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Pore-Filled Nanoporous Silica Colloidal Films with Enantioselective Permeability

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Abstract. We prepared nanoporous silica colloidal films whose nanopores were filled with polymer brushes containing chiral selector moieties in the side chains, or with a chiral polypeptide. Both types of polymers were grown inside the nanopores using surface-initiated polymerization and thus were covalently attached to the nanopore surface. We studied the enantioselective permeation in the resulting pore-filled films and found that they possess a relatively high enantioselectivity. Increasing the number of chiral selectors inside the nanopores and preventing through solution diffusion by pore-filling with polymers did not lead to increased enantioselectivity compared to that observed for silica colloidal films whose nanopores were surface-modified with a monolayer of chiral selectors. This suggests that the enantioselectivity depends solely on the energy difference between the enantiomer/selector complexes and that through solution diffusion plays a minor role in the transport of enantiomers, which occurs predominantly through site hopping.

Introduction

The ability to obtain enantiomerically pure compounds is of high importance in the preparation of new drug molecules.[1] Although advances in stereoselective synthesis provide new and efficient ways to obtain a desired enantiomer,[2] chiral separation of racemic mixtures[3] is still the most widely used industrial technique to produce single enantiomers. Despite their utility, these separation techniques, which include crystallization and chromatography, are labour, material and energy-intensive and are usually difficult to scale up. Membrane-based separations[4–8] provide an attractive alternative method for chiral separations. Chiral membrane separations of enantiomer mixtures are based on the difference in non-covalent binding energy between each enantiomer and a selector moiety,[9–11] or on the preferential inclusion into a cavity within a porous organic or inorganic material.[3]

Presently used enantioselective membranes[12–15] most often consist of a porous material supporting either a liquid phase containing chiral selector molecules, or carrying surface-bound selector moieties. The latter, much more robust enantioselective membranes contain selector moieties introduced by coating the pores with a thin layer of a chiral polymer,[16] by covalently grafting the selector to the membrane,[17–21] may be prepared as a porous polymeric films that incorporate chiral selectors,[22–24] or by molecularly imprinting a polymer.[25,26] Optically active polyelectrolyte multilayer membranes[27] and nanotube membranes surface-modified with antibodies[28,29] have also been shown to separate enantiomers.

For practical applications, chiral membranes should possess a high surface area, low mass transfer resistance, good mechanical strength and high selectivity.[30] In this respect, nanoporous silica colloidal membranes may provide an ideal medium for chiral separations. Indeed, silica colloidal crystals are formed via self-assembly of silica spheres into a close-packed face-centered cubic (fcc) lattice with a void fraction of 0.26[31] and contain ordered arrays of three-dimensional interconnected nanopores whose size can be controlled by changing the size of the silica spheres used to assemble the colloidal crystal, whose molecular flux remains significant even when the pore size is sufficiently small to impart chemical selectivity,[32] and whose surface can be easily modified through standard siloxane chemistry[33] to impart permselectivity.[34,35] Silica colloidal membranes can be prepared as thin films,[32] suspended,[36,37] and free-standing membranes.[38,39]

Earlier, we described[40,41] nanoporous silica colloidal films modified with a monolayer of chiral selectors.[42] These films exhibited good chiral selectivity, transporting one enantiomer of a pair up to 4.5 times more efficiently than the other, while maintaining a high molecular flux. We demonstrated that the transport in these films occurs via a facilitated mechanism,[28,29] with chiral selectors serving as fixed-site carries that allow enantiomers to hop from one selector to the next and thus cross the membrane.[43,44] The stereoselective non-covalent interactions between enantiomers and surface-bound chiral selectors result in higher binding energy for one enantiomer in a pair, leading to it being transported more efficiently across the chiral membrane (i.e. the enantiomer interacting stronger with surface-immobilized chiral selectors is transported with a higher rate).[40]

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In the present work, we explored silica colloidal films in which the entire nanopore space is filled with a polymer carrying multiple chiral selectors. As was demonstrated in our previous study,[41] the maximum coverage of monolayer chiral selector moieties on the surface of silica spheres was 6–8 molecules/nm^2. While the grafting density of a polymer is unlikely to exceed this number, the presence of side-chains containing chiral selector moieties may significantly increase the total number of the sites capable of chiral recognition on the surface of the colloidal, which in turn may lead to increased enantioselectivity. In addition, filling the colloidal nanopores with a polymer would prevent through solution diffusion across the membrane, which may further improve the selectivity.

