

## Novel Microporous Polymers for NO<sub>x</sub> Adsorption

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### Abstract

*In this paper, we synthesized hypercross-linked conjugated chromophores with light absorption characteristics during cross-linking of aromatic monomers, such as naphthalene with dimethoxy methane, Phloroglucinol with terephthaldehyde and Phloroglucinol with dichloro-p-xylene from Friedal-Crafts reaction. DRS UV Vis spectroscopy confirms conjugated quinonoid matrix by their broad light absorption characteristics extending from 1000 to 200 nm. Absorbance maximum occurred close to 400 nm. So, the catalyst functions to cross-link the monomers by -CH<sub>2</sub>- bridges and subsequently dehydrogenate the bridges to form quinonoids. The FTIR spectroscopy showed their characteristic quinonoid vibrations between 1600 and 1700 cm<sup>-1</sup>. From the thermogravimetric analysis, thermal stability of the microporous polymers was found to be good. Their SEM images showed microspheres of 1 to 5 μm size built with tiny particles. Their surfaces were not smooth. The maximum NO<sub>x</sub> sorption of 13% was obtained for the hypercross-linked polymer of Phloroglucinol with dichloro-p-xylene.*

**Key words:** *conjugated quinonoid chromophores, hyper cross-linked polymers, NO<sub>x</sub> adsorption, scanning electron microscopy*

### 1. Introduction

As the world waits for viable clean energy solutions for the transportation sector, consumption of petroleum continues to rise dramatically. Pollution from combustion of gasoline and diesel can be broadly categorized into the inevitable (CO<sub>2</sub>) and the byproducts arising from impurities in the hydrocarbons and/or undesired combustion byproducts (SO<sub>x</sub>, NO<sub>x</sub>, particulate matter). NO<sub>x</sub> has been widely known as a typical pollutant that has caused a detrimental environmental effect on the earth for several decades [1]. Nitrogen oxides (NO<sub>x</sub>) are formed from the reaction of nitrogen and oxygen in air during combustion processes, such as in power plants and automotive engines [2-4]. In areas of high motor vehicle traffic, the amount of NO<sub>x</sub> emitted into the atmosphere can be quite significant resulting in smog and acid rain and the formation of tropospheric ozone. Despite the fact that NO is unstable thus its self decomposition should be thermodynamically favored (2NO → N<sub>2</sub> + O<sub>2</sub>, G = -86 kJ/mol) [5], appropriate catalytic systems are necessary in order to reduce the high activation barrier accompanied with the decomposition reaction (364 kJ/mol) [6].

Significant efforts have been made on the catalytic removal of NO<sub>x</sub>, with a extensively established approach being the selective catalytic reduction using a different reducing agents, such as CO, hydrogen, ammonia and hydrocarbons. CO is present in the exhausts of several combustion processes and under certain limitations to exhibits a good reducing activity

converting NO to N<sub>2</sub>, while it is oxidized into CO<sub>2</sub>, thus limiting the amounts of two important air pollutants. The use of hydrocarbon is also considered a valuable alternate due to safety in handling compared to several other reducing agents. To this extent we have approach NO<sub>x</sub> adsorption using hypercross-linked aromatic polymers.

With the main objective of microporous organic polymers for NO<sub>x</sub> sorption, we have been involved in the cross-linking of naphthalene with dimethoxy methane, Phloroglucinol with terephthaldehyde and Phloroglucinol with dichloro-p-xylene in the presence of Friedel Crafts catalyst, FeCl<sub>3</sub>. All the synthesized hypercrosslinked quinonoids were characterized by FTIR, DRS-UV, SEM, TGA and NO<sub>x</sub> adsorption studies.

## 2. Experimental

### 2.1. Synthesis of Hypercross-linked Polymer, Poly(Naphthalene + Dimethoxy methane)

1 g of naphthalene and 2.4 g of dimethoxy methane were dissolved in 40 mL of 1, 2 dichloroethane in a 100 mL RB flask, and the mixture was vigorously stirred using a magnetic stirrer. Then 3.0 g of anhydrous ferric chloride was added to it, and the flask was attached to a reflux condenser carrying a calcium chloride guard tube. The flask was heated at 40 °C in a temperature controlled mantle for 4 h and then temperature was raised to 80 °C. The reaction was continued for 20 h, the flask cooled, and the mixture filtered under suction. The residue was washed with 5% HCl in water, methanol and acetone mixture in the ratio 3:1:1 for four times, then with water and finally with acetone, and dried in the oven at 100 °C for 12 h.

