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Citation: Zhao, Yanchuan et al. "Porous Organic Polymers via Ring Opening Metathesis Polymerization." ACS Macro Letters 7, 3 (February 2018): 300–304 © 2018 American Chemical Society

As Published: <http://dx.doi.org/10.1021/ACSMACROLETT.8B00041>

Publisher: American Chemical Society (ACS)

Persistent URL: <https://hdl.handle.net/1721.1/121277>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

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Porous Organic Polymers *via* Ring Opening Metathesis Polymerization

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Supporting Information Placeholder

ABSTRACT: Highly porous and solution processable organic polymers that can be structurally tailored for various applications are in great demand. Previously reported strategies to prepare porous polymers usually rely on a high level of cross-linking or structurally rigid polymer backbones. We now demonstrate that one-dimensional linear polymers with flexible backbones having rigid non-complementary sidechains prepared through ring opening metathesis polymerization can be highly porous. This new strategy allows facile access to diversified porous organic polymers having tunable mechanical/chemical properties bearing different functionalities.

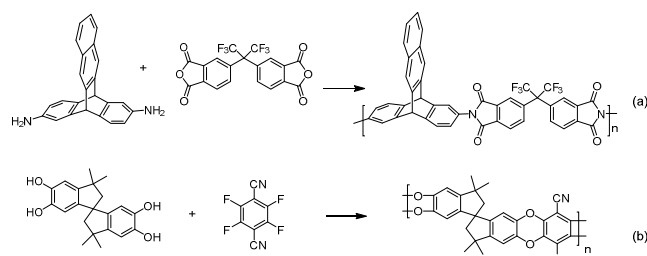
Organic porous materials have found increasing applications in separation,¹ catalysis,² sensing³ and environmental purification.⁴ Highly tunable and solution processable porous materials that can be customized for diverse applications are in great demand. As a result of the excellent structural diversity and the cost-effective synthesis, one-dimensional (1D) linear polymers are most widely used for industrial applications. The development of highly efficient and controllable polymerization methods, such as ring-opening olefin metathesis polymerization (ROMP), atom-transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer polymerization (RAFT) have allowed facile access to structurally tunable polymers with diverse functions.⁵ Despite the ease of preparation and structural diversity, 1D linear polymers usually have low surface areas as a result of the flexible nature of the polymer, which promotes dense-packing in the solid state. In fact, the use of structurally rigid building blocks⁶ and ladder-typed backbone⁷ is a common wisdom to achieve non cross-linked porous organic polymers (Scheme 1a,b). However, the structural tunability of these polymers is limited.⁸ Herein, we disclose that highly tunable and solution processable polymers with high surface area can be directly prepared through ROMP (Scheme 1c). The resulting polymers are highly soluble in common organic solvents and possess Brunauer-Emmett-Teller (BET) surface areas as high as 780 m²/g. The versatility of this strategy is further demonstrated by the use

of postpolymerization functionalization and copolymerization to achieved a diversified family of porous organic polymers.

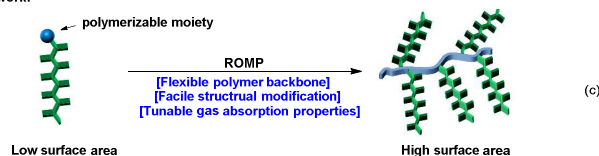
ROMP is among the most efficient controlled living polymerization methods.⁹ Despite the wide application, its use in preparing porous organic polymer is scarcely explored. We hypothesize that a porous ROMP polymer could be achieved if rigid, stereorandom, and noncompliant moieties are densely incorporated to the polymer backbone such that the folding of the polymer to the collapsed state is prevented (Scheme 1c). Furthermore, interpenetrations between the side chains are restricted by the unique topology of these polymers, thereby leading to materials of high surface area.

Scheme 1. A comparison between rigid mainchain and ladder-typed porous polymers with our designed porous polymer synthesized through ROMP.

