Microporous Materials

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# Reverse Engineering of Conjugated Microporous Polymers: Defect Structures of Tetrakis(4-ethynylphenyl)stannane Networks

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*Dedicated to Professor Todd B. Marder on the occasion of his 60th birthday*

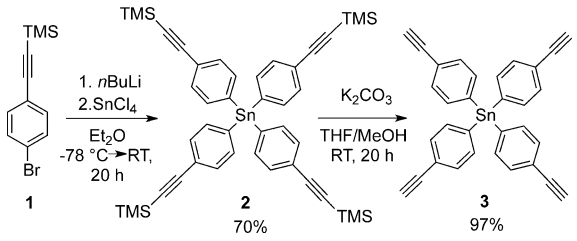
***Abstract:*** *Two different conjugated microporous polymers (CMPs) based on tetrakis(4-ethynylphenyl)stannane as the repeating unit were synthesized and their BET surfaces and thermal properties were investigated. The first direct method to elucidate the molecular structure of the organic linkers between the tin centers by digestion of the CMP is described. Selective cleavage of the tin–carbon bonds with chloroacetic acid afforded the isolated bridging units and provided insight into the surprisingly varied chemical composition of these networks.*

In the biosciences, sequence analysis is a critical tool for obtaining information about biomacromolecules; the sequencing of DNA and proteins and identification of the building blocks was one of the achievements that led to a much deeper knowledge of their structures and functions.[1–4] For artificial polymers, the backbones are often composed of C–C bonds. With few exceptions,[5] these linkages are not amenable to digestion and analysis, which would give an idea about defect structures or possible branching. In the past decade, conjugated microporous polymers (CMPs) have become increasingly important owing to their versatile applications in gas storage, heterogeneous catalysis, and molecular separations.[5–9] Pore size, density, and surface area are specifically tunable through the choice of organic monomers of different strut length and structure.[10–12] Nevertheless, little is known about the structure–property relationships of these networks because of a lack of methods to directly investigate their molecular structure.[13] Since CMPs are fundamentally insoluble and infusible, it is impossible to obtain any sequence and/or structural information unless preordained structural elements, ready for digestion, could be incorporated into the monomers.

Recently, a series of microporous polymers was synthesized by Sonogashira–Hagihara coupling[9] or alkyne–alkyne homocoupling reactions.[10,14] Several groups have reported conjugated microporous poly(phenylene butadiynylene)s, prepared through a $Pd^{II}/Cu^{I}$-catalyzed homocoupling reaction in the absence of an additional oxidant,[15–17] but the elucidation of the real molecular structure of polymers is quite difficult owing to their insolubility, and therefore only few attempts have been made to evaluate the exact composition of CMPs.[15] However, since the properties of these materials are a direct consequence of their molecular composition, structure determination is important with regard to the rational design of novel specialized or general CMPs, as well as from a fundamental, conceptual point of view.

In this work, we acquired sequence information for CMPs by using chemical digestion. Two CMPs containing tin as the center of their tetrahedral modules were synthesized and their molecular structures were investigated. Quantitative cleavage of the tin–carbon bond enables a direct comparison of two formally identical materials: **P1** was synthesized through a homocoupling reaction of tetrakis(4-ethynylphenyl)stannane **3**, and **P2** was obtained by reacting a prefigured diyne structure that is not affected by the polymerization reaction.

For the synthesis of **3**, we adopted a procedure developed by Bräse et al. to furnish the tetrahedral tin module in good yields (Scheme 1).[18–19] **P1** was synthesized through $Pd^{II}/Cu^{I}$




***Scheme 1.*** Synthesis of precursors for **P1**. TMS = trimethylsilyl.

catalyzed homocoupling of **3** according to the method reported by Cooper et al. for their homocoupled conjugated microporous polymers (HCMPs); the reaction proceeds without the use of an oxidant and under exclusion of oxygen and water (Scheme 2).[15] Notably, the authors already hypothesized that significant defect structures and not only butadiyne linkers are formed under Sonogashira–Hagihara

