

*Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)*

MALEIMIDE TYPE POLYMERS BASED ON N-(3-ACETOXY-4-CARBOXY-PHENYL)MALEIMIDE

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Three maleimide type polymers have been prepared by starting from N-(3- acetoxy- 4-carboxy-phenyl)maleimide. The first one was prepared by free radical polymerization of this monomer, followed by chemical modification of the resulting homopolymer with *p*-amino-azobenzene. The second one was prepared by the reaction of the same homopolymer with metal (II) acetates. Finally, the third polymer was prepared by copolymerization of the monomer with divinylbenzene. The structures of these polymers were identified by IR, ¹H-NMR and UV spectroscopy. Their molecular weight values and thermal stability are also discussed.

INTRODUCTION

N-substituted maleimides (RMI)s, which belong to 1,2-disubstituted ethylenic compounds, are attractive monomers for designing special vinyl co-polymers. The maleimide ring can serve as a vehicle for many functional groups and for their pre-defined distribution in a polymer backbone through free radical polymerization.¹ Maleimide polymers and copolymers have found use in the area of electronics for the aerospace and aircraft industry. The general properties of this class of polymers include tractability, high thermal stability, high durability, good water resistance, fire resistance, and radiation resistance.² In addition, the maleimides are relatively cheap materials.

On the other hand, functional polymers, members of the salicylic acid family, show chelation, catalytic, thermochromic or photochromic properties. Therefore, the maleimide structures with same active groups can function as stabilizers, complexing agents, pharmaceuticals or catalysts.³ The chelating capacity of such a reactive polymaleimide has been investigated.⁴

Macromolecular metal chelates are new functional materials of supramolecular chemistry for strongly upcoming nanotechnologies. These polymers are perspective in many areas: microelectronics, membrans technology, medicine, high disperse finely conducting coverings, materials with magnetic, antistatic, tribochemical, ferromagnetic or non-linear optical properties, gaseous sensors, selective sorbents, superconductors and other. It is known that metalloorganic stabilizers were used for photo- and thermostabilization of polyolefines, polyamides and polystyrene-based materials. The excellent coordination capability of the carboxylic group with metals is well known.⁵⁻⁷ The polymeric nature of the metal dicarboxylate salts depends mainly on the coordination number of the metal ion as well as on the number of ligands from the system; the steric factors and the method of preparation have to be taken into account, as well.⁸ Organic complexes of Ni (II) are most well-known, but other metalloorganic compounds of Cu, Co, Mn are also very much studied. The complexing ability of polymers implies the separation process of metal ions and, generally, occurs in two steps: the complexing of a polymer with metal ions and filtration of the complexes through membranes of appropriate selectivity.⁹ For removal or selective adsorption of the metal ions, the

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multifunctional ligands are very important. From the analytical, coordination and environmental chemistry points of view, they can be useful due to differences in