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Novel flexible styrenic elastomer cation-exchange material based on phenyl functionalized polystyrene-butadiene copolymer

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ABSTRACT

The sulfonated phenyl functionalized polystyrene-butadiene random copolymer was synthesized for application as flexible ion-exchange material. The polymer was prepared through phenyl functionalization via thiol-ene reaction and sulfonation of the base polystyrene-butadiene copolymer with different vinyl contents and phenyl contents. Sulfonation on phenyl functionalized polystyrene-butadiene copolymer was carried out in 1,2-dichloroethane at room temperature using the acetyl sulfonate as the sulfonation agent which was prepared from the reaction of acetyl acetate with sulfuric acid. The sulfonation degrees were adjusted from 7.3 mol% to 24.3 mol% determined by elemental analysis (EA) with great ion exchange capacity (0.60–2.26 meq/g), conductivity (0.47–6.1 mS/cm) and lower water uptake (5.1–12.8 wt.%). These excellent characteristics lead to great potential using as the flexible ion-exchange material.

Introduction

Ion exchange materials are the polymers containing cationic or anionic functional groups, which play an important role in an active separator in various industries because of their superior selectivity for specific ions and wide applicability in fuel cells, desalination of seawater, recovery of valuable metals from effluents and other purposes [1–4]. Nafion (Dupont), a perfluoroether sulfonic acid polymer has been the most frequently used as the ion-exchange material due to its superior chemical/mechanical stability and high proton conductivity, but the high cost of the material is still one of the barriers against practical industry applications [5–7]. An important direction in new ion exchange material development is the preparation of homogeneous membrane based on sulfonated aromatic polymers with much lower cost.

Recently, various investigations have been pointed out the utility in sulfonated aromatic polymers, such as polystyrene [8], poly(ether ether ketone) [9,10], polyimide [11], poly(phenyleneoxide) [12], poly(ether sulfone) [13–16] and poly[(sodium 4-styrensulfate)-methacrylic acid-methyl methacrylate] [17]. Also, a number of investigations have demonstrated that increasing the sulfonic acid content in the polymer results in increased ion-exchange capacity with low-cost [18,19]. Among them, the sulfonated polystyrene is most widely used as ion exchange material due to its good chemical stability and excellent characteristics for functionalization. However, the membranes of highly sulfonated aromatic backbone polymer swell excessively in water and have poor mechanical properties. Also, a styrene-divinyl benzene copolymer has been used due to its improved mechanical properties and decreased swelling compared to PS [20]. But the expensive and brittle property limits its utility in ion exchange material. Therefore, to overcome these problems, it is necessary to develop membranes with flexibility, low cost and relatively high ion exchange capacity.

Styrene-butadiene rubber (SBR) is one of the most versatile copolymer rubber compounds, produced from a copolymer of styrene and butadiene. It exceeds all other synthetic rubbers in consumption due to its excellent elasticity and resistant to abrasion. The styrene moieties in SBR have provided the sulfonation feasibility, which could be regarded as the potential flexible ion exchange materials [21].

Herein we report on a novel process for the formation of an improved gel-free sulfonated phenyl functionalized polystyrene-butadiene random copolymer (PSB-T-S) having flexibility and

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relatively high ion-exchange capacity. Moreover, compared with Nafion, PSB(L)-T-S would have the advantages on price (~\$1.50/lb), and PSB(L)-T-S would also the advantage on mechanical property compared with sulfonated polystyrene or its derivative of styrene-divinylbenzene copolymer because SBR is a synthetic rubber which has excellent elasticity, physical and viscoelastic properties. By using SBR as the base material, the flexible PSB(L)-T-S film could be easily obtained. The synthesis process comprises: (1) The introduction of phenyl groups into polystyrene-butadiene random copolymer (PSB) via thiol-ene reaction to form phenyl functionalized PSB (PSB-T) in order to introduce more sulfo groups into the polymer backbones; (2) The PSB-T was sulfonated by using acetyl sulfonate to form sulfonated polymer (PSB-T-S).

Experimental

Materials

Styrene, tetrahydrofuran (THF), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) were stored over freshly ground calcium hydride (reagent grade, Aldrich) with stirring for at least one day and then distilled into a two-neck reactor fitted with silicone rubber seal and a Rotofol® stopcock just before use by the high-vacuum line (10^{-6} Torr). Methanol, 2-propanol (extra grade, Samchun) was degassed on the vacuum line and then bubbled over one hour with nitrogen gas. Solutions of sec-butyllithium (1.4 M in cyclohexane, Aldrich) were analyzed using the direct titration method with 2-butanol. l, 10-phenanthroline was used as the indicator [22]. 2,2-Azobis(4-methoxy-2,4-dimethyl- valeronitrile) (V-70) was purified by recrystallization from ethanol. Benzyl mercaptan (BM), 1,3-butadiene, 1,2-dichloroethane (DCE), *N,N*-dimethylformamide (DMF), sufur acid (95%), acetic anhydride were purchased and used without further purification.