Previous approach:



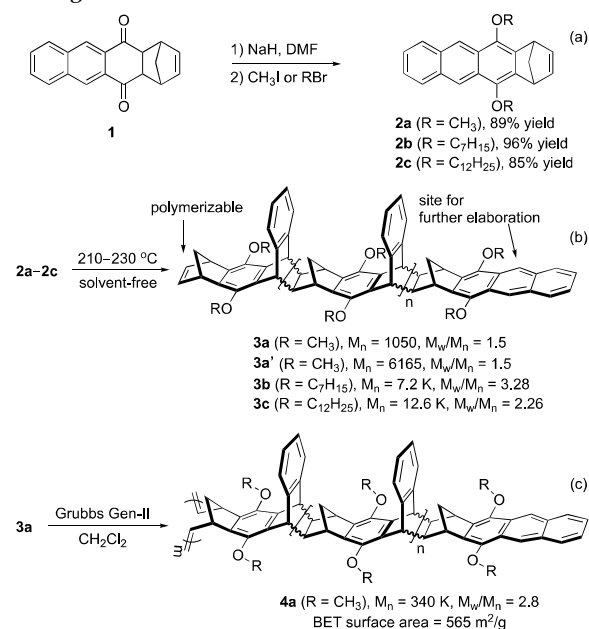
This work:



A three-dimensional stereorandom molecule with an annulated norbornyl moiety was targeted as monomeric unit for our polymer design. However, the preparation of a shape persistent structures that are sufficiently large is a prerequisite for our approach. The self-oligomerization of norbornyl-anthracenyl moieties (Scheme 2a,b) was utilized to prepare the monomeric units for our designed polymer. Although the

use of oligomeric mixtures as the monomers is likely to result in polymers with high polydispersities, the increased structural irregularity may be beneficial to increase porosity. Norbornene derivatives (**2**) with different substituents were first prepared

Scheme 2. Monomers and the porous polymer prepared through ROMP.



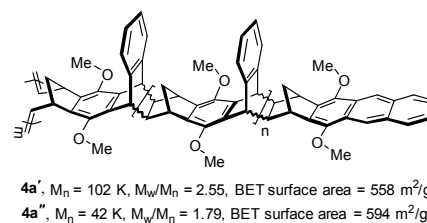
pared by alkylating diketone¹⁰ (**1**) with the aim to test the influence of the side chains on the oligomerization and porosity (**Scheme 2a**). A solvent-free melt phase oligomerization of **2** proved to be effective. Solution phase Diels-Alder polymerization reactions at ambient pressures suffer from slow reaction rates and low conversion.¹¹ Interestingly, the molecular weight of the resulting oligomer increases as the alkyl substituent becomes longer. For instance, the oligomerization of **2a** bearing methyl groups gave oligomer **3a** with a molecular weight of 1050 Dalton (ca. 3 repeating units), whereas the oligomer produced from **2c** under the same conditions possessed a molecular weight of 12.6 K (ca. 21 repeating units) (**Scheme 2b**). This is attributed to the long alkyl groups effectively decreasing the crystallinity and lowering the melting point of **2** to increase motility of the monomers and growing polymer during the reaction (**Scheme 2b**).

In order to investigate the surface area of oligomers **3** and the influence of the ROMP on the porosity, N₂ adsorption was measured at 77 K. BET analysis of the isotherms showed that the surface areas of **3b** and **3c** are too low to be measurable, whereas oligomer **3a** displays a BET surface area of 4 m²/g. These results indicate that the long flexible chains diminish the porosity and should be avoided in the preparation of high surface area materials (**Scheme 2b**). This behavior was also found for other porous organic polymers.¹² To examine if the low surface area of oligomer **3a** is attributed to its low molecular weight, oligomer **3a'** with a higher molecular weight of 6.2 K is prepared by extending the Diels-Alder oligomerization over 2.5 days. To our surprise, only a minimal increase of the surface area was observed with BET surface area of 9 m²/g for **3a'**. This indicates that a rigid three dimensional ladder-typed backbone is not sufficient to achieve high po-

rosity. We next tested the feasibility to prepare high surface polymers by ROMP of oligomers **3a-3c**. Interestingly, in presence of second-generation Grubbs catalyst,¹³ only oligomer **3a** gave the corresponding polymer, whereas no polymerizations occurred with oligomers **3a',b,c**. This result indicates the ROMP is sensitive to the size of the side chains and the polymerization may be inhibited by the steric hindrance of large monomers. Nevertheless, the ROMP of **3a** afforded a high molecular weight polymer with significantly increased porosity. The BET surface area of the resulting polymer **4a** was determined to be 565 m²/g, demonstrating the feasibility of our designed strategy in preparing highly porous materials.

