HYPERCROSSLINKED POLYMERIC FOAMS
PREPARED BY FRIEDEL-CRAFTS
POLYCONDENSATION

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Porous materials are widely used in industry and government for chemical separations, processing and monitoring, environmental cleanup and remediation, energy efficiency, and conservation. Porous materials used in these applications include: foams, filters, membranes, absorbents, ion exchange resins, molecular sieves, zeolites, catalyst supports, sensors, and electrodes. Organic analogues to inorganic zeolites would be a significant step forward in engineered porous materials and would provide advantages in range, selectivity, tailorability and processing. A novel process for preparing hypercrosslinked polymeric foams has been developed via a Friedel-Crafts polycondensation reaction. A series of rigid hypercrosslinked foams have been prepared using simple rigid polyaromatic hydrocarbons such as benzene, biphenyl, m-terphenyl, diphenylmethane, and polystyrene, with p-dichloroxylene as the crosslinking agent. After drying the gels, the resulting foams are robust and rigid. Their densities range from 0.3g/cc to 0.5g/cc. Nitrogen adsorption studies have shown that by judiciously selecting monomers and crosslinking agent along with the level of crosslinking, the pore size and distribution along with total surface area of the foam can be tailored. Surface areas range from 160 to 1,200 m\(^2\)/g with pore sizes ranging from 6Å to 250Å. Further evidence of this has been confirmed by high resolution TEM.

**ABSTRACT.** Please be BRIEF—150 words maximum if possible. Title of paper should be ALL CAPS; author(s) listed by first name, middle initial, last name; indicate address w/zip code. SINGLE SPACE, BLACK INK.
HYPERCROSSLINKED POLYMERIC FOAMS PREPARED BY FRIEDEL-CRAFTS POLYCONDENSATION

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Introduction

There are numerous efforts in the materials science community directed towards producing well-defined materials that are engineered at the sub-micron level. Hyperbranched and hypercrosslinked polymers are two prominent examples. Polymer scientists are now able to manipulate polymers at the nanometer level by producing hyperbranched monodisperse entities with well defined sizes, structures, and functionalities. Hyperbranched polymers are truly intriguing from a theoretical standpoint. Preparation of hyperbranched structures requires expensive starting materials, numerous synthetic steps, and rigorous purification procedures often to obtain just a few milligrams of product. Hypercrosslinked polymers are also receiving attention because polymer scientists are attempting to produce rigid, non-porous, truly microporous materials. A straightforward polycondensation, known as Friedel-Crafts polycondensation, provides a simple, yet versatile, method for preparing rigid hypercrosslinked poly(aryl-ylene methylene) foams. This straightforward polycondensation, as known as Friedel-Crafts polycondensation, has been applied to similar aromatic systems in an effort to obtain linear poly(aryl-ylene methylene). In this early work, researchers were unable to prevent crosslinking and typically recovered insoluble, infusible polymers. Even the lightly crosslinked polymers swell upon standing in various solvents, uptake a variety of substances from solution, and possess high thermal stabilities.

Experimental

Material

All of the polyaromatic hydrocarbons, crosslinking agents, catalyst, and all solvents were purchased from Aldrich, except for the three polystyrene precursors which were purchased from Polysciences. Air Products supplied the carbon dioxide. Unlike previous syntheses, all the reactants, solvents and catalyst were used as supplied.

Samples were typically prepared by first dissolving the PAH and XL in dichloroethane. The concentrations of PAH and XL were varied from 0.10g/cc to 0.20g/cc in the precursor solution. Tin tetrachloride, used as the Friedel-Crafts catalyst, was added at this point. This solution was allowed to react for 10 - 24 hours at 60°C. Once the gel had cured, any catalyst and unreacted monomers were extracted from the gel using a solvent such as acetone or methanol. This solvent was removed from the gel via supercritical extraction with carbon dioxide.

Methods

Surface area analysis was done using a Micromeritics ASAP 2010 Surface Area Analyzer. Nitrogen adsorption measurements were performed at 77°K. Surface areas were calculated according to theory as developed by Brunauer, Emmett, and Teller (BET). Micropore volume and area distributions were calculated according to Horvath - Kawazoe (H-K) theory. The Barrett, Joyner, and Halenda (BJH) method was used in determining the pore volume and area distributions for the mesopores. Thermal analysis measurements were run on a Polymer Laboratories TGA in air and argon with a heating rate of 10°C/min. Micrographs were obtained using a Jeol TEM. Samples were stained with ruthenium tetroxide in order to improve contrast.

Results and Discussion

A novel process for preparing hypercrosslinked polymeric foams has been developed via a Friedel-Crafts condensation reaction. A series of rigid free-standing hypercrosslinked foams have been prepared using simple rigid polyaromatic hydrocarbons such as benzene, biphenyl, m-terphenyl, diphenylmethane, and polystyrene, with p-xylenechloethane as the crosslinking agent. Varying the ratio of XL:PAH from 1.5:1 to 2/1 increases the surface area of the resulting foam. An increase in the surface area resulting from additional crosslinks can be seen as an increase in the surface area of the smaller pores of polystyrene, as shown in Fig. 1. The effect of the crosslink ratio on the surface area is not as great as the choice of monomers, as shown in Figure 2. Initial polymerizations were conducted at 60°C for 16 hrs. in glass molds. This presents a novel method of preparing hypercrosslinked polymers by Friedel-Crafts Polycondensation. The preparation of rigid gels using this technique has never been documented in the literature. Prior art in this area gives rise to materials that are either powders or resins.

