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Templating Mesoporous Silica with Chiral Block Copolymers and Its Application for Enantioselective Separation

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In this paper we describe the synthesis of chiral mesoporous silica based on chiral block copolymers of poly(ethylene oxide) and of D-phenylalanine (PEO-*b*-D-Phe) as a surfactant template. The resulting porous structures are characterized by nitrogen sorption experiments, transmission electron microscopy, and small-angle XRD. It is shown that chiral block copolymers of PEO-*b*-D-Phe are effective as a surfactant template for the preparation of silica materials with highly ordered periodic mesoporous structures of hexagonal symmetry with a pore size of ca. 5 nm and high surface areas of ca. 700 m^2/g. The enantioselectivity feature of this porous silica, after the extraction of the chiral copolymers, was examined by selective adsorption of enantiomers and racemic solutions of valine. The selective adsorption was measured by circular dichroism (CD) spectroscopy. A chiral selectivity factor of 2.34 was found with the D enantiomer of valine adsorbed preferably.

Introduction

The discovery of the role of stereochemistry in chemistry goes back to the late 1850s, when Pasteur reported on the different destruction rates of dextro and levo ammonium tartrate by the mold *Penicillium glaucum*.[1] The interest in chirality and its consequences have increased during recent decades due to scientific and economic reasons.[2] Developing new and efficient methods to produce enantiomerically pure compounds is critical for the development of new materials, particularly pharmaceuticals, agrochemicals, and flavors.[3] Generally, chiral compounds are prepared either from available chiral starting materials generated during a reaction by asymmetric catalysis or by the chiral resolution of the enantiomers using various separation methods. Asymmetric synthesis[4] is, in principle, the most cost-effective method of producing single-isomer products. However, despite its obvious advantage, asymmetric synthesis has one limitation: namely, it gives high enantiomeric purity only for exceptionally enantioselective reactions. The resolution of isomers can be achieved by various processes[5] based on physical, chemical, and biological techniques. New chromatographic techniques[6] commonly based on the strategy of linking chiral compounds to a solid substrate, and using the resultant material to selectively bind one enantiomer, were developed recently. Chiral polymers[7,8] are used in several chiral applications such as nonlinear optical applications, chiral separations,[9] and molecularly imprinted polymers (MIPs).[10,11] We demonstrated recently the potential application of chiral double hydrophilic block copolymers[12] and chiral polymeric microspheres[13] to control chirality throughout crystallization, in particular for racemic crystals. One of the most common uses of chiral polymers is for the preparation of MIPs. In spite of the fact that molecular imprinting methods allow materials to be prepared with high affinity and selectivity for a given target molecule, some of these materials' limitations prevent their use in real applications. Such limitations are, for example, extensive nonspecific binding, slow mass transfer, low sample load capacity, and poor recognition in aqueous systems.

One way to overcome these limitations is to employ molecular imprinting methods for the preparation of chiral porous materials. Template-based approaches to the preparation of amorphous, nanoporous silicas is defined by Brinker et al.[14] as, "a central structure about which a network forms in such a way that removal of the template creates a cavity with morphological and/or stereochemical features related to those of the template". It is clear from this definition that template-based approaches can result in the formation of chiral nanoporous structures. For example, Alvaro et al.[15] used chiral binaphthyl precursors with TEOS for the preparation of optically active porous material that linearly rotate polarized light. Corma et al.[16] used chiral trialkoxysilane grafting onto mesoporous silica materials, forming a whole range of chiral catalysts.

In addition, there were recent reports on antibody-based bionanotube membranes for enantiomeric drug separation.[17] However, to the best of our knowledge, none of these systems was effective in chiral separation. More recently, a general method for chiral imprinting of sol−gel thin films exhibiting enantioselectivity was developed by Avnir's group. In a series of articles, Avnir et al.[18,19] showed that template molecules such as propranolol, 2,2,2-trifluoro-1-(9-anthryl)ethanol, DOPA, and tyrosine can be used to prepare a chiral imprint sol−gel matrix. The shape of the chiral matrix is maintained when the template molecule is extracted. Therefore, the porous materials formed

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are enantiopure; i.e., the cavity left inside the sol−gel films can discriminate between optical enantiomers. For instance, in a sample of an (*S*)-imprinted propranolol sol−gel thin film, the (*S*) film recognized (*S*)-propranolol better and the (*R*) imprinted film recognized better (*R*)-propranolol with a discrimination ratio of about 1.5. Similarly, TiO_2 thin films imprinted by chiral carboxylic acids were also reported, and enantioselectivity was observed.[20] A variety of other imprinting approaches for the preparation of chiral porous materials,[21−27] including polymers[28] and dendrimers,[29] was studied Although a variety of interesting and exciting approaches to the chiral synthesis of porous materials and the use of those materials for chiral separation have been reported, much more can still be accomplished.

