

How to maintain the morphology of styrene-divinylbenzene copolymer beads during the sulfonation reaction

Ana Jaqueline Barreto de Oliveira^a, Alcino Palermo de Aguiar^{a,*},
Mônica Regina Marques Palermo de Aguiar^b, Luiz Claudio de Santa Maria^{b,*}

^a*Departamento de Engenharia Química, Instituto Militar de Engenharia, Praça General Tibúrcio, 80, Rio de Janeiro/RJ, CEP 22290-270, Brazil*

^b*Instituto de Química, Universidade do Estado do Rio de Janeiro Rua São Francisco Xavier, 524, Rio de Janeiro/RJ, CEP 20559-900, Brazil*

Received 24 May 2004; received in revised form 2 December 2004; accepted 9 December 2004

Available online 25 December 2004

Abstract

This work aims to describe the use of acetyl sulfate as sulfonating reagent of microporous beads based on styrene (STY) and divinylbenzene (DVB) which were prepared by aqueous suspension copolymerization. The copolymer was chemically modified by two different sulfonating agents, namely sulfuric acid and acetyl sulfate which is prepared “in situ” by mixing acetic anhydride and sulfuric acid. The morphologic features of resin beads were analyzed by optical microscopy (OM) and by scanning electron microscopy (SEM). The sulfonic group incorporation into the copolymer network was verified by infrared spectroscopy (FTIR) and quantified by using a standardized NaOH solution. The bead morphology maintenance depends on the sulfonating agent and reaction conditions.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Polymers; Porosity; Sulfonation reaction; Poly(styrene-co-divinylbenzene); Morphology

1. Introduction

Functionalized polymer networks have gained great importance in many fields of scientific research as well as in industrial applications. These applications will highly increase due to the variety of possible modifications in chemical and physical properties of these materials [1]. Cross-linked copolymers with different porosity prepared from styrene (STY) and divinylbenzene (DVB) are of major interest, taking into consideration their use for preparing ion exchange resins by the introduction of diverse functional groups (polar or not) as such as alkyl, benzoyl, acetyl,

hydroxymethyl and sulfonic derivatives [2]. These copolymers can be mainly employed as catalytic support [3] and for solid-phase extraction (SPE) [4–7].

At low dilution and small DVB content, the obtained copolymer beads are generally microporous or gel-type. The diluent thermodynamic affinity for STY-DVB copolymer determines positively its porous structure and swelling properties. It is a well-known fact that the introduction of functional groups like-SO₃H into the STY-DVB matrices changes their network morphology [8–12]. The sulfonic group into the STY/DVB copolymer bead structures can be introduced by chemical modification with different sulfonating agents, such as concentrated sulfuric acid [1,3,7,13,14], sulfur trioxide [8] and chlorosulfonic acid [12,15–18]. However, during the modification reaction, it is possible to affect or even destroy completely the bead morphology due to the action of sulfonating agent and reaction conditions.

Our group has investigated the STY/DVB copolymer sulfonation with 8% of cross-linking degree. The sulfonating agents employed were: concentrated sulfuric acid or

* Corresponding authors. Alcino Palermo de Aguiar is to be contacted at Departamento de Engenharia Química, Instituto Militar de Engenharia, Praça General Tibúrcio, 80, Rio de Janeiro/RJ, CEP 22290-270, Brazil. Fax: +55 21 25467059. Luiz Claudio de Santa Maria, Instituto de Química, Universidade do Estado do Rio de Janeiro Rua São Francisco Xavier, 524, Rio de Janeiro/RJ, CEP 20559-900, Brazil. Fax: +55 21 2587 7227.

E-mail addresses: alcino@ime.eb.br (A.P. de Aguiar), lscm@uerj.br (L.C. de Santa Maria).

acetyl sulfate. In this respect, to the best of our knowledge the acetyl sulfate has been reported as sulfonating agent particularly for molecular low weight compounds or for polymers without cross-link [19]. In the present work, we have investigated the efficiency of both sulfonating agents and their effects on the bead morphology.

