



Highly microporous free-radically generated polymeric materials using a novel contorted monomer



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ABSTRACT

A novel, free-radically polymerizable, contorted monomer was synthesized in two steps from bisphenol A. In a simple precipitation polymerization process making use of solvent as a porogen, homopolymerization of this contorted monomer (SBI-DV) resulted in polymeric networks with surface areas as high as 850 m²/g and with $S_{A_{\text{micro}}}/S_{A_{\text{BET}}}$ values as high as 0.65. Comparative DVB based polymeric networks produced under similar conditions had equally as high $S_{A_{\text{BET}}}$ but $S_{A_{\text{micro}}}/S_{A_{\text{BET}}}$ values of 0.35. In addition, copolymeric networks were produced using varying molar monomer ratios of SBI-DV/DVB. The degree of microporosity in the resulting copolymeric networks correlated with the amount of SBI-DV used in their formation.

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1. Introduction

The unique adsorptive characteristics found in materials with substantial interconnected microporosity (pore diameters < 2 nm) has driven the interest in microporous materials for many years. While the field of microporous materials encompasses a wide diversity of materials, the desire to tailor the amounts, sizes and chemistry of these micropores has resulted in the emergence of microporous organic polymers as a new category of microporous materials [1]. The different kinds of microporous organic polymers include hypercrosslinked polymers (HCPs) [2,3], polymers of intrinsic microporosity (PIMs) [4,5], covalent organic frameworks (COFs) [6–8], conjugated microporous polymers (CMPs) [9] and porous aromatic frameworks (PAFs) [8,10]. These microporous organic polymers are of interest for a number of applications including gas storage [11–16] and separation [4,14,17–19], heterogeneous catalysis [20–23] and sensors [24–27].

Of these classes of microporous organic polymers, HCPs are of particular interest due to their excellent chemical stability, the diversity of functional groups that can be incorporated into their structure and the relative ease of producing them on large scale. Most HCPs are made by one of two routes: 1) self-condensation of monomers with or without a crosslinking agent [11] and 2) crosslinking of pre-formed polymers which may or may not be lightly crosslinked [28,29]. The most common chemical reaction used to

prepare HCPs via either route is Friedel-Crafts alkylation. While this chemistry makes use of relatively low cost reagents (for example, FeCl₃), the typical conditions require excess stoichiometric amounts of the Lewis acid in halogenated solvents. In many cases, for a given mass of an HCP desired, two to three times that weight of the Lewis acid is needed for the reaction. The atom inefficiency, the need for excessive washing to remove reagents and the use of halogenated solvents are all non-ideal for the large scale production of these types of HCPs.

Free-radical polymerization is a route commonly used to make polymeric materials on an industrial scale. This synthetic process for making polymers is atom efficient and does not require post-polymerization clean-up steps. Suspension polymerization utilizing porogens has been shown to be a useful way to produce resins with diverse porosity [30]. The identity of the porogen used (good vs. bad solvent), the amount of the porogen used and the extent of crosslinking can be manipulated to generate resins with macro-, meso- and/or microporosity. Ideal conditions to favor micropore formation with this methodology include use of a high concentration of crosslinker in conjunction with a high ratio of porogen/monomer where the porogen is a good solvent for both the monomer and the growing polymer. The highest surface areas have been demonstrated by both suspension [31] and solvothermal [32–34] polymerization conditions utilizing high concentrations of divinylbenzene (80% or greater of the total monomer weight). The resulting HCPs (crosslink density greater than 40% [35]) can have surface areas as high as 1100 m²/g, but their pore size distribution is still dominated by small mesopores (diameters 2–10 nm) even

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though they contain significant amounts of microporosity.

