Cyclophane as a conformationally twisted monomer in high performance polymers

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Abstract

Intrinsic microporosity in polymers is defined as "a continuous network of interconnected intermolecular voids, which forms as a direct consequence of the shape and rigidity of the component macromolecules". Our approach to creating intrinsic microporosity is by the use of a novel conformationally twisted cyclophane monomer for the synthesis of polybenzimidazoles which may have potential applications as membranes for selective proton or lithium ion transport.

Keywords: *Intrinsic microporosity, Free volumes, Paracyclophane, Polybenzimidazoles*

Introduction

Porous polymers are polymeric materials containing one or more types of pores. Opportunity to create high value applications provide an incentive for developing reliable methods for preparation of porous polymers, with designed pore architectures, customized framework and pore surface functionalities.[1] Several important structural characteristics of porous polymers are important for defined applications. These include, pore geometry, pore size, pore surface functionality and polymeric framework structure including composition, topology, and functionality. Recently, Intrinsically microporous polymers (IMP) have attracted attention as a class of new materials for creating microstructured and microporous polymers.[2] Intrinsic microporosity in polymers is defined as "a continuous network of interconnected intermolecular voids, which forms as a direct consequence of the shape and rigidity of the component macromolecules".

Poly(benzimidazole)s (PBIs) are a class of high-performance polymers which have been receiving increasing interest during the last years due to their high potential as constituents of membrane materials. In earlier work, porous PBIs were mainly prepared through the template method by use of soft templates.[3]

Our approach to maximizing intrinsic microporosity has been to design polymers with highly contorted molecular structures to provide "awkward" macromolecular shapes that cannot pack efficiently. Such intrinsically microporous PBI's may find useful applications as membranes for selective transport of proton (in fuel cells) and transport of lithium ions (as separator films for lithium ion batteries).

[2.2] *para*-Cyclophane is a key compound of the cyclophane family partly because of the ease of its synthesis.[4] The most important features of this class of compounds are the electronic interaction of the closely stacked π systems and the high amount of molecular strain which manifests itself in the distortion of the benzene rings into a boat shape. As cyclophane is a twisted bulky structure, its incorporation into rigid polymer networks is expected to result in packing defects and large free volume leading to the appearance of accessible microporosity.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. FTIR spectra were obtained on a Perkin-Elmer 1600 spectrometer. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates.

Materials

[2.2] *para*-Cyclophane was obtained from Aldrich, 3,3'-diaminobenzedene (Sigma), isophthalic acid (Sigma), polyphosphric acid (Sigma), N,N-dimethylacetamide (Sigma) were used as received. The chemical structure of aromatic dicarboxylic acid 4, 16-dicarboxyl[2.2] *para*-cyclophane used in this work is well established.

Results and discussion

The derivatization of cyclophane was accomplished via electrophilic bromination

as originally described by Reich and Cram.[5] Reaction was carried out using 2 equiv of bromine and was kept overnight in refluxing condition and monitored by thin layer chromatography. Pure pseudo-*para*-dibrobromo [2.2] cyclophane was separated by recrystallization process and the structure was established by single crystal XRD (**Figure 1**). The synthetic procedure of 4, 16-dicarboxyl[2.2] *para*- cyclophane is found to depend on the concentration of n-BuLi.

The synthetic procedure used for polybenzimidazoles is outlined in **Scheme 1**. Polymerization of p-dicarboxy [2.2] *para*-cyclophane in different mole percent with isophthalic acid and 3,3'-diaminobenzidine in polyphosphoric acid at 180°C gave poly (benzimidazo1e) PBI-I (5 % cyclophane di carboxylic acid) and PBI-II (10 % cyclophane dicarboxylic acid). Polyphosphoric acid solvent is selected for polymerization because a full conversion could be obtained well below the strain release temperature of the [2.2] *para* cyclophane. The reference copolymer m-PBI was synthesized in the same manner at 200 °C. **Figure 2** shows the ^{1}H NMR spectrum of 10 mole % cyclophane dicarboxylic acid containing PBI where 3 imidazole protons exhibited a singlet at 13.27 δ, ppm, 16 aromatic protons of isophthalic acid and 3,3'-diaminobenzidene exhibited a multiplet between 9.16-7.65 δ, ppm, 6 aromatic protons of cyclophane dicarboxylic acid exhibited a triplet between 6.89-6.61 δ, ppm.

The copolymers were fully amorphous in nature and showed single glass transition temperatures (Tg). The results of thermogravimetric analysis (TGA) given in **Figure 3** indicate that poly(benzimidazole)s as a class possess outstanding thermal stability. The onset degradation temperature (Td) of the PBI II is about 590 °C and the weight loss is about 63 % at 900 °C. A small weight loss in the temperature range 270 °C is also observed. This can be ascribed to the homolysis of cyclophane ring (**Scheme 2**) leading to crosslinking. Inherent viscosity measurements of the copolymers were performed in DMAc at 30 °C with a concentration of 0.2 g/dL. The value obtained for PBI I and PBI II are 0.54 and 0.6 dL/g, respectively.

