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Comparative study of strong anion exchange hypercrosslinked poly(HEMA-*co*-EGDMA-*co*-VBC) and strong anion exchange poly(Styrene-*co*-EGDMA-*co*-VBC): Synthesis and characterization

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Abstract: Strong anion exchange hypercrosslinked of poly(HEMA-*co*-EGDMA-*co*-VBC) (PHEV) and strong anion exchange hypercrosslinked of poly(styrene-*co*-EGDMA-*co*-VBC) (PSEV) were prepared *via* amination reaction with dimethylbutyl amine (DMBA) as the amination agent in dried toluene. The resins were characterized by SEM, FTIR, BET and elemental analysis. SEM results showed that there was no significant change of the particles shape after amination reaction for both strong anion exchange hypercrosslinked PHEV and strong anion exchange hypercrosslinked PSEV. Specific surface area (SSA) of strong anion exchange hypercrosslinked PHEV increase from 1035 m^2/g to 1090 m^2/g when amination reaction take place. However, SSA of strong anion exchange hypercrosslinked PHEV decreased from 124 m^2/g to 27 m^2/g. From FTIR spectra, significant drop occurred at 1265 cm^{-1} band after amination reaction of strong anion exchange hypercrosslinked PSEV but SSA of strong anion exchange hypercrosslinkedPHEV showed slightly significant drop. Elemental analysis showed that nitrogen content of strong anion exchange hypercrosslinked PHEV significantly increase from 0.10% to 1.46% resulted to high IEC value. Meanwhile, nitrogen content in strong anion exchange hypercrosslinked PSEV only showed small increment in nitrogen content from 0.36% to 0.63% led to low IEC value.

Keywords: *Hypercrosslinked polymer; Amination reaction; Strong anion exchange resin.*

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Introduction

Since years ago, considerable interest has been developed in the synthesis of ion-exchange resin having selective properties and containing selective functional groups.The main application for strong anion resin is in separation process. Quaternary ammonium is ammonium cation with four alkyl group or aryl group attached to the nitrogen atom and it carries positive charge that suitable for many applications and being known as strong anion resin. Many studies showed that positive charges in resin have potential to be used in many applications. For example, in sulfur removal,[1] phosphorus removal in wastewater,[2]separation of actinides elements in sediments and biological materials,[3] and even be used to decrease the acid value of crude low-calorie cocoa butter to an acceptable level.[4]Most of the strong anion resins used in the studies is commercially available.

Generally, conventional copolymers sorbent available commercially such as D202 anion exchange resin and Amberlite IRA 420 are normally based on styrene-divinylbenzene (DVB) copolymer which these resins show hydrophobic characteristic. This hydrophobicity is more efficient in the retention of non-polar compounds.

Meanwhile, hydrophilic polymers contain polar functional groups and it is more useful for retention of polar compounds.[5,6] Development of resin containing hydrophilic characteristic have been done since a few year ago and have received great attention from many researchers.[7,8]

Commercially ion exchange resin available also can be either gel-type or macroporous structure and usually have hydrophobic characteristics. Drawback of such ion-exchange resin is that it has limitedhydrophilic character which is in separation application, such resin useful for retention non-polar compound only and have low specific surface area (SSA). Gel-type resin have higher (SSA) (>1000 m^2/g)[1][9,10]and macroporous structure have lower than 600 m^2/g.[11]

Hypercrosslinked polymers have a great attention due to they have a few striking features such as it is display high specific surface area, very low density, chemical and mechanical stability. Thus, they were classified as a new generation of porous polymer and replace the conventional porous polymer since discovery by Davankov late 1960s.[12] Because of the unusual features of hypercrosslinked polymer, they have a vast opportunity in terms of applications for example in chromatography columns, separation and also used as

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starting material/precursor to synthesis ion exchanger resin.[11]

Starting material upon hypercrosslinking reaction or functionalization reaction can be synthesized in many ways. The polymerization techniques included dispersion polymerization and suspension polymerizationcan be carried out as the preparation of precursor resulting in different size and morphology.In this comparative study, we describe how the precursors derived from two different polymerization techniques effects on stronganion exchange hypercrosslinked resin.

