

Formation of Helical Mesopores in Organic Polymer Matrices

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The synthesis of mesoporous materials with well-defined pore size is a widely studied topic. Such materials are of great importance in everyday life as well as for industrial applications, such as catalysis, adsorption, or membrane filtration. They have been largely developed for inorganic materials due to the use of organic templates.¹ The synthesis of mesoporous organic materials with organic templates, although less developed, has also allowed the synthesis of interesting materials.² Most often the templates are amphiphilic surfactants or block copolymers, and the resulting pores, shaped after the phase separation, are either cylindrical or spherical; examples of other shapes are rare. The synthesis of large helical pores was accomplished in silica, using self-assembled chiral surfactants³ or with ionic liquids⁴ as templates. Organic templates have been used to pattern the formation of helical pores in inorganic tubular nanoparticles,⁵ but no equivalent voids have been prepared in all-organic materials. In this paper, we address the possibility of forming helical pores in a polymer matrix.

When a template is used to form mesopores in a polymer network, the main difficulty is the removal of the template out of the resin; therefore, it has to be chosen wisely. For this purpose, Möller⁶ proposed the use of organogelators. These self-assembling molecules⁷ spontaneously form fibrillar objects in various solvents, including some monomers, but the templating aggregates can be dissociated in other solvents and hence are more easily leached out after the matrix polymerization. This work was exemplified only by a few syntheses of nanoporous resins using organogelators as templates.^{8,9} Some authors⁹ specifically tried to apply this strategy to helical self-assemblies from a chiral gelator, but the shrinking of the matrix during polymerization resulted in the loss of the chiral shape of the pores. Despite these difficulties, we have used gelators to template resins because they offer great variability in the shape of their assembly. We have recently shown¹⁰ that the 3,5-bis(5-hexylcarbamoylpentyloxy)benzoic acid decyl ester (BHPB, Figure 1) self-assembles in organic solvents, such as alkanes. It forms nanotubes with diameters of about 30 nm and lengths of several micrometers and helical tapes at lower concentrations (Figure 1).

The possibility of forming helices from BHPB was tested in several monomer/cross-linker mixtures. The formation of these fibrillar objects results, at the macroscopic level, in the formation of gels, which allows the rapid screening of several monomers. The monomers which precipitate or solubilize BHPB must be disregarded. From these tests, we found that BHPB formed thermoreversible gels in ethylene glycol diacrylate (EGDA) at concentrations of 5% per weight; BHPB dissolves in EGDA when heated, and a self-supporting gel forms when the solution is cooled back to 25 °C. The gel melts again when heated, which indicates that it is formed through noncovalent self-assembly and does not result from the polymerization of the monomer.

The gel matrix was polymerized by photoinitiation which avoids any thermal treatment that could dissociate the nanotubes; the helical tapes were formed in a mixture of EGDA and initiator Irgacure

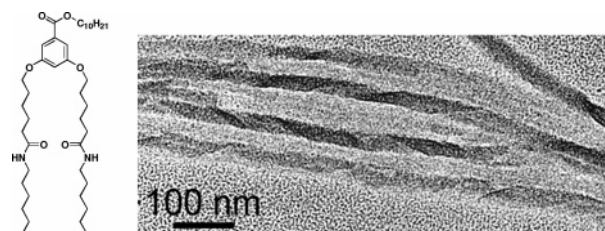


Figure 1. Structure of BHPB and TEM of helical tapes formed in C₆H₁₂ and in EGDA.

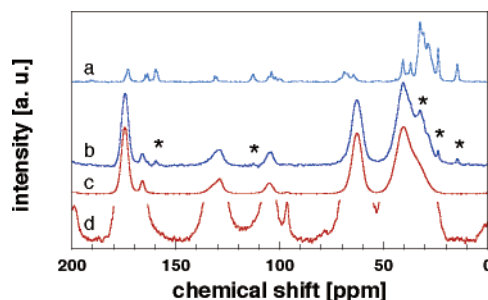


Figure 2. CPMAS NMR: (a) BHPB (template); (b) pEGDA resin containing BHPB; (c) same after extraction; (d) expanded 10 times. Stars: peaks of the template.

651 (benzil dimethylacetal), and the resulting gel was polymerized by UV irradiation to yield a transparent, hard, and glassy material.

The removal of the template was achieved by extraction of the resin with CH₂Cl₂, which dissociates BHPB. The extraction was performed for 24 h and yielded an opaque resin. The extractable material analyzed by NMR displayed mainly initiator and BHPB (Supporting Information S1). The weight of the extractable corresponded to a quantitative recovery of the compounds. This shows that the template is effectively extracted. After a second 24 h extraction, the leaching solvent did not show any traces of BHPB, indicating that the extraction is complete. The removal of the template was followed by CPMAS NMR. The spectra of the templated resin before extraction exhibit peaks that belong to the polymeric matrix along with peaks of the template (Figure 2). The spectrum of the extracted matrix shows the drastic decrease of the peaks of BHPB that corresponds to an extraction of at least 97% of the template. These results prove that, despite a high cross-linking density, the template can be efficiently removed.

