

FUNCTIONAL MICRO- AND NANOPARTICLES – A POSSIBLE TOOL FOR NANOSTRUCTURED MATERIALS

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The application of several water-soluble poly[(N-acylimino)ethylene] (PROZO) macromonomers in the preparation of polymer micro- and nanoparticles with narrow size distribution, or as intermediates in the synthesis of polymer supported catalysts is presented. Different heterogeneous polymerization techniques were applied to obtain polymeric microspheres with controlled characteristics.

The use of surface functionalized microspheres for the immobilization of nanosized metal catalysts (Pt) or for the recovery of poisoning or valuable metals from their diluted aqueous solutions (Pt⁴⁺) were exemplified for core-shell polymeric particles - polystyrene latexes (PSt) with poly[(N-acetylimino)ethylene] (PMOZO) grafts.

A recently developed approach for the preparation of manganese-polymer supported catalysts of high efficiency in the olefin epoxidation reaction, based on molecularly imprinted polymer technique, together with the chelating properties of the PROZO polymers and their derivatives are also presented.

INTRODUCTION

Branched polyethylenimine and 2-oxazoline polymers have histories of more than seventy or thirty years, respectively. However, they were only recently used for the preparation of new polymeric materials corresponding to the actual requirements.¹⁻³ Poly[(N-acylimino)ethylene]s (PROZO), especially, are known as materials with large applicability in technical and also biomedical domains (dispersants, nonionic surfactants, compatibilizers, biocatalysts, sorbents etc.). Due to the specific properties (precisely controlled synthesis by living cationic polymerization of 2-substituted-2-oxazolines (ROZO), biocompatibility or low toxicity, facile modification to polyethylenimine – polymer with chelating properties, also able to immobilize biocompounds) PROZO derivatives may intermediate the preparation of multifunctional polymeric materials with controlled structure and functionality, emerging in *smart* polymeric materials. The high versatility of the cyclic imino ethers, able to perform a large range of ring opening reactions (double isomerization polymerization, no-catalyst alternating copolymerization *via* a zwitterion intermediate, ring-opening addition reactions), and the specific features of the living polymerization

systems allowed the formation of various polymeric architectures with defined structure – macromonomers and telechelics, block and graft copolymers, networks, dendrimers, star polymers, hyperbranched polymers.¹⁻³ Multisensitive hydrogel systems^{4,5}, PROZO – silica hybrid materials⁶, stable supramolecular assemblies like Langmuir monolayers⁷, are only some of the recent interesting results in the field.

The design and synthesis of new polymers, especially tailor-made, intended to be used for specific tasks, as a tool in the preparation of controlled nanostructured and responsive surfaces with specific (multi)functionalities, are of topical interest. In this context, the present paper focuses on the application of several water-soluble poly[(N-acylimino)ethylene] macromonomers^{8,9} in the preparation of polymer micro- and nanoparticles with narrow size distribution, or as intermediates in the synthesis of polymer supported catalysts.

EXPERIMENTAL

Materials

Styrene (St, Merck) and acrylic acid (anhydrous – AA, Fluka) were purified by vacuum distillation, dried on MgSO₄ and stored over molecular sieves at 4°C.

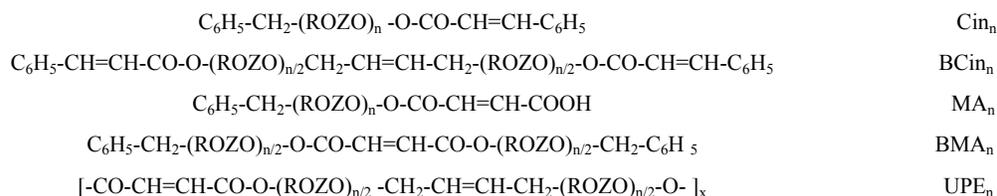
Ethylene glycol-dimethacrylate (EGDMA), trimethylolpropane trimethacrylate (TRIM-Aldrich) and pentaerythritol triacrylate (PETRA- Aldrich) were washed with 1M aqueous sodium hydroxide to remove the inhibitor, with water until neutral pH, dried on $MgSO_4$, passed through alumina columns and stored on molecular sieves at 4°C.

