger diameter) were less adsorbed than  $Cu^{2+}$  ions (with a smaller diameter).



Fig. 5 Distribution coefficients on the adsorbent as function of initial concentration of metals; m = 0.14 g, V = 100 ml, t = 24 h; sulfonation conditions: 1V/E PS:2ClSO<sub>3</sub>H, T = 60 °C, t = 420 min.

### CONCLUSIONS

The problem of environmental pollution by polymer waste can be resolved by its chemical modification into useful products. The obtaining of effective cation exchange resins for metal ions treatment from chemically modified polymer wastes could be one of the ways.

By using silica sulfuric acid as the sulfonating agent for PS modification, it is possible to obtain a product that can be used for purification of water. The synthesized resins cause a decrease of concentration of the solved impurities. The IEC of sulfonated PS derivatives is similar to commercial ion exchangers. Moreover silica sulfuric acid simplifies the reaction in comparison with the conventional sulfonation methods.

It is noteworthy that the shape of the plot from FT-IR spectra yields information about the properties of the PS sulfonation product.

## ACKNOWLEDGMENTS

This work was supported by the Committee of Scientific Research in Poland and the University of Silesia in Katowice, Poland (BW/ICh/08).

# REFERENCES

- 1. Y. A. Elabd, E. Napadensky. Polymer 45, 3037 (2004).
- 2. R. Neihof. J. Colloid Interface Sci. 58, 916 (1954).
- 3. W. Bajdur, W. Sułkowski. In ynieria Ochrona Środowiska 1, 115 (1999).
- 4. F. Lafuma. Polimery 43, 104 (1998).
- 5. J. Randtke. J. Am. Water Works Assoc. 80, 40 (1998).
- 6. M. A. Zolfigol. Tetrahedron 57, 9509 (2001).
- 7. Z. Su, X. Li, S. L. Hsu. Macromolecules 27, 287 (1994).

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- 8. G. Zundel. *Hydration and Intermolecular Interaction*, pp. 169–172, Academic Press, New York (1969).
- 9. J. H. Wang, M. H. Yang, R. J. Lee. Polym. Test. 16, 147 (1997).
- 10. J. C. Yang, M. J. Jablonsky, J. W. Mays. Polymer 43, 5125 (2002).
- 11. M. A. Jama, H. Yücel. Sep. Sci. Technol. 24, 1393 (1990).