### 2.2. Synthesis of Poly(phloroglucinol + terephthaldehyde)

1 g of phloroglucinol mixed with 1 g of terephthaldehyde in the presence of 1,4-dioxane solvent and the mixture was stirred continuously and kept in oven at 100 °C for 6 hours. The yellow-orange precipitate was collected through filtration using acetone as the solvent. The sample was then dried in vacuum oven at 100 °C for 12 h.

### 2.3. Synthesis of Poly(phloroglucinol + dichloro-p-xylene)

In a typical procedure, 1 g of phloroglucinol and 0.99 g of dichloro-p-xylene were dissolved in 20 mL of 1, 2 dichloroethane in a 100 mL round bottom flask, and the mixture was vigorously stirred. Then 3.0 g of ferric chlorides (catalyst) was added to it, and the flask was attached to the reflux condenser with calcium chloride guard tube. The flask was heated initially at 40 °C for four hours and then temperature raised to 80 °C for another 16 hours. After completion of the reaction, the product was filtered under suction. The filtrate was washed several times with water, methanol and acetone mixture and dried in an oven at 100 °C for 12 h.

### 2.4. Characterization

Ultraviolet-visible diffuse reflectance (DRS UV-Vis) spectra were recorded on SCINCO Neosys 2000 spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded at room temperature with 4 cm<sup>-1</sup> resolution between 4000 and 400 cm<sup>-1</sup> in a FT-IR spectrometer (Nicolet IR 200). The morphologies of the samples were studied by SEM after gold coating using a FEI Quanta 200 instrument operating at 30 keV and equipped with an EDX detector.

## 2.5. NO<sub>x</sub> Adsorption

For NO<sub>x</sub> adsorption study, Rubotherm high pressure thermogravimetric analyzer was used. Prior to the experiment, the samples were pre heated at 150 °C. The adsorption was monitored at room temperature feeding the NO gas (Figure 1).

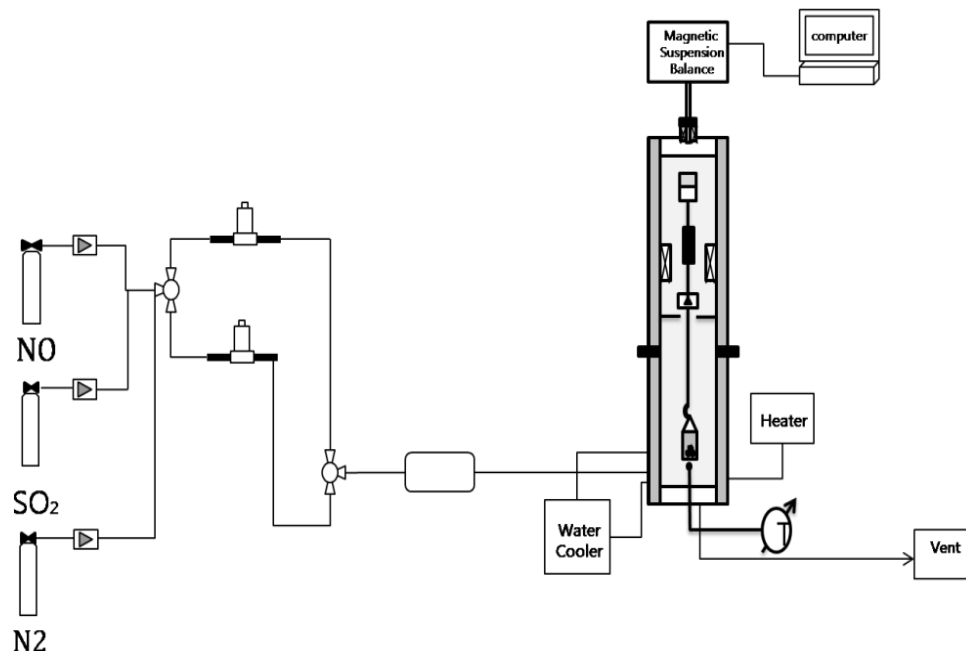
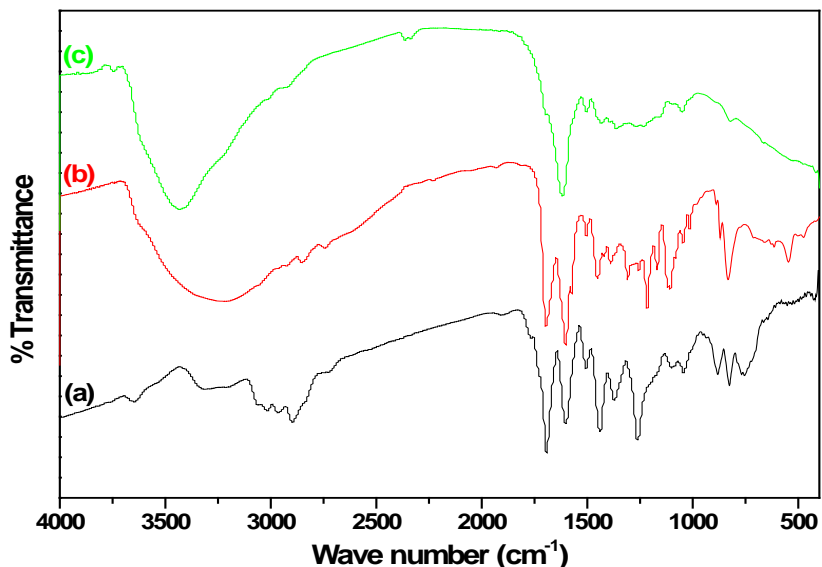


