Microporous Materials

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Hole Control in Microporous Polymers**

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gas adsorption · hypercrosslinked polymers ·
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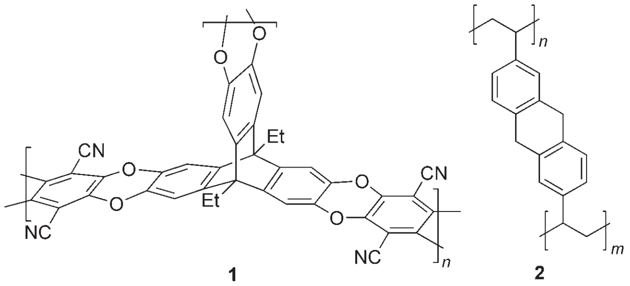
ultramicropores

Microporous materials that have large specific surface areas and pores with molecular dimensions are of interest for applications that range from selective membranes to molecular sieves to catalysts to photonic crystals. Especially their potential utilization as physisorptive storage media for hydrogen (H_2), widely viewed as the fuel of the future, has sparked a recent flurry of activities that target the development of new lightweight microporous materials with small and well-controlled pore dimensions. Most of the materials that are currently used in commercial applications are inorganic; zeolites and activated carbon are the most prominent examples. Organic polymers represent a desirable alternative, since they combine low density with good mechanical properties and ease of processing. Furthermore, their chemical nature can be broadly tailored, making it easy to create surfaces that attract or repel specific molecules. However, until recently it was impossible to gain control over their porosity and especially their pore sizes. Several new approaches have lately emerged to solve this problem. Research has rapidly led to the development of materials with specific surface areas that exceed those of activated carbons (3000 $m^2 g^{-1}$) and with H_2 storage capacities that approach the US Department of Energy target for 2010 (6 wt% at 77 K and 10 bar). More than one paradigm has been shifted along the way, the last one by Cooper and co-workers, who reported that control over pore size can be achieved in amorphous conjugated polymer networks.[1]

Because of their higher surface energies, microporous materials generally exhibit a much lower thermodynamic stability than more condensed phases. In the case of inorganic zeolites, this problem is overcome by the kinetic trapping of metastable network structures in which the framework is sufficiently rigid to keep the pores open. Organic macromolecules, in contrast, are usually characterized by high translational and conformational mobility. Hence, most polymers collapse into dense, nonporous materials upon solidification. High rigidity, bulkiness, nonplanarity, and contorted architectures frustrate efficient packing of macromolecules so that interconnected voids can form. Budd, McKeown, and co-workers recently demonstrated that polymers with intrinsic microporosity (PIMs) can be created on the basis of these design rules and through the exploitation of simple and efficient dioxane-forming reactions.[2] Several candidates were studied, including the cross-linked ladder-type polymer **1** (Scheme 1). The internal surface area of some of these easily accessible polymers is in excess of 1000 $m^2 g^{-1}$, and apparent micropore size distributions reveal average pore diameters of about 0.7 nm or less. The small pore diameter is especially advantageous for H_2 storage, where a high concentration of such ultramicropores helps to maximize the physisorption of the small H_2 molecule. Indeed, the hydrogen storage capacity of some of the investigated materials (2.7 wt% at 77 K and 10 bar) is remarkably high. Their microporosity is independent of their processing history, which confirms that the property is intrinsic and arises from the rigid macromolecules' inability to completely fill the voids.



1 2

Scheme 1. Examples of polymers with intrinsic microporosity (PIMs) studied by Budd, McKeown, and co-workers (**1**)[2] and the hyper-crosslinked polymers (HCPs, **2**) investigated by the groups of Cooper[3] and Fréchet.[4]

Hypercrosslinked polymers (HCPs) represent another class of organic microporous materials with large specific surface areas. The most important examples are the so-called Davankov-type resins, which are prepared by the Friedel–Crafts alkylation of chloromethylated polystyrene in the presence of a solvent (**2**, Scheme 1). The microporosity is the result of the hypercrosslinked network's high rigidity, which prevents collapse of micropores formed by the solvent upon drying. While such materials have long been commercially

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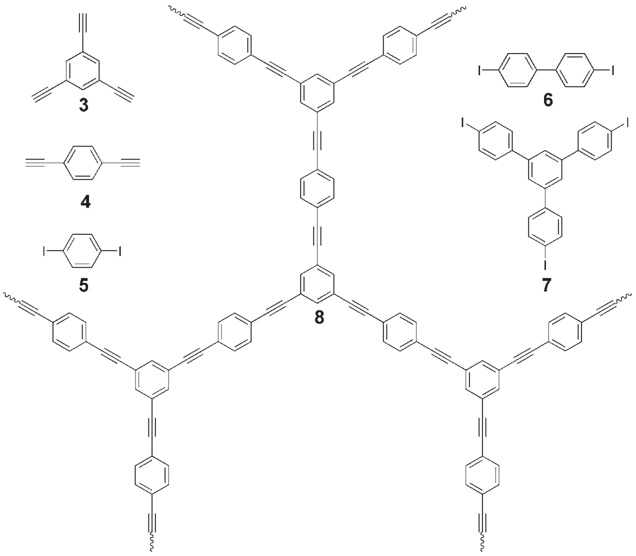
used as the basis for ion-exchange resins and adsorbents, it was not until recently that their high H_2 storage capacity—similar to that of PIMs—was independently discovered by the groups of Cooper[3] and Fréchet.[4] PIMs and HCPs are formed under kinetic control and accordingly are fully amorphous. The micropores in these materials generally display broad size distributions and were thought to be difficult to control, making it challenging to optimize PIMs and HCPs for membranes, gas storage, and other applications for which judicious control over pore size is crucial.

