SYNTHESIS OF POLYMER SUPPORTED –TRANSITION METAL CATALYSTS FOR OLEFIN EPOXIDATION

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Polymer supported Mn catalysts were synthesized by different methods and their characteristics were comparatively investigated. Precipitation polymerization and postpolymerization complexation, alternatives belonging to molecularly imprinting polymers (MIP) strategy, like sacrificial spacer route, were some of the involved preparation methodologies. The products properties were studied for different polymerization conditions (i.e. nature and concentration of the functional monomer). Spectral and thermal analysis techniques, as well as scanning electron microscopy (SEM) observation were used for the characterization of the resulted heterogeneous compounds. A polymer-Cu(II) complex was also prepared in order to elucidate the structure of the Mn-based catalysts. Preliminary tests on the use in olefin epoxidation were run.

INTRODUCTION

The separation and reuse of usually expensive catalysts have pointed to the immobilization of homogeneous complexes on solid supports as one of the most accessible challenges. Different attempts were developed with this aim. One of the most used alternatives implies the bonding of active sites to a heterogeneous organic or inorganic surface dotted with functional groups, acting as ligands for suitable metal containing moieties, polymers being between the most envisaged catalyst support materials. The growing interest of the scientific community for the supported metal complexes originates in the advantages they offer – robustness, increased stability, facile separation and potential recovery, minimization of deactivation pathways.[1] Mn(III) – based catalytic systems may be mentioned among the polymer supported catalysts of increased interest, due to their use in stereoselective oxidation reactions.[1] Chatterjee and Mitra[2] studied the epoxidation of 1-hexene by using Mn(III) (salen complexes). Kureshi et al. reported the use of dissymmetric Mn(III) and Ru(III) chiral Schiff-base complexes in asymmetric epoxidation of styrene.[3] Mn (salen) complexes were used since 1990 in the catalytic asymmetric epoxidation of olefins, mainly conjugated with an aromatic ring.[1,4] To reach high selectivity and efficiency, recent strategies based on molecularly imprinting polymers (MIP) and metal containing monomers (MCM) (derived from salen) were used to prepare catalytically active metal – polymer complexes containing Mn(III) moieties for epoxidation of unfunctionalized olefins or styrene.[5-8]

Polymer supported manganese was synthesized *via* template polymerization involving acrylic acid and vinylimidazole as functional monomers to afford a catalyst with superoxide dismutase activity.[9] Thus, the possible application of such metal – polymer systems as enzyme mimics, able to catalyze important biochemical reactions, was pointed out.

The present paper presents a comparative study on the synthesis, characterization and preliminary results on the evaluation of some new Mn(III) supported catalysts in olefin epoxidation reaction. The molecularly imprinting polymer (MIP) strategy, as well as the immobilization of Mn(III) on polymeric linear supports, was applied. Some copper(II) complexes were also prepared for comparison. Water-soluble poly(4-vinyl benzoic acid) (pVBA), poly(acrylic acid) (pAA), hydrolyzed poly(pentaerythritol tri- or tetraacrylate) (pPETRA or pPETEA) or insoluble polymers (i.e., microparticles with inner cavities of controlled

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dimension and functionality) were used as a support. Screening a series of metal complexes for olefin epoxidation is expected to allow the identification of several catalysts with improved activity and selectivity.

EXPERIMENTAL

Materials

Acrylic acid (anhydrous, AA – Fluka) was purified by vacuum distillation, dried on $MgSO_4$ and stored over molecular sieves at 4°C.

Divinyl benzene (DVB – Aldrich), pentaerythritol triacrylate (PETRA – Aldrich), pentaerythritol tetraacrylate (PETEA – Aldrich) were washed with 1M aqueous sodium hydroxide to remove inhibitor, washed with water until neutral pH, dried on $MgSO_4$, passed through alumina columns and stored on molecular sieves at 4°C.

4-Vinylbenzoic acid (VBA – Aldrich), manganese(III) acetate dihydrate ($Mn(OAc)_3 \cdot 2H_2O$ – Aldrich), copper acetate ($Cu(OAc)_2 \cdot nH_2O$ – Aldrich), 2,2'-azo-bis(isobutyronitrile) (AIBN – Aldrich) were used without further purification. The solvents (methanol, ACS spectrophotometric grade – Aldrich, anhydrous ethanol – Kenetyl AB, anhydrous toluene – Aldrich, acetonitrile, HPLC grade, ACN – Aldrich) and hydrochloric acid (37%, Labasco) were used as received.

Iodosobenzoic acid and stilbene (Aldrich) were used without further purification. All aqueous analysis solutions were prepared using double-distilled water.

