Versatile Postmodification of Conjugated Microporous Polymers Using Thiol-yne Chemistry

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Ⓢ *Supporting Information*

ABSTRACT: Radical thiol-yne chemistry is used for the modification of microporous networks with aliphatic alcohols. The degree of functionalization can be tuned by varying the reacted amount of thiol. Porosity analysis indicates that the microporosity can be preserved within a certain range, however, a decrease in pore size is observed.
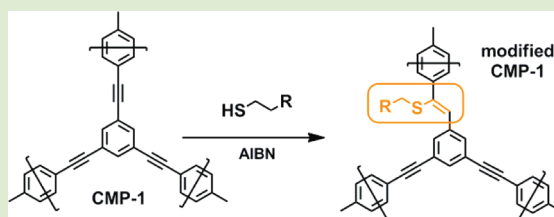
Conjugated microporous polymers (CMPs) gained a lot of interest during the last years due to their combination of high porosity with an outstanding chemical stability.[1] Typically, CMPs are synthesized by metal catalyzed polycondensation reactions, for example, Sonogashira-Hagihara coupling of multifunctional aryl halides with aryl ethynylenes,[2,3] or by Suzuki coupling of multifunctional aryl halides with bisboronic acids.[4,5] Recently, there was an increased interest in preparing functional microporous polymer networks to achieve benefits over mere surface area. One way to achieve functionality is to use functional comonomers.[6−8] This approach works fine for a rather large of variety of monomers, but does sometimes fail because of incompatibility of the used metal-catalyzed cross-coupling reaction with the functional monomer. Another (economical) drawback is the use of functional monomers in large quantity, which is not always required to obtain functionality of the final material.

Postfunctionalization of organic materials was studied extensively during the last years and was often undertaken using so-called "click" chemistry. Despite the well-known Huisgen reaction (copper catalyzed 3 + 2 cycloaddition of azides),[9] which was recently also used for the functionalization of microporous polymer beads (by reaction of terminal ethynyl groups),[10] there was recently also more and more interest in the radical thiol + X chemistry, where X can be, for instance, a double or a triple bond.[11,12]

CMPs that are synthesized by the Sonogashira-Hagihara coupling method are based on triple bonds and should therefore be able to be directly modified by radical thiol-yne chemistry. Indeed, a comparable modification of conjugated double bonds in phenylene-vinylene type polymers was reported in 2005.[13] It was reported that the emission color of the polymers could be significantly changed by the thiol—ene reaction. It should also be noted that nucleophilic addition of HBr to triple bonds of poly(arylene ethynylene)s (PAE) was already reported in 1994.[14]

A radical thiol-yne modification of CMPs based on arylene—ethynylene should result in (i) morphological changes (due to the changed connection geometry, see Scheme 1), which

should effect the porosity and (ii) in changed optical properties. To analyze the various effects, we prepared a large batch of CMP-1 by reaction of 1,3,5-triethynylene benzene (1) and 1,4-dibromo benzene (2; Scheme 1). The reaction was performed using diisproylamine (DIA) instead of triethylamine (TEA), which resulted in higher specific surface areas. The resulting CMP-1 was then reacted with varying amounts of thioethanol (C_2SH, 3) or 6-mercaptohexanol (C_6SH, 4). The reaction was initiated by azoisobutyronitrile (AIBN; 1 equiv per thiol) and performed in toluene at 90 °C for 24 h. After cooling, the solid was filtrated, washed and analyzed after drying (evaporative drying). Analysis was done by various methods, as will be discussed below. We modified CMP-1 by reacting it with 0.5, 1, or 1.5 equiv of thiol-compounds (C_2SH or C_6SH) per triple bond, assuming ideal stoichiometry of CMP-1. The success of the reaction was estimated by elemental analysis, FTIR and Raman spectroscopy. Elemental analysis showed a decreasing carbon-to-sulfur ratio (C/S) with increasing thiol reactant (Figure S1). It should be noted that a C/S ratio of ∼8 can be calculated if one thioethanol molecule would be attached per repeating unit of the polymer network (containing 3 triple bonds). Reaction of 1.5 eq thiol per triple bond yields a C/S ratio of ∼22 for thioethanol and ∼24 for 6-mercaptohexanol, which indicates that only one out of 8−9 triple bonds reacted with a thiol. This rather low degree of functionalization is nevertheless reflected in the observable porosity of the modified polymer networks as will be discussed below. Spectroscopic analysis of the networks revealed also a successful modification. FTIR spectroscopy could prove the presence of alkyl CH_2 groups and OH groups. (Figure 1). Furthermore, a strong but somewhat broad band arises at ∼1660 cm^{-1} which might be attributed to the presence of double bonds.