In the current publication we describe the synthesis and application of well-ordered chiral mesoporous silicas templated by chiral block copolymers of poly(ethylene oxide) block (PEO) and blocks of chiral D-phenylalanine (PEO-*b*-D-Phe). Block copolymers, particularly double hydrophilic block copolymers, are a new class of amphiphilic polymers of rapidly increasing importance with unique and fascinating properties, potentially connecting materials science, pharmacy, biochemistry, and polymer science.[30−32] Their chemical structure may be adapted for a wide range of applications covering different aspects such as the stabilization of colloids, crystal growth modification, induced micelle formation, and polyelectrolyte complexing toward novel drug carrier systems. As the potential of this novel polymer class is still relatively unexplored, it can be expected that more applications will arise due to the possibility of adapting the chemical structure to either the desired substrate in contact with water or to the stimulus for the induction of structural changes. In this paper we describe the first application of chiral block copolymers as template surfactants for the synthesis of mesoporous silica. Furthermore, we demonstrate that chiral mesoporous silica could be applied for the enantioselective separation of enantiomers and racemic solutions.

Experimental Section

Preparation of Chiral Block Copolymers. The synthesis of the chiral block copolymers of amino acids was carried out by a method previously reported by Antonietti and co-workers.[33] The most frequently used route toward copolymers with polypeptide block segments is by the ring-opening polymerization of protected amino acid *N*-carboxyanhydrides (NCAs), initiated by an aminofunctional polymer.

Synthesis of the *N*-Carboxyanhydride (NCA) of D- or L-Phenylalanine. A solution of triphosgene (0.30 g; 0.0021 mol) in 30 mL of THF was added to a suspension of D- or L-phenylalanine (1 g; 0.0042 mol) in 10 mL of THF. The mixture was stirred for 3 h at 50 °C under argon atmosphere. After 1 h the suspension developed into a transparent solution, and the solvent was evaporated under reduced pressure. The product was crystallized from THF/*n*-hexane. The crystalline product was dissolved in 15 mL of cold ethyl acetate and washed with a cold solution of sodium bicarbonate in water (0.5%, 100 mL). The layer of ethyl acetate was isolated, and the solvent was evaporated under reduced pressure. The product was recrystallized three times in a mixture of THF/*n*-hexane and dried at room temperature under vacuum (yield 82%).

Synthesis of Copolymer Poly(ethylene oxide)-(*block*)-poly-(D-phenylalanine). A solution of the NCA of the phenylalanine (0.395 g; 0.0015 mol) in 5 mL of THF was added to a solution of α-methoxy-ω-amino-poly(ethylene glycol) (0.5 g; 0.0001 mol; M_w = 5000 g/mol) in 10 mL of THF. The mixture was stirred over 3 days at 40 °C under argon atmosphere. The solvent was evaporated under reduced pressure, and the product was dissolved in 2 mL of THF and precipitated in petroleum ether (or *n*-hexane) (yield 62%).

Preparation of Chiral Mesoporous Silica. Chiral mesoporous silica was synthesized using a chiral surfactant based on block copolymers of chiral phenylalanine and PEO as the template and TEOS as the precursor for silica. In a typical synthesis, the chiral block copolymer (1 mmol) was dissolved in deionized water (32 g) and stirred at room temperature. A volume of 0.1 M HCl (0.14 mmol) was added to the chiral block copolymer solution under vigorous stirring at room temperature. After the mixture was stirred for 1 h, 1.40 g of TEOS (0.14 mmol) was added to the solution and the mixture was stirred at 40 °C for 4 h. The mixture was allowed to react at 40 °C under static conditions for 20 h. The chiral mesostructured product thus formed was cured at 80 °C for an additional 24 h. The product was recovered by centrifugal separation and dried under vacuum. The extraction process for the removal of the chiral block copolymer was carried out by stirring the as-prepared material in a chloroform solution for 48 h at 40 °C. The solid material was washed three times with water, recovered by centrifugal separation, and dried under vacuum.