TEM micrographs reveal the preservation of the pore system in the co-PBI network **(Figure 4).** TEM micrograph of porous PBI indicates porous bicontinous sponge-like network. For all the samples, the distribution of the pores is not uniform.

Membrane Preparation

1 wt % polymer solution was dissolved at 80 ^{o}C in 10 mL of DMAc. The solution was stirred overnight and then filtered before being cast onto a clean glass plate. The solvent was evaporated at 180 ^{o}C overnight under nitrogen flux and then heated gradually to 200 ^{o}C and maintained at this temperature for 1 h. After cooling to room temperature, the membrane was unstuck from the glass plates by immersion in water. To remove the residual solvent, the membrane was dried under high vacuum for 5 h at 120 °C and then immersed in water and methanol.

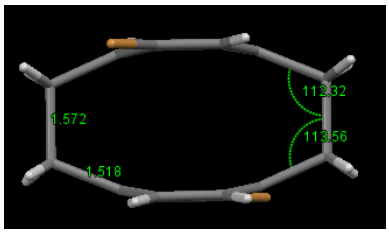
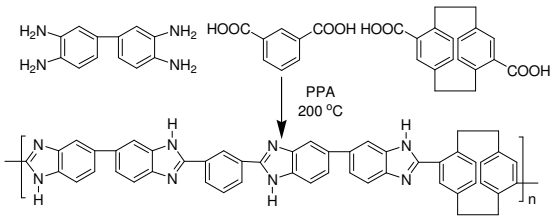


Figure 1. Crystal structure of pseudo para-dibrobromo [2.2] cyclophane with bond angle and bond length.



Scheme 1. Synthesis of polybenzimidazole based on 3,3'-diaminobenzidine, 4,16-dicarboxyl[2.2]paracyclophane and isophthalic acid.

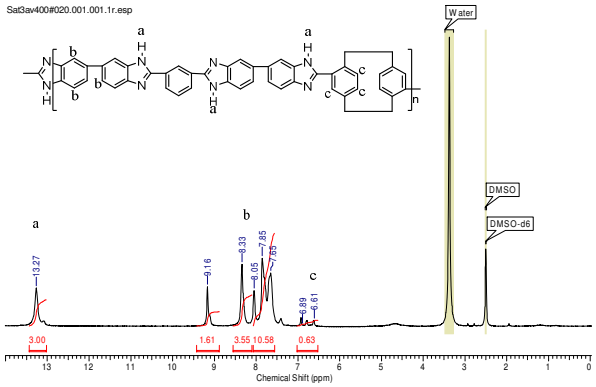


Figure 2. ^{1}H-NMR (DMSO-D$_6$) spectrum of co-polybenzimidazole based on 3, 3'-diaminobenzidine, cyclophane dicarboxylic acid (10 mole %) snd isophthalic acid.

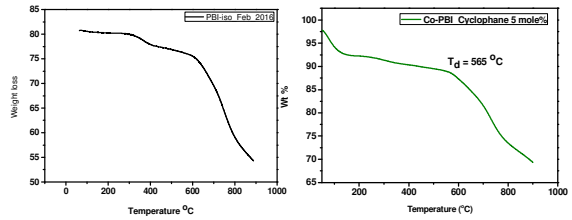
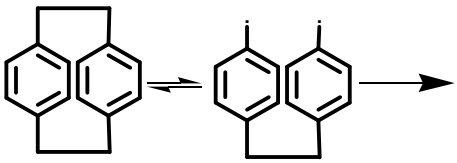


Figure 3: TGA curve of co-poybenzimidazole PBI-II and PBI-I .



Scheme 2. The paracyclophane units of the poly(benzimidazole) may undergo homolysis and combine in an intermolecular fashion to give the desired ethylene ladder crosslinks.

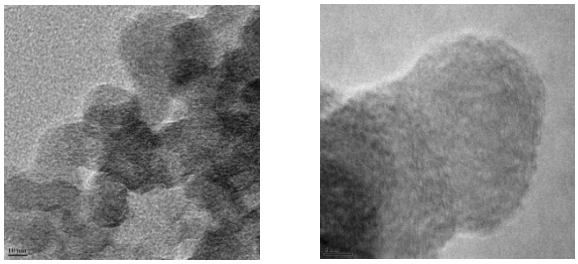


Figure 4. TEM micrographs of mesoporous PBI networks.

Table 1. Thermal characteristics of m-PBI, PBI-I and PBI-II.

Polymer	T_d (°C) (onset)	Tg (°C)
m-PBI	600	438
PBI-I	565	427
PBI-II	590	411

Conclusions

Copoly-benzimidazoles were successfully synthesized using upto 10 mol % 4, 16-dicarboxyl[2.2] *para*-cyclophane as a conformationally twisted comonomer. This polymer, consist of sites of contortion within a rigid amorphous polymer backbone. These copolymers could be cast in the form of a free standing film. The polymer has been characterized for its molecular and thermal properties.

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