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Preparation and Characterization of Hypercrosslinked Poly (HEMA-*co*-EGDMA-*co*-VBC)

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Abstract

Objectives: The aims of this paper was to produce hydroxyl hypercrosslinked polymers with high specific surface area derived from poly(HEMA-*co*-EGDMA-*co*-VBC) precursor beads. **Methods:** This was achieved using hypercrosslinking reaction and the beads were characterized by FTIR, SEM and BET analysis. **Findings:** The BET analysis showed that specific surface area increasing from ~5 m^2/g to 310 m^2/g when amount of VBC increased up to 90 wt%. However, when amount of EGDMA increasing from 40 wt% to 100 wt%, specific surface area decreasing from 310 m^2/g to ~61 m^2/g. SEM images also showed that when increasing EGDMA content, hypercrosslinked polymer still can retain precursor shape with satisfied quality. The catalyst ratio was varied between 1:1 to 3:1 mole ratio (based on $-CH_2Cl$ content) and from the results obtained, there are no significant effect on specific surface area and morphology of hypercrosslinked polymer when ratio of catalyst increased. From FTIR spectra, reduction peak at 1265 cm^{-1} resulted from methylene bridges formed in all experiments proved that hypercrosslinking reaction was successfully carried out. **Application/Improvement:** Hypercrosslinked polymer will be used in functionalization reaction to produce quaternary ammonium resin.

Keywords: Hypercrosslinked hydrophilic polymer, Hypercrosslinking reaction, Morphology hypercrosslinked polymer Specific surface area

1. Introduction

Hypercrosslinked polymers are highly crosslinked synthetic porous macromolecules formed upon the exhaustive intramolecular crosslinking of linear or lightly crosslinked polymeric precursors in a thermodynamically 'good' solvent. Porous polymer particles are used in wide range of important scientific and everyday applications. Because of its extensive used, there is an unequivocal need for the development and implementation of new synthetic approaches for the production of porous polymers. A novel type of hypercrosslinked polymer differ from typical styrene-divinylbenzene copolymer that obtained by extensively post-crosslinking of polymer chains in the presence of a good solvent. This material can be obtained from using an 'internal' bis electrophile[1] or with 'external' bis-electrophile[2].

Since 2004, new methods of hypercrosslinking reaction have emerged originating from the work of[1,3]. The overall strategy of this method involved the development of precursor polymer particles using Vinyl Benzene Chloride (VBC) to produce polymer particles with restricted level of crosslinking. Then this polymer will be further crosslinked extensively in a thermodynamically 'good' solvent which is Dichloroethane (DCE) has been used intensively by many researchers to exploit the chloromethyl group as an 'internal' electrophile source and $FeCl_3$ being used as the efficient Lewis acid catalyst. This process involved conversion of chloromethyl group into methylene bridge where chlorine atom utilized

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as a leaving group to form a methylene bridge; that lead to the formation of pores inside the precursor[2,4,5]. These methylene bridges are installed between adjacent aromatic residues whilst the precursor in swollen state resulting high specific surface area.

Conventional porous polymer particles or polymeric sorbent available commercially are normally based on styrene-divinylbenzene copolymers that shows hydrophobic characteristic. This hydrophobicity is more efficient to holding non-polar compounds than the polar compounds[6,7]. Therefore, the aim of this study is to investigate the effect of reaction parameters including amount of VBC, amount of EGDMA and lewis acid catalyst ratio on the specific surface area and morphology of hypercrosslinked hydrophilic polymer.

