



## Preparation of Anion-Exchange Resin from Styrene-Divinylbenzene Copolymer with High Cross Linking Structure

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### ABSTRACT

Styrene-divinylbenzene copolymer is a special macroporous strong base anion resin crosslinked with divinylbenzene that is specially selective for hydrophobic anions. It shows good mechanical strength and an excellent resistance to osmotic and thermal shock. The amination reactions were done by chloro dimethyl ether solvent at 45°C. TGA and FTIR techniques were used to investigate the thermo gravimetric analysis and structures of obtained resins, respectively. The exchange capacities of anion exchange resins (X-16) are 312 meq/100g as determined by titration method. Then 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 intact after amination reaction.

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### Introduction

Anion exchange materials are strong base depending on tertiary amine group, they reused in ion exchange systems where strong base predominate because it give more economical removal of sulfates and chloride ions. Chlorides and sulfates are the natural substances found in the sea water bodies in varying amounts. However, their concentrations are significantly high. Many techniques have been adopted in order to reduce the amount of chlorides and sulfates in sea water like reverse osmosis, coagulation, precipitation, electro dialysis and so on. However, these techniques are physico – chemical in nature, and are cost consuming capital cost wise as well as maintenance cost wise. Therefore, this part of the study directed to replace the traditional techniques by the prepared anion exchange resins for the removal of chlorides and sulfates from seawater via study the suitability of prepared resins as a sorbent for chloride ion removal, also, variations in the efficiency of sorption with respect to different pH, concentration and time were studied. Suspension polymerization is a heterogeneous radical polymerization process that uses mechanical agitation to mix a monomer or mixture of monomers in a liquid phase, such as water, while the monomers polymerize, forming spheres of polymer. This process is used in the production of many commercial resins, including polyvinyl chloride (PVC), a widely used plastic, styrene resins including polystyrene, expanded polystyrene, and high-impact polystyrene, as well as poly(styrene-acrylonitrile), polystyrene divinylbenzene copolymer resins and poly(methyl methacrylate)[1].

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 S–DVB comonomers, 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].

The reaction mixture consists of two phases, a liquid matrix and monomer droplets. The monomer and initiator are insoluble in the liquid phase, so they form drops within the liquid matrix. A suspension agent is usually added to stabilize the monomer droplets and hinder monomer drops from coming together. The reaction mixture usually has a volume ratio of monomer to liquid phase of 0.1 to 0.5. The liquid phase acts as a heat transfer agent, enabling high rates of polymerization with little change in the temperature of the polymerizing solution. The reactions are usually done in a stirred tank reactor that continuously mixes the solution using turbulent pressure or viscous shear forces. The stirring action helps to keep the monomer droplets separated and creates a more uniform suspension, which leads to a more narrow size distribution of the final polymer beads. The polymerization is usually carried to completion.[3] The kinetics of the polymerization within an individual bead is similar to those of typical radical polymerization [4].

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, 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

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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 [6–8]. For example, it was shown that water solubilized in reverse micelles can be used as a diluent in the production of porous S–DVB copolymer beads by suspension polymerization. Depending on the amount of water solubilized in the micelles, the size of the water droplets inside the S–DVB monomer mixture was varied. Thus, the size of the pores was 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 was produce free-radicals that 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. This work aimed to produce resin with high porosity via using high percentage of cross linking agent. The new prepared resins will having a high thermal stability for long time in addition to high exchange capacity towered monovalent and polyvalent anions. The prepared anion PS-DVB resins were characterized using infrared spectroscopy, thermal stability and electro scan microscope.

## Experimental

### Materials

Styrene, chloromethyl methyl ether (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. 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].

#### Chloromethylation of Copolymer Resins:

2.0176 g of resins, 2.5 ml of chloromethyl methyl ether, 1.1530 g of ZnCl<sub>2</sub> and 10 ml of nitrobenzene were added to a 50 ml flask equipped with refluxing condenser and anhydrous CaCl<sub>2</sub> tube. After stirring at room temperature for 5–10 min, the chloromethylation reaction was carried out at 45°C for 4 hours. After that, 0.5770 g of ZnCl<sub>2</sub> was added to the system, the polymerization was carried out at 80°C for 12 hours. The resulting polymer washed with hot deionized water, and extracted with acetone in a Soxhlet apparatus. The product was dried under vacuum to give 2.3907 g of resin [17].

