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Manganese distribution in polystyrene beads prepared by copolymerization with cross-linking dendritic salens using laser ablation inductively coupled plasma mass spectrometry

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Abstract

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) with an ArF 193-nm excimer laser was used to determine the Mn content of polystyrene beads (diameter ca. 400 µm) obtained by radical cross-linking suspension copolymerization of chiral, dendritically styryl-substituted salens with styrene and loading with $Mn(OAc)_2/LiCl$ to give polymer-bound Mn-Salen complexes (p-**1**· and p-**2** · Mn(Cl)). The beads were used to catalyze the enantioselective epoxidation of styrene to the corresponding epoxide. The spatial distribution of Mn (and Li) in freshly prepared, in multiply used (up to 20 times), or in “reloaded” beads was measured by drilling with laser craters (ablation) of ca. 40 µm into whole beads or into beads cut in half and analyzing the vaporized and ionized material in a plasma (detection limits down to 10 µg/g and depth resolution down to 0.3 µm/pulse). The following results were obtained: (i) the Mn content is evenly distributed within the freshly prepared and loaded beads; (ii) the high-performance polymer (p-**2** · Mn(Cl)) leaches Mn down to a constant value of ca. 25% of the original content after 15 sequential uses; (iii) the low-performance polymer (p-**1** · Mn(Cl), a hydroquinone derivative) loses almost all Mn after six runs; (iv) reloading of beads with Mn causes increased Mn content only on the outer layers of the particle; (v) leaching occurs by loss of Mn, increasing from the surface to the center of the beads. It was demonstrated for the first time that LA-ICP-MS is well suited to assessing element distribution inside individual beads containing catalytically active transition metal sites and to detecting spatial changes upon multiple use.

Keywords: Laser ablation; Plasma mass spectrometry; Mn and Li analysis; Polymer-bound catalysts; Chiral Mn–salens; Dendrimers; Distribution of catalytic sites in polystyrene beads

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1. Introduction

Chiral Mn–Salen complexes are among the most useful catalytic systems for enantioselective olefin epoxidation [1]. Much effort has been directed towards immobilization of such complexes, for example in or on inorganic materials, such as SiO_2 or zeolites [2], in a polysiloxane membrane [3], or on polystyrene [4].

In 1997, we introduced a novel concept for the immobilization of chiral ligands in polystyrene (PS): the ligand of choice is placed in the core of a styryl-substituted dendrimer, which is suspension-copolymerized with styrene (Fig. 1a). We expected that the steric congestion around the catalytic centers within the polymer network would be reduced in comparison to the more conventional approach of copolymerizing a monostyryl-substituted ligand with styrene and divinyl benzene as cross-linker (Fig. 1b).

This approach has been realized with the chiral ligands TADDOL [5] and BINOL [6], giving rise to immobilized catalysts of unprecedented performance upon multiple applications in a variety of test reactions. Most recently, we have also reported on the immobilization of Salen by our method, as outlined in Fig. 2 [7]. Salen complexes of Cr, Mn, and Co have turned out to be most useful, and immobilized complexes are especially attractive because they should reduce,

