Efficient, "One-Pot" Synthesis of Suspension Crosslinked Sulfonated Polystyrene via a Friedel–Crafts Reaction

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SYNOPSIS

A suspension technique leading to macronet ionic resins is described based on a single reactor process. The procedures demonstrate sulfuric acid as a polar suspending medium that can act as a sulfonating agent, a Friedel-Crafts catalyst, and a crosslinking agent. The sulfonation reaction was finally completed using sulfuric acid excess, or oleum 65%. High yields were obtained for the crosslinking and the sulfonation reaction, while the final products were characterized by using ion-exchange capacity measurements, U.V. spectra, and determination of the degree of crosslinking. The number average molecular weight between crosslinks and the ion-exchange capacity $H^+ \rightarrow Na^+$ of the resins was decreasing by increasing the nominal crosslinking ratio. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Macronet structures can be obtained by the introduction of bulky groups between the styrene units of linear polystyrene via Friedel–Crafts reactions. Processes like these lead to three-dimensional polymer networks, which appear to exhibit advantages compared to the conventional styrene–divinylbenzene (S–DVB) copolymers.[1-5] 1,4-Dichloromethyl-2,5-dimethylbenzene (DCMDMB) has been shown to be a desirable crosslinking agent[6-12] for polystyrene (PS) modification. Friedel–Crafts crosslinking of PS can be performed in solution, by using various solvents and catalysts[7-11] until gelation occurs. However, it is afterward necessary to crush the products to the appropriate particle-size distribution needed for the following sulfonation reaction, since rather small particles are required to achieve a high-yield final product in a short time. More uniform products are obtained by a suspension reaction in various media,[8,10] but the PS particles have to be isolated before the introduction of the sulfonic group.[12]

Novel efficient processes have been developed for the synthesis of crosslinked sulfonated polystyrene, which are based in the use of concentrated sulfuric acid as a suspending medium, a Friedel–Crafts catalyst for the crosslinking reaction of polystyrene (PS), and simultaneously as a sulfonating agent. The present communication describes "one-pot" syntheses of suspension crosslinked sulfonated PS.

EXPERIMENTAL

Materials

Linear PS was purchased by Dow Chemical Hellas, with $M_n = 1.18 \times 10^5$ and a polydispersity index of 2.25. 1,4-Dichloromethyl-2,5-dimethylbenzene (DCMDMB) was prepared by chloromethylation of p-xylene, according to the technique reported by Peppas and Valkanas.[6]

"One-Pot" Process

Crosslinking

Five grams of linear PS and DCMDMB, at a ratio varied between 1 and 32% w/w, were dissolved in 15 mL of 1,2 dichloroethane (DCE, analytical grade, Merck) at 50°C within 90 min, using a 400 mL three-neck flat-bottom flask, equipped with magnetic stirrer, gas inlet tube, thermometer, and closed feeding system. Nitrogen was used for 15 min, passing over the reaction mixture to remove oxygen and moisture. Then, 15 mL of concentrated sulfuric acid 95–97% (pro analysi, Merck) was added to the apparatus at constant temperature 50 ± 1°C, without a simultaneous air inlet. After the addition of sulfuric acid, the vessel was heated in a water bath at the same temperature for 4 h, agitating in 150 rpm for 25 min. Agitation stopped after 25 min due to gel formation

followed by absorption of the suspending medium. The obtained product consisted of spherical particles swollen in the excess of sulfuric acid.

Sulfonation

Afterward, sulfonation was performed using either sulfuric acid or sulfur trioxide (oleum) as sulfonating agent.

(i) Sulfonation using sulfuric acid. Fifty milliliters of sulfuric acid 95–97% was added to the reaction mixture, at $78 \pm 1°C$ and 60 rpm for 20 min. While the reaction proceeded, the sulfonating agent was absorbed by the PS particles. The final product consisted of brown-colored spherical particles.

(ii) Sulfonation using sulfur trioxide. Forty milliliters of DCE was added to the reaction mixture to ensure a uniform dispersion of the sulfonating agent. Subsequently, the appropriate DCE was added to 15.3 mL of oleum 65% (analytical-grade Merck) to form a 30 mL solution. This mixture was added to the reaction vessel and the system remained for 90 min at $30 \pm 1°C$ and 100 rpm agitation. The final product also consisted of brown-colored spherical particles, dispersed in the DCE excess.

The resins were precipitated in portions in ice-cooled water at $0°C$ to achieve a light-colored product and to reduce the osmotic shock, washed with $CHCl_3$, then with $1N$ HCl solution, and dried at $105°C$ for 24 h for the removal of any residual solvent.