2. Materials and Methods

2.1 Materials

The reagent used for suspension polymerizationwere 2-hydroethylmethacrylate (HEMA) (97% grade) contains 200 ppm monomethyl ether hydroquinone, ethylene glycol dimethacrylate (EDGMA) (98% grade) contains 90-110 ppm of monomethyl ether hydroquinone, 4-vinylbenzyl chloride (VBC), (97% grade), poly(N-vinylpyrrolidone) 55 (PVP) (MW ~55,000), and benzoyl peroxide (BPO) (75% grade). The chemicals were obtained from Sigma Aldrich. Toluene (99.5% grade) was obtained from HmBG Chemical. Distilled water was used as solvent. All chemicals except HEMA, EDGMA and BPO were used without purification. HEMA and EDGMA were purified by going through aluminium oxide column and benzoyl peroxide was purified by recrystallization from chloroform, which was also obtained from Sigma Aldrich.

In hypercrosslinking 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) and methanol (99.8% grade), from Sigma-Aldrich, sodium hydrogen carbonate (99.8% grade) supplied by VWR and distilled water. All of them were used as received.

2.2 Precursor Synthesis

Precursor used in hypercrosslinking reaction was synthesized using suspension polymerization[8]. In suspension polymerization, 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 °C for 24 hours.

2.3 Hypercrosslinking Reaction

Hypercrosslinking reaction method were based on previous reported method[9]. For the hypercrosslinking reactions, 1.5 g of the precursor particles were added to 30 mL of 1,2-dichloroethane (DCE) in a five necks round-bottomed (250 mL) and left to swell with constant flow of nitrogen gas at room temperature for 1 hour. After one hour, $FeCl_3$ (1:1, 2:1, and 3:1 mole ratio based on chlorine content of particles) was added and the mixture heated at 80 °C for 18 hours. The hypercrosslinked particles were recovered using filter paper and washed with methanol and aqueous HNO_3 at pH 2. The particles were then left in soxhlet extractor with acetone overnight and were washed again with methanol and diethyl ether. Then the particles were dried in oven at 50°C for 24 hours.

2.4 Particles Characterization

The morphology of the polymer particle was captured by using Field Emission Scanning Electron Microscopy (FESEM) analysis. The analysis was carried out at a condition of 60x magnification. The functional group presence in the particles was identified using Nicolet iS50 (Thermo Scientific) Fourier transforms infrared spectroscopy analysis (FTIR). Bruker, S8 Tiger X-ray Flourescence analysis (XRF) was used to monitor the amount of chlorine presence in the particles. Specific surface area of the hypercrosslinked polymer was characterized by using a Brunauer-Emmett-Teller (BET) treatment of nitrogen sorption isotherm data generated to measure the specific surface area.

3. Results and Discussion

3.1 Effect of EGDMA content on Hypercrosslinked Particles

Prior to hypercrosslinking reaction to occur, the precursor should have an ability to swell in thermodynamic good solvent to allow the catalyst diffused into the precursor displacing chlorine from the backbone. Swellability usually depends on the content of the crosslinking monomer in the initial mixture. Increasing the amount of crosslinker will cause the precursor harder to swell.

Figure 1 shows FESEM images of polymer after hypercrosslinking reaction. Hypercrosslinked polymer managed to retain their initial shape even after 18 hours of reaction time. This happened due to abundance of crosslinker amount used during precursor synthesis. The crosslinker responsible to hold the polymer chain together, preventing it from collapsing in swollen state. This observation was similar with other group that proved macroporous structure managed to retain the shape after hypercrosslinking reaction[10].

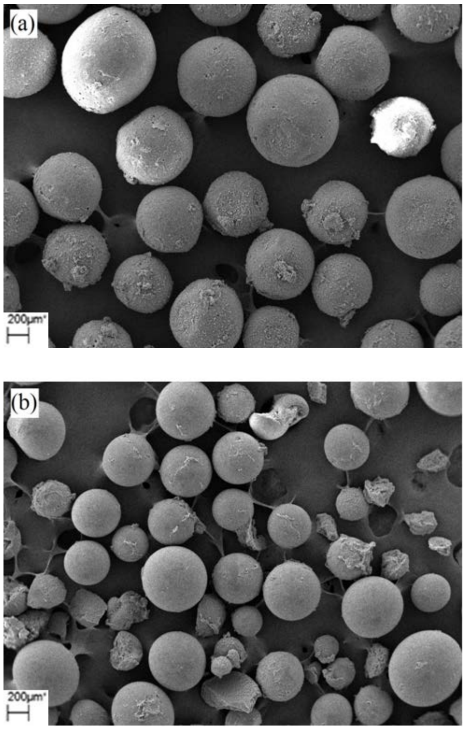


Figure 1. Morphology of hypercrosslinked polymer after hypercrosslinking reaction. (a) 40 wt% EGDMA. (b) 100 wt% EGDMA.