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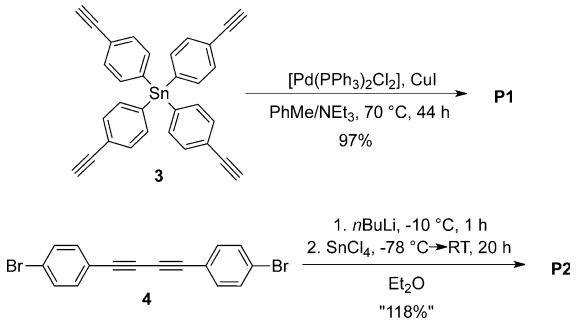



***Scheme 2.*** Syntheses of the polymers **P1** and **P2**.

conditions with $Pd(PPh_3)_2Cl_2$, copper(I)iodide, and triethylamine, but it was difficult to get proof thereof.[16] To explore the structure of polymers that were synthesized under these diyne coupling conditions, we introduced tin centers. The tin–carbon bond is easily cleaved, thus allowing digestion of the CMPs and investigation of the structure of the liberated organic connectors. We additionally prepared the control CMP **P2**, which should only feature diyne linkers (Scheme 2). Halogen–metal exchange, as exploited by Kaskel et al., has already enabled access to some element organic frameworks (EOFs) containing tin without diyne structures.[5,19] Our monomer **4** contains a pre-established diyne motif, which was not affected by treatment with *n*-butyl lithium and tin(IV)chloride and therefore was assumed to be a suitable monomer for the preparation of **P2**.

In contrast to **P1**, which appeared as a dark brown crude solid, **P2** was obtained as a fine, bright orange powder. Neither CMP showed any fluorescence under UV light. The color difference suggests a more uniform material for **P2**, which is corroborated by the respective powder UV/vis spectra (see the Supporting Information). Both polymers exhibit a peak at $\lambda \approx 320$ nm, which arises from their monomeric aromatic repeat components. However, **P2** possesses a well-defined charge transfer band ($\lambda = 400$–$650$ nm), whereas the inhomogeneous composition of **P1** leads to a steady decline in absorbance caused by various overlaps in the absorbance range.

The excess yield (>100%) of **P2** is explained by residual bromine of about 5% (probably in the form of trapped LiBr) within the polymer, as determined by elemental analysis. However, it is also possible that there are $R_3Sn$-OH and $R_2Sn(OR)_2$ residues present as a result of incomplete reaction of the tin-(IV)chloride with the organic lithium compound formed from **4**, and this could also explain the excess yield.

The IR spectrum of **P1** still features an alkyne band at $\tilde{\nu} = 3300\ cm^{-1}$, which corresponds to unreacted terminal alkyne groups within the polymer. Such bands were not found for **P2** because of its alternative preparation method based on a preconfigured diyne structure for the monomer (see the Supporting Information).

**P1** and **P2** show similar thermogravimetric behavior and both decompose at 370 °C, which is in line with the HCMPs synthesized by Cooper et al. Measurements of the Brunauer–Emmet–Teller (BET) surfaces gave similar curve shapes (Figure 1), although a hysteresis was observed for **P1**. The small deviation is probably due to the

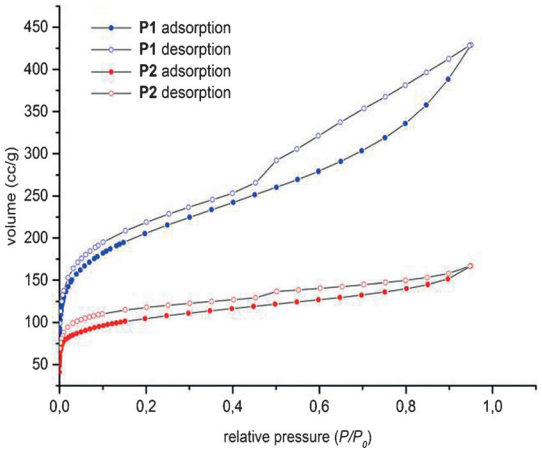
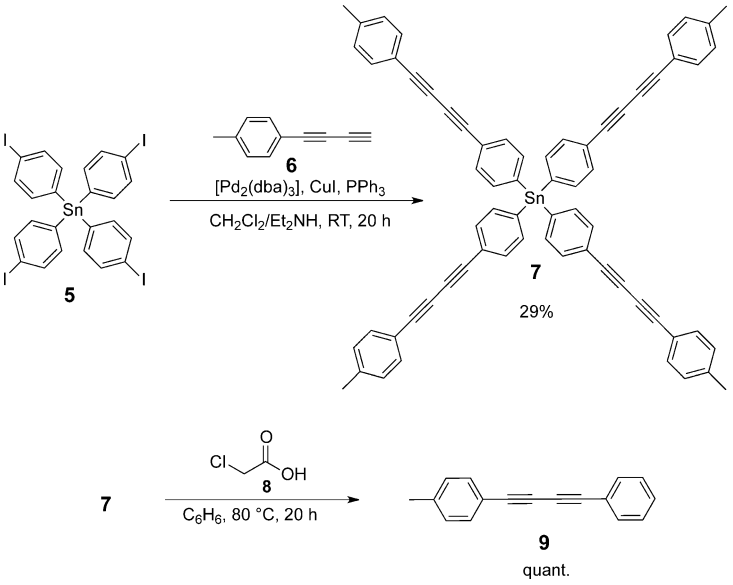