Inorganic reagents of analytical quality (platinum precursor, hydrogen hexachloroplatinate(IV) hydrate, $H_2PtCl_6 \cdot 6H_2O$ - Aldrich, manganese acetate dehydrate, $Mn(OAc)_3 \cdot 2H_2O$ - Aldrich, sodium perjodate - Aldrich) and the initiators (kalium persulfate - $K_2S_2O_8$, Aldrich, and 2,2'-azo-bis(isobutyronitrile) - AIBN, Aldrich) were used without further purification.

The solvents (methanol, spectrophotometric grade - Aldrich, anhydrous ethanol - Kenetyl AB, anhydrous toluene - Aldrich, methylene chloride - Aldrich, acetonitrile HPLC

grade - Aldrich, ACN) and hydrochloric acid (37%, Labasco) were used as received.

Precisely controlled macromonomers were synthesized, taking into account the living character of the cationic polymerization of the 2-substituted-2-oxazolines, by the quenching of the oxazolinium species in 2-methyl-2-oxazoline (MOZO) or 2-ethyl-2-oxazoline (EOZO) polymerization with cinnamic acid or with maleic acid.^{8,9} Poly(4-vinylpyridine - co - divinyl benzene) (beads of $\Phi = 0.4$ mm) was used as a macromolecular proton scavenger. The synthesis approach was proved to be not only convenient, but also efficient, a quantitative functionalization and high yields (> 85 %) being achieved. Depending on coupling reaction conditions, *i.e.* by varying the functionality of the initiating system and the ratio of the nucleophile to oxazolinium ends, mono-, bi- or multifunctional macromonomers, with the structures presented below, were obtained:



Iodosobenzoic acid and stilbene (Aldrich), were used for the epoxidation tests without further purification. All aqueous solutions were prepared using double-distilled water.

Poly(acrylic acid) surface grafted poly(trimethylolpropane trimethacrylate) particles (PTRIM/PAA) were prepared according to literature, by a two step polymerization method.¹⁰ Initially, trimethylolpropane trimethacrylate was polymerized in an ethanol-toluene 9:1 v/v mixture (1.5 mol/L), using AIBN as initiator (1.5% relative to monomer). The second step consisted in the grafting of a functional monomer (acrylic acid) on polyTRIM particles, which posses residual unpolymerized double bonds.

The polystyrene microparticles with poly[(N-acetylimino)ethylene] shell used as a Pt catalyst support or sorbent were prepared by soapless emulsion polymerization (recipe: St - 5 g, water - 95 g, MA_{15} - 0.5 g or 0.2 g respectively, $K_2S_2O_8$ - 0.1 g, 75°C, 6 h, inert atmosphere - N_2)¹¹. The resulted microparticles were separated and purified by centrifugation and repeated washing with bidistilled water. The polystyrene latex with PNAI grafts at the surface was submitted to acid hydrolysis after redispersion in 10 wt% aqueous solutions of hydrochloric acid, 6 h, at 60°C. According to spectral and analytical data, the particles resulted after hydrolysis contained 2.5 wt% ethylenimine units in the hydrophilic shell.

Poly(acrylic acid), polymer bearing carboxylic functional groups, able to interact with metal ions, was synthesized by the polymerization of acrylic acid in benzene solution (10 wt %), at 60°C, under inert atmosphere (N_2), for 4 h. AIBN (4 wt% with respect to monomer) was used as initiator. The crude product was washed with benzene and acetone, separated by centrifugation, dried and characterized. Yield: 97 %.