Experimental Techniques. Gel permeation chromatography (GPC) measurements were carried out using a SP-Thermo Separation Products chromatograph, consisting of a UV detector (Model UV 100 at 254 nm) and with IR detector. Five milligrams of the dried polymer was dissolved in 1 mL of chloroform. Then 20 μL of the chloroform polymer solution was injected into the GPC column. Samples were eluted acetate buffer: pH 7, T = 25 °C through a 4 × HEMA-BIO column (10^4 Å pore size) at a flow of 1 mL/min. The molecular weights were determined relative to standards of PEO (Sigma Aldrich) using a Winer-286 computer program.

We used a Bruker AXS D8 Advance diffractometer (using Cu Kα λ = 1.5418 Å radiation) operating at 40 kV/40 mA, with a graphite reflected beam monochromator and variable divergence slits for powder X-ray diffraction analysis. Data were collected from 0.5 to 5° (2θ) with a resolution of 0.02°. Transmission electron microscopy (TEM) images were acquired on a JEOL 840 instrument at an acceleration voltage of 200 kV. We performed Fourier transform infrared (FTIR) measurements with a Varian spectrophotometer at room temperature with KBr pellets. The surface area was measured at 77 K (liquid nitrogen) on a Micromeritics instrument (Gemini 2375) after the samples had been evacuated at 120 °C for 12 h. From the adsorption isotherm, the Barrett, Joyner, and Halenda theory (BJH) was used to calculate the mesopore volume and its size distribution. NMR spectra were measured on a Bruker DXP 300 MHz spectrometer. Circular dichroism measurements were carried out with a Jasco J-715 spectrometer (Model 6025) using a cylindrical quartz cell (0.1 mL) at room temperature. Thermogravimetric analysis (TGA) measurements were performed with a ThermoONIX Gaslab 300 thermogravimetric analyzer. Light scattering measurements of the block copolymers were performed at room temperature with a Coulter N4Plus dynamic light scattering instrument.

Results and Discussion

In this study we prepared and employed a chiral polymer based on a PEO (M_w = 5000g/mol) block and a block of D-phenylalanine. The synthesis of the chiral block copolymers was carried out by previously reported methods.[33] The reaction sequence for the preparation of chiral block polymer is shown in Scheme 1. In general, the chiral block copolymers were

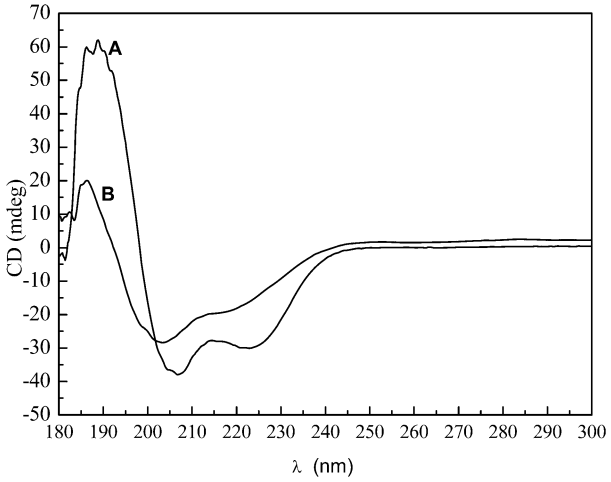
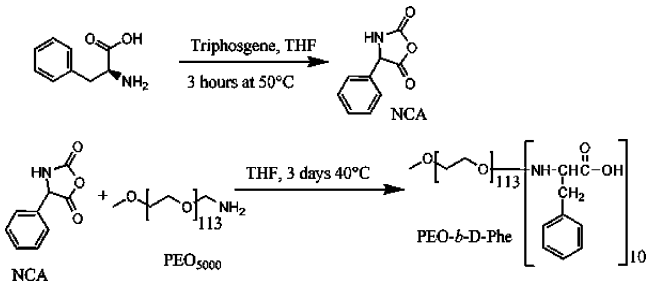


Figure 1. Circular dichroism of block copolymers PEO_{113}-*b*-D-Phe_{10} at (A) pH 2.0 and (B) pH 5.5.