Characterization of Products

The kinetics of the crosslinking reaction was then studied. Nitrogen was purged over the reaction mixture, at a rate of 1.5 l/h. A reservoir containing approximately 40 mL of distilled water was used to scrub the HCl produced by the reaction. Water was replaced by a fresh source at the appropriate times. The reservoir content was titrated against a standardized $AgNO_3$ solution. To each aliquot, 1.5 mL of $NaHCO_3$ 4% w/v solution was added to adjust the pH.

The molecular weight between crosslinks was calculated by the Flory–Rehner equation, using the swelling data in the polar solvents. The swelling degree of the sulfonated products was determined gravimetrically. The particles were swollen in $2N$

NaCl excess for 24 h at $25°C$. Then, the gels were filtered off in a 3G4 glass filter under vacuum for 1 min for the removal of the residual solvent, covered to avoid solvent evaporation, and weighted. Afterward, the gels were washed with distilled water, filtered off, dried at $105°C$ for 24 h, and reweighted to determine the solvent free weight of the polymer. The porosity of the networks was also measured by uptake experiments of a nonswelling solvent (cf. benzene). A Hitachi U 2000 double-beam spectrophotometer was used to record ultraviolet spectra. The measurements consisted of 0.02% w/v solutions in $CHCl_3$ (analytical grade) in the range of 250–310 nm. The scanning speed was 100 nm/min and the polymers subjected to spectra analysis were well purified by precipitation in methanol, filtered off, washed three times with $n\text{-}C_7H_{16}$, and dried at $60°C$ for 12 h. The degree of sulfonation was obtained by ion-exchange capacity measurements employing a batch procedure. Actually, 0.1–0.3 g of sulfonated resin was added to 40 mL of a $0.5N$ NaCl solution for 4 h at $25°C$. The polymers were filtered off and washed with NaCl solution, and the filtrate was titrated against a standardized KOH solution.

RESULTS AND DISCUSSION

Product Morphology

In Figure 1, photographs of the crosslinked sulfonated particles are depicted as swollen by water. The lines inside indicate a 1 mm distance. It is observed
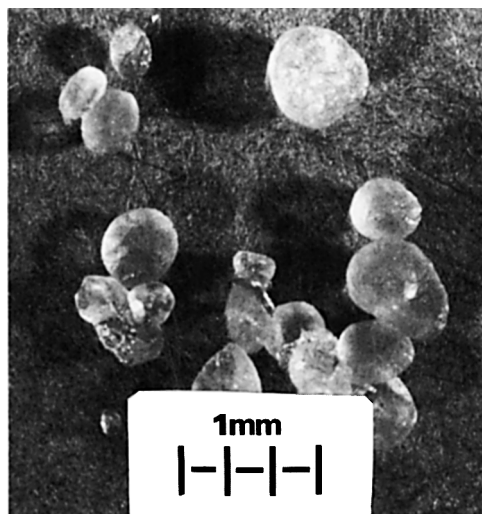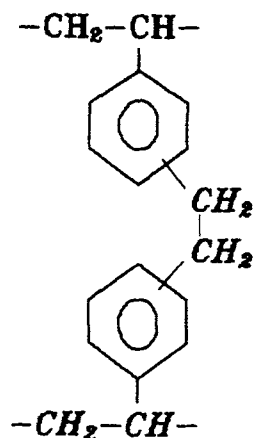

Figure 1 The appearance of the product obtained by "one-pot" synthesis (150 rpm, $50°C$, sulfuric acid as sulfonating agent, 2% crosslinking agent) swollen in water.

−CH₂−CH−

CH₂

CH₂

−CH₂−CH−

Structure (I)

−CH₂−CH−

CH₂

H₃C−

CH₃

CH₂Cl

Structure (II)

that most of the swollen particles are in a spherical form, due to the action of sulfuric acid as the suspending medium. Aggregates of two or more spherical particles can also exist.

Kinetics

The kinetics of the crosslinking reaction was studied by determining the liberation of HCl titrimetrically, considering that 1 mol of HCl evolved corresponds to 1 mol of the chloromethyl group reacted. For this relationship to exist, it is necessary that the chlorinated solvent does not react with the polymer chains under these conditions (structure I). Rabek and Lucki[13] proved that at a high concentration of Friedel–Crafts catalysts, like AlCl₃, crosslinking of PS is caused by chlorinated solvents. To examine this, experiments were performed using PS solutions and concentrated sulfuric acid, without the presence
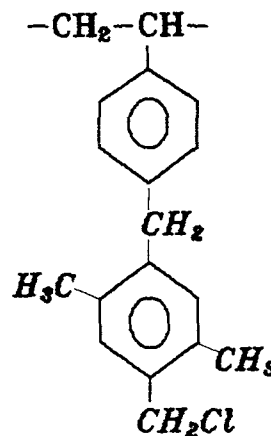
of a crosslinking agent. In fact, evolution of HCl was not observed under the reaction conditions for 12 h. Besides, by heating the polymer solution at 50°C with the presence of sulfuric acid after 75 min of stirring, gelation occurred attributed to sulfone-type crosslinking (structure II), which was also analyzed and proved by calculating the molecular weight between crosslinks.

