



## Preparation of Cation-Exchange Resin from Styrene-Divinylbenzene Copolymer Obtained by Suspension Polymerization Method

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### ABSTRACT

Suspension Polymerization was used for the synthesizing of cross-linked polystyrene-divinylbenzene (PS-DVB) containing 16% DVB. For application of these resins as columns' filler in ion-exchange chromatography; the sulfonation reactions were done by acetyl sulfate and in the presence of methylene chloride as solvent at 60°C. The exchange capacities of cation exchange resins X-16 (CE=225 meq/100g) was determined by titration procedure. The structure of PS-DVB resin was investigated by scanning electron microscope (SEM) technique. The SEM images showed that the porous structure of PS-DVB resin was approximately maintained intact after sulfonation reaction. TGA and FTIR techniques were used to investigate the thermo gravimetric analysis and structures of obtained resins, respectively.

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### Introduction

Ion-exchange resins are used to replace the magnesium and calcium ions found in hard water with sodium ions. When the resin is fresh, it contains sodium ions at its active sites. When in contact with a solution containing magnesium and calcium ions (but a low concentration of sodium ions), the magnesium and calcium ions preferentially migrate out of solution to the active sites on the resin, being replaced in solution by sodium ions. This process reaches equilibrium with a much lower concentration of magnesium and calcium ions in solution than that before. The suspension polymerization technique has generally been used for the preparation of macroporous copolymer networks in the form of beads of diameter ranging between 0.1 and 1.5 mm. The copolymerization and crosslinking reactions taking place in the monomer–diluent droplets result in the formation of beads having a glassy, opaque, or milky appearance. The beads are then extracted with a good solvent to remove the soluble polymers and the diluent from the network. Mainly, water-insoluble monomers have been used in the synthesis of macroporous copolymers. In addition to the widely used PS–DVB co monomers, the classical suspension polymerization technique is the method of choice in which an aqueous phase containing additives is utilized as the continuous phase of the reaction. A precipitation polymerization method can also be used to make porous particles 4–7 mm in size [1]. Several diluents or diluent mixtures have been used for the preparation of hydrophobic porous particles including aliphatic and aromatic hydrocarbons, alcohols, esters, etc. Although the inert diluent must be soluble in the monomer mixture (organic phase) and insoluble in the continuous water phase, the organized surfactant assemblies such as inverse micelles can be used to capture monomer-insoluble diluents such as water inside the organic phase. Thus, the crosslinking copolymerization in

the continuous phase of a water-in-oil microemulsion also yields macroporous networks [2–3]. The nature of the porous structure is largely dependent on the microstructure of the micro emulsion [4, 5]. Short chain alcohols have been used as co surfactants together with conventional surfactants for the formation of micro emulsions [6–7]. For example, it was shown that water solubilized in reverse micelles can be used as a diluent in the production of porous PS–DVB copolymer beads by suspension polymerization. [8] By this technique, sodium bis (2-ethylhexyl) sulfo succinate (a surfactant commonly known as Aerosol OT or AOT) is used as the surfactant for the formation of reverse micelles. Depending on the amount of water solubilized in the micelles, the size of the water droplets inside the PS–DVB monomer mixture is different. Thus, the size of the pores is controlled by adjusting the water content in the reverse micelles prior to polymerization [2,9–10]. The free-radical crosslinking copolymerization (FCC) system for the production of macroporous copolymers includes a mono vinyl monomer, a divinyl monomer (crosslinker), an initiator, and the inert diluent. The decomposition of the initiator produces free-radicals which initiate the polymerization and crosslinking reactions. After a certain reaction time, a three-dimensional network of infinitely large size may start to form. The term 'infinitely large size', according to Flory, [5] refers to a molecule having dimensions of an order of magnitude approaching that of the containing vessel. At this point (the gel point) the system (monomer–diluent mixture) changes from liquid to solid-like state. Continuing polymerization and crosslinking reactions decreases the amount of soluble reaction components by increasing both the amount and the crosslinking density of the network. After complete conversion of monomers to polymer, only the network and the diluent remain in the reaction system.