SCHEME 1: Synthesis of Block Copolymer of Poly(ethylene oxide)−D-Phenylalanine (PEO-*b*-D-Phe)



synthesized via the ring-opening polymerization of D-phenylalanine *N*-carboxyanhydride monomer with α-methoxy-ω-amino-poly(ethylene glycol) as a macroinitiator.

The block copolymers were optically active and ^{1}H NMR, IR spectra, and elemental analysis confirmed their structures. Based on the ^{1}H NMR spectrum of the block copolymer and GPC analysis, the number of amino acid units in the block is calculated to be 10 on average. The PEO_{113}-*b*-D-Phe_{10} copolymers show a high polydispersity index (PDI) of ca. 1.47, mainly due to the broad distribution of the molecular weights of the polypeptide block. It should be mentioned that with the recently introduced organo nickel based initiating system bipy-Ni(COD)[34] and other transition metal complexes,[35] the NCA polymerization of block copolymers is much better controlled and produces well-defined polypeptides with a PDI < 1.2 compared to the method we used.

The block polymers were highly water-soluble in concentrations ranging from 0.1 to 0.5 mg/mL. The secondary structures of the chiral block copolymers in aqueous solutions were analyzed with circular dichroism (CD) spectroscopy. In Figure 1 the CD spectra of PEO_{113}-*b*-Phe_{10} at pH 2.0 and at room temperature are shown. In principle, synthetic peptides can adopt three main types of secondary structures: α-helix, *β*-sheet, and random coil. The structure depends on the measurement conditions, mainly on the pH, or the temperature. Overall polypeptide block length is important for the secondary structure; it is known that a peptide chain of at least 10 amino acids is necessary to allow formation of a α-helix. The CD spectrum of the chiral block copolymers PEO_{113}-*b*-Phe_{10} at room temperature and at pH 2 is shown Figure 1A. At this pH , the secondary structure of the chiral block copolymers was 80−85% α-helix and 10−15% random coil, as calculated according to the literature,[36,37] based on the two minima at λ = 209 and 222 nm. At pH 5 (Figure 1B) the secondary structure shows most probably a mixture of random coil structure (60%) and α-helix (40%). Thus, it seems that low pH values stabilize α-helix structure in our block copolymers, which agrees well with the behavior of other synthetic chiral copolymers such as in PEO−poly-(L-glutamic acid)[33] structures in water.

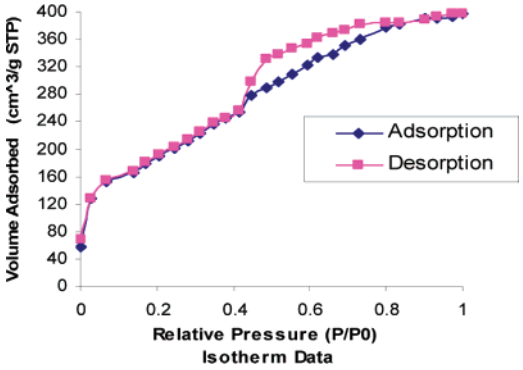


Figure 2. Nitrogen adsorption/desorption isotherm (BET) of chiral mesoporous silica (BET, 726 m^2/g, pore diameter 5 nm).

Finally, the micellar dimensions of the PEO_{113}-*b*-D-Phe_{10} copolymer in an aqueous solution and at pH 2 (2.5 mg/mL) were investigated by dynamic light scattering, and the formation of spherical micelles of diameter ca. 10 nm were observed. Overall, these results are in agreement with the behavior of a synthetic block copolymer of amino acid structures in water.[30,38]

Chiral mesoporous silica containing the chiral block copolymers was synthesized, as described in the Experimental Section. A key step in the synthetic procedure is the extraction of the chiral block copolymer surfactant. Generally, surfactant removal in the synthesis of mesoporous silica can be achieved either by solvent extraction or by calcination. In this work the chiral block copolymers were removed by solvent extraction by placing the samples in a chloroform solution for 48 h at 40 °C. To ensure the full removal of the chiral block copolymer surfactant, the IR spectra of the chiral polymer material and of the silica after extraction were measured. In Figure S1 (see Supporting Information) we present the results of these measurements. The IR spectrum of the chiral polymer reveals three absorption peaks at 3300, 1690, and 1100 cm^{-1}. The absorption bands are assigned to the Ar−H, amide−C═O, and N−H, C−N, stretching vibrations of the block copolymer, respectively. These absorptions disappear after the extraction process, as evidenced in Figure S1. The IR data clearly demonstrate that the extraction process successfully removes the surfactant molecules from the pores.

