Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2010**, *43*, 6943–6945 **6943**
DOI: 10.1021/ma101361b

Preparation of Clickable Microporous Hydrocarbon Particles Based on Adamantane

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Received June 19, 2010
Revised Manuscript Received August 1, 2010

Microporous materials have diverse applications such as gas storage, separation, and catalysis.[1−3] Zeolites and activated carbons have traditionally been used for these applications. Recently, metal−organic frameworks (MOFs) have attracted much attention owing to their regular porosity and large surface areas.[4,5] However, under practical application conditions MOFs suffer from chemical instability, mainly due to the nature of a coordination bond. This weakness can be overcome by using a covalent bond to constitute the framework. Therefore, a significant research effort is currently being directed at synthesizing physicochemically stable, microporous organic materials.[6] Moreover, organic materials have a weight advantage over MOFs, which contain metal elements.

Microporous organic materials have been prepared in forms of highly cross-linked polymers,[7−13] rigid polymers composed of fused-ring components,[14−16] and 2D or 3D crystalline organic frameworks.[17,18] Highly cross-linked polymers can be obtained by polymerization of multifunctional monomers. For example, multifunctional aromatic compounds were polymerized by the palladium-catalyzed coupling reactions to give microporous cross-linked structures.[10−12] Alternatively, polymer chains could be cross-linked in a swollen state to give microporous hyper-cross-linked networks. Polystyrene and polyaniline have been used for the synthesis of hyper-cross-linked polymers.[7,9] Rigid polymers bearing stiff kinks also showed microporous porosity. Hexaazatrinaphthylene-, cyclotricatechylene-, and triptycene-based polymers are typical examples.[14,16]

The overall material performance for the gas adsorption appears to be governed by a combination of morphology, pore structure, material elements, and surface area. Herein, we report clickable, microporous, hydrocarbon particles consisting of carbon and hydrogen. We were able to control the particle morphologies by varying the polymerization conditions and to functionalize the surface by utilizing a click process.

Adamantane is a bulky hydrocarbon, consisting of four cyclohexanes fused into a chair conformation. Because of its rigid and highly symmetrical structure, adamantane was expected to be a promising building block for the preparation of a microporous organic framework. Scheme 1 shows the synthesis of the polymer. 1,3,5,7-Tetrakis(4-iodophenyl)adamantane (**1**) was prepared from 1,3,5,7-tetraphenyladamantane according to the literature.[19] Sonogashira coupling reaction with diethynylbenzene was used to polymerize compound **1**.

The polymerization was carried out in either a miniemulsion or a solution state. The miniemulsion method[20] produced spherical microporous particles with a diameter of 500−700 nm, as observed in the scanning electron microscopic (SEM) image of Figure 1a. A noncontinuous phase of the miniemulsion system was achieved by mixing an aqueous solution of cetyltrimethylammonium bromide and two different organic solvents, toluene and triethylamine (TEA). Compound **1** and the palladium catalyst were dissolved in toluene and 1,4-diethynylbenzene in TEA. When an attempt was made to use only toluene as an organic solvent, the coupling reaction did not occur.

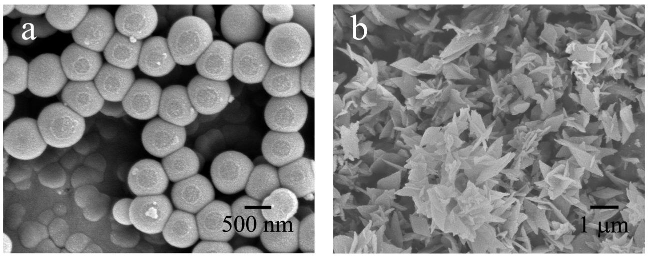
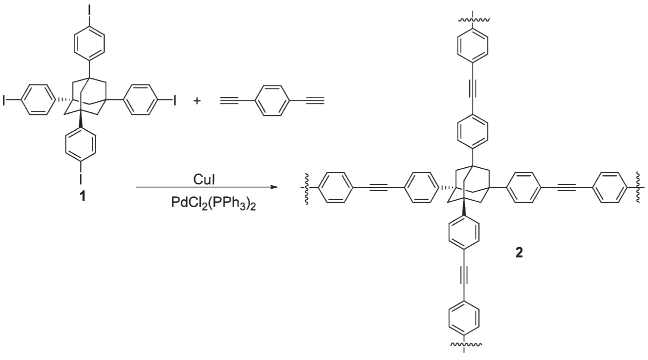