Figure 1. Pictorial Representation of NO<sub>x</sub> Adsorption Setup

## 3. Results and Discussion

### 3.1. FTIR

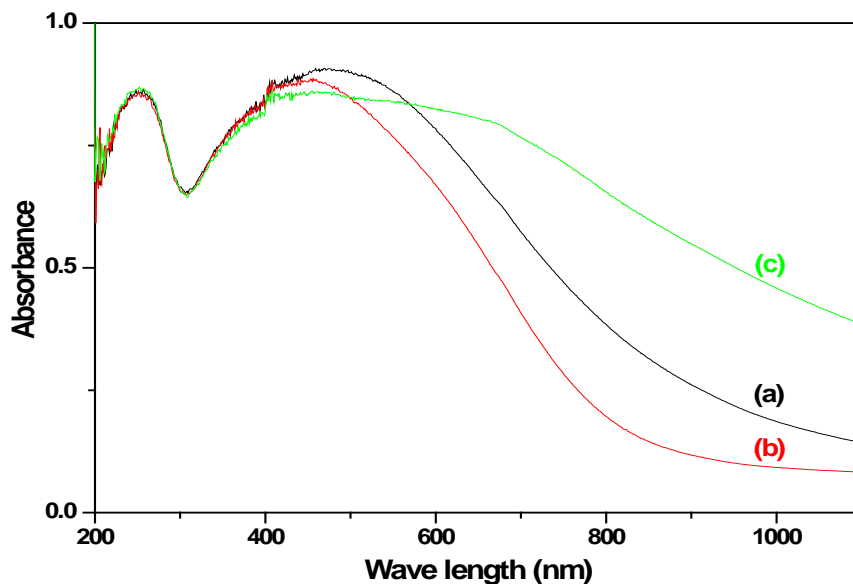
The FTIR spectrum of the polymer, Naphthalene + Dimethoxy methane (Figure 2(a)) showed peaks for aromatic and aliphatic C-H stretching vibrations just above and below 3000cm<sup>-1</sup>, but they are weak. It is due to quinonoid formation, evidenced by the peaks between 1600 and 1700cm<sup>-1</sup>. The peaks due to -CH<sub>2</sub>- bending modes just below 3000 cm<sup>-1</sup> were also weak. The aromatic-C-H bending vibration just below 1000 cm<sup>-1</sup> was also weak illustrating nearly saturation of the substitution. The spectrum (Figure 2(b)) of phloroglucinol-terephthaldehyde also showed similar features. The broad envelope around 3400 cm<sup>-1</sup> was due to phenolic O-H stretching vibration. The aromatic C-H stretching vibration just above 3000 cm<sup>-1</sup> was nearly lost evidencing substitution in all the three free aromatic carbons. The quinonoid bands between 1600 and 1700 cm<sup>-1</sup> illustrates that the terephthaldehyde bridge is converted into a quinonoid. The FTIR spectrum (Figure 2(c)) of Phloroglucinol-Bis-dichlobenzene also showed a broad band around 3400 cm<sup>-1</sup> due to phenolic O-H stretching. Here too the chromatic C-H stretching vibration just above 3000 cm<sup>-1</sup> is lost illustrating complete substitution in the ring. The -CH<sub>2</sub>- stretching vibrations just below 3000 cm<sup>-1</sup> was weak. The intense band about 1600 cm<sup>-1</sup> with the shoulder in its high energy portion illustrates its transformation to quinonoid. It is also supported by absence of peaks due to aromatic C-H bending modes below 1000 cm<sup>-1</sup>.