Equipment and instrumentation

IR spectra were recorded using a Spectrum 2000 (Perkin Elmer) FT-IR spectrometer. The obtained polymeric particles were characterized using a Jeol JSM-5400 scanning electron microscope (SEM). Samples were previously sputtered with a Pt thin protecting film (Denton vacuum, Desk II sputtering system). The particle size and size distribution were calculated with the formula:

$$Dn = \sum NiDi/\sum Ni , \quad Dw = \sum NiDi^4/\sum NiDi^3, \quad PI = Dw/Dn$$

Thermal characterisation of the studied materials (differential scanning calorimetry – DSC and thermogravimetric analysis – TGA) was performed with a Mettler DSC 820 and a TGA/SDTA 851^e instrument, respectively. Before testing, the samples were heated at 110°C to eliminate the absorbed moisture. The registration was carried out under nitrogen flow (10 and 50 l/min, respectively) by using a heating rate of 10°C/min.

Evaluation of the manganese ions content in residual and washing solutions was performed by spectrophotometric measurements at $\lambda = 524$ nm.

Polymer supports preparation

MIP synthesis by the sacrificial spacer method

The application of the sacrificial spacer method[10] involved the development of a three step synthetic procedure, consisting of (a) copolymerization of the crosslinker (DVB) with the functional monomer (PETRA or PETEA), (b) hydrolysis of the resulted copolymer and (c) complexation of the hydrolyzed sample with manganese salt.

Copolymers of PETRA and PETEA with DVB were prepared in ethanol/toluene 9:1 v/v mixture, using AIBN as an initiator (2 wt % relative to total monomer). A concentration of 3.5% wt/v total monomer/solvent mixture was adopted. Four different molar ratios were used, considering the final composition of the inorganic/organic hybrid material and the feed compounds involved (crosslinker/functional monomer/ manganese salt), i. e. 92/4/4, 80/10/10, 70/15/15 and 60/20/20, respectively. The reaction mixtures were purged 10 min with nitrogen and then were maintained under inert atmosphere at 60°C, with stirring (1000 r/min), for 6h. The resulted polymer particles were separated by centrifugation, washed with methanol and acetone to remove the non-reacted monomer, dried in vacuum, weighed and characterized.

The polymer particles were then subjected to alkaline hydrolysis in aqueous NaOH solution (2.5 wt % copolymer particles in 2N NaOH solutions in 1:2 v/v water/methanol mixture), or with sodium alcoholate in methanol, at reflux temperature. The hydrolyzed microparticles were washed with 10% HCl solution and distilled water until neutral pH. The usual yield was of 75-90%.

Homopolymers synthesis

Water-soluble linear polymers bearing carboxylic functional groups, able to interact with the metal (manganese or copper) ions, were synthesized by the polymerization of the appropriate monomers, i.e. acrylic acid or 4-vinylbenzoic acid, in benzene solution (10 wt %), at 60ºC, under inert atmosphere (N_2), for 4 and 20 h, respectively. AIBN (4 wt % with respect to monomer) was used as initiator. The crude products were washed with benzene and acetone, separated by centrifugation, dried and characterized. Yield: 97% and 90%, respectively.

The acrylic monomers PETRA and PETEA were polymerized in alcohol/toluene mixtures (9/1 v/v) in similar conditions. Then they were hydrolyzed with NaOH solution (2.5 wt % copolymer particles in 2N NaOH solutions in 1:2 v/v water/methanol mixture). The hydrolyzed homopolymers were precipitated first with acetone and then carefully washed with 5N HCl and acetone/water mixture. Yield: 70%.

Preparation of the resin complexes

For the complexation of the p(PETRA-co-DVB) and p(PETEA-co-DVB) hydrolyzed polymer particles, solutions of 10 mg/ml of $Mn(OAc)_3 \cdot 2H_2O$ in ACN were used, while for homopolymers complexation (pAA, pVBA, pPETEA, pPETRA) the solutions salt content was raised to 20 mg/ml. The reaction mixtures were maintained under stirring for 6h at 60°C and 10h at room temperature. Periodically, inert gas was purged in order to remove the resulted acetic acid.

The prepared complexes were separated by centrifugation and extracted with acetonitrile. When uptake of the manganese salt wasn't total, the washing solutions were submitted to photocolorimetric titration.

To obtain the Cu(II) complex, the sodium polymer salt was submitted to an ion-exchange reaction with Cu acetate in an aqueous solution. A batch method was used. 0.8 g pPETRA – Na salt – were dispersed in 20 ml aqueous solution containing 0.772 g $Cu(OAc)_2$ by 10 min sonnication and the mixture was stirred at room temperature for 24h.

