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Synthesis of Perfectly Alternating Copolymers for Polymers of Intrinsic Microporosity†

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Copolymer's properties are controlled not only by co-monomers' composition but also their sequence distribution along the chain. We hereby report a strategy to the synthesis of perfectly alternating PIMs copolymer, an important class of material for gas separation membrane. We achieve this copolymer microstructure through two-pot synthesis process via ABA trimer intermediate. For comparison, both alternating and statistical copolymers with same composition were prepared and characterized with ^{1}H and ^{13}C NMR, FT-IR, MALDI-ToF, GPC, TGA, DSC and WAXD. The present work offers new method for repeating unit sequence control in step growth polymerization system.

Polymers of Intrinsic Microporosity (PIMs) are a unique family of pure organic macromolecules featured in ladder-shape, stiff and contorted backbones.[1] As a result, PIMs exhibit a large amount of free volume and large accessible surface area intrinsically.[2] Since 2004,[1a,1b] PIMs have stimulated a great deal of interest in materials science due to its intrinsic microporosity. Especially in the field of gas membrane separation, PIMs exhibit exceptionally high permeability and moderate selectivity.[3] Additionally, many PIMs enjoy their solubility in common organic solvents, thus their applications are broadened by this solvent-processable nature.[4]

Currently, chemistry of PIMs has been focused on new monomer structures, copolymerization, post-polymerization modification and cross-linking.[5] A wide range of PIMs statistical copolymers were synthesized by pairing different co-monomers in one-pot and varying their co-monomer feed ratios in order to tailor their solubility and gas transport performance. Although the overall compositions of the copolymers obtained correspond to those of the co-monomers

feed ratio, the sequence distribution of the different repeating units along the copolymer chains is lack of control. It is believed that macroscopic properties of copolymers are influenced by their arrangement of repeating units. There are many examples showing that alternating copolymers differ from their corresponding random ones in terms of thermal, mechanical, optical, and even biological property.[6] We hypothesis that the arrangement of repeating unit could also have an impact on gas transport properties.

Many smart and creative strategies, especially in chain-growth polymerization, have been developed for this target. Catalysts have been designed and successfully synthesized to produce alternating ethylene/propylene copolymer[7], ethylene/α-olefin copolymers, alkenes and carbon monoxide copolymer[8], and also the polycarbonate from epoxides and carbon dioxide.[9] Ring-opening polymerization strategies were also envisaged to access alternating copolymers from appropriate pre-constructed cyclic monomers.[10] Less straightforwardly, conjugated alternating copolymers were achieved through multi-step synthesis.[11]

Herein, we report a strategy to the synthesis of PIMs copolymer with well-defined alternating fashion. We achieve this copolymer microstructure through two-pot synthesis process via ABA trimer intermediate. To the best of our knowledge, this is the first synthesis example of sequence-controlled PIMs copolymer.

As detailed in Scheme 1, the biscatechol monomer **TTSBI** was firstly sandwiched by two tetrafluoro monomers **TFTPN** to form an ABA type monomer **TFTTSBI**, and then, homo-polymerization ~~is~~ was conducted between the new ABA monomer **TFTTSBI** and the second biscatechol monomer **DETA**.

The key intermediate ABA monomer **TFTTSBI** was prepared based on our previous study on AB-type monomer.[12] **TTSBI** was treated with two equivalents of potassium hydroxide to form a di-potassium phenoxide salt, which was subsequently added to a solution of **TFTPN** in acetonitrile to give **TFTTSBI**. It is known that the reactivity of electron-deficient aryl halide (Ar-F) is subject to considerable decrease after the

