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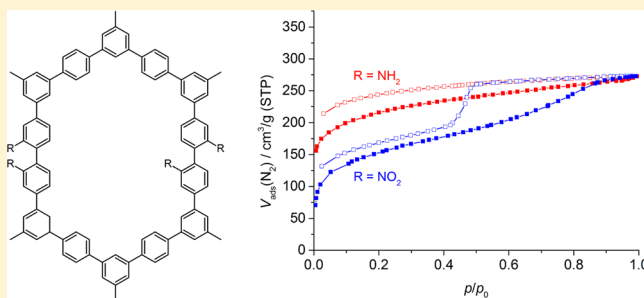
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## Tailoring Pore Structure and Properties of Functionalized Porous Polymers by Cyclotrimerization

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## S Supporting Information

**ABSTRACT:** Porous polymers were prepared by cyclotrimerization reaction in molten *p*-toluenesulfonic acid. Their properties could be tailored by functionalization of the aromatic diacetyl monomers. Thus, a range of homo- and copolymers based on hydrogen-, amine-, or nitro-functionalized 4,4'-diacetylbiphenyl derivatives and 1,4-diacetylbenzene was synthesized. The pores size could be tuned from mainly microporous to hierarchical micro- and mesoporous or even hierarchical micro- and macroporous. BET surface areas up to 720 m<sup>2</sup>/g and total pore volumes up to 1.76 cm<sup>3</sup>/g were achieved. The formation of different pore types was related to the solvent–monomer/polymer interactions, which is shown by <sup>15</sup>N solid state MAS NMR spectroscopy and SEM. Other physical properties such as surface polarity and thermal stability were influenced by the different monomers as well.



## ■ INTRODUCTION

In the past decade, porous polymers such as porous polymer networks (PPNs), covalent organic frameworks (COFs), covalent triazine-based frameworks (CTFs), organic frameworks by cyclotrimerization (OFCs), porous aromatic frameworks (PAFs), and others have attracted much attention because of their great application potential due to their easy processability as well as their high chemical and thermal stability.<sup>1–7</sup> This includes gas storage and separation, catalysis, and recently also their usage in energy storage systems.<sup>8–11</sup> Most of the porous polymers are stable toward moisture as compared to COFs with oxygen–heteroatom bonds.<sup>12</sup> Because of their chemical robustness, porous polymers can be functionalized by a variety of postsynthetic approaches even under harsh conditions, which is an advantage compared to metal–organic frameworks.<sup>13</sup> This allows the optimization of properties for a specific purpose. For example, Lu et al. showed that the postsynthetic modification of PPN-6 with alkyl amino groups increases the CO<sub>2</sub> adsorption at 298 K and 1 bar from 5.4 to 15.8 wt % for PPN-6 and PPN-6-CH<sub>2</sub>DETA, respectively.<sup>14</sup> Another possibility is the functionalization of the aromatic backbone by reacting the porous polymer with nitric acid. The resulting nitro groups can be subsequently reduced with tin(II) chloride yielding amino-functionalized porous polymers. Using this procedure, El-Kaderi and co-workers were able to achieve an average ratio of 0.54 nitrogen atoms per initial phenyl ring.<sup>13</sup> The disadvantage of a

