CONF-960376--3

LA-UR-95- -3568

Title:

HYPERCROSSLINKED POLYMERIC FOAMS PREPARED BY FRIEDEL-CRAFTS POLYCONDENSATION

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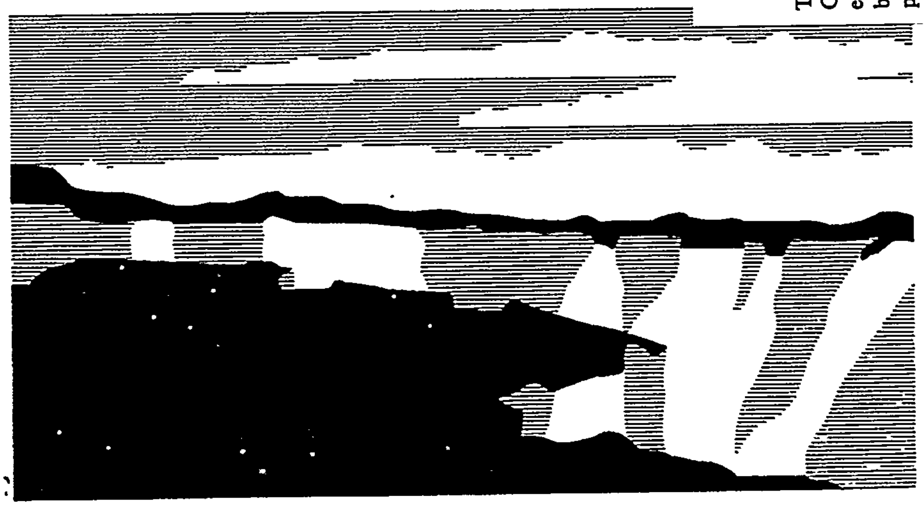
Submitted to:

American Chemical Society
Spring National Meeting
New Orleans, LO
March '96



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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 remidiation, 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.

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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 control porosity in rigid-rod polymers and organic-inorganic hybrids at the nanometer level using low temperature condensation reactions or sol-gel processing techniques. While some successes are noted, the starting materials can be expensive or difficult to synthesize. In addition, the crosslinking reactions are cumbersome and not amenable to large scale preparations.

Although promising, these novel hyperbranched and hypercrosslinked polymers are still unable to compete with commercially available macroporous materials including lightly crosslinked polystyrene resins which are commonly used in separations, chromatography and ion exchange. Surprisingly, highly or hypercrosslinked forms of polystyrene are relatively unknown and are not commonly used for separations. However, there are several reports describing truly phenomenal properties in hypercrosslinked polystyrene which suggest that these materials may be superior to traditional polystyrene resins.[1-3] Hypercrosslinked polystyrenes have extraordinarily high surface areas, swell in thermodynamically unfavorable solvents, absorb dyes and hydrocarbons, and readily absorb gases. These phenomena, which are not observed in linear or lightly crosslinked polystyrene resins and beads, are attributed to the high frequency of rigid crosslinks which do not allow the polymeric network to collapse. This leaves a true microporous material with extraordinarily high surface areas and exceptional absorptive capacity. Despite these wonderful properties, several drawbacks are apparent. The microstructure cannot easily be varied since the pore sizes and volumes are determined solely by the length and structure of the crosslinking agent. Robust, easily tailorable, microporous, rigid, hypercrosslinked polymeric materials do not exist.

A simple, one step process from inexpensive raw materials to microporous hypercrosslinked polymers has been developed. Polycondensation of rigid polyaromatic hydrocarbons (PAHs) using rigid aromatic crosslinking agents (XLs) provides a simple, yet versatile, method for preparing rigid hypercrosslinked poly(arylene methylenes) foams. This straightforward polycondensation, known as Friedel-Crafts polycondensation, has been applied to similar aromatic systems in an attempt to obtain linear poly(arylene methylenes). In this early work, researchers were unable to prevent crosslinking and typically recovered insoluble, infusible polymers.[4-5] 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 synthesis[1-5], 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)[6]. Micropore volume and area distributions were calculated according to Horvath - Kawazoe (H-K) theory[7]. The Barrett, Joyner, and Halenda (BJH)[8] 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 tetraoxide in order to improve contrast.

Results and Discussion

A novel process for preparing hypercrosslinked polymeric foams has been developed via a Friedel-Crafts polycondensation 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*-xylylenedichloride 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 represents 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.

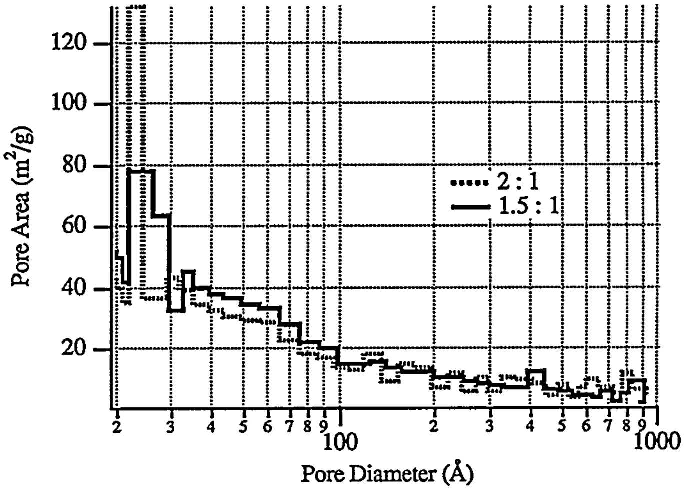

Fig. 1. Pore size distribution for polystyrene crosslinked with dichloroxylene at molar ratios of 1.5:1 and 2:1.