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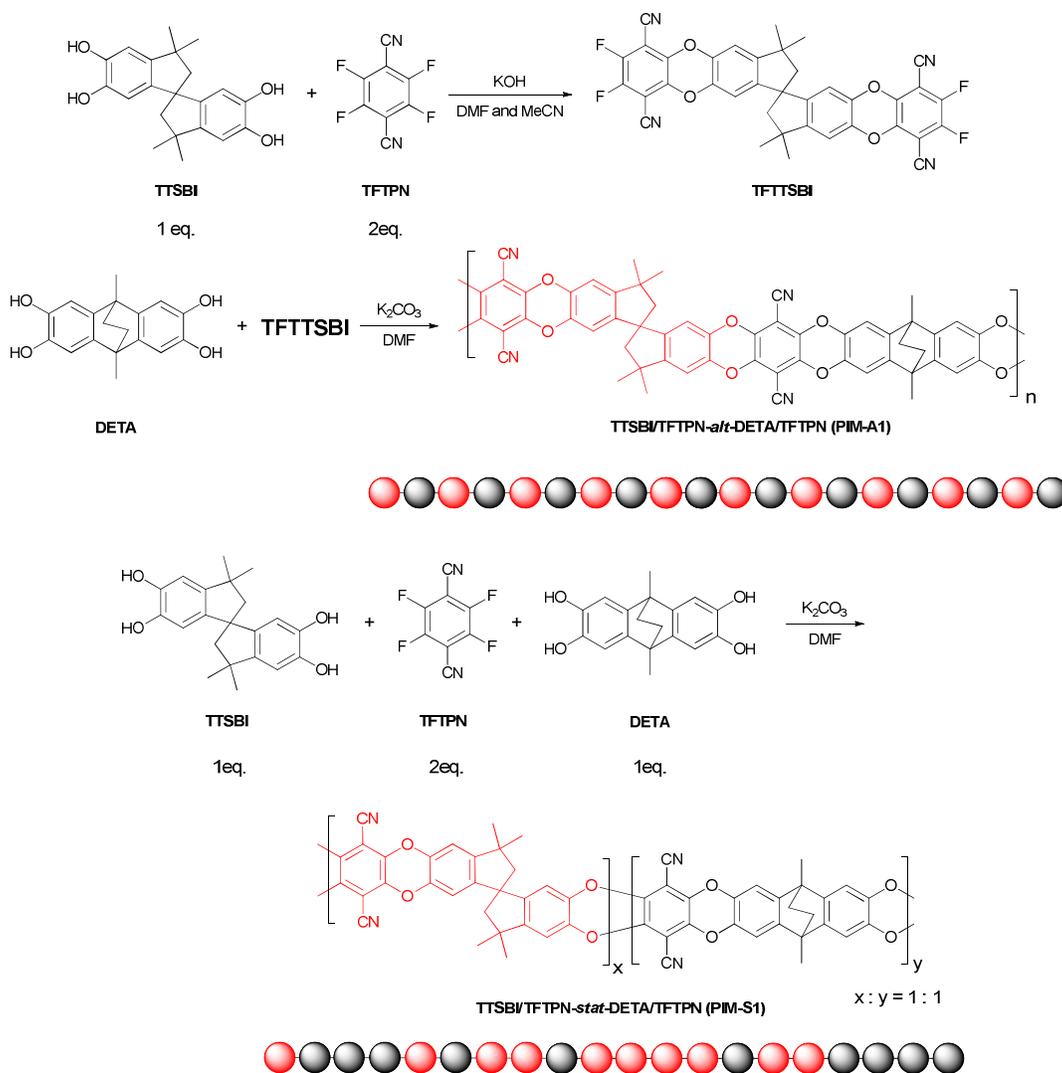
Scheme 1 Synthetic routes of **PIM-A1** and **PIM-S1**.

introduction of electron donating groups (Bbenzodioxane). Therefore, **TFTTSBI** is much stable and less reactive than **TFTPN** towards **TTSBI**. The subtle chemoselectivity exists among them. Furthermore, acetonitrile, as a non-solvent of the product, was selected to promote the precipitation of **TFTTSBI** from the reaction mixture. This strategy aims not only to isolate the product in a facile way, but also to suppress side reaction of **TFTTSBI** forming longer larger oligomers. The synthesis of the key compound **TFTTSBI** was achieved directly at an excellent yield of 80%, without employing any protecting group or intermediate. (Detailed experimental procedures see ESI).

Subsequently, the novel alternating copolymer **TTSBI/TFTPN-alt-DETA/TFTPN** was successfully synthesized using **TFTTSBI** and **DETA** as tetrafluoro monomer and biscatechol monomer, respectively, following the polymerization protocol described by Budd and McKeown.[1b] For direct comparison purpose, the choice of second biscatechol monomer for PIMs copolymer

synthesis is **DETA** since the statistical copolymer version of **TTSBI/TFTPN-stat-DETA/TFTPN** (named as **PIM1-CO1-50** in its original paper) has been prepared by Fritsch et al.[5h, 13] In the following discussion, the alternating copolymer **TTSBI/TFTPN-alt-DETA/TFTPN** and the statistical copolymer **TTSBI/TFTPN-stat-DETA/TFTPN** are coded as **PIM-A1** and **PIM-S1**, respectively.

