

# Template-Free Tuning of Nanopores in Carbonaceous Polymers through Ionothermal Synthesis

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The synthesis of micro- and mesoporous organic materials with well-defined pore size and structure is currently a major challenge in materials science. Because of their purely organic nature, such systems are expected to introduce new opportunities that expand on those of their well-known inorganic analogues.<sup>[1]</sup> Since the pioneering work on polystyrene-derived resins, macroporous polymers (pore diameter >50 nm) became a well-established family of porous materials.<sup>[2]</sup> Here, the porosity arises mainly from microphase separation during the polymerization reaction.<sup>[3]</sup> On the other hand, studies on hyper-crosslinked polystyrene networks further confirmed that it is also possible to generate microporous (pore diameter <2 nm) organic materials with high surface area.<sup>[4]</sup> Owing to several recent studies, these findings were extended to different type of polymers, from polymers with intrinsic microporosity to covalent organic frameworks.<sup>[5–12]</sup>

It is, however, much more difficult to design mesoporous organic materials (i.e., with pores in the range of 2–50 nm). Generally, mesoporous materials such as silica are synthesized through a soft templating approach,<sup>[13–17]</sup> whereas carbons or polymer networks usually require the use of silica-based hard templates,<sup>[1,18–20]</sup> but some reports with a soft templating approach were recently reported as well.<sup>[21–23]</sup> Although this methodology led to interesting materials, it is practically a “no-go” for industrial applications because of its complexity and high cost. Therefore, a template-free preparation of mesoporous organic materials is still highly desired.

Recently, we have shown that high-temperature ionothermal polymerization of simple aromatic nitriles, such as terephthalonitrile, can be used to produce carbonaceous polymer networks with well-defined bimodal micro- and mesoporosity.<sup>[24]</sup> Thus, highly porous materials could be obtained (surface area up to 3 000 m<sup>2</sup> g<sup>-1</sup>) containing 4–5 nm mesopores beside the generic, scaffolded 1.5 nm micropores. The dynamic self-organized formation of the mesopores leads to a quite narrow mesopore distribution, but the size of the mesopores could not be tuned. It is the purpose of the present Communication to show that the ionothermal polymerization of cyanobiphenyl monomers in an extended condition range allows a more flexible tuning of the

mesopore size in carbonaceous polymers from 5 to >20 nm as a function of the reaction conditions. Thus, organic materials with tuneable mesoporosity can be prepared through a direct, template-free approach.

As previously reported,<sup>[8]</sup> the polymerization of dicyanobiphenyl in an excess of ZnCl<sub>2</sub> (10 equiv.) at 400 °C for 40 h produces an amorphous material with high surface area and porosity. From its nitrogen sorption isotherm, it was found that mesopores are formed at higher reaction temperatures (600 °C) in addition to the micropores found as an exclusive event at standard conditions. A study of the influence of the experimental conditions for the DCBP (Scheme 1) monomer to understand and adjust mesopore formation is therefore presented here.

