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Crosslinked PS-DVB microspheres with sulfonated polystyrene brushes as new generation of ion exchange resins

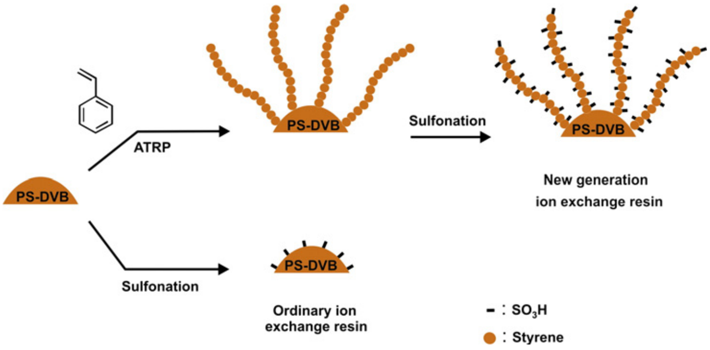
Ozlem Ozer, Ahmet Ince, Bunyamin Karagoz, Niyazi Bicak *

Istanbul Technical University, Department of Chemistry, Maslak 34469, Istanbul, Turkey

HIGHLIGHTS

- ► SI-ATRP of styrene yields polystyrene brushes on PS-DVB microspheres.
- ► Sulfonation of the brushes gives high capacity cation exchange resins.
- ► These new resins carry ion exchange groups on flexible graft chains.
- ► Whereas in ordinary resins the exchanging groups are located on bead surface.
- ► Flexibility of the graft chains makes the ion exchange faster.

GRAPHICAL ABSTRACT



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ABSTRACT

Generation of sulfonated linear polystyrene brushes on poly (styrene–divinylbenzene) (PS-DVB) microspheres and their ion exchange characteristics are reported, for the first time. Two resin materials bearing different chain lengths of sulfonated linear polystyrene brushes were prepared by surface initiated atom transfer radical polymerization (ATRP) of styrene from PS-DVB microbeads (210–420 μm) and followed sulfonation. Bromoacetyl groups (0.81 mmol g^{-1}) incorporated to the microbeads via acetoxymercuration route were employed as ATRP initiating sites to create non-hydrolyzable linkages between the PS graft chains and bead core. The standard analytical methods and FT-IR spectroscopy techniques were used for characterization of the materials.

Ion exchange characteristics (capacity, kinetics and regeneration behaviors) of the resulting materials were investigated in exchange with some divalent metal ions such as Ca (II), Mg (II), Ni (II) and Cu (II) ions in water. Correlation of the exchanged metal concentrations with the sulfonic acid group contents, implied formation of metal mono and disulfonate moieties in the exchange process. High capacities (as high as 1.5–2 times of the commercial resins) and rapid equilibration of the ion exchanges (i.e. less than 1 min) were determined as typical characteristics of the newly designed ion exchange materials.

1. Introduction

Utilization of ion exchange resins in water processing has been one of the traditional arts in industry. Historically, alumina-silicates and phenol-formaldehyde based ion exchange materials introduced in 1940's have been replaced almost completely with PS-DVB based resins in recent years [1,2]. Sulfonic acid functional PS-DVB resins, so called “strong-acid cation-exchange resins” have also found extensive use as solid acid catalysts in many chemical processes, such as dehydration of alcohols to olefins or ethers [3], alkylation of phenols [4], addition of alcohols to olefins [5], manufacturing of bisphenol-A from phenol and acetone [6] and so on. The subject has been reviewed a few times. Gelbard [7], Alexandratos [8], Olah et al. [9] and Chakrabarti and Sharma

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* Corresponding author. Tel.: +90 2122853261; fax: +90 2122856386.
E-mail address: bicak@itu.edu.tr (N. Bicak).

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[10] gave detailed accounts on the applications of polystyrene-based ion-exchange resins ranging from alkylation of aromatic nucleus with olefins and alkyl esters, isomerization of alcohols to synthesis of esters, acetals, thioacetals and ethers. Ion exchange resins have also found broad application in "ion chromatography", which is a powerful analytical tool for precise assessment of ions especially in blood or urine [11,12]. Another application area of ion-exchange materials is "ion-exchange membranes" in which a swollen polyelectrolyte gel carrying sulfonic acid or quarternary amino groups involve in the ion exchange processes. Combination of such systems with electrodialysis allows large-scale water desalination [13,14]. Ongoing efforts in the area have led to emerging perfluorinated sulfonic acid resins such as Nafion® and Amberlyst-15. Having Hammett acidity (H_0) of 12, these materials show "super acid" behavior and excellent catalytic effect in organic reactions [15]. These materials have been demonstrated to provide good proton transfer media in the fuel cells [16].

Perhaps the most significant development in this area is commercialization of a new class of polymers, "hypersol macronets" in recent years by Purolite Company. These resins obtained by post crosslinking of styrene–divinylbenzene polymers in swollen state exhibit very high surface area (up to 900 $m^2\ g^{-1}$) and isoporous network structure as reported by Tsyurupa and Davankov [17,18]. Recently the "Macronet" concept has been adopted for preparing nonfunctional nanoporous styrene–divinylbenzene resins capable of reversible hydrogen storage [19].