Figure 1. SEM images of the adamantane-based microporous polymer prepared (a) in a miniemulsion state and (b) in a solution state.

Scheme 1. Synthesis of an Adamantane-Based Microporous Polymer



For the solution polymerization, the same two organic solvents (i.e., toluene and TEA) and catalyst were used. Because of its cross-linked nature, the polymer was precipitated during the reaction. The rate of the reaction was dependent on the ratio of the two solvents. At a higher TEA concentration, the reaction proceeded faster and thereby precipitation occurred in the earlier stage. For example, in a 7/3 (v/v) mixture of TEA/toluene, most polymers were precipitated in 1 h. However, at a ratio of 3:7, the precipitation began to occur in 2 h. In most cases, platelike particles were obtained. Figure 1b shows a typical SEM image of the resulting polymer particles obtained in a 1/1 (v/v) mixture of TEA/toluene.

The polymer structures were characterized by ^{13}C CP/MAS NMR and FT-IR specroscopy. Figure 2 shows the solid-state ^{13}C NMR spectrum of the polymer. Aromatic carbons, $C_{ar}{-}C{\equiv}C$, were observed at around 124 ppm and aromatic ring carbons bonded to the adamantine ring at around 149, 137, and 131 ppm. Ethynylene units, $-C{\equiv}C-$, were observed at 90 ppm. Adamantane carbon peaks appeared at 44 and 38 ppm. The FT-IR study showed that the bands at 2100 cm^{-1} for $C{\equiv}CH$ triple-bond stretching modes of diethynylbenzene almost disappeared after polymerization, while the bands for $C{\equiv}C$ triple-bond stretching modes of disubstituted acetylene groups appeared at 2200 cm^{-1}.

Polymer **2** had good thermal stability. A 5% weight loss temperature determined by thermal gravimetric analysis was around 340 °C (Supporting Information Figure 1S). A small weight loss (2%) was observed below 100 °C probably due to entrapped volatile molecules.

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The porous structure of the polymers was investigated by a cryogenic N_2 adsorption/desorption experiment. Figure 3a shows the N_2 adsorption and desorption isotherms for the resulting polymers. All particles exhibited type I adsorption/desorption isotherm. Both isotherm graphs showed hysteresis, suggesting a bottlelike pore shape. The surface area of the spherical particles was higher than that observed for the platelike particles. The Brunauer−Emmett−Teller (BET) surface areas of the spherical particles and the platelike particles were 665 and 442 m^2/g, respectively. The pore size distribution calculated by the Horvath−Kawazoe method indicated the presence of micropores with a mean width of about 0.6 nm [Figure 3a (inset)].

