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ORIGINAL PAPER

Effect of reaction time and temperature on the morphology and ion-exchange capacity of polystyrene beads sulfonated using different sulfonating agents

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Abstract Monodisperse polystyrene (PS) beads 2.5 μm in size were synthesized by dispersion polymerization. The PS beads were chemically modified by three different sulfonating agents, namely, concentrated sulfuric acid, acetyl sulfate, and chlorosulfonic acid. When they were sulfonated using chlorosulfonic acid, the concentration of sulfonic acid (SO_3^-) groups on the PS beads increased from 0.5 to 2.25 meq/g as the treatment time was increased from 10 to 360 min at 0 °C. As the reaction temperature was increased, the ion-exchange capacity (IEC) of the sulfonated PS beads increased. However, it can be seen that they lost their spherical shape. The PS surface was modified by the introduction of the SO_3^- groups to give an IEC of up to 2.28 meq/g, which provides 1.1×10^{10} SO_3^- groups per bead, without any deformation of their spherical shape.

Keywords Sulfonation · Polystyrene bead · Ion-exchange capacity

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Introduction

Polymeric materials have unique properties such as a low density, light weight, and high flexibility and are widely used in various industrial systems. However, in many cases, the hydrophobic nature of most polymer surfaces causes problems related to adhesion, wetting, printability, and coating [1]. Functionalized polymers have gained great importance in many fields of scientific research, as well as for industrial applications, and their importance will doubtless continue to increase, because of the variety of possible modifications of their chemical and physical properties. Already, the techniques used for the surface modification of polymers developed in the plastics, electronics, and biomaterials industries have enabled a wide variety of surface functionalized materials to be produced with added value and the promise of new functions [2].

Various approaches have been proposed to modify polymers including UV-irradiation, chemical oxidation, graft copolymerization, and plasma treatment to introduce functional groups such as carboxyl, amine, hydroxyl, and sulfonate moieties [3–6]. However, it should be mentioned that the use of physical methods usually incurs high preparation costs for the equipment and technical difficulties in exposing all sides of the beads to the source. On the other hand, grafting copolymerization and chemical oxidation are simpler and more controllable than other methods [7].

Sulfonation is the most common method used for the incorporation of sulfonic acid (SO_3H) groups onto aromatic polymer chains via electrophilic substitution [8]. Many researchers have used sulfonation to prepare electrolyte membranes, which require high proton conductivity. In this case, the polymeric materials are often dissolved in various solvents and then thin films are prepared using spin coating and bar coating [9, 10]. For example, Chen et al. reported the preparation of a new composite proton exchange membrane by casting a sulfonated polystyrene (SPS) solution with suspended micron sized particles of a crosslinked SPS ion-exchange resin [11]. When SPS beads are adopted as a specific biotechnology and electro-device, the ion exchange capacity (IEC) of the functional PS surface is likely to be one of the key factors determining the adsorption of metal ions or enzymes to the SPS surface. Furthermore, the maintenance of the polymer's spherical shape is also important [12, 13].

Sulfonic acid groups can be introduced onto PS beads by chemical modification with different sulfonating agents, such as concentrated sulfuric acid, acetyl sulfate, and chlorosulfonic acid [14–16]. However, during the sulfonation, it is possible for the PS bead morphology to be affected or even deformed, due to the action of the sulfonating agent and reaction conditions.

We report the efficiency of various sulfonating routes using different sulfonating agents, viz. concentrated sulfuric acid, acetyl sulfate, and chlorosulfonic acid, as well as their effects on the PS bead morphology.

Experimental

Materials

2,2-Azobisisobutyronitrile of analytical grade (AIBN: Junse Chemical) was used as an initiator without further purification. Styrene monomer, poly(vinylpyrrolidone) (PVP, Mn: 40,000), chlorosulfonic acid, acetic acid, sulfuric acid, 1,2-dichloroethane, acetic anhydride, and ethanol were obtained from Aldrich and used as received.