We have chosen atom transfer radical polymerization (ATRP) to produce polymer brushes inside the nanopores since this technique has been widely used to grow polymer brushes covalently attached to various surfaces.[45–49] We demonstrated previously[48] that the growth of polymer brushes inside the pores of the colloidal crystal does not affect its lattice.

Results and Discussion

We designed and synthesized the methacrylic monomer **1S** (Figure 1) containing a chiral selector moiety based on the chiral selector that exhibited good selectivity in our previous studies.[40,41] In order to model the polymerization reactions that would take place inside the nanopores of a colloidal film we modified 200 nm silica spheres with chlorobenzyl ATRP initiator moieties (Figure 2) following the previously reported procedure (Scheme 1).[47] The surface coverage for the initiator was estimated as ca. 4 molecules/nm^2 based on the weight loss of 2 % measured by thermogravimetric analysis (Figure 3). The initiator-modified silica spheres were used in the surface-initiated ATRP of the chiral monomer **1S**.

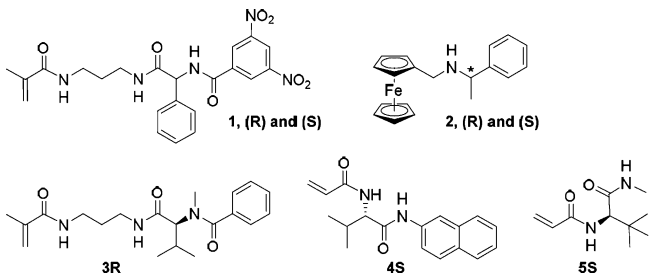


Figure 1. Chiral monomers used in ATRP modification of colloidal films and chiral probe used for cyclic voltammetry measurements.

The IR spectra of the polymer-modified silica spheres showed the C-H stretch in 3000–2800 cm^{-1} region, indicative of the polymer brushes on silica surface. The polymer brush was visible in the TEM images of the resulting particles (Figure 2), and its thickness after 25 min of polymerization could be estimated, by measuring the low density corona around the silica particles, as ca. 10 nm. The TGA analysis (Figure 3) of the poly(**1S**)-modified particles showed 16 % weight loss after 25 min of polymerization corresponding to the polymer brush thickness of ca. 12 nm.

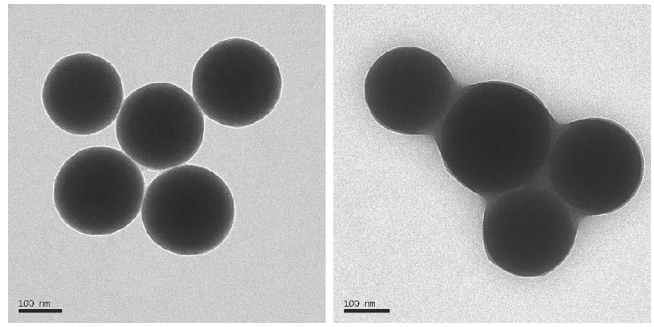
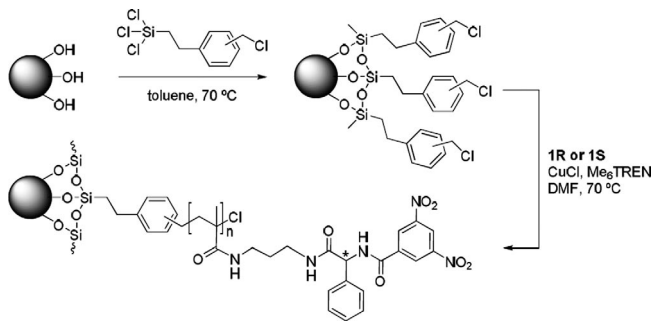


Figure 2. TEM images of initiator-modified SiO_2 spheres (left) and SiO_2 spheres with poly(**1S**) grown for 25 min. Scale bar = 100 nm.



Scheme 1. Preparation of chiral polymer-modified silica spheres by surface-initiated ATRP.

