ORGANIC LETTERS

2008
Vol. 10, No. 13
2641−2643

Novel Spirobisindanes for Use as Precursors to Polymers of Intrinsic Microporosity

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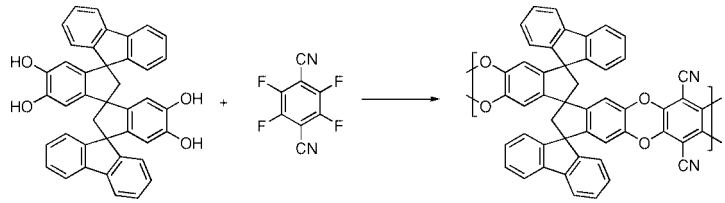
Received March 15, 2008

ABSTRACT



The synthesis of novel spirobisindane-based monomers for the preparation of polymers of intrinsic microporosity (PIMs) with bulky, rigid substituents is described. Polymers derived from monomers containing spiro-linked fluorene substituents display enhanced solubility and microporosity due to additional frustration of packing in the solid state.

Microporous materials derived from organic precursors are of increasing interest and several distinct aproaches have been adopted to achieve their preparation.[1–5] Over the past few years, we have developed a class of organic microporous material termed Polymers of Intrinsic Microporosity (PIMs). PIMs are materials which combine the high internal surface area of conventional microporous materials, such as zeolites or activated carbons, with the processability of polymers.[6–9] They have potential applications as heterogeneous catalysts,[10,11] hydrogen storage materials[12–15] and as polymer membranes,[16] especially for the separation of gases.[17] The microporosity of PIMs is due to their rigid and contorted macromolecular structures which cannot fill space efficiently, leaving molecular-sized interconnected voids. The rigidity is enforced by the polymer being composed of fused rings

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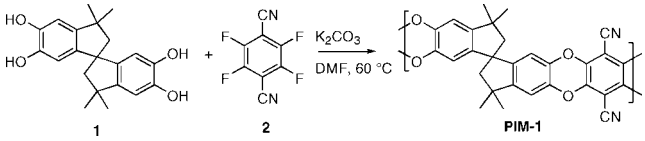
10.1021/ol800573m CCC: $40.75
Published on Web 06/03/2008

and the nonlinear structure arises from the incorporation of 'sites of contortion' such as spiro-centers. One of the most useful spiro-containing monomers, 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spiro-bisindane **1**, is readily prepared by the acid-mediated reaction between catechol and acetone and is commercially available.[18–20] For example, **1** reacts with 2,3,5,6-tetrafluoroterephthalonitrile **2** to give PIM-1 (Scheme 1), which is the archetypal and most studied PIM.[6] This polymerization reaction produces fused dioxan rings as linking groups via highly efficient aromatic nucleophilic substitution.

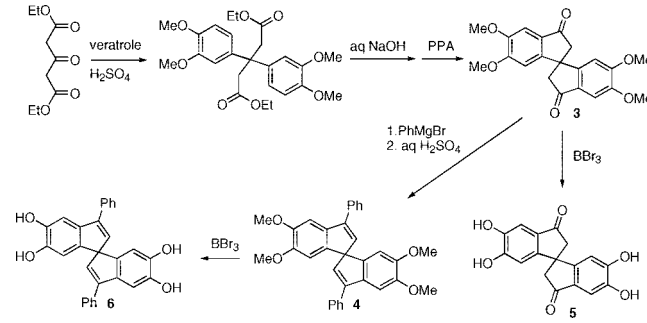
Scheme 1. Synthesis of PIM-1



In order to gain insight into the effect of the macromolecular structure on the degree of microporosity, we desired a range of PIM-1 analogues in which bulky, rigid groups are attached to the polymer. In particular, we wished to determine whether the addition of such groups creates greater microporosity due to further frustration of macromolecular packing or, alternatively, reduces microporosity by simply filling space. In order that the steric or electronic effects of the new substituents do not adversely effect the successful polymerization reaction, it is best to place the bulky groups (e.g., phenyl or spirofluorenes) at the 3,3′-positions of the 1,1′-spiro-bisindane units in place of the methyl groups of PIM-1. Hence, novel monomers based on 5,5′,6,6′-tetrahydroxy-1,1′-spirobisindane are required. These monomers may also be of interest for the other established applications of spirobisindane **1**, such as being precursors to self-assembled cyclic structures,[21–23] as chiral ligands,[24–27] as model systems to investigate spiro-conjugation[28,29] and as HIV-1 integrase inhibitors.[30]

The remarkably simple synthesis of monomer **1**, in which two catechol and three acetone molecules are assembled in a straightforward, one-pot reaction, was first reported by Baker in 1934.[19] Simple adaptations of this procedure (e.g., using a mixture of catechol, acetone and a ketone containing bulky aryl groups) are unlikely to succeed due to the preference for acetone toward acid-mediated self-condensation to give phorone, which is a suspected intermediate in the formation of **1**.[19,20] Instead, we decided to explore the potential of using the addition of an aryl Grignard reagent to the known 5,5′,6,6′-tetramethoxy-spiro(bisindane)-3,3′-dione **3** for the introduction of bulky groups. Baker prepared **3** in five steps with the last step being an inefficient oxidation of 5,5′,6,6′-tetramethoxy-spiro(bisindane) using chromium trioxide.[31] As a more satisfactory alternative, we found that the dione **3** is prepared from diethyl 1,3-acetonedicarboxylate in three steps (Scheme 2), with 35% overall yield, by acid-mediated reaction with veratrole,[32] followed by simple hydrolysis and a double intramolecular Friedel-Craft acylation mediated by PPA. Phenyl magnesium bromide added smoothly to **3** to give the dehydrated bisindene **4** after acidic workup. Monomers **5** and **6** are readily prepared from **3** and **4**, respectively by treatment with BBr_3.