#### Amination of Chloromethylated Copolymer:

A 250 mL round bottom flask fitted with magnetic stirrer was charged with 5 g of polymer beads, 150 ml of acetonitrile and 30ml of tri ethylamine, then the mixture was purged with nitrogen, deaerated under vacuum and the entire setup was placed in an oil bath over a magnetic stirrer and the mixture was refluxed at 70°C for 3 days with a continuous sweep of nitrogen into the reaction flask. The quaternized beads were filtered and successively washed with acetonitrile and methanol followed by drying under vacuum at 60°C [18].

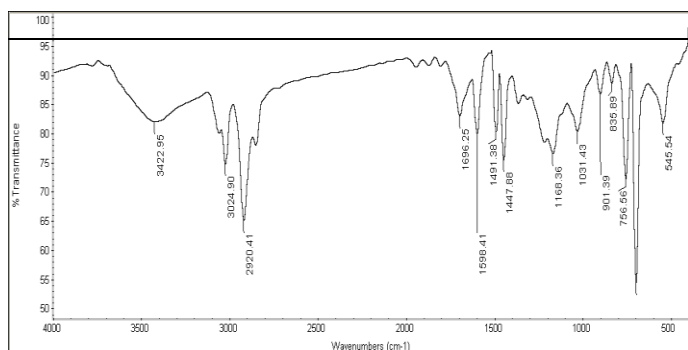
## Results and Discussion

The FTIR spectra of poly styrene shown in Figure 1 appear stretching absorption peaks at 3024.38 cm<sup>-1</sup> for alkenyl C–H, and two peak at 752.02 cm<sup>-1</sup>, 905.37 cm<sup>-1</sup> for disubstituted Benzene ring. Absorption peaks of PS-DVB in Figure 2 show absorption peaks at 3021.97–2916.43 cm<sup>-1</sup>, 1442.99 cm<sup>-1</sup>,

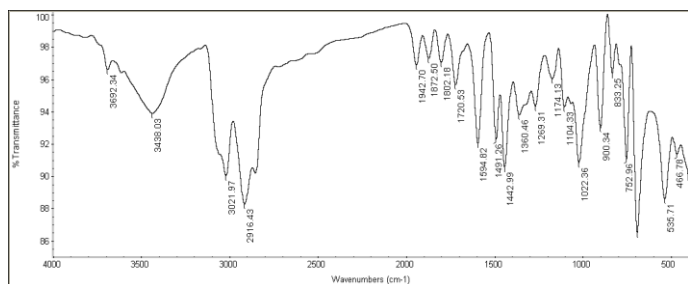
1491.26  $\text{cm}^{-1}$  and 1594.82  $\text{cm}^{-1}$  that corresponds to the stretching and bending aromatic  $-\text{CH}_2-$ ,  $-\text{CH}-$  bands, respectively

Figures 3 represent the IR adsorption peaks of chloromethylated polystyrene di vinyl benzene resin and aminated polystyrene di vinyl benzene as anion exchange resin, respectively. In this respect, the two spectrum are typically with slight difference for the latter, i.e., tow stretching weak bands appear at 1259 and 1260  $\text{cm}^{-1}$  may represent the chloromethyl group, two stretching vibration peak appear at 695–700  $\text{cm}^{-1}$  for C–Cl bond, and one beak at 3024.38 corresponding to aromatic  $-\text{CH}$ , the difference appear in the spectrum of aminated polystyrene di vinyl benzene hence the additional bands appear at 892  $\text{cm}^{-1}$  and 3442.57  $\text{cm}^{-1}$  may corresponding to aromatic  $-\text{NH}$  group.

