Reassessing the Physicochemical Properties of Ordered Mesoporous Polymer and Copolymer Nanocasts

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In Memory of Prof. Dr.-Ing. Jens Weitkamp

Nanocasting is a convenient way for preparing highly porous, nanostructured soft materials. Mesoporous polymer nanocasts have been reported for over a decade, however, several aspects remain to be explored further. To do so, we report a comprehensive investigation of the physicochemical characteristics of high surface area functional organic polymers and copolymers obtained by nanocasting. Divinylbenzene, styrene and chloromethyl styrene were selectively polymerized within the pores of mesoporous SBA-15 or KIT-6 silicas. Following template removal, the resulting materials were characterized. The nanocast mesoporous polymers were also modified to introduce functional groups. The success of the functionalization was assessed analytically and by model catalytic tests. The study points to the advantages of the hard templating method for structuring organic materials but also its limitations.

Keywords: Adsorption, Mesoporous polymers, Nanocasting, Nanopores, Polydivinylbenzene, Sulfonation

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1 Introduction

Organic polymers can be adapted to a wide variety of applications because there is a large choice of monomers and they have the capacity to be functionalized for a specific use. Furthermore, many applications require a material with the ability to be processed into various shapes and sizes, which is possible for organic polymers. Heterogeneous catalysis is a possible field of application for functionalized polymers (e.g., as support, acid/base catalyst, etc.) [1–4]. However, bulk polymers exhibit low specific surface area and very low or inexistent pore volume that limit their utilization as catalysts. For a long time, research groups have tried to introduce structuration at the nanoscale to organic polymer materials, and especially generate nanopores [5]. One early attempt made by Zhu et al. [6] consisted of using inverse micelles and polymerizing cross-linked styrene between the micellar aggregates. Another way was to use silica nanoparticle as templates. For that, Johnson et al. [7] have sintered silica particles and polymerized divinylbenzene (DVB) or pure ethylene glycol dimethacrylate (EDMA) in the interstices between the spheres. With that process, porous polyDVB and polyEDMA exhibiting pores of 35 nm (i.e., the size of the silica particles) were obtained. However, only a high cross-linking degree was suitable to generate a porous polymer. Currently, the synthesis and application of nanoporous organic polymers and their composites remain areas of intense research activity [8–23]. Nevertheless, hard templating strategies appeared to be a suitable pathway to generate nanostructured polymeric materials and soft materials in general [24].

In 1999, Ryoo and coworkers [25] showed the possibility of using ordered mesoporous silica as a hard template for preparing high-surface-area mesoporous carbon materials. Selected monomers or precursors were impregnated within the template pores, and subsequently, the precursors were
solidified by polymerization or decomposition. The silica template was then removed with a treatment using hydrofluoric acid or a strong base such as NaOH. This method appeared ideal for the preparation of materials like metals, oxides, carbons, and polymers, which are difficult to organize at the nanoscale by direct synthesis methods. These compositions are usually more sensitive to hydrolysis, redox conditions, sintering or phase transitions, and the thermal step can lead to collapse of the material mesostructure, and thus, loss of the porosity [26, 27]. Regarding polymers, Johnson et al. [28] had used first MCM-41 for casting phenol-formaldehyde polymer rods. The resulting materials were disordered but consisted of well-shaped polymer nanorods. Kim et al. [29] have then tried to replicate mesoporous silica to form ordered mesoporous polymers. In their case, the polymer replica materials presented nitrogen physisorption isotherms with low adsorption capacity and no capillary condensation step, suggesting the absence of a truly mesoporous material [30]. This work was rather preliminary, and more precise information about this system and substantial improvement were required. As a possible alternative, two groups, Zhao et al. [31] and Tanaka et al. [32, 33], independently demonstrated the preparation of ordered mesoporous organic polymers by direct soft templating strategies through evaporation induced self-assembly process.

