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Published on Web 02/04/2005

Enantioselective, Chirally Templated Sol−Gel Thin Films

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Abstract: Enantioselective surfactant-templated thin films were fabricated through the sol−gel (SG) process. The enantioselectivity is general in the sense that it discriminates between pairs of enantiomers not used for the imprinting process. The chiral cationic surfactant (−)-*N*-dodecyl-*N*-methylephedrinium bromide (**1**) was used as the surfactant template, and after its extraction chiral domains were created. The chiral discriminative feature of these films was examined by challenging with pure enantiomer solutions for rebinding. Selective adsorption was shown using (*R*)- and (*S*)-propranolol, (*R*)-**2** and (*S*)-**2**, respectively, and (*R*)- and (*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol, (*R*)-**3** and (*S*)-**3**, respectively, as the chiral probes. The selective adsorption was measured by fluorescence analysis, and the chiral selectivity factors were found to be 1.6 for **2** and 2.25 for **3**. In both cases, (*R*)-enantiomer was adsorbed preferably. The resulting material was characterized by transmission electron microscopy, by diffraction, and by surface area measurements, and was found to be semicrystalline with short-range ordered domains (50 Å) of hexagonal symmetry.

1. Introduction

Recently, we reported the successful imprinting of sol−gel thin films with a variety of molecules,[1,2] including chiral ones. Thus, films that were imprinted with a specific enantiomer showed clear preference to its re-adsorption, as compared to the opposite enantiomer. Here, we move an important step forward and describe the preparation of thin films which are generally enantioselective, where the chirally imprinted cavities can discriminate between enantiomers of molecules not used in the imprinting process, and completely different from the imprinting one. Chirally templated thin films are important for biomedical studies, for chiral catalysis, and for evaluating enantiomeric excess. The approach we use follows the preparation of porous (derivatized) silica matrices by templating with high concentrations of a surfactant, which has been a major direction in recent materials science. Interest in these materials stems from the many demonstrated useful applications, including shape selective catalysis, molecular sieving, chemical sensing and selective adsorption.[3−13] Sol−gel methodologies emerged as the preferred route of synthesis of these materials because they entail mild reaction conditions and offer a wide selection of metal alkoxide monomers, with which one can tailor chemical functionalities to the final porous material. The resulting templated sol−gel matrix can be obtained in various forms: monoliths, ground powders, or thin films. The latter, the topic of this report, have been fabricated by dip- or spin-coating[14−16] and offer advantages, which originate from the submicrometer thickness, including fast diffusion and transport needed for sensing.

Successful attempts to template chiral cavities within silica were reported, beginning with Curti et al. in 1952,[17] who obtained 30% enrichment of the templating enantiomer, continuing, for instance, in the studies of Che et al.,[18,19] Jung et al.,[20−23] Katz et al.,[24] Kunitake et al.,[25] Markowitz et al.,[26] and

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10.1021/ja0454384 CCC: $30.25