From FTIR spectra, for both samples HHP1 (40 wt% of EGDMA) and HHP2 (100 wt% of EGDMA), the intensity peak at 1265 cm^{-1} band that assign to chloromethyl group (-CH_2Cl) has been significantly reduced after hypercrosslinking reaction shown in Figure 2. This showed that conversion of methyl group to methylene bridge have been successful formed. These results also have a good agreement with BET results which both hypercrosslinked particles (HHP1 and HHP2) has increment in SSA values shown in Table 1, indicator the formation of methylene bridge.

However, precursor with lower amount of EGDMA has higher Specific Surface Area (SSA) after hypercrosslinking reaction compared to precursor that contain higher amount of EGDMA.

This factor contributed by increasing the swellability of precursor in thermodynamic 'good' solvent[11]. Higher degree of crosslinker limits the precursor to swell during initial stage of hypercrosslinking reaction, thus prevent diffusion of catalyst into the precursor. Therefore, the precursor containing 40 wt% EGDMA have higher SSA compared to 100 wt% EGDMA.

3.2 Effects of VBC Content on Hypercrosslinked Particles

In this study, four precursors with different VBC contents have been studied to investigate their effect on hypercrosslinked polymer. The VBC amounts were varies between 5 wt and 90 wt% at fixed crosslinker content. From FESEM images shown in Figure 3, it shows after hypercrosslinking reaction, the entire precursor still managed to retain their shape and morphology. This proved that co-monomer (VBC) did not affect the morphology of hypercrosslinked polymer and presence of crosslinker (40 wt% EGDMA) in precursor also holds the polymer chain together thus give extra rigidity preventing it from collapse during hypercrosslinking reaction.

In hypercrosslinking reaction, the pendent chloromethyl groups originated from VBC in the precursor were subsequently consumed to produce the hypercrosslinked particles. From Figure 4(a), even though the chlorine peak for 5 wt% of VBC does not show any reduction in intensity at 1265 cm^{-1} even after hypercrosslinking reaction, however, BET analysis show slightly increasing in value of specific surface area from ~5 m^2/g to 16.831 m^2/gas shown in Table 2. This proves that conversion of chlorine to methylene bridge still occurred but slightly increment of SSA. This might be due to the presence of very small amount of VBC (0.86% of chlorine).