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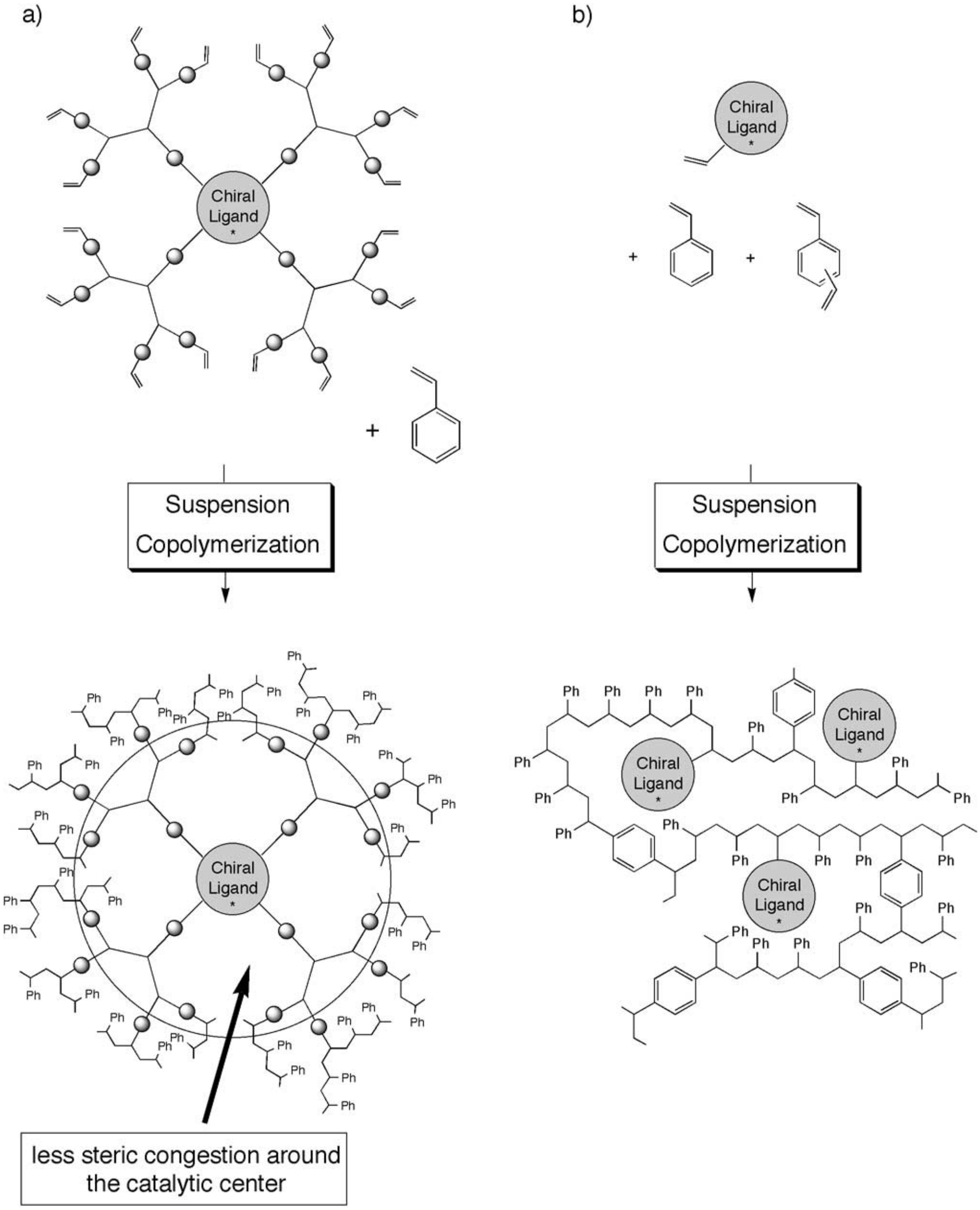

Fig. 1. Two approaches to the immobilization of chiral ligands in polystyrene: (a) conventional approach, copolymerization of a monostyryl-substituted ligand with styrene and divinyl benzene, and (b) novel approach, copolymerization of a cross-linking dendrimer with styrene.

or even avoid contaminations of products with these toxic elements.

Thus, we have prepared spherical beads of the polymers p-**1** and p-**2** with an average diameter of 400 µm from the corresponding monomers **1** and **2** and styrene (Fig. 3b). The beads, containing the Salen moieties, were loaded with Mn (by treatment with $Mn(OAc)_2$ and LiCl) to give the complexes p-**1**· and p-**2** · Mn(Cl), which exhibited excellent catalytic activity in the epoxidation of various olefins, with enantioselectivities matching those observed under homogeneous conditions [7]. There was, however, a big difference between these two immobilized complexes upon recycling in the enantioselective styrene epoxidation (Fig. 3a): only p-**2** · Mn(Cl) could be applied many times without significant loss of enantioselectivity. Only the first 10 recycling steps are shown, but the polymer p-**2** · Mn(Cl) was used 20 times, with only 8% loss of enantioselectivity, which dropped to nil with p-**1** · Mn(Cl) (Fig. 3c); in parallel the conversion under standardized conditions (reaction rate!) decreased with p-**1** · Mn(Cl), but not with p-**2** · Mn(Cl) [7].