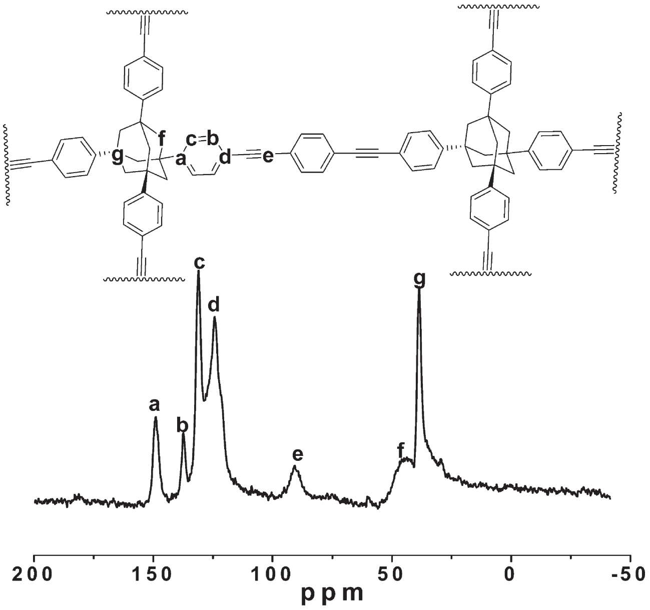


Figure 2. Solid-state ^{13}C NMR spectrum of polymer **2**.

In hydrogen uptake, the spherical particles also showed better performance. From the hydrogen adsorption isotherms shown in Figure 3b, the hydrogen uptake was 0.82 and 0.65 wt % at 77 K and 1 bar for the spherical particles and the platelike particles, respectively.

Since the particles have terminal ethynyl groups, they were further functionalized by using a click reaction. A copper(I)-catalyzed, azide−alkyne cycloaddition reaction is an attractive tool to provide such particles with diverse functionality because the reaction proceeds smoothly with high yield even under mild conditions.[21] In addition, azide compounds with various functional groups are synthetically available. Scheme 2 shows an example of functionalization of the particles via click chemistry. In this reaction, we used an azide with a fluorescent group as an exemplary functional group.

Azide compound **3** was prepared from 5-aminofluorescein and nitrous acid according to the literature.[22] The click reaction of a spherical particle of polymer **2** with azide **3** was carried out in DMSO at 60 °C in the presence of copper sulfate. The product was isolated by filtration and purified by washing with water, methanol, and THF. We were unable to determine the degree of functionalization by ^{13}C CP/MAS NMR or FT-IR spectroscopy. But the high coupling efficiency of the

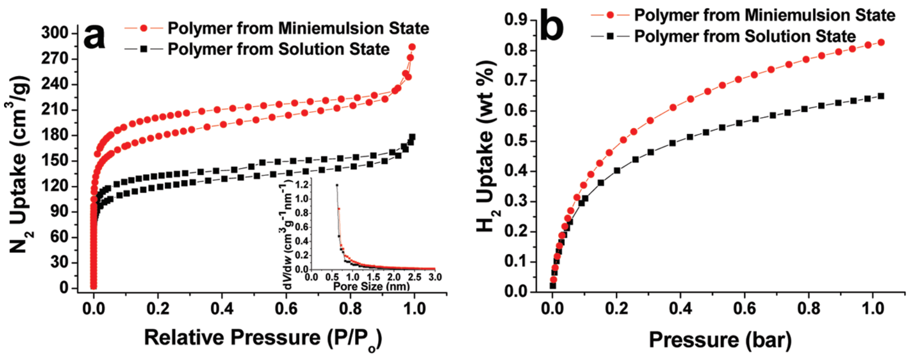
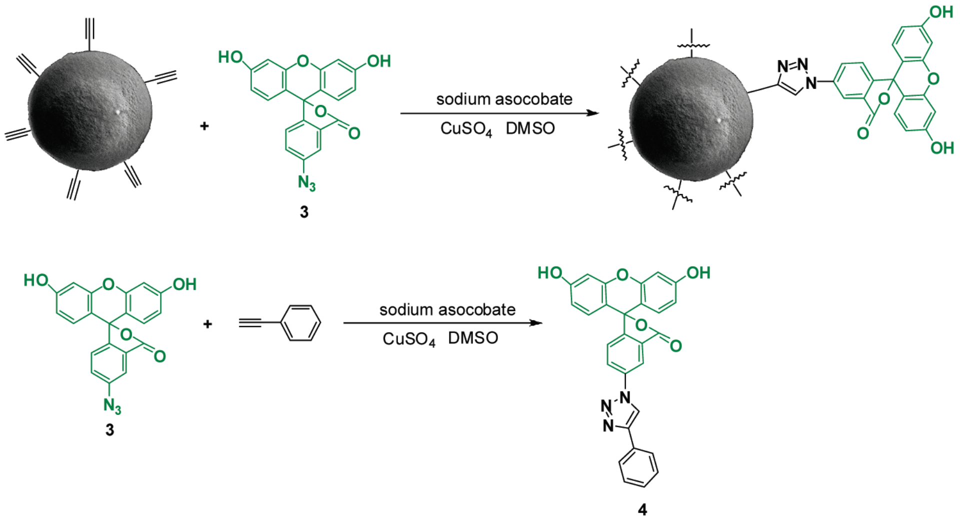