Poly(pentaerythritoltriacrylate)/manganese catalyst was prepared by precipitation polymerization (3.5 % wt/v total monomer/solvent mixture, *i. e.* ethanol/toluene 9:1 v/v, using as an initiator 2 %wt AIBN relative to total monomer, inert atmosphere, 60°C, with stirring - 1000 r/min, for 6 h), followed by alkaline hydrolysis of the separated, dried microparticles in aqueous NaOH solution (2.5 wt %

copolymer particles in 2N NaOH solutions in 1:2 v/v water/methanol mixture, at reflux). The hydrolysis was monitored by FT-IR. When maximum hydrolysis degree was achieved, the polymer salt was washed with acetone, treated with 5N HCl and dried (total yield, 70%).

To obtain Mn^{3+} polyacrylic resin complexes, the mixtures of the solutions of $Mn(OAc)_3 \cdot 2H_2O$ in absolute ethanol (10 mg/ml) and the corresponding polymeric materials were maintained 2 h at 60°C, followed by 2 h at 65°C, at a stirring rate of 1000 r/min. The reaction mixtures were periodically purged with nitrogen to remove the generated acetic acid. The polymer particles were purified by repeated centrifugation-washing cycles using methanol, acetonitrile and dichloromethane to extract the unpolymerized monomers, soluble oligomers and uncomplexed manganese acetate. The prepared complexes were separated by centrifugation and extracted with acetonitrile. When uptake of the manganese salt was not total, the washing solutions were submitted to photocolometric titration.

Equipment and instrumentation

IR spectra were recorded on a Spectrum 2000 (Perkin Elmer) FT-IR spectrometer.

The obtained polymeric particles were characterized with a Jeol JSM-5400 scanning electron microscope (SEM) or with a transmission electron microscope (TEM) TESLA BS 513 A. The particle size and size distribution were calculated with the formula:

$$D_n = \sum NiDi / \sum Ni, \quad D_w = \sum NiDi^4 / \sum NiDi^3, \quad PI = D_w/D_n$$

The thermal characterization of the studied materials (differential scanning calorimetry - DSC and thermogravimetric analysis - TGA) was performed with a Mettler DSC 820 and TGA/SDTA 851° instrument, respectively. The registration was carried out under nitrogen flow (10 and 50 L/min, respectively) by using a heating rate of 10°C/min.

The Pt amount immobilized on the polymeric catalytic supports by alcoholic reduction (refluxing alcoholic

hexachloroplatinic acid solutions at 110°C, in the presence of the selected water-soluble copolymer or latex) was evaluated by analyzing the clear supernatant resulted by samples centrifugation, after a treatment with specific analytic reagents (SnCl₂ and concentrated HCl). The absorbance measurements were performed with a S 104D spectrophotometer at $\lambda = 403$ nm. A similar analytical protocol was applied for the determination of Pt(IV) ions retention from aqueous solutions in the sorption experiments (performed by a batch method).

The evaluation of the Mn content was performed by chemical analysis of the washing waters or by atomic absorption spectrometry (Perkin–Elmer Atomic Spectrometer 3300).

RESULTS AND DISCUSSION

Micro- and nanoparticles

Polymer micro- and nanoparticles are used in different applications, *i.e.* in environment management, technical areas or biomedical related domains.¹² Chemical or physical approaches may be used for their preparation. Among the useful techniques, the heterogeneous copolymerization of a main monomer with a water-soluble functional comonomer or macromonomer is one of the most appropriate tools for the synthesis of functional latexes, due to the possibilities offered to control the particle size, size distribution and surface functionality.^{12,13} The addition of water-soluble PROZO macromonomers (PEOZO or PMOZO macromonomers with styryl or butadiene end group, amphiphilic PROZO macromonomers with styryl or vinyl ester reactive group) to the recipe of dispersion or soapless emulsion copolymerization with styrene, methyl methacrylate or vinyl acetate results in the preparation of polymeric microspheres with narrow size distribution or even monodisperse particles.¹⁻³