Simple leaching of Mn and/or oxidative destruction of the Salen moiety **1** (containing a hydroquinone–ether moiety) may be reasons for the poor performance of the p-**1** · Mn(Cl) complex.

The following general and specific questions about our complexes, dendritically incorporated into PS, arose: (i) Are the chiral ligands and their complexes evenly distributed throughout the PS beads? (ii) Is Mn leaching from the Salen

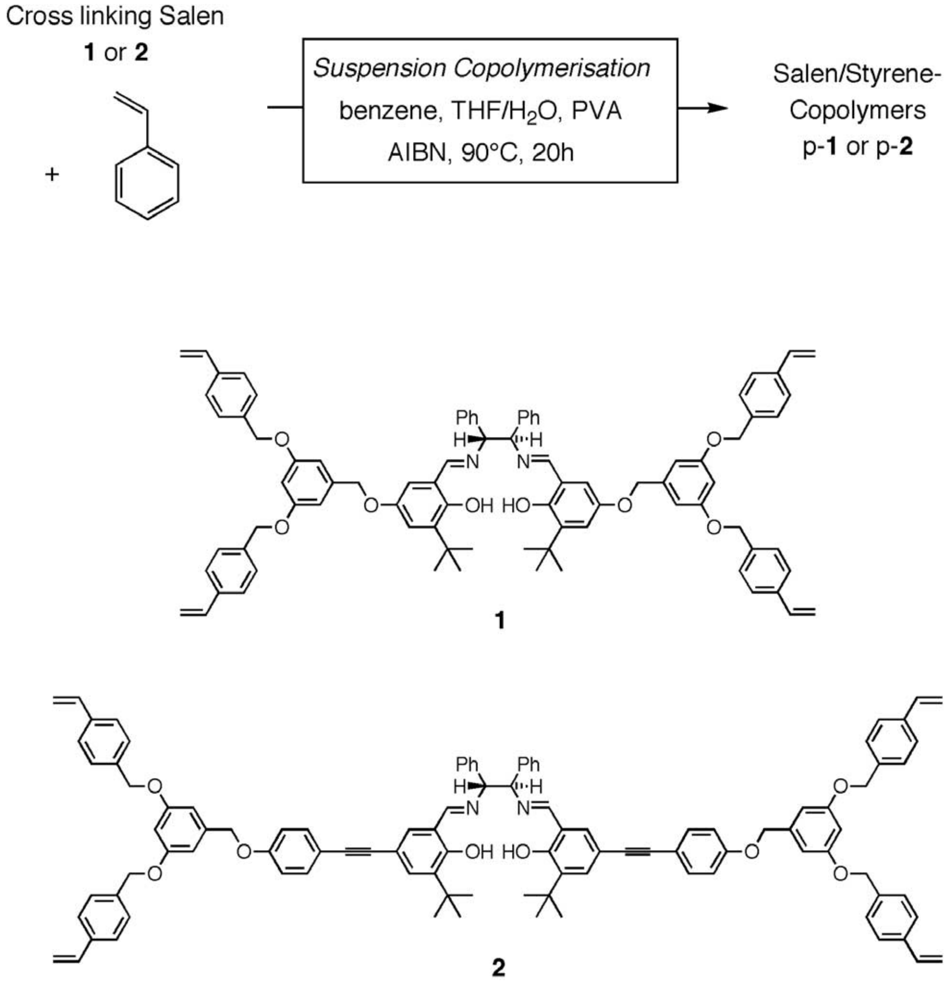

Fig. 2. Suspension copolymerization of Salen cross-linker **1** or **2** with styrene to give Salen/styrene copolymers p-**1** or p-**2**. THF = tetrahydrofuran, PVA = poly(vinyl alcohol), AIBN = azoisobutyronitrile.

ligands in the polymer upon multiple applications? (iii) If yes, can the beads be successfully recharged with Mn? (iv) Does the distribution of Mn within the beads change upon multiple use? (v) Do Li ions play a role in epoxidation with Mn–Salen (bimetallic catalysis)?

