Nanostructured Polymers Prepared Using a Self-Assembled Nanofibrillar Scaffold as a Reverse Template

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We describe the preparation of nanostructured polymeric materials by polymerizing a monomer within a scaffold composed of self-assembled nanofibrils. 1,3:2,4-Dibenzylidene sorbitol (DBS) is an inexpensive sugar derivative that can form nanofibrillar networks in a variety of organic solvents at relatively low concentrations. Here, we induce DBS nanofibrils in styrene and then thermally initiate the free-radical polymerization of the monomer. The polymerization proceeds without any evidence of macroscopic phase separation, ultimately yielding a transparent solid of polystyrene. Within this material, intact DBS nanofibrils (diameter 10−100 nm) are preserved, as shown by atomic force microscopy (AFM). The DBS fibrils can also be subsequently extracted from the polymer, leaving behind a network of nanoscale pores. The porosity of the resulting polymer has been characterized by the BET technique.

Introduction

Over the last two decades, there has been a great deal of interest in the subject of polymerization within complex fluids, that is, within fluids that contain nano- or microscale assemblies or aggregates. Examples of such assemblies include micelles, microemulsion droplets, vesicles, liquid crystalline aggregates, or nanofibrillar networks.[1−13] One can envision polymerizing a monomer either inside of these assemblies, or on their surface, or all around them. While the first two cases represent a "templating" strategy, the third represents a "reverse templating" approach. One motivation for the reverse templating approach has been the creation of nanoporous polymers by polymerizing a monomer around the pertinent assemblies, followed by removal of the assemblies in a washing or extraction step. In a perfect scenario, pores are created in the polymer that bear the imprint of the original assemblies. Such "molecular imprinting" has been in vogue for a number of years, especially in the context of sensor applications. Nanoporous polymers could also prove useful in a variety of other applications, including their use as membranes, mesoporous catalysts, or stationary phases for chromatography.[14−16]

Our interest here is in the polymerization of a monomer in the presence of nanoscale assemblies such as micelles or nanofibrils, with an eventual goal of creating nanoporous polymers. A key question is whether such polymerizations can be conducted while preserving the assemblies. In other words, do the assemblies break apart, aggregate, coalesce, or transform in shape while the polymerization reaction proceeds? Indeed, one does often find that as polymerization proceeds in an initially clear and homogeneous sample, there is the onset of phase separation, turbidity, or other visible heterogeneities. These macroscopic changes are generally indicative of large-scale aggregation or destabilization of the assemblies. Ensuring stability in size, shape, and structure of the nanoassemblies during polymerization is thus a crucial challenge.[5−7] In this context, aggregates of amphiphilic molecules (surfactants, lipids) such as spherical micelles or wormlike micelles are generally quite fragile, which precludes their use as reverse templates. Fibrils formed by small, organic molecules through hydrogen bonding or other interactions are expected to be relatively sturdy in comparison, making them amenable to reverse templating efforts.

It is now well-known that a range of low-molecular-weight organic molecules ("organogelators") are capable of self-assembling into nanoscale or microscale fibrils in organic solvents.[17−20] The fibrils are typically held together by physical interactions, which may include hydrogen bonding and stacking. A few reverse templating studies have already been conducted with such systems, in which monomer(s) have been polymerized in the presence of organogelator fibrils. For example, John et al.[10] recently reported a study on a two-component gelator and divinylbenzene (DVB), where thin films of this liquid mixture were polymerized using UV radiation. It was shown that the fibrils (∼200 nm in diameter) remained intact in the final polymer material. Subsequently, upon solvent extraction of the fibrils, pores corresponding to an imprint of the fibrils were left behind in the polymer. These are interesting results, although the size scale of the fibrils is rather large (for this reason, the samples were reported to be turbid even before polymerization).