A modification of particle dimensions took place, smaller, light blue coloured fine new particles being formed. A complete Cu(II) uptake took place. The product was separated by centrifugation, washed repeatedly with water, dried, analyzed by FT-IR and thermal techniques.

Epoxidation tests

0.1 g Mn-supported catalyst was dispersed in 5 ml dichloromethane and stirred for 30 min at room temperature. 1 mmol stilbene and 0.1 mmol oxidant reactive (iodosobenzoic acid) were then added dropping-wise and the reaction was continued with stirring for 2h. The reaction development was monitorized by thin layer chromatography (TLC), using *cis*-stilbene and *trans*-stilbene (Fluka) as standard samples.

RESULTS AND DISCUSSION

Supported catalysts by molecularly imprinting polymer technique. Sacrificial spacer alternative

One way to overcome the limitations of conventional molecular imprinting is to use an approach where the underlying chemistry is not sensitive to the presence of water. Byström et al.[11] prepared divinyl benzene-based polymeric beads with sterol acrylates by aqueous suspension polymerization, followed by the conversion of the resulting copolymers to "template polymeric reducing agents" by reductive cleavage of the acrylate ester bond and attachment of the metal hydride center to the resultant hydroxyl groups. The produced compounds showed a high degree of stereochemical control in the reduction of steroid ketones.

Here, the presynthesized functional polymeric support intended for the catalytic complex was prepared by the copolymerization of tri- or tetrafunctional pentaerythritol acrylates (PETRA or PETEA) with divinyl benzene, followed by hydrolysis of the esteric groups to carboxylic ones and complexation of the chelating groups inner the formed cavities. The copolymerization data and the characteristics of the poly(acrylate-co-DVB) particles are compiled in Table 1.

As can be seen, the size of the poly(PETEA-co-DVB) particles is decreasing from sample 4,4T to 20,4T, due to an increased compactness, related to an increased content in the polyfunctional acrylate units. As revealed by SEM observations, all generated particles are uniform and have a compact structure as compared to the hydrolyzed particles, which have an increased porosity (Fig. 1).
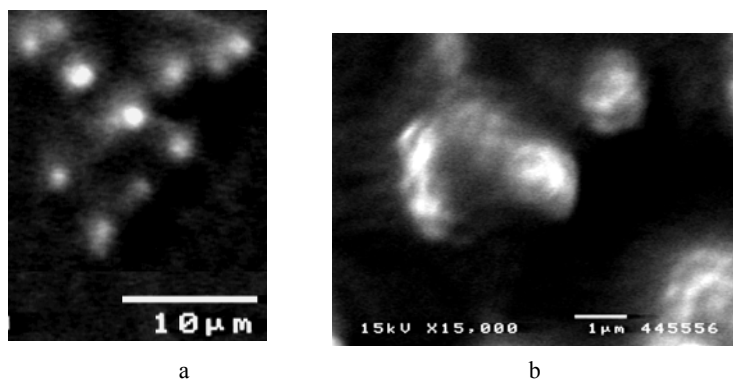

a   b

Fig. 1 – SEM microphotographs of copolymer particles (a) before (sample 2) and (b) after hydrolysis (sample 8).

The hydrolysis process was monitored by FT-IR spectrometry. As can be seen from the spectra of the initial copolymers and of the hydrolysed products presented in Fig. 2 (a, b) the peak situated at 1731.4 cm^{-1} in the initial sample, ascertained to the esteric C=O groups, was replaced by a new peak situated at 1703-1705 cm^{-1}, of higher intensity, due to the C=O stretching in the carboxylic groups. The peaks specific to the C-O-C stretching in the polyacrylates from 1253, 1152 and 1062 also disappeared, being replaced by a large band, of lower intensity, in the 1230-1170 cm^{-1} range.

The hydrolysed compounds were then complexed with appropriate amounts of manganese acetate (equivalent to Mn(III) complexes) in absolute ethanol, under inert atmosphere. All the obtained complexes present characteristic colours (given by the used metallic salt, totally different from the initial polymer, which is white in the solid state). The observed colours varied from beige to brown, with increasing concentration of added manganese. The hybrid materials were characterized by spectral technique and thermal analysis. In the FT-IR spectra the complexation is confirmed by the appearance of specific signals of increased intensity situated at 1557 cm^{-1}, 1415 cm^{-1}, 657 cm^{-1} and 616 cm^{-1} (Fig. 2c).

