

Effect of Catalyst Concentration and Reaction Time on One-Step Synthesized Hypercrosslinked Polyxylene

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Abstract: A meso- and microporous hypercrosslinked polyxylene was synthesized *via* Friedel-craft reaction in the presences of iron(III) chloride as a Lewis acid catalyst. Dichloro-*p*-xylene, which has both benzene ring and chlorine functional groups, was used as monomer for the one-step synthetic process. A different amount of catalyst was used for polymerization and hypercrosslinking reaction. Yield and properties of the hypercrosslinked polyxylene were affected by the concentration of catalyst. Maximum yield of hypercrosslinked polyxylene was 65.4% above 30 wt%/monomer. Maximum Brunauer-Emmett-Teller (BET) surface area was 1168.37 m²/g at 40 wt%/monomer. Micropore volume and peak diameter at maximum differential volume, determined using Horvath-Kawazoe (H-K) method, were 0.2324 cm³/g and 0.55 nm, respectively.

Keywords: hypercrosslinked, catalyst concentration, reaction time, meso- and microporous, friedel-craft reaction.

Introduction

Porous materials are of great interest because of their potential applications in adsorption of small molecules,¹ gas separation,² catalysis,³ chromatography,⁴ and electronics.⁵ Especially, high performance porous materials with high surface area and nanosize pore have recently become a central topic in the field of adsorption study, and many kinds of porous materials were investigated including carbon,⁶ zeolites,⁷ metal-organic frameworks (MOFs),⁸ and organic polymers.⁹ Among these materials, hypercrosslinked polymer is one of notable materials due to its high and unique adsorption properties. In general, hypercrosslinked polymer has high surface area above 1,000 m²/g and has both meso- and micropores.^{10,11} Also, as opposed to inorganic absorbents, swelling capability in polar and nonpolar media and extremely low true density are important non-classical properties of hypercrosslinked polymer.^{12,13} For this reason, hypercrosslinked polymers has been used as sorbents for cleaning of water pollution,¹⁴ dialysis,¹⁵ chromatography,¹⁶ ion exchanger,¹⁷ and template for preparation of nanoparticle.¹⁸ Recently, hydrogen storage property was reported: hypercrosslinked polymer adsorb around 2.75 wt% H₂ at 77 K and 10 bar.¹¹ This storage value is higher than organic polymers, which has intrinsic microporosity.

An initial report of the synthesis of hypercrosslinked polymer appeared in 1970.¹² Davankov *et al.* reported that

hypercrosslinked polymers have been obtained by crosslinking linear polystyrene chains in solution or in swollen state using bifunctional compounds such as 1,4-bis-chloromethyldiphenyl, monochlorodimethyl ether, dimethylformal, and tris-(chloromethyl)-mesitylene. These crosslinking agents react with phenyl rings *via* a Friedel-crafts reaction and form bridge between the polystyrene chains. This type polymer is called "Styrosob"¹⁹ or "Davankov resin".¹¹ Warshavsky *et al.* synthesized hypercrosslinked polysulphone.²⁰ After halomethylation of aromatic compounds in polysulphone chain, partial self-crosslinking reaction occurred in the presence of a Friedel-crafts catalyst. Also, hypercrosslinked properties of other network polymers, such as hypercrosslinked polyarylates and arylene-bridged polysilsesquioxane, were studied.²¹⁻²³

Normally, synthesis of hypercrosslinked polymers, especially polystyrene based materials, is followed by a two-step process: polymerization of linear polymer that contains aromatic groups and post-crosslinking with bridge molecules in the presence of a Lewis acid catalyst. This general method takes a long time and is complicated. Also, excess amount of catalyst in the crosslinking step is another problem in the cleaning process. Elimination of Lewis acid catalyst is hard and needs a great amount of solvent. Hence, reduction of the process and optimization of the catalyst are warranted in preparing hypercrosslinked polymers.