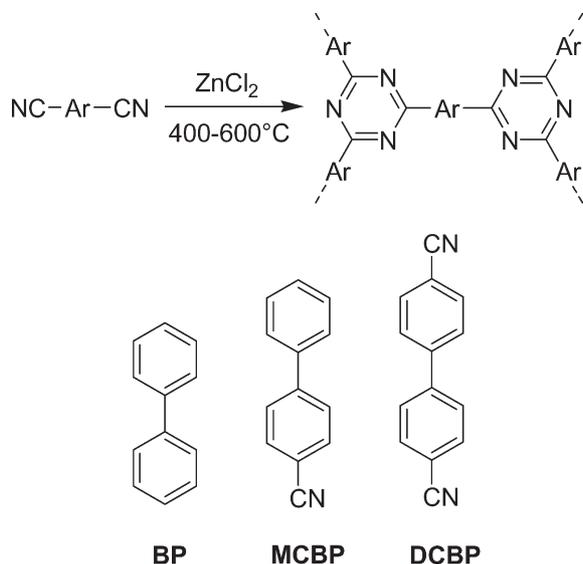
First, the influence of the salt/monomer ratio was investigated under standard conditions at 400 °C. As seen from the nitrogen adsorption-desorption isotherms and the corresponding non-local-density functional theory (NL-DFT) pore-size distributions (see Supporting Information Fig. S1a and S1b), an increasing salt content induces a gain of “super-micropores” (i.e. of the order of 2 nm in size), but the variations are comparably small. The corresponding numerical data are summarized in Table 1. The results show that the mesoporosity is only significant when an excess of the salt is used (ca. >10 equiv.), yet the mesopore size distribution is broad. In turn, the appearance of mesoporosity in addition to microporosity induces a growth of the surface area from 1 150 to 1 710 m<sup>2</sup> g<sup>-1</sup>. These values are, however, lower than the one previously reported.<sup>[8]</sup> We attribute this to the influence of the heating rate and of the heating device that is used. Comparative experiments were thus carried out to substantiate this influence (Table 1, entry 3 and 6). The data clearly show that a fast heating (without heating rate) to 400 °C enables higher surface areas. Therefore, all experiments were carried out using a 1 h heating time to the desired temperature, as no further changes were found for longer times.

As previously found for the polymerization of 1,4-dicyanobenzene,<sup>[8]</sup> also for DCBP, higher reaction temperatures generate mesoporosity in addition to microporosity. The DCBP monomer features, however, more flexibility, as a strong influence of the monomer concentration on the mesopore size was found at 600 °C. The shape of the nitrogen adsorption-desorption isotherms (Fig. 1a) completely changes from 2 to 20 equivalents of salt, clearly reflecting an extreme increase of the size of the mesopores.

Whereas a type I isotherm (characteristic for a purely microporous material) is found for 2 equivalents, type IV isotherms are observed when higher amounts of salt are used. An H<sub>2</sub> hysteresis loop is observed until 10 equivalents, evolving to a

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**Scheme 1.** Schematic representation of the formation of polytriazines from aromatic nitriles and monomers used in this study.

H<sub>3</sub>-type hysteresis for higher amounts of salt. Whereas the mesoporous contribution stays relatively small for 2 equivalents, a significant population of mesopores centred at ca. 6 nm diameter appears for 5 equivalents (Fig. 1b and 1c). At 10 equivalents, the maximum of the pore size distribution is displaced to ca. 20 nm. Finally, super-mesopores are produced for 15 and 20 equivalents, for which the size distribution is difficult to characterize by nitrogen sorption. The values of the surface area are almost identical to the one from the samples prepared at 400 °C. In turn, the total pore volume is increasing, reaching values up to 4.5 cm<sup>3</sup> g<sup>-1</sup>. It can also be seen that the microporous contribution is smaller, indicating that at 600 °C mesopores are formed at the

cost of micropores, which even induces a lowered surface area for high amounts of salt.

The formation of the mesopores can be directly related to a change of the scaffolded covalent structure, as at high temperatures carbonisation reactions, i.e., C–C bond formations between the aromatic rings, can occur. Moreover, a biphenyl moiety can behave as a diene and undergo cycloaddition reactions.<sup>[25]</sup> This reaction pathway leads to modification of the chemical nature of the polymers towards more extended, stiff aromatic systems. This is in agreement with the formation of larger pores, which rely on stiff subunits to open up the pores against capillary pressure and collapse.

Elemental analysis (see Experimental section, Table 2) showed a characteristic depletion of the nitrogen content with increasing temperature and amount of salt. As already reported, energy dispersed X-ray (EDX) analysis revealed that aqueous work-up efficiently removes all of the salt (see Supporting Information Fig. S4). At 600 °C, also a significant diminution of the hydrogen content is observed. A striking feature is that the amount of residual mass (that is not burned in elemental analysis and analyzed) decreases with a decrease in the amount of nitrogen, indicating that the residual mass results from the resistance against oxidation of the nitrogen-rich material.

