Synthesis of a Nanoporous Polymer with Hexagonal Channels from Supramolecular Discotic Liquid Crystals**

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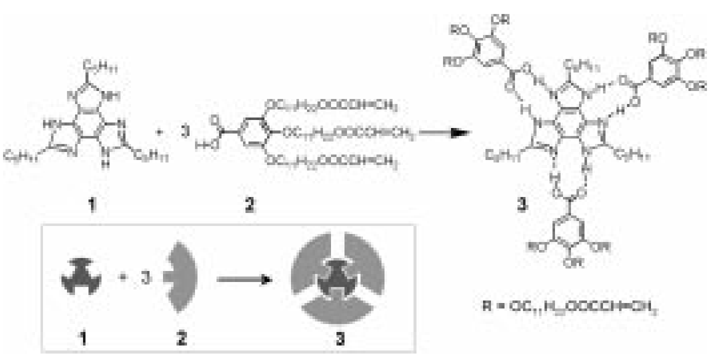
The design and synthesis of new materials with controlled nanostructures is a subject of intense research.[1, 2] Organic materials with ordered nanometer-sized pores have useful applications in such areas as separation and catalysis.[3] Recently, Gin and co-workers reported an elegant method for preparing nanoporous organic materials with regular channels that involved cross-linking amphiphilic monomers in lyotropic liquid crystalline phases.[4] They have also demonstrated that such materials are not only useful in preparing nanocomposites,[4d,e] but can also function as efficient heterogeneous catalysts.[4f,g]

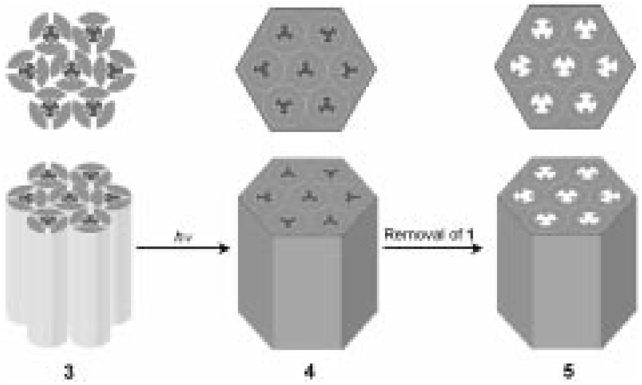
Our interests in discotic liquid crystals[5] led us to synthesize supramolecular liquid crystalline materials with hexagonal columnar mesophases that were self-assembled from long-chain alkoxybenzoic acids and a benzotri(imidazole) core through formation of intermolecular hydrogen bonds.[6] Based on this work, we now report a simple and novel way to prepare nanoporous organic materials with hexagonal channels. In this method, a large, flat organic core of a polymerizable supramolecular discotic liquid crystal serves as a template and the ordered channels are easily created by removing the template core after formation of a cross-linked polymer matrix. To the best of our knowledge, the synthesis of nanoporous materials by this route has not been investigated.

The benzotri(imidazole) core **1**[7] and polymerizable alkoxybenzoic acid **2**[4c] form a 1:3 supramolecular complex (**3**; Scheme 1) through hydrogen-bonding interactions. The complex **3** shows a thermotropic liquid crystalline phase from 23.0 to 74.7 °C on heating,[8] which has been confirmed by differential scanning calorimetry, polarized optical microscopy, and X-ray diffraction studies. The X-ray diffraction study of **3** by using synchrotron radiation reveals first and second diffraction peaks at 33.5 and 19.4 Å, respectively, with a reciprocal spacing ratio of $1{:}\sqrt{3}$. This ratio is consistent with a hexagonal columnar (Col_h) mesophase with a lattice constant (or an intercolumnar distance) of 38.7 Å. A diffuse halo is observed in the wide-angle region at $2\theta = 20°$ as a result of the liquidlike properties of the molten aliphatic chains.



Scheme 1. Supramolecular discotic liquid crystal **3** formed from **1** and **2**.

Irradiation of **3** in a liquid crystalline phase with UV light induces polymerization of the acrylate moieties at the termini of the alkoxy chains to give **4** (Scheme 2). About 70 % of the acrylate moieties in **4** are estimated to be polymerized, as judged by FT-IR spectroscopic analysis.[9] The cross-linked polymer **4** maintains the hexagonal columnar structure with essentially the same lattice constants (Table 1).



Scheme 2. Synthesis of nanoporous polymer **5** with hexagonal columnar channels from supramolecular discotic liquid crystal **3**.

Table 1. X-ray diffraction data of **3**, **4**, and **5**.

