immediately in the dark at room temperature (12 h). Crystals form as small lemon-yellow cubes in the case of **1** and as colorless cubes in the case of **2**. Elemental analysis and spectroscopic investigations were complicated by the presence of finely dispersed Sn metal in samples of the complexes and by their sparing solubility in organic solvents. For **1**: Yield 0.10 g, 19% (on the basis of 2-aminopyrimidine). Decomposition occurred at about 250°C to give a brown solid. IR (Nujol, NaCl): no N–H str; ^{119}Sn MAS-NMR (relative to $SnCl_2/D_2O$, 148.99 MHz, 8 KHz spin speed); $\delta = 353.7$ (Sn^{VI}, Sn(1)), -180.4 (Sn^{II}, Sn(2,3,4)); elemental analysis: calcd: C 27.9, H 2.3, N 19.6; found: C 25.5, H 2.2, N 17.3. For **2**: Yield 0.10 g, 19% (on the basis of 2-amino-5-methylpyridine). Decomposition occurred at about 150°C to give a brown solid. IR (Nujol, NaCl): no N–H str; elemental analysis: calcd: C 34.3, H 2.8, N 13.3; found: C 33.7, H 3.1, N 12.3.

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How Important is the Inert Matrix of Supported Enantiomeric Catalysts? Reversal of Topicity with Two Polystyrene Backbones[**]

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The development of efficient polymer-supported chiral reagents and catalysts has become an important research topic.[1, 2] This is a result of the advantages of heterogeneous systems for large-scale reactions and of the availability of new materials and methods provided by the advances in combinatorial chemistry.[3]

The preparation of these kinds of functionalized resins involves the immobilization of a modified chiral auxiliary in a polymeric matrix by grafting or copolymerization.[1–4] The role of the polymeric backbone is sometimes underestimated, but it is known that the chemical and textural properties of the polymer affect the efficiency of the supported species.[2] Therefore, important changes in the catalytic activity of a compound can be expected upon its immobilization. Although much less is known about the role played by the

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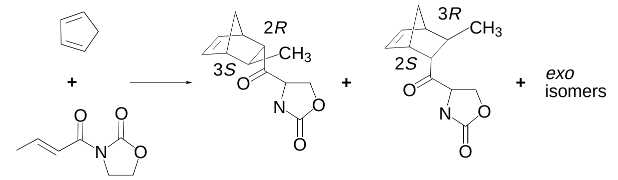
polymeric backbone in the stereochemical outcome of the reaction, the effects of immobilization can be important. A decrease in stereoselectivity, in particular enantioselectivity, is often obtained for polymeric reagents or catalysts. However, we have observed how the changes in activity associated with structural variations in the chiral auxiliary do not always follow the trends expected from solution studies.[5] Here we report on the preparation of monolithic columns containing enantioselective Ti-TADDOLate catalysts that show a very high stability, and on the first example, to our knowledge, of an even more drastic effect as seen by the reversal of topicity observed for a Ti-TADDOLate upon immobilization on two different polystyrene matrices.

Since the seminal work of Seebach and other researchers Ti-TADDOLates have become a very important and versatile class of chiral catalysts with application for a broad range of enantioselective organic transformations.[6] Recently, several groups, including us, have been involved in the preparation of polymeric Ti-TADDOLate analogues so that the advantages associated with the heterogeneous systems might be utilized.[7]

Initially, Ti-TADDOLates **6** derived from polymers **4** prepared by grafting of a modified TADDOL **1** (Scheme 1) onto a polystyrene–divinylbenzene (PS-DVB) matrix were used as catalysts in the Diels–Alder reaction of cyclopentadiene and 3-crotonoyl-1,3-oxazolidin-2-one [Eq. (1)]. In general, the reactions were nonenantioselective, except for those TADDOL derivatives bearing bulky aryl groups at the α positions (Table 1), which may be a consequence of the conformational restrictions imposed by these groups. The 2*R*,3*S* isomer was obtained as the major product using catalysts containing the 3,5-dimethylphenyl moiety at the α positions (entries 1–3), while Ti-TADDOLates containing other groups gave the 2*S*,3*R* isomer as the major product (entries 5–7) using catalysts containing the naphthyl group. This observation seems to be related to the presence of 3,5-dimethylphenyl groups at the α positions and an aromatic group in the 2-position of the acetal ring.[8]

Table 1. Results obtained for the Diels–Alder reaction (1) of Ti-TADDOLates considered in this work.