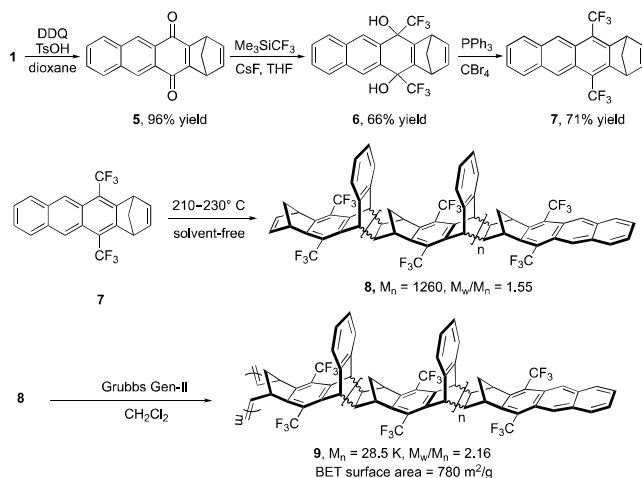
Encouraged by the result, we next examined the influence of the molecular weights of polymer **4a** on its surface area. By varying the amount of Grubbs catalyst, polymers **4a'** and **4a''** with respective molecular weights 102 K to 42 K were prepared (**Scheme 3**). Although we had anticipated that the surface area would increase with the degree of polymerization, different molecular weight samples of polymer **4a** all possess similar BET surface areas (558 – 594 m²/g). This observation illustrates that the topology of polymer **4** is more important than the molecular weight in increasing the surface area.

Scheme 3. The influence of molecular weight on the surface area of polymer **4**.



The modular synthesis of anthracene annulated norbornene **2** allows facile structural modifications to increase the diversity of the porous ROMP polymers. As conformational freedom is usually undesirable when preparing porous materials, the free rotating of methoxy group potentially deteriorates the porosity. On the other hand, recently investigations showed that the introduction of fluorine atoms or fluorinated moieties to porous materials has a significant influence on their swelling and gas absorption properties.¹⁴ Therefore, fluorinated ROMP

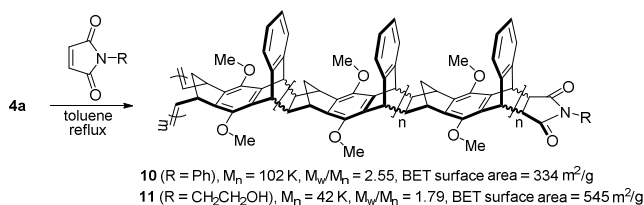
Scheme 4. Fluorinated porous polymer prepared through ring opening metathesis polymerization.



polymers are promising candidates to achieve high performance porous polymers. The oxidation of **1** with following by the nucleophilic trifluoromethylation gave a CF₃-substituted diol (**6**), which underwent aromatization to afford the trifluoromethylated anthracene derivative (**7**) for the oligomerization.¹⁵ By design, the replacement of the OMe groups with the bulkier CF₃ groups reduces the rotational freedom and shortens the side chains, which could be an effective way to prevent interpolymer penetrations. Consistent with our design, the fluorinated polymer ROMP **9** possesses a BET surface area of 780 m²/g, which is significantly higher than **4a** bearing OMe groups. The modification of substituents provides an attractive means to tune the porosity of our ROMP polymers.

The postpolymerization modification is a straightforward way to increase the structural diversity of polymeric materials. However, applying this strategy to porous polymers is largely unexplored. The ROMP polymers presented here retain anthracenyl end groups, which allows facile structural elaboration through Diels-Alder reactions. By using different maleimide derivatives, various functional group could be successfully incorporated into the porous polymer **4a** (Scheme 5). It is noteworthy that the surface areas of the modified polymers **10**, **11** are comparable to that of **4a**. Therefore, our postpolymerization functionalization method could provide facile access to porous polymers with diverse functionalities.

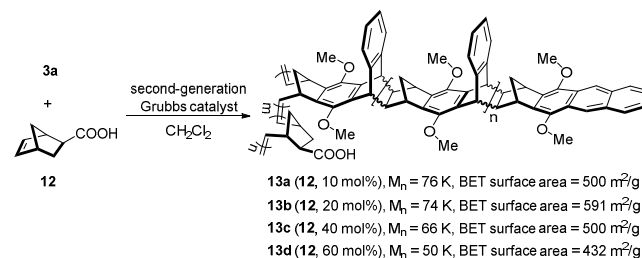
Scheme 5. Structural modification of polymer **4a** through end group functionalization.