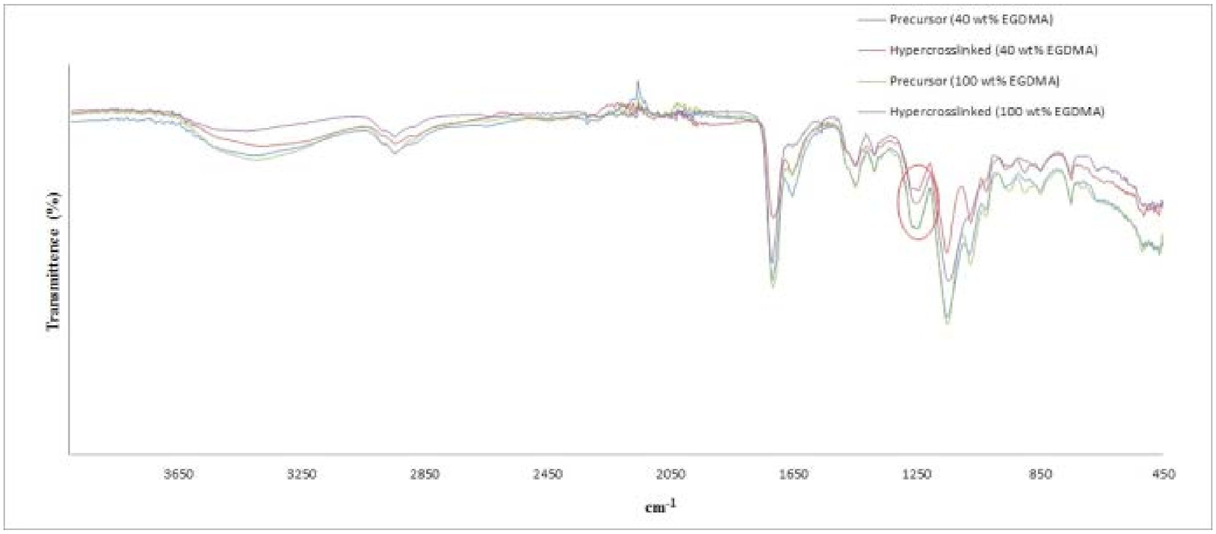


Figure 2. FTIR spectra for 40 wt% EGDMA and 100 wt% EGDMA precursor before and after hypercrosslinking reaction.

Table 1. BET analysis of hypercrosslinked polymer at different EGDMA contents at fixed VBC and HEMA content

Sample	EGDMA[a] (wt%)	HEMA (wt%)	VBC (wt%)	Cl[b] (%)	BET SSA (m^2/g)[c]	BET SSA (m^2/g)[d]	Yield (%)
HHP1	40	80	20	4.3	~5	67.1	76
HHP2	100	80	20	4.31	~5	60.5	79

[a] Based on monomer feed (HEMA+VBC)
[b] Percent of chlorine obtained from XRF result
[c] SSA of precursor
[d] SSA of hypercrosslinked polymer