Scheme 2. Improved Synthesis of the Pivotal Intermediate 5,5′,6,6′-Tetramethoxytetraphenyl-1,1-spiro-bisindane-3,3-dione **3** and Tetrahydroxy Monomers **5** and **6**



Monomer **7** which contains two spiro-fused bisfluorenes is an attractive target to demonstrate any potential benefits of large, rigid substituents on polymer microporosity. Its synthesis was achieved by adaptation of the established method of preparing spiro-bis(fluorene)s by the addition of 2-biphenyl Grignard reagent to fluorenones and subsequent formation of the spiro-center by an intermolecular Friedel-Craft alkylation.[33,34] Addition of excess 2-biphenyl magnesium bromide to **3** proceeds slowly even under rigorous conditions and a complex mixture of products is obtained following conventional aqueous workup. However, treatment of the crude mixture with Eaton's reagent gave a reasonable yield of the desired precursor **8** (40%) together with the monoadduct **9** (50%), which could be recycled to provide

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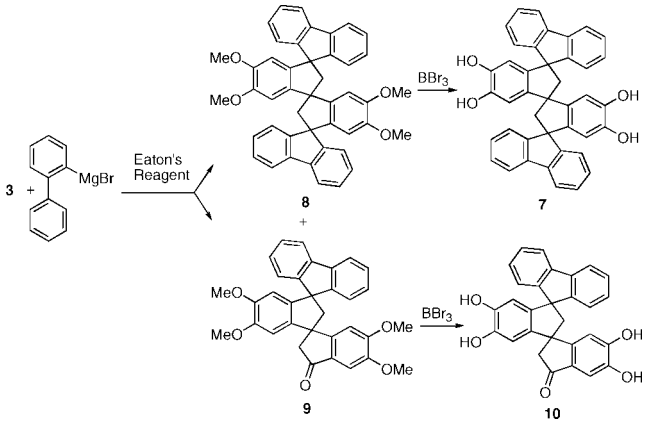
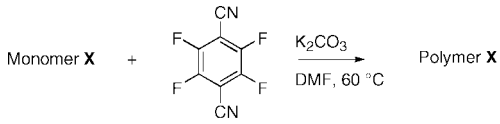
further batches of **8**. The complex mixture obtained from initial Grignard addition clearly contained a significant amount of the desired carbinol intermediate. On demethylation with BBr_3, **8** and **9** provide the desired monomer **7** and the unsymmetrical monomer **10**, respectively (Scheme 3).

Scheme 3. Synthesis of Spiro-Fused Fluorene-Based Monomers



Polymers derived from the novel monomers **5**, **6**, **7** and **10** were prepared by copolymerization with monomer **2** using the condition previously optimized for the synthesis of PIM-1. The properties of these polymers are given in Table 1.

Table 1. Properties of the Novel PIMs



polymer **X** (monomer **X**)	$M_w \times 10^3$ (g mol^{-1})	solubility	surface area (m^2 g^{-1})
PIM-1 (**1**)	180[a]	THF, $CHCl_3$	780
polymer **5**(**5**)	*b*	cH_2SO_4	501
polymer **6**(**6**)	*b*	quinoline	560
polymer **7**(**7**)	75[a]	THF, $CHCl_3$	895
polymer **10**(**10**)	*b*	NMP, quinoline	656

[a] Relative to polystyrene standards. [b] Not soluble in a solvent compatible with gel permeation chromatography (GPC).

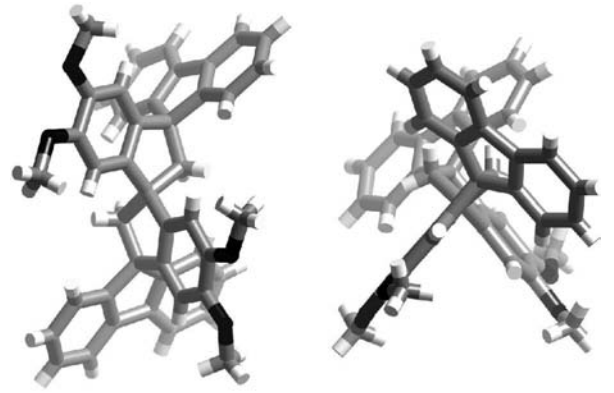


Figure 1. Two views of the molecular structure of **8** from a single-crystal X-ray diffraction study (oxygen atoms in black) showing the triple spiro-containing hydrocarbon framework.

The polymers derived from **5** and **6** are both insoluble in all common solvents with the exception of hot quinoline and conc. H_2SO_4, whereas the polymer derived from **7**, like PIM-1, is freely soluble in $CHCl_3$ and THF. The polymer derived from **10** is soluble in high-boiling solvents (e.g., NMP and quinoline) at room temperature. In powder form all polymers show significant microporosity as demonstrated by nitrogen adsorption isotherms collected at 77 K. Polymers derived from **5**, **6** and **10** exhibit less surface area than PIM-1, which may reflect greater cohesive interactions between polymer chains due to the polar ketone groups (from monomers **5** and **6**) or blocking of available microporosity by the phenyl groups (from monomer **10**). In contrast, the polymer derived from monomer **7** displays enhanced surface area as compared to PIM-1, which suggests that the rigid, spiro-fused fluorene units increase free volume by reducing further the packing efficiency of the polymer chains. Studies are in progress to determine whether the greater microporosity of this polymer offers advantages for applications such as hydrogen storage or gas separation. In addition, further PIMs designed using this useful paradigm are being prepared.

Acknowledgment. We thank EPSRC for funding.

Supporting Information Available: Experimental details and characterization data for all monomers and polymers.This material is available free of charge via the Internet at http://pubs.acs.org.

OL800573M