The main crosslinking reaction starts with grafting of the crosslinking agent to the polymer backbone (structure III). The remaining chloromethyl group can react either with a styrene unit of

−CH₂−CH−

S

O

O

−CH₂−CH−

Structure (III)

−CH₂−CH−

CH₂

H₃C−
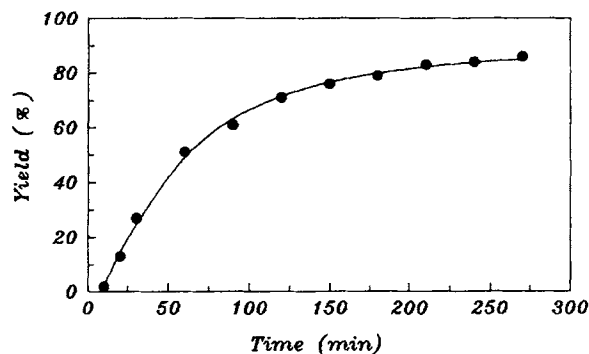
CH₃

CH₂

−CH₂−CH−
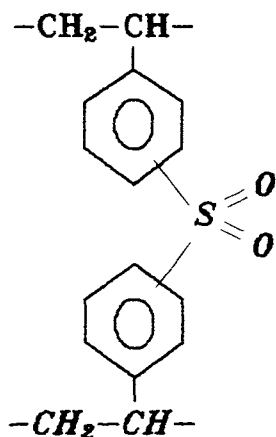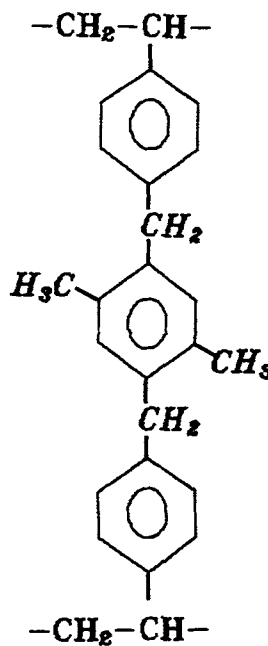
Structure (IV)

Figure 2 Crosslinking reaction yield as a function of time (50°C, sulfuric acid concentration = 3 mL/g PS, 4% crosslinking agent).

the polymer chain or with another molecule of DCMDMB. Since the second reaction is nonprobable because of relative concentration in the majority of the networks, which is low (see also Table I) and because of reduced reactivity caused by steric inhibition due to the methyl groups in the DCMDMB, we considered structure **IV** as the most probable.

The graph in Figure 2 represents the reactivity determined as hydrogen chloride liberation. In expanding reaction times, the HCl evolution observed is related to mass transfer efficiency through the swollen particles.

Molecular Structure

The average molecular weight between crosslinks ($\bar{M}_c$) of the products after crosslinking and sulfonation in a "one-pot" process was determined using a modified Flory–Rehner equation[14]:

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{\ln(1 - v_{2,s}) + v_{2,s} + x_1 \cdot v_{2,s}^2}{(V_1/\bar{v}) \cdot \left(\mu_{2,s}^{1/3} - \frac{\mu_{2,s}}{2}\right)} \quad (1)$$

where V_1 is the molar volume of the swelling agent; $\bar{v}$, the specific volume of the polymer; x_1, the Flory interaction parameter; $\bar{M}_n$, the number-average
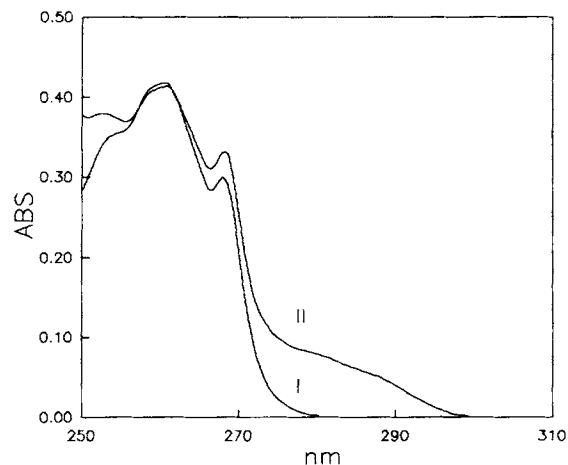

Figure 3 Ultraviolet spectra of linear (I) and grafted (II) polystyrene.

molecular weight of the linear polymer; and $v_{2,s}$, the equilibrium volume fraction of polymer in the swollen particles.