PS bead synthesis

Styrene monomer (30 mL) and PVP (3.0 g) were charged into a 500 mL, four-necked reaction vessel, and then dissolved in ethanol. The AIBN concentration was 1 wt% relative to the total amount of monomer. The polymerization temperature was fixed at 60 °C in an oil bath with a fixed agitation speed of 150 rpm. After the completion of the polymerization, the resulting PS beads were obtained by centrifugation at 3,500 rpm and washed repeatedly with deionized water and ethanol in order to remove the remaining styrene monomer, and finally dried using a freeze-dryer.

Sulfonation of PS beads

The synthesized PS beads were sulfonated using three different sulfonating agents: concentrated sulfuric acid (method A), acetyl sulfonate (method B), and chlorosulfonic acid (method C).

Method A

First, the PS beads (1 g) were swollen with 30 mL of acetic acid in a 100 mL three-necked reaction vessel. Concentrated sulfuric acid (10 mL) was then added under mechanical stirring. The PS beads were then treated with concentrated sulfuric acid for a designated reaction time and the system heated until the desired temperature was attained. In order to prevent any damage being caused to the SPS beads, they were washed very carefully with deionized water and dried using a freeze-dryer.

Method B

The sulfonating agent was first prepared by the addition of concentrated sulfuric acid to a mixture containing acetic anhydride and 1,2-dichloroethane in an ice bath. The solution became viscous and pale blue. The prepared acetyl sulfate was added dropwise, under mechanical stirring, into a three-necked reaction vessel containing the PS beads (1 g). The PS beads were then treated with acetyl sulfate for a designated reaction time and the system heated until the desired temperature was attained. The SPS beads were washed with deionized water and finally dried using a freeze-dryer.

Method C

PS beads (1 g) were dropped into chlorosulfonic acid in a three-necked vessel equipped with a mechanical stirrer, thermometer, and addition funnel. The PS beads were then treated with chlorosulfonic acid for a designated reaction time and the system heated until the desired temperature was attained. When it was complete, the reaction was terminated by adding ethanol. Finally, the SPS beads were washed with deionized water and dried using a freeze-dryer.

Determination of ion-exchange capacity

For the measurement of the IEC (meq of SO_3H/g) by the acid–base titration method [17], the SPS beads (1 g) were immersed in 50 mL of saturated sodium chloride (NaCl) solution and the mixture was stirred for 24 h to allow the H^+ ions to exchange with the Na^+ ions. The released H^+ ions were titrated with 0.1 M sodium hydroxide (NaOH) solution. The IEC was calculated from the consumed NaOH via the following equation:

$$\mathrm{IEC} = \frac{\text{Consumed NaOH (mL)} \times \text{molarity of NaOH}}{\text{Dried polymer weight (g/meq)}} \qquad (1)$$

Characterization

Scanning electron microscopy (SEM, Hitachi, S2400) was used to analyze the size of the PS beads and the morphology of the SPS beads. Fourier transform infrared spectroscopy (FT-IR, Bruker, IFS-66/S) was utilized to analyze the structures of the PS and SPS beads.

Results and discussion

The PS beads were synthesized by dispersion polymerization. Their average size and molecular weight (M_w) were ca. 2.5 μm and 209,000, respectively. As can be seen in Fig. 1, the PS beads were perfectly spherical and smooth without any aggregation and their size distribution was fairly monodisperse.

Figure 2 shows the SEM images of the SPS beads synthesized using different sulfonating agents. When concentrated sulfuric acid and chlorosulfonic acid were used (Fig. 2a, b, respectively), the SPS beads retained their spherical shape and their surface remained smooth without any visible deformation slits being formed on them. However, the PS beads sulfonated by acetyl sulfate (method B) were deformed and lost their spherical shape (Fig. 2c).