In order to answer these questions we have applied laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), one of the most sensitive analysis techniques for solid materials, to determine the Mn and Li distribution in the polystyrene beads. LA-ICP-MS, a still widely unknown analytical tool for elemental analysis of polymeric materials, has been successfully applied in various areas, such as forensics, materials science, and geology [8–10]. New developments in the field of excimer laser ablation systems [11] allow the controlled ablation of ng amounts of solid materials, which are vaporized and ionized in an inductively coupled plasma. The advantage of this technique is the access to local information on major, minor, and trace elements and their distribution. Typical limits of detection of 10 ng/g are achievable, which depends on the element of interest and the spatial resolution of the sampling process. Much progress has been made in the understanding of the ablation process, aerosol transport, and excitation and a large number of quantitative analyses have demonstrated the potential of this technique, especially with short-wavelength UV lasers [12,13].

The aim of this work was the determination of the distribution of Mn and Li in beads of polystyrene-bound Mn–Salen complexes during recycling of the corresponding polymer-bound catalysts in enantioselective catalysis. Thus, bulk and local analyses were carried out on the bulk material and individual beads. Furthermore, the contamination of the polymer with other trace elements such as Pd was determined to investigate the purity of the material (a Pd complex had been used as a catalyst for cross-coupling reactions in the preparation of Salen cross-linker **2**).

2. Experimental

Bulk measurements of the polystyrene beads were carried out with an IRIS/AP ICP optical emission spectrometer (ICP-OES, Thermo Jarrell Ash): ca. 25 mg of material, i.e., ca. 30 beads, was digested with a 6:1 mixture of con-

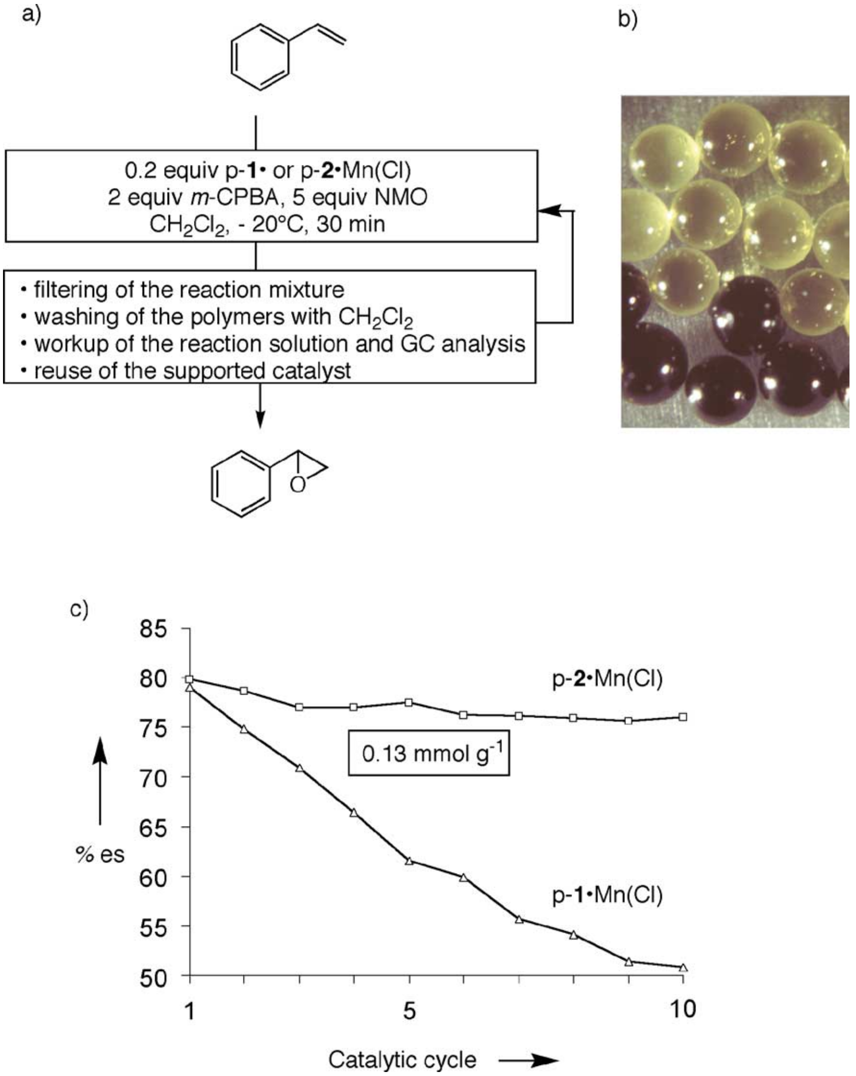

Fig. 3. (a) Multiple application of Mn–Salen polymers p-**1**· and p-**2** · Mn(Cl) in the enantioselective epoxidation of styrene; (b) polymer beads of p-**1** before (yellow) and after (black) loading with Mn; and (c) enantioselectivities with which styrene oxide is formed during recycling of polymers p-**1**· and p-**2** · Mn(Cl) with a loading degree of 0.13 mmol/g.

