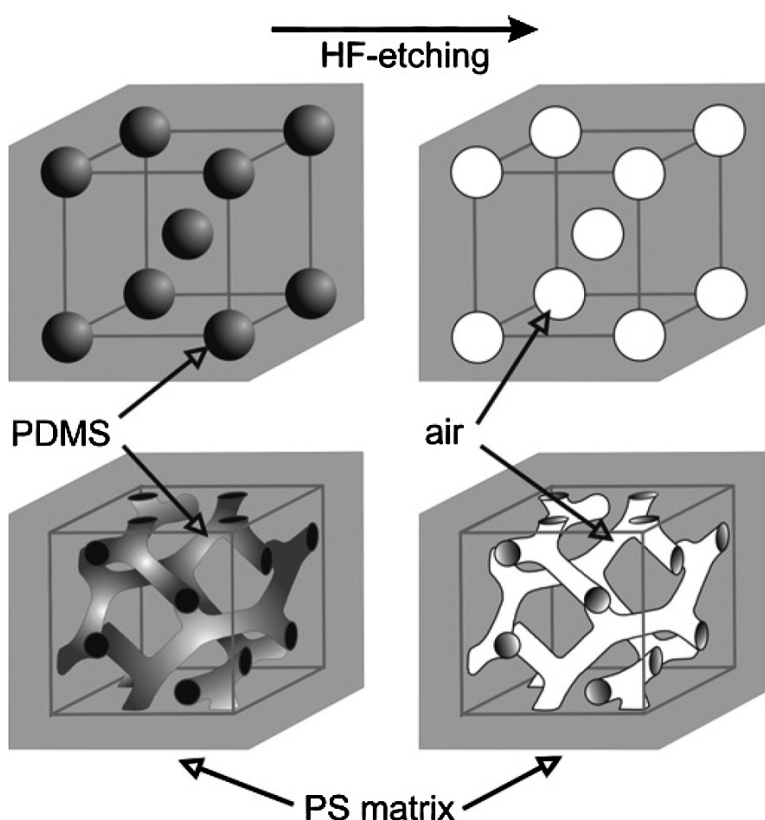


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Nanoporous Materials with Spherical and Gyroid Cavities Created by Quantitative Etching of Polydimethylsiloxane in Polystyrene–Polydimethylsiloxane Block Copolymers

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A substantial part of the scientific polymer literature in the last 15–20 years reports on diblock copolymers and their morphologies. The interplay between block immiscibility and connectivity generates a rich variety of nanophase-separated mesoscopic morphologies.¹ The design of the molecular weight and composition of these polymers – for example, via “living” anionic polymerization² – permits control of the resulting morphologies. The minority component in two such structures self-organizes into spherical domains or gyroid interpenetrating networks, as illustrated on the left side of Figure 1. Here, we report a new procedure for preparing samples, macroscopic in all three dimensions, of nanoporous materials (NPM) with spherical or gyroid cavities, as shown on the right side of Figure 1.

Possible nanotechnological applications could utilize the characteristic mesomorphic porous structures derived after selective etching of one block in diblock copolymers. Potential applications include templates for electronics, special dielectric materials, substrates for catalysis, design of nanoreactors, microfiltration membranes, and use in medical diagnostics. The literature reports on at least three ways to prepare nanoporous polymers from diblocks: ozonolysis of polydienes,³ UV-etching of poly(methyl methacrylate),⁴ and hydrolysis of polyesters.⁵ While the UV-etching technique was only reported to work on submicrometer thick samples, the other two procedures were reported to work on submillimeter thick films too. Percolation of a nonsolvent from the outer surface through the etched phase is necessary for these three techniques, either in the etching step⁵ or during removal of the etching products.^{3–5}