Figure 3 shows the IEC (meq of SO_3H/g) of the sulfonated beads plotted as a function of the sulfonation treatment time. It can be seen that the IEC value increases with increasing reaction time for all three sulfonating agents and that the IEC values for both concentrated sulfuric acid and acetyl sulfate are lower than that for chlorosulfonic acid, which exhibits a maximum value of 2.28 meq/g after a

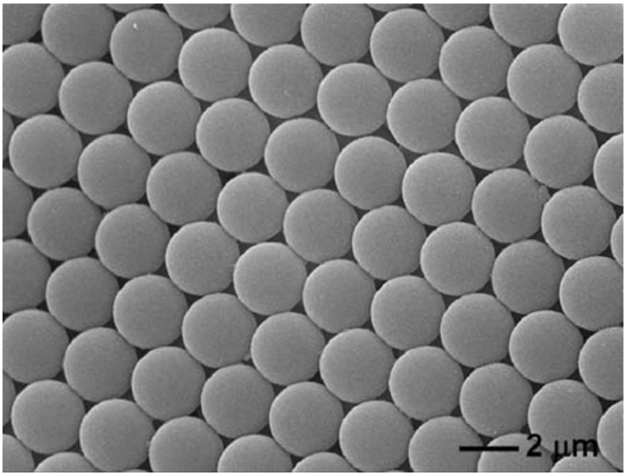


Fig. 1 SEM image of PS beads synthesized by dispersion polymerization

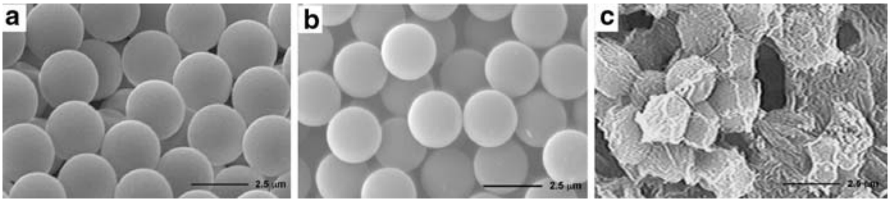


Fig. 2 SEM images of PS beads after the sulfonation process by various sulfonating agents **a** PS beads sulfonated by concentrated sulfuric acid, **b** PS beads sulfonated by chlorosulfonic acid, and **c** PS beads sulfonated acetyl sulfate

treatment time of 360 min at 0 °C. In order to obtain a higher IEC, we examined the IEC value as a function of the sulfonation temperature using chlorosulfonic acid. As can be seen in Fig. 4, the IEC values abruptly increase with increasing reaction temperature and it was found that the maximum value of the SPS beads was 5.96 meq/g at 90 °C.

However, although the PS beads exhibited a high IEC value, it can be seen in Fig. 5 that their original perfectly spherical structure changed to an oval one. It is reasonable to suppose that it was difficult for the PS beads to maintain their spherical shape under the strong reaction conditions and high temperature.

The number of SO_3^- ions $\left(N_{SO_3^-}\right)$ formed on the surface of the PS beads can be estimated to be

$$N_{SO_3^-} = m\,\mathrm{IEC}\,N_A, \tag{2}$$

where m and N_A are the mass of a PS bead and Avogadro's number, respectively.

Their IEC values, number of sulfonic acid groups, and reaction conditions are summarized in Tables 1, 2, 3, respectively. In addition, the $\left(N_{SO_3^-}\right)$values of the SPS