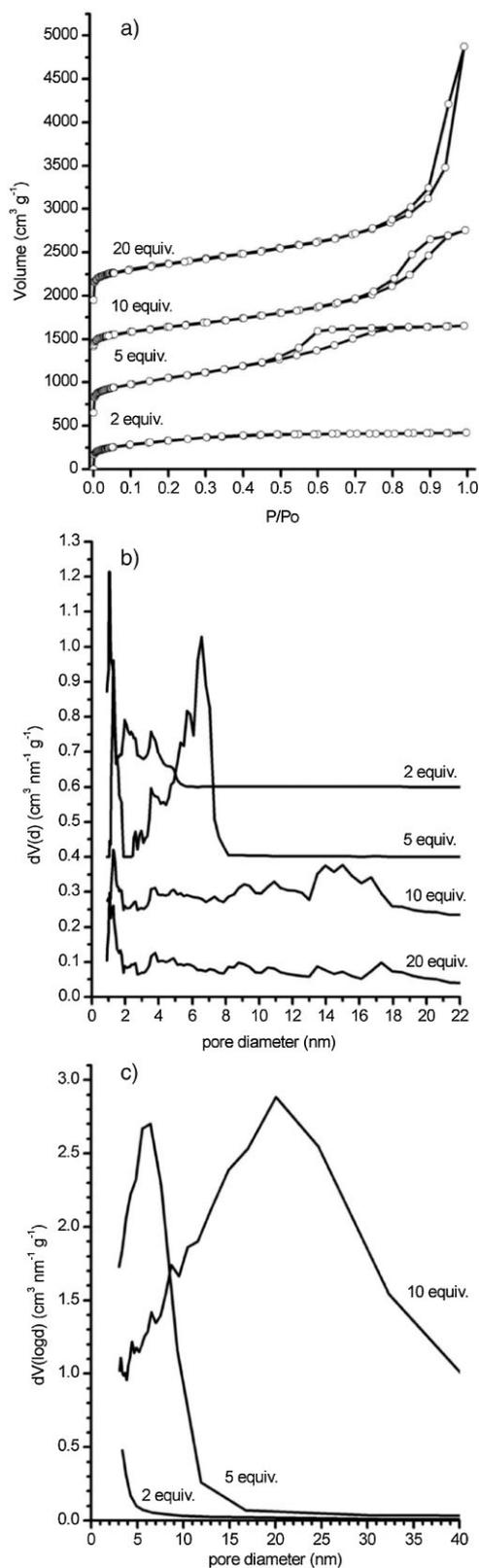
Overpressure in the reaction flask was detected for almost every experiment. This can be explained by the formation of high amounts of hydrogen as a result of C–C coupling reactions. These reactions may follow a different mechanism, involving radicals, metal-mediated C–H bond activation, or Diels-Alder/aromatization reactions (Scheme 2).<sup>[25]</sup> Note that the Diels-Alder reactions are catalyzed by Lewis acids.<sup>[26]</sup>

The reactivity of a monofunctional monomer was investigated to obtain evidence of this additional reaction channel, which at high temperatures results in a shift of the structural features from a polyaryltriazine polymer to a carbonaceous polymer network. Thereto, experiments were carried out with 4-cyanobiphenyl and

**Table 1.** Porous characteristics of the materials prepared from DCBP at different temperatures and concentrations.

Entry	Temperature [°C]	ZnCl <sub>2</sub> [mol. equiv.]	S <sub>BET</sub> [m <sup>2</sup> g <sup>-1</sup> ]	S <sub>BET</sub> [e] (micro) [m <sup>2</sup> g <sup>-1</sup> ]	Total Pore Volume <sup>[f]</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	Microporous Volume <sup>[e]</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	Average Pore Diameter [nm]
1[a]	400	2	1 150	840	0.57	0.4	2
2[a]	400	5	1 140	730	0.64	0.37	2.2
3[a]	400	10	1 710	705	1.2	0.42	2.8
4[a] (MCBP)	400	10	1 130	420	1.5	0.24	5.3
5[a]	400	20	710	490	0.4	0.24	2.2
6[d]	400	10	2 120	790	1.7	0.51	3.3
7[b]	600	2	1 170	600	0.65	0.31	2.2
8[b]	600	5	1 400	290	1.55	0.2	4.4
9[b]	600	10	1 240	235	2.25	0.14	7.2
10[b] (MCBP)	600	10	675	285	1.67	0.14	10.0
11[b] (BP)	600	10	0	–	0	–	–
12[b]	600	15	1 260	340	2.76	0.19	8.8
13[b]	600	20	1 510	340	4.5	0.2	12.1
14[c]	400/600	5	1 630	400	1.29	0.22	3.2
15[c]	400/600	10	1 625	200	2.42	0.15	6.3
16[c]	400/600	20	1 430	205	2.96	0.14	8.3