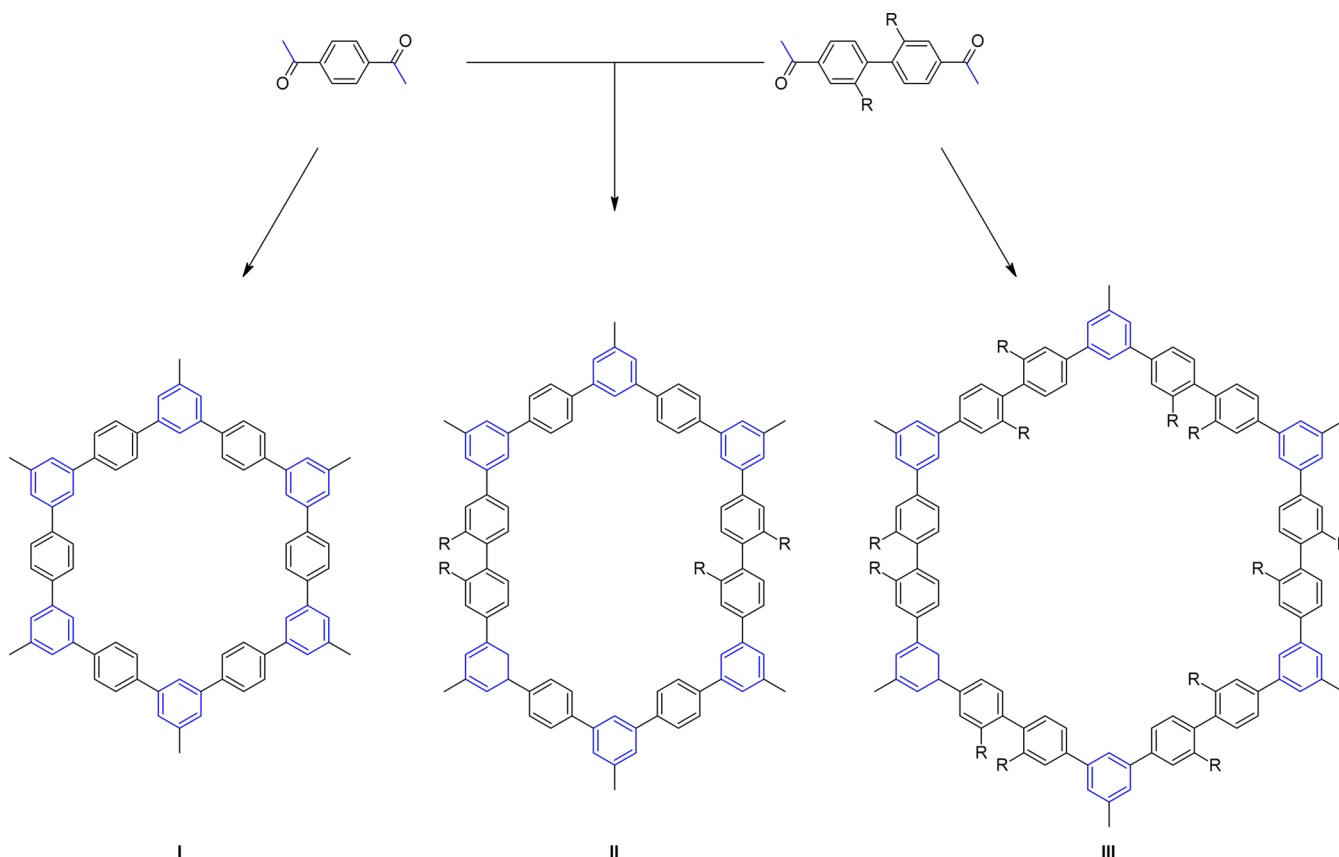
postsynthetic modification is the random incorporation of the functional groups. Therefore, a more reliable approach is the use of functionalized monomers. Recently, Garibay et al. used the so-called *de novo* approach for preparing amine-functionalized PAFs.<sup>15</sup> They used (4-bromo-3-(bromomethyl)phenyl)-tris(4-bromophenyl)methane as monomer containing a benzylic bromine which easily undergoes nucleophilic substitution. After polymerization they obtained a hydroxyl-functionalized PAF. Using a phthalimide-functionalized monomer, they were able to prepare an amine-containing network by postsynthetic reaction with hydrazine. Another approach includes the use of azide-containing monomers and postsynthetic modification by click reaction with alkynes.<sup>16</sup> Cooper and co-workers have shown that functionalized monomers, e.g. amine, nitro bearing monomers, can be used in palladium-catalyzed Sonogashira–Hagihara cross-coupling.<sup>17,18</sup> These are rare examples for the direct use of amine functionalized monomers because those monomers often undergo undesired side reactions. Beyond that, other functional groups such as esters, hydroxyl groups, or pyridine have been successfully incorporated in porous polymers.<sup>18,19</sup>

A reaction that is known not to be affected by amine or nitro groups is the aldol condensation of aromatic acetyl

Received: March 10, 2014

Revised: June 2, 2014

Published: June 17, 2014



**Figure 1.** Idealized reaction scheme of the cyclotrimerization: (I) homopolymerization of 1,4-DAB (OFC-1), (II) co-condensation of 1,4-DAB and 4,4'-DABP, molar ratio 2:1 (DUT-92 family), and (III) homopolymerization of 4,4'-DABP (DUT-93 family). R = H, NO<sub>2</sub>, and NH<sub>2</sub>.

compounds.<sup>20,21</sup> Rose et al. have reported the preparation of porous polymers by cyclotrimerization, for instance of 1,4-diacetylbenzene in molten *p*-toluenesulfonic acid.<sup>4</sup> In the following we report the preparation of functionalized porous polymers by using amine- or nitro-modified aromatic diacetyl compounds. Because of the functional groups, not only the polarity but also the pore structure could be tailored. DUT-92(NO<sub>2</sub>) (DUT = Dresden University of Technology), a copolymer of two monomers 1,4-diacetylbenzene (DAB) and 4,4'-diacetyl-2,2'-dinitrobiphenyl (DABP-(NO<sub>2</sub>)<sub>2</sub>), has micro- and mesopores whereas the corresponding amine-functionalized DUT-92(NH<sub>2</sub>) is mainly microporous.

## EXPERIMENTAL SECTION

**Materials.** 4-Bromo-3-nitroacetophenone (99%) was purchased from ABCR, 1,4-diacetylbenzene (99%), copper (99.5%, ~40 mesh), and DMF (extra dry, 99.5%) from Sigma-Aldrich, 4,4'-diacetylbi-phenyl (98%), *p*-toluenesulfonic acid (98%), and tin(II) chloride dihydrate (98%) from Alfa Aesar, and iodine (resublimated) from Acros Organics. Copper was activated according to a literature procedure.<sup>22</sup> All other chemicals were used as received.