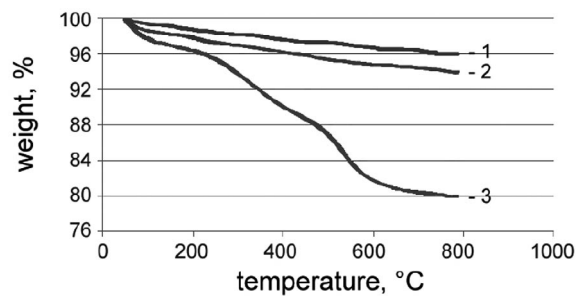


Figure 3. TGA of unmodified (1), initiator-modified (2) and poly(**1S**)-modified SiO_2 spheres with polymer grown by surface-initiated ATRP for 25 min (3).

The thickness of the polymer brushes was also measured as a function of polymerization time using dynamic light scattering (DLS). DLS measurements for silica spheres modified with the poly(**1S**) grown for 5 min gave the polymer brush thickness of 26 nm. A longer polymerization time (25 min) resulted in polymer brush thickness of 48 nm. The difference between the polymer thickness in solution (DLS) and in the dry state (TGA and TEM) suggests that the polymer chains are swollen in the solvent. This is important since polymer brushes can only be used for separations when they swell in the solvents used. For nanoporous colloidal films formed from 200 nm silica spheres, the distance from the centre of the pore projection to the nearest silica sphere surface is 16 nm. Thus, polymer chains allowed to grow for more than five minutes are expected to reach the length sufficient to completely fill the nanopores.

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To test the enantioselective permeability of polymer-modified nanoporous colloidal films, we modified the surface of silica colloidal films assembled on the surface of Pt electrodes with initiator moieties and conducted surface-initiated polymerizations of **1S** and **1R**. Based on the results obtained for surface-initiated ATRP in colloidal solutions, the polymerization time of twenty-five minutes was chosen for the pore-filling of the colloidal films. We believe that the moderate initiator surface coverage described above should lead to moderately dense polymer brushes,[50] which in turn should ensure that both the interior and exterior brush regions are accessible to the enantiomers permeating through the nanopores.

We found the resulting pore-filled films to be mechanically stable as was evidenced by our ability to use them repeatedly in various solutions without cracking or peeling from the glass support. Also, a significant effort was required to remove the films from the glass surface, thus suggesting that the polymerization worked as "chemical sintering" for the colloidal assemblies.

Cyclic voltammetry was used to investigate the enantioselectivity of the resulting pore-filled films by measuring the limiting current of the redox-active chiral probe **2** (Figure 1) for the electrodes carrying poly(**1R**)- or poly(**1S**)-filled colloidal films (Figure 4A), in a way similar to that used to investigate the enantioselectivity of colloidal films modified with monolayers of chiral selectors.[40,41] The enantioselectivity of the poly(**1R**)-filled colloidal films, defined as the ratio of the limiting currents for the S and R enantiomers of chiral probe **2**, was 2.2. This is similar to the enantioselectivity found for colloidal films modified with a monolayer of chiral selectors analogous to **1R**.[40] We observed a reversal of enantioselectivity when the chirality of the selector moieties attached to the polymer was changed from R to S (Figure 4B). A similar behavior has been observed previously for colloidal films modified with monolayers of chiral selector moieties,[40] which confirmed that similar phenomena are taking place once the pores are filled with polymers carrying chiral selectors in their side-chains. The selectivities of **1R**- and **1S**-modified colloidal films were somewhat different, a phenomenon that has been reported for chiral stationary phases used in liquid chromatography[51] and in our studies of chiral silica colloidal films.[40]

We repeated the above enantioselectivity experiments with several electrodes, obtaining semi-quantitative reproducibility in the absolute and relative changes between the different electrodes. Additionally, control experiments were conducted with electrodes carrying initiator-modified colloidal films and in all cases we observed no permselectivity, with both enantiomers of the chiral probe **2** diffusing through the colloidal film at the same rate, as illustrated in Figure 5. Thus, the observed enantioselective permeability can be attributed solely to the presence of the polymer chains carrying chiral selector moieties and filling the interstitial voids within the silica colloidal films and affecting the diffusion of the enantiomeric permeants.