Materials and Methods

Materials

The reagent used for non-aqueous dispersion (NAD) polymerization and suspension polymerization (SP)were styrene (99% grade) supplied by Aldrich (Steinheim, Germany), 4-vinylbenzyl chloride (VBC) (95% grade) supplied by Fluka (Steinheim, Germany), methanol (99.7% grade), ethanol (95% grade), poly(N-vinylpyrrolidone) 55 (PVP) (MW ~55,000), Triton X-305 and 2,2'-azobisisobutyronitrile (AIBN) (97% grade)was supplied by BDH (Poole, UK) and purified by recrystallization from methanol, 2-hydroethylmethacrylate (HEMA) (97% grade) contains 200 ppm monomethyl ether hydroquinone and benzoyl peroxide (BPO) (75% grade)purified by recrystallization from chloroform were obtained from Sigma Aldrich, Toluene (99.5% grade) was obtained from HmBG Chemical and distilled water. Inhypercrosslinking reactions, the reagents used were anhydrous 1,2-dichloroethane (DCE) (99% grade), and Ferum (III) chloride, ($FeCl_3$) (98% grade), were supplied by Sigma-Aldrich.Dried toluene (99.8% grade), dimethylbutylamine (DMBA) (99.8% grade), and methanol (99.8% grade), from Sigma-Aldrich, sodium hydrogen carbonate (99.8% grade) supplied by VWR and distilled water were used in amination reaction.All of them were used as received.

Resin preparation

In precursor polymerization, the spherical particles used as swellable precursors in the production of strong anion exchange resin, were synthesized using non-aqueous dispersion polymerisation (NAD) and suspension polymerisation (SP).[9,13] In NAD polymerizations, all of the styrene, stabilizer, co-stabilizer, initiator, and half of the VBC and ethanol were added into a 500 mL five-necked, round-bottomed flask fitted with an overhead stirrer, condenser and nitrogen inlet. The flask was then placed into an oil bath set at 70 °C, and stirred. EGDMA and the second portion of VBC were dissolved in the remaining half of ethanol at 70 °C under nitrogen inlet. One hour after polymerization had begun, EGDMA and VBC were added into the reaction vessel and reaction was carried out until 24 hours. The polymer particles that formed were washed twice with ethanol and twice with methanol by centrifugation. The particles were filtered using vacuum filtration on a 0.22 µm nylon membrane filter and dried overnight in oven at 40 °C.

In SP, dispersion medium was prepared by dissolving PVP in distilled water. Then toluene was mixed with HEMA, BPO, EDGMA, and VBC. The mixture then being transferred into the dispersion medium placed in 250 mL five-necked, round-bottomed flask fitted with a condenser and nitrogen inlet and magnetic stirrer. The reactor was flushed by nitrogen for 30 minutes before the flask was put into the oil bath. Polymerization process was conducted at 75 °C for 6 hours with constant stirring speed at 300 rpm.After polymerization, the microsphere then washed by distilled water and methanol before dry in oven at 40 °Cfor 24 hours.

The hypercrosslinking reactions the precursor particles (~1.2 g) were added into a round- bottomed flask containing DCE (40 mL) and left to swell fully under nitrogen for 1 hour. Then, $FeCl_3$ (in a 5% molar excess relative to chloromethyl groups) suspended in DCE (40 mL) was added. The mixture was then heated rapidly to 80 °C and reaction was carried out for 18 hours. After cooling, the hypercrosslinked particles were filtered and washed with MeOH, and then washed several times with aqueous HNO_3 (pH 2). Then, the hypercrosslinked polymer were extracted overnight with acetone in a Soxhlet extractor and dried overnight in *vacuo* at 40 °C.[9]

In typical amination reaction, hypercrosslinked polymer (~ 0.5 g) and dried toluene (80 mL) were placed in a round bottomed- flask (100 mL) and the mixture left under N_2 for 1 hour to wet the beads. Then, dimethylbutyl amine (DMBA) (in 5 molar excess relative to $–CH_2Cl$) was added into the solution. The mixture then was heated rapidly to 85 °C and kept this temperature for 18 h. The aminated beads were filtered and washed with toluene, MeOH, MeOH:H_2O and then washed several times with aqueous 5% (w/v) $NaHCO_3$ and water. Then the aminated beads were then extracted overnight with acetone in a soxhlet extractor before drying overnight in oven at 40 °C.