In this paper, we describe an efficient and versatile reverse templating approach with a different organogelator that forms true nanoscale fibrils. The organogelator is 1,3:2,4-dibenzylidene sorbitol (DBS), shown in Figure 1, a butterfly-shaped molecule derived from the sugar-based alcohol, D-glucitol. DBS self-assembles into nanofibrils via hydrogen bonding, and a network of such fibrils is formed at low concentrations in a variety of nonpolar organic solvents and polymers.[21−26] The fibril diameter has been found to range from 10 to 800 nm depending on the solvent. In the present work, we induce fibrils of DBS in styrene,

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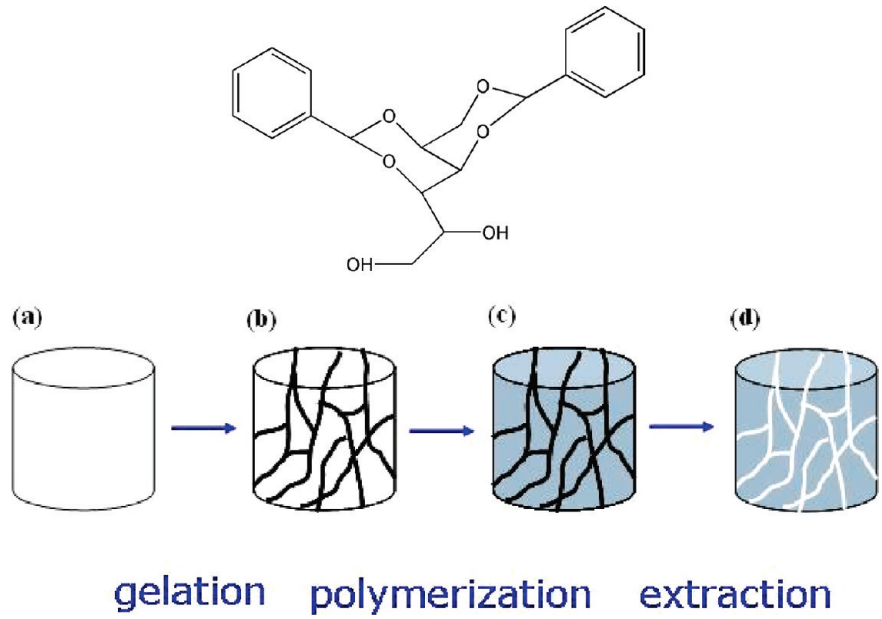

Figure 1. Chemical structure of 1,3:2,4-dibenzylidene-D-sorbitol (DBS). Schematic diagram of the steps used in this paper; (a) a homogeneous solution of DBS molecules dissolved in a liquid monomer/initiator mixture at high temperature, (b) the formation of DBS organogels (3-D nanofibrillar networks) after cooling to room temperature, (c) resulting polymers within DBS organogels by thermally initiated free-radical polymerization, (d) final porous polymers after the extraction of DBS organogels.

a conventional monofunctional monomer. We then polymerize the styrene within the fibrillar scaffold using thermally initiated free-radical polymerization. Importantly, we find that the polymerization proceeds without any evidence of macroscopic phase separation or destabilization of the fibrils. The presence of intact DBS fibrils in the final polymer is further confirmed by atomic force microscopy (AFM). We then attempt to extract the DBS fibrils from the polystyrene using a solvent extraction methodology and measure the porosity of the resulting material using the BET technique. Figure 1 illustrates the series of steps described in this paper. The net result is to imprint the fibrillar structure of DBS onto polystyrene.

Experimental Methods Section

Materials. DBS (1,3:2,4-dibenzylidene-D-sorbitol) was obtained from Milliken Chemicals. Styrene and benzoyl peroxide (BPO) were of reagent grade and were obtained from Aldrich and Fluka, respectively.

Polymerization. The organogel samples were prepared by dissolving different amounts of DBS in styrene at 100 °C on a hot plate under constant agitation (200 rpm). After the DBS dissolved, the initiator BPO (1.0 wt %) was added to the samples. At this high temperature, the BPO easily dissolved in styrene in a few seconds; then, the samples were removed from the hot plate and cooled to room temperature very quickly to suppress the polymerization so that gelled samples could be obtained. Thereafter, the sample was polymerized by heat at 80 °C for 1 day.

Rheological Measurements. The rheological properties of DBS/styrene organogels were measured using a Rheolab MC 100 instrument (Paar-Physica, Stuttgart, Germany) under oscillatory shear. The frequency spectra were collected over 0.01−100 rad/s at 25 °C, and strain amplitudes were maintained at 2%.