The structure of the samples was studied by TEM of ultrathin sections (nominal thicknesses between 40 and 80 nm). The reference sample, pure photopolymerized pEGDA, displayed a homogeneous structure (Supporting Information S2). The samples containing BHPB exhibited individual structures. These objects were light-colored compared to the surrounding matrix, which indicates a lower electron density since no dye or contrasting agent was added to the preparations. The first kind of objects that could be observed were oblate ones (Figure 3a, black arrow). Their length was between 500 nm and 1 μm and their width between 30 and 50 nm. These

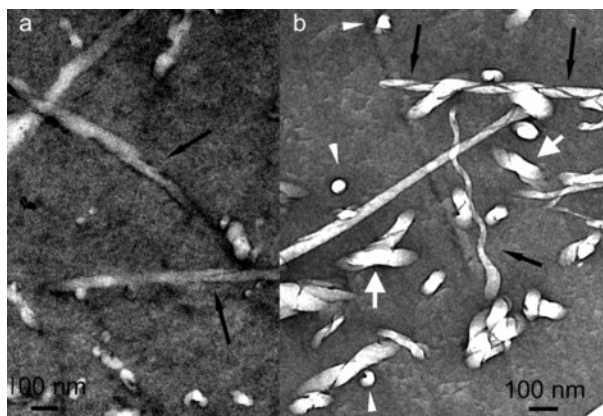


Figure 3. TEM of microsections of the resins. (a) with templates; (b) after leaching out the template. Black arrows: helical tape (a) and helical pores (b) viewed perpendicular to their axis. White arrows: same objects, tilted. White arrow heads: helical pores, viewed along their axis.

structures are the self-assembled templates included in the resin. The same objects were observed in the leached resins (Figure 3b) but with a stronger contrast between the objects and the matrix and clean-cut outlines. They are the voids left after the dissolution of the templates. They display classical patterns corresponding to the projection of helical tapes. Many other objects appeared shorter (Figure 3, white arrow heads). They correspond to the same helical pores but with different angles with respect to the electron beam since the tapes have an isotropic distribution. This assignment can be verified on tomographic reconstructions.

Such a tomogram is supplied in the Supporting Information as an mpg sequence. It shows that the white circles (Figure 3, white arrow) are not cylindrical pores but instead a top view of helical pores running perpendicular to the section. Most of the observed holes have a helical shape. The microscopic studies demonstrate that the polymer matrix reproduces the details of the molded structures with a good resolution, which can be estimated to be 3 nm.

At concentrations of 5 wt % in BHPB, the specific area was found to be 5 m²/g. In order to obtain larger areas, resins containing 50 wt % template were prepared. At this higher concentration, the templates only form cylinders. N₂ sorption isotherms of these resins were recorded and showed that the specific area of the samples before extraction was below the detectable threshold (0.5 m²/g) but equaled 50 m²/g after extraction. This result also demonstrates the possibility to form materials with high porosity using these self-assembled cylinders as templates. The porosity appears only after removal of the template. TEM of thin sections of these samples (Supporting Information S3) showed an increased density of pores. These pores are cylindrical and have an isotropic spatial distribution. The measurement of the BJH pore size distribution (Figure 4) showed a narrow distribution centered around 31 nm, very close to the diameters of the template, which shows that the porosity can be tuned by the size of the template.

In this study, we have shown that self-assembled helices can be used as templates to form helical pores in organic matrices. The imprints were obtained with a high resolution, most likely facilitated

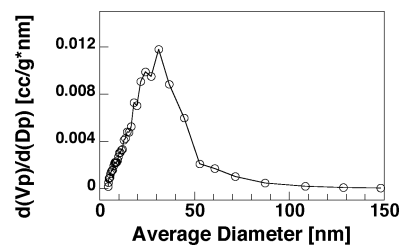


Figure 4. Pore size distribution of the resins imprinted with 50 wt % BHPB.

by the choice of a high cross-linking density network, which prevents any shrinking of the matrix. Due to the high resolution of the imprints, these materials can in turn be used as templates to form inorganic nanoparticles, and this possibility will be investigated in forthcoming work.

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Supporting Information Available: Experimental details for the preparation of the resins; NMR of the extractable; TEM of the pure pEGDA and of the 50 wt % BHPB–pEGDA resin; and mpg sequence of the 3D reconstruction by tomography. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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