Scheme 1. Synthesis of CMP-1 and Its Modification by Thiol-yne Chemistry
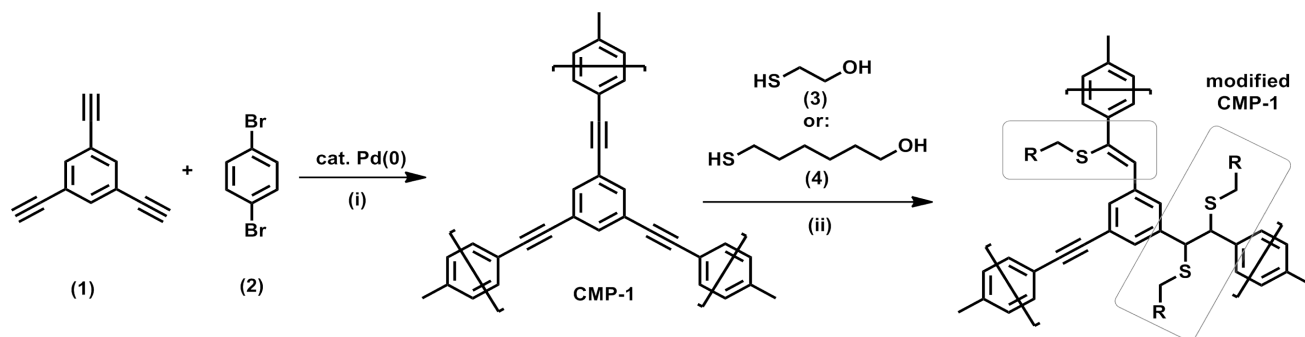
The possible binding schemes obtained from 1- or 2-fold thiol attack per triple bond are highlighted. Synthesis conditions: (i) Pd(PPh$_3$)$_4$, CuI, DMF, DIA, 90 °C, 5 d; (ii) 1 equiv AIBN per thiol, toluene, 90 °C, 24 h.
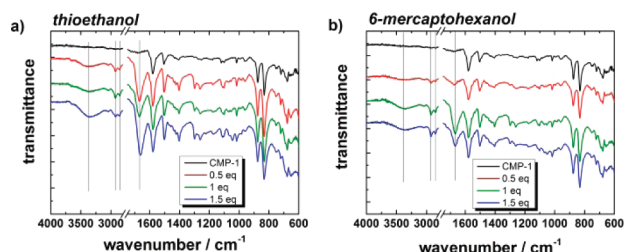

Figure 1. FTIR spectra of CMP-1 and (a) the thioethanol-modified derivatives and (b) the 6-mercaptohexanol-modified derivatives.

Raman spectroscopy can be an additional spectroscopic tool for the analysis of the modification reaction. However, the measurements were strongly affected by the fluorescence of the samples, which is a common feature of PAEs and was also reported for hyperbranched PAE and CMP-1 earlier (see corresponding photoluminescence spectra within the Supporting Information).[2,15] No qualitative statement could be derived from the spectra of the modified networks, except for CMP-1 reacted with 5 equiv thioethanol (C$_2$SH_5.0, see below), where the −C≡C− band at ~2200 cm^{-1} almost vanished from the spectrum, proving efficient reaction (Figure S2). Furthermore, there are major changes at the broad band between 1100 and 1200 cm^{-1}. The Raman spectrum of C$_2$SH_5.0 features a main band at 1186 cm^{-1}, which is close to a typical band of poly(paraphenylene vinylene)s (PPV) at 1174 cm^{-1}.[16]

Based on the results of the elemental analysis and the spectroscopic analysis, we conclude that the modification is possible and results (at the used amounts of thiol compounds) in the formation of double bonds, while there is no significant evidence for 2-fold substitution, which would yield C−C single bonds, as indicated in Scheme 1.

Thermogravimetric analysis was also employed to determine the degree of functionalization. Changes in the decomposition patterns compared to unmodified CMP-1 were observed (onset of decomposition at lower T), but quantitative analysis was not possible due to an overlap of the decomposition steps of the aliphatic chains and the aromatic network.

The microporosity of the materials was analyzed by means of CO$_2$ adsorption/desorption at 273.15 K and by N$_2$ adsorption/desorption at 77.3 K.[17]

The porosity data derived from the measurements is summarized in Table 1 and representative gas adsorption/desorption isotherms are depicted in Figure 2 (for further data, please see the Supporting Information).

Table 1. Porosity Data obtained from Gas Adsorption/Desorption Experiments

material	S_{BET}/m^2 g^{-1}	V_{pore}^{a}/cm^3 g^{-1}	S_{GCMC}/m^2 g^{-1}	V_{pore}^{b}/cm^3 g^{-1}
CMP-1	1200	0.465	590	0.24
C$_2$SH_0.5	998	0.384	755	0.304
C$_2$SH_1.0	943	0.365	659	0.259
C$_2$SH_1.5	907	0.352	600	0.238
C$_2$SH_5.0^c	325	0.118	n.d.	n.d.
C$_6$SH_0.5	884	0.341	570	0.226
C$_6$SH_1.0	860	0.329	531	0.212
C$_6$SH_1.5	688	0.264	315	0.13