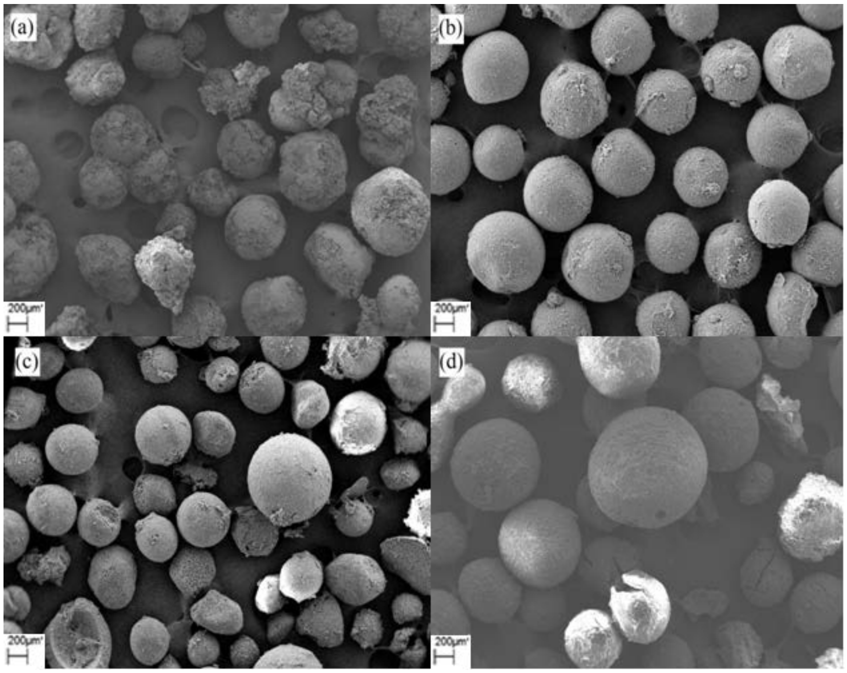
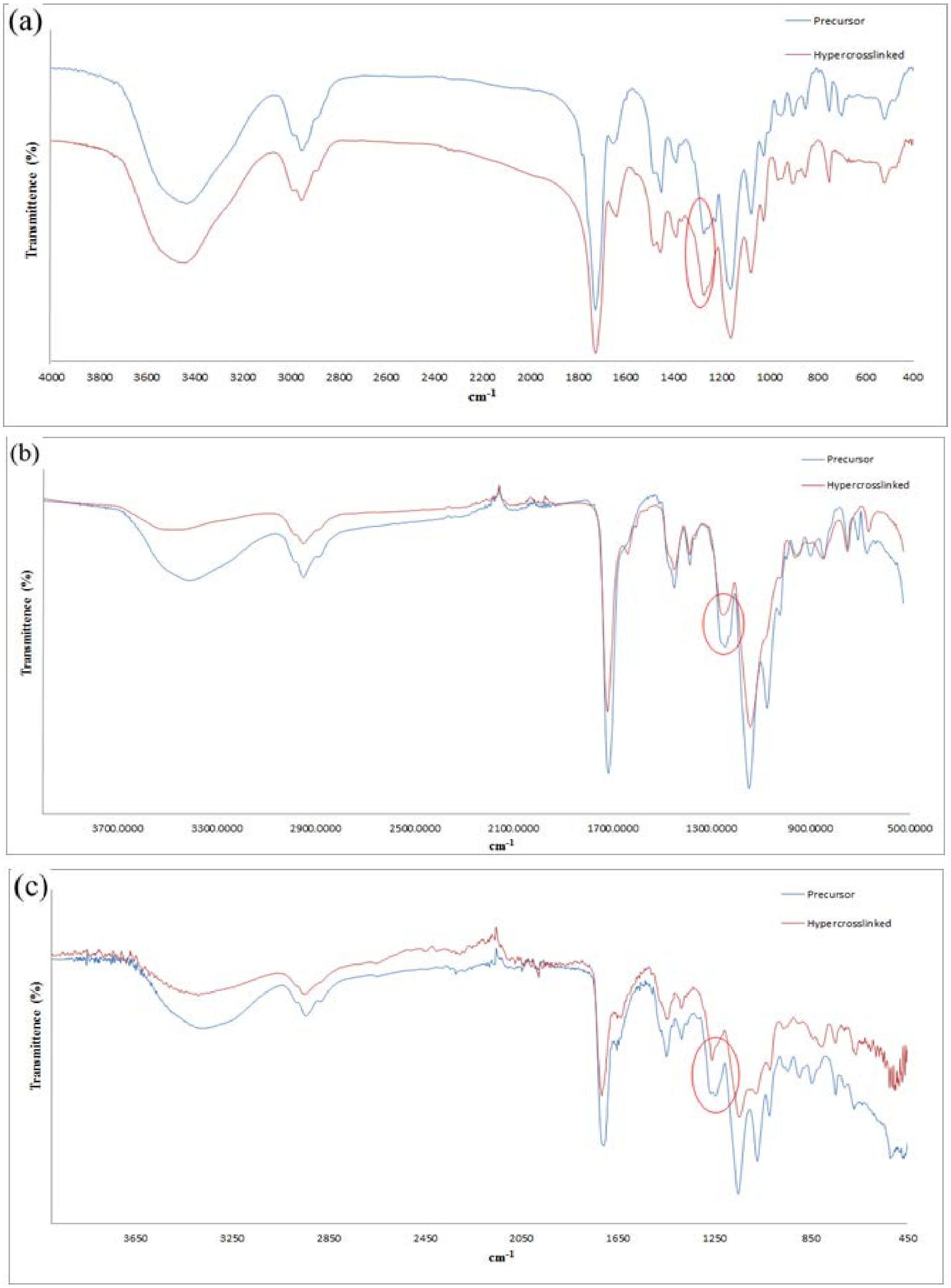


Figure 3. Morphology of hypercrosslinked polymer after hypercrosslinking reaction. (a) 5 wt% VBC. (b) 20 wt% VBC. (c) 40 wt% VBC. (d) 90 wt% VBC.