**Figure 2. FTIR Spectra of (a) Naphthalene + Dimethoxy Methane, (b) Phloroglucinol + Terephthaldehyde and (c) Phloroglucinol + Dichloro-p-xylene**

### 3.2. DRS-UV

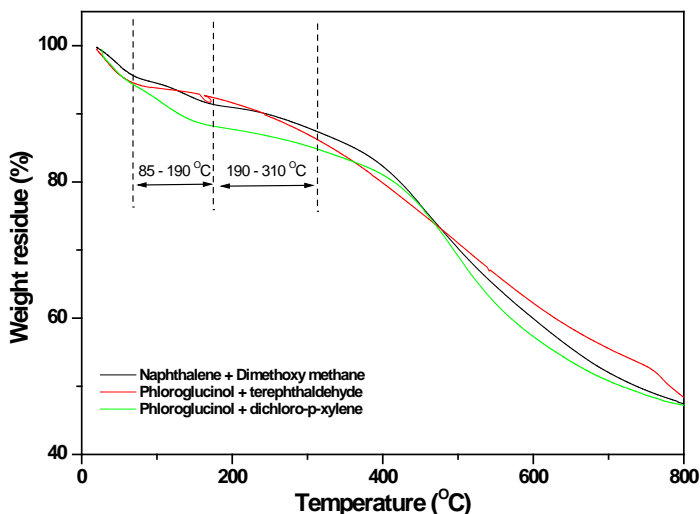
The DRS UV Vis spectra of the polymers (Figure 3) showed broad light absorption extending from 1000 to 200 nm. It confirms formation of hyper cross-linked conjugated quinonoid chromophores. We are proud to mention that we are the discoverers of these polymers. We expect large hope for them in the future for different applications. In Naphthalene + Dimethoxy methane, the naphthalene ring is transformed to quinonoid. In the other two polymers the bridges are converted into quinonoids.



**Figure 3. DRS-UV Visible Spectra of (a) Naphthalene + Dimethoxy Methane, (b) Phloroglucinol + Terephthaldehyde and (c) Phloroglucinol + dichloro-p-xylene**

### 3.3. TGA

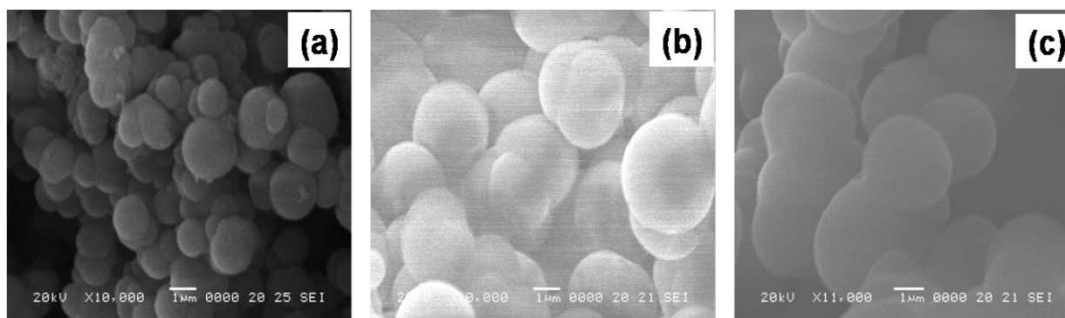
The results of are of the polymers are illustrated in Figure 4. They showed nearly similar characteristics. The initial weight loss between 30 and 250 °C was due to desorption of entrapped solvents. Desorption over a large range of temperatures confirms they are microporous. The major weight loss above 310 °C was due to their decomposition. So, these polymers can be exploited for sorption applications upto 310 °C.