Characterization

The morphology of the polymer particle was captured by using CARL ZEISS Scanning Electron Microscopy (SEM). The SEM images of poly(styrene-*co*-EGDMA-*co*-VBC) particles were captured using SEM at 3.95X, 2.48kX, and 1.64kX magnification. The SEM images of poly(HEMA-*co*-EGDMA-*co*-VBC) particles were captured using SEM at60X and 50X magnification. The functional group presence in the particles was identified using Nicolet iS50 (Thermo Scientific) Fourier transforms infrared spectroscopy analysis

(FTIR). Specific surface area of the hypercrosslinked polymer was characterized by using a Brunauer-Emmett-Teller (BET) (Micromeritics ASAP 2010 BET ANALYZER).The amounts of nitrogen presence in the particles were determined using elemental analysis equipment from Elementar Germany.

Results and Discussion

Morphology and specific surface area (SSA) of particles

Figure 1 and Figure 2 shows morphology of strong anion exchange resin. As can be seen in Figure 1a and 1b, hypercrosslinked poly(styrene-*co*-EGDMA-*co*-VBC) (PSEV) particles cannot retain the original shape upon hypercrosslinking reaction. This occurred due to amount of crosslinker that presence in the backbone of polymer very small resulting to the particles aggregated. However, there were no significant changes observed on hypercrosslinked particles before and after amination reaction take place (Figure 1b and 1c). The presence of high degree of crosslinking in the backbone of polymer formed during hypercrosslinking reaction provide extra rigidity to the particles. Therefore, when the solvent is removed from the system, the collapse of the hypercrosslinked PSEV particles been avoided.[14]

Figure 2 shows images of strong anion exchange hypercrosslinked PHEV. In all reaction stages (SP to amination reaction), the particles managed to retain their shape. The hypercrosslinked polymer can retain the original shape because it contributed by the presence of high amount of crosslinker during precursor synthesis. Similar results have been obtained by other researchers.[11,13]Meanwhile, structure of strong anion exchange hypercrosslinked PHEV further strengthen by the presence of extra crosslinked chain formed during hypercrosslinking reaction. After amination process, the surface of the particles become smoother and the pore became less prominent at the surface (Figure 2c).

Table 1 depicted the specific surface area (SSA) before and after amination for both strong anion exchange hypercrosslinked PSEV and PHEV. SSA for precursor in both cases around ~5 m^2/g which prove that the precursors are non-porous in dry state. For PSEV, the precursors were easier to swell in solvent during hypercrosslinking reaction compared to macroporous PHEV due to small amount of crosslinker presence in precursor.This causing more chloromethyl group being transformed to methylenebridge and subsequently formed pores.[15]However, for PHEV, the precursor containing high amount of crosslinker resulting the particles more rigid and less swell in solvent. This contributes to less conversion of chloromethyl group to methylene bridges. Therefore, hypercrosslinked PSEV have more SSA compared to hypercrosslinked PHEV.

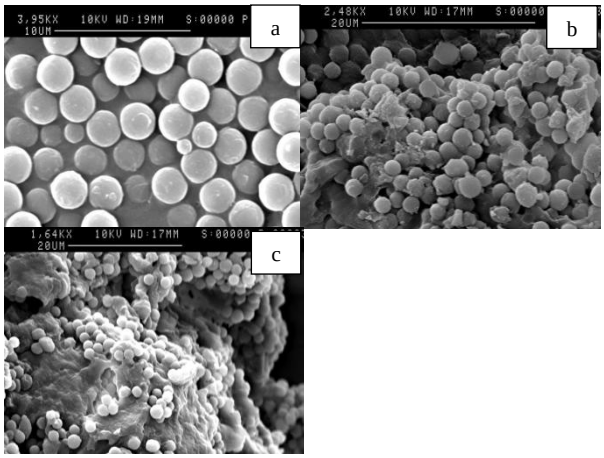


Figure 1: SEM imagesof PSEV: a) PSEV precursor at 3.95kX magnification, b) hyper cross linked particles at 2.48kX magnification, and c) hyper cross linked aminated particles at 1.64kX magnification.