A complementary approach towards the development of organic microporous materials with well-defined pores is based on the idea of mimicking the architecture of inorganic zeolites. The development of crystalline metal–organic frameworks (MOFs), which are formed under thermodynamic control, represents a significant step in this direction.[5] As detailed in the preceding Highlight by Mastalerz,[6] Yaghi and co-workers recently extended this concept to two-[7a] and three-dimensional[7b] crystalline covalent organic frameworks (COFs). These highly ordered materials indeed exhibit large surface areas (greater than 4000 $m^2 g^{-1}$) and well-controllable (ultra)micropore sizes, but their successful synthesis requires very careful design.

Cooper and co-workers recently reported the synthesis of conjugated microporous poly(arylene ethynylene)[8] (PAE) networks, which are formed under kinetic control and thus display no long-range order.[1] Despite this, their pore size appears to be rather well defined and controllable, defying the notion that order is a prerequisite for control over pore size. Thus, these materials may combine the advantages of PIMs (ease of synthesis, chemical stability) with those of COFs (control over pore size). Cooper's group synthesized a series of conjugated cross-linked PAEs using the palladium-catalyzed Sonogashira–Hagihara cross-coupling reaction between di- and trifunctional aryl ethynylenes (**3**, **4**) and aryl halides (**5**–**7**, Scheme 2).[9]



Scheme 2. Monomers **3**–**7** used by Cooper and co-workers for the synthesis of microporous poly(arylene ethynylene) (PAE) networks and a segment of the polymer **8** formed by the polymerization of **3** and **5**.[1]

The networks (e.g. **8**) were created by connecting 1,3,5-substituted benzene nodes with rigid phenylene ethynylene struts. The length of these struts was varied by increasing the number of phenylene moieties from one to three through molecular control at the monomer level. Microporosity of the PAE networks was confirmed by nitrogen sorption studies. Quite surprisingly, the nitrogen sorption isotherm, internal surface area (830 $m^2 g^{-1}$), and pore size distribution of a PAE formed from monomers **3** and **5** were all similar to those of a two-dimensional COF reported earlier by Yaghi.[7a] Moreover, the fraction of ultramicropores decreased with increasing strut length. Thus, although these polymers are completely amorphous, they share many of the features of highly crystalline COFs.

To rationalize this behavior, Cooper and co-workers explored a number of structural models for their cross-linked PAEs. Atomistic simulations suggest that the three-dimensional nature of these PAE networks arises from a combination of the struts bending out of the benzene-node planes, from the dihedral angle between struts on adjacent nodes, from bending of the struts themselves, and from deviations from the 120° angles imposed by the *meta* substitution pattern of the benzene rings (Figure 1).

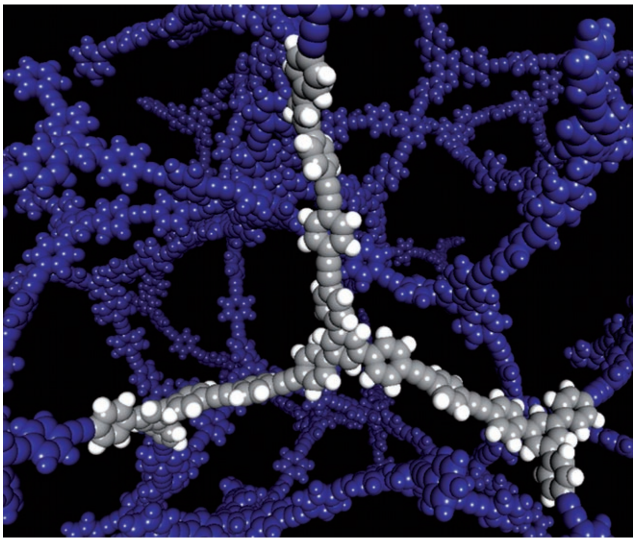


Figure 1. Node–strut topology for a simulated network fragment of a polymer formed by the reaction of monomers **4** and **7**. A 1,3,5-substituted benzene node connecting three other nodes through rigid struts is highlighted.[1]

The finding that order is not a prerequisite for control over the microporous properties of organic networks opens new possibilities for the design of such materials. The conjugated PAE networks studied by the Cooper group appear to bridge the gap between COFs on the one hand and PIMs and HCPs on the other. The results suggest that the differences between these systems may not be as fundamental as previously thought. It is unclear to what extent the pore size distribution can be narrowed in disordered polymer networks, but the results appear to open the door for the further development of a broad range of materials with controlled pore dimensions.

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