The method described here is based on the removal of poly(dimethylsiloxane) by the reaction with an excess of anhydrous hydrogen fluoride (HF) (Please notice precautions!).⁶ It works especially well for bulk-etching. Percolation of the etched microphase to the outer surface is not required. Therefore, this method permits – for the first time – one to prepare bulk nanoporous polymers of secluded spherical voids. In the case of polystyrene–poly(dimethylsiloxane) (PS–PDMS) block copolymers, it selectively removes the PDMS block. The use of anhydrous HF is known as an analytical tool for determining the composition of alkylsiloxanes,⁷ but it has not been previously reported in the context of block copolymers. The etching of PS–PDMS samples⁸ with anhydrous HF was accomplished using standard HF equipment⁹ for cleaving synthetic peptide-resins.¹⁰ The reaction products as well as the excess HF were removed afterward by applying vacuum overnight.¹¹ We present results on two not preoriented block copolymers: PS–PDMS-2 (mass fraction of PDMS $w_{\text{PDMS}} = 0.05$, number average molar mass $\bar{M}_n = 40$ kg/mol, polydispersity index

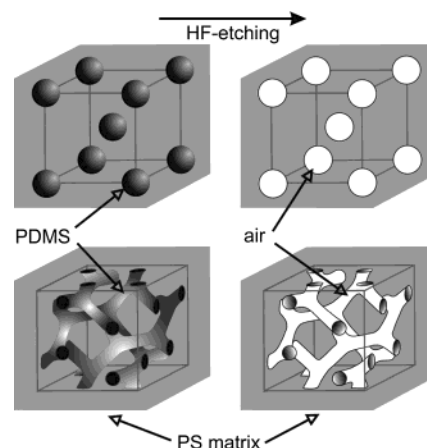
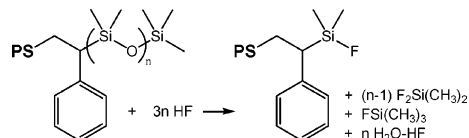


Figure 1. Schematics of two equilibrium morphologies in PS–PDMS diblock copolymers: spheres (top) and gyroid (bottom). HF-etching removes the PDMS component and renders a nanoporous material (NPM).

Scheme 1. The Expected Reaction between PS–PDMS and Excess HF (A C–Si Bond as Shown Binds the Two Blocks)



PDI = 1.08) and PS–PDMS-7 ($w_{\text{PDMS}} = 0.35$, $\bar{M}_n = 8.2$ kg/mol, PDI = 1.04).¹¹

The expected reaction products between PDMS and HF are water, dimethyldifluorosilane, and trimethylfluorosilane (Scheme 1). Notice that after complete etching, it is expected that each PS chain bear one dimethylfluorosilyl capping-unit. ¹H NMR (Figure 2), mass difference, size exclusion chromatography (SEC), and X-ray photoelectron spectroscopy¹¹ were used to characterize the materials before and after etching. The most significant results obtained by these analyses are as follows: (1) PDMS is completely etched by HF. (2) The drastic reduction of the signal around 0 ppm from methylsilane protons in Figure 2 is evident; otherwise, the spectra are virtually identical. The remaining small signal at 0 ppm for the etched samples is most probably due to the dimethylfluorosilyl capping-unit. The area under this signal is consistent with 0.5–0.6 capping units per PS chain. This discrepancy from the expected value of 1 is presently not clear. (3) SEC analysis permits one to estimate the extent of the PS cross-linking side reaction during HF-etching to roughly 1 cross-link per 3000 styrene units.¹¹

Small angle X-ray scattering (SAXS) is a powerful technique for analysis of mesoscopic structures.¹² It renders the symmetry of the sample, but also probes the whole bulk macroscopically. Figure

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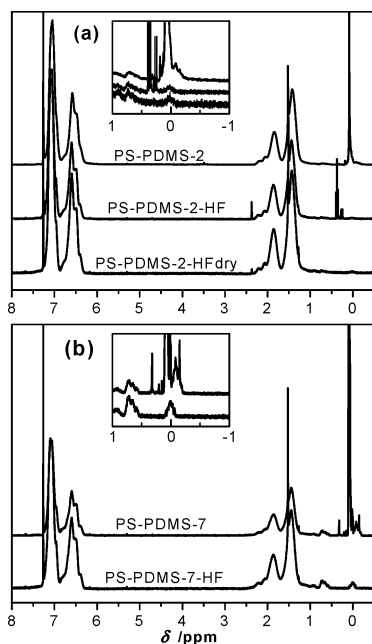