2. Experimental part

2.1. Materials

STY and DVB (grade of 45% of DVB isomers, containing a mixture of DVB and ethylvinylbenzene) were kindly donated by Petroflex and Niriflex, respectively, and used as received. α, α' -Azo-bis-isobutyronitrile (AIBN, donated by Metacril, Brazilian) was purified by recrystallization from methanol. 2-Hydroxyethyl-celullose (HEC, Cellosize QP100MH) was donated by Union Carbide and used as received. The other reagents were commercially purchased, namely IR120 plus sulfonic resin (Sigma-Aldrich, exchange capacity=1.9 mmol/g of resin, value offered by supplier), gelatin, sodium chloride, propanone, 1,2-dichloroethane, acetic anhydride, methanol, isopropanol, toluene, concentrated sulfuric acid, glacial acetic acid, spectroscopic potassium bromide (Vetec Química Fina, Brazil) with P.A. degree and used as received. Aqueous solutions were prepared using distilled deionized water.

2.2. Copolymer synthesis

The aqueous suspension copolymerizations of STY/DVB was carried out in a 1 L, three-necked, round-bottomed flask glass reactor fitted with mechanical stirrer, reflux condenser with a silicon oil seal at its top. Aqueous phase (AP) was composed by gelatin (0.06 wt.% in relation to AP) and 2-hydroxyethyl-celullose (0.15 wt.% in relation to AP) and NaCl (0.6 wt.% in relation to AP). The organic phase (OP) was composed by STY 3 (0.82 mol), DVB (0.18 mol), toluene employed as diluent (50% v/v in relation to the monomers) and AIBN used as initiator (1.0 mol% in relation to the monomers). OP was added slowly to AP previously prepared under stirring at room temperature, employing AP/OP ratio=4/1. These two phases were maintained under stirring (300 rpm) at room temperature during 10 min. Hence the suspension copolymerization system was kept under stirring at 65 °C during 24 h. The resin beads was thoroughly washed with warm water (8 portions of 500 mL) and with propanone (3 portions of 500 mL) and dried at 60 °C.

2.3. Copolymer beads sulfonation

The copolymers based on STY/DVB were sulfonated using two distinct methodologies employing two different sulfonating agents: concentrated sulfuric acid (Method A)

[1,3,7] and acetyl sulfate (Method B) [19]. In both cases the copolymer beads were previously swollen with glacial acetic acid or 1,2-dichloroethane during 24 h.

2.3.1. Method A

Previously the copolymer beads (3 g) were swollen with 30 mL of glacial acetic acid or 1,2-dichloroethane in a 250 mL, three-necked, round-bottomed flask glass reactor. Concentrated sulfuric acid (50 mL) was added slowly, under mechanical stirring, at room temperature. The system was warmed slowly until reach the desired temperature. The beads were filtered off, washed with warm water, then extracted with methanol in a Soxhlet (around 30 cycles) and finally dried at 60 °C. The synthesis parameters, such as swelling agent, temperature and the time of reaction were presented in Table 1.

2.3.2. Method B

Firstly, the sulfonating agent was previously prepared by the addition of concentrated sulfuric acid in a mixture containing acetic anhydride and 1,2-dichloroethane, in ice bath. The resultant solution has become viscous and pale yellow. The prepared acetyl 4 sulfate was added slowly, under mechanical stirring, at room temperature, in a 250 mL, three-necked, round-bottomed flask glass reactor containing the swollen copolymer (3 g) in 1,2-dichloroethane. The system was warmed slowly until reach the desired temperature. The beads were filtered off, washed with warm water, then extracted with methanol in a Soxhlet (around 30 cycles) and finally dried at 60 °C. The synthesis parameters, such as swelling agent, proportion between resin and sulfonating agent, temperature and the reaction time were presented in Table 2.

2.4. Characterization of copolymer modified and unmodified

The unmodified copolymer beads were characterized by apparent density (d_a) and swelling degree, which was determined in a graduated cylinder [18]. The swelling degree (%S) of copolymers in acetic acid and 1,2-dichloroethane was calculated from the following relation $\%S = [(v_1 - v_0)/v_0] \cdot 100$, where v_1 is the volume of swollen resin after 24 h and v_0 is the volume of dry state [18]. The

Table 1
Sulfonation reaction of the STY/DVB copolymers using concentrated sulfuric acid

Reaction number	Swelling agent	Temperature (°C)	Time (h)	EC ^a (mmol/g of resin)
RM01	Acetic acid	100	1.5	1.0
RM02	Acetic acid	120	1.5	2.1
RM03	Acetic acid	85	1.5	0.4
RM04	Acetic acid	50	8	0.3
RM05	Acetic acid	27	24	0.2
RM06	1,2-Dichloroethane	85	2	2.2

^a EC=exchange capacity.

Download English Version:

<https://daneshyari.com/en/article/9808695>

Download Persian Version:

<https://daneshyari.com/article/9808695>

[Daneshyari.com](https://daneshyari.com)