Despite being of significant interest, the soft templating strategy has, however, still some limitations (e.g., specific monomers and synthesis conditions, reproducibility, scale). On the other hand, advances in the control of polymerization of vinyl-based monomers confined within the mesopores of SBA-15 silica [34] have paved the way for an improved preparation of nanostructured organic mesoporous polymers. In their work from 2006, Sozzani and coworkers [35] reported the preparation of individual polymer micro-objects obtained through replication (i.e., nanocasting) of nanoporous silica with well-defined particle morphology. The polymers were shown to retain, over the scale of several micrometers, the complex shapes of the initial inorganic particles during the replication process. However, the authors could not preserve the initial mesostructure of the silica materials used as hard template, which reflects the findings of Johnson [28] and Kim [29] discussed above. Actually, the possibility of shape retention during nanocasting was not very surprising since Ryoo and coworkers had already demonstrated in 1999 that CMK-type carbon could easily maintain the shape of the initial silica particles [25]. For instance, MCM-48 silica single crystals could beautifully be replicated into carbon equivalents. As the carbon precursors were often polymers, it could be expected that shape retention is possible in the case of polymers as well. Subsequently, Ryoo and coworkers reported in 2010 the successful synthesis of highly ordered mesoporous polymer nanocasts using different mesoporous silicas as templates, e.g., KIT-6, SBA-15, and MCM-48 [36]. They demonstrated the importance of using a silica template with sufficiently large mesopores (> 5 nm) to allow an efficient ("faithful") replication and high pore ordering. Furthermore, only materials with 3D pore network, i.e., KIT-6, were considered suitable templates. In that study, however, the authors described that to achieve high quality polymer replicas, a posttreatment of the parent silica surface with trimethylchlorosilane (TMSCl) (i.e., silylation) was needed. Following this development, we were intrigued to verify whether the TMS modification could be avoided, and thus pristine silicas used directly for the hard templating process. Furthermore, questions regarding the details of the polymer porosity and the possibility of extending the method to design multifunctional copolymers remained to be answered. Therefore, we have initiated a comprehensive study of the preparation, characterization, and functionalization of nanocast mesoporous polymers (NMPs). Different NMPs were prepared on the basis of divinylbenzene (DVB) with various cross-linking degrees (i.e., with or without comonomers), and their porosity was tailored depending on synthesis parameters. Pristine silicas, such as 2D hexagonal SBA-15 [37, 38] and 3D cubic KIT-6 [39], could directly be employed as hard template without difficulties. The cross-linking degree of the polymer was adjusted (i.e., through copolymerization) to improve the capacity for (post)functionalization. Emphasis was placed on the characterization of the materials in terms of their porosity and functions, although the mesostructured ordering was also assessed using electron microscopy methods. The inclusion of multiple functional groups, such as sulfonic acids, phosphonic acids and amines, was carried out to generate (bi)functional mesoporous resins and their properties were assessed.

2 Results and Discussion

2.1 Synthesis and Characterization of the Materials

For the sake of clarity, the nanocast polymer materials synthesized in this study are summarized in Tab.1 together with their nomenclature. The first step for the preparation of NMPs is to prepare a suitable highly ordered mesoporous silica which will be used as the hard template. The second step is to properly and selectively fill the pore system with polymer precursors (monomers). The third step is to perform a solidification of the pore-loaded precursors. Finally, the last stage of the process is to selectively remove the silica template, using HF or concentrated NaOH, to liberate the pore system of the replicated polymeric materials. KIT-6 and SBA-15 silicas were chosen because they exhibit interconnected pore structures (i.e., with a 3D network character). KIT-6 shows a 3D cubic pore structure [40, 41] and SBA-15, aged at elevated temperature (> 120°C), exhibits bimodal porosity that confers a 3D character to the pore network [42–45]. Their pore size and their interconnectedness can be changed easily with a variation of the aging temperature and aging duration. When the
aging temperature is increased or the aging time is longer, the pore size increases and the proportion and size of interconnecting intrawall pores may be larger. At the same time, the wall thickness of silica decreases with an increase of the aging temperature (through densification/condensation within the walls). Alternatively, the wall thickness may also be tuned by varying the ratio of silica precursor to Pluronic P123, used as a structure-directing agent, in the synthesis. With higher amount of silica precursor, the wall thickness will be larger [38, 43]. This allows the possibility to selectively tune the silica templates according to the requirement for the nanocasting procedure. Therefore, SBA-15 silica was prepared with an aging step at 140 °C and with a molar ratio (r) of TEOS/P123 = 75. The SBA-15 sample prepared in such a way has a lot of wide interconnections but also sufficient wall thickness [42, 43, 46]. The isotherms of the different silica templates are shown in Fig. S1 in the Supporting Information (S1). All isotherms show steep capillary condensation steps indicating the high quality of the materials. All of them exhibit a type IV(a) isotherm with H1 hysteresis loop [30]. As expected, the pore condensation step in the KIT-6 isotherms shifts to higher P/P₀ when the aging temperature is increased, indicating the augmentation in pore size. At the same time, the total pore volume and the surface area evolves markedly with increasing aging temperatures. Tab. S1 summarizes the physicochemical parameters derived from the N₂ physisorption measurements for the different hard templates. Structural characterization of the mesoporous silicas by low-angle powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) can be found elsewhere [40, 41, 43]. Overall, the characterization data of the mesoporous silica templates are in good agreement with the literature [36–46].