centrated nitric acid (suprapur 65%, Merck AG, Germany) and hydrogen peroxide (suprapur 30%, Merck AG, Germany) in an ETHOS microwave oven (MLS-Mikrowellen-Laborsystems, Germany). One of the samples was used as an external quality control for all further measurements.

The Mn and Li distribution patterns within individual polystyrene beads were determined with an ArF 193-nm excimer laser ablation system (GeoLas, MicroLas, Göttingen, Germany) [12] coupled to an ELAN 6100 DRC (Perkin–Elmer Corp., Norwalk, USA). Typical operating conditions of the instruments can be found in the literature [14]. Polystyrene beads, previously analyzed by ICP-OES, and the NIST 612 reference glass were applied as external calibration standards. Mass transport, excitation, and ionization were corrected by internal standardization using ^{7}Li and ^{13}C as matrix elements. The beads were ablated using a crater diameter of 40 µm and a laser pulse repetition rate of 5 Hz at a laser fluency of 10 J/cm^2. The sample ablation rate is material-dependent and was determined to be 200 nm per pulse. In total, seven isotopes (^{7}Li, ^{13}C, ^{23}Na, ^{27}Al, ^{55}Mn, ^{57}Fe, ^{105}Pd) were measured; Na, Al, Fe, and Pd served as indicators for the purity of the material. Various samples of polymer beads of p-**1** · Mn(Cl) and p-**2** · Mn(Cl) at different stages of recycling in the enantioselective epoxidation of styrene were ablated in order to check the remaining Mn and Li concentration by LA-ICP-MS. Furthermore, some beads of the polymer p-**1** · Mn(Cl) were cut in the middle and mounted on Scotch tape after they had been reloaded with Mn following their use in 10 runs. From the rim, center, and rim parts of the beads individual analyses were carried out in order to determine the element distribution within the beads. The limits of detection for the individually measured elements were determined to be between a few ng/g (Pd) and a few µg/g (Mn, Li, Na, Al); all concentrations reported herein were at least 4–5 times above limits of detection.

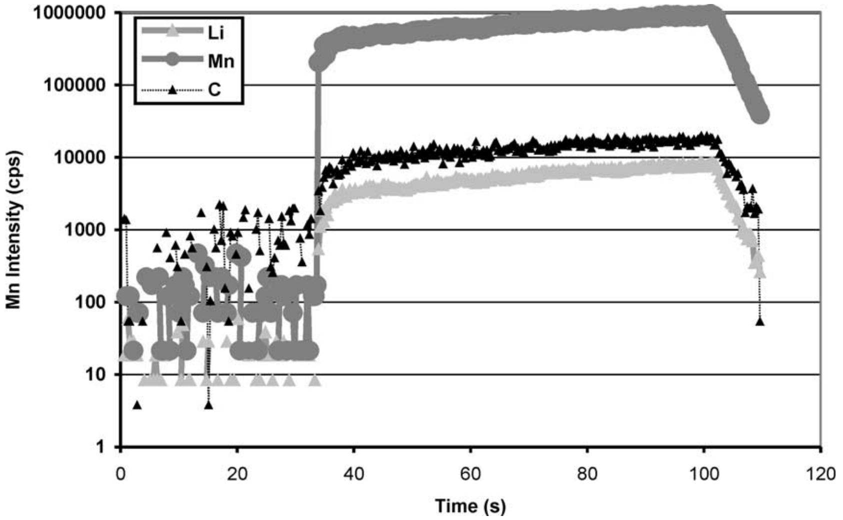

Fig. 4. Time-dependent signal for Mn, Li, and C on p-**2** · Mn(Cl) acquired using LA-ICP-MS. The increase of the intensity of all measured elements is due to the crater broadening during the laser drilling into the sample.