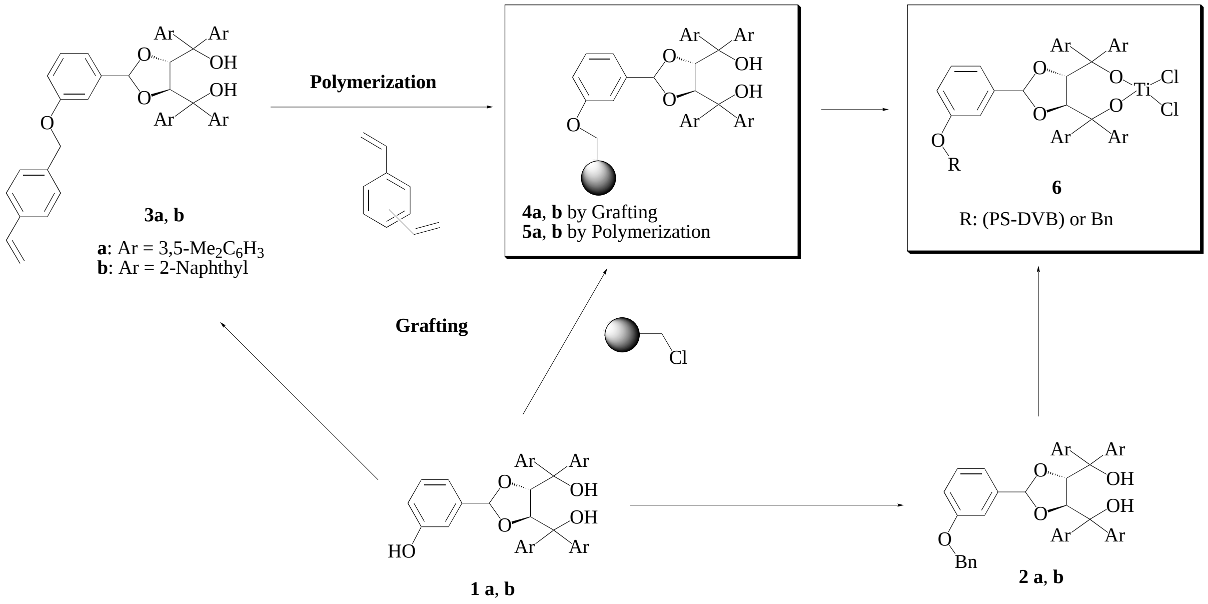


(1)

Entry	Starting TADDOL	Ar	Conversion [%]	*endo*:*exo*	*ee* [%]
1	**2a** solution	3,5-$(CH_3)_2C_6H_3$	100	71:29	38 (2*R*,3*S*)
2	**3a** solution	3,5-$(CH_3)_2C_6H_3$	99	82:18	3 (2*R*,3*S*)
3	**4a** grafting	3,5-$(CH_3)_2C_6H_3$	98	71:29	17 (2*R*,3*S*)
4	**5a** monolith	3,5-$(CH_3)_2C_6H_3$	100	80:20	18 (2*S*,3*R*)
5	**1b** solution	2-naphthyl	99	87:13	25 (2*S*,3*R*)
6	**2b** solution	2-naphthyl	96	74:26	61 (2*S*,3*R*)
7	**4b** grafting	2-naphthyl	50[a]	83:17	40 (2*S*,3*R*)
8	**5b** monolith	2-naphthyl	96	79:21	40 (2*S*,3*R*)

[a] Low conversion of the dienophile as a result of the total consumption of cyclopentadiene after 24 h.