A mesoporous polymer was synthesized following a one-step impregnation method and was prepared first using KIT-6 aged at 80 °C for two days. The process of nanocasting can be followed nicely by gas adsorption (e.g., N₂ at –196 °C) as shown in Fig. S2. Fig. S2A presents the sorption data of the selected KIT-6 template (KIT-6-80), Fig. S2B the resulting composite before HF washing, and Fig. S2C the final NMP1-80 prepared with 100 % DVB as a single monomer. From these gas adsorption data, one can deduce that the pores of KIT-6 were completely filled with the polymer because the condensation step and the hysteresis loop vanished (Fig. S2B). The total pore volume (TPV) of the resulting composite material is 0.05 cm³ g⁻¹; this is in the range of nonporous granular materials. After HF washing, Fig. S2C again reflects a type IV isotherm with a hysteretic behavior. This indicates the presence of a mesoporous polymer and proves the success of the polymer nano-replication, i.e., the nanocasting. This NMP made with 100 % DVB exhibits a specific surface area (S BET) of 416 m² g⁻¹, a total pore volume of 0.43 cm³ g⁻¹, and a pore width of 3.7 nm. Although not particularly accurate, the Barrett-Joyner-Halenda (BJH) method was used first in order to allow comparison with literature data. For more accurate pore size analysis, the use of NLDFT methods [30, 41, 47, 48] is otherwise strongly advised (vide infra). The pore size distribution (PSD, Fig. S2D) obtained for the silica template showed a narrow distribution with a peak at 7.2 nm while NMP1 has a wider distribution centered around 3.7 nm. The NMP pore size would somewhat reflect the wall thickness of the silica template. These data agree very well with the BJH values reported by Ryoo for a similar system but based on TMS-modified KIT-6 [36]. Furthermore, NMP1-80 has wider pore size than the materials reported by Kim et al. [29] (e.g., 1.7 nm) for the replication of MCM-48 silica, but smaller than soft-templated polymers (e.g., 6.7 nm) [31]. Similarly, pure KIT-6 synthesized with different aging temperatures can be used to efficiently prepare different NMPs. Fig. 1A combines isotherms of NMP1 prepared with KIT-6 templates aged at 60, 80 and 100 °C. For comparison, Fig. S3 shows the respective carbon materials (i.e., CMK-8 [39, 40, 49] prepared with the same silicas. A difference is observed in the shape of the isotherms of NMP1 and CMK-8 samples. All NMP1 materials show a triangular hysteresis loop, while the CMK-8 samples exhibit a well-resolved type IV(a) isotherm with H1 type hysteresis. Compared to the carbon analogs, the NMPs exhibit rather low pore volumes, much lower surface areas, and the capillary condensation steps are not very pronounced. Moreover, the condensation step in the isotherms of the CMK-8 materials moves to lower relative pressures with increasing aging temperature of the templates, which reflects the decreasing wall thickness of the template used, leading to smaller pore sizes (Fig. S3). This effect is less obvious for the NMPs, and only NMP1-100 has a slightly smaller pore size than the two others and

| Table 1. General names and nomenclature of the NMP samples. |
|--------------------------------------------------------------|
| Material code     | Description                                      |
| NMP1-60          | NMP templated from KIT-6 aged at 60°C           |
| NMP1-80          | NMP templated from KIT-6 aged at 80°C           |
| NMP1-100         | NMP templated from KIT-6 aged at 100°C          |
| NMP2-140         | NMP templated from SBA-15 (aged at 140°C)       |
| NMP1-60-PCMS-30  | NMP1-60 copolymerized with 30 mol % PCMS       |
| HSO₃⁻·NMP2-140   | Sulfonated NMP2-140                             |
| EDA-NMP1-60-PCMS-30 | Aminated NMP1-60 from a material with 30 mol % PCMS |
| (HO)₂PO-HSO₃⁻·NMP2-PS-15-PCMS-15 | Bifunctional phosphonated/sulfonated NMP2-140 from a material with 15 mol % PS and 15 mol % PCMS |

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a broader PSD (Fig. 1B and Tab. 2). The evolution of the pore volume (TPV) for these two series of materials follows an opposite trend, that is, the pore volume of the CMK-8 is decreasing with increasing aging temperature of the silica template, while it increases for the NMPs from 60, to 80 and 100 °C. For the CMK-8 samples, this evolution could be rationalized by the progressive decrease in pore size of the replica while the carbon wall thickness increases. In case of the NMPs, the reason for the opposite evolution is unclear and may be related to differences in mesostructure/network stability. Clearly, the rigidity of the nanocast polymer network is an important parameter here and organic polymers, being less rigid, need larger connections (in the silica template) for maintaining their mesostructure. The isotherm of NMP prepared with SBA-15 (NMP2-140, Fig. 1C), shows a well-defined capillary condensation step. The isotherm shape is similar to that of the carbon material (CMK-3) [50] prepared from the same template (Fig. 1C), except for the much lower adsorbed volume. The hysteresis loop of NMP2-140 is however resembling that of the NMP1 samples. CMK-3 has a substantially higher pore volume and a higher surface area than the corresponding NMP (Tab. 2).

We observed differences in terms of pore sizes between the NMP series and their carbon equivalents (Figs. 1 and S3, Tab. 2). The values vary much when comparing the BJH to modern NLDFT methods. However, taking DFT analyses as a more reliable pore size analysis, it appears that the NMP1 series shows slightly smaller pore size than their CMK-8 equivalents, whereas the pore size of NMP2-140 is slightly larger than that of the carbon (Fig. 1D). These differences may be due to several factors, such as the influence of the high-temperature pyrolysis step on the silica (i.e., densification, contraction) or the stability of the mesoporous polymer network after template removal. In particular, the shape of the isotherms of the NMPs can be influenced by the rigidity of the materials. Soft materials, such as organic polymers, are clearly less rigid than carbon materials. Van der Waals-type interactions [51] within the organic polymer nanostructure can also lead to partial collapse or local aggregation in the materials and, ultimately, reduce the porosity. Moreover, the PSDs (Figs. 1B and S3B) indicate the width of the peak was smaller for CMK-8 than NMP1. Here, it seems the rigidity of the carbon materials ensures a better pore definition and a more constant space between the walls of the replica.