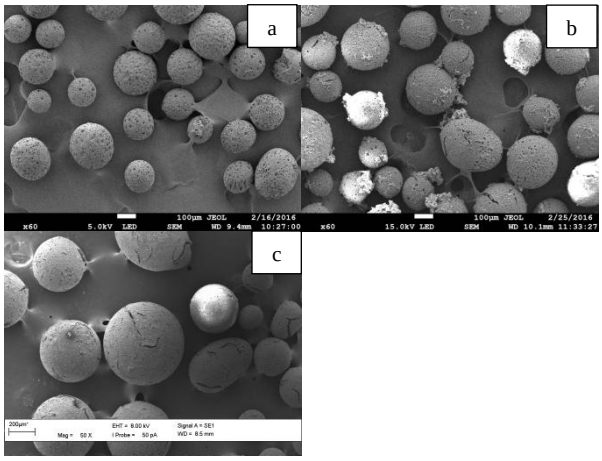


Figure 2: SEM images of PHEV: a) PHEV precursor at 60X magnification, b) hyper cross linked particles at 60X magnification, and c) hyper cross linked aminated particles at 50X magnification.

The SSA before amination strong anion exchanges hypercrosslinked PSEV exceeding 1000 m^2/g. After amination, SSA slightly increasing probably it arises from additional crosslinking which contribute to increasing in SSA instead of the porous structure of strong anion exchange hypercrosslinked polymer itself. Similar result was also reported in literature.[16-18] However, for strong anion exchange hypercrosslinked PHEV, the SSA decreased significantlyfrom 124 m^2/g to 27 m^2/g. This might be caused by the bulky functional group arise from DMBA block the pore of the particles. Despite of decreasing in SSA, smoother surface of the resin also can be seen in Figure 2c which it most probably due to the particle poreshave been covered by DMBA.

Table 1: BET analysis of hypercrosslinked PSEV a hypercrosslinked PHEV resin before and after amination.

Sample	SSA[a] (m^2/g)	SSA[b] (m^2/g)	SSA[c](m^2/g)	Yield (%)
PSEV	~5	1035	1090	65.00
PHEV	~5	124	27	78.19

[a]SSA of precursor

[b]SSA of hypercrosslinked PSEV and PHEV

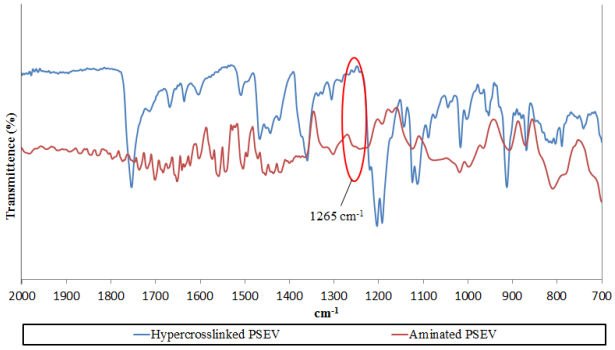
[c]SSA of strong anion exchange hypercrosslinked PSEV and PHEV