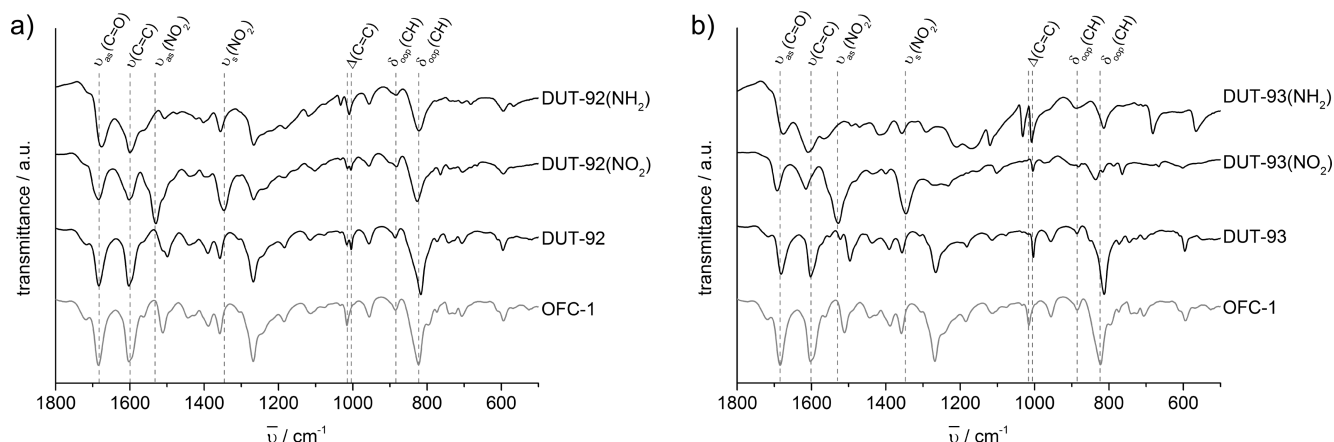
**Methods.** Nitrogen physisorption experiments were carried out either on a Quantachrome Instruments Nova 4000e or on a Quantachrome Instruments Quadrasorb SI. Water physisorption measurements were done using a Quantachrome Hydrosorb 1000. Prior to measurements the samples were degassed at 150 °C for at least 12 h.

Liquid NMR spectra were recorded on a Bruker DRX 500 P (<sup>1</sup>H at 500.13 MHz, <sup>13</sup>C at 125.76 MHz). The spectra were referenced against the deuterated solvent. Solid state <sup>15</sup>N CP-MAS spectra were recorded on a Bruker Ascend 800 spectrometer at a magnetic field of 18.8 T, with <sup>15</sup>N resonance frequency of 81.11 MHz and a <sup>1</sup>H

resonance frequency of 800.13 MHz. A 3.2 mm probe head was used. All measurements were carried out at a MAS rotation frequency of 12 kHz and at 298 K (<sup>1</sup>H–<sup>15</sup>N contact time: 2 ms). The spectra were referenced to the ammonium signal of <sup>15</sup>NH<sub>4</sub><sup>15</sup>NO<sub>3</sub> (358.5 ppm<sup>23</sup>). Solid state <sup>13</sup>C MAS spectra were recorded on a Bruker Avance 400, with <sup>13</sup>C resonance frequency of 100.61 MHz and a <sup>1</sup>H resonance frequency of 400.13 MHz. For <sup>13</sup>C HPDEC MAS spectra a 7 mm probe head was used. The measurements were done at a MAS rotation frequency of 5 kHz and at 298 K. <sup>13</sup>C CP MAS spectra were recorded using a 4 mm probe head. All measurements were done at a MAS rotation frequency of 10 kHz and at 298 K. The <sup>13</sup>C MAS spectra were referenced to adamantane. For electron paramagnetic resonance (EPR) measurements, the samples were transferred into EPR quartz tubes. EPR spectra were recorded with an X-band ( $\nu_{mw}$  9.475 GHz) Bruker Elexys E580 spectrometer at 298 K. FT-IR spectra were recorded on a Bruker Vertex 70 in the range from 4000 to 400 cm<sup>−1</sup> (resolution 2 cm<sup>−1</sup>, KBr). Elemental analyses were performed on a Hekatech EA 3000 Euro Vector CHNS. TG-DTA was carried out using a STA 409 (Netzsch) from room temperature to 800 °C (heating rate of 5 K/min under synthetic air). For TG-MS analysis a STA 409 PC Luxx (Netzsch) was coupled with a QMS 403C Aeolos (Netzsch). Scanning electron microscopy (SEM) was performed using a ZEISS DSM-982 Gemini.

**Polymerization.** The cyclotrimerization was performed based on a literature procedure.<sup>4</sup> In a typical reaction for OFC-1 5.924 g (30.5 mmol, 5 equiv) *p*-toluenesulfonic acid and 1.00 g (6.1 mmol, 1 equiv) 1,4-diacetylbenzene were mixed and transferred to a glass vial. This vial was evacuated and refilled three times with argon prior to heating to 120 °C for 24 h in a drying oven (heating ramp: 100 K/h). After cooling to room temperature the vial was destroyed. Soxhlet extraction with ethanol for 24 h gave the polymer as a red solid. Yield: 770 mg.