Note that, for all the polymer replicas, the isotherms are non-reversible at the low relative pressure range between $P/P_0 = 0.05–0.4$. This is rather common for soft materials and polymers and usually attributed to the small infiltration and entrapment of N$_2$ in the polymer structure (i.e., absorption in the volume), remaining in the material under the adsorption/desorption experiments.

The pronounced difference in adsorption capacity observed when comparing carbon and polymer replicas may be attributed to several factors. First, the carbon materials exhibit quite large sorption capacities at low relative pressures due to the presence of micropores within the carbon rods that are building the network. This is a general feature of this type of mesoporous carbon prepared using, for example, sucrose or furfuryl alcohol as the carbon source [50, 52]. The other contribution to the lower capacities might be due to the presence of non-porous polymer among the material. This can be verified by electron microscopy investigations (see below).

TEM images obtained for the NMP1-80 and NMP2-140 materials are depicted in Fig. 2. These TEM images prove the excellent ordering of the mesoporous polymers. Overview images confirmed that only mesostructured polymer is observed without the presence of disordered
bulk material. High-resolution images of the NMP1-80 sample illustrated in Fig. 2a show clearly a mesostructure reflecting the cubic phase of the parent silica template. Images taken along the [111] and [110] incidences of the cubic phase demonstrate the effectiveness of the replication of the KIT-6 mesostructure (3D cubic Ia3d symmetry) particularly well [36]. Similarly, the hexagonal mesostructure of SBA-15 aged at 140 °C is very well replicated in the NMP2-140 sample, as visible on the images in Fig. 2b showing a highly ordered hexagonal packing of connected polymer rods.

The high-resolution SEM images (Fig. 3) confirm the TEM data and demonstrate furthermore the extend of the nanocasting process over large domains. Both particle morphology and mesostructure are retained in the nanocast polymers. The SEM images of NMP2-140 show well-aligned polymer rods and some connections or bridges between the rods are visible in the magnification (Fig. 3b), which reflects the high interconnectivity of the SBA-15 template aged at high temperature (140 °C). In addition, these SEM images reveal that the pores reaching to the surface of this particular SBA-15 sample are open (i.e., no curved closed channels are seen) [53] (Fig. 3a, left) and numerous defects (irregular pores/cavities in the walls or connections) seem visible on the particle surface along the channel direction (Fig. 3b, left image). In the case of KIT-6-80 and its replica, NMP1-80, the 3D open pore structure is clearly visible from the surface of both materials (Fig. 3c). The image of NMP1-80 shows very well the casting/molding of the highly branched mesopore channels with their 3D interconnectivity (see also magnified image, Fig. S4 in the SI).

Replication is successful in the case of the KIT-6 template irrespective of the aging temperature applied for the synthesis of the template. This is expected, since the KIT-6 porous structure is a 3D interconnected network (from symmetry and pore organization). However, in the case of the 2D hexagonal SBA-15 template, the replication is proven to be more difficult if the silica is not prepared with an elevated aging temperature [29, 36]. High aging temperature results in a silica matrix with increased pore size and, most importantly here, increased

### Table 2. Summary of the physicochemical properties of NMPs and CMKs (from N2 sorption at –196 °C) prepared with various silica templates (see SI for details).

| Material | \( S_{\text{BET}} \) \([\text{m}^2\text{g}^{-1}]\) | \( \text{TPV} \) \([\text{cm}^3\text{g}^{-1}]\) | Pore size DFT-\text{C-des} \([\text{nm}]\) | Pore size DFT-\text{ads} \([\text{nm}]\) | Pore size DFT-des \([\text{nm}]\) | Pore size BJH \text{ads} \([\text{nm}]\) |
|----------|----------------|----------------|-------------------|-------------------|-------------------|-------------------|
| NMP1-100 | 635            | 0.59           | 4.7               | 4.2               | 4.6               | 2.8               |
| NMP1-80  | 416            | 0.43           | 4.7               | 4.8               | 4.6               | 3.7               |
| NMP1-60  | 366            | 0.36           | 4.8               | 4.7               | 4.6               | 3.4               |
| NMP2-140 | 516            | 0.61           | 4.8               | 4.9               | 4.8               | 3.7               |
| CMK-8-100| 1040           | 1.09           | 5.1               | n/a               | n/a               | 3.7               |
| CMK-8-80 | 1197           | 1.31           | 5.6               | n/a               | n/a               | 4.5               |
| CMK-8-60 | 1207           | 1.58           | 5.8               | n/a               | n/a               | 4.7               |
| CMK-3-140| 1244           | 0.95           | 4.7               | n/a               | n/a               | 3.2               |

Figure 2. High-resolution TEM images of a) NMP1-80-(DVB-100) (on the left, along the [111] incidence, and right, along the [110] incidence of the 3D cubic mesophase), and b) NMP2-140-(DVB-100) (2D hexagonal).
connection size and/or occurrence. Therefore, for a successful replication of SBA-15, a material aged at 140 °C was employed. The extensive pore network interconnectivity of SBA-15 prepared under these conditions [43–45] could supply sufficient rigidity to the polymer replicas after silica removal. On the other hand, using a high ratio of TEOS to P123 increases the wall thickness, and so it compensated a bit the effect of high temperature to allow sufficient pore size for NMP2. The resulting NMP2 replica shows particularly large rod sizes and interconnectivity (Figs. 2 and 3). Further information about the long-range order and the nature of the organization of the pore system can be gathered from powder XRD analyses. Fig. S5 shows the low-angle XRD patterns for a series of these materials. The silica-polymer composite obtained after complete filling of the pores shows almost no XRD signal indicative of proper pore filling. After silica removal, the mesostructured ordering is recovered for all the NMPs, as XRD patterns characteristic of mesostructured materials are obtained.

