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Letter

A viable route to designable chiral macromolecular supports: implications for supported metal catalysis

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Abstract

Chemically and structurally designed chiral microporous matrices can be obtained upon aminolysis with enantiomerically pure amino acids of an activated ester functionality pendant from the backbone of precursor cross-linked copolymers.

Keywords: Chiral supports; Macromolecular supports; Metal catalysis; Supported catalysts

Enantioselectivity in metal catalysis can be achieved when the active metal centers are placed in a chiral environment in such positions that their reactivity can become enantiomerically discriminating. In homogeneous catalysis this condition is achieved when suitable ligands are present inside the metal co-ordination sphere. In heterogeneous catalysis either the active metal centers are dispersed inside a chiral support or the surface of the catalyst crystallites is allowed to adsorb a chiral substance (modifier) [1,2].

Although numerous chiral polymeric materials are currently utilized in chromatographic applications [3], they appear to have been only marginally utilized as supports in heterogeneous enantioselective catalysis ([1], see Ref. [4] for an example).

Matrices based on synthetic cross-linked polymers can be made chiral upon the attachment of low molecular weight chiral pendants. The procedures which have been mainly employed so far are based either on laborious reactions of chloromethylation of cross-linked polystyrene followed by functionalization or on the ring-opening reaction between chiral amino acids and the epoxy groups which are present in preformed resins obtained from glycidyl α,β unsaturated esters [3].

We report in this paper on a new, expectedly general strategy to chiral predesigned macro-

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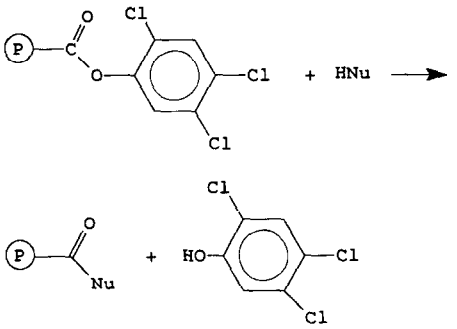
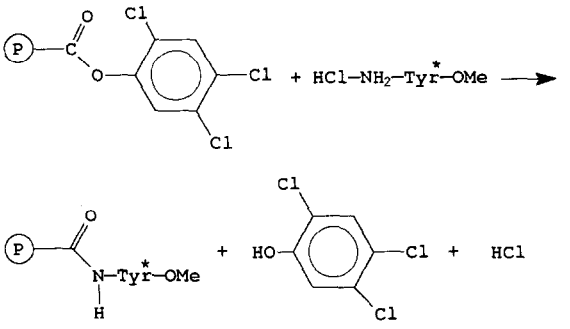


Scheme 1.



Scheme 2.

and microporous resins, which is based on the aminolysis with chiral amino acids of trichlorophenyl methacrylate repeating units.

The strategy stems from the seminal work of Arshady [5] who in the eighties provided convincing proof of its versatility in the preparation of lipophilic, hydrophilic, amphiphilic [6] multifunctional resins (Scheme 1), upon starting from *preformed* co-polymers containing ester functionalities featured by a good leaving group such as trichlorophenate.

It was clear to us that the proper choice of a chiral nucleophile could make reaction in Scheme 1 the way of access to a great variety of finely designable chiral matrices. In this communication we will illustrate the viability of reaction in Scheme 1 upon reacting a microporous poly-STY–TCPA–DVB resin (STY = styrene, 47%; TCPA = 2,4,5-trichlorophenyl acrylate, 50%; DVB = divinylbenzene, 3%) (molar percentages) with L and D-tyrosine methyl ester hydrochloride (**L1** and **D1**), Scheme 2.

P was prepared by γ-ray irradiation of a proper mixture of the monomers and the cross-linker up to ca. 100% polymerization yield [1] and then characterized with FTIR, SEM and elemental analysis. The strong ester ν_{CO} band at 1764 cm^{-1} is very useful for a qualitative record of the progress of the reaction in Scheme 2. This reaction is carried out in DMF at 40°C for 69 h. The conversion of **P** into **P-1L** was monitored by means of elemental analysis and FTIR [2] The 1764 cm^{-1} band almost completely disappears and is replaced by a composite one at 1650–1670 cm^{-1} (ν_{CO} amidic), and the ν_{CO} band of the incorporated methyl ester functionality is well evident at 1740 cm^{-1}. Remarkably, the functionalization degree of **P-1L**, as estimated from the percentage of the residual chlorine, fits with the IR observation and turns out to be 94.5%. Resin **P-1L** was carefully characterized by means of circular dichroism measurements. Unfortunately, although CD experiments are simple for soluble species, they pose serious sampling problems for insoluble materials [7–9]. However, we could obtain satisfactory results upon recording CD spectra of **P-1L** dispersed in KBr discs. Possible artifacts deriving from scattering phenomena were allowed for by averaging the signal upon rotation of the disc in a plane perpendicular to the incident beam. Indeed, the sign and intensity of the solid-state

[1] Resin **P** is prepared according to the basic suggestions contained in Ref. [4], but under γ-ray irradiation. The reaction mixture (STY, 3.75 g; TCPA, 4.00 g; DVB, 0.25 g; chlorobenzene; 5.60 g) is purged with nitrogen and exposed for 48 h to a ^{60}Co γ-ray source at a dose rate of 0.50 $Gy \cdot s^{-1}$, up to ca. 100% polymerization yield. The resin obtained, a colorless and rather elastic material, is washed several times with methanol and then shrunk with diethyl ether. The material is eventually crushed with an impact grinder, dried and sieved to 180 μm.