Separately, incorporation of non-planar (contorted) structural motifs in rigid ladder polymers results in polymers which are intrinsically microporous (PIMs) [4,5]. The inefficiency of polymer chain packing with these rigid, contorted polymers results in the formation of a significant amount of free-volume in the form of interconnected micropores. The origin of the work reported here comes from the desire to combine the concepts of using porogen templating with poorly packing contorted monomers to make highly microporous polymeric networks via free radical polymerization. Herein is described (a) the design and synthesis of a free-radically polymerizable contorted monomer based on the spirobisindane structural motif, (b) homopolymerization of this novel contorted monomer in the presence of various porogens and characterization of the porosity of the resulting homopolymeric networks and (c) copolymerization of this novel contorted monomer with divinylbenzene in various monomer ratios in the presence of ethyl acetate as porogen and the characterization of the porosity of the resulting copolymeric networks.

2. Experimental

2.1. Materials and synthesis

3,3,3',3'-tetramethyl-1,1'-spirobisindane-6,6'-diol (SBI-diol) was prepared as previously reported [36]. All other chemicals were commercial and used as received.

2.1.1. Synthesis of perfluoromethane-1-sulfonic acid 6'-(perfluoromethane-1-sulfonyloxy)-3,3,3',3'-tetramethyl-1,1'-spirobisindane-6-yl ester (SBI-bistriflate)

In a 250 mL round bottomed flask, 5.00 g (16.2 mmol) of SBI-diol and 4.76 mL (58.8 mmol) of pyridine were dissolved in 150 mL of methylene chloride (CH_2Cl_2). The flask was placed in an ice/water bath. To this solution was added dropwise 7.93 mL (47.1 mmol) of trifluoromethane sulfonic anhydride (TFMSA). After the addition was complete, the flask was removed from the ice/water bath. The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 1 h. The reaction was stopped by adding 10 mL of aqueous hydrochloric acid (HCl) (10% by weight).

The resulting mixture was partitioned between CH_2Cl_2 and a saturated aqueous solution of sodium bicarbonate (NaHCO_3). The organic layer was isolated, dried over anhydrous sodium sulfate (Na_2SO_4) and filtered. The filtrate was condensed under reduced pressure and dried under high vacuum at room temperature for 3 h. The resulting tan solid (SBI-bistriflate) weighed 8.51 g (yield: 92%). ^1H NMR (500 MHz, CDCl_3) δ 7.17 (d, $J = 8.3$ Hz, 2H), 7.08 (dd, $J = 8.3$, 2.3 Hz, 2H), 6.55 (d, $J = 2.3$ Hz, 2H), 2.26 (ABq, $J = 13.2$ Hz, 4H), 1.34 (s, 6H), 1.29 (s, 6H). ^{13}C NMR (125.8 MHz, CDCl_3) δ 152.4, 151.8, 149.2, 123.8, 120.7, 116.9, 59.2, 57.6, 43.5, 31.5, 30.0. ^{19}F NMR (470.5 MHz, CDCl_3) δ -73.0. GC/MS (EI): M^+ calculated for $\text{C}_{23}\text{H}_{22}\text{O}_6\text{F}_6\text{S}_2$: 572.0757, found 572.0772.

2.1.2. Synthesis of 3,3,3',3'-tetramethyl-1,1'-spirobisindane-6,6'-divinyl (SBI-DV)

In a 250 mL round bottomed flask, 5.00 g (8.73 mmol) of SBI-bistriflate was dissolved in 75 mL of anhydrous *N,N*-dimethyl formamide (DMF). To this solution was added 6.13 mL (21.0 mmol) of vinyltributyl tin and 2.22 g (52.4 mmol) of lithium chloride (LiCl). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for 5 min before adding 0.614 g (875 μmol) of bis(triphenylphosphine)palladium (II) chloride. The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. After reacting for 24 h at room temperature, the reaction was stopped by pouring the reaction mixture into

150 mL of deionized water. A precipitate formed.