Previously, PMOZO macromonomers were tested as stabilizers in the dispersion

copolymerization with styrene and as comonomers in the soapless emulsion copolymerization with the same main monomer. In all cases an improved stability, narrower particle size distribution and lower particle size were realized as compared to those obtained in their absence.^{9,14,15} Typical micrographs are shown in Fig. 1. A thorough, comparative study evidenced that the characteristics of the colloidal system and of the prepared microparticles are strongly dependent on macromonomer structure, its average molecular weight and its concentration in the system. Thus, by changing the synthesis parameters and recipe formulation, a wide range of polymer particles, with diameters in the micrometer range, surface enriched with hydrophilic, biocompatible PMOZO chains, can be prepared. Some of the most important results are included in Table 1. The involved factors of influence are specified. As can be seen, the best results in the stabilization of heterogeneous polymerization systems were achieved by the use of monofunctional macromonomers, *i. e.* of Cin_n type in dispersion copolymerization^{8,14} and of MA_n type in soapless emulsion copolymerization¹⁵, respectively. As compared to the polymerization systems using PMOZO macroazoinitiators,^{11,15, 16} a higher solid content (until 15 wt % vs. 4.5 wt %), and higher yields (> 85% vs. maximum 60 wt %) are reached. In soapless emulsion recipes the concentration of the PMOZO macromonomer may be varied in a large range, in agreement with the required surface functionality, while in dispersion polymerization and when using PMOZO macroazoinitiators an optimum value is recommended, corresponding to a maximum solid yield and the narrowest particle size distribution which may be reached in the involved polymerization system.

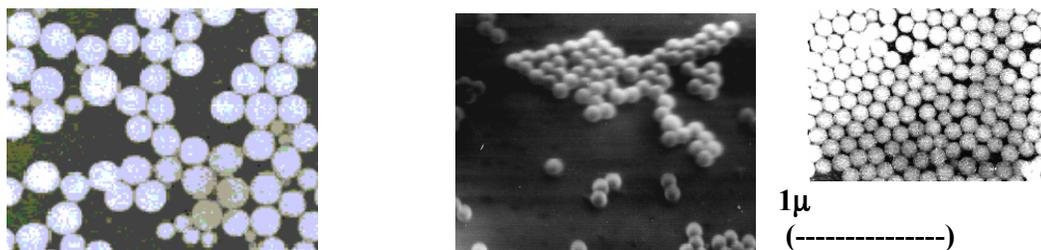


Fig. 1 – Typical micrographs of soapless emulsion polymerization systems of styrene without macromonomer (a) and with 10 wt% macromonomer MA₄₀, relative to monomer, as viewed by SEM (b) or TEM (c).¹¹ Polymerization conditions: 5% St, K₂S₂O₈ – 2% relative to monomers, 75°C, Ar, 6h.

Table 1
Heterogeneous polymerization data

Polymerization system	Factors of influence	Effect on : Dn ^a	PI ^b	Observations
Dispersion polymerization	macromer structure			Stabilization efficiency
	macromer concentration →	↘	↘	Cin~BCin>MA>BMA>>UPE
	macromer dimension →	↘	↘	Dn: 500-1000nm
	medium polarity →	↘	min	Dn = 462 nm; PI = 1.02
	initiation mode			3 wt% Cin ₄₀ relative to monomers
	initiator concentration →	↘	↘	
	monomer nature	↘	↘	
Soapless emulsion polymerization	macromer structure			Stabilization efficiency
	macromer concentration →	↘	↘	MA>BCin~Cin>BMA>>UPE
	macromer dimension →	↘	↘	Dn = 100-400nm Dn = 120; PI = 1.002 10 wt % MA ₄₀ relative to monomers
Microemulsion polymerization	macromer presence	↘	↘	Dn = 12-50nm; Dw = 40nm; PI = 1.1 SDS/monomer = 0.08 wt/wt Cin ₂₅ /SDS = 2:1 wt/wt 0.002g SDS/ml – w SDS – sodium dodecyl sulfate

a- $Dn = \sum Ni Di / \sum Ni$; $Dw = \sum Ni Di^4 / \sum Ni Di^3$; b- $PI = Dw/Dn$