[2] Resin **P** (1.00 g) is added to a suspension of **L1** (2.32 g) in dimethylformamide (DMF, 5 ml). The slurry is kept under vigorous stirring for 69 h at 40°C, after which time the liquid phase is removed upon filtration. **P1-L** is washed with DMF (5×5 ml), methanol (5×5 ml), diethyl ether (5×5 ml) and eventually dried under vacuum. The yield of displacement of trichlorophenol was higher than 90%. The same procedure has been employed to prepare resin **P-1D**.

spectra closely reflect those obtained for L-Tyr–OMe in solution (Fig. 1).

In order to further check the success of the reaction in Scheme 2, we also synthesized matrix **P-1D**, for which satisfactory CD spectra could also be obtained (Fig. 1).

The internal (nanometric scale) morphology and molecular accessibility of **P-1L** was preliminarily investigated with ISEC (inverse steric exclusion chromatography) [10,11] in THF. This swelling medium has been chosen in view of the results of bulk expanded volume experiments. ISEC data are collected and depicted in Fig. 2. The structural information stemming from those technique is represented by the distribution in the swollen polymer mass of the volumes of a number of fractions of different density (Fig. 2). The volume of the swollen gel can be calculated from ISEC data as the sum of the volumes of each polymer fraction and in this case it turns out to be 2.7 ml · g^{-1}. This value is

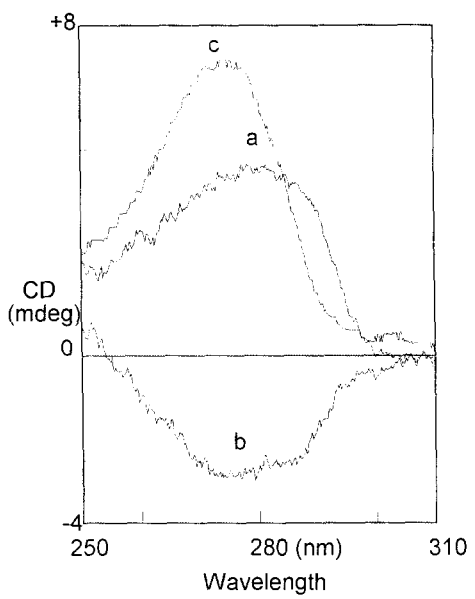


Fig. 1. CD spectra of resins **P-1(L)** (curve a), **P-1(D)** (curve b) dispersions in KBr discs at a polymer concentration of 10 mg/g KBr. The spectra are averaged over at lest 10 different radial orientations of each sample. The CD spectrum of L-Tyr–OMe in methanol solution (curve c, conc. 0.9 mM) is reported for comparison.

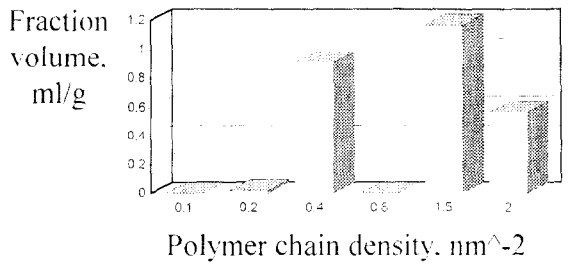


Fig. 2. ISEC pattern exhibited by **P-1(L)** in THF, at room temperature. The chain density is expressed as nanometers of polymer chains per cubic nanometer of swollen material, i.e. polymer chain plus THF-filled voids.

in a reasonably good agreement with the actual volume of the swollen gel, 2.59 ml · g^{-1}, which can be measured independently as the difference between the total volume of the chromatographic column and the elution volume of totally excluded standard solutes (dead volume). This agreement substantiates the validity of the ISEC-derived model for the description of the internal morphology of the resin [11] and, at the same time, it gives a strong indication of the fact that the chiral resin does not contain significant fractions of unswollen domains, which would have not been detectable by this technique.

The chiral resin in THF appears to possess a polydisperse internal morphology featured by three major domains in which the polymer chains density is 0.4, 1.5 and 2.0 nm^{-2}, respectively. The relatively more dense domains represent ca. 70% of the total gel volume, but still the remainder possesses a relatively low chain density (0.4 nm^{-2}) and it is therefore expected to be easily accessible to solutes of substantial sizes.

The preliminary data presented here appear to be very promising both in terms of synthetic viability of the proposed strategy and of the general accessibility of the microporous domains of the chiral resins prepared therefrom. We are presently synthesizing chiral anionic exchange resins suitable for the effective dispersion of catalytically active metal centres.

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References

[1] H.U. Blaser, Tetrahedron Asymm., 2 (1991) 843.
[2] For very recent examples, see (a) T. Tarnai, A. Tungler, T. Mathè, J. Petrò, R.A. Sheldon and G. Toth, J. Mol. Catal. A, 102 (1995) 41; (b) M.A. Keane, Langmuir, 10 (1994) 4560.
[3] W.H. Pirkle and G.S. Mahler, in D.C. Sherrington and P. Hodge (Eds.), Syntheses and Separations using Functional Polymers, Wiley, Chichester, 1988.
[4] S. Itsuno, M. Sakakura and K. Ito, J. Org. Chem., 55 (1990) 6047.
[5] R. Arshady, Adv. Polym. Sci., 111 (1993) 1.
[6] R. Arshady, Adv. Mater., 3 (1991) 182.
[7] J. Bartus, D. Weng and O. Volg, Monatsh. Chem., 185 (1984) 671.
[8] P.K. Khan and S. Beychok, J. Am. Chem. Soc., 17 (1968) 4168.
[9] R. Kuroda and Y. Saito, Bull. Chem. Soc. Jpn., 49 (1976) 433.
[10] K. Jeřàbek, Anal. Chem., 57 (1985) 1598.
[11] A. Biffis, B. Corain, M. Zecca, C. Corvaja and K. Jeřàbek, J. Am. Chem. Soc., 117 (1995) 1603.