Characterization of the ABA monomer **TFTTSBI** was pursued by using ^{1}H, ^{13}C, ^{19}F NMR and HRMS. ^{1}H NMR (Figure S1) and ^{13}C NMR (Figure S2) results agreed well with the target structure. The ^{19}F NMR spectrum displays single peak at -134.85 ppm, which indicated all fluorines in the molecule have same chemical environment. Compared to the chemical shift of the fluorines of the stating material (**TFTPN**) which is at −128.2 ppm, the fluorine signal of **TFTTSBI** shifts to a higher field considerably (ca. 6.65 ppm). Clearly, due to the benzodioxane formation, **TFTTSBI** experienced a higher electron density. Hence a lower reactivity of aryl fluoride as a leaving group is

expected and the formation of ABA monomer could be afforded selectively in a good yield.
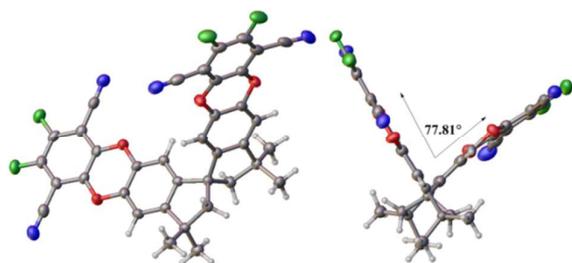

Fig. 1 The molecular structure of **TFTTSBI** as determined by X-ray crystallography demonstrating gross structural features (left) and a view orthogonal to the benzene ring (right) to emphasize the dihedral angle.

Single crystals of **TFTTSBI** were obtained by slow diffusion of n-hexane into its chloroform solution in vial. As shown in Figure 1, **TFTTSBI** has a symmetrical structure. Interestingly, by analysing the XRD data, the dihedral angle between the two benzene rings of spirobisindane on **TFTTSBI** is 77.81° while the corresponding dihedral angle is 71.87° for AB-type monomer [12] and 85.0° for the biscatechol monomer **TTSBI**, respectively. [14] The substantial difference in dihedral angle value in these three spirobisindane containing monomers evidently suggests the relative flexibility of the spiro center. This agrees well with the broad energy well of spirobisindane dihedral angle in contrast to that of other bridged bicyclic units, such as Tröger Base (TB) and ethanoanthracene (EA).[3b] This flexibility could translate to the less shape-persistence of PIMs backbone containing spirobisindane units, hence impairing the properties of these PIMs on gas separation.

Gel permeation chromatography (GPC) was used to determine the molecular weight of polymer products. Both copolymers displayed broad GPC chromatogram with similar number average molecular weight presumably due to the formation of cyclic oligomer during polymerization. (**PIM-A1**: M_n=16000, M_w=51000, M_w/M_n=3.2; **PIM-S1**: M_n=17000, M_w=63000, M_w/M_n=3.7) Interestingly, there is no evidence to distinguish between **PIM-A1** and **PIM-S1** by means of FT-IR and ^{1}H NMR (Figure 2a and 2b). Furthermore the ^{13}C NMR analysis also hardly differentiate the alternating and statistical PIMs copolymers (Figure S8, respectively). The enlarged partial ^{13}C NMR spectra arguably shows a insignificant chemical shift between C1 of **PIM-A1** (δ_C = 139.31 ppm, Figure S8c) and C1' of **PIM-S1**, (δ_C = 139.34 ppm, Figure S8d). However, the true identity of those copolymers can be evidently revealed by Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-ToF) mass spectrometry. As shown in Figure 3, the copolymers exhibit totally different patterns on their MALDI-ToF spectra. All the ~~mass~~ signals observed in the spectra are cyclized oligomers according to their m/z values. The result of **PIM-A1** cleanly revealed mass peaks of various sizes of cyclic **PIM-A1** oligomers. And most importantly, the adjacent spacing between each pair is equal to the mass of repeating unit (878 Da), which corresponds to the total molar mass of **TFTTSBI** and