In other syntheses, the same reaction scheme was followed, but instead of 1,4-diacetylbenzene, 4,4'-diacetylbi-phenyl or a mixture of



**Figure 2.** IR spectra of OFC-1 (gray) and DUT-92 family (a) OFC-1 (gray) and DUT-93 family (b).

both monomers was used, with a molar ratio between acid and functional groups of 2.5 to 1.

The synthesis of the functionalized DUTs is described in the following: For the preparation of DUT-92( $\text{NO}_2$ ), 66.8 mg (0.41 mmol) 1,4-diacetylbenzene, 65.8 mg (0.20 mmol) 2,2'-dinitro-4,4'-diacetyl biphenyl (**1**), and 582.5 mg (3.00 mmol) *p*-toluenesulfonic acid were mixed and transferred to a glass vial. The vial was evacuated and refilled three times with argon prior to heating to 120 °C for 24 h in a drying oven (heating ramp: 100 K/h). After cooling to room temperature, the vial was destroyed. Soxhlet extraction with ethanol for 24 h gave the polymer as a black solid. Yield: 110 mg.

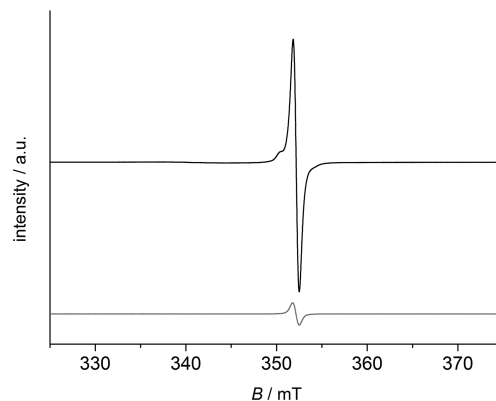
## RESULTS AND DISCUSSION

The different porous polymers reported herein were prepared by aldol condensation of diacetyl aromatic compounds. As catalyst and solvent, molten *p*-toluenesulfonic acid at 120 °C under inert atmosphere was used.<sup>4</sup> For this kind of polymerization it is crucial for the monomer to dissolve in the melt without decomposition but not necessarily to melt. Hence, monomers with melting points above 120 °C can be used, such as 4,4'-diacetyl biphenyl (DABP, melting point: 191 °C<sup>24</sup>).

After polymerization the *p*-toluenesulfonic acid could be removed by Soxhlet extraction yielding porous monoliths. The amine-functionalized polymers still contain *p*-toluenesulfonic acid even after extraction with ethanol for 48 h.

**Structural Investigations.** IR measurements confirm the successful (co)polymerization. The characteristic out-of-plane bending vibrations of 1,3,5-trisubstituted benzene rings at approximately 880  $\text{cm}^{-1}$  are present in all samples (Figure 2). By comparing the IR spectra of the monomers and the polymers, the vibration at around 1510  $\text{cm}^{-1}$  can be attributed to a vibration of the DAB unit whereas the vibration at 1500  $\text{cm}^{-1}$  could be attributed to the trisubstituted benzene ring.<sup>25,26</sup> The shift of the band at 1510 to 1500  $\text{cm}^{-1}$  and from 1015 to 1000  $\text{cm}^{-1}$  indicates the copolymerization. This is further confirmed by a shift of the out-of-plane bending frequency at 825  $\text{cm}^{-1}$  to lower wavenumbers by increasing the amount of DABP and thus the number of *para* connected benzene rings. In the case of the nitro-functionalized monomer the characteristic vibrations of the nitro groups at 1530 and 1350  $\text{cm}^{-1}$ —the asymmetric and symmetric stretching vibration, respectively—prove the copolymerization.<sup>13</sup> In all reported polymers, some carbonyl groups (1690  $\text{cm}^{-1}$ ) remain, as it has been reported for OFC-1.<sup>4</sup> They can be attributed to terminal acetyl groups and to the dimerization product of two acetyl groups forming an  $\alpha,\beta$ -unsaturated carbonyl compound.

The attempt to determine the degree of conversion of the carbonyl groups using HPDEC excitation  $^{13}\text{C}$  solid state MAS spectroscopy failed; the spectrum consists of an intense, but unusually broad, signal (Figure S1). This broad signal is supposed to be caused by unpaired electrons. Using EPR spectroscopy, it was possible to quantify the amount of radicals varying between  $1.72 \times 10^{16}$  and  $6.40 \times 10^{17}$  spins/g for OFC-1 and DUT-92( $\text{NO}_2$ ), respectively (Figure 3).<sup>27</sup> The higher



**Figure 3.** Quantitative EPR spectra at 298 K of DUT-92( $\text{NO}_2$ ) (black) and OFC-1 (gray).

radical content in DUT-92( $\text{NO}_2$ ) might be due to additional resonance structures including the nitro groups. One reason for the presence of unpaired electrons might be a partial decomposition during synthesis. However, this would lead to isolated radicals which are not stabilized over an aromatic system as is the case for our system.