In our study, a hypercrosslinked polyxylene was synthesized by Friedel-craft reaction using Iron(III) chloride as a Lewis acid catalyst (Figure 1). Organic molecules that have both aromatic ring and halogen group were used as mono-

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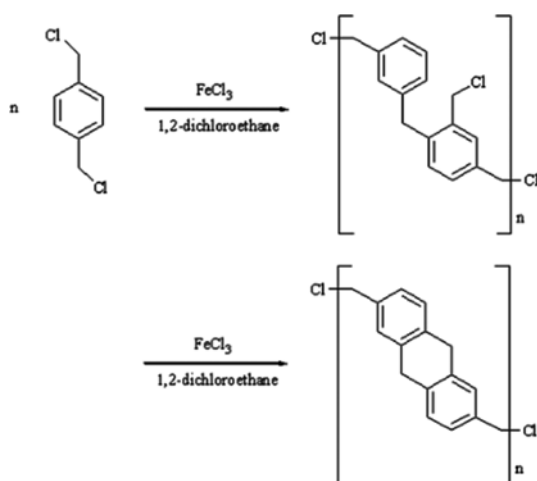


Figure 1. Scheme of synthesis the hypercrosslinked polyxylylene from dichloro-*p*-xylylene molecules.

mers for one step synthesis. Dichloro-*p*-xylylene, being a simple molecule, was selected to be a suitable monomer. Hypercrosslinked polyxylylene had been reported in reference,^{21,24} in these previous literatures, the changes of BET surface area in comparison with before and after Friedel-Craft reaction were studied with varied DCE amounts, but there is insufficiently researched about reaction condition such as catalyst concentration and reaction time, *etc.* and microporosity. The control of catalyst concentration is important in the preparation of hypercrosslinked polymers, and reaction time is a critical factor on the changing BET surface area.

In this study, the effect of catalyst concentration and crosslink reaction time on one-step hypercrosslinked polyxylylene was researched.

Experimental

Materials. Dichloro-*p*-xylylene (98%) monomer was purchased from Across Inc., USA. 1,2-Dichloroethane and iron (III) chloride, which are solvent and Lewis acid catalyst, respectively, were purchased from Sigma-Aldrich Inc., USA. Methanol for the cleaning process was purchased from SK chemical, Korea. Double-distilled and deionized (DI) water was produced from DirectQ3, Millipore, USA and used in removing the catalyst. All chemicals were used as received without further purification.

Synthesis of Hypercrosslinked Polyxylylene. In a double-jacketed glass reactor, 5 g of dichloro-*p*-xylylene was dissolved in 30 g of 1,2-dichloroethane. The catalyst solution (concentration of iron(III) chloride in 45 g of 1,2-dichloroethane was controlled 5 to 40 wt%/monomer) was added in reactor, and the mixed solution was stirred and maintained at 30 °C for at least 12 h. Hydrochloric acid gas, a byproduct of condensation polymerization, was push out from reactor by nitrogen gas and collected for safety (Caution: hydrochloric acid is very dangerous). When

the reaction was completed, product was washed with methanol and DI water. The final cleaned sample was dried in a vacuum oven.

Characterization. Structure of molecules (before and after polymerization) was studied by FTIR spectroscopy using TENSOR27, Bruker, Germany. The morphology of hypercrosslinked polyxylylene was imaged by field-emission scanning electron microscopy (FE-SEM) using JSM-6500F, JEOL Inc., Japan and Transmission electron microscopy (TEM) using JEM-2000EXII, JEOL Inc., Japan. Surface area and pore size of hypercrosslinked polymers were determined by ASAP 2020, Micromeritics Inc., USA. Size distribution and volume of micropore were determined with argon gas by ASAP 2010, Micromeritics Inc., USA.

Results and Discussion

Polymerization of Hypercrosslinked Polyxylylene. Initial solution of monomer with dichloroethane was transparent and a light-yellow color. When the catalyst dissolved in dichloroethane was mixed, reaction initiated and the solution rapidly turned to dark violet. Viscosity of mixed solution was increased with reaction time and phase of mixture was converted from liquid to a gel-like state. After the cleaning step, final product was formed to brownish powder.