Synthesis of styrene-butadiene copolymer

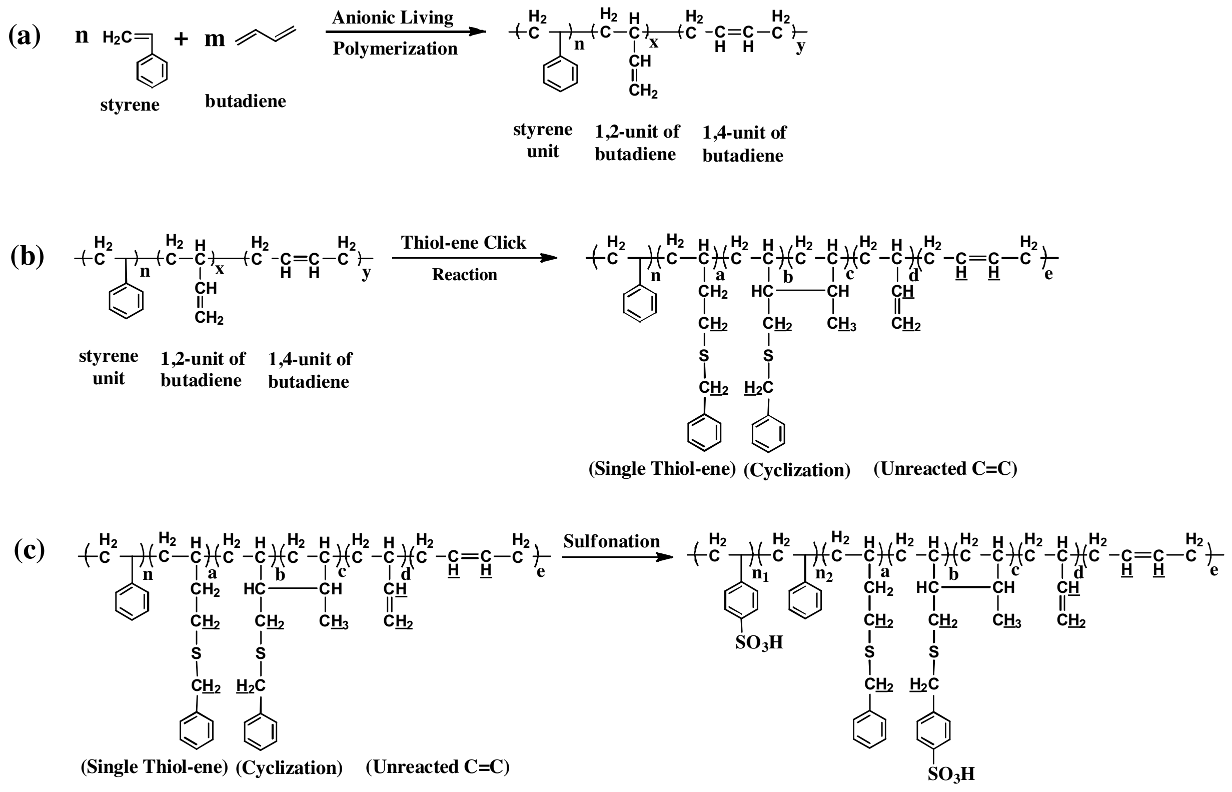
Polystyrene-butadiene copolymer (PSB) were prepared via anionic polymerization. Buchi glasuster reactor was equipped with a mechanical stirrer, nitrogen stream tube and temperature control via cooling ethylene glycol. The composition of styrene and butadiene (25/75, mol/mol) was premixed in cyclohexane with 10 wt.% of monomer concentration. This polymerization system was initiated by adding *s*-butyllithium (*s*-BuLi), followed by the addition of 0.42-fold THF ([THF]/[Li] = 0.42) or 1-fold TMEDA ([TMEDA]/[Li] = 1) at 50 °C. The mixture was stirring for another 8 h, quenched with degassed methanol. The resulting PSB was purified by repeated precipitation from methanol three times to remove initiator system, then dried in a vacuum oven at 60 °C to constant weight.

Phenyl functionalization of polystyrene-butadiene copolymer

The phenyl functionalized polystyrene-butadiene copolymer (PSB-T) was synthesized from the base PSB with 8.8% and 57.1% vinyl contents via thiol-ene reaction. The PSB was dissolved in 500 ml pure THF under nitrogen atmosphere, followed by the addition of BM and V-70 at the ratio of [BM]/[vinyl]/[V-70] = 5/1/0.3. The functionalization was carried out at 40 °C for 24 h and cooled down at 0 °C. The result PSB-T was purified by repeated precipitation from methanol three times to remove unreacted BM and initiator system, then dried in a vacuum oven at 60 °C to constant weight.

Sulfonation of phenyl functionalized polystyrene-butadiene random copolymer

The resulting PSB-T samples were dissolved in 150 ml of 1,2-dichloroethane, followed by the bubbling with nitrogen gas for



Scheme 1. Synthesis of sulfonated phenyl functionalized styrene-butadiene copolymer.

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