We carried out a series of high-resolution gas adsorption measurements including data collected in the low relative pressure range to investigate the presence of possible microporosity. Representative data focusing on the NMP2-140 sample are shown in Fig. 4. A complete isotherm, including micropore region at low relative pressure is shown in Fig. 4A. The isotherm exhibits a well resolved triangular hysteresis loop, with steep capillary condensation step [30, 47]. Desorption seems to take place under critical conditions, i.e., desorption occurs spontaneously due to instability of the meniscus of the condensed pore fluid (i.e., lower tensile strength effect) or cavitation effects [54, 55]. The isotherm represented in the log scale shows the occurrence of almost no micropore adsorption volume (Fig. 4B). The NMPs appear to be only mesoporous, as opposed to the microporous-mesoporous CMKs. PSDs are difficult to accurately determine for organic polymer materials. Figs. 4C and 4D compare PSD curves and cumulative pore volumes obtained from the classical BJH method and different NLDFT models. The BJH method is known to generally underestimate the values by about 25 % or more [56] and is not suitable to determine pore size characteristics below 2 nm (i.e., the micropore range visible in Fig. 4C for the BJH data is meaningless). On the other hand, modern methods based on DFT modeling, which consider fluid-fluid and fluid-solid interactions at the molecular level and under pore confinement, are considered more accurate, especially in the range of pores below 10 nm [30, 47, 48, 57]. However, the DFT models available do not necessarily consider the proper surface nature (e.g., silica/oxide or carbon, instead of organic polymers) and adsorption potentials suitable to describe the behavior of organic materials. Nevertheless, the different DFT models (i.e., carbon, silica) do not differ much in terms of the obtained value of mode pore size. A widening of the PSD towards lower pore size is visible in the case of a carbon-based DFT kernel. Overall, the DFT analyses do not suggest microporosity and provide a more reasonable mode pore size in the range of 4.5–5 nm (rather than 3.7 nm obtained by BJHads).

Thermogravimetric analysis coupled with differential thermal analysis (TGA-DTA) (Figs. S6 and S7) confirms that the materials consist entirely of organics with no residue remaining after high temperature treatment. This excludes the possibility that the XRD reflections could originate from the presence of residual silica. The decomposition of the material happens in three steps. The first step, around 250 °C, is a small gain of weight created by the adsorption of oxygen and the creation of some carboxylates and/or carbonyls. The second and the third steps are exothermic and happen around 350 °C and 550 °C, respectively, corresponding to the combustion of the polymer under air. Between

Figure 3. High-resolution SEM images of a, b) the parent SBA-15 silica aged at 140 °C (left) and the NMP2-140 replica (right), and c) the parent KIT-6-80 (left) and the resulting NMP1-80 replica (right).
the different samples, only a small difference exists, with the NMPs showing slightly different onset of decomposition, i.e., different thermal stability, depending on the parent silica template used; NMP1-60 being apparently the most stable thermally.

One of the main parameters for preparing a high-quality replica is the DVB monomer loading inside the template. A typical synthesis uses 100% of the total pore volume of the silica template. However, to verify the influence of polymer loading, the monomer loading quantities were changed in the interval of 50 to 110 % of the TPV, inside SBA-15 or KIT-6. Fig. S8 shows the isotherms for these NMP samples and Tab. S2 compiles their porosity characteristics. For 110 %, no results were obtained because after polymerization, the silica/polymer composite material remained as a bulk solid impossible to be separated, crushed, or recovered. For the other samples, some variations in the TPV and $S_{BET}$ were observed when the loading decreases, but it is non-systematic (i.e., increase in TPV for NMP1-80 down to 80 % vs. a progressive decrease for NMP2). This may be attributed to the fact that some regions of the template are not sufficiently replicated. Furthermore, the quality of the materials changes a lot, as visible from the evolution of the shape of the isotherms. The isotherm opens at high relative pressures when the loading is 90 % or below. Non-reversible isotherm in the high-pressure range indicates a relatively wide distribution of pore sizes and possible defects in the structure. Thus, parts of the replica become less rigid and induce loss of TPV. Only 50 % of DVB loading did not allow to produce a stable nanocast.