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## Experimental

### Materials

Styrene (Merck), Benzoyl peroxide were supplied (Merck, as cross-linking agent), and used without further purification, Dichloromethane, Acetone, Trimethylamine, Toluene, from Egyptian market and were used as received. Multi-wall carbon nano tubes were supplied from Pristine MWCNTs was synthesis in EPRI in Nano lab purity of 95 wt. % an average diameter of 15 nm and lengths ranging from 0.5  $\mu\text{m}$  to 1  $\mu\text{m}$  with most of the materials closer to 1  $\mu\text{m}$ . Surfactant, Hydroxyl propyl cellulose (HB) (Merck), and Sodium dodecyl benzene sulfonate (SDS).

### Methods:

#### Synthesis of Polystyrene (PS):

Suspension polymerization of polystyrene seeds was carried out in a 250 mL round bottom flask at 75°C for 6 hours. Hydroxyl propyl cellulose (HB) (1 wt. %) was dissolved in distilled water solution (150 mL) and loaded into the reactor. Styrene (14 g) and Benzoyl peroxide (BPO) (0.12 g) were added, and the mixture solution was homogenized at 600 rpm using a mechanical stirrer to form the stable microspheres. The polymerization products were rinsed with ethanol and centrifuged repeatedly to remove any non-reacted styrene and HB. The PS microspheres were then dried in a vacuum oven at room temperature for 48 hours [11-13].

#### Synthesis of Polystyrene Divinylbenzene (PS-DVB) copolymer beads:

The PS-DVB copolymer beads were prepared by suspension polymerization technique. The initiator (Benzoyl peroxide) was dissolved in the monomers (styrene and Divinylbenzene) and the diluents. This mixture was added to the suspension solution formed by dissolving one of cellulose derivatives in deionized water. Then all were poured in 1L four neck flask fitted with a mechanical stirrer, nitrogen inlet, condenser, thermometer, and pressure indicators, and the reaction mixture was heated to 75°C and was allowed to proceed at this temperature for 6 hours and at 90°C for another 18 hours under nitrogen atmosphere with constant stirring at 300 rpm. After that, the copolymer beads were filtered and washed with dilute HCl solution and enough quantity of hot water and extracted with acetone, then dried at 150°C and sieved. In order to measure the toluene regain, the copolymer beads were swollen to equilibrium in toluene for at least one week. Then, they were washed first with acetone and finally with pure methanol [14-15].

#### Synthesis of PS-DVB and PS-DVB-CNT beads:

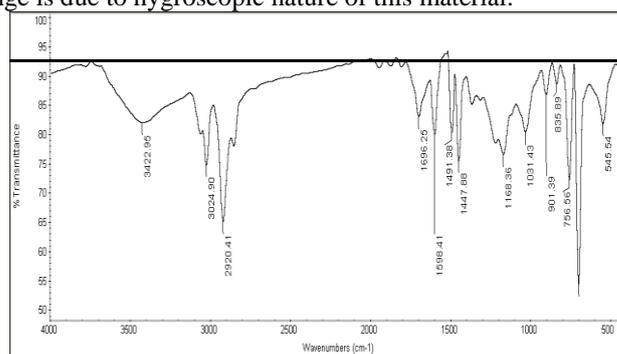
2 g polymer of PS seeds was placed in a 500mL three neck flask. Then, the emulsified solution containing 30mL SDS aqueous solution (0.2%, w/v) was added and stirred overnight. Afterwards, another emulsified mixture consisted of 30 g organic compounds and 250 mL HB aqueous solutions (1%, w/v) were prepared by an Ultrasonic Compact Hielscher UP200Ht (200W, 26 kHz) and poured into the flask for swelling. The organic compounds consisted of styrene, divinylbenzene, MWCNTs, toluene, BPO and SDS. The amount of toluene equaled to the sum of styrene and divinylbenzene, while BPO was only 1.5% of the sum (w/w). The amount of SDS was 0.25% of the HB aqueous solution (w/v). The amount of MWCNTs, which were 1% (w/w), were attempted to prepare PS-DVB-CNT particles. After 24 hours the temperature was increased to 70 °C under nitrogen atmosphere and lasted another 24 hours. Subsequently, the resulting beads were washed successively with hot water and alcohol. Then the beads were extracted with toluene for 48 hours. After washing and drying,

the resulting particle size of the stationary phase was about 20Mm [12, 16].