In order to elucidate the mechanism of enantioselective transport within the colloidal nanopores filled with poly(**1S**), we studied the dependence of the selectivity and flux of the chiral probe **2** through the colloidal films on its concentration in the 0.1–18 mM range (Figure 6A). The molecular flux of permeants increased linearly with the concentration of the chiral probe until it reached ca. 5 *mM* (Figure 6B). Further increase in the probe concentration did not result in higher transport rates, while the enantioselectivity decreased. We can rationalize these observations in terms of the fixed-site theory of facilitated transport.[28,29,43,44] According to this theory, for the transport across the membrane by hopping between the fixed-site carriers high selectivity is to be expected at low permeant concentrations while at high concentrations saturation of the receptors occurs and the transport rate flattens, which corresponds to our observations. Our results also suggest that an optimal ratio of available chiral selectors to the concentration of the diffusing probe may exist. This ratio could be found with variation of the grafting densities or the brush lengths of the polymer modifiers to maintain low through solution diffusion without hindering the transport across the membrane.

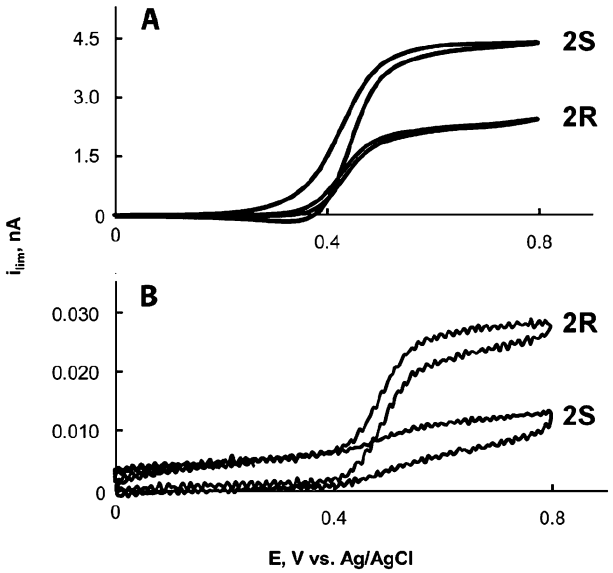

Figure 4. Overlay of the voltammetric responses of a Pt microdisk electrode carrying a colloidal film pore-filled with (A) poly(**1S**) and (B) poly(**1R**).

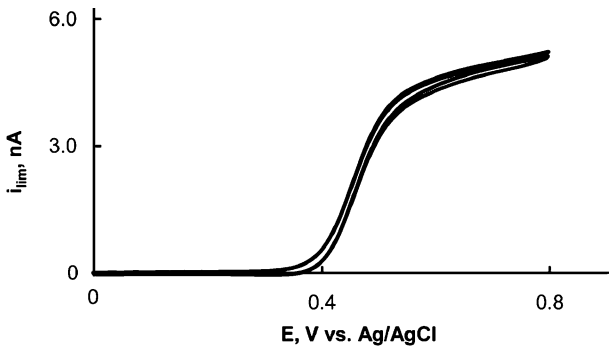

Figure 5. Overlay of the voltammetric responses of a Pt microdisk electrode for **2S** (black) and **2R** (grey) after modification of the colloidal film surface with ATRP initiator moiety 1-(trichlorosilyl)-2-[*m*/*p*-(chloromethyl)phenyl]ethane.

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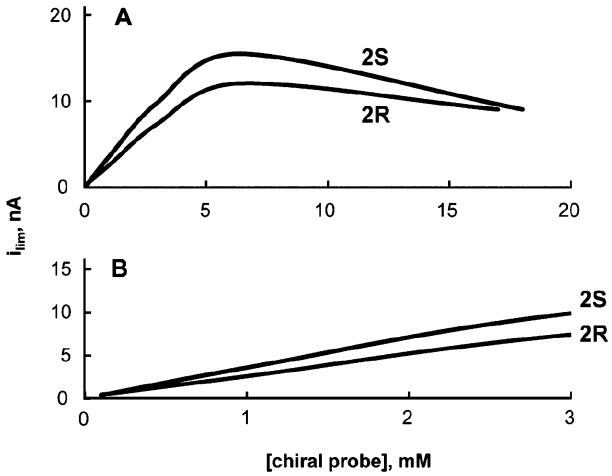