Compared to the studies in porosity, studies in hypercrosslinked polymer morphology are rarer. Generally, morphologies of hypercrosslinked polymer, which is prepared by two step process, are structured in the nearly identical form from its original.^{10,25} Surface roughness of hypercrosslinked polymer was the same as, if not slightly rougher than, the uncrosslinked resin. In the case of hypercrosslinked polyxylylene, it had highly rougher surface and irregular pore structure (Figure 2(a)). Size distribution of mesopore had a broad range of 20 to 50 nm as seen in SEM image. From the TEM image, meso- and microporous structure was also determined (Figure 2(b)). Bright spots, which are smaller pores (< 10 nm), were spread throughout the polyxylylene. These small pores are the significant factor that yields high surface area and pore volume of hypercrosslinked polyxylylene.

The variations of FTIR spectra give evidence to prove the

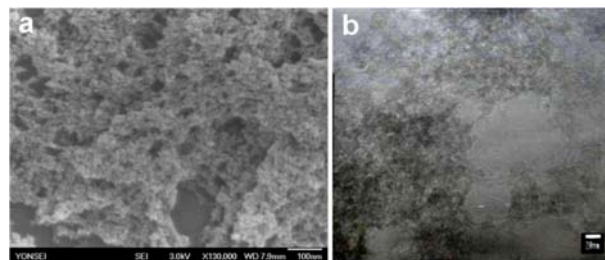


Figure 2. (a) FE-SEM image of hypercrosslinked polyxylylene in 20 wt%/monomer. (b) TEM image of hypercrosslinked polyxylylene in 20 wt%/monomer ($\times 200,000$).

synthesis of hypercrosslinked polyxylene. It was difficult to analyze the molecular structure through NMR, due to its high insolubility. There are two important differences between in the molecular structure before and after the reaction. The first is the detachment and elimination of Cl- group. During the Friedel-craft reaction, chlorine functional group comes together with a benzene ring of another monomer, and HCl molecule is eliminated. Hence, intensity of C-Cl band at 670 cm^{-1} decreased after reaction; also, peak intensity at 1265 cm^{-1} dropped because of decreasing number of CH_2Cl bond. The latter is the increased number of substitution bond to the benzene ring. Dichloro-*p*-xylene has two functional groups on the benzene ring in *para* formation. After crosslinking reaction, the benzene ring of one monomer to another are interconnected in a network of bridging bonds. Therefore, there could be more than three substitutions on benzene ring. The peak at 854 cm^{-1} , which denotes the vibration of C-H band in benzene ring with *para*-type functional groups at, decreased. New peaks that appear at 815 and 894 cm^{-1} mean that more than three functional groups are attached to the benzene ring.

Effect of Crosslinking Reaction Time. Reaction time is yet to be mentioned in hypercrosslinked polymer researches. There were two steps of reaction: preparation of polymer resin and crosslinking with bridge molecules. Especially, crosslinking time was long enough to set up for entire reaction of bridge molecules. But, one-step reaction using bifunctional monomer did not need a long time to prepare the hypercrosslinked polymer. Figures 4 and 5 respectively show the yield and BET surface area with reaction time. These will be used to simply explain the change in the property of hypercrosslinking throughout the reaction.