Table 2

Complex characteristics

Sample	Homopolymers	Yield (%)	Dn ^a (nm)	PI ^a	Mn retained (%)	Color
PAA _c	Poly(acrylic acid)	75	3.54	1.4	11	dark brown
PETRA _c	Hydrolyzed poly(pentaerytritol triacrylate)	85	3.07	1.2	30	dark brown

a - from TEM registration; b - according to the mentioned analytical procedure

Such functional, monodisperse microparticles have the ability to self-assembly creating nanoscopically patterned thin films, with application in novel **bottom up** lithography techniques.¹⁷

The synthesized nonfunctional PMOZO macromonomers were also tested (to our knowledge, for the first time) as co-surfactant in microemulsion polymerization systems, using sodium dodecyl sulfate (SDS) as the main surfactant and methyl methacrylate (MMA) and butyl methacrylate (BMA) as comonomers.¹⁸ The introduction of the PMOZO derivative allowed the diminishing of the amount of the main surfactant required and a lowering of the nanoparticles diameters. An improvement of both surface functionality and film forming ability, due to the presence of the hydrophilic, biocompatible PMOZO chains, may be also considered.

Polymer supported catalysts

Supported metal complexes continuously attracted the interest of a growing part of the scientific community for the advantages they offer: robustness, increased air and moisture stability, facile separation and potential recovery, minimization of deactivation pathways.¹⁹⁻²¹ Using organic copolymers as supports for transition metal complexes allows the conjugation of a controllable flexibility of the matrix with the possibility to fine-tune its physical properties (polarity, swellability, morphology, etc.).

Stable hybrid platinum nanocatalyst - polymer systems were prepared by the reduction of

alcoholic solutions of H_2PtCl_6 in the presence of water-soluble poly[(N-acetylimino)ethylene] based graft copolymers or of polystyrene latexes with PMOZO surface grafts. The water-soluble amphiphilic copolymers (*i.e.* PSt/PMOZO copolymers with 9 wt% St units) may be employed for the generation of colloidal Pt nanocatalysts ($D_n = 26$ nm, $PI = 4.5$), as PSt nanoparticles with PNAI surface grafts are efficient in the immobilization of Pt nanoparticles to form tricomponent systems, *i.e.*, metal nanoparticles/latex support/hydrosoluble protective polymer.²²

The immobilization of metal particles was demonstrated by transmission electron microscopy and spectral techniques. To find the best reaction parameters, the reduction process was monitored by analytical methods. The comparative study of ultrafine platinum particles immobilization on polystyrene latexes and on polystyrene latexes with superficial PMOZO grafts, not hydrolyzed or partially hydrolyzed to polyethylenimine (PEI), evidenced differences in the behavior of polymer supports, pointing on the advantages offered by the last ones, related to PEI ability to coordinate with Pt.

Figure 2 presents the TEM micrographs of the crude products obtained after the reduction of H_2PtCl_6 in the absence and in the presence of PSt/PMOZO particles ($D_n = 246$ nm, $PI = 1.06$) or water-soluble amphiphilic copolymers. The aggregation of Pt nanoparticles, present in the first case, is avoided for the Pt nanoparticles protective polymer systems. The stability and Pt immobilization efficiency of PSt/PMOZO particles are higher as compared to those obtained for PSt latexes.