Figure 3. (a) N_2 adsorption/desorption isotherms at 77 K (inset: pore-size distribution curves). (b) H_2 adsorption isotherms at 77 K.

Scheme 2. Postmodification of the Polymer Particle by a Click Reaction



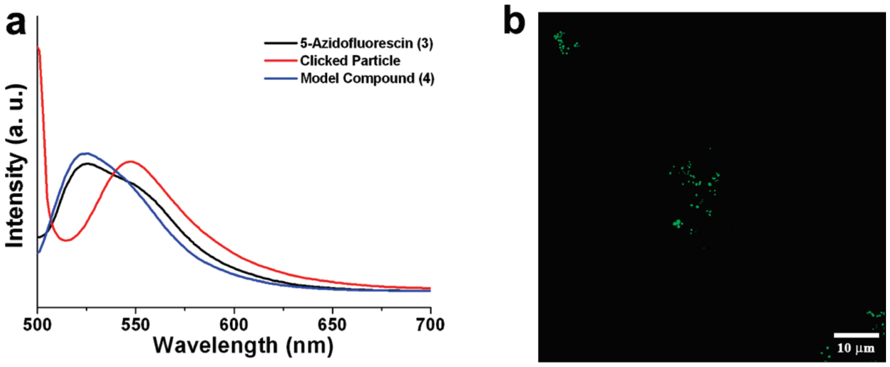


Figure 4. (a) Fluorescence spectra of 5-azidofluorescein (**3**), model compound **4**, and the clicked particle (λ_{ex} = 490 nm). (b) CLSM image of the clicked particle.

reaction was confirmed by a model reaction of azide **3** with ehtynylbenzene, where compound **4** was obtained almost quantitatively (Scheme 2). After functionalization, the surface area of the particle was only slightly decreased by about 15 m^2/g, suggesting that the microporous structure was not changed significantly.

Figure 4a shows the fluorescence spectra of 5-azidofluorescein (**3**), model compound **4**, and the functionalized particle. 5-Azidofluorescein showed the maximum fluorescence emission at around 525 nm when excited at 490 nm. Model compound **4** also showed a similar fluorescent emission pattern, but the fluorescence emission band of the clicked particle was shifted to the longer wavelengths, with the maximum emission at around 547 nm. This shift may have resulted from interactions between the fluorophore attached onto the solid particle surface and the aromatic groups of the polymer. The fluorescent emission of the clicked particles was visualized by confocal laser scanning microscopy (CLSM). Figure 4b shows the CLSM images of the fluorescent particles. As expected, the particles were strongly fluorescent due to the presence of a fluorescein group covalently attached to the polymer.

In a conclusion, we prepared clickable microporous hydrocarbon particles based on an adamantane building block. The particle morphologies were controlled by varying the polymerization conditions. Spherical particles with a high surface area were obtained by the polymerization in a miniemulsion state. The polymer particles were easily modified via the click reaction, which provides a potential tool to tailor the chemical and physical properties of porous particles to meet the requirements of specific applications.

Acknowledgment. This research was supported by grants from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy and from the Midcareer Researcher Program through NRF grant (No. 2010-0017552) funded by the Ministry of Education, Science and Technology, Republic of Korea.

Supporting Information Available: Experimental procedures of the synthesis of polymer **2** and model compound **4**; TGA thermogram of polymer **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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