[a] 25 to 400 °C in 1 h then 400 °C during 40 h. [b] 25 to 600 °C in 1 h, then at 600 °C during 20 h. [c] 25 to 400 °C in 1 h, then at 400 °C for 20 h, 400 to 600 °C in 1 h, then at 600 °C for 1 h. [d] Fast heating to 400 °C. [e] determined by NL-DFT. [f] at P/P<sub>0</sub> = 0.99.

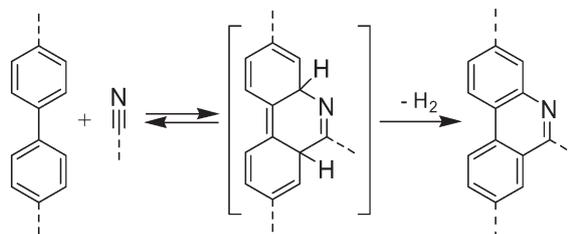


**Figure 1.** a) Nitrogen sorption isotherms (ordinate offset  $350 \text{ cm}^3 \text{ g}^{-1}$ ). b) NL-DFT pore size distributions (ordinate offset  $0.2 \text{ cm}^3 \text{ nm}^{-1} \text{ g}^{-1}$ ) and BJH pore size distribution for the materials obtained from different concentrations of DCBP. (Conditions:  $600^\circ\text{C}$ , 20h)

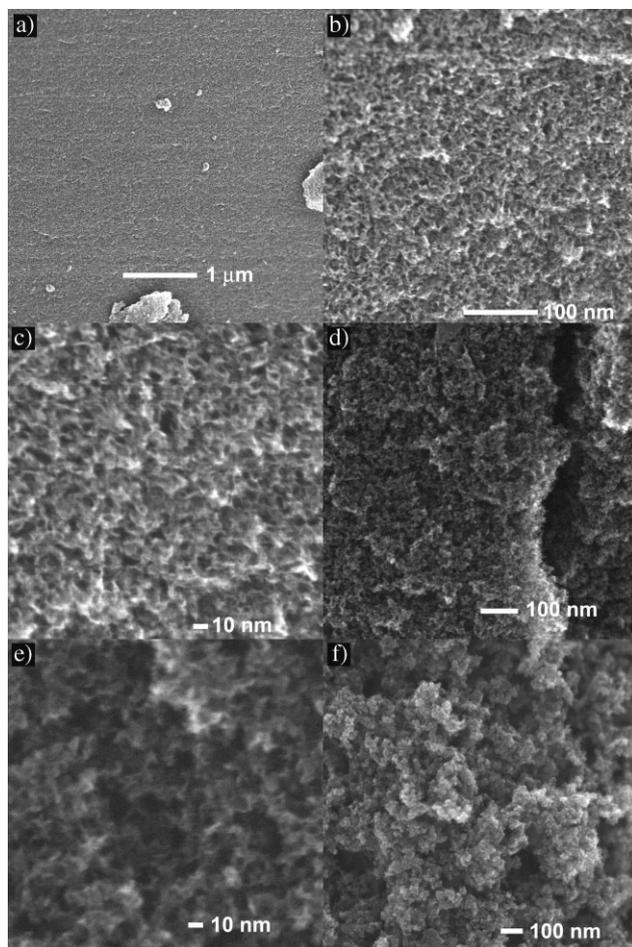
**Table 2.** Combustion elemental analysis.