(a)
Precursor
Hypercrosslinked
Transmittence (%)
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
cm^{-1}
(b)
Precursor
Hypercrosslinked
Transmittence (%)
3700.0000
3300.0000
2900.0000
2500.0000
2100.0000
1700.0000
1300.0000
900.0000
500.0000
cm^{-1}
(c)
Precursor
Hypercrosslinked
Transmittence (%)
3650
3250
2850
2450
2050
1650
1250
850
450
cm^{-1}

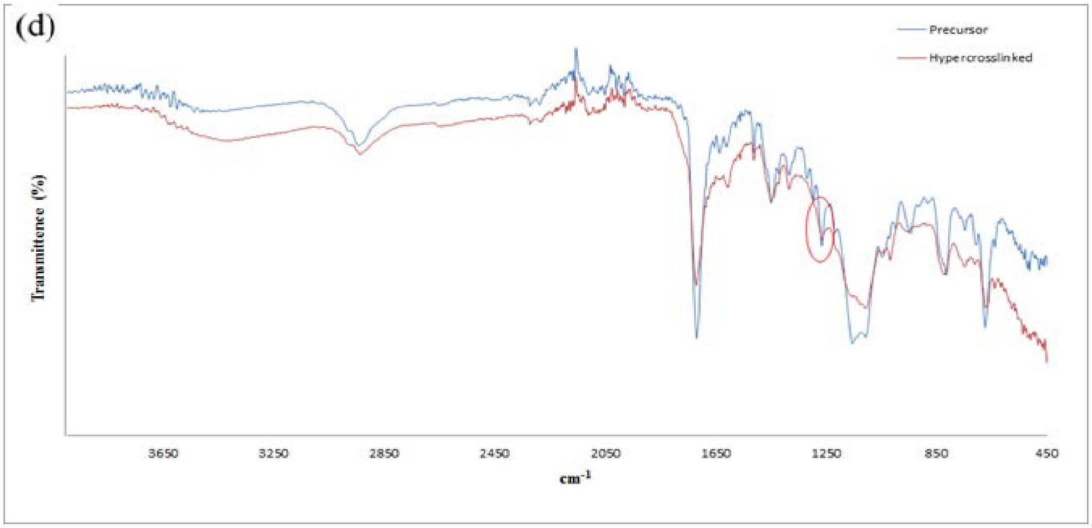


Figure 4. FTIR spectra for precursor before and after hypercrosslinking reaction. (a) 5 wt VBC. (b) 20 wt% VBC. (c) 40 wt% VBC. (b) 90 wt% VBC.

Increasing the amount of VBC to 20 wt%, shows a decrease in intensity for chloromethyl band in FTIR shown in Figure 4(b). The result was in-line with finding by other researchers[9,12,13]. Reduction in chloromethyl intensity peak showed that methylene bridge formed during reaction. The result was further supported by BET specific surface area result. BET analysis showed increasing in value of specific surface area (SSA) from ~5 m^2/g before hypercrosslinking reaction to 67.111 m^2/g after hypercrosslinking reaction.

The chloromethyl peak in 40 wt% VBC precursor has more prominent intensity compared to the two previous precursors (5 wt% VBC) shown in Figure 4(c). It was expected due to more chlorine have been attached to backbone (11.21% chlorine) of precursor polymer. Therefore after hypercrosslinking reaction, the decrease of the chloromethyl intensity peak should be more significant compared to 5 wt% VBC and 20 wt% VBC precursor. The FTIR result showed exactly as expected, more significant reduction in intensity can be observed. The observation in FTIR spectra was further confirmed by comparing the SSA of precursor and hypercrosslinked polymer which the SSA was increased from 5 m^2/g to 133.537 m^2/g shown in Table 2.