Yield of hypercrosslinked polyxylene rapidly increases

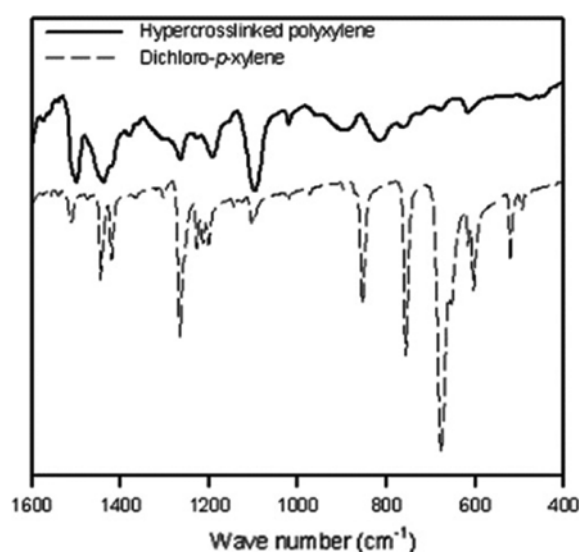


Figure 3. FTIR spectrum of dichloro-*p*-xylene and hypercrosslinked polyxylene (20 wt%/monomer).

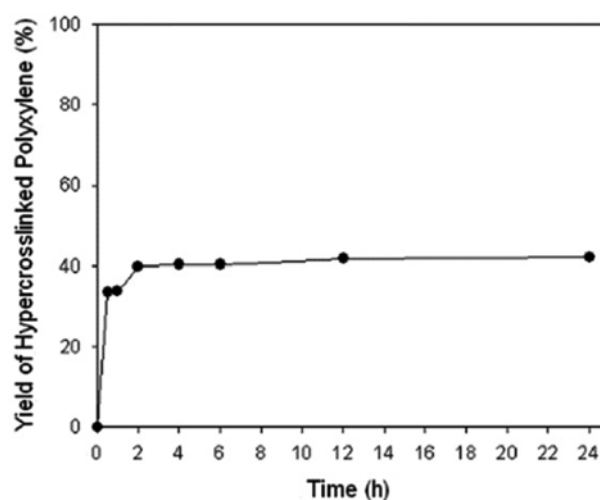


Figure 4. Yield of hypercrosslinked polyxylene via Friedel-craft reaction with reaction time in 10 wt%/monomer.

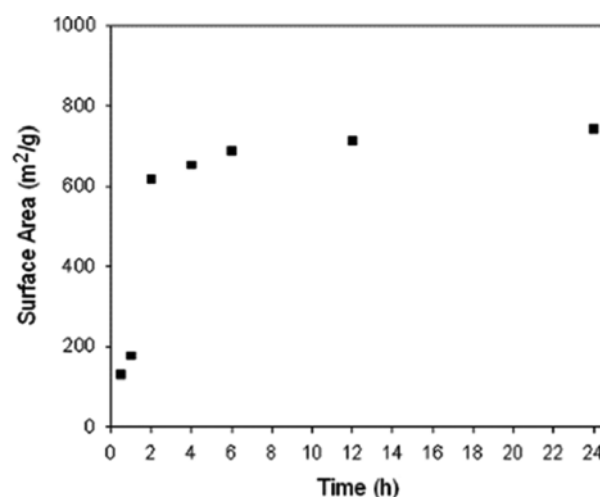


Figure 5. BET surface area of hypercrosslinked polyxylene via Friedel-craft reaction with reaction time in 10 wt%/monomer.

with reaction time at initial step of reaction because preparation of hypercrosslinked polyxylene using Friedel-craft reaction is a condensation polymerization. It is sometimes called 'self-condensation' due to the monomer polymerizing with its own kind. In case of 10 wt% sample, the yield of hypercrosslinked polyxylene was about 33% at 30 min, and reached maximum yield point of 40% in 2 h. The surface area of the hypercrosslinked polyxylene increased in a similar manner as the yield. Surface area of growing samples was below $200\text{ m}^2/\text{g}$, which is a lower value than the maximum yield. However, different from the yield data, surface area of hypercrosslinked polyxylene was further increased even after the time of maximum yield. The additional increase in surface area is about $100\text{ m}^2/\text{g}$ at 12 h. From the Figures 4 and 5, roles of Lewis acid catalyst in self-condensation polymerization and hypercrosslinking can be

seen. The first hour of the reaction was mainly self-condensation polymerization, hence yield of hypercrosslinked polyxylylene rapidly increased. Hypercrosslinking also happened in early in the reaction, but not to the extent of the polymerization. This can be deduced from Figure 5, surface area data. Further into the reaction, rate of polymerization is decreased and hypercrosslinking reaction accelerates. After the completion of polymerization, hypercrosslinking continues and properties of hypercrosslinked polymer also increase.