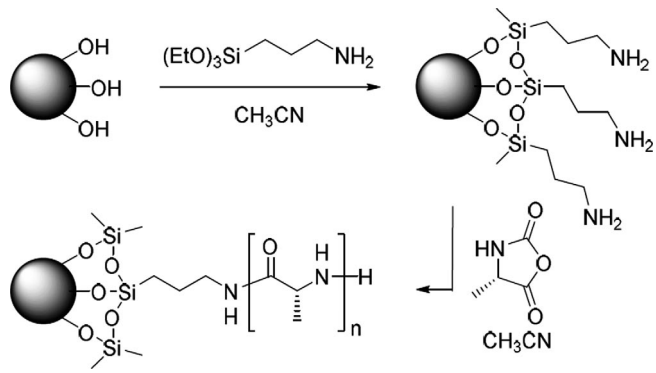
Figure 6. Limiting current of **2S** and **2R** for poly(**1S**)-modified colloidal films for (A) 0.1–18 mM and (B) 0.1–3 mM concentration of **2S** and **2R**.

The structure of the chiral selector moiety may have a significant effect on the enantioselective membrane permeability due to the variations in the strength of the non-covalent interactions between the selector and permeating enantiomers.[42] To test this notion for the pore-filled colloidal films, we prepared monomers **3R**, **4S** and **5S**, chosen as analogues of chiral selectors used in our earlier studies.[40,41] They formed polymer brushes on silica surface with thickness (Table 1) similar to that of poly(**1R**). Poly(**3R**)-filled colloidal films, most similar in structure to poly(**1R**)-filled films, showed a similar enantioselectivity, while poly(**4S**)- and poly(**5S**)-filled films showed a lower enantioselectivity, likely due to their reduced ability to interact via hydrogen bonding, van der Waals interactions and π–π stacking. Overall, these permselectivity values are comparable to those observed in monolayer-modified colloidal films,[40,41] antibody-modified nanotubes membranes,[52] and compare favorably to the results obtained for optically active polyelectrolyte membranes.[53]

Table 1. Thickness of polymers formed by ATRP on the surface of silica spheres measured by DLS, and enantioselectivity ($i_{lim(S)}/i_{lim(R)}$) obtained by cyclic voltammetry for pore-filled nanoporous silica colloidal films.

monomer	polymer thickness, nm	enantioselectivity
1R	48 ± 13	2.20 ± 0.04
1S	48 ± 13	0.55 ± 0.01
3R	87 ± 14	1.80 ± 0.03
4S	34 ± 9	0.83 ± 0.01
5S	93 ± 5	0.59 ± 0.05

Finally, we prepared poly(L-alanine)-filled colloidal films. This chiral polypeptide has been prepared on the surface of porous silica and used as a stationary phase for chiral HPLC separations.[54,55] The grafting of poly(L-alanine) on the surface of the silica colloidal films has been achieved by surface-initiated polycondensation of L-alanine *N*-carboxyanhydride from the aminated silica surface,[56] as shown in Scheme 2. Our previous studies of this polymerization reaction on silica spheres revealed that poly(L-alanine) brushes reach ca. 35 nm length after 1 hour of polymerization.[57]. Thus, we prepared poly(L-alanine)-filled colloidal films and studied their enantioselective permeability by cyclic voltammetry, as described above. Representative voltammograms for both enantiomers of the chiral probe 2 are shown in Figure 7. The poly(L-alanine)-filled colloidal films displayed a modest enantioselective permeability of ca 1.5, which could be attributed to the inherent chirality and hydrogen-bonding ability of the polymer and to the fractional helicity it can adopt on surfaces.[58]



Scheme 2. Preparation of poly(L-alanine) modified silica spheres.

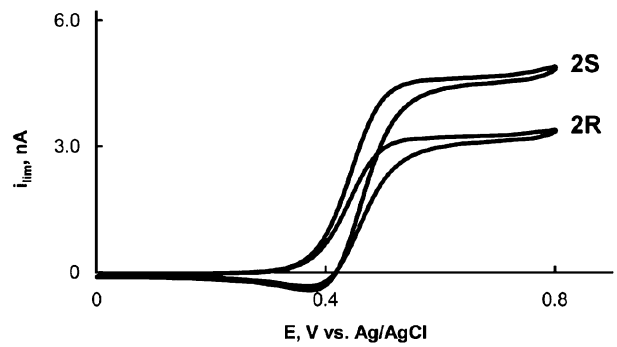


Figure 7. Overlay of the voltammetric responses of a Pt microdisk electrode for **2S** and **2R** after pore-filling of the colloidal film with poly(L-alanine).