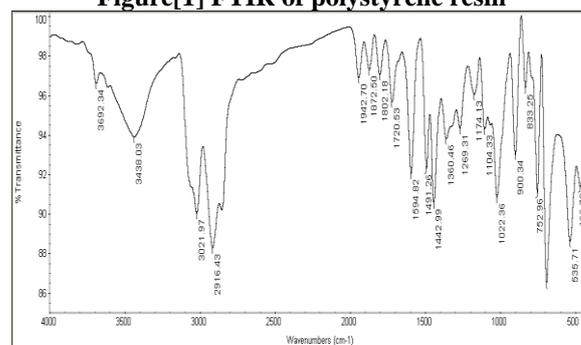
## Results and Discussion

### FTIR Analysis:

The FTIR spectra of poly styrene shown in Figure 1 appear stretching absorption peaks at 3024.38  $\text{cm}^{-1}$  for alkenyl C-H, and two peak at 752.02  $\text{cm}^{-1}$ , 905.37  $\text{cm}^{-1}$  for disubstituted Benzene. Absorption peaks of PS-DVB in Figure 2 show absorption peaks at 3021.97–2916.43  $\text{cm}^{-1}$ , 1442.99  $\text{cm}^{-1}$ , 1491.26  $\text{cm}^{-1}$  and 1594.82  $\text{cm}^{-1}$  that corresponds to the stretching and bending aromatic –CH<sub>2</sub>–, –CH– bands, respectively Absorption peaks for sulfonated PS-DVB represents S=O stretching vibration around 1123.63  $\text{cm}^{-1}$  as broad band (Figure 3). Weakness of the skeletal benzene ring vibration band at 1499.39  $\text{cm}^{-1}$  might be due to higher percentage of sulfonated portion in comparison to polystyrene part in the cross-linked core. The broad band in 1640.36–1716.00  $\text{cm}^{-1}$  range is due to hygroscopic nature of this material.

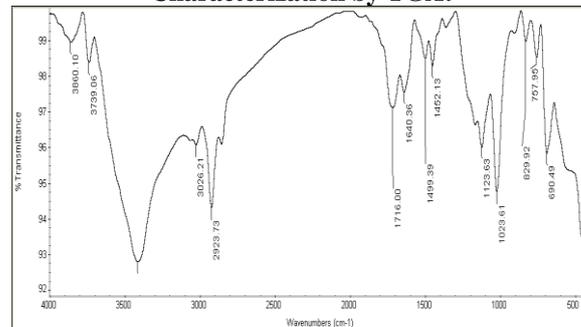


Figure[1] FTIR of polystyrene resin



Figure[2] FTIR of polystyrene di vinyl benzene resin.

### Characterization by TGA:



Figure[3] FTIR of sulfonated polystyrene di vinyl benzene resin

The TGA analysis of PS-DVB in (Figure 4) showed decomposition in two steps, the first step started at 266 °C and ending at 466 °C, meanwhile the second step started at 466 °C and ending at 600°C, this means that about 99.8% of total sample decomposed and the remaining 0.11%.

As showed if Figure 5 at 90°C the X-10 cation-exchange resin gave a weight loss of 7% which was attributed to dehydration of the hydrophilic resin surface. At 590°C an

overall weight loss 25% showed which was attributed to isolation of sulfonation group. This resin exhibited thermal stability up-to 390°C. After 390°C the degradation of resin was occurred.