The thermostability of the coordinated complexes decreases as compared to the initial polymer support (Fig. 3) and with increasing the metal content (Fig. 4).
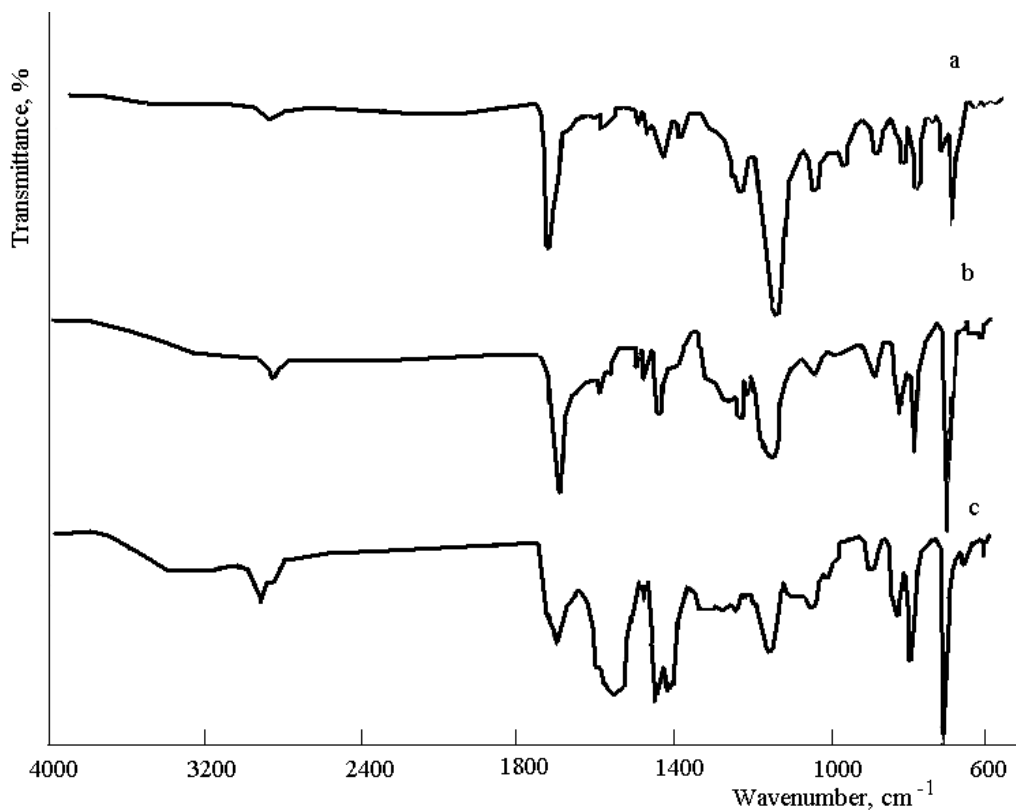
Fig. 2 – FT-IR spectra of samples based on copolymer 15,4T:
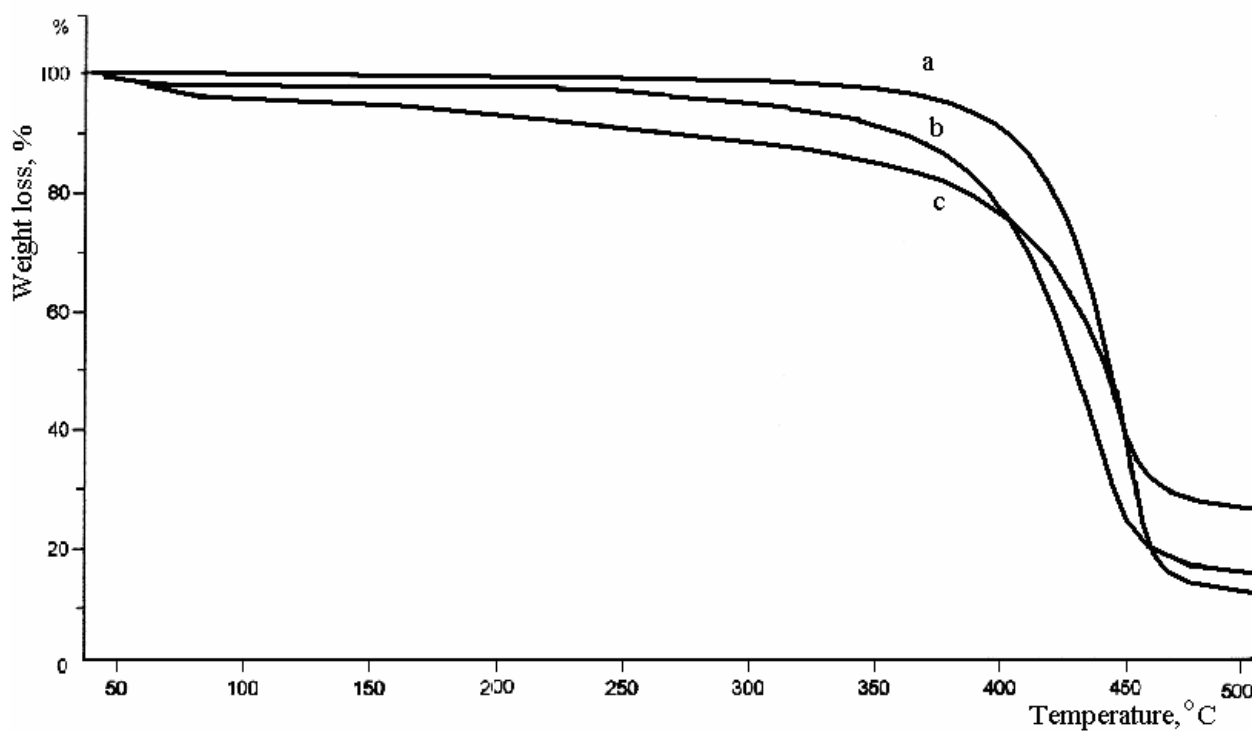a) initial, b) after hydrolysis, c) after complexation (sample 6).