In some cases chiral-supported catalysts prepared by the polymerization of chiral auxiliaries have been reported to give better asymmetric inductions than those prepared through grafting, particularly those catalysts with high degrees of cross-linking.[3, 5] We assayed this strategy using the vinylic derivatives **3** as the chiral monomers in order to improve the enantioselectivity obtained with our catalysts (Scheme 1). We carried out bulk polymerizations to obtain monolithic columns of **5** with appropriate porosity so as to avoid diffusion problems in the polymeric matrix.[9] These could act as stable, easily recoverable microreactors, that were even useful under continuous flow conditions. Different monomeric compositions (DVB/**3**), porogenic agents (1-dodecanol/toluene), and polymerization conditions were assayed. Other studies have described that the addition of toluene to 1-dodecanol in the



Scheme 1. Synthesis of homogeneous and heterogeneous TADDOL derivatives.

porogenic mixture generally results in the formation of smaller pores.[9] This effect was also observed by us.

Monoliths with the desired morphology and properties were obtained using a mixture containing 40 % of monomers (DVB/**3** 60/40, no styrene was used) and 60 % of the toluene/1-dodecanol porogenic mixture (9 wt % of toluene). The column prepared in this way using azobisisobutyronitrile (AIBN) as the initiator showed an average pore size of 1100 nm, which gave a back pressure of 47 psi for a 1 mL min^{-1} flow rate. The corresponding Ti-TADDOLate **6** was prepared from this supported TADDOL by reaction with $TiCl_2(i PrO)_2$. A titration of the excess of $TiCl_2(i PrO)_2$ used in this step, showed a quantitative loading of Ti in the monolithic column (0.4 mmol g^{-1}).

This polymeric Ti-TADDOLate showed an activity comparable to that found for related homogeneous and heterogeneous catalysts in the Diels–Alder reaction of cyclopentadiene and 3-crotonyl-1,3-oxazolidin-2-one. The activity of such catalysts can be maintained almost unaffected for several months, simply by keeping the monolithic column closed (under an argon atmosphere; Figure 1). This result clearly highlights the great potential of those materials for use in catalytic systems, especially if we consider that they allow reactions to be carried out in a column, and, accordingly, to proceed in a continuous flow system.

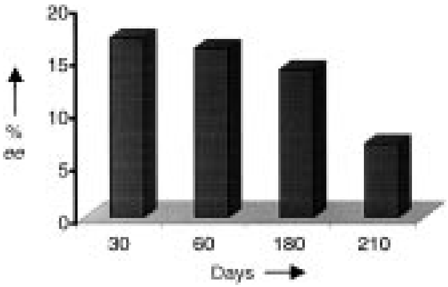


Figure 1. Time-dependent activity of the monolithic column derived from TADDOL **5a** as a catalyst in the Diels–Alder reaction [Eq. (1)].

One of the most remarkable observations was, however, that the major isomer obtained with the monolithic column was the 2*S*,3*R* isomer, instead of the 2*R*,3*S* isomer that was obtained with the grafted polymer **4a** as well as with the homogeneous analogues (namely, **2a** and **3a**).[10] Therefore, this reversal of topicity can be attributed to the polymeric matrix. This is the first example of a resin-supported enantioselective catalyst for which the morphology of the polymeric backbone determines the topicity of the resulting products. A simple explanation could be related to the introduction of some kind of main-chain chirality arising from the presence of the chiral monomer. Different approaches to the preparation of polymeric chiral reagents and catalysts using imprinted polymers or resins with main-chain chirality have been described.[11] However, this change in topicity is only observed for TADDOLates containing 3,5-dimethylphenyl groups at the α-positions. The use of TADDOLates **2b**, **4b**, and **5b** containing 2-naphthyl groups at the α positions gave much better enantioselectivities, but no change in topicity was observed (Table 1). Thus, what can be the reason for this specific behavior of polymer **5a**? The change in the TADDOL substitution could modify the level of chirality in the chiral main chain. On the other hand, the reversal in topicity is observed in homogeneous catalysis for TADDOLs containing the 3,5-dimethylphenyl moiety as a result of the presence or absence of a phenyl group in the 2-position of the acetal ring. This effect seems to be attributed to the existence of π-stacking interactions between this phenyl group and one of the 3,5-dimethylphenyl substituents.[8] Accordingly, polymerization of **3a** to form part of a very rigid, cross-linked matrix may increase the steric crowding in the close proximity of the acetal and make these π-stacking interactions more difficult, favoring the obtention of the 2*S*,3*R* cycloadduct. The situation will be different for polymers obtained through grafting procedures as more flexible networks are used and functionalization takes usually place at the more accessible lightly cross-linked regions.