The ROMP method for the preparation of porous organic polymers also offers the ability to introduce various functionalities through copolymerization. Owing to the excellent functional group tolerance of the Grubbs' ROMP catalysts, sensitive and reactive moieties could be incorporated with high fidelity. In order to test the feasibility of this approach, oligomer **3a** was copolymerized with varying amounts of 5-

norbornene-2-carboxylic acid (**12**). We find that the copolymerization was not affected by the acidic carboxylic groups, giving copolymers with molecular weights ranging from 76K to 50K (Scheme 6). The successful incorporation of **12** into the resulting polymers was confirmed by infrared (Figure S2 in SI) and NMR analysis. It was found that the copolymer with a high content of **12** possessed a lower molecular weight, which is consistent with the fact that **12** is much smaller than oligomer **3a**. Considering that the incorporation of **12** significantly increases the conformational freedom of **13**, lower surface areas relative to that of **3a** were anticipated for copolymers **13**. Although this is true for most of the copolymers shown in Scheme 6, the surface area of copolymer **13b** containing 20 mol% of **12** is higher than that of **3a**. This interesting behavior is attributed to interactions between the carboxylic groups, which may promote the formation of rigidified three-dimensional hydrogen bonded network in solid state.

Scheme 6. Preparation of porous ROMP polymer through copolymerization



Considering the high surface area and polarizable aromatic components of our ROMP polymers and we expect these materials should be able to absorb organic vapors. In order to test the absorption performance of our ROMP porous polymers, various organic vapors at low concentrations (500 ppm) were directed into a chamber containing the polymers and the purging was continued for 1h, after which the mass change of the polymers were measured. Activated carbon was selected as a reference as a result of its known utility as an absorbance material. As illustrated by the results shown in Figure 1, the mass changes of activated carbon after exposure are small (<1%), which illustrates the challenge associated with the absorption of vapors at low concentrations. In contrast, polymer **4a** displays high absorption capabilities with a strong preference for aromatics over acetonitrile and ethanol. After exposure, a mass increase of 7.7% and 14.5% were observed, respectively for benzene and toluene. This observation reflects the hydrophobic aromatic character of polymer **4a**, which allows extensive π - π and C-H- π interactions with aromatic gas molecules. In order to demonstrate the feasibility to tune the gas absorption properties through our copolymerization strategy, the performance of polymer **13c** bearing carboxylic acids groups was examined under the same experimental conditions. Owing to the introduction of carboxylic groups, we expect that the hydrogen-bonding and dipole interactions between polymer **13c** and gas molecules will be more favorable than that of **3a**. Consistent with our hypothesis, the absorption of acetonitrile and ethanol was selectively enhanced with polymer **13c** and was accompanied by a slight decrease in absorption of aromatics as a result of

the decreased hydrophobicity of the polymer (**Figure 1**). This example illustrates the possibility to rationally tune the gas absorption capability of the polymer by introducing selective functionality.

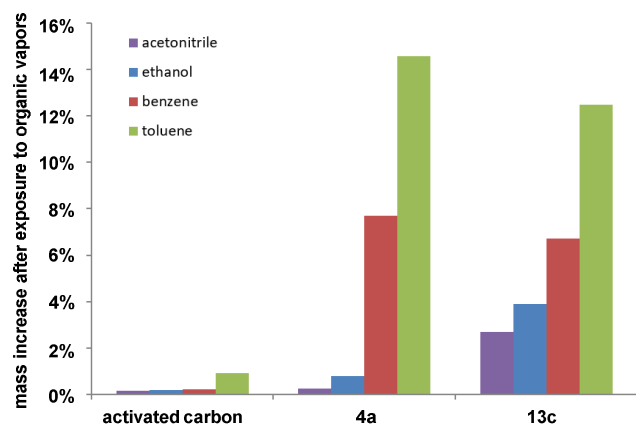


Figure 1. Gas absorption ability of activated carbon, **4a**, and **13c**.

In summary, we have developed a new strategy for the preparation of solution processable porous organic polymers. The polymerization of structurally rigid nonporous units through ROMP provides access to structurally tunable polymers with high surface areas. The copolymerization approach allowed manipulation of the gas absorption properties through incorporation of carboxylate functionality. The ease of preparation and the scope of structural diversity constitute a new approach to porous polymers with tailored properties.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

Y.Z. and Y.H. contribute equally to this work. The authors declare the following competing financial interest(s): A patent has been filed on the polymers and their applications in gas absorption.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation through award DMR-1410718.

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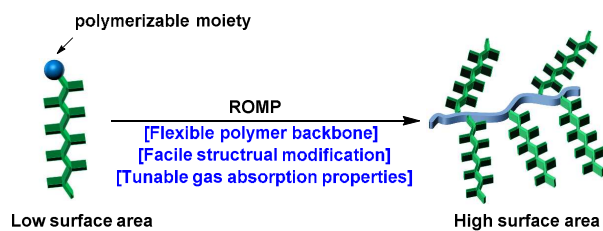
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