It was considered that, sulfonic acid functional polyelectrolytes tethered to solid microspheres might show interesting ion exchange and catalytic behaviors. In such a structure, flexibility and partial mobility of polyelectrolyte brushes are expected to provide nearly homogenous reaction conditions and rapid interaction with the target ions. There appears no report on synthesis of such ion exchange materials, so far. This would be the first report on designing of such topologically new ion exchange resins.

Since sulfonic acid group is a strong acid, the poly(sulfonic acid) brushes will be fully ionized and take expanded form due to Coulombic repulsion between the graft chains. The result of this phenomenon would be a rapid ion exchange. To prove this assumption, in the present work, we studied design of a special resin with a crosslinked PS-DVB bead core and a hydrophilic shell layer consisting of sulfonated PS brushes. Ion exchange behaviors of the sulfonate groups located on partially mobile polystyrene brushes were investigated and compared with those of commercial ion exchange resin, Amberjet 1200Na.

2. Experimental

2.1. Materials

Divinylbenzene (DVB, E. Merck) and styrene (Aldrich) were redistilled under vacuum prior to use. Bromoacetyl bromide (Aldrich), Azobis(isobutyronitrile) (AIBN, Fluka), P_2O_5 (E. Merck), mercuric acetate (E. Merck), Amberjet 1200Na and all the other chemicals were used as purchased, unless otherwise stated. CuBr was freshly prepared as given in the literature [20]. The ATRP ligand, H-TETA (1, 1, 4, 7, 10, 10-hexakis [hexyl1, 4, 7, 10-tetraazadecane]) was prepared by action of triethylene tetramine upon 1-bromohexane as described before [21]. The starting material, crosslinked PST-DVB (10%) microspheres were prepared by suspension polymerization using Gam Arabic as stabilizer, according to literature method [22]. The bead product was dried, sieved and 210–420 μm size of fraction was used for the sulfonation in the next step.

2.2. Characterizations

FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer. Metal concentrations were assigned either by complexometric methods using EDTA as complexing reagent or by atomic absorption spectroscopy technique, using Shimadzu AA-6300 atomic absorption spectrometer. In the complexometric determinations, the equivalence points were assigned by using special indicator of each metal ion, given in the text books. Kinetic measurements were carried out by conductometric method using Hanna Instruments HI-9812-5 pH/EC/TDS/°C Meter. Photo images of the new resin material were recorded using Olympus Biological Microscope CX-31.

2.3. Incorporation bromoacetyl groups onto PS-DVB microsphere

Incorporation of bromoacetyl groups into PS-DVB microspheres was performed in three steps, i) acetoxymercuration by action of mercuric acetate in glacial acetic acid, ii) exchange of acetate ion with chloride using saturated NaCl solution and iii) followed reaction with bromoacetyl bromide, as reported before [22].

2.4. Determination of the bromine content

The bromoacetyl group content of the resulting bead product was assayed by gravimetric analysis of bromide, in which bromide ion was first liberated by boiling 0.42 g of the bromoacetylated bead sample with 10 mL methanolic NaOH solution (5 M) for 8 h. The mixture was filtered and washed with distilled water (10 mL) and neutralized with nitric acid. The filtrate and washings were combined and the solution was concentrated by evaporation 2/3 of the original volume. Dry weight of silver bromide precipitated by 15 mL $AgNO_3$ solution (0.1 M) revealed 0.81 mmol bromine per gram of the polymer.

2.5. Surface initiated ATRP of styrene from PS-DVB microspheres

This was performed according to the procedure reported elsewhere [22]. In a 100-mL three-necked canonical flask equipped with a reflux condenser and a nitrogen inlet, 5.0 g bromoacetylated bead sample and 40 mL styrene (0.35 mol), 2.53 g (4.05 mmol) H-TETA and 0.58 g CuBr (4.05 mmol) under nitrogen atmosphere were added. The reaction was conducted at 90 °C under continuous stirring for 6 and 24 h. The reaction mixture was then allowed to cool to room temperature, diluted with 50 mL THF and filtered. To remove copper residues the product was transferred into acetic acid THF mixture (2:1) and shaken on a shaker for 1 h. The mixture was filtered, washed with THF (40 mL), methanol (40 mL) and ether (30 mL). The products were dried overnight at 60 °C under vacuum.

2.6. Sulfonation of the resin with PS brushes

Seventy mL of H_2SO_4 (96%) was mixed with 7.1 g P_2O_5 (0.05 mol) and stirred for 30 min and cooled to 0 °C in an ice-bath. Meanwhile 10 g of bead sample with PS surface brushes was swelled in 60 mL CH_2Cl_2 for 30 min. The acid mixture was slowly added to this mixture at 0 °C and left to stand for 14 h at room temperature. The acid residues were removed by filtration. The sulfonated beads were added portion wise to 500 mL of ice water while stirring vigorously. The product was collected by filtration and washed several times with water (5×250 mL). The product was stored in wet state, as in the case for the commercial ion exchangers.

2.7. Determination of the sulfonic acid contents

Acid content of the resin samples was determined by titration method. In a typical procedure, 0.5 g resin sample was added to 10 mL 1.0 M NaOH solution and shaken for 1 h at room temperature. The mixture was filtered and 2.0 mL of the filtrate was titrated with 0.1 M HCl solution using phenolphthalein as a color indicator. The titer consumptions, 13.6 and 15.8 mL revealed a sulfonic acid contents of 3.0 and 4.3 mmol g^{-1} for the low and high grafted samples respectively.