This result was further substantiated by BET measurements. Nitrogen adsorption−desorption isotherms were measured for the as-prepared and the extracted materials. The nitrogen physisorption isotherm of the chiral mesoporous product is shown in Figure 2. It reveals a typical type IV isotherm with a hysteresis, which is characteristic for mesoporous silica templated by block copolymers. Specific surface areas of 261 and 726 m^2/g were measured for the as-prepared and the extracted materials. Pore diameters of 5 nm were calculated from desorption branch of the BET (see Figure S2), which are consistent with estimations based on high-resolution (HR) TEM images.

To ensure the full removal of the chiral polymer via the solvent extraction process, we also performed thermogravimetric and elemental analysis measurements on the extracted chiral silica. The results of the elemental analysis measurements showed no indication of the presence of carbon (ca. 1% carbon),

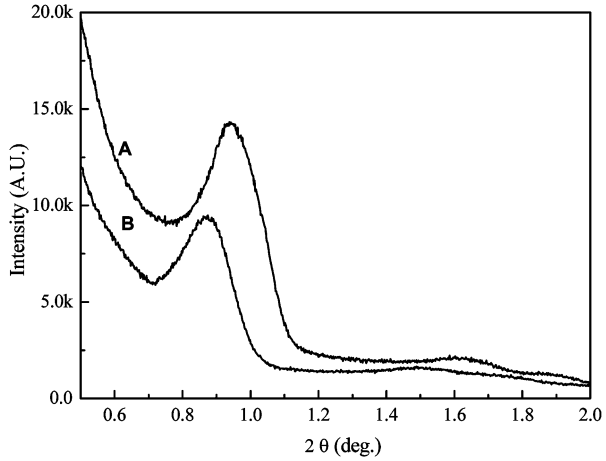


Figure 3. Powder small-angle X-ray scattering patterns of mesoporous silica (A) after removal of the copolymer and (B) the as-prepared material.

proving the full removal of the chiral block copolymer. Figure S3 presents the thermogravimetric analyses of the porous silica obtained after polymer removal, showing approximately 18% weight losses in a temperatures range of 50−130 °C which is associated with the loss of water. No other weight losses at higher temperatures up to 500 °C that could be attributed to loss of carbon residues were observed.

The bulk structure of the mesoporous chiral silica was characterized by small-angle X-ray diffraction. Small-angle X-ray diffraction patterns of as-synthesized chiral mesoporous silica before and after extraction are shown in Figure 3. The powder X-ray diffraction pattern of the chiral mesoporous silica exhibits three sharp reflections in the low-angle region ($2\theta < 2°$), indicating a high degree of mesostructural order. The diffraction patterns of the extracted sample exhibit stronger intensities than the corresponding peaks of the as-synthesized material. This is due to the enhanced contrast in the electron density after the removal of the polymer surfactant from the matrixes. The low-angle XRD patterns of the as-prepared chiral silica (Figure 3A) show one intense diffraction peak at $2\theta = 0.878$, indexed to a (100) plane, and two well-resolved weak diffraction peaks at $2\theta = 1.523$ and 1.865, corresponding to (110) and (200) planes. The extracted sample displays three well-resolved peaks at $2\theta = 0.943$, 1.630, and 1.912, indexed as 100, 110, and 200 reflections, based on the two-dimensional hexagonal *p6mm* unit cell, indicating that this mesoporous silica has a highly ordered hexagonal structure and that the crystallographic ordering of the mesoporous is retained on extraction. However, the slight shift of the diffraction peaks of the extracted materials toward larger 2θ angles indicates a slight shrinkage of the cell dimension.