Fig. 3 – Typical thermograms of samples based on copolymer 20,4T:
a) the initial copolymer; b) the hydrolysed form and c) the resulting complex with manganese
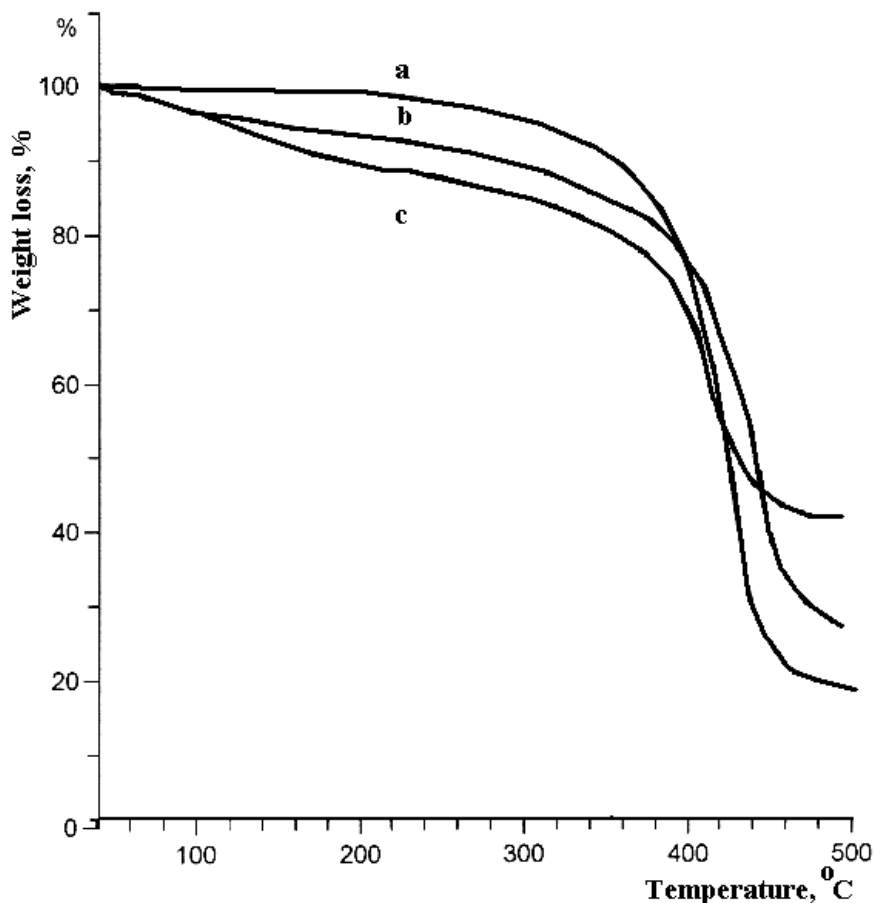
Fig. 4 – Typical thermograms of the complexed samples (a) 4,3T; (b) 20,4T; (c) 40,4T.