Effect of Concentration of Lewis Acid Catalyst. The concentration of Lewis acid catalyst is the main factor in the synthesis of hypercrosslinked polyxylylene. Normally, catalyst remains after the Friedel-Craft reaction. But, due to the swelling and adsorption properties of the hypercrosslinked polymer, the catalyst may be lost in its activity in the reaction. In literatures,^{12,25} mole of catalyst and the number of bridging group between aromatic ring and chlorine functional group is fixed in a 1:1 ratio. In this research, concentration of catalyst adjusted from 5 to 40 wt%/monomer. The yield of hypercrosslinked polyxylylene was governed by the concentration of catalyst. (Figure 6) Below 20 wt%/monomer, yield increased to 62.7%. Above 30 wt%/monomer, maximum yield point was 65.4% and remained at this level even though concentration of catalyst was increased.

Properties of hypercrosslinked polyxylylene were also affected by concentration of Lewis acid catalyst. Figure 7 shows the nitrogen adsorption and desorption isotherms for the hypercrosslinked polyxylylene. From the isotherm data, all samples could be classified as Type IV and H₂ hysteresis loop,²⁶ which shows that it is a mesoporous and interconnected networks of pores of different size and shape. Total amount of nitrogen adsorption increased with the concentration of catalyst.

The apparent surface area and t-plot data for the polymer was measured by nitrogen adsorption at 77 K (Table I).

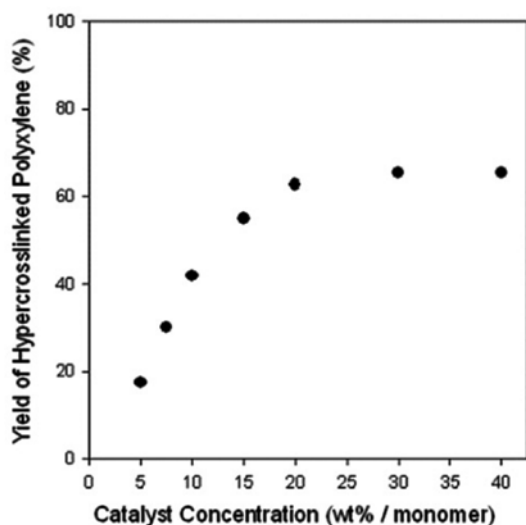


Figure 6. Yield of hypercrosslinked polyxylylene *via* Friedel-Craft reaction in various concentrations of Lewis acid catalyst.

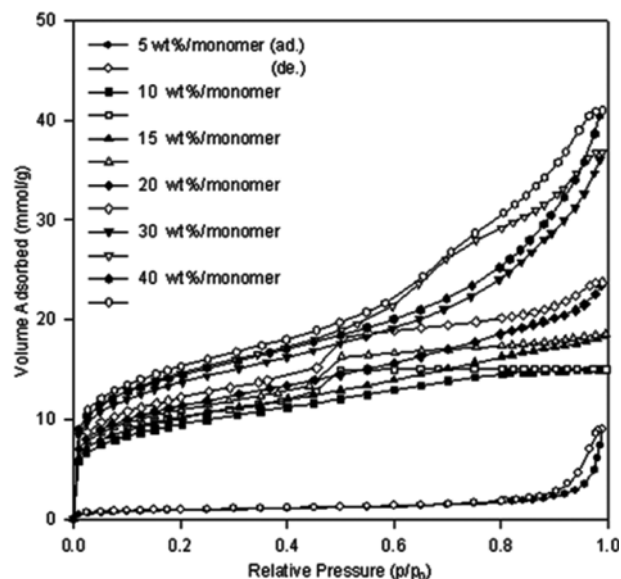


Figure 7. Nitrogen adsorption (filled symbols) and desorption isotherm (open symbol) of hypercrosslinked polyxylylenes at 77 K.