Additional work is being carried out to better understand the reasons underlying this behavior and to obtain more examples of such a change in topicity. However, the present results clearly show the high potential of monoliths for the preparation of heterogeneous chiral catalysts and highlight the important role of the polymeric network in the course of the reactions. In our experiments, the presence of the polymeric matrix provided a way to drastically increase the stability of the Ti catalyst and, in one example, to induce a reversal of the topicity.

Experimental Section

Preparation of the monolithic polymer rods: TADDOL **3** (0.400 g) was dissolved in toluene (0.487 g). Then DVB (0.600 g) and 1-dodecanol (1.012 g) together with AIBN (1 wt % with respect to the monomers) were added to obtain a homogeneous solution. The polymerization mixture was purged with nitrogen for 3 min and poured into a mold. The stainless steel tubular molds were sealed at the two ends, and placed in a vertical position into a water bath. The polymerization was allowed to proceed for 23 h at 70 °C. The seals were removed and fittings attached to the tube before it was connected to a high-pressure pump. THF was pumped through the column at a flow rate of 1 mL min^{-1} to remove the porogenic solvents and any other soluble compounds.

General procedure for the Diels–Alder reaction (1) with polymeric catalysts obtained by polymerization: A solution of $TiCl_2(i PrO)_2$ was inserted in a syringe pump and passed in a continuous flow (0.6 mL h^{-1}, $V =$ 9 mL) through the monolithic column (previously washed with dry toluene for 1 h at 20 mL h^{-1}), then the column was washed with dry toluene (3 h, 20 mL h^{-1}) to remove the excess of titanium. A solution of 3-crotonoyl-1,3-oxazolidin-2-one and cyclopentadiene in dry toluene was loaded onto the monolithic column and the reaction mixture was maintained within the column for 24 h. The column was then washed with dry toluene to remove the products. The solvent was eliminated under reduced pressure, and the conversion, the *endo*/*exo* ratio, and the enantioselectivities were determined by ^1H NMR spectroscopy and chiral HPLC (Chiralcel OD).

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Polymeric Layers Catenated by Ribbons of Rings in a Three-Dimensional Self-Assembled Architecture: A Nanoporous Network with Spongelike Behavior

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The current interest in the crystal engineering of polymeric coordination networks[1] stems from their potential applications as zeolite-like materials[2] for molecular selection, ion exchange, and catalysis, as well as in the intriguing variety of architectures and topologies. Particularly attractive are the novel types of supramolecular intertwinings observed in these species, that still need a rational classification. According to Batten and Robson[3] an "interpenetrating framework" is comprised of motifs that are infinite and inextricably entangled, that is, they cannot be separated without breaking links. On this basis, we must exclude some interesting polymeric entanglements recently described, including polymeric catenanes,[4] infinite double helices,[5] two-dimensional clothlike warp-and-weft sheets,[6] and other noteworthy supramolecular architectures.[7] For "true" interpenetrating networks, however, different classes can be envisaged. The dominant type ("class A") is represented by 2D or 3D species that are comprised of a limited number of individual frames of equal topology that interpenetrate into an array with the same original dimensionality as in, for example, *n*-fold parallel interpenetrating hexagonal layers ($n \leq 6$) or diamondoid nets ($n \leq 9$).[3] Other types of interpenetration have been observed in coordination polymers that are reminiscent of molecular catenanes and rotaxanes. Some examples of polymeric catenated species are illustrated in Figure 1. In contrast to the class A interpenetrated nets, these examples all show the following features: 1) the constituent motifs have a lower dimensionality than that of the resulting architectures; 2) each individual motif is intertwined only with the surrounding ones and not with all the others, as "a ring in a chain"; and 3) the concept of "*n*-foldicity" cannot be used in the same sense as for class A.[13] We report here on a new member of this class of catenated motifs, **1**, obtained from the self-assembly of copper(II) sulfate and 1,3-bis(4-pyridyl)propane (bpp).

$[Cu_5(bpp)_8(SO_4)_4(EtOH)(H_2O)_5](SO_4)\cdot EtOH\cdot 25.5\,H_2O$ **1**

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