Table 1

Copolymerization of PETRA and PETEA with DVB. Characteristics of the Mn-hydrolyzed polymer complex

No.	Code	Copolymer particles							Complex
		Functional monomer PETRA	PETEA	Crosslinker	η^a	Dn	Dw	PI	Mn^b
		(g)	(g)	(g)	(%)	(μm)	(μm)		(%)
1	4,3T	0.12		1.20	84	1.4	1.5	1.06	1.6
2	4,4T		0.14	1.20	75	2.8	3.8	1.34	2.1
3	10,3T	0.30		1.04	67	1.7	2.2	1.30	3,1
4	10,4T		0.35	1.04	73	1.7	1.9	1.05	3.2
5	15,3T	0.45		0.91	89	1.9	2.3	1.20	3.2
6	15,4T		0.52	0.91	86	2.5	3.1	1.24	3.4
7	20,3T	0.60		0.78	87	2.2	3.0	1.38	6.0
8	20,4T		0.70	0.78	85	1.9	2.0	1.05	5.8
9	40,4T		1.40	0.26	90	2.0	2.1	1.05	8.5

[a]- polymerization yield
[b]- analytic determination

Concentrated complexes as polymer supported catalysts in epoxidation

To elucidate the structure of the complex involved and to conclude on the effect of shape and composition of the polymer chain used as support on the catalytic efficiency of the resulting material, a comparative study on four homopolymers – poly(4-vinylbenzoic acid) (pVBA), poly(acrylic acid) (pAA), hydrolysed poly(pentaerythritol tetraacrylate) (pPETEA) and poly(pentaerythritol triacrylate) (pPETRA) – was

performed. In the last case, the complex with copper acetate was also investigated with the aim to better understand the Mn-polymer complex structure and behaviour.

Retention by chelating may be accomplished in virtue of the presence of one or more donor atoms able to coordinate the polyvalent metal ions. Coordination or ion-exchange reactions were used to generate the metal-ligand chelates, i.e. the Mn – polymer and Cu – polymer complexes, respectively. In the first case, the reactions were carried out in acetonitrile solution at moderate

temperature (60-65ºC), in inert atmosphere, the equilibrium shifting to complex formation being achieved by periodic elimination of generated CH_3COOH from the system (by nitrogen purge). For the same reason a high concentration of the reactants in the system was adopted. The Cu complex with hydrolyzed poly(pentaerythritol triacrylate) was obtained by an ion-exchange reaction in aqueous solution.

The main characteristics of the realized materials are presented in Table 2.

Table 2

Homopolymers complexes characteristics

Code	Homopolymer support		Hybrid metal-polymer microparticles				
	Homopolymers	Yield[a] (%)	Dn (nm)	PI	Cu[b] (%)	Mn[b] (%)	Colour
pVBA	Poly(4-vinylbenzoic acid)	96	3.3	1.3		12	dark brown
pAA	Poly(acrylic acid)	75	3.5	1.4		11	dark brown
pPETRA	Hydrolyzed poly(pentaerythritol triacrylate)	95	1.5	1.1	31		intense blue
		85	3.1	1.2		30	dark brown
pPETEA	Hydrolyzed poly(pentaerythritol tetraacrylate)	90	2.5	1.3		32	dark brown

[a]- polymerization yield
[b]- analytic determination

The products structure was confirmed by investigations performed by FT-IR technique (Fig. 5) and thermal analysis (Fig. 6)

The resulted complexes present similar characteristics. In the FT-IR spectra (Fig. 5) the main signals ascertained to manganese complexes formation are situated at 1530 -1560 cm^{-1} and in the 1393 - 1420 cm^{-1} range (1561 cm^{-1}, 1420 cm^{-1} – pAA complex; 1553 cm^{-1}, 1393 cm^{-1}– pVBA complex; 1556 cm^{-1}, 1420 cm^{-1} – hydrolyzed pPETRA complex, 1530 cm^{-1}, 1400 cm^{-1} - hydrolyzed pPETEA complex) attributed to ν_{as} and ν_s (O-C=O) mode in the newly formed carboxylate groups. Specific are also the signals in the 600 - 660 cm^{-1} domain, ascertained to Mn presence, i. e. δ O-C=O and ν Mn-O (667 cm^{-1}, 615 cm^{-1} – pAA complex; 662 cm^{-1}, 618 cm^{-1} – pVBA complex; 657 cm^{-1}, 615 cm^{-1} – hydrolyzed pPETRA complex; 676 cm^{-1}, 615 cm^{-1} – hydrolyzed pPETEA complex). The presence of the signals at 1707 cm^{-1} and 1695 cm^{-1} in the spectra of the complexes formed with pAA and pVBA was related to the presence of uncomplexed, free COOH groups. However, almost 97 % of the added equivalent amount of Mn(III) salt was consumed. The signals situated at 1730 cm^{-1} and 1149 cm^{-1}, attributed to ν C=O and ν C-O-C stretching vibrations in pPETRA and pPETEA

esteric groups, disappeared. Also, the signal bands specific to acrylic compounds from 903, 831, 797.5 cm^{-1}, were replaced, according to the previously mentioned data.

According to the spectroscopic criterium[12] one may assume that a bidentate, polynuclear structured coordinative complex was generated.