Figure 2. ^1H NMR traces before (PS–PDMS-2, PS–PDMS-7) and after (PS–PDMS-2-HF, PS–PDMS-7-HF) HF-etching. The signals from H_2C –Si around 0 ppm (see insets with curves in the same vertical order as in the main plot) strongly indicate that the etching reaction is quantitative. The trace for PS–PDMS-2-HF contains a group of sharp signals at 0.3–0.4 ppm that most probably derive from methylfluorosilane etching products captured in the PS matrix (long diffusion time from the spherical holes through the PS matrix).¹¹ These were removed after evacuation following dissolution of PS–PDMS-2-HF (PS–PDMS-2-HF_{dry}).

3 shows background-corrected and normalized SAXS profiles for samples of PS–PDMS-2 and PS–PDMS-7 before and after etching. In both cases, the SAXS data give undisputable evidence that the structure of the PS matrix remains in the HF-treated samples. The scattering of the HF-treated samples reproduces the features of the scattering from the original diblocks, but it is intensified dramatically. A scattering intensity enhancement of about 2 orders of magnitude is expected from an estimate of the enhanced contrast factor between PS and air as compared to PS and PDMS. Two additional PS–PDMS samples (not shown) gave identical results.¹¹ The original morphology of the PS matrix is conserved after HF-etching.

In conclusion, we have presented a new method for the preparation of porous nanostructures of polystyrene. The voids originate from domains of PDMS in self-organized PS–PDMS block copolymers. The morphology of PS is fully conserved after etching of PDMS, as ascertained by SAXS. The method is well suited for preparing samples of macroscopic dimensions; a 0.5 mm thick film of PS with secluded spherical voids was thus prepared for the first time.

The method has potential for application to other materials containing alkylsiloxane moieties. A polydiene component would be highly desirable in many situations, because of the possibility of introducing functional groups by subsequent reactions on the double bonds. Preliminary experiments with polydiene–PDMS block copolymers are showing encouraging results.

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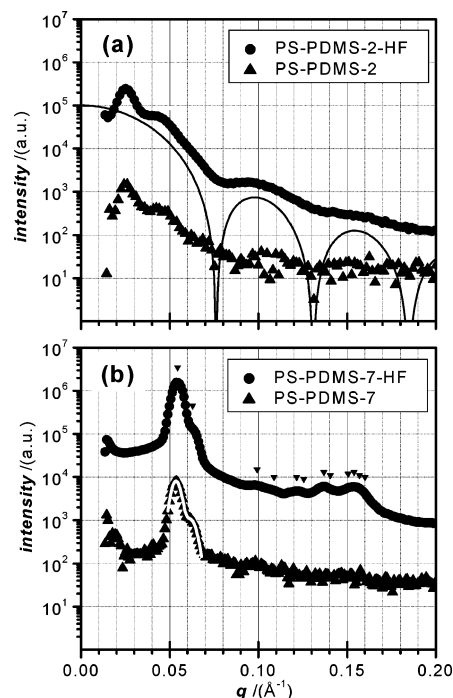


Figure 3. Scattering profiles of PS–PDMS-2 and PS–PDMS-7 before (▲) and after (●) HF-etching. (a) The two profiles are consistent with a morphology of spherical domains¹³ expected from the PDMS volume fraction in PS–PDMS-2. The solid line shows the (vertically displaced) calculated form-factor scattering from spheres of radius 6 nm. (b) The upside-down triangles mark the positions of scattering peaks from the $Ia\bar{3}d$ gyroid symmetry, and the white line shows a Gaussian fit of the [211] and [220] peaks. Both profiles are consistent with the gyroid morphology, in agreement with PDMS volume fraction and molar mass of PS–PDMS-7. The lattice constant was estimated to 28 nm.

with scanning electron microscopy (SEM) imaging.¹¹ We also appreciate the valuable comments made by the reviewers on the first manuscript.

Supporting Information Available: Procedure for sample preparation and HF-etching; size exclusion chromatography data; NMR and SAXS profiles of additional PS–PDMS samples; XPS, AFM, and SEM data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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