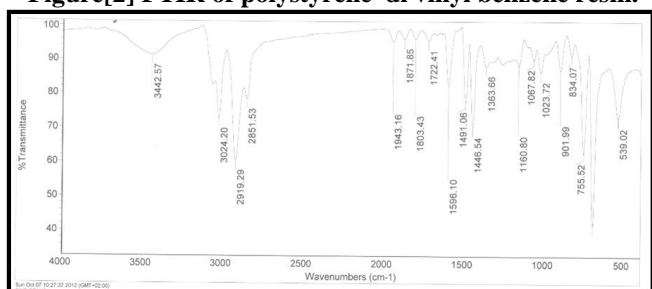
The TGA analysis of PS-DVB in Figure 4 showed decomposition in two steps, the first step started at 266 °C and ending at 466 °C, meanwhile the second step started at 466 °C and ending at 600°C, this means that about 99.8% of total sample decomposed and the remaining 0.11%. As showed if Figure 5 at 90°C the X-10 anion-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 amination group. This resin exhibited thermal stability up-to 390°C. After 390°C the degradation of resin was occurred.



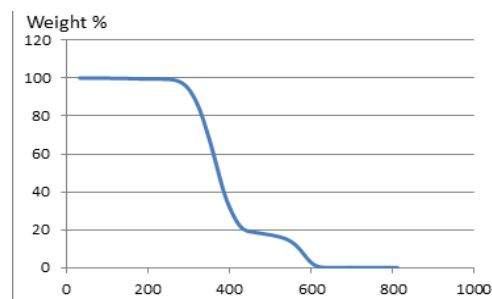
Figure[1] FTIR of polystyrene resin



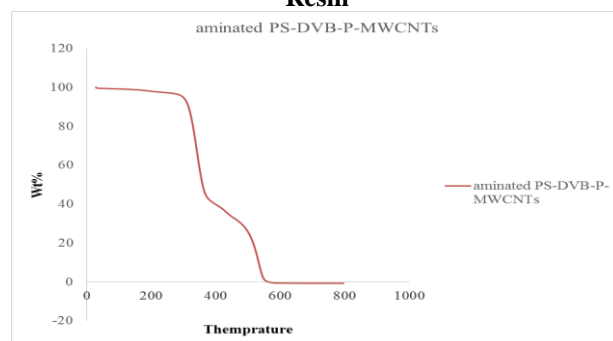
Figure[2] FTIR of polystyrene di vinyl benzene resin.



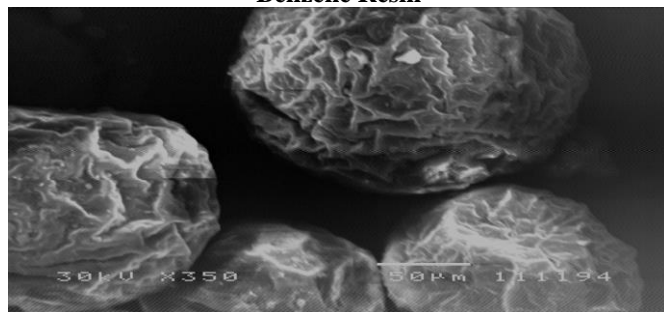
Figure[3] FTIR of aminated polystyrene di vinyl benzene resin



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



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



Figure[6] SEM of polystyrene di vinyl benzene resin.

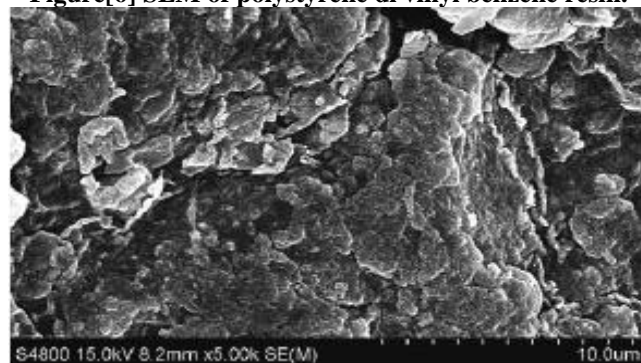


Figure [7] SEM section of anion exchange resins.

Figure 6 showed the scanning electron micrographs (SEM) of PS-DVB (16%) copolymer compound. As could be seen in the Figure 6 cross-linked PS-DVB had high porous surface. The X-16 anion exchange resin had the porous surface along with the holes irregularly distributed.

### Conclusion

In this work, anion-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 anion exchange resins were demonstrated by SEM. It was found that the amount of DVB affected on the degree of thermal stability and anion exchange capacity of resins as illustrated by

TGA analysis. The obtained exchange capacities of X-16 are 2.25meq/g. In addition to TGA, SEM and FTIR spectroscopy techniques investigate the irregular structure of the resins pores.

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