DETA minus four hydrogen fluoride condensate. In contrast, multiple mass peaks are found in cyclic **PIM-S1** oligomer due to various possibilities on combination of repeating units. Moreover, for the alternating copolymer, the spirobisindane units and ethanoanthracene units must come in pairs (n is the number of pairs); as a result, no mass signals for **PIM-A1** could be found at the range of odd-numbered x+y values in **PIM-S1**, such as x+y=5, 7, and 9.
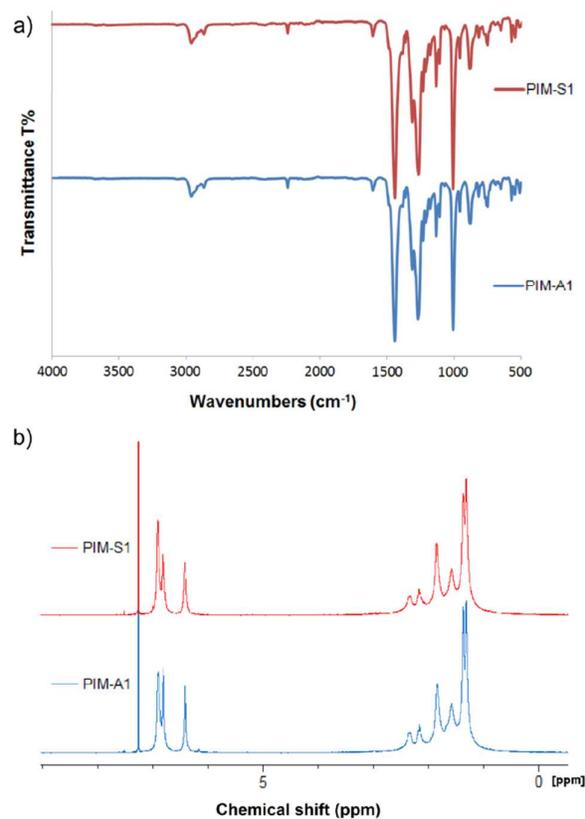

Fig.2 (a) FT-IR spectra of **PIM-A1** and **PIM-S1**. (b) ^{1}H NMR spectra of **PIM-A1** and **PIM-S1**.