Table I. Porous Structure Parameters for Hypercrosslinked Polymers^a

Amount of Catalyst (wt%/monomer)	A_{BET} (m ² /g)	$A_{Lang.}$ (m ² /g)	A_t (m ² /g)	V_t (cm ³ /g)
5	73.50	94.87	30.47	0.0126
10	762.17	1002.14	375.09	0.1660
15	821.07	1043.13	384.91	0.1707
20	903.49	1222.59	450.49	0.2081
30	1100.62	1441.45	522.39	0.2359
40	1168.37	1476.99	554.54	0.2395

^aNitrogen was used to adsorb as gas at 77 K. T-plot method data has correlation coefficient above 0.999.

Hypercrosslinked polyxylylene surface area was within the range given in other literature.¹² Surface area and micropore volume of hypercrosslinked polyxylylene increased with the increase in the concentration of catalyst. Behavior of porosity increment by catalyst concentration was similar with yield data, but there was a slight increase in porosity above 30 wt%/monomer. Maximum value of BET surface area and t-plot micropore volume was 1168.37 m²/g and 0.2395 cm³/g, respectively, at 40 wt%/monomer. Comparing this article with previous literature²¹ using SnCl₄ Lewis acid catalyst, the maximum surface area of this work was higher than that obtained by previous study. The reason of that was different of solubility and molecular size of Lewis acid catalyst. These order of activity of Lewis acid are FeCl₃ > AlCl₃ > SnCl₄ based on this criterion.²⁷

Figure 8 shows meso- and micropore volume with pore size through cumulative graph by density functional theory

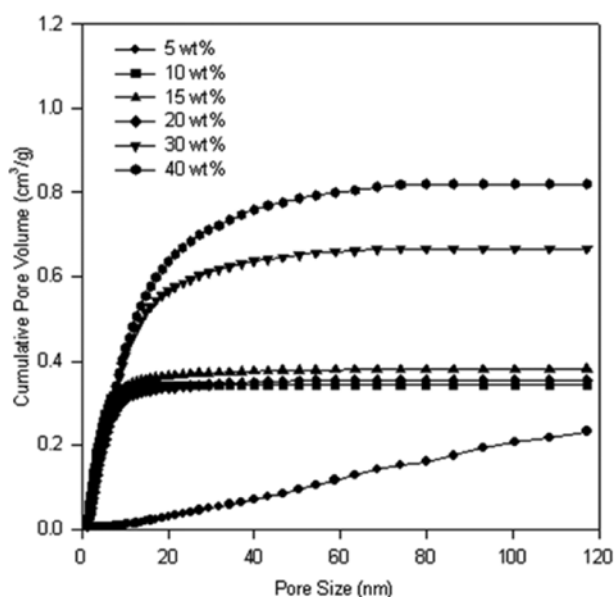


Figure 8. Mesopore distribution for the hypercrosslinked polyxylene calculated by the DFT theory.

(DFT) method. In range of 10 to 20 wt%/monomer, trend of total pore volume and volume distribution were similar. Total pore volume was about $0.34 \text{ cm}^3/\text{g}$ and meso- and micropores were mostly distributed below 15 nm. Above 30 wt%/monomer, there were more mesopores above 15 nm; so, the total pore volume increased while the pore volume distribution broadened.

One step synthesis of hypercrosslinked polyxylene can be explained from the yield and adsorption data. When monomers are converted into polymers, they obtain swelling properties. With the growth of hypercrosslinked polymer, amount of swelled solvent was increased. For this reason the polymer has a gel-like characteristic. Therefore, in the mixed solution of monomers and catalyst the movement molecules were limited. Also, hypercrosslinked polymer had micropores, which are a factor for good absorbent to small molecules such as iron(III) chloride. By the limitation of solution movement and adsorption of catalyst, polymer growth is restricted. Residual monomer and oligomer, which respectively are unreacted or slightly reacted molecules, were eliminated in the cleaning step. When amount of catalyst was increased, unabsorbed catalyst molecules yield of hypercrosslinked polyxylene. In addition, excessive amount of catalyst may result in untailed crosslinking structure, hence the formation of relatively large mesopores and broad pore size distribution in the hypercrosslinked polyxylene.