Conclusions

We prepared nanoporous silica colloidal films pore-filed with polymers containing chiral selector moieties in the side chain, and with a chiral main chain. We used surface-initiated polymerization to prepare the polymers, which thus were surface-immobilized. Overall, pore-filled silica colloidal films showed enantioselective permeability similar to that of the colloidal films functionalized with a monolayer of chiral selectors. We did not observe significant differences in chiral selectivity for different chiral polymers. Thus, we conclude that the enantioselective permeability in pore-filed films depends solely on the energy difference between the enantiomer/selector complexes, which similar in monolayer- and polymer-modified colloidal films. While the capacity for chiral recognition within the polymer-filled colloidal films might have increased, the relative permeation rates for enantiomers remain the same.

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Moreover, although the interstitial space of the colloidal nanopores is filled with the polymer, dramatically reducing the possibility of through solution diffusion compared to the monolayer-modified colloidal films, the enantioselective permeability does not increase. This suggests that through solution diffusion plays a minor role in the transport of enantiomers, which occurs predominantly through surface hopping. Our observations are valuable for the future design of membranes for chiral separations, and for the optimization of enantioselective separations.

In present work, we used silica colloidal films deposited on glass-shrouded platinum microelectrodes in order to investigate the transport of enantiomers through polymer-modified colloidal nanopores. For the actual chiral separations, such films can be prepared on a porous support. Alternatively, free standing silica colloidal membranes[59] can be modified with chiral selector moieties for chiral separations of enantiomers.

The enantioselectivity of ca. 2 obtained for pore-filled silica colloidal films is moderately high but would require their use in a series of membranes in chiral separations to achieve high enantiomeric purities. We are presently working on increasing this selectivity by modifying the structure of chiral selector moieties present in the polymer side-chains, and on the preparation of free-standing chiral colloidal membranes.

Experimental Section

Materials and Characterization. All reagents were obtained from commercial sources except for Me_6TREN.[60] The preparation of compounds **1–5** and of L-alanine N-carboxy anhydride is described in Supporting Information. Solvents were dried following established procedures. All reactions were performed under the N_2 atmosphere. 18 MΩ·cm water was obtained from a Barnstead "E-pure" water purification system. Transmission electron microscopy (FEI Philips Tecnai T-12) and dynamic light scattering (PSS NICOMP 380/ZLS) were used for size characterization of the silica spheres. A Branson 1510 sonicator was used for all sonications. UV/Vis measurements were performed using an Ocean Optics USB2000 or USB4000 instrument. Thermogravimetric data were collected using a TA Instruments TGA 2950 Thermogravimetric Analyzer.

Preparation and modification of 200 nm silica spheres in solution. Silica nanoparticles were prepared following the literature procedure.[61] A solution of tetraethoxysilane (TEOS) in absolute ethanol was rapidly poured into a stirred mixture of ammonia and water in absolute ethanol at room temperature. The final concentrations of the reagents were 0.2 M TEOS, 0.4 M ammonia and 17 M water. The reaction mixture was stirred for 18 hours. The silica spheres were isolated by repeated centrifugation and resuspension in absolute ethanol. The diameter of the spheres was found to be 205 ± 6 nm using dynamic light scattering (DLS). Amine fictionalization of silica spheres was achieved by treatment with a solution of 0.056 M 3-aminopropyltriethoxysilane in dry acetonitrile at room temperature for 17 hours followed by centrifugation and resuspension in acetonitrile. The presence of amino groups was confirmed by treating the silica spheres with dansyl chloride, followed by fluorescence measurements, as described previously.[62]

Colloidal Film electrodes. Pt microdisk electrodes (25 μm in diameter) shrouded in glass were prepared by first attaching a 1.0-mm-diameter Cu wire (Alfa Aesar) to a 25μm-diameter Pt wire using Ag paint (DuPont). The Pt wire was then flame sealed in a glass capillary; the capillary was bent into a U-shape, and the middle was cut orthogonal to the length of the capillary with a diamond saw to expose the Pt disk. The resulting electrodes were polished with Microcut Paper disks (Buehler), from 240 to 1200 grit in succession, until the surface was free from visible defects. The colloidal films were deposited onto the Pt and the glass shroud by placing the electrodes vertically into 1.5 wt.-% colloidal solution of silica spheres in ethanol. The vials were placed under a crystallization dish and the solutions were allowed to evaporate for 3 days in a vibration-free environment.