FTIR Analysis

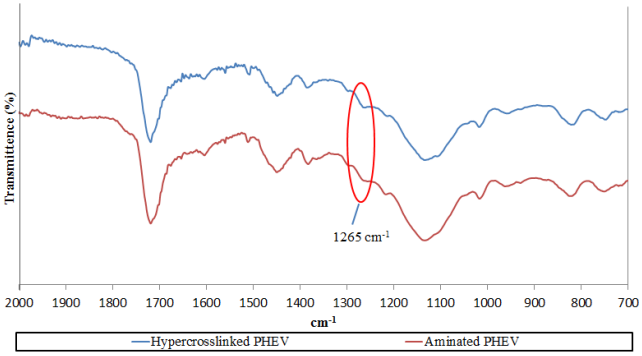
The spectra of strong anion exchange hypercrosslinked PSEV and PHEV before and after amination reaction are shown in Figure 3. Both polymers have characteristic absorption bands at 1265 cm^{-1} and 733 cm^{-1} arise from stretching vibrations of C-Cl bonds and 975 cm^{-1} is ascribed to CH_2 vibration that present in hypercrosslinked polymer before amination.[17]For strong anion exchange hypercrosslinked PSEV (Figure 3a),slightly reduction at band 1265 cm^{-1} can be observed. This probably because of chlorine residues in hypercrosslinked polymer decreased (high SSA, Table 1) resulting low conversion of chlorine groups to amine groups. However, for strong anion exchange hypercrosslinked PHEV (Figure 3b) the reduction in intensity at band 1265 cm^{-1} clearly can be observed due to the high residue chlorine inside hypercrosslinked polymer. General speaking, the reduction of intensity at band 1265 $cm^{-1}$was due to the reaction between Cl groups and their adjacent H cause additional Cl loss.[11]The loss of Cl was replaced by DMBA. In the both cases, DMBA was successfully attach at the backbone of polymers.

Ion Exchange Capacity (IEC) and nitrogen content

An increasing of nitrogen percentage was observed from hypercrosslinked polymer to strong anion exchange hypercrosslinked for PSEV and PHEV (Table 2). This was as expected which Cl was replaced by DMBA thus provide increasing in nitrogen content. Nitrogen content slightly increased from 0.36% to 0.63% after amination reaction for strong anion exchange hypercrosslinked PSEV. Meanwhile, for strong anion exchange hypercrosslinked PHEV, the nitrogen content significant increase from 0.10% to 1.46% (Table 2).



(a)



(b)

Figure 3: FTIR analysis for hypercrosslinked and aminated resin: a) PSEV; b) PHEV.

The significant increase in nitrogen content observed at strong anion exchange hypercrosslinkedPHEV probably due to high chlorine residue inside the hypercrosslinked polymer prior amination reaction. Therefore, more amine groups can take place during amination reactions. This result also in a good agreement with FTIR and SSA results of such polymer (Table 1 and Figure 3b).

The elemental results also in good agreement with the ion exchange capacity (IEC) (Table 2) for both strong anion exchange hypercrosslinked PHEV and PSEV. High amount of nitrogen indicates that more ion exchange site available in the particles. Ion exchange site available for strong anion exchange hypercrosslinked PSEV was determined to be around 0.193 mmol/g while ion exchange site available for strong anion exchange hypercrosslinked PHEV was determined to be around 9.97 mmol/g. The difference in IEC values was due to high amount of chloromethyl group available at hypercrosslinked PHEV to allow amine groups take place chlorine groups site during amination reaction. Therefore, more DMBA were attached to the polymeric backbone compared to strong anion exchange hypercrosslinked PSEV. Attachment of DMBA into the polymeric backbone formed positively charge nitrogen group (quarternary ammonium group) which provide ion exchange site.

Table 2: Nitrogen content for both PSEV and PHEV resin (before and after amination) and their ion exchange capacity (IEC).

Sample	Nitrogen content (%)		IEC[a] (mmol/g)
	Hypercrosslinked	Aminated	
PSEV	0.36	0.63	0.193
PHEV	0.10	1.46	9.970

Conclusion

From SEM, both strong anion exchange hypercrosslinked PSEV and PHEV manage to retain their shape after amination reaction. This contributed by the presence of high degree crosslinking after hypercrosslinking reaction. Meanwhile, SSA for hypercrosslinked PSEV higher than hypercrosslinked PHEV but after amination reaction SSA lower than strong anion hypercrosslinked PHEV. From FTIR spectra, quarternary ammonium groups were successful attached at the polymer backbonein both cases.Strong anion hypercrosslinked PHEV also containing higher nitrogen content and IEC compared to strong anion hypercrosslinked PSEV.This prove for existence of more N^+ functional group at the backbone and more ion exchange site available in strong anion hypercrosslinked PHEV polymer.

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