One of unique result is lower limit of catalyst concentration for synthesis of hypercrosslinked polyxylene. 5 wt%/monomer sample showed different behaviors to that of a sample with higher concentrations. The final product of the 5 wt%/monomer sample had a brighter, ocher color. BET surface area and t-plot micropore volume are $73.50 \text{ m}^2/\text{g}$

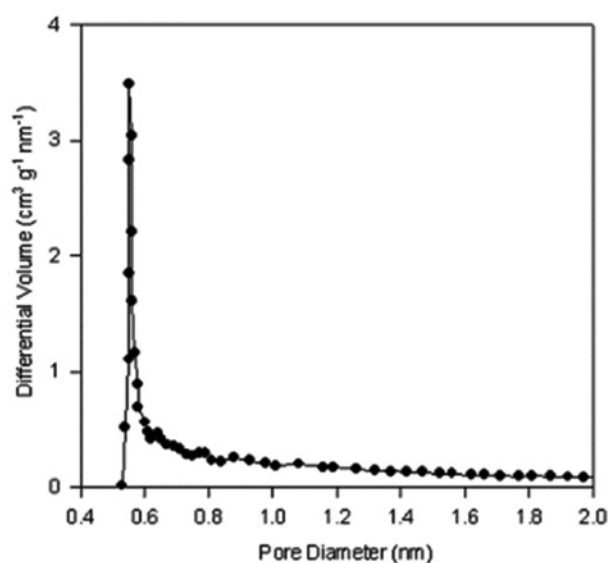


Figure 9. Micropore size distribution for the hypercrosslinked polyxylene calculated by the H-K method (carbon slit pore model).

and $0.0126 \text{ cm}^3/\text{g}$, respectively, which were 10 times lower than values in high concentration samples. Also, pore size was distributed above 50 nm, which is a macropore region. Therefore, there is a threshold catalyst concentration where the polymer becomes a high performance hypercrosslinked polymer somewhere between 5 and 10 wt%/monomer.

Figure 9 shows the micropore size distribution for the sample as calculated by the H-K method. The hypercrosslinked polymer had a pore diameter of 0.55 nm at the peak of maximum differential volume and a relatively broad micropore size distribution. The micropore volume for the hypercrosslinked polymer at an argon partial pressure (P/P_0) of 0.057 was determined as $0.2324 \text{ cm}^3/\text{g}$ at 87 K. It is matched with result of porosity using nitrogen gas. For reference,¹¹ a typical hypercrosslinked polystyrene has a median pore diameter of 0.789 nm and micro pore volume is about $0.48 \text{ cm}^3/\text{g}$ ($P/P_0 = 0.053$, nitrogen at 77 K).

Conclusions

Hypercrosslinked polyxylene was synthesized from dichloro-*p*-xylene monomers by self-condensation polymerization without bridge molecules *via* Friedel-craft reaction. These monomers, which have both benzene ring and halogen groups, were converted into a polymer in the presence of a Lewis acid catalyst. The yield of hypercrosslinked polyxylene increased with the concentration of catalyst, and the maximum yield was 65.4%. Due to adsorption and swelling, which are characteristic properties of hypercrosslinked polymers, limited the yield during self-condensation polymerization. Above a certain threshold amount of catalyst, porosity of hypercrosslinked polyxylene was found to increase as the catalyst concentration increased. Maximum values of BET surface

area and t-plot micropore volume were 1168.37 m²/g and 0.2395 cm³/g. Using the H-K method, hypercrosslinked polyxylylene had a broad micropore distribution and a peak diameter of 0.55 nm at the maximum differential volume.

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