The nanoscale structure of the chiral porous silicas was characterized using HR-TEM. Typical micrographs of the porous silica are shown in Figure 4. The micrographs clearly show that the structure consists of spherical pores of ca. 5 nm in diameter, arranged in a highly hexagonal fashion. It assumed that this diameter corresponds in a first approximation to the size of the collapsed spherical chiral block copolymers' micelle. It is worth mentioning that the pore structure is obviously continuous and also supported by BET measurements, which are not evident from the simple TEM picture of the template consisting of packed spheres.

The structural homogeneity of the periodic chiral mesoporous material was investigated by ^{29}Si MAS NMR. A typical ^{29}Si MAS NMR spectrum of a solvent-extracted chiral mesoporous material is shown in Figure S4. The ^{29}Si MAS NMR spectrum exhibits three characteristic peaks. As shown in Figure S4, the resonance lines representing Q4 (siloxane, (SiO)4Si), Q3 (single silanol, (SiO)3SiOH), and Q2 (geminal silanol, (SiO)2Si(OH)2) silicons are observed in their usual spectral positions. The absence of addition peaks indicates the successful extraction of the polymer.

In summary, we conclude that chiral block copolymers of PEO_{113}-*b*-D-Phe_{10} are effective for the preparation of mesoporous silica materials. It was shown that they are highly ordered, periodically mesoporous structures with a pore size of ca. 5 nm and specific surface areas in the range of 700 m^2/g. The mesoporous structure was obtained under acidic conditions using a chiral block copolymer as a supramolecular structure-directing agent.

In the next stage we examined the chiral recognition ability of our chiral mesoporous silica. We chose DL-valine, a small chiral molecule, as a representative case to demonstrate the chiral recognition ability of the mesoporous silica. DL-Valine is used to probe the specific chiral interactions with the surface chirality of the imprinted mesoporous silica due to the similarity of the valine, in terms of polarity, hydrophobicity, and acidity, to the chiral template molecule. In general, chiral binding and selectivity of enantiomers to chiral mesoporous silica can be tested with various analytical tools such as fluorescence analysis and isothermal titration calorimetry (ITC).[39,40]

In this work, we selected circular dichroism (CD) spectroscopy as the method for exploring the chiral recognition of our chiral silica. We performed selective chiral adsorption measurements of enantiomers and also of racemic solutions of valine. The evaluation of the amount of adsorbed molecules onto the chiral mesoporous silica was determined by circular dichroism (CD) spectroscopy. Adsorption measurements were carried out as follows: aqueous solutions of 300 mmol of the L or the D enantiomer were prepared and their optical activities were measured. To both solutions, 2 mg/mL chiral silica (after chiral copolymer extraction) was added and the optical activity of the solutions was probed as a function of time. The adsorption dynamics curve of the valine enantiomers is shown in Figure 5. As can be seen from this figure, the amount of the adsorbed valine *Q* (in millimoles per gram of the chiral silica) increases rapidly during the first 4 h in both enantiomers. In the second stage (4−16 h) the rate of adsorption decreases progressively and reaches a maximum value at 16 h. After that, the system reaches an equilibrium state with equal rates of adsorption and desorption, while *Q* remains constant. A comparison of the adsorption measurements for the L and D enantiomers clearly demonstrates a stereoselective uptake of the enantiomers by the chiral silica, which displays a significant difference in the adsorption kinetics of the enantiomers. For example, after 8 h, approximately 160 mmol of D-valine was adsorbed, while at the same time 65 mmol of the L-valine was adsorbed. Overall, the chiral silica recognizes D-valine better than it recognizes L-valine. Based on equilibrium concentrations for L and D enantiomers, an equilibrium discrimination ratio of 2.39 is calculated. This enantioselectivity value is reasonable and suffices for carrying out successful enantiomeric separation.[41]

In a similar manner, we also performed chiral adsorption measurements of alanine enantiomers onto the chiral silica. Generally, the adsorption kinetics and the chiral resolution factor of alanine enantiomers are very similar to those of valine. From the above results of the adsorption measurements on chiral silica, we can deduce two important conclusions. First, it is demonstrated that the templated cavity is able to recognize the chirality