In the majority of cases, highly colored gels were formed upon polymerization. In some cases, transparent gels were formed suggesting a very small pore size. The colors of gels ranged from light pink to deep purple. Shrinkage did occur upon polymerization due to the high contractive forces of the highly crosslinked networks. This shrinkage sets up stresses in the material which leads to cracking. In order to provide a membrane for separation studies these materials needed to be monolithic. By tailoring the catalyst concentration and reaction conditions, rigid foams were produced which were then machined into coupons for membrane testing. Initial studies on membranes prepared from these materials shows that diffusion of hydrocarbons is by an active transport mechanism. This would extend the use range of these hypercrosslinked materials over those that have been previously prepared.

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 m^2/g, whereas an analogous air dried foam had a surface area of only 7 m^2/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 m^2/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.

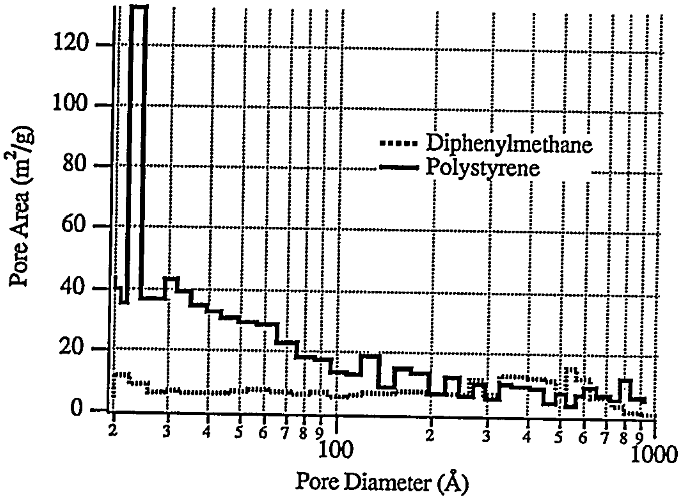

Fig. 2. Comparison of pore size distributions for a low surface area foam, diphenylmethane, and a high surface area foam, polystyrene.

Table 1. Surface Areas of Hypercrosslinked Foams

Resin	Monomer	xl density *	BET SA (m^2/g)	H-K pore (Å)	BJH pore (Å)
27BB	bibenzyl	1.50	159.9	7.1	215.5
27BP	biphenyl	1.50	291.5	6.7	211.8
27DM	diphenylmethane	1.50	291.9	10.1	259.9
27TPB	triphenylbenzene	1.50	311.4	6.6	122.6
1DM	diphenylmethane	2.00	370.2	6.6	144.6
1BP	biphenyl	1.75	570.6	7.4	153.9
9BP	biphenyl	2.00	603.3	7.2	125.0
1TPB	triphenylbenzene	2.00	636.2	6.8	112.4
27B	benzene	1.50	692.1	6.2	155.7
27PSL	PS-50k	1.50	994.8	6.2	128.6
5PSH	PS-280k	2.00	1,096.0	6.5	148.3
5PSL	PS-50k	2.00	1,204.4	6.0	105.8

* - 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.

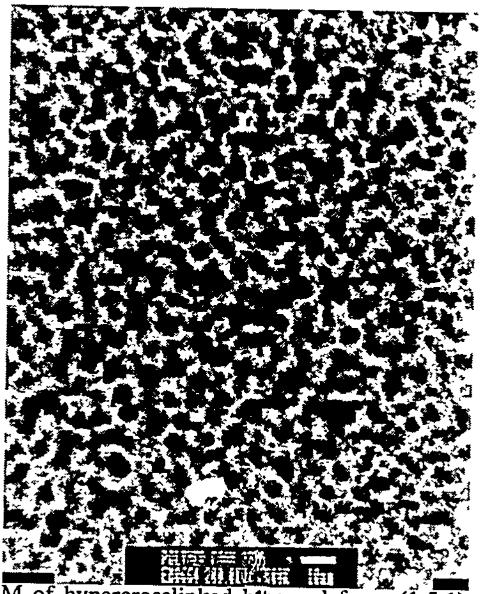

Fig. 3. TEM of hypercrosslinked bibenzyl foam (1.5:1) stained with ruthenium oxide. (Scale bar = 10 nm)

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 m^2/g to 1,200 m^2/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

TEM micrographs were acquired by Kerry Siebein, whose dedication towards obtaining better images is greatly appreciated. Funding for this project has been made possible by the Department of Energy via Lab Directed Research & Development project 94-218 at Los Alamos National Labs.

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