2.2 Functionalization of the Nanocast Polymers

For specific applications, it is important to be able to introduce functionalities into the polymer materials. To create functionalized nanocast mesoporous polymers, two methods were explored. A first modification was attempted directly by varying the nature of the monomers. Because sufficient mechanical stability is required, the selected monomer should be combined with the co-monomer that was used previously, e.g., DVB. The second method is to add functionalities by post-synthetic reaction on the nanostructured replica. For that, the NMP used may be the fully cross-linked polymer or a copolymerized NMP, both containing units that can receive new functional groups. The first co-monomer used was styrene (Sty), as it was performed in the work of Ryoo et al. [36]. Fig. 5A shows the $N_2$ isotherms of the NMP1 replicas prepared with different percentages of styrene. NMP1-80 (100 % DVB) and NMP1-80-PS-10 show isotherms with similar shape and that exhibit approximately the same pore volumes and surface areas. For other samples, the TPV and $S_{BET}$ surface area decrease substantially with an increase in quantity of the styrene monomer (see Tab. 3). This observation may be attributed to the rigidity of NMPs that could decrease because of the reduced amount of the DVB cross-linker. Noticeably, NMP1-80-PS-30 is the material with the lowest content of DVB available that still leads to a satisfying mesostructure. The same concept applies to NMP1-80 prepared with PCMS as a co-monomer (Tab. 3). However, here, NMP1-80-PCMS-10 is the material with the highest possible amount of co-monomer while preserving high porosity values. It was, however, possible to

![Figure 4. A) Nitrogen physisorption isotherm at –196 °C (77 K) of NMP2-140 measured over the full pressure range. B) Same isotherm represented in log scale. C) Different pore size distribution curves, as indicated, and D) respective cumulative pore volumes.](image-url)
prepare a good quality NMP1-60-PCMS-30 material, using KIT-6 aged at 60°C instead of 80°C. The reason for the better stability remains elusive, as the wall thickness of the KIT-6-60 template is wider than KIT-6-80 [40] and creates a bigger space between polymer rods. Furthermore, the nanocasting strategy enables this way the direct preparation of bi-functional copolymers. This is achieved by the combination of PS and PCMS, together with polyDVB. For instance, NMP2-140-PS-15-PCMS-15 shows a well resolved isotherm (Fig. 5B), high porosity and high surface area (Tab. 3). The distribution of the different monomer moieties in the copolymer (Styrene and CMS) is not known so far. However, these results confirm that it is possible to modify the cross-linking degree for NMPs and, at the same time, prepare multiple copolymers.

Alternatively, functional groups can be introduced by a posttreatment realized on the NMP materials after silica removal. For example, cross-linked polyDVB can directly be sulfonated, either in concentrated sulfuric acid, as performed already in the work of Ryoo et al. [36], or with a solution of acetyl sulfate (see SI for details). Sulfonation may be performed at different temperatures depending on the sulfonation agent chosen: 85°C for conc. H2SO4, or for more moderate conditions, 40°C for acetyl sulfate. However, less degradation appears in the isotherm (Fig. 6) of NMP2-140 (100% DVB) treated with concentrated sulfuric acid rather than with ace-

**Table 3.** Physicochemical properties of functionalized NMP samples (from N2 sorption at –196°C) prepared by copolymerisation and/or post-functionalization.

| Materials                          | \(S_{\text{BET}}\) [m\(^2\)g\(^{-1}\)] | TPV [cm\(^3\)g\(^{-1}\)] | Pore size DFT-C-des [nm] | Pore size DFT-ads [nm] | Pore size DFT-des [nm] | Pore size BJH ads [nm] |
|-----------------------------------|----------------------------------------|---------------------------|--------------------------|------------------------|------------------------|------------------------|
| NMP1-PS-10                        | 429                                    | 0.44                      | 4.9                      | 4.7                    | 4.6                    | 3.5                    |
| NMP1-PS-20                        | 407                                    | 0.40                      | 4.9                      | 4.7                    | 4.6                    | 3.3                    |
| NMP1-PS-30                        | 352                                    | 0.34                      | 4.9                      | 4.7                    | 4.4                    | 3.3                    |
| NMP1-PCMS-10                      | 286                                    | 0.24                      | 4.9                      | 4.9                    | 4.9                    | 3.3                    |
| NMP1-PCMS-20                      | 92                                     | 0.06                      | 4.4                      | 4.7                    | 4.9                    | 3.3                    |
| NMP1-PCMS-30                      | 45                                     | 0.04                      | 4.9                      | 4.9                    | 4.9                    | 3.4                    |
| NMP1-60-PCMS-30                   | 313                                    | 0.25                      | 4.9                      | 4.9                    | 4.9                    | 3.2                    |
| NMP2-PS-15-PCMS-15                | 439                                    | 0.38                      | 4.9                      | 4.8                    | 4.8                    | 3.3                    |
| EDA-NMP1-60-PCMS-30               | 431                                    | 0.32                      | 4.9                      | 4.9                    | 4.9                    | 3.2                    |
| (EtO)\(_2\)PO-NMP2-PS-15-PCMS-15  | 386                                    | 0.26                      | 4.9                      | 3.7                    | 4.5                    | 2.8                    |
| (HO)\(_2\)PO-HSO\(_3\)-NMP2-PS-15-PCMS-15 | 285                                   | 0.20                      | 4.9                      | 3.8                    | 4.7                    | 2.9                    |
| HSO\(_3\)-NMP2-(DVB-100)a)       | 434                                    | 0.34                      | 4.4                      | 4.9                    | 4.9                    | 3.2                    |
| HSO\(_3\)-NMP2-(DVB-100)b)       | 483                                    | 0.37                      | 4.6                      | 4.3                    | 4.8                    | 3.1                    |
| HSO\(_3\)-NMP2-PS-30c)           | 321                                    | 0.21                      | 2.9                      | 3.6                    | 3.4                    | 2.2                    |
| HSO\(_3\)-NMP2-PS-30d)           | 436                                    | 0.29                      | 3.0                      | 3.7                    | 3.6                    | 2.5                    |