As compared to the $Cu(OAc)_2 \cdot nH_2O$ specific bands in the FT-IR spectrum of the Cu-poly(pentaerythritol triacrylate) complex, the signals situated at 1604.5 cm^{-1} and 1445 cm^{-1} (multiplet), attributed to ν_{as} and ν_s (O-C=O) stretching vibrations in the original salt, are shifted to higher frequencies, i.e 1561 cm^{-1} and 1407.5 cm^{-1} (Fig. 5D). A similar trend can be observed in the 600-700 cm^{-1} range. The signals at 692 cm^{-1} and 628.5 cm^{-1} were replaced by signals situated at 682.4 cm^{-1} and 593 cm^{-1}. The signals situated at 3440 and 3333 cm^{-1} are ascertained to the water included in the complex structure. Thus, it may be concluded that the equivalence of the two coordinated groups is maintained in the generated Cu-polymer complex.

The proposed structures are confirmed by the DSC and TGA data (Fig. 6). Thus, while the decomposition of poly(pentaerytritol triacrylate) homopolymer takes place in a single step (89% weight loss) in the 370-460ºC range, its Mn

complex presents a more complex decomposition process: first, a 4% weight loss, attributed to the crystallization water, takes place at 225-227ºC, and then a 40.5% weight loss, ascertained to the decomposition of the carboxyl ligand groups, can be observed in two steps situated at 250-340ºC and 380-450ºC. The residual amount of about 53%, decomposing after 500ºC, mainly corresponds to Mn oxides.
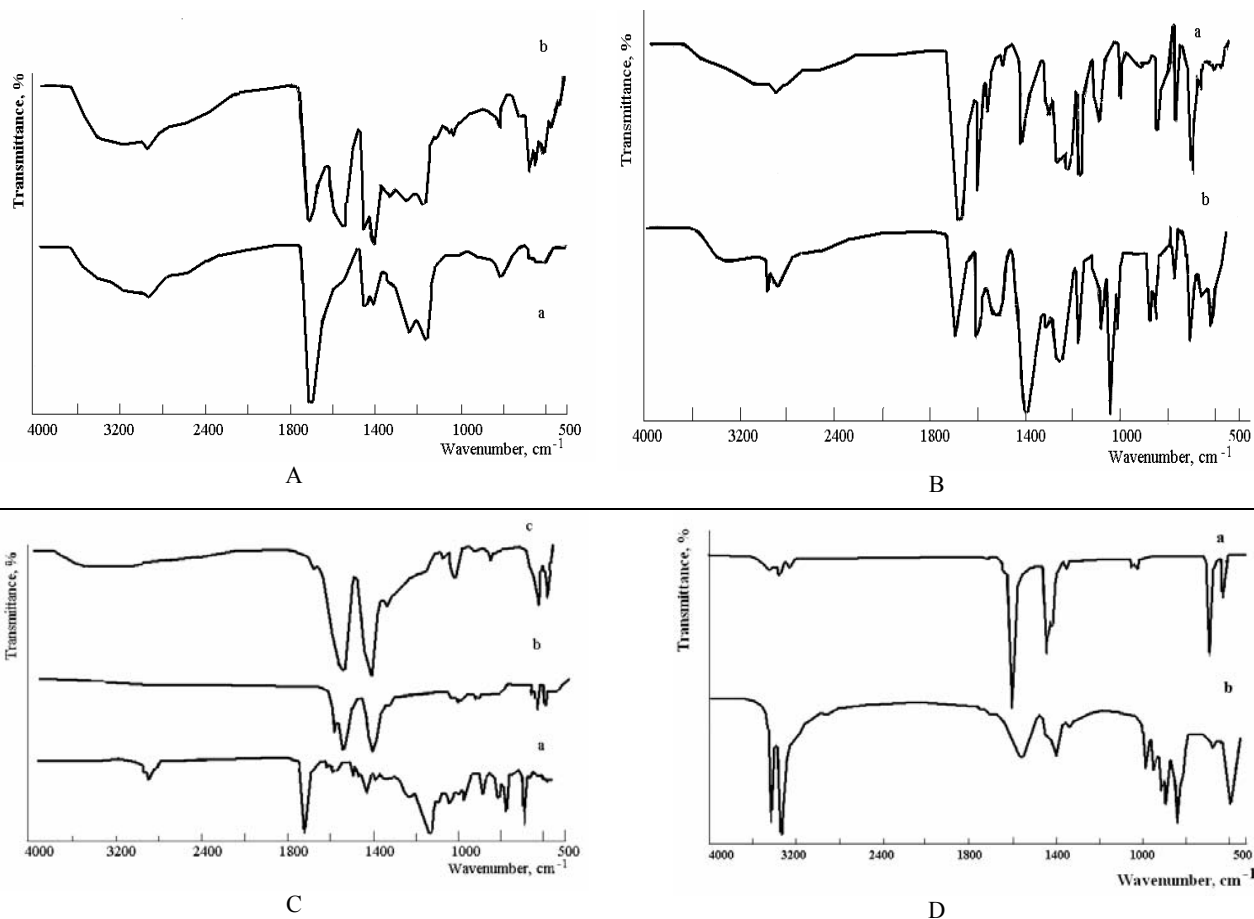