3. Results and discussion

In the bulk digested sample, concentrations corresponding to the amount of applied Mn (0.77 ± 0.007 wt%) and Li (0.02 ± 0.003 wt%) were measured with polymer beads of p-**2** · Mn(Cl) prior to use in catalysis. $(PdCl_2(PPh_3)_2$ had been used as catalyst in a Sonogashira cross-coupling reaction for the preparation of Salen cross-linker **2** [7]). Repeated digestions of different polymer beads showed that there is low variability in the bulk composition, indicating a homogeneous distribution of Mn and Li throughout the polymeric material. We then applied LA-ICP-MS to determine the concentrations of Mn and Li within various samples of polymer beads taken from different catalytic runs. Other elements, such as Pd, were detected at concentration levels of less than 200 ng/g, with a decrease to 160 ng/g during recycling (leaching of these trace elements from the polystyrene beads during multiple use).

A typical transient signal for the process of drilling into the beads with the laser is shown in Fig. 4. The increasing intensity of all elements is related to the total sample uptake and is caused by a crater broadening, typical for all kinds of polymer samples. The ratio of the elements signifies a homogeneous distribution of Li and Mn with respect to the polystyrene matrix, which was measured on a sample before use in catalysis. The drilling of the laser is progressively from the sample surface into the beads. The drill-time is linearly related to the depth and indicates the element variation. From the start to the end of the signal indicates a distance, which is more than 0.25 mm. These drillings were carried out from different sites of the beads and therefore indicate a very homogeneous distribution of Mn within the beads used for catalysis.

The dependence of the element concentration of Mn and Li within polymer p-**2** · Mn(Cl) upon multiple use of the beads in the enantioselective epoxidation of styrene is summarized in Fig. 5. Each data point represents five measurements, consisting of 30 s of drilling into each bead studied. The concentrations obtained with polymer samples taken from the reaction mixtures at intervals between run 1 and run 20 show that the Mn content has decreased by 50% after six catalytic cycles to finally 25% of its original value after 15 cycles. Analyses of beads that had been used 20 times in the epoxidation of styrene prove that there is no further Mn leaching. A similar trend was observed for the Li concentrations. The decrease of the Li concentration to 1/5 of the original value within the first three runs is, however, significantly larger; after six catalytic cycles the concentration remains constant within ±10%.

The experiments with polymer p-**1** · Mn(Cl) are summarized in Fig. 6. The starting Mn concentration was slightly different from that in polymer p-**2** · Mn(Cl). In addition, beads of p-**1** · Mn(Cl) were reloaded with Mn and Li after the 10th catalytic run (by washing with $Mn(OAc)_2$ and LiCl) and subjected to LA-ICP-MS measurements before and after

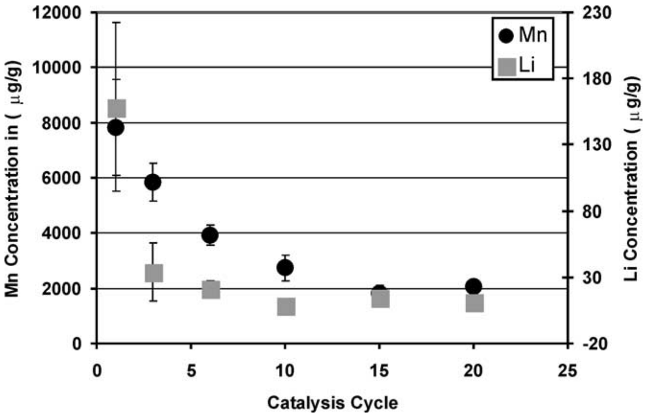

Fig. 5. Mn and Li concentrations in samples of polymer p-**2** · Mn(Cl) during recycling. Various samples from individual runs were analyzed and each value represents five parallel determinations.