A thermally induced [2 + 2] cycloaddition is a more reliable explanation (Figure S2). This cycloaddition, which is normally forbidden in the ground state, can be catalyzed among others by Lewis acids.<sup>28</sup> As molten *p*-toluenesulfonic acid is a relatively strong Lewis acid it might catalyze the reaction. Moreover, the reaction mechanism of the cyclotrimerization of acetylbenzene is postulated to occur by a transition state in the enolate form. This enolate form could also take part in the [2 + 2] cycloaddition.

Elemental analyses reveal only small differences between theoretical and experimentally determined composition (Table 1). These differences can be explained by two facts: First, the theoretical values are calculated for a hypothetical fully

Table 1. Theoretical (Calculated Assuming Complete Conversion) and Experimental (CHNS) Composition of the Polymers

	theoretical				experimental				
	C	H	N	O	C	H	N	O	S
OFC-1	95.21	4.79			82.25	5.23	0.00	12.52	
DUT-92	95.12	4.88			88.05	4.96	0.00	6.99	
DUT-92(NO <sub>2</sub> )	79.40	3.70	5.14	11.75	75.53	3.98	4.38	16.11	
DUT-92(NH <sub>2</sub> )	89.23	4.99	5.78		77.73	5.08	3.78	11.82	1.56
DUT-93	95.02	4.98			88.28	5.13	0.00	6.59	
DUT-93(NO <sub>2</sub> )	65.76	2.76	9.59	21.90	63.36	3.12	8.87	24.65	
DUT-93(NH <sub>2</sub> )	82.73	5.21	12.06		66.14	4.97	6.58	17.04	5.28

condensed polymer, and second, the polymer adsorbs water as detected by TG and water physisorption experiments. For DUT-92(NO<sub>2</sub>) and DUT-92(NH<sub>2</sub>) a third reason might be that DAB is preferentially incorporated in the polymeric network, decreasing the nitrogen to carbon ratio. In the case of DUT-93(NO<sub>2</sub>) this difference is much lower. Even after Soxhlet extraction for 48 h with ethanol or after additional alkaline treatment in the amine-containing porous polymers, some *p*-toluenesulfonic acid remains, as can be seen from the CHNS analysis (Table 1).

**Thermal Stability.** The introduction of additional functional groups affects the thermal stability. The decomposition of the nitro-functionalized porous polymers began at about 300 °C, whereas the nonfunctionalized and amine-functionalized porous polymers are stable up to approximately 350 °C (Figure 4 and Figure S3). The lower thermal stability is related to the

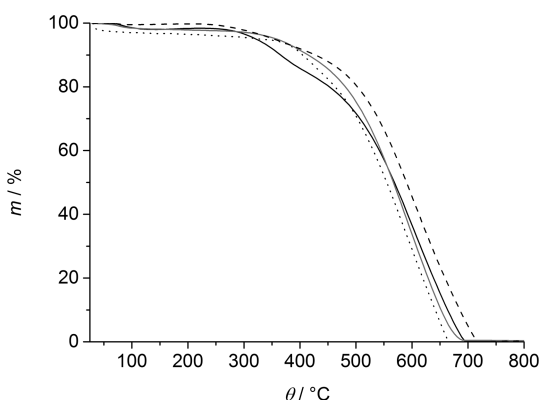


Figure 4. TG curve of OFC-1 (dotted line), DUT-92 (dashed), DUT-92(NO<sub>2</sub>) (solid line, black), and DUT-92(NH<sub>2</sub>) (gray) under synthetic air.

combustion or decomposition of the nitro-functionalized aromatic moieties. It is known from literature that nitro aromatic compounds start to decompose above 200 °C.<sup>29</sup> Wirth et al. reported that nitro-substituted *p*-polyphenylene decomposes above 250 °C.<sup>30</sup> In the TG-MS spectra the overall maximum for the quasi-multiple ion detection (QMID) signal of nitrogen monoxide is at around 350 °C (Figure S4). For carbon dioxide and water, the other products of the combustion of the porous polymer, only shoulders can be detected at this temperature. The corresponding maxima of intensity lie above 570 and 670 °C for water and carbon dioxide, respectively. The weight loss below 200 °C is due to desorption of water. In the MS spectra of DUT-92(NO<sub>2</sub>) mainly water is detected at about 100 °C (Figure S4).