Atomic Force Microscopy (AFM). Samples for AFM were prepared by a procedure similar to that described above but with the polymerization conducted on a substrate. A DBS−styrene mixture containing 1% BPO was deposited on a silicon wafer by spin coating at 1700 rpm for 20 s at room temperature. The wafers were then placed in a closed chamber at 80 °C for 1 day to polymerize the styrene. AFM imaging of the polymerized samples containing DBS fibrils was done under ambient conditions with a Digital Instruments D3100 SPM system operating in tapping mode using OTESP (Olympus Tapping Mode Etched Silicon Probea) tips from Veeco Instruments. The tips were used at resonance frequencies of 300 kHz. The silicon cantilever in the AFM had a spring constant of 42 N/m, and the scan rate was 1 Hz.

BET Analysis of Porous Polymers. Porous polymer samples were prepared by extraction of the DBS fibrils (see text for details). These samples were analyzed using a Coulter SA-3100 instrument. The technique involves gas adsorption experiments using nitrogen, and the data were analyzed in terms of the BET isotherm to determine the specific surface areas in the samples.

Results and Discussion

Self-Assembly. While self-assembly of DBS fibrils occurs in a variety of organic liquids, all studies up to this point have focused on unreactive organic media. Our approach, on the other hand, was to induce the formation of a nanofibrillar DBS network in organic liquid monomers bearing polymerizable groups. The monomer that we have used is styrene. Figure 2 shows a photograph of a sample containing 2 wt % DBS in styrene. Note that the sample is transparent and capable of holding its weight in the inverted vial, indicating that it is a stiff organogel at room temperature. Dynamic rheological measurements confirm the gel-like behavior of the sample. The plot in Figure 2 shows the storage modulus G' and the loss modulus G'' as functions of frequency ω. As is typical of a gel,[27] we observe that G' is practically independent of ω and that G' is greater than G'' at all ω. It is thus clear that DBS forms a physical gel in styrene, with a plateau modulus (value of G') of about 1 MPa. Evidently, the gelation is due to the presence of a volume-filling three-dimensional network of DBS nanofibrils in the sample, as has been observed with DBS in other organic solvents. Also, on the basis of earlier studies,[22−25,28] it is known that the dominant interactions responsible for

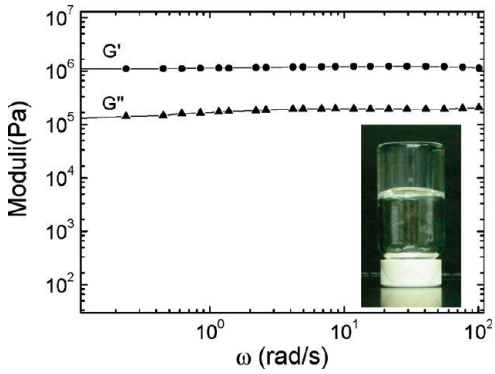

Figure 2. Photograph of a sample containing 2 wt % DBS in styrene. Dynamic rheological data, elastic modulus G' (circles), and the viscous modulus G'' (triangles) as functions of frequency ω for the styrene sample containing 2 wt % DBS at 25 °C.

connecting the DBS molecules within the nanofibrils are the hydrogen-bonding interactions of their hydroxyl groups. Similar gel formation occurs in styrene at higher DBS concentrations as well, with the gel modulus increasing with increasing DBS concentration.

Polymerization. The next step involved free-radical polymerization of the liquid monomer in the presence of DBS fibrils. Toward this end, we added the thermal initiator BPO to the styrene + 2% DBS mixture and polymerized the sample at 80 °C (see Experimental Methods Section). The polymerization temperature is a factor to control the polymerization process. We find that the samples will remain transparent when the polymerization temperature is at 80 °C. If the polymerization temperature is lower, the samples become turbid, and macroscopic phase separation happens. On the other hand, as the polymerization temperature is higher (for example, above 100 °C), the gel samples will melt and become solutions. This is because the gel dissolution temperature (gel to sol transition temperature) is around 105 °C (determined by the rheological measurement). Therefore, in this study, 80 °C is chosen as the polymerization temperature. Moreover, the gelled sample was completely soluble in methanol, in which polystyrene (PS) cannot dissolve, indicating that the polymerization of styrene was mostly suppressed after the sample was quickly removed from the hot plate and cooled to room temperature. During the polymerization process, the gel remained transparent. Note that the optical clarity of the initial gel reflected the nanoscale dimensions of the fibrils present. The fact that the sample stayed transparent during polymerization is significant because it strongly suggested that the same fibrils were preserved in the final material. No turbidity or macroscopic phase separation was detected during polymerization, in contrast to many other reverse templating schemes involving assemblies such as micelles or microemulsion droplets.[3,5,6]