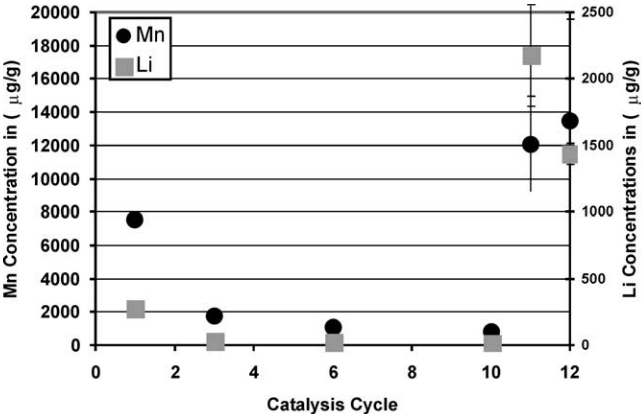

Fig. 6. Mn and Li concentrations in samples of polymer p-**1** · Mn(Cl) in multiple applications. Run 11 represent the values found directly after reloading of the beads with Mn and prior to use, and run 12 represents the Mn and Li concentrations measured with samples of p-**1** · Mn(Cl) after reloading, before the 11th catalytic cycle.

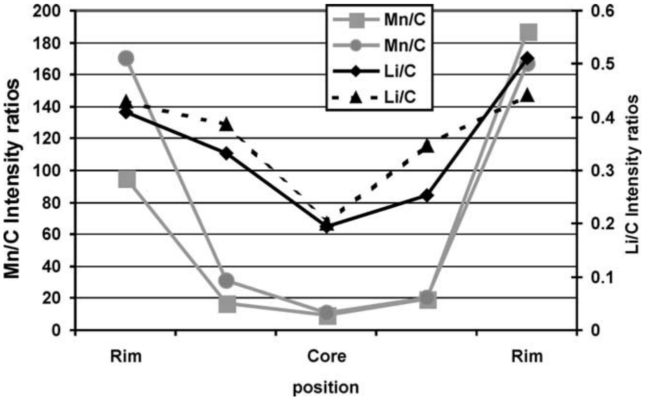

Fig. 7. Mn/C and Li/C distribution within individual polystyrene beads. Five 40-µm ablation craters were placed across the beads. The "reloading" p-**1** · Mn(Cl) leads to a Mn increase in the surface area of the beads.

the 11th catalytic cycle. Comparison of Figs. 5 and 6 clearly shows the same trend, loss of Mn and Li during recycling of the polymer-bound catalysts. Both polymers show very fast leaching of Li within the first three runs by almost one order of magnitude; the degree of leaching of Mn from the beads is, however, much more pronounced with p-**1** · Mn(Cl) than with p-**2** · Mn(Cl).

There is a surface effect in the reloading of beads of polymer p-**1** · Mn(Cl) with Mn and Li after run 10 (Fig. 7): After reloading, the polystyrene beads were cut in the middle to determine the spatial Mn and Li distribution. Across beads (diameter of 400 µm) five to six ablation spots of diameter 40 µm each were placed, and the resulting Li/C and Mn/C ratios of two different polymer beads are presented in Fig. 7. This measurement, which was repeated on a number of individual beads, shows that both elements, Li and Mn, are significantly enriched on the bead surface and that there is a minimal concentration in the center of the beads. The ratios of the corresponding elements to the matrix element carbon was used to make sure that the changes of Li and Mn concentrations are not ablation- or sampling-dependent.

From the analytical results presented above the following answer to the questions presented in the Introduction can be given: (i) The Mn–Salen complexes are homogeneously distributed throughout the polymer resin: constant Mn intensities are found when drilling through the polymer beads of both p-**1**· and p-**2** · Mn(Cl) prior to use (e.g., Fig. 4). All of the available Salen ligand centers are complexing Mn: the experimentally determined Mn loading (0.77 wt% in the case of p-**2** · Mn(Cl)) matches very well the theoretical Mn-content (0.71 wt%) calculated from the relative amounts of monomers used in the copolymerization. (ii) Mn is leaching from both polymers p-**1**· and p-**2** · Mn(Cl) during recycling in the enantioselective epoxidation of styrene; the loss of Mn is much more pronounced with polymer p-**1** · Mn(Cl) than with p-**2** · Mn(Cl) (Figs. 5 and 6), compatible with the fact