**Physisorption.** All materials show the typical swelling behavior of a nonrigid porous polymer. The nonfunctionalized

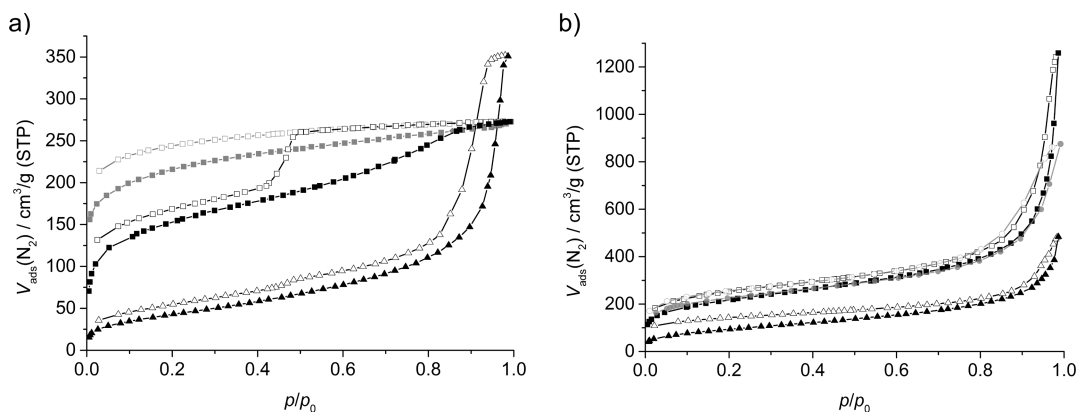
polymers OFC-1, DUT-92, and DUT-93 can be classified as a mixture of type I and type II isotherms according to IUPAC classification (Figure 5b).<sup>31</sup> As the content of DABP increases, the system becomes more flexible, and in addition partial interpenetration of the networks might occur, resulting in a reduced specific surface area of 320 m<sup>2</sup>/g for DUT-93 (Table 2).

As can be seen from the nitrogen physisorption isotherm at 77 K, the surface areas of DUT-92(NO<sub>2</sub>) and DUT-93(NO<sub>2</sub>) are lower than those of the corresponding nonfunctionalized porous polymers DUT-92 and DUT-93 (Figure 5). In addition the partial replacement of DABP by DABP-(NO<sub>2</sub>)<sub>2</sub> leads to a meso- and microporous material in the case of DUT-92(NO<sub>2</sub>). The nitrogen physisorption isotherm shows a type IV/H4 isotherm behavior without any large meso- and macropores.<sup>31</sup> A specific surface area of 500 m<sup>2</sup>/g and a total pore volume up to 0.45 cm<sup>3</sup>/g were achieved. The sharp step in the desorption branch at partial pressures between 0.4 and 0.5 is most likely caused by cavitation inside the porous polymeric framework. This shows that at least a part of the mesopores is only accessible through micropores.<sup>32,33</sup> In contrast, DUT-92(NH<sub>2</sub>) can be classified as a type I isotherm with a specific surface area of 700 m<sup>2</sup>/g.<sup>31</sup>

By completely replacing DAB and DABP with DABP-(NO<sub>2</sub>)<sub>2</sub>, the amount of micro- and mesopores is dramatically reduced. Consequently, the specific surface area is reduced to 170 m<sup>2</sup>/g. Because of the higher amount of large meso- and macropores, the total pore volume remains nearly constant with approximately 0.50 cm<sup>3</sup>/g.

Cooper and co-workers also reported a change in the isotherm type for a series of conjugated microporous polymers, but they related this effect to the use of different solvents or different reactivity of the brominated compared to the iodated monomer.<sup>17,18</sup> They showed that different solvents, e.g. dioxane or toluene, result in different polymerization degrees leading to different pore systems. In our case, the solvent is the same for all presented polymers. The differences thus have to be related to the functional groups of the monomers. When DAB and/or DABP are used, no additional interaction between *p*-toluenesulfonic acid as solvent and the monomers occurs apart from the interaction through the acetyl group. Compared to DAB and DABP, DABP-(NO<sub>2</sub>)<sub>2</sub> and DABP-(NH<sub>2</sub>)<sub>2</sub> can also interact with the solvent through the nitro or amine groups. The first one can interact through dipole or hydrogen bond interactions, whereas the latter one can form ionic bonds. Solid state <sup>15</sup>N MAS NMR spectra of DUT-92(NH<sub>2</sub>) before and after the removal of *p*-toluenesulfonic acid show a difference in the shift of the amino groups (Figure 6 and Figure S5). In the spectra of the nonpurified DUT-92(NH<sub>2</sub>), a shift of −331 ppm indicates the complete protonation of the amino groups, yielding ammonium groups. After Soxhlet extraction, the signal



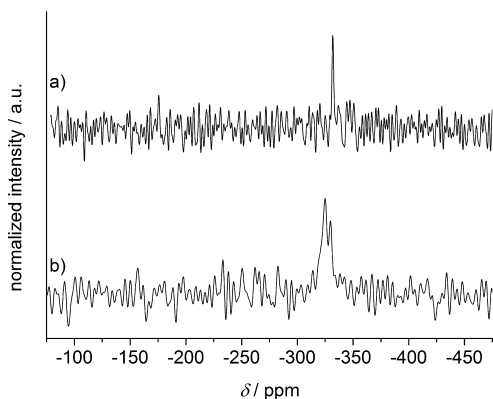


**Figure 5.** (a) Nitrogen physisorption isotherms (77 K) of DUT-92(NO<sub>2</sub>) (square, black), DUT-93(NO<sub>2</sub>) (triangle, black), and DUT-92(NH<sub>2</sub>) (square, gray). (b) Nitrogen physisorption isotherms of OFC-1 (circle, gray), DUT-92 (square), and DUT-93 (triangle). Adsorption points are symbolized by filled symbols and desorption points by unfilled symbols.