To further investigate their difference on morphology, WAXD was conducted and revealed both copolymers are amorphous. (Fig. 4a) The values of d-spacing were calculated by means of Bragg's law indicating slight different d-spacing for **PIM-A1** and **PIM-S1**. (7.5Å and 7.3Å respectively) In addition, the thermal properties of **PIM-A1** are similar to that of **PIM-S1** as measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The onset temperature of decomposition is around 300 °C and the decomposition rates increase considerably after 420 °C for both copolymers. (Fig. 4b) Although the general thermal degradation behaviours are quite similar, **PIM-A1** performs a faster rate of decomposition than that of **PIM-S1** after 420 °C. This phenomenon could be
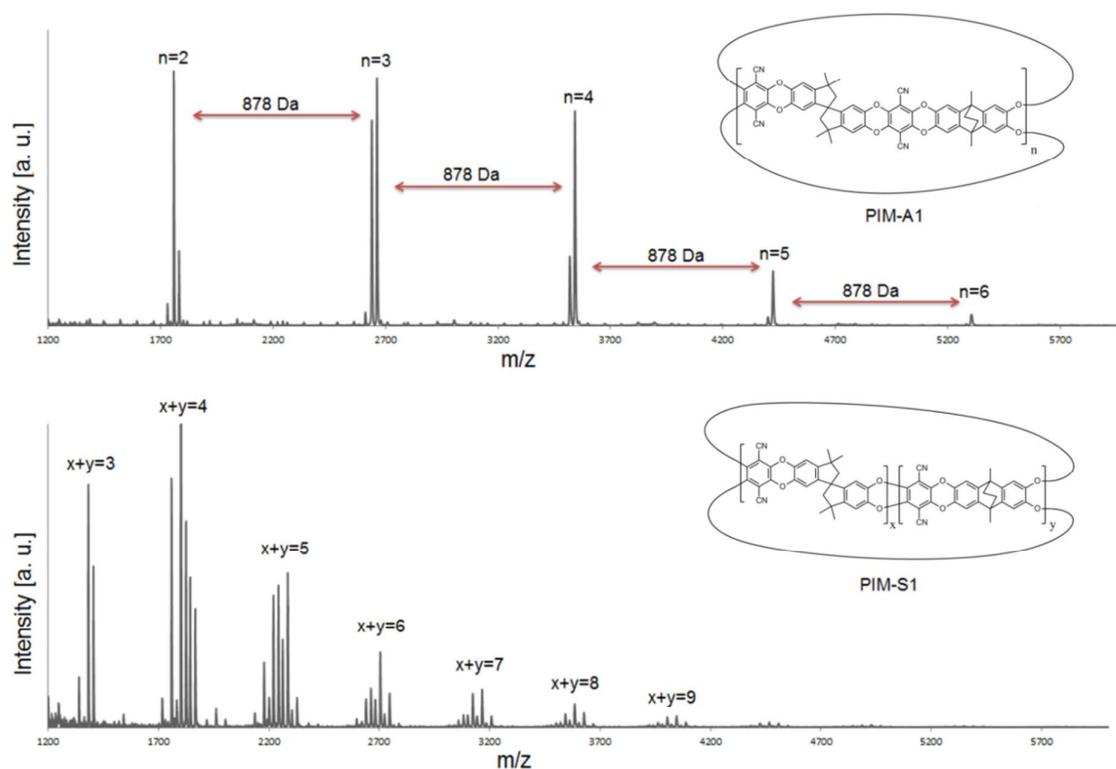
Fig.3 MALDI-ToF mass spectra of **PIM-A1** (top) and **PIM-S1** (bottom).
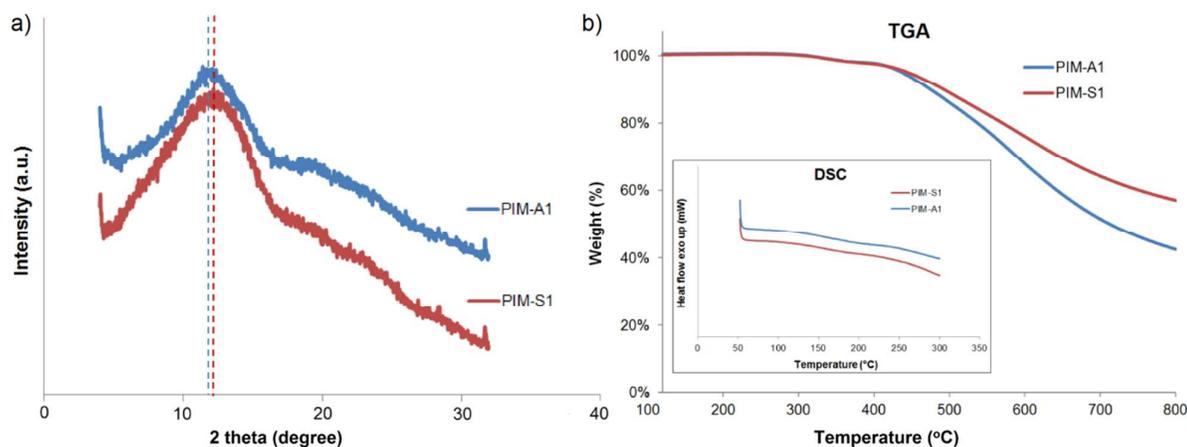

Fig.4 (a) WAXD of **PIM-A1** and **PIM-S1**. (b) Thermogravimetric analysis thermograms (TGA) of **PIM-A1** and **PIM-S1** and differential scanning calorimetry (DSC) thermograms of **PIM-A1** and **PIM-S1**.

due to the alternating copolymer has unified chain microstructures. In the thermograms of DSC, no discernible glass transition was found for the polymers between 50 °C to 300 °C. (Fig. 4b inset)

Conclusions

In summary, the first example of alternating copolymer of PIMs was accomplished in a two-pot synthetic pathway via ABA trimer intermediate. By making use of chemoselectivity the ABA monomer was synthesized at a yield of 80% and was thoroughly characterized including single-crystal XRD. Both copolymers, **PIM-A1** and **PIM-S1**, were successfully prepared. The chain microstructures of the alternating **PIM-A1** were revealed ~~using~~ by MALDI-ToF. The mass patterns were

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distinctively different between **PIM-A1** and **PIM-S1**. The present work offers an interesting way to produce PIMs copolymer comparing to the commonly employed one pot copolymerization route.   Further efforts to deeply investigate the effect of this well-defined PIMs copolymer on gas permeability and selectivity are in progress.

Acknowledgement

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A two-pot synthetic strategy was developed to accomplish sequence control in a completely alternating fashion for co-polymers of intrinsic microporosity.

TTSBI/TFTPN-alt-DETA/TFTPN (PIM-A1)