***Figure 1.*** $N_2$ adsorption and desorption isotherms measured at 77 K for **P1** (blue) and **P2** (red).

small particle size. The BET surface areas for **P1** and **P2** were found to be $747\ m^2g^{-1}$ and $385\ m^2g^{-1}$, respectively. Cooper and co-workers measured surface areas of about $800\ m^2g^{-1}$ for their HCMPs. The differing values for **P1** and **P2** provide additional evidence for the different molecular structures of the two polymers.

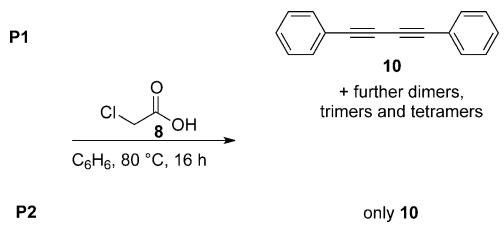
To identify defect structures within the synthesized materials, we developed a procedure for tin–carbon bond cleavage based on work by Srivastava et al.: model compound **7** was heated in anhydrous benzene with chloroacetic acid **8**, resulting in quantitative formation of diyne **9** (Scheme 3).[20] Control experiments were performed by heating compounds **3** and **4**, phenylacetylene, and styrene in the presence of chloroacetic acid **8** to exclude side reactions of the acid with the organic products of the polymer degradation.




***Scheme 3.*** Synthesis and cleavage of model compound **7**.

We employed the digestion reaction to analyze the structures of **P1** and **P2**. The reaction suspensions were heated under reflux overnight and then purified by column chromatography. Reaction of **P2** quantitatively gave the expected organic linker **10** without side products (see the Supporting Information for GC–MS and NMR spectra after the cleavage reaction). By contrast, digestion of **P1** resulted in a range of organic compounds; only 6% of the expected diyne **10** was found along with large amounts of enyne oligomers in the GC–MS spectrum of the raw digest (Scheme 4).

Several dimers (*m*/*z* 204), trimers (*m*/*z* 304, *m*/*z* 306), and one tetramer (*m*/*z* 406) of phenylacetylene were identified. We were able to separate the dimer, trimer, and the tetramer fractions by column chromatography (Figure 2). The three




***Scheme 4.*** Cleavage reaction of **P1** and **P2**.

dimeric enynes **11**–**13** of the first fraction were identified by comparison with reported NMR spectra and a GC–MS database.[21–24]

The ratio of dimers **11**/**12**/**13** was determined to be 0.5:1.5:1.5 (NMR spectrum before purification, Table 1). Furthermore, we detected several signals for different trimers of phenylacetylene in the GC–MS spectrum of the second fraction, two at *m*/*z* 304 and five at *m*/*z* 306, thus indicating two enediynes and five dienynes (Figure 2). The identities of the enediynes **13** (pink) and **15** (bright green), and the

***Table 1:*** Ratios of the identified dimers and trimers, as determined by NMR spectroscopy (before purification) with hexamethylbenzene as a standard.

| Dimers | **11** | **12** | **13** | Trimers | **14** | **15** | **16** | **17a–d** |
|---|---|---|---|---|---|---|---|---|
| NMR ratio | 0.5 | 1.5 | 1.5 | | 0.35 | 0.8 | 2.2 | 1:1:0.8:0.8 |

dienyne **16** (violet) were confirmed by comparison with literature data.[25–27] However, there are no reports on NMR spectra of the other possible isomers. The brown colored signals in Figure 2 were thus assigned to the two isomers of hexa-3,5-dien-1-yne-1,3,5-triyltribenzenes **17a**,**b** on the basis of the characteristic multiplets appearing at $\delta = 5.0$–$5.5$. ppm that feature a typical splitting of geminal hydrogen atoms, and supporting NMR spectra simulation.