Nanostructure. To probe whether the fibrils were indeed present in the polystyrene matrix, we conducted AFM studies of the final polymerized material (on films deposited on silicon wafers; see Experimental Methods Section). Figures 3 and 4 show AFM height and phase images of polymerized samples made within scaffolds of 1 and 2 wt % DBS. The images correspond to 2 μm × 2 μm areas, and in both cases, we can observe extensive nanofibrillar networks. The nanofibrils appear to be quite stiff, and their diameters range from 10 to 100 nm, which are similar to the sizes observed for DBS fibrils in some organic solvents and polymer melts.[22−25] These images demonstrate that the nanofibrils are indeed preserved during polymerization, consistent with our visual observations of a clear and homogeneous sample. Also, the AFM images show no evidence of large, microscale aggregates or bundles of the nanofibrils.

Closer examination of Figures 3 and 4 using AFM Nanoscope image analysis software shows that the minimum diameter size of the nanofibrils observed by AFM is around 10 nm, and the maximum is around 100 nm. Figures 3 and 4 are the typical AFM results. Mostly, the diameter sizes are very close, but AFM software reveals subtle differences. In the 1 wt % DBS sample (Figure 3), we find that the average diameter of the nanofibrils is around 20 nm. On the other hand, in the 2 wt % DBS sample (Figure 4), the nanofibrils measure about 30 nm in diameter on average. (The average diameters were obtained by averaging at least five measurements of different nanofibrils.) Thus, the nanofibrils are slightly thicker at the higher DBS concentration, and similar results have been observed before for DBS fibrils in certain solvents using electron microscopy.[24] The increase in diameter is probably due to the lateral bundling of primary nanofibrils into higher-order aggregates. The results imply an ability to control nanofibril size through the system composition, which can be particularly useful for reverse templating studies (see below).

Template Extraction and Analysis of Porous Polymer. Finally, we attempted to extract the DBS fibrils from the polystyrene so as to create a porous polymer having pores in

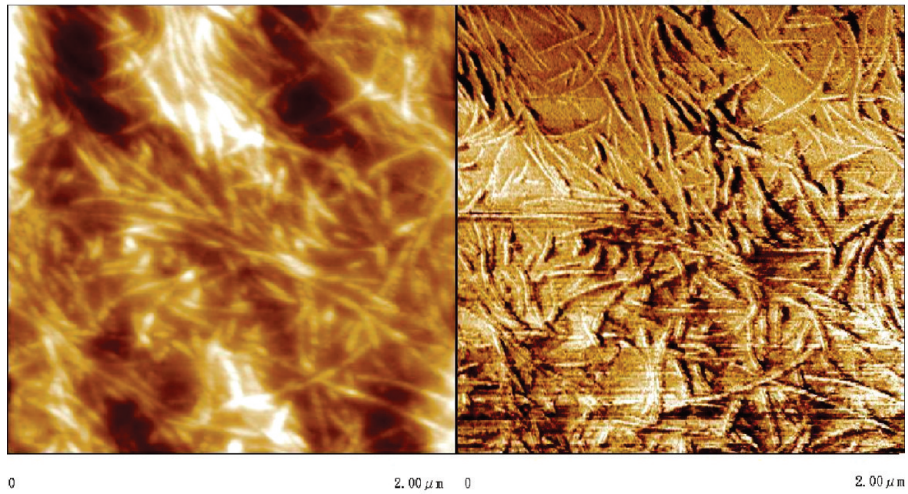

Figure 3. AFM height and phase images in 2 μm × 2 μm areas of the polymerized sample with 1 wt % DBS.