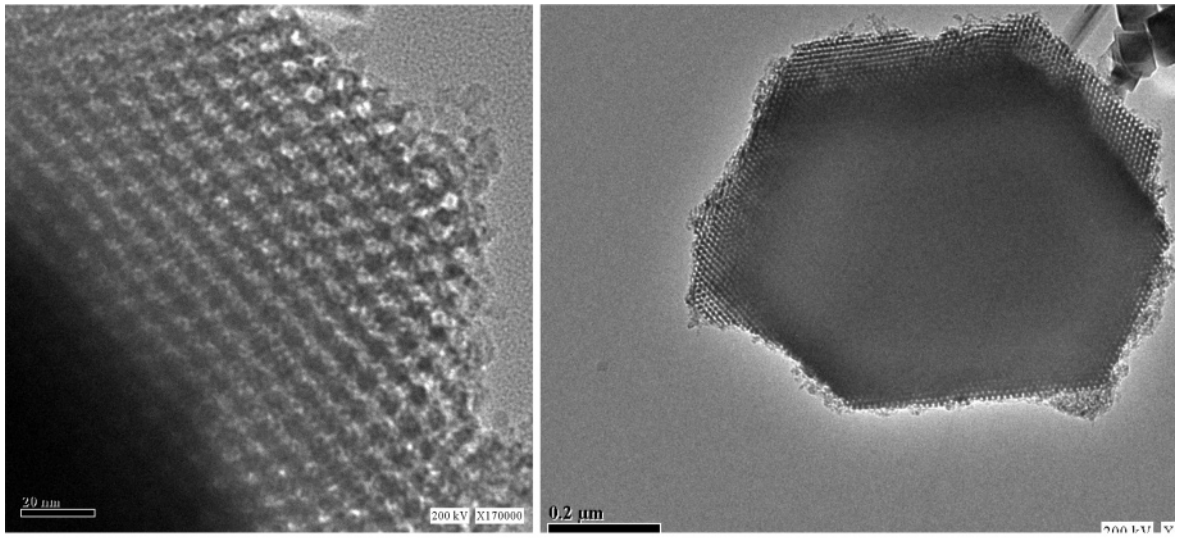


Figure 4. TEM images: (A) high resolution (B) low resolution of chiral silica made from PEO_{113}-*b*-D-Phe_{10} after chiral copolymer extraction. The light area corresponds to the pores, while the dark area corresponds to the walls.

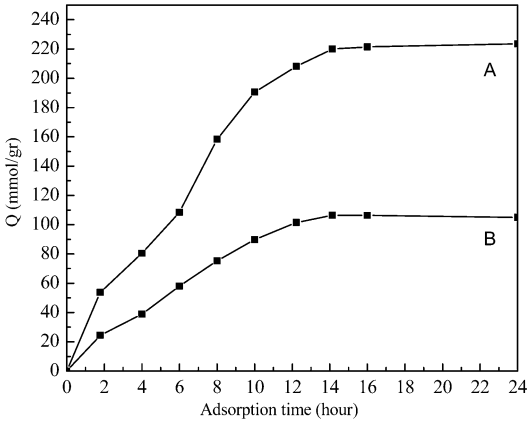


Figure 5. Curve of adsorption dynamics from a solution of valine enantiomers into the chiral-imprinted silica: (A) D-valine and (B) L-valine.

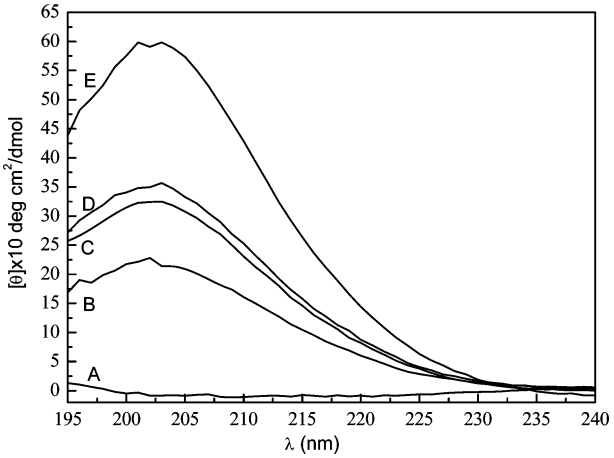


Figure 6. CD spectrum of a DL-valine solution with chiral silica as function of time: (A) 1, (B) 4, (C) 8, (D) 12, and (E) 16 h.