Fig. 5 – FT-IR spectra of: A: a) poly (acrylic acid); b) the corresponding complex with Mn; B: a) poly(4-vinyl benzoic acid); b) its complex with Mn; C: a) poly(pentaerythritol triacrylate); b) the complex of hydrolyzed poly(pentaerythritol triacrylate) with Mn; c) the complex of the hydrolyzed poly(pentaerythritol tetraacrylate) with Mn; D: a) $Cu(OAc)_2 \cdot nH_2O$; b) Cu(II) − hydrolyzed poly(pentaerythritol triacrylate) complex.
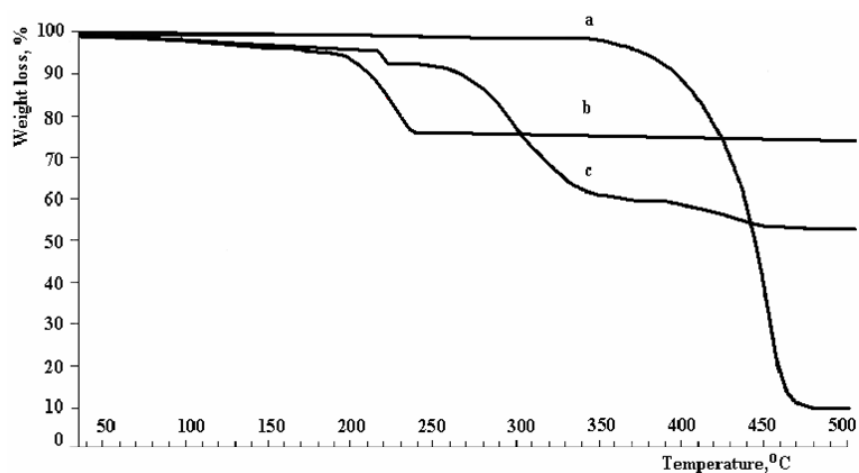

Fig. 6 – Typical thermograms for: a) poly(penthaerythritol triacrylate), b) Cu(II) − hydrolyzed poly(pentaerythritol triacrylate) complex, c) Mn − hydrolyzed poly(pentaerythritol triacrylate) complex.

For the Cu-poly(pentaerytritol triacrylate) complex the destruction of the two equivalent ligand groups linked to the Cu(II) ions takes place in the 195-235ºC range (weight loss, 18.6%) after the elimination of water (5% crystallization water). The weight loss process is connected with the strong endothermic effects observed in the DSC plot. The residual amount of 77% at 500 ºC is related to the high content in inorganic material.

Preliminary tests in olefin epoxidation of stilbene[13] gave a relatively low yield (40%) when sample 9 (Table 1) was used as a catalyst. However, yields higher than 70% were obtained for the Mn based complexes of poly(acrylic acid) and hydrolysed poly(pentaerythritol triacrylate), with a high stereoselectivity in the last case for the trans isomer.

Further studies are in progress. The copper catalyst, considered as a possible alternative, will be also tested for comparison.

CONCLUSION

Two synthesis alternatives were applied in order to achieve the synthesis of metal - polymer supported catalysts: 1) use of a molecular imprinting polymer strategy (sacrificial spacer route) followed by complexation with appropriate metal salts, and 2) direct complexation of soluble polymer supports. The complexation is an equilibrium process and can be controlled by reaction parameters (temperature, reaction duration, concentration of the partners, periodic elimination of the generated low molecular compound – the acetic acid).

A comparison between the complexes generated with contribution of Mn(III) or Cu(II) salts pointed on the increase of the ionic nature in the last case. The ligand groups are equivalent in Cu(II) complexes. With manganese, a similar coordinative complex was formed, independent on polymer support nature and specific structure. The performed investigations suggest a bidentate, polynuclear structure.

The random coil conformation of the liniar polymer chains with pendant chelating groups yielded an incomplete complexation of the functional groups, a lower catalytic efficiency and stereoselectivity in the epoxidation reaction of olefins as compared to the cluster-like structure of the hydrolysed poly(pentaerythritol triacrylate).

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