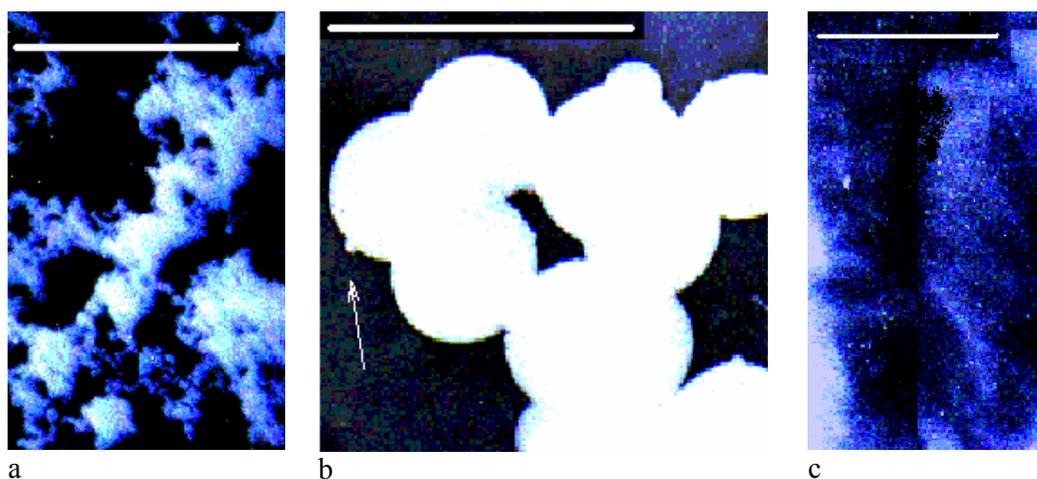


Fig. 2 – Typical TEM micrographs of a) aggregated Pt-nanocatalyst particles; b) PSt/PMOZO latex supported Pt nanocatalyst; c) Pt nanoparticles protected by PSt-g-PNAI copolymer with 9 wt% PSt units content.²² Bar - 1 μ m (a, b) and 0.5 μ m (c).

The study of the sorption process on PSt latex with partially hydrolyzed PNAI shell (PSt-PNAI, h latex,) indicated that this new polymeric material can be used as an effective sorbent material for the treatment of Pt(IV)-bearing aqueous streams.²³ The sorption of Pt(IV) on the core-shell beads was proved to depend on solution pH, on initial Pt(IV) concentration and on contact time. It was found that the sorbed amount and percentage of Pt(IV) recovery from the aqueous solutions increase with increasing pH and initial concentration, and reach a maximum at pH = 10, at $C_0 = 300\text{mg Pt(IV)/L}$, with a sorption half-time of ≈ 90 min (Fig. 3).²³ The equilibrium distribution of Pt(IV) between the sorbent and solution can be described by using the Langmuir model of monomolecular layer adsorption. The apparent free energy of sorption process suggests the affinity of chelating resin against Pt(IV) ions. The sorption data indicated the applicability of a pseudo-second order kinetics.

One of the recently developed methods to prepare polymer supported catalytic systems is the molecular imprinting.²⁴ The general procedure supposes the building of a polymeric material with inner cavities of controlled type and dimension by the following three synthesis steps: (1) preparation of a covalent conjugate or of a non-covalent adduct between a functional monomer and a template molecule; (2) polymerization of this monomer-template conjugate (or adduct); (3) removal of the template from the polymer.

To achieve the specific structure of the final material, functional and crosslinking monomers are used. Many new catalytic systems of high efficiency and stereoselectivity were obtained according to this strategy.^{19,24}

Screening a series of Mn complexes for olefin epoxidation is expected to allow the identification of several catalysts that are capable of high activity and selectivity. The molecularly imprinted polymer (MIP) strategy, as well as the immobilization of Mn (III) on/inner functional polymeric microspheres, were applied for the synthesis of these organic/inorganic hybrid materials. Five types of samples were prepared: (1) hybrid materials resulted by copolymerization; (2) polymer supported catalysts with N containing ligands (based on poly[(N-acylimino)ethylene] or polyethyleneimine; (3) hybrid materials synthesised by a sacrificial spacer alternative of molecularly imprinting polymer technique; (4) complexes of functional homopolymers (linear or

crosslinked); (5) core-shell microparticles with the catalytic active sites disposed in the shell.