**Figure 4. Thermogravimetric Analysis Hypercross-linked Polymers**

### 3.4. SEM

The SEM images of the polymers are shown in Figure 5. There were microspheres of varying dimensions. The surface of the spheres reflects that each sphere is made of tiny particles. The micropores between the particles become the cause for adsorption. The spheres of Phloroglucinol + dichloro-p-xylene are very much fused, and so it is expected to yield high NO sorption. Actually each particle of the sphere is a hyper cross-linked conjugated quinonoid. The particles are insoluble in dichloroethane, so during polymerization they reach a particular size, escape from the solvent and associate to form a sphere.



**Figure 5. SEM Images of (a) Naphthalene + Dimethoxy Methane, (b) Phloroglucinol + Terephthaldehyde and (c) Phloroglucinol + dichloro-p-xylene**

### 3.5. NO<sub>x</sub> Adsorption

The NO adsorption characteristics of the polymers are illustrated by plotting time versus wt% in Figure 6. The polymer, Phloroglucinol-Bis-chloromethyl benzene, showed higher percentage of adsorption than others. The interaction of O–H groups might not be the cause, as Naphthalene + Dimethoxy methane polymer showed higher value than Phloroglucinol + terephthaldehyde. Their specific surface area, in addition to fusion of spheres, as evidenced from SEM images, might be the cause for it. Fused spheres can better take NO as their deep pores can better retain molecules inside. So, microporous polymers have high scope for removing NO from the exhaust.

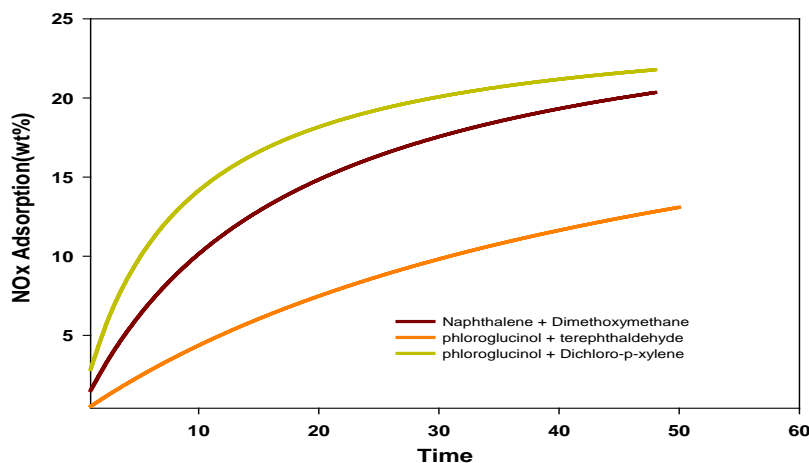


Figure 6. NO<sub>x</sub> Adsorption Study for Hypercross-linked Polymers

## 4. Conclusions

Hence, with the above results we are to conclude that three hypercross-linked polymers were successfully synthesized from their respective monomers for NO<sub>x</sub> adsorption. DRS UV Vis spectroscopy clearly reveals that conjugated quinonoid matrix was formed by their broad light absorption characteristics. From the FTIR spectroscopy, the characteristic quinonoid vibrations between 1600 and 1700 cm<sup>-1</sup> was observed. Thermal stability of the microporous polymers was found to be adequate. SEM images showed microspheres of 1 to 5μm size built with tiny particles. Their surfaces were not smooth. The maximum NO<sub>x</sub> sorption of 13% was obtained for the hypercross-linked polymer of Phloroglucinol with dichloro-p-xylene. Hence the prepared hypercross-linked microporous polymers are better candidate for NO<sub>x</sub> adsorption.

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