In addition, the FTIR spectra for 90 wt% of VBC hypercrosslinked polymer showed that chloromethyl group almost completely disappeared from the backbone of precursor polymerdue to very significant reduction of chloromethyl peak at 1265 cm^{-1}shown in Figure 4(d). Compared to other precursor (HHP3, HHP4 and HHP5), HHP6 has the most significant reduction in intensity due to many chlorine atom attached to the backbone of precursor polymer (21.22% of chlorine atom). The BET result also reflects the observation obtained from FTIR result. The SSA of precursor was increased from ~5 m^2/g to 310.155 m^2/g.

The trend of SSA was showed to be increased when percentage of VBC increase as shown in Table 2. This was expected as high residual chlorine content in the products; hence the level of methylene bridging is also high. The observation was in agreement with the trend reported by[10,12]. As conclusion, the relationship between amount of VBC in monomer feed was linear as depicted shown in Figure 5, similar observation reported by[11].

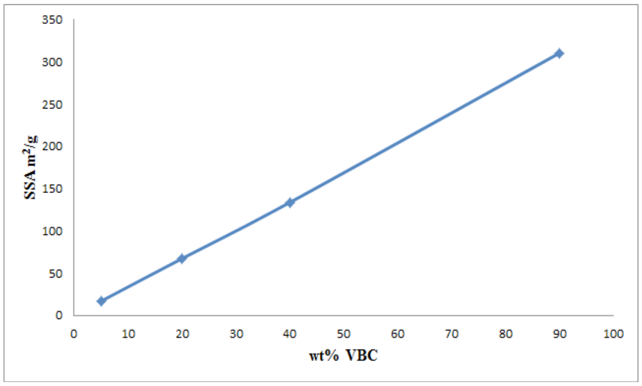


Figure 5. Relationship between VBC content of precursor and SSA after hypercrosslinking reaction.

Table 2. BET result for hypercrosslinked polymer at different VBC content at fixed EGDMA and HEMA content

Sample	%VBC[a]	%Cl[b]	BET (m^2/g)[c]	BET (m^2/g)[d]	Yield (%)
HHP3	5	0.86	~5	16.8	74
HHP4	20	4.3	~5	67.1	79
HHP5	40	11.21	~5	133.5	75
HHP6	90	21.22	~5	310.2	73

[a] Based on monomer feed (HEMA+VBC)
[b] Actual chlorine content obtained from XRF analysis.
[c] SSA of poly(HEMA-*co*-EGDMA-*co*-VBC) precursor
[d] SSA of hypercrosslinked polymer

3.3 Effect of Lewis Acid Catalyst Ratio on Hypercrosslinked Particles

Past research reveals that $FeCl_3$ is consistently the most active Lewis acid catalyst[12] in preparation of hypercrosslinked polymer. From literatures, typically the mole ratio of catalyst and mole ratio of chlorine originated from functional group was fixed at 1:1[12]. In this study, the ratios of catalyst were varied between to 2:1 and 3:1 to investigate their effect on hypercrosslinked polymer

SSA of hypercrosslinked polymer increasing up to 76.548 m^2/g when amount of catalyst used in hypercrosslinking reaction increased. Similar trend also reported by other researcher[14_ENREF_15]. When amount of catalyst was increasing, more catalyst diffuse inside the polymer, leading to more methylene bridge formed.

However, the formation of methylene bridge was also depend on number of chlorine presence in the backbone of precursor. As shown in Table 3, there are slightly increment in specific surface area in all samples which the differences of SSA between HHP7 and HHP8 was ~9% and between HHP8 and HHP9 was only ~3%. This is because of the presence of percentage of chlorine in precursor polymer backbone low around 4%. However, when percentage of chlorine content increasing, SSA of the particles also increased. This fact can be supported by amount of catalyst depend on amount of chlorine content that present in precursor. As conclusion, increasing the ratio of catalyst only cause a little effect on SSA.