Compound	Temp.	*hkl*	d_{obs} [Å]	Mesophase parameter [Å]
3	60 °C	(100)	33.5	$a = 38.7$
		(110)	19.4	
		halo	4.4	
4	RT	(100)	33.4	$a = 38.6$
		(110)	19.3	
		halo	4.4	
5	RT	(100)	32.8	$a = 37.8$
		(110)	18.9	
		halo	4.3	

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Sonication of **4** in a mixture of methanol and 3 N HCl results in the removal of the benzotri(imidazole) core **1** from **4** to produce the porous polymer **5**. The removal of the benzotri(imidazole) core has been confirmed by ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy (Figure 1 a, b): the peak at $\delta = 118$ almost disappears and the intensity of the signal at $\delta = 150$ decreases substantially. The former peak corresponds to the central benzene core of **1** and the latter corresponds to the imidazole carbon atom, the chemical shift of which overlaps with that of the carbonyl carbon atoms of the benzoate group in **5**. The amount of extracted benzotri(imidazole) core **1**, as determined by UV/Vis spectroscopy, indicates that approximately 90% of the core is removed from **4**.

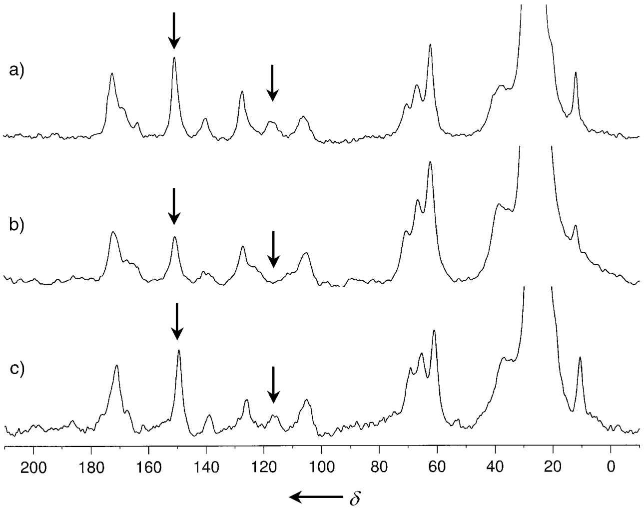

Figure 1. ^{13}C CP/MAS NMR spectra of a) **4**, b) **5**, and c) **4** reconstituted from **5** and **1**.

Most importantly, the de-cored polymer **5** shows an X-ray diffraction pattern nearly identical to those of **3** and **4** (Table 1), which indicates that **5** maintains the same hexagonal columnar structure. Each of the columns in **5** has a channel with an effective diameter of about 10 Å. The reconstitution of the core is achieved by incubating **5** in a solution of **1** for 24 h. The ^{13}C CP/MAS NMR spectrum of the reconstituted sample shows that intensities of the signals at $\delta = 118$ and 150 are almost identical to those in **4**. The amount of reincorporated **1** is estimated to be 70–80% of that in **4**. On the other hand, the tri-N-methylated derivative of **1** is only slightly incorporated into the channels of **5** under similar conditions.[10] These results suggest that the porous polymer **5** effectively recognizes the original template **1**.

We have performed preliminary gas permeability measurements to demonstrate the porous nature of **5**. The N_2 gas permeability constant measured for a membrane of **5** is approximately $2 \times 10^{-9}\,\mathrm{cm^2\,s^{-1}\,cm^{-1}\,Pa^{-1}}$, which is about four orders of magnitude higher than that for low-density polyethylene.[11] The high gas permeability confirms the porous nature of the film of **5**.[12] Further characterization of the pores in **5** by imaging techniques, such as transmission electron microscopy and atomic force microscopy, and by sorption experiments are in progress.

In summary, nanoporous cross-linked polymers with hexagonal columnar channels have been prepared by a new method that uses thermotropic supramolecular liquid crystals as templates. The size and shape of the channels as well as the functional groups lining the channels are expected to be controlled with carefully designed template cores. Helical channels with one-handedness may also be introduced.[13] Such nanoporous polymers with highly ordered channel structures may find useful applications in many areas including recognition, separation, catalysis, and synthesis of nanocomposites.

Experimental Section

3: Compounds **1** and **2** were synthesized according to the literature.[4c, 7] A mixture of **1** (80.9 mg, 0.198 mmol) in methanol and **2** (499 mg, 0.593 mmol) in $CHCl_3$ was stirred for 30 min. The solvent was then removed under reduced pressure. The residue was redissolved in $CHCl_3$ and the solution was stirred for 30 min. Evaporation of the solvent produced **3** in a quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.91$ (d, 7 H), 1.21–1.46 (m, 194 H), 3.21 (d, 4 H), 4.01 (d, 20 H), 4.10 (t, 18 H), 5.77 (d, 8 H), 6.08 (m, 8 H), 6.36 (d, 8 H), 7.37 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.41$, 22.78, 26.49, 29.02, 29.68, 29.79, 29.95, 30.02, 30.76, 38.01, 39.48, 65.12, 69.51, 73.87, 108.83, 120.98, 126.93, 129.03, 130.87, 142.59, 153.12, 166.76, 170.81, 171.80; IR (KBr): $\tilde{\nu} = 1729$ (C=O), 1636 cm^{-1} (C=C); MS (matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF)): *m*/*z*: 2939.1 [M^+].