The $v_{2,s}$ was calculated by the expression[15]

$$\frac{1}{v_{2,s}} = \frac{1}{v_{2,app}} - dp \cdot p \quad (2)$$

where $\mu_{2,app}$ is the apparent volume fraction of the polymer in the swollen state; p, the porosity of the network in cm^3/g; and dp, its density. These quantities were measured gravimetrically, as described in the Experimental section. For swelling experiments, a concentrated aqueous NaCl solution was prepared to eliminate the ionic contribution of the sulfonic groups to swelling in the polar solvents. The solvent molar volume was 19 mL/mol,[9] its density was 1.084 g/cm^3, while the Flory's interaction parameter for sulfonated polystyrene approaches to 0.5.[9] The number-average molecular weight of the linear polymer was 1.18×10^5. It was assumed that the density of the network was that of the linear analog, experimentally determined as 1.05 g/cm^3. Thus, the specific volume was 0.95 cm^3/g.

Table I Molecular Weight between Crosslinks in Crosslinked Sulfonated PS

X	$\mu_{2,app}$	p	$v_{2,s}$	$\bar{M}_c$	$\bar{M}_{c,t}$	$\bar{M}_{c,t}/\bar{M}_c$
0.005	0.078 ± 0.003	0.121	0.079	25400	41600	1.6
0.01	0.109 ± 0.006	0.202	0.112	13000	20800	1.6
0.02	0.165 ± 0.004	0.135	0.169	4700	10400	2.2
0.02	0.158 ± 0.004	0.115	0.161	5300	10400	2.0
0.04	0.205 ± 0.005	0.205	0.214	2400	5200	2.2
0.08	0.228 ± 0.010	0.194	0.239	1700	2600	1.5
0.16	0.303 ± 0.014	0.184	0.322	700	1300	1.9

Table II Sulfonation Reaction Conditions and Ion-Exchange Capacity

No.	% w/w Crosslinking Agent	Sulfonating Agent	Temp (°C)	IEC (meq/g)
1	1	H_2SO_4	78	5.33 ± 0.10
2	2	H_2SO_4	78	5.26 ± 0.03
3	4	H_2SO_4	50	4.13 ± 0.09
4	4	H_2SO_4	78	4.85 ± 0.05
5	4	SO_3	30	4.72 ± 0.02
6	8	H_2SO_4	78	4.70 ± 0.15
7	16	H_2SO_4	78	4.56 ± 0.16
8	32	H_2SO_4	78	4.39 ± 0.05

The theoretical molecular weight between crosslinks ($\bar{M}_{c,t}$) was calculated using the equation[15]

$$\bar{M}_{c,t} = 2Mo/X \qquad (3)$$

where Mo is the molecular weight of the styrene unit, and X, the molar ratio of the crosslinking agent to polymer units. The results of these calculations are presented in Table I. In this table, rows 1–3 and 5–7 were performed in the "one-pot" cross-linking and sulfonation procedure using concentrated sulfuric acid as the sulfonation agent, whereas row 4 was performed using oleum 65%. The results of Table I show a substantial increase in the densities of crosslinks compared to the calculated $\bar{M}_{c,t}$, which is attributed to be due to sulfone crosslinking represented in structure **II**.

The ultraviolet spectra of the material in early stage (3 min crosslinking reaction time), when mostly grafting had occurred, were also taken using the solution technique for the wavelength range of 250–310 nm. The spectra of the grafted PS was compared to that of the linear polymer in Figure 3. The shoulder observed at 278 nm characterizes PS grafted in the p-position.[11]

Properties

The prepared crosslinked and sulfonated spherical particles in the "one-pot" procedure were also tested for ion-exchange properties for H^+ and Na^+. The results obtained are summarized in Table II. High ion-exchange capacities (IEC) are observed that depend upon the degree of sulfonation and the degree of crosslinking. Sample 3 corresponds to the product of the crosslinking reaction at 50°C. It is obvious that sulfuric acid acts also as the sulfonating agent under the reaction conditions. Further treatment is required without isolation or purification of the crosslinking products, employing sulfuric acid or oleum to obtain high ion-exchange capacity prod-

ucts. Therefore, the procedures described above are indicative of a simple and reliable approach to sulfonated ion-exchange resins.

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