Temperature ( $^\circ\text{C}$ )	Equivalents of $\text{ZnCl}_2$	C	N	H	C/N	C/H	Resid.
400	2	70.8	8.36	3.46	9.9	1.7	17.4
400	5	67.5	7.08	2.91	11.1	1.9	22.5
400	10	79.0	6.21	3.00	14.9	2.2	12.8
400	10direct	84.2	5.41	2.18	18.2	3.2	8.2
400	10mono	84.2	3.33	3.33	29.5	2.1	9.1
400	20	79.0	5.98	3.03	15.4	2.2	12.0
600	2	72.4	5.90	1.53	14.3	3.9	20.2
600	5	75.5	4.98	1.49	17.7	4.2	18
600	10	83.6	5.21	1.6	18.8	4.3	9.5
600	10 mono	87.8	2.24	1.54	45.7	4.7	8.4
600	15	83.9	4.77	1.4	20.5	5.0	9.9
600	20	89.9	3.56	1.32	29.5	5.7	5.2
400/600	5	84.6	3.35	1.28	29.5	5.5	10.8
400/600	10	85.0	3.58	1.22	27.7	5.8	10.2
400/600	20	85.4	4.27	1.40	23.3	5.1	9.0
Calc. $\text{C}_{14}\text{H}_8\text{N}_2$	/	82.3	13.72	3.95	7	1.5	/

with 1,1'-biphenyl as reference-monomer sources. With biphenyl, only a very low conversion was observed at  $400^\circ\text{C}$  (ca. 10%) into black amorphous, nonporous carbon. At  $600^\circ\text{C}$ , full conversion was observed, but the polymerization system was not homogeneous (total phase separation) and resulted in a nonporous material. Under these reaction conditions, the pure 4-cyanobiphenyl leads to cross-linked, porous materials, which are less perfect and also exhibit a lower surface area. In this case, the crude reaction mixture is obtained as a foam instead of a monolith. It must be underlined that simple trimerization towards the triazine would here only result in a soluble low-molecular-weight product, while only rather complete secondary reactions involving the biphenyl-system can explain the presence of a black, fully condensed carbonaceous material. In the case of 4-cyanobiphenyl, a huge amount of gas is produced as a side product, which was evident from the high overpressure when the ampoules are opened. Thus, the presence of the two nitrile functions is favorable, but not required. However, the presence of at least one nitrile function is necessary to obtain a homogeneous reaction mixture in the salt melt and, in turn, porosity. The formation of large pores of the "foam type" is presumably due to the onset of phase separation between the forming carbonaceous polymer and the salt phase. As phase separation should have an influence on the morphology of the materials, high-resolution scanning electron microscopy



**Scheme 2.** Schematic representation of a possible Diels-Alder reaction between a biphenyl and a nitrile.



**Figure 2.** HR-SEM pictures of the samples prepared from DCBP with 5 equivalents (a–c) and 10 equivalents (d,e) of  $\text{ZnCl}_2$  and from MCBP with 10 equivalents  $\text{ZnCl}_2$  at  $600^\circ\text{C}$  (f).

(HRSEM) investigations were carried out. Transmission electron microscopy (TEM) investigations could indeed only reveal the highly porous character of the materials (see Supporting Information, Fig. S2a and S2b).

From Figure 2a it can be seen that the materials are highly homogeneous; macroscopic heterogeneities are absent on all scales. The mesopores with sizes of up to 5 nm nicely manifest in the picture of the sample prepared from DCBP at  $600^\circ\text{C}$  with 5 equivalents of  $\text{ZnCl}_2$  as an interconnected, droplet-like porosity (Fig. 2b and 2c). The bigger 10 nm pores of the material prepared from DCBP at  $600^\circ\text{C}$  using 10 equivalents of  $\text{ZnCl}_2$  are seen in Figure 2d and 2e. Such porosity morphologies are similar to those of gels obtained from spinodal demixing<sup>[2]</sup> and favorable for transport and permeation. On the other side, the material prepared from MCBP under similar conditions shows a different morphology, that is, polymer “droplets” with an interstitial pore structure (Fig. 2f). These observations undoubtedly show that the mesoporosity is formed through phase separation, and that the variation of the affinity of the material with the salt will direct the pore morphology. A good affinity of the organic material with the salt is required, which in the present system is provided by the cyano group- and nitrogen moieties.