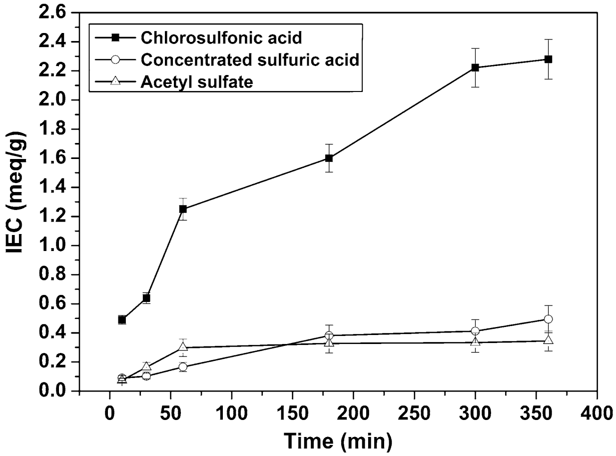
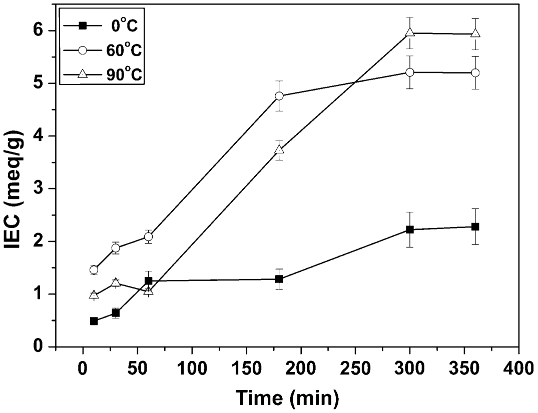


Fig. 3 Ion-exchange capacity (IEC) measured as a function of reaction time at 0 °C: PS sulfonated by concentrated sulfuric acid, PS sulfonated by acetyl sulfate, and PS sulfonated by chlorosulfonic acid

Fig. 4 Ion-exchange capacity (IEC) measured as a function of reaction temperature with chlorosulfonic acid



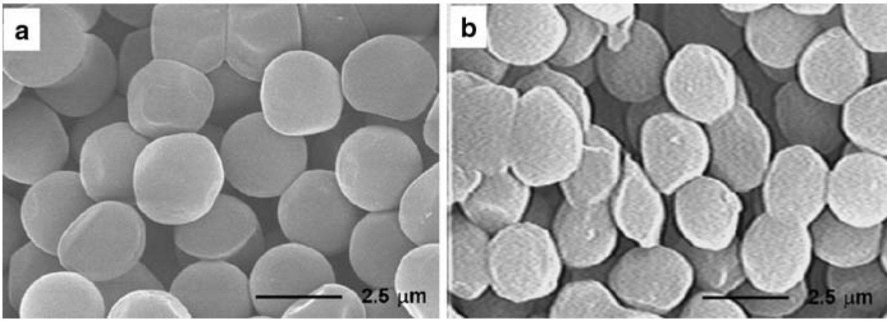


Fig. 5 SEM images of PS beads after sulfonation by chlorosulfonic acid at different temperatures **a** PS sulfonated at 60 °C and **b** PS sulfonated at 90 °C

Table 1 Sulfonation conditions of the PS beads using concentrated sulfuric acid

Concentrated sulfuric acid, temperature: 0 (°C)						
Reaction time (min)	10	30	60	180	300	360
IEC (meq/g)	0.02	0.04	0.04	0.05	0.05	0.05
Number of SO_3^-	1.0×10^8	2.0×10^8	2.0×10^8	2.5×10^8	2.5×10^8	2.5×10^8

Table 2 Sulfonation conditions of the PS beads using acetyl sulfate

Acetyl sulfate, temperature: 0 (°C)						
Reaction time (min)	10	30	60	180	300	360
IEC (meq/g)	0.09	0.100	0.17	0.17	0.18	0.18
Number of SO_3^-	4.5×10^8	5.0×10^8	8.5×10^8	8.5×10^8	9.0×10^8	9.0×10^8