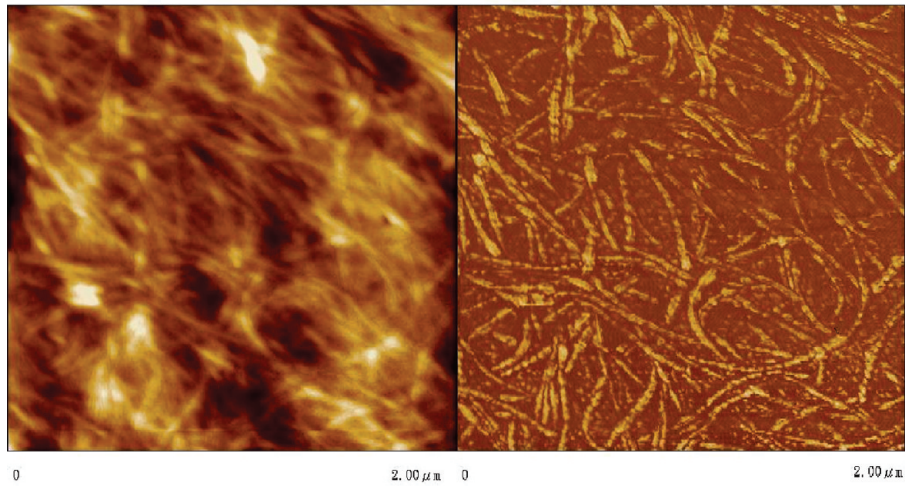

Figure 4. AFM height and phase images in 2 μm × 2 μm areas of the polymerized sample with 2 wt % DBS.

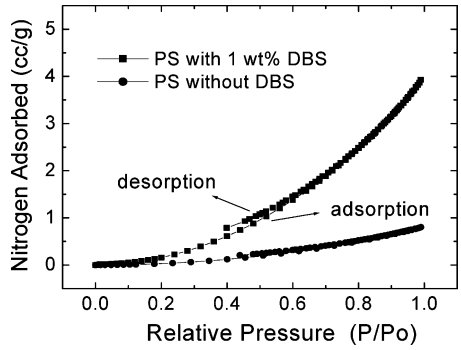

Figure 5. The adsorption−desorption hysteresis loops of polystyrene without and with 1 wt % DBS.

the place of the fibrils. For this, we ground the polymer using a ball milling machine (Retsch, PM 100) and then immersed the ground polymer in warmed ethanol (50 °C) for 1 week, with the ethanol being changed every day. The DBS fibrils were expected to dissolve away upon contact with warm ethanol. The final powder was dried and sieved before characterization. To determine whether this material was indeed porous, we carried out adsorption−desorption experiments on it with nitrogen gas. The results are shown in Figure 5, and for comparison, we also ran a control, that is, a sample of polystyrene with no DBS and synthesized under the same conditions (including the washing and drying steps). The control polystyrene showed identical adsorption and desorption curves, which is typical of a nonporous material. On the other hand, a different behavior was seen for the PS-DBS material, which was made with 1% DBS followed by extraction of the nanofibrils. Here, the adsorption and desorption curves did not overlap and instead showed a hysteresis loop. Also, the amount of gas adsorbed was much higher for the PS-DBS sample compared to the control.

The specific surface area (S) was calculated by the following equation[29,30]

$$S = \frac{V_M \times N_A \times A_M}{M_V} \quad (1)$$

where V_M is the volume of monolayer, N_A is the Avogadro's number, A_M is the molecular area of an adsorbed N_2 molecule (16.2 Å^2),[29] and M_V is the gram molecular volume (22414 mL). V_M is obtained from the BET equation[30]

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_M} + \frac{(C-1)P}{(CV_M)P_0} \quad (2)$$

where P is the equilibrium pressure of adsorbent gas, P_0 is the saturated vapor pressure of adsorbent gas, V is the gas volume of adsorption in equilibrium pressure, and C is the constant related to the enthalpy of adsorption. A specified range of P/P_0 is chosen (0.05−0.2), and from the slope and intercept of the plot of $P/V(P_0 - P)$ versus P/P_0, the two constants V_M and C could be evaluated. From eqs 1 and 2, we were able to calculate a specific surface area, which was found to be 3.1 m^2/g. A corresponding calculation with the control gave a considerably lower value of about 0.5 m^2/g. These results are encouraging and suggest the feasibility of reverse templating with DBS to create porous polystyrene.

Conclusions

We have demonstrated an interesting method of using organogels to generate transparent polymer solids simply by polymerizing the liquid monomer and removing the gel fibers. Thermal-initiated polymerization was employed in this study because it required no special UV-exposure apparatus. Samples could easily be prepared in standard glass vials and heated. Moreover, this thermal-initiated polymerization resulted in highly transparent polymer solids retaining the organgogel's nanostructure. AFM results show that the DBS network consisted of nanofibrils measuring from 10 to 100 nm in diameter. Finally, porous polymer was obtained by leaching away the DBS fibrils, and the specific surface area of the polymer was characterized by the BET method.

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