Further control of the pore size is exerted by carrying out the reaction in a two-step heat treatment, where the reaction mixture is first heated to  $400^\circ\text{C}$ , and then matured and reorganized by heating to  $600^\circ\text{C}$ . For DCBP this can also be applied to tune the pore size (see Supporting Information, Fig. S3a and S3b). As shown from the BJH distributions, the maximum of the pore size distribution can be lowered by this method, for example from 15 to 10 nm at 10 equivalents. This is in line with the fact that fast heating produces larger pores (see Table 1, entry 3 and 6). The surface area and porosity remain almost the same compared to the samples prepared by a single-step heat treatment.

In conclusion, a template-free synthesis of porous polymer/carbon-materials was presented, leading to nonperiodic, but well-defined mesoporosity with a broad range of pore sizes and favourable pore connectivity. The simple process of ionothermal polymerization of cheap nitriles at various temperatures allows the convenient preparation of a broad set of materials with a very homogeneous micro-, meso-, or macroporosity, where the size of the mesopores can be tuned in the range of 5 to  $>20$  nm. It was reasoned that the key feature that allows the formation of this mesoporosity is the adjustment of the phase separation between the salt phase and the organic material by its nitrogen content. The presence of a sufficient amount of nitrile functions is decisive for ensuring a good homogeneity of the reaction mixture and controlling the affinity of the organic material with the salt phase. Owing to the low cost of this process, the here presented method for generating well-defined porosity should open new opportunities for the design of nanofoams with tunable porosity, which could be applied in large-scale industrial applications, such as insulating materials, catalyst supports, or as sorption materials.

## Experimental

**Chemicals:** Zinc chloride (ABCR, anhydrous, 98%) was stored in a glove box and used as received. 4,4'-dicyanobiphenyl (DCBP), 4-cyanobiphenyl (MCBP) and biphenyl (BP) were purchased from Aldrich and used as received.

**Characterization:** Elemental analyses were obtained from a Vario El elemental analyzer. Nitrogen-sorption measurements were collected either on a Quantachrome Quadrasorb apparatus at 77K. BET surface areas were determined over a P/P0 range as described before [27]. The samples were degassed at  $200^\circ\text{C}$  for 15 h before measurement. NLDFT pore-size distributions were determined using the carbon/slit-cylindrical pore model of the Quadrawin software. A Nabertherm L3/11 oven was used as heating device. TEM was carried out on an Omega 912 (Carl Zeiss, Oberkochen, Germany). EDX spectra were measured on the TEM instrument with an EDXS spectrometer. HRSEM was performed on a JEOL JSM-7500 microscope in the high vacuum mode. The acceleration voltage was set to 15 kV.

**Synthesis of the Polytriazine Networks:** In a typical experiment, the monomer and  $\text{ZnCl}_2$  were transferred into a quartz ampoule ( $3\text{ cm} \times 12\text{ cm}$ ) under an inert atmosphere. The ampoule was evacuated, sealed, and heated to the desired temperature during 20 h. The ampoule was then cooled down to room temperature and opened. **Caution:** for temperatures higher than  $500^\circ\text{C}$ , the ampoules are under pressure, which is released during opening of the ampoule. The reaction mixture was subsequently grounded and then washed thoroughly with water to remove most of the  $\text{ZnCl}_2$ . Further stirring in diluted HCl for 15 h was carried out to remove the residual salt (total elimination of the salt residue was confirmed by EDX analysis, see Supporting Information, Fig. S4). After this

purification step, the resulting black powder was filtered, washed successively with water and THF, and dried in vacuum at 150 °C. The typical isolated yield was 80%.

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