General procedure for surface-initiated ATRP on silica spheres. The preparation of 200 nm silica sphere using a Stöber method has been described elsewhere.[40,41] A monolayer of ATRP initiators was introduced on the surface of these silica spheres by treating a suspension of the particles in toluene with 1.5 equivalents of (1-(trichlorosilyl)-2-*m*/*p*-(chloromethyl)phenyl]ethane). Following 18 h of stirring at 70 °C, the initiator-modified spheres were isolated via centrifugation, washed by 4 cycles of centrifugation and resuspension in toluene, methanol, dichloromethane and acetone in order to remove any adsorbed initiator, then dried in vacuo. The polymerization solutions were prepared as follows: CuCl (0.50 mg, 4.7 μmol) and Me_6TREN (3.2 mg, 14.0 μmol) were dissolved in anhydrous deoxygenated DMF (1.0 mL) and the mixture was sonicated for 3–4 min to facilitate the formation of the organometallic catalyst. In a separate vial, the chiral monomer (470 μmol) was added to a suspension of initiator-modified silica spheres (50 mg) in DMF (4.0 mL). The contents of both vials were degassed via four freeze/pump/thaw cycles and subsequently combined and sonicated to obtain a uniform suspension. The reaction mixture was then stirred at 70 °C and aliquots were taken after 5, 10, 15, 20 and 25 min. Polymer functionalized-silica nanoparticles were precipitated in methanol, washed with large amounts of methanol, distilled water and acetone then dried in vacuo. The resulting particles were then characterized using SEM, TEM and DLS in addition to TGA and IR spectroscopy.

General procedure for surface-initiated ATRP in colloidal films. The preparation of colloidal films via vertical deposition of 200 nm silica sphere on the surface of platinum microdisk electrodes has been described elsewhere.[40,41] A monolayer of ATRP initiators was introduced onto the surface of the spheres forming the colloidal film by immersing the electrodes in a 60 mM solution of 1-(trichlorosilyl)-2-*m*/*p*-(chloromethyl)phenyl]ethane in dry toluene. After 18 h at 70 °C the initiator-modified electrodes were soaked in dry toluene and acetonitrile to remove any adsorbed initiator and dried. The ATRP solution was prepared in a three-neck round-bottom flask by dissolving CuCl (0.50 mg, 4.7 μmol), Me_6TREN (3.2 mg, 14.0 μmol) and the chiral monomer (470 μmol) in dry degassed DMF (5.0 mL). Following further degassing by four freeze-pump-thaw cycles, initiator-modified colloidal electrodes were immersed in the solution and the reaction mixture was gently stirred at 70 °C for 25 min, after which they were thoroughly rinsed with DMF, acetonitrile and dichloromethane.

Surface-initiated polymerization of L-alanine in colloidal films. Silica colloidal films deposited on the surface of Pt microelectrodes were modified with primary amines by immersing them in a 56 mM solution of 3-aminopropyltriethoxysilane in acetonitrile for 17 h under gentle stirring. Following extensive rinsing and drying the amine-modified electrodes were immersed in a 4.7 μM solution of L-alanine N-carboxyanhydride in DMF (NCA:amine molar ratio of 1:10) under the nitrogen atmosphere. The reaction mixture was gently stirred at room temperature for 3 h after which the electrodes were rinsed with distilled water, soaked in dichloromethane and dried.

Cyclic Voltammetry Measurements. The flux of permeants across colloidal films was measured using a 2-electrode cell and an Ag/AgCl reference/counter electrode. A Par Model 175 Universal Programmer and Dagan Cornerstone Chem-Clamp potentiostat were used to conduct the measurements. All solutions were purged with N_2 to remove dissolved O_2. The voltammetric responses of the bare, colloidal film-modified, and pore-filled colloidal film-modified Pt electrodes were measured in 1.0×10^{-3} M dichloromethane solutions of the (*R*) and (*S*) enantiomers of compound **2** using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as supporting electrolyte. Measurements were conducted with several electrodes to test the reproducibility in the absolute and relative changes in limiting current.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of compounds **1–5**.

Acknowledgments

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