All NMP1 samples were from KIT-6 at 80°C, except when specified. All NMP2 samples were from SBA-15 at 140°C. a) HSO\(_3\)-NMP2 treated at 85°C in conc. H\(_2\)SO\(_4\); b) HSO\(_3\)-NMP2 treated at 40°C with acetyl sulfate; c) HSO\(_3\)-NMP2-PS-30 treated at 40°C with acetyl sulfate; d) HSO\(_3\)-NMP2-PS-30 treated at 85°C in conc. H\(_2\)SO\(_4\)
Acid sites concentrations and S content determined for sulfonated NMP materials.

| Samples                                  | Acid sites, titration [mmol g⁻¹] | S content, CHNS [mmol g⁻¹] |
|------------------------------------------|----------------------------------|-----------------------------|
| HSO₃-NMP2 treated at 40 °C in acetyl sulfate | 2.08                             | 1.96                        |
| HSO₃-NMP2 treated at 85 °C in conc. H₂SO₄ | 1.98                             | 2.25                        |
| HSO₃-NMP2-PS-30 treated at 40 °C acetyl sulfate | 2.17                             | 2.03                        |
| HSO₃-NMP2-PS-30 treated at 85 °C conc. H₂SO₄ | 2.16                             | 2.43                        |
| (HO)₂PO-HSO₃-NMP2-140-PS-15-PCMS-15       | 2.05                             | 2.22                        |
assigned to C–Cl bond. In the EDA-PCMS spectrum, these two peaks seem to be reduced. In addition, a band at 1686 cm⁻¹ could be attributed to NH bending. Moreover, the thermal degradation process of both materials is quite similar regarding the temperature of decomposition, but the DTA signals are different (Fig. S11C, D). Despite the incomplete substitution, it could be interesting to test the resulting mesoporous aminated polymer in selective adsorption processes (e.g., metal extraction, CO₂ capture, oxygenates removal) [60–64] or base catalysis [65].

Finally, by using a PS-PCMS-based copolymer material, it should be possible to generate a bi-functional mesoporous polymer through similar post-synthetic treatment. Polystyrene and chloromethylstyrene can be sulfonated and phosphonated, respectively [66, 67]. Diethyl phosphonate groups can replace the chlorine atoms through the Arbuzov reaction [68]. Subsequently, the resulting ethyl phosphonate may be hydrolyzed to generate phosphonic acid groups. At the same time, the polystyrene and polyDVB fractions can simultaneously be sulfonated, if chlorosulfonic acid is employed as the hydrolysis agent. After this acid hydrolysis, two kinds of acid groups, e.g., sulfonic and phosphonic acids, are thus present in the resulting modified NMP. The isotherm of such a bi-functional material reveals after hydrolysis a partial degradation of the porous structure (Fig. 5 B). Nevertheless, the bi-functional polymer still shows acceptable S_BET and TPV, mesopores and some interesting acid properties. The total acid content measured by titration equals 2.05 mmol g⁻¹. Sulfur content obtained by CHNS amounts to 2.22 mmol g⁻¹. The phosphorus amount obtained by ICP analysis was 0.233 mmol g⁻¹. From these numbers, it is thus possible that the hydrolysis of the phosphonate ester was not complete. Solid-state ³¹P MAS NMR spectrum (Fig. S12) provides additional evidence of the presence of phosphorous. The single peak at 25.88 ppm fits to a phosphoryl group coupled with two alkoxy groups, in the case of the (RO)₂PO-NMP2-140-PS-15-PCMS-15 (with R = Et or Bu). After acid treatment, the peak of the sulfonated/hydrolyzed material shifted to higher ppm (29.78). This shift is consistent with the hydrolysis of the alkoxy groups into a phosphonic acid, however, from these NMR data, it cannot be concluded that non-hydrolyzed phosphonate species would be remaining in the material.