Table 3 Sulfonation conditions of the PS beads using chlorosulfonic acid

Chlorosulfonic acid						
Temperature 0 (°C)						
Reaction time (min)	10	30	60	180	300	360
IEC (meq/g)	0.49	0.64	1.3	1.60	2.22	2.28
Number of SO_3^-	2.5×10^9	3.2×10^9	6.5×10^9	8.0×10^9	1.1×10^{10}	1.1×10^{10}
Temperature 60 (°C)						
Reaction time (min)	10	30	60	180	300	360
IEC (meq/g)	1.49	1.88	2.09	4.76	5.21	5.20
Number of SO_3^-	7.5×10^9	9.4×10^9	1.0×10^{10}	2.4×10^{10}	2.6×10^{10}	2.6×10^8
Temperature 90 (°C)						
Reaction time (min)	10	30	60	180	300	360
IEC (meq/g)	0.97	1.21	1.05	3.73	5.95	5.96
Number of SO_3^-	4.9×10^9	5.3×10^9	5.3×10^9	1.9×10^{10}	3.0×10^{10}	3.0×10^{10}

beads with IEC values of 0.05, 2.28, and 5.96 meq/g were estimated from Eq. 2 to be 2.5×10^8 SO_3^-/bead, 1.1×10^{10} SO_3^-/bead, and 3.0×10^{10} SO_3^-/bead, respectively. Consequently, chlorosulfonic acid is preferred over the other sulfonating agents, viz. concentrated sulfuric acid and acetyl sulfate, because it affords a wide range of IEC values in a controllable manner without any deformation of the spherical shape.

The FT-IR spectra of the pristine PS beads and the PS beads sulfonated by chlorosulfonic acid are shown in the wavelength range from 500 to 1,500 cm^{-1} (Fig. 6). The prominent peaks at 1,375, 1,172, 1,006, 834, and 576 cm^{-1} confirmed the formation of sulfonic acid groups on the surface of the PS beads. In particular, the observation of the peak at 576 cm^{-1} indicates the attachment of the sulfonic acid groups to the *para* position of the PS [17–19].

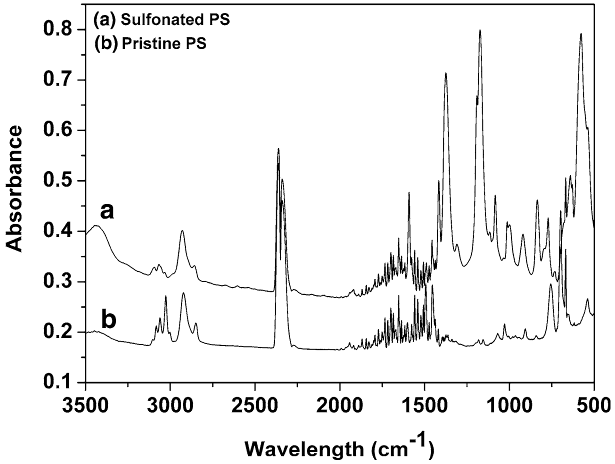


Fig. 6 FT-IR spectra of *a* the pristine PS beads and *b* PS beads sulfonated by chlorosulfonic acid

Conclusion

In this study, the effects of the reaction time and reaction temperature on the IEC value and morphology of PS beads sulfonated by three different sulfonating agents, viz. concentrated sulfuric acid, acetyl sulfate, and chlorosulfonic acid, were investigated. It was found that the degree of sulfonation of the PS beads increased with increasing reaction time for all three sulfonating agents. In order to obtain SPS beads with a higher IEC value, we controlled the reaction temperature. The IEC value of the SPS beads was found to increase significantly with increasing reaction temperature. The maximum IEC value of the SPS beads was 5.96 meq/g at 90 °C, however, their morphology was affected by the high temperature. Using chlorosulfonic acid, the PS surface was able to be modified by introducing sulfonic acid groups (SO_3^-) to give PS beads with an IEC of up to 2.28 meq/g, providing 1.1×10^{10} sulfonic acid groups per bead, without deforming their spherical shape. Consequently, chlorosulfonic acid is preferred over the other sulfonating agents because it affords a wide range of IEC values in a controllable manner without any deformation of the spherical shape. This study shows the potential of sulfonating PS beads with chlorosulfonic acid for use in various applications.

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