^{a}Obtained from total N$_2$ uptake at p/p^0 = 0.1. ^{b}Obtained from the GCMC model based on the CO$_2$ adsorption isotherms. ^{c}Freeze-dried material; n.d.: not determined

The analysis of the starting material, CMP-1, indicated significant microporosity. By comparison of the N$_2$ and CO$_2$ derived specific surface areas, a significant mismatch becomes visible. As CO$_2$ sorption can, however, probe only the narrowest micropores (smaller than 1 nm) reliable, this indicates that larger micropores are also present in the material.[17] The N$_2$ adsorption/desorption isotherms also imply the presence of undefined mesopores, as indicated by the presence of the hysteresis loop. However, this is purely an effect of the applied drying method (evaporative drying). If freeze-dried, the hysteresis loop is missing (see Figure S6), but a much steeper increase at high relative pressures is observed. This indicates that the drying method mainly influences the macrostructure, that is, the stability of the interstitial voids between the polymer particles. Evaporative drying seems lead to some compacting which can explain the observed mesoporosity. To sum up, the here prepared CMP-1 is mainly microporous (with micropores covering the whole size range) but has also some ill-defined mesopores.

Upon modification, we observe a slight decrease of the determined BET surface areas, which was to be expected. Contrary, the specific surface area determined by CO$_2$ adsorption is rising at low degree of modification (0.5 equiv), but follows to decrease at higher levels of functionalization. This effect might be attributed to a change in pore morphology/size, which would be in line with the introduction of guest, but also with the expected geometrical change upon switching from triple bonds toward double bonds. The impact of switching the network geometry on the observable porosity was recently demonstrated.[18]
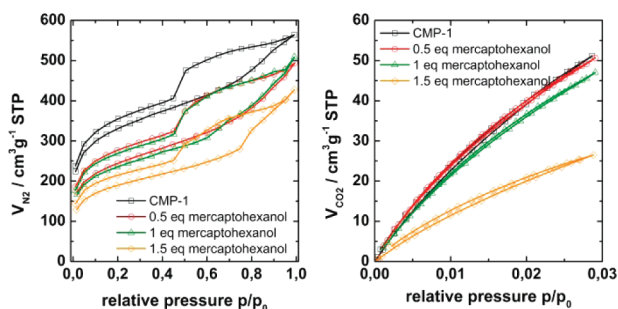
Figure 2. (Left) N_2 adsorption/desorption isotherms obtained at 77.3 K; (right) CO_2 adsorption/desorption isotherms obtained at 273 K.

The here observed changes, indicate an increase of the fraction of small micropores (higher or stable CO_2 uptake) at the cost of the larger micropores. This might have its origin in diffusion and steric effects. First, diffusion in the larger micropores is presumably faster. This leads to preferred functionalization of the larger pores, which consequently become smaller in size. Steric reasons, that is, taking the size of the molecule to enter the pores (especially C_6SH) into account would also result in a preference of larger pores in first approximation. This conclusion is also evident, when looking at the carbon dioxide isotherms in more detail Figure S7). Comparison of the CO_2 adsorption branches of CMP-1 and C_6SH modified CMP-1 (0.5 equiv) shows that both materials show a comparable CO_2 uptake. However, the isotherms cross each other, with the modified material having a steeper increase at low relative pressures (corresponding to a larger fraction of very small pores).[19,20]

The tendency toward pore-filling becomes just evident for the material reacted with 1.5 equiv 6-mercaptohexanol, where the BET (688 $m^2\ g^{-1}$) as well as the CO_2 adsorption derived surface area (315 $m^2\ g^{-1}$) decreased significantly, compared to the starting compounds.

We were also interested, whether it is possible to achieve higher degree of functionalization. CMP-1 was hence reacted with 5 equiv of thioethanol. The resulting material had still an apparent BET surface area of 325 $m^2\ g^{-1}$ (after freeze-drying). Raman spectroscopy indicated, however, that almost all $-C\equiv C-$ were converted (Figure S8).

To be finally sure, that the observed effects are indeed due to the thiol-yne modification, we also treated a sample of CMP-1 with AIBN but without adding any thiol compounds. No significant change in porosity was observed (Figure S9), indicating that the observed changes are indeed due to the thiol-yne addition.

In conclusion, this works presents a first example how porous polymers can be postfunctionalized *on-demand* using thiol-yne chemistry. The porosity can be largely preserved, depending in the size and amount of the molecule to be introduced. Future work targets the introduction of other functionalities. First experiments using cysteamine hydrochloride were undertaken, but not successful so far, presumably due to radical scavenging by some free amines.

An attractive outlook would also target the covalent functionalization of optically active materials inside a fluorescent microporous matrix. This could result in much more stable energy-harvesting systems, compared to the so far realized simple pore-filling approaches.[5,21,22] Other potential applications might be found in the field of tunable gas/vapor selectivities or targeted incorporation of catalytically active species (e.g., metal binding sites).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, materials and methods, further analytical data (gas adsorption data, RAMAN spectra, TGA data, elemental analysis data, PL spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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