![Fig. 1. Pore size distribution for polystyrene crosslinked with dichloroethane at molar ratios of 1.5:1 and 2:1.](image-url)
The foams were then processed and dried using several techniques. Air, oven, or vacuum-drying successfully removes solvent; however, the gels tend to crack significantly leaving cracked foam articles. Supercritical drying of the solvent-wetted gels using carbon dioxide leaves uncracked rigid foam pieces. Foams which were supercritically dried had surface areas in excess of 500 m²/g, whereas an analogous air dried foam had a surface area of only 7 m²/g. After drying, a rigid free-standing foam article remains. Their densities range from 0.3g/cc to 0.5g/cc. The increase in density is due primarily to the shrinkage upon polymerization.

The foams are not transparent and are typically lighter in color (white to yellow) following drying. Sorption studies have shown that by judiciously selecting monomers and crosslinking agent along with the level of crosslinking, the pore size and distribution along with total surface area of the foam can be tailored. As shown in Table 1, surface areas range from 160 to 1,200 m²/g with pore sizes ranging from 6Å to 1,000Å. Further evidence of this has been confirmed by high resolution TEM, shown in Figure 3.

**Table 1. Surface Areas of Hypercrosslinked Foams**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Monomer</th>
<th>xl density</th>
<th>BET SA (m²/g)</th>
<th>H-K pore (Å)</th>
<th>BJH pore (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27BB</td>
<td>bibenzyl</td>
<td>1.50</td>
<td>159.9</td>
<td>7.1</td>
<td>215.5</td>
</tr>
<tr>
<td>27BP</td>
<td>biphenyl</td>
<td>1.50</td>
<td>291.5</td>
<td>6.7</td>
<td>211.8</td>
</tr>
<tr>
<td>27DM</td>
<td>diphenylmethane</td>
<td>1.50</td>
<td>291.9</td>
<td>10.1</td>
<td>259.9</td>
</tr>
<tr>
<td>27TPB</td>
<td>triphenylbenzene</td>
<td>1.50</td>
<td>311.4</td>
<td>6.6</td>
<td>226.2</td>
</tr>
<tr>
<td>1DM</td>
<td>diphenylmethane</td>
<td>2.00</td>
<td>370.2</td>
<td>6.6</td>
<td>144.6</td>
</tr>
<tr>
<td>1BP</td>
<td>biphenyl</td>
<td>1.75</td>
<td>370.6</td>
<td>7.4</td>
<td>153.9</td>
</tr>
<tr>
<td>9BP</td>
<td>biphenyl</td>
<td>2.00</td>
<td>603.3</td>
<td>7.2</td>
<td>125.0</td>
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<tr>
<td>1TPB</td>
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<td>2.00</td>
<td>636.2</td>
<td>6.8</td>
<td>112.4</td>
</tr>
<tr>
<td>27B</td>
<td>benzene</td>
<td>1.50</td>
<td>692.1</td>
<td>6.2</td>
<td>155.7</td>
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<tr>
<td>27PSL</td>
<td>PS-50k</td>
<td>1.50</td>
<td>994.8</td>
<td>6.2</td>
<td>128.6</td>
</tr>
<tr>
<td>5PSH</td>
<td>PS-280k</td>
<td>2.00</td>
<td>1,096.0</td>
<td>6.5</td>
<td>148.3</td>
</tr>
<tr>
<td>5PSL</td>
<td>PS-50k</td>
<td>2.00</td>
<td>1,204.4</td>
<td>6.0</td>
<td>105.8</td>
</tr>
</tbody>
</table>

* - where crosslink density is reported as ratio of XL/PAH

Due to highly crosslinked nature of these materials, the thermal stability has been found to be much greater than that of conventionally crosslinked materials. TGA has shown that in air there is less than a five percent weight loss at 500°C and between thirty and seventy percent at 1,000°C.

**Fig. 2.** Comparison of pore size distributions for a low surface area foam, diphenylmethane, and a high surface area foam, polystyrene.

**Fig. 3.** TEM of hypercrosslinked bibenzyl foam (1.5:1) stained with ruthenium oxide. (Scale bar = 10 nm)

**Conclusions**

Pore size and distribution can be judiciously chosen by careful choice of monomers and reaction conditions. Surface areas of these hypercrosslinked foams range from 160 m²/g to 1,200 m²/g. More important is the fact that these foams are robust in nature and can be machined into coupons for use as membranes. Current work includes direct casting of membranes as well as functionalization of the surfaces of these materials.

**Acknowledgments**

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**References**