In summary, tin-containing cleavable CMPs were synthesized and characterized. The organic linkers between the tin centers of **P1** were identified after cleavage of the tin–carbon bonds. Except for a small amount of diphenylbutadiyne **10**, mostly enyne-based dimers, trimers, and tetramers of phenylacetylene were detected after digestion of **P1**. The presence of a range of enynes provides evidence that the polymerization conditions do not result in the homocoupling reaction of diynes. However, with **P2**, we created a network containing diyne motifs, which was also verified by the new method of selective cleavage of the tin–carbon bond. We can now elucidate the molecular structures of CMPs, which will be helpful for future investigations concerning their structure–property relationships. Knowing the exact composition of CMPs will fundamentally facilitate the design of desired properties in these materials. The method presented here is not limited to CMPs based on tin centers but should also be applicable to silicon-containing CMPs by employing fluoride as a cleaving reagent. It should also be possible to digest ester, ether, or amide-containing CPMs, thus making this a powerful and broadly applicable method.

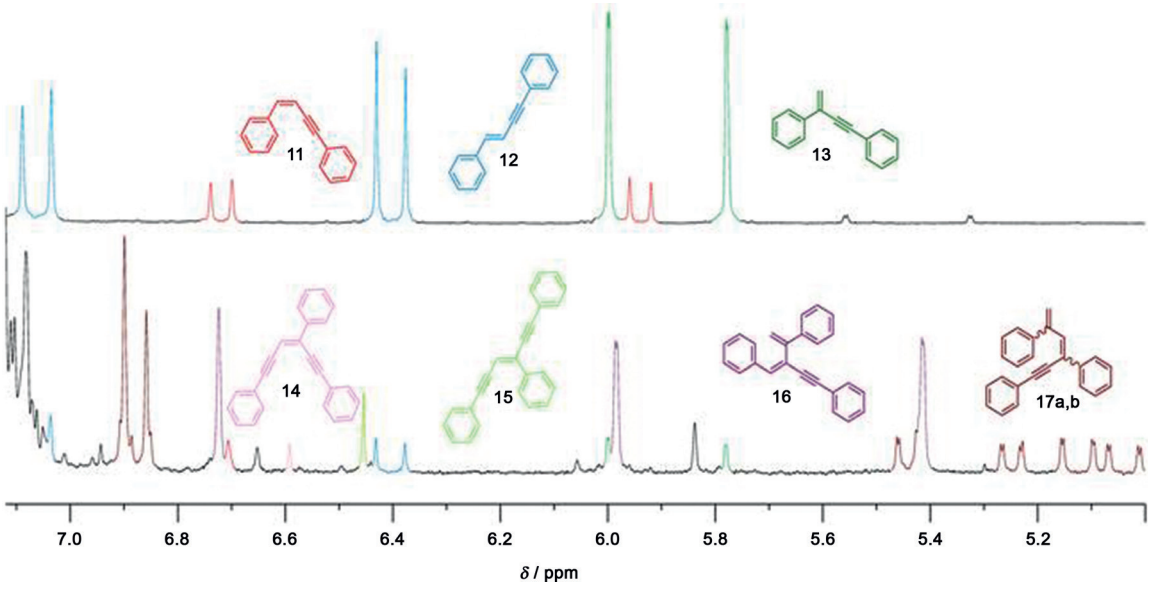



***Figure 2.*** NMR spectra of the isolated fractions after column chromatography. Top: Fraction 1 contains dimers of phenylacetylene. Bottom: Fraction 2 contains a range of trimers.

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**Keywords:** defect structures · homocoupling · microporous materials · polymers · structure elucidation

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