The aqueous layer and precipitate were extracted with diethyl ether (Et_2O) (3×200 mL). The organic layers were combined. The organic layer was then stirred vigorously at room temperature with an equal volume of aqueous potassium fluoride (KF) (10 g/100 mL) for 1 h. A gray-white precipitate formed, and the mixture was vacuum filtered. The filtrate was then placed back in a separatory funnel and the organic layer isolated. The organic layer was then dried over anhydrous Na_2SO_4 and filtered. The filtrate was condensed under reduced pressure to yield a white solid. This solid was further purified by silica gel chromatography. The material was loaded onto a silica gel column (8×25 cm), and the column was eluted with 5% ethyl acetate (EtOAc)/95% petroleum ether (PE) (vol/vol). Fractions containing the pure SBI-DV were combined, condensed under reduced pressure and dried under high vacuum at room temperature to yield 2.38 g (yield: 83%) of SBI-DV as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.34 (dd, $J = 7.9$, 1.6 Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 6.85 (d, $J = 1.6$ Hz, 2H), 6.64 (dd, $J = 17.6$, 10.9 Hz, 2H), 5.62 (dd, $J = 17.6$, 1.0 Hz, 2H), 5.12 (dd, $J = 10.9$, 1.0 Hz, 2H), 2.32 (ABq, $J = 13.1$ Hz, 4H), 1.42 (s, 6H), 1.36 (s, 6H). ^{13}C NMR (125.8 MHz, CDCl_3) δ 152.3, 150.8, 136.9, 125.1, 122.3, 122.0, 112.9, 59.5, 57.5, 43.3, 31.6, 30.2. GC/MS (EI): M^+ calculated for $\text{C}_{25}\text{H}_{28}$: 328.2186, found 328.2200.

2.1.3. Synthesis of divinylbenzene (DVB) based porous polymeric networks

In a 40 mL vial, 0.948 g (7.28 mmol) of divinylbenzene (DVB) (80%, technical grade) and 13.0 mg (79.2 μmol) of azoisobutyronitrile (AIBN) was dissolved in 20.0 mL of EtOAc. The polymerization mixture thus consisted of an EtOAc solution of DVB at 5.0 wt% solids and 1.4 wt% AIBN (based on the amount of DVB). The polymerization mixture was bubbled with nitrogen for 10 min. The vial was then capped and placed in a sand bath at 100 °C. The polymerization was heated at this elevated temperature for 16 h. A white precipitate had formed and was isolated by vacuum filtration and washed with EtOAc.

The solid was placed in a 40 mL vial and 20 mL of EtOAc was added to the vial. The vial was shaken on a wrist shaker for two hours at room temperature. The solid was again isolated by vacuum filtration and washed with EtOAc. The solid was placed in a 40 mL vial and 20 mL of EtOAc was added to the vial. The solid was shaken on a wrist shaker overnight. The solid was again isolated by vacuum filtration and washed with EtOAc. The solid was then dried under high vacuum at 90 °C overnight. Typical yields for the production of DVB based porous polymeric networks were 75–85% calculated based on the weight of the dried, isolated material compared to the mass of monomers used in the polymerization mixture. This polymeric network based on divinylbenzene is referred to as PDVB.

2.1.4. Synthesis of SBI-DV based porous polymeric networks

A 5.0 mg/mL solution of benzoyl peroxide (BPO) was made by dissolving 50.1 mg of BPO in 10 mL of EtOAc. In an 8 mL vial, 0.200 g (609 μmol) of SBI-DV was dissolved in 1.80 mL of EtOAc. To this solution was added 800 μL of the BPO/EtOAc solution. The polymerizable composition thus consisted of an EtOAc solution of SBI-DV at 7.9 wt% solids and 2 wt% BPO (based on the amount of SBI-DV). The polymerizable composition was bubbled with nitrogen for 10 min. The vial was then capped and placed in a sand bath at 80 °C. The polymerizable composition was heated at this elevated temperature for 17 h. A white precipitate had formed and was isolated by vacuum filtration and washed with EtOAc.

The solid was placed in a 20 mL vial and 10 mL of EtOAc was added to the vial. The vial was shaken on a wrist shaker for one hour at room temperature. The solid was again isolated by vacuum filtration and washed with EtOAc. The solid was placed in a 20 mL

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