**Table 2.** BET Surface Areas as Well as Pore Volumes of the Synthesized Polymers

	BET <sup>a</sup> (m <sup>2</sup> /g)	V <sub>N<sub>2</sub></sub> <sup>b</sup> (cm <sup>3</sup> /g)	V <sub>N<sub>2</sub></sub> <sup>c</sup> (cm <sup>3</sup> /g)	V <sub>H<sub>2</sub>O</sub> <sup>b</sup> (cm <sup>3</sup> /g)	Ξ/1 <sup>d</sup>	n <sub>CO<sub>2</sub></sub> <sup>e</sup> (mmol/g)
OFC-1	780 ± 30	1.06 ± 0.09	1.54 ± 0.27	0.19 ± 0.03	0.12	0.87
DUT-92	720 ± 20	1.14 ± 0.10	1.76 ± 0.19	0.12 ± 0.03	0.07	1.11
DUT-92(NO <sub>2</sub> )	500 ± 20	0.44 ± 0.03	0.44 ± 0.03	0.29 ± 0.04	0.67	0.87
DUT-92(NH <sub>2</sub> )	700 ± 10	0.42 ± 0.04	0.42 ± 0.05	0.29 ± 0.01	0.69	1.67
DUT-93	320 ± 20	0.49 ± 0.08	1.02 ± 0.32	0.03 ± 0.02	0.04	0.88
DUT-93(NO <sub>2</sub> )	160 ± 10	0.42 ± 0.06	0.50 ± 0.05	0.17 ± 0.07	0.34	0.84
DUT-93(NH <sub>2</sub> )	nonporous	nonporous	nonporous	0.20 ± 0.01		1.66

<sup>a</sup>Determined at  $p/p_0 = 0.3$ . <sup>b</sup>Determined at  $p/p_0 = 0.97$ . <sup>c</sup>Determined at  $p/p_0 = 0.99$ . <sup>d</sup>Degree of pore filling:  $\Xi = V_{N_2}/V_{H_2O}$ . <sup>e</sup>Determined at  $p = 760$  mmHg. All values given are mean values determined by at least two independent measurements except for CO<sub>2</sub> physisorption measurements.



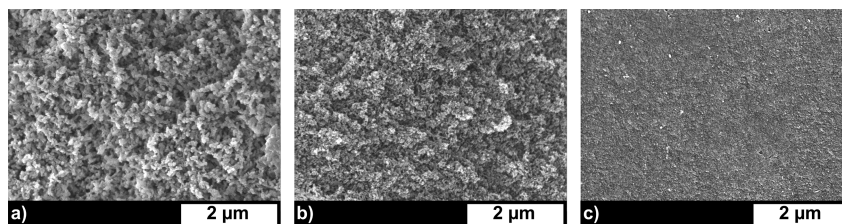
**Figure 6.** <sup>15</sup>N CP MAS spectra of (a) crude DUT-92(NH<sub>2</sub>) (60 000 scans) and (b) purified DUT-92(NH<sub>2</sub>) (60 000 scans).

becomes much broader and is split into two signals, at −324 ppm, corresponding now to an amine group, and at −330 ppm, corresponding to the remaining ammonium groups.<sup>34</sup> The

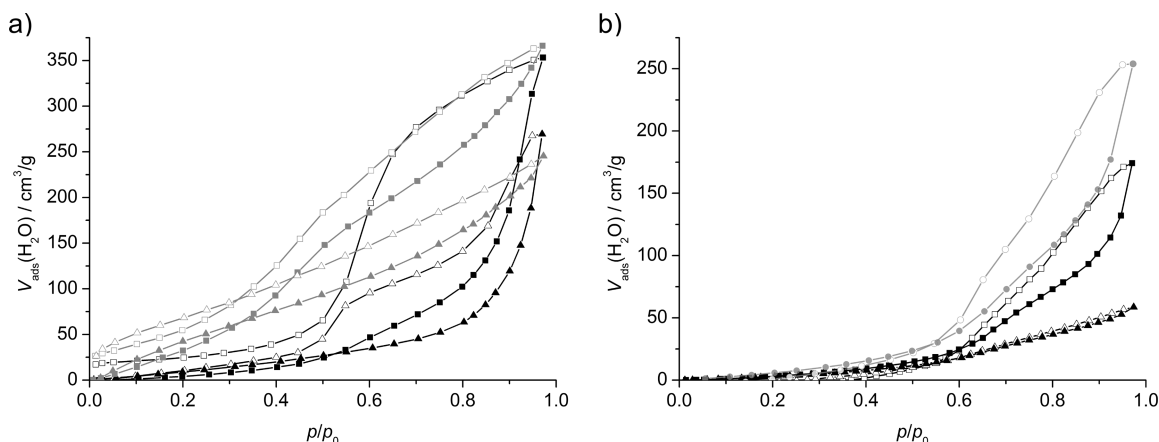
broader line width might be a hint for a higher number of possible conformations of the amino group and thus a higher flexibility. Probably, there are also some ammonium groups formed by ionic interaction with *p*-toluenesulfonic acid. This is supported by the fact that there is still some sulfur in the polymeric network after work-up as has been shown by elemental analysis (Table 1).