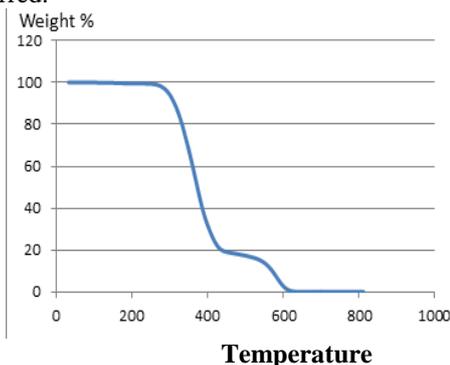
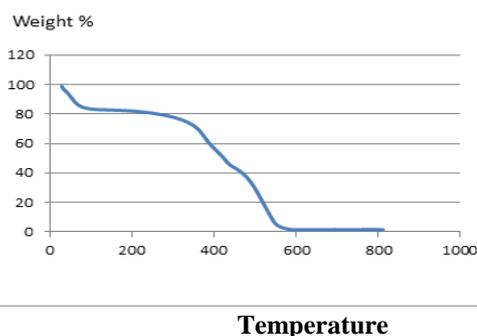


Figure [4] TGA analysis of Poly Styrene Di Vinyl Benzene Resin



Figure[5] TGA analysis of sulfonated Poly Styrene Di Vinyl Benzene Resin

#### SEM analysis:

Figures 6, 7 showed that the scanning electron micrographs (SEM) of PS-DVB (16%) copolymer compound and its sulfonated resins. As could be seen in the Figures, the cross-linked PS-DVB had high porous surface. The X-16 cation exchange resin had the porous surface along with the holes irregularly distributed.

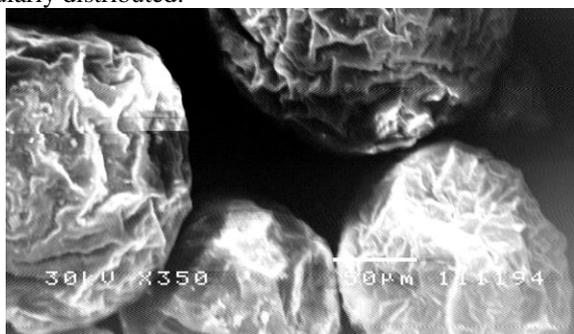


Figure [6] SEM of polystyrene di vinyl benzene resin

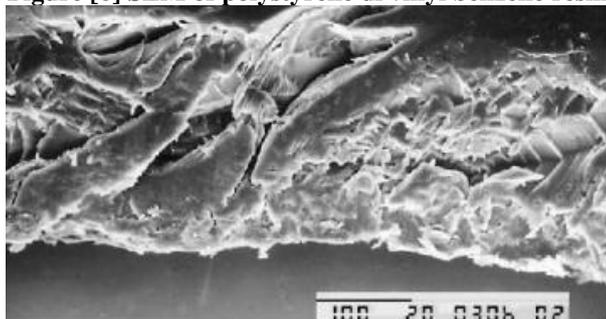


Figure [7] SEM section of cation exchange resins.

#### Exchange capacity:

During the titration of prepared resins (PSDVB-SO<sub>3</sub>H) with 0.01 mol L<sup>-1</sup> NaOH solutions in methanol it's observed that the

cationic exchange capacity of PS-DVB SO<sub>3</sub>H recorded 225.6 meq./100-g.

#### Conclusion

In this work, cation-exchange resins copolymer (styrene-divinylbenzene) was obtained by suspension polymerization method. The influences of high cross-linking reactions on internal morphology of styrene-divinylbenzene copolymers and cation exchange resins were demonstrated. The amount of DVB affected on degree of the thermal stability and anion exchange capacity of resins. The obtained exchange capacities of X-16 are 2.25meq/g, respectively. TGA, SEM and FTIR Spectroscopy techniques were used to investigate the structure of the resins.

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