Table 3. BET analysis of hypercrosslinked polymer at different catalyst ratio at 40 wt% EGDMA and 20 wt% VBC

Sample	Catalyst Ratio	BET (m^2/g)	Yield (%)
Precursor	N.A.	~5	86
HHP7	1:1	67.1	78
HHP8	2:1	74.1	72
HHP9	3:1	76.5	77

Based on Figure 6, all the samples obtained from different catalyst ratios showed reduction in intensity of $-CH_2Cl$ peak in FTIR spectra. This observation indicates that methylene bridging process occurred in all cases. FTIR results also were in-line with SSA where the most significant reduction for 1265 cm^{-1} band at 3:1 of catalyst ratio.

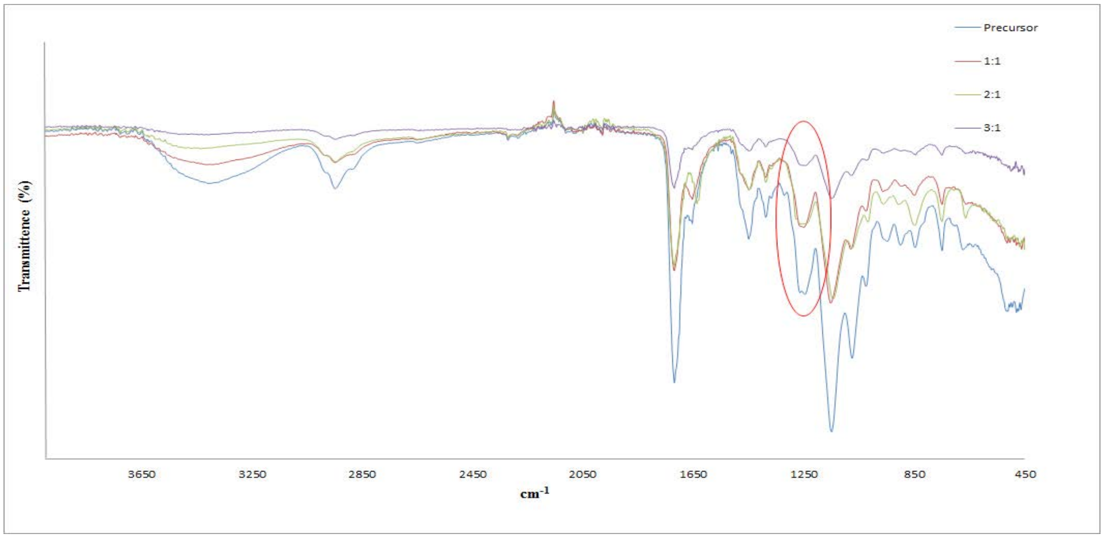


Figure 6. FTIR spectra for hypercrosslinked polymer with different catalyst ratio.

4. Conclusion

Hypercrosslinked Poly(HEMA-*co*-EGDMA-*co*-VBC) hydrophilic polymer was successfully synthesized using hypercrosslinking reaction. All the precursor used showed increasing in SSA after undergo hypercrosslinking reaction. However, increasing the amount of EGDMA reduce the ability of precursor to swell, cause smaller increment in SSA compared to low EGDMA in precursor. To obtain the highest SSA, the amount of VBC should be increased as up to 90 wt%. This provides by more chlorine atoms as electrophile source for hypercrosslinking reaction. Meanwhile, only a small increment in SSA was observed by increasing the amount of $FeCl_3$ due to limitation of chlorine atoms in the backbone. Thus, using 1:1 catalyst ratio to $–CH_2Cl$ group was enough to allow the hypercrosslinking reaction to occur. The International Conference on Fluids and Chemical Engineering (FluidsChE 2017) is the second in series with complete information on the official website[15] and organised by The Center of Excellence for Advanced Research in Fluid Flow (CARIFF)[16]. The publications on products from natural resources, polymer technology, and pharmaceutical technology have been published as a special note in volume 2[17]. The conference host being University Malaysia Pahang[18] is the parent governing body.

5. Acknowledgement

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