As all amino groups are protonated during synthesis, the formed oligomers and short polymers should be better soluble in molten *p*-toluenesulfonic acid through ion pair formation. These ion pairs are built up by interaction of ammonium and *p*-toluenesulfonic acid anions. As a consequence during synthesis there is less macrophase separation. Such a macrophase separation would lead to larger meso- or even macropores.

This lets us conclude that the interaction between solvent and monomer is crucial for the pore formation. The better the monomer–solvent and especially the polymer–solvent interaction is, the less macrophase separation occurs. This is further confirmed by SEM images (Figure 7 and Figure S6). The nonfunctionalized polymers have the highest amount of



**Figure 7.** SEM images of DUT-93 (a), DUT-93(NO<sub>2</sub>) (b), and DUT-93(NH<sub>2</sub>) (c); 20 000-fold magnification.



**Figure 8.** (a) Water vapor physisorption isotherms at 298 K of DUT-92-NO<sub>2</sub> (square, black), DUT-93-NO<sub>2</sub> (triangle, black), DUT-92-NH<sub>2</sub> (square, gray), and DUT-93-NH<sub>2</sub> (triangle, gray). (b) Water vapor physisorption isotherms at 298 K for OFC-1 (circle, gray), DUT-92 (square), and DUT-93 (triangle).

interparticular space, which is a clear hint for macrophase separation during polymerization. For the nitro-functionalized polymers the particles are denser packed, and thus the interparticular space is reduced. In contrast, the amine-functionalized polymers shows hardly any space in between the polymer particles even at higher magnification (Figure S7). Hence, the particle size is reduced, too.

Using water vapor physisorption experiments, we were able to show that the porous polymers became more hydrophilic by incorporation of polar groups. In the case of DUT-92(NH<sub>2</sub>) and DUT-93(NH<sub>2</sub>), the water uptake already starts at very low partial pressures below 0.1, pointed out by a considerable initial slope (Figure 8 and Figure S8). This indicates a more polar surface due to the amine groups.<sup>35,36</sup> In contrast, the nitro functionalization did not result in an earlier water uptake compared to the unfunctionalized polymers. But the slope of the adsorption branch below  $p/p_0 = 0.2$  is higher with respect to the unfunctionalized polymer, indicating a slightly polar surface. This can also be seen in the TG trace as the mass loss due to water desorption occurs at higher temperatures (Figure 4 and Figure S3). Also, the degree of pore filling increases from 12% for DUT-92 to approximately 70% for DUT-92(NO<sub>2</sub>) and DUT-92(NH<sub>2</sub>) (Table 2). These values were calculated using the pore volumes at relative pressures of 0.95 determined by nitrogen physisorption at 78 K and water vapor physisorption at 298 K. For nonfunctionalized and nitro-functionalized polymers, the isotherm can be characterized as type III isotherm (Figure 8).<sup>4</sup>

An increased content of biphenyl moieties from OFC-1 to DUT-93 results in a lower water uptake and thus in a higher hydrophobicity. In addition, the surface area decreases, too, which lowers the water uptake above  $p/p_0 = 0.5$ . Taking this into account, the difference in hydrophilicity between the two nitro-functionalized polymers could be explained by the more hydrophobic nature of the biphenyl backbone of DABP-(NO<sub>2</sub>)<sub>2</sub> and the lower surface area (Table 2). These two effects cannot be counterbalanced by the increased numbers of hydrophilic nitro groups.

To prove the porosity of DUT-93(NH<sub>2</sub>), CO<sub>2</sub> physisorption experiments were carried out at 25 °C (Figure S9). Indeed, DUT-93(NH<sub>2</sub>) shows a CO<sub>2</sub> uptake at 25 °C of 1.66 mmol/g, which is approximately twice as high as the uptake of DUT-93 and DUT-93(NO<sub>2</sub>). Also, DUT-92(NH<sub>2</sub>) has the highest CO<sub>2</sub>

uptake in the DUT-92 family (Table 2). The increase in CO<sub>2</sub> uptake within a family of porous polymers is in good agreement with published data for pure amine-functionalized polymers.<sup>15</sup> Compared to oligoamine-tethered PPNs, the increase reported here is much lower due to the lower number of nitrogen atoms.<sup>14</sup>

## CONCLUSION

In summary, the strategy of using functionalized monomers in synthesis instead of a postsynthetic modification has several advantages. Most important we were able to show that by changing the molar ratio of different monomers or the functionalization of the monomers, not only the pore surface but also the pore geometry is controllable. Therefore, the polymer can be tuned toward an optimization in target molecule uptake, based on a well-defined pore system. Moreover, we have shown that the shape of the pores is strongly influenced by the interaction between monomers/polymer and solvent. A stronger interaction leads to a better solubility and therefore avoids the macrophase separation of polymer and solvent leading to (large) meso- and/or macropores. In addition, the degree of functionalization is more homogeneous compared to postsynthetic modification.

## ASSOCIATED CONTENT

### Supporting Information

Synthesis procedures as well as NMR spectra, TG traces, SEM images, and water vapor and carbon dioxide physisorption isotherms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors are grateful to Dr. I. Kunert and M. Welz for thermal analyses. This work was partially funded by the European Social Fund (ESF) and the Free State of Saxony (Project No. 080940507).

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