of various molecules having a different chirality from that of the templating molecule. Another interesting observation is that the chiral-imprinted silica also adsorbs enantiomers with a chirality opposite that of the templated molecule. Although the nonspecific adsorption is far lower in comparison with chiral specific adsorption, it still indicates the presence of nonchiral sites. It is clear that, due to the amorphous nature of the silica, not all the binding sites are identical: the sites may, for instance, have domains with different accessibilities as well as nonchiral sites. In addition, the formation of nonchiral sites can result from the incompleteness of the silica monomer−chiral template association. It is obvious that some amount of the silica monomer is not associated with the chiral template, and as a consequence, only part of the chiral template added to the silica monomer mixture gives rise to selective chiral binding sites. It should be mentioned that the chiral silica preparation is different from that of the covalent chiral imprinting of polymers, where, theoretically, all of the template sites should be associated with a templated binding site. In general, the existence of nonochiral sites can explain the adsorption of valine and alanine enantiomers with the opposite chirality of the templated chiral block copolymer.

Finally, we performed chiral adsorption measurements of racemic solutions of valine to demonstrate the chiral resolution capability of the mesoporous silica. Solutions of 300 mmol of the racemic (DL) valine and 2 mg/mL chiral silica were mixed together, and the optical activity of the solution as a function of time was measured. The results of those experiments are shown in Figure 6. Analyses of the CD spectra verify high chiral discrimination of the chiral silica. The enantiomeric excess (ee, percent) of the solution increases with time, and at equilibrium, an ee of about 40% of the L enantiomer in solution is achieved. This proves that solid chiral silica is enriched with the D enantiomer; namely, the D enantiomer is preferentially absorbed to the chiral silica. The results demonstrate the high enantioselective discrimination of the chiral silica for the enantiomer pairs. However, in spite of the high enantiomeric excess of ca. 40% observed in our chiral silica, the kinetics of the molecular recognition process is very slow. For example, after 1 h a very low value of enantiomeric excess (ee of 5%) is detected and the maximum enantiomeric excess is attained after 16 h. This slow chiral resolution kinetics is the main disadvantage for technological applications. For most applications of specific molecular recognition, rapid chiral resolution kinetics is important. For example, in chemical chiral sensors the response time depends on the association rate between the chiral sensor and the target analyte. Furthermore, in chiral catalysis the binding kinetics will determine the maximum rate of the

chemical transformation, and in chromatographic separations it will influence the spreading of the chromatographic peaks. It is clear that improvements aimed at increasing the chiral binding kinetics will have a significant impact on the performance of our chiral silica and for its use in chiral separation techniques.

Conclusion

The impact of chirality on almost any chemical and biological process is well recognized and has significant ramifications in many fields of economic interest. Because of the increasing demand for enantiomerically pure compounds, efficient strategies for analytical and preparative separations of enantiomers are required. A number of new chiral separations based on the use of chiral porous silica materials have appeared in the field of chiral technology. Nearly all aspects of this technology, including synthesis, separation, and analysis, can benefit greatly from the use of chiral porous materials. In this work we have described the preparation of chiral porous materials and demonstrated their enantioselectivity property in the resolution of racemic solutions. We showed that chiral block copolymers based on a PEO block and phenylalanine are good surfactant templates for the fabrication of chiral mesoporous materials with high surface areas as well as narrow pore size distributions.

Chiral mesoporous silica has shown high enantioselectivity after the extraction of the chiral copolymers, as examined by the selective adsorption of valine enantiomers. The chiral resolution of a valine racemic solution was measured by CD spectroscopy, and a high enantiomeric excess of ca. 60% of the D enantiomer of valine was found. It is obvious that, besides the very high surface area, high capacity, and technical accessibility of these chiral materials, they should also exhibit higher mechanical and thermal stabilities than the molecularly imprinted polymers, and therefore could be used as stationary phases in chromatography. Therefore, it is clear that in the near future a variety of new approaches for chiral resolution based chiral mesoporous materials will be developed, and our work is part of the general trend in the development of this methodology.

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Supporting Information Available: FTIR, TGA, and MAS NMR spectrum of the chiral mesoporous silica after removal of the copolymer and pore size distributions of the mesoporous silica. This material is available free of charge via the Internet at http://pubs.acs.org.

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