The goal was to find the best alternative by studying the effect of the preparation method on the performance of the final imprinted material. All polymer – supported catalysts were characterized by FT-IR, thermal and analytical methods. The size and size polydispersity of the heterogeneous beads were evaluated through SEM examination.

The hybrid materials resulted by the precipitation copolymerization of a multifunctional monomer (*i.e.*, EGDMA) with the preformed manganese - chelate or with the functional monomer in the presence of Mn(III) salt gave poor results. This behavior was related to the low content in manganese ions in the final products and the low accessibility of the active sites. The chelate having a higher relative reactivity as compared to the comonomer was preferentially disposed inner the particle covered with a dense PEGDMA shell. The presence of acetic acid in the polymerization system with *in situ* generated coordinative complex gave rise to low copolymerization yields, acting as an inhibitor.

Another investigation adapted a recent methodology, developed by Kabanov research group²⁵ for the synthesis of sorbents, for the preparation of catalytic systems for olefin epoxidation. It makes use of both molecularly imprinting technique and specific interactions which occur between PROZO or PEI chains and manganese ions.

The present proposed synthetic approach consists in a previous formation of a coordination complex (P1) by the participation of PROZO macromonomers of UPE type and Mn salt, followed by its copolymerization with a multifunctional monomer (ethyleneglycol dimethacrylate) (Fig. 4).²⁶

The resulted nanostructured hybrid microparticles, with diameters of aprox. 1-2 μm , considered as catalyst P2, were submitted to acid hydrolysis, and the new material containing cavities with inner ethylenimine groups (P3) was recomplexed with manganese triacetate dihydrate to give a second catalytic system (P4). The process was monitored by the FT-IR technique by comparing the signals areas for the free functional groups to those of the chelated ones. The application in the epoxidation of stilbene (in the presence of iodosobenzene acid as an oxidant) gave yields in the range of 70% - 95% and a high stereoselectivity for the *cis* isomer.

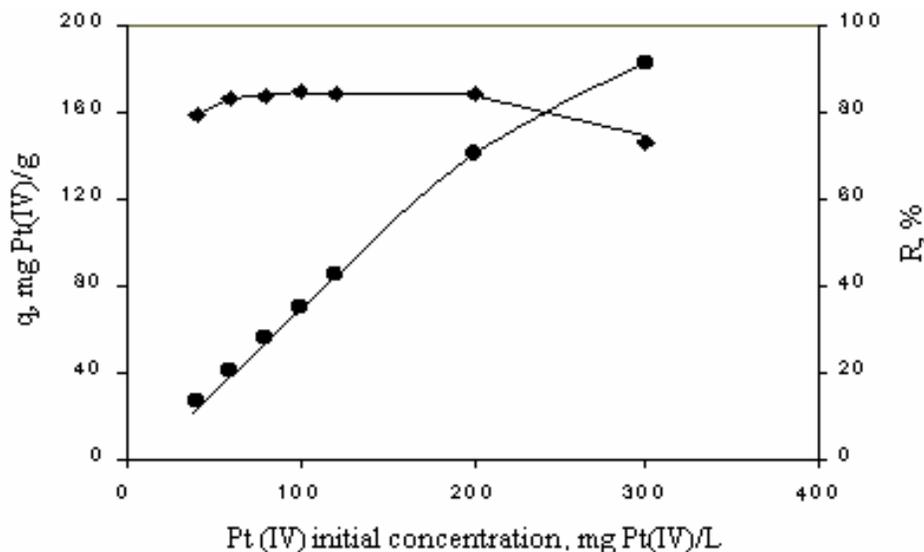


Fig. 3 – Effect of the initial Pt (IV) concentration on the sorption process. (●) q , mg/g; (◆) R , %
 $q = \frac{C_0 - C}{G} \cdot V \cdot 10^{-3}$ (mg/g) - the amount of Pt(IV) retained by 1 g polymer $R = \frac{C_0 - C}{C} \cdot 100$ (%) - the percentage of Pt(IV) retained on polymeric microspheres where C_0 and C are the Pt(IV) concentration in solution before and after the sorption process.