4: Compound **3** was placed between two glass plates at 30 °C. This sample showed the characteristic texture of a columnar liquid crystalline phase. The sample was irradiated with UV light (365 nm) for 3 h to give a polymer film which was detached from the glass plates and washed with $CHCl_3$ and methanol to produce **4**. ^{13}C CP/MAS NMR (125 MHz) $\delta = 4.87$, 11.90, 24.23, 27.44, 38.05, 62.12, 66.75, 70.56, 105.92, 118.22, 127.49, 139.97, 150.33, 168.26, 171.95; IR (KBr): $\tilde{\nu} = 1728$ (C=O), 1637 cm^{-1} (C=C); elemental analysis (%) calcd for $C_{171}H_{270}N_6O_{33} \cdot H_2O$: C 69.51, H 9.36, N 2.83; found: C 69.11, H 9.32, N 2.65.

5: Compound **4** was soaked in a mixture of aqueous 3 N HCl (12.5 mL) and methanol (12.5 mL) and then sonicated for 9 h before washing with $CHCl_3$, methanol, and water to produce **5**. ^{13}C CP/MAS NMR (125 MHz): $\delta =$ 12.26, 27.28, 38.18, 62.12, 66.43, 105.45, 127.16, 140.53, 150.40, 171.60. The amount of **1** removed from **4** was determined by UV/Vis spectroscopy.

Reconstitution of the core in **5**: The porous polymer **5** after soaking in a 0.010 M solution of **1** in $CHCl_3$/MeOH (9/1) was shaken for 24 h at room temperature and finally washed with $CHCl_3$ and methanol. Reconstitution of the core was confirmed by ^{13}C CP/MAS NMR spectroscopy (see Figure 1 c). The core was removed from the reconstituted sample and quantified using the same procedure described above in order to estimate the amount of **1** incorporated into **5**.

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[10] Incorporation of **1** and its tri-N-methylated derivative (**1′**) into **5** was studied by soaking **5** in $CDCl_3/CD_3OD$ containing either one equivalent of **1** or **1′** in a sealed NMR tube. The amount of **1** or **1′** remaining in solution was monitored by ^{1}H NMR spectroscopy by using bromoform as an internal standard. About 40% of **1** was found to be incorporated into **5** after 40 h, whereas almost no **1′** was incorporated. Similarly, 1,3,5-benzenetricarboxylic acid, which is the right size to fit into the channels, is only slightly incorporated into **5**.

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Enantioselective Incorporation of Azobenzenes into Oligodeoxyribonucleotide for Effective Photoregulation of Duplex Formation**

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Various organic molecules have been introduced into oligodeoxyribonucleotides (ODNs) by means of linkers to provide new functionalities.[1] We already reported that the *cis* → *trans* isomerization of an azobenzene moiety in the side chain of ODNs could reversibly photoregulate the formation and dissociation of its duplex: a *trans*-azobenzene moiety in the ODN stabilizes the duplex, whereas the *cis* form destabilizes it.[2] By using this modified ODN as a modulator, a T7 DNA polymerase reaction could also be photoregulated.[3] For even more effective photoregulation, the change in melting temperature ΔT_m induced by the *trans* → *cis* isomerization should be enhanced. A promising strategy for this purpose is to introduce multiple azobenzene groups into the ODN. However, the modified ODN was previously synthesized from the corresponding racemic mixture of phosphoramidite monomers, which were obtained from a prochiral diol as starting material (Scheme 1 A). Thus, two diastereomers were inevitably produced.[4] Since their photoregulation capabilities are significantly different,[2a] the azobenzene moieties should be enantioselectively incorporated into the ODN for more effective photoregulation. With these racemic phosphoramidite monomers, it is practically impossible to synthesize diastereochemically pure ODNs containing multiple azobenzene groups, and hence the optically pure phosphoramidite monomer is essential.

We chose threoninol as the linker (Scheme 1 B) for two reasons: 1) optically pure diols can be synthesized from the corresponding D- or L-threonine, and 2) perturbation of the framework of our previous prochiral linker (Scheme 1 A) is minimized.[5] Both L- and D-threoninol were used as optically pure linkers, and two azobenzene moieties were enantioselectively introduced. It was shown that a D-threoninol-tethered azobenzene moiety induces much larger ΔT_m on photoisomerization than does an L-threoninol-tethered one.

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