2.3 Acid Catalysis Tests Using Sulfonated Materials

The ion-exchange and acid properties of the synthesized sulfonated NMPs should be evaluated. The esterification of hexanoic acid with benzyl alcohol, in competition with the alcohol etherification, was chosen as typical example to verify the catalytic activity of the materials, as it was used previously for nanocast polymers and composites as well [34, 36, 69]. The following samples were tested: HSO₃-NMP2 with 100 % of DVB and HSO₃-NMP2 with 30 % PS, the commercial Amberlyst™ resin (~ 4 mmol S g⁻¹), sulfuric acid (homogeneous conditions), and a mesoporous polymer-silica composite material prepared according to Choi et al. and Kleitz et al. [34, 70] (see Experimental section). Most of the tests were conducted at 75 °C in toluene, except for some cases in hexane at 40 °C. All catalysts were tested in the same conditions in terms of solvent quantity, stirring speed and H²/S concentration. The reactions were followed by GC-MS. In toluene, all catalysts yielded good conversions, in the range of 90 % to 100 %
within 24 h (Fig. 8A). As expected, the tests performed at 40 ºC in hexane resulted in a lower conversion. The fastest conversion is however observed with the mesoporous polymer-silica composite material. This may be attributed to its higher specific surface area and higher pore volume compared to the other samples (444 m² g⁻¹ and 0.61 cm³ g⁻¹). However, these NMPs are still better catalysts than Amberlyst™ and compare well to concentrated sulfuric acid. Clearly, the S_BET values of HSO₃-NMP2-DVB-100 and HSO₃-NMP2-PS-30 are around 430 m² g⁻¹ and around 320 m² g⁻¹, respectively, whereas the Amberlyst™ resin has a much lower S_BET of 53 m² g⁻¹. Selectivity to the ester of the NMPs (Fig 8B) was higher than that obtained with other materials and can almost compare to conc. H₂SO₄. As the catalysts were compared under the same conditions (for a given solvent), differences are attributable to the accessibility of the acid sites on the surfaces, and a high density of acid sites in the solid seems to favor the undesired formation of the ether, in accordance with the hypothesis of Choi et al. [34]. Overall, we observed a slightly improved catalytic performance as compared to the NMPs reported by Ryoo et al. [36], especially in terms of ester selectivity. Since porosity characteristics and acid concentrations (S mmol g⁻¹) are comparable, the reasons for these differences are unclear, and might be attributed to different density or distribution of the acid sites in our materials.

From the recycling test, one can see that the reagents are still converted, but conversion has significantly decreased compared to the first run (Fig. S13A). This can be attributed to the fact that the catalyst showed a loss in porosity after long immersion in the solvent at warm temperature (toluene at 75 ºC) (see Fig. S13B). In hexane at 40 ºC, the problem is less important, but it still exists. On the other hand, HSO₃-NMP2 (100 % DVB) is rather stable at these temperatures (e.g., 75 ºC) in acetonitrile according to the physiosorption data (Fig. S13B). Thus, it seems that the use of polar solvents could be less detrimental for the mesoporous framework of the HSO₃-NMP materials than apolar solvents. However, the reagents had limited solubility in acetonitrile (see Experimental in SI for more details).

3 Conclusion

The aim of this contribution was to assess the synthesis, the mesostructure and porosity characterization, and the possibilities of functionalization of nanocast mesoporous polymers. We discussed the different parameters involved in the nanocasting synthesis and re-evaluated the resulting physicochemical characteristics of the obtained materials in a critical way. In comparison to previous reports, the work demonstrates that native mesoporous silica (e.g., large pore KIT-6 and SBA-15 silicas) can be used with no difficulties, without the need for surface silylation, as efficient templates for the preparation of well-ordered mesoporous polymers. In agreement with the literature, it appears that highly cross-linked polymer systems (e.g., > 70 % DVB) are required for ensuring the stability of the replica. As such, copolymerization with non-cross-linking monomers remains quite limited. However, it is still possible to introduce different functional monomers to tailor the physicochemical properties and reactivity of the resulting nanocasts. Furthermore, we observed that the extent of the copolymerization possibility (i.e., how much co-monomer can be introduced together with DVB) depends on the type of monomer (e.g., styrene vs. CMS), as expected, but also on the silica chosen as the template (here KIT-6 aged at 60 ºC seems to be more suitable). Pore size tailoring, on the other hand, is limited in a narrow range. This is a significant drawback of this rather tedious synthesis method in comparison to direct soft templating methods. Moreover, advanced porosity characterization demonstrates the absence of micropores in the polymer nanocasts, and the isotherm hysteresis behavior seems to be influenced by network effects, suggesting variations in pore size and opening. For pore size analysis, modern DFT methods are considered more accurate than the classical BJH method, which underestimated the mode pore size substantially. Both carbon-based models and silica/oxide models may be implemented, and their fit compared, since the polymer surface polarity varies depending on the composition and functions introduced. Moreover, to get insights into the molec-
ular structure of the synthesized porous polymers, it would be of interest to investigate molecular weight, molecular weight distribution and polydispersity of the different materials obtained. However, these NMPs are highly cross-linked polymers that are generally insoluble, making such analyses challenging.

Overall, through nanocasting, interesting multifunctional mesoporous polymers could be prepared. Some of these NMPs may have potential for diverse applications, e.g., selective sorption, catalysis, metal scavengers. However, at the moment, the stability of the porous polymer mesostructures is still limited (especially the solvent stability), and should be validated under different conditions and, if possible, improved. Compared to other strategies to produce nanoporous organic polymers with high surface area [19, 23, 31], the nanocasting has limitations (e.g., tedious and costly synthesis procedure, limited tailoring of pore size, limited scale-up, low stability), however, it offers also some advantages in terms of pore ordering, tailoring of mesostructure, some flexibility in composition and function, and shape replication process, all of which could be of interest for the design and use of advanced porous organic nanostructures.

Supporting Information

Supporting Information for this article can be found under DOI: https://doi.org/10.1002/cite.202000238. This section includes additional references to primary literature relevant for this research [71–77].

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