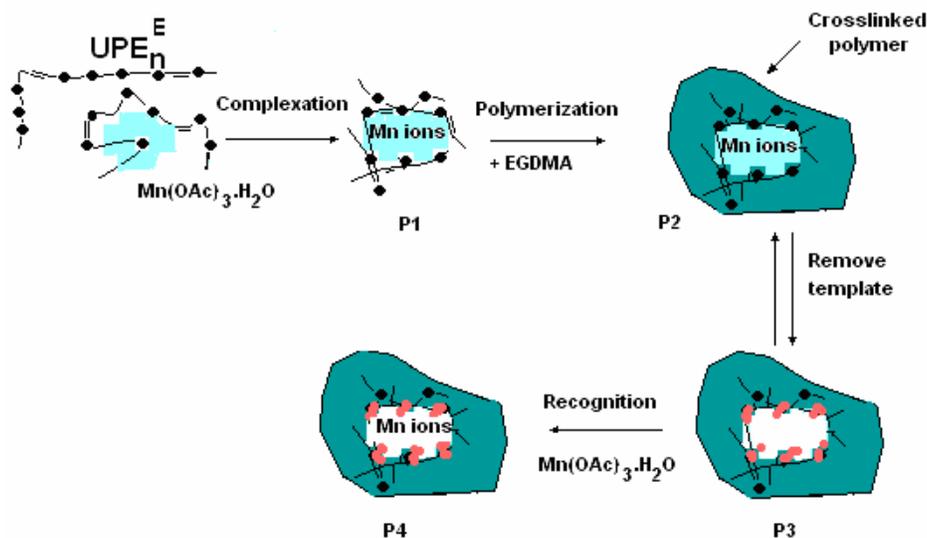


Fig. 4 – Manganese polymer supported catalyst – preparation scheme.

An improved stereoselectivity was also obtained in the epoxidation reaction of olefins for the polymer supported catalyst consisting in hydrolyzed poly(pentaerythritol triacrylate)/manganese ions complex (over 70% yield, 70/30 *trans* isomer in the epoxidation reaction of stilbene) as compared to the system formed by PAA/manganese ions, attributed to the *cluster-like* structure of the former.²⁷ The random coil conformation of the linear polymer chains with pendant chelating groups in PAA yielded an

incomplete complexation of the functional groups (Table 2), a lower catalytic efficiency and stereoselectivity. The spectroscopic and thermal analysis data suggest that in the complex with hydrolyzed PETRA the Mn carboxylate acts as a bidentate, as well as an unsymmetric bridging group, *i.e.*, the involved Mn complex has a polynuclear structure.²⁸

On the contrary, no significant yield was registered in stilbene epoxidation performed in the presence of core-shell PTRIM/PAA microparticles

after a previous complexation with the coordinative complex P1, based on the known H-bond interaction between poly[(N-acylimino)ethylene] and poly(acrylic acid).²⁹

CONCLUSIONS

Thanks to their peculiarities, *i.e.*, controlled dimension and functionality, facile modification to polyethyleneimine - polymer with chelating ability, water-soluble poly[(N-acylimino)ethylene] macromonomers are serious candidates in the design of new functional microspheres with a narrow size distribution. Their use in the preparation of polymer supported catalysts was investigated. It was demonstrated that the application of new strategies, like molecular imprinting, allows the design of systems with a high catalytic efficiency and stereoselectivity.

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