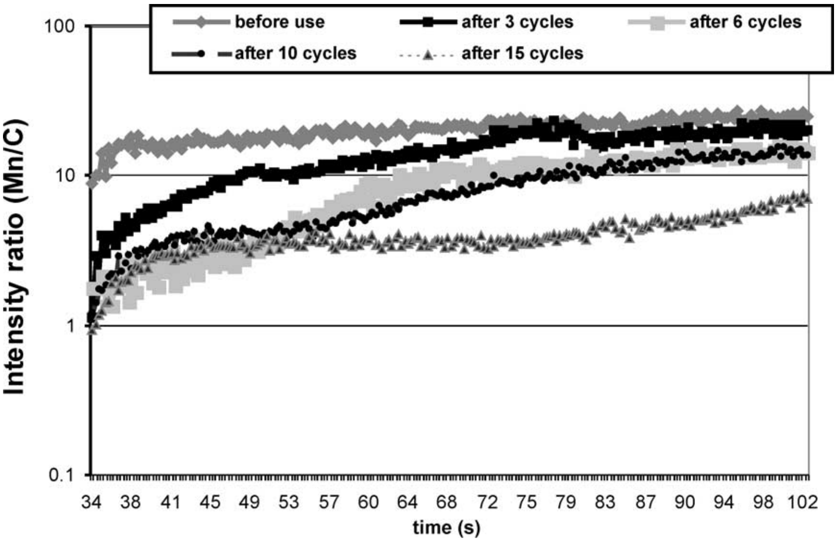

Fig. 8. Mn/C signal variation on p-**2** · Mn(Cl), indicating the drilling process into the beads with a depth resolution of better than 1 µm/laser pulse. The distribution of Mn after various numbers of cycles in comparison to an unused polymer indicates a process of surface-enhanced leaching of Mn.

that the catalytic activity of p-**1** · Mn(Cl) decreased rapidly, whereas p-**2** · Mn(Cl) gave rise to a rather constant performance during the first 10 recycling steps (Fig. 3c). (iii) In an attempt to reload polymer p-**1** · Mn(Cl) with Mn after 10 recycling steps the beads were treated with $Mn(OAc)_2$ and LiCl in DMF/EtOH. Unlike in the first loading of freshly prepared beads, only the outer layers of the beads were reloadable with Mn (Fig. 7); i.e., diffusion of substrates and solvents into the polymer network becomes more and more hindered by multiple use of the beads. Also, the polymeric material, after reloading with Mn, gave rise neither to an increase of enantioselectivity nor of conversion in the test reaction. The Salen ligands in polymer p-**1** are irreversibly deactivated. Since the cross-linker **1** contains a hydroquinone substructure, an oxidative decomposition is likely to occur, and by introducing an alkinyl group between dendritic branch and Salen core in cross-linker **2** the stability toward oxidation in the polymer is increased: p-**2** · Mn(Cl) has a stable performance (Fig. 3c) and there is much less leaching of Mn than with p-**1** · Mn(Cl) (Figs. 5 and 6). (iv) Since the LA-ICP-MS measurements have a depth resolution of less than 1 µm, the degree of Mn leaching in different parts of the polymer beads after several runs could be determined: it mainly occurs from the outer layers (Fig. 8). (v) Very probably, Li ions (LiCl has been used in the loading of the polymers with Mn) do not play a role in the epoxidation with Mn–Salen. In the case of bimetallic catalysis a Li content of 0.09 wt% might have been expected, corresponding to a loading of 0.13 mmol Mn per g polymer; the Li content of uniform distribution was, however, found to be only 0.02 wt% in p-**2** · Mn(Cl), prior to the first use in catalysis (Fig. 4), and it decreased very rapidly in the first few applications.

4. Conclusion

The experiments described here show that analysis of polystyrene beads by laser ablation ICP-MS is a highly effective analytical tool for the fast and routine investigation of polymer-bound catalysts. For the first time it is possible to determine element distributions inside individual beads which were used for catalytic reactions. Previously, it was only possible to determine the metal content of polymer-bound catalysts by bulk analysis, and no information about the distribution of metal throughout the resin was available. LA-ICP-MS provides detailed information about concentration changes at levels of 0.7–0.002 wt% with a depth resolution of less than 1 µm and a spatial resolution of 40 µm. Thus, not only can the metal distribution within the polymer network prior to use of the catalyst be determined, but also the change and site of metal concentration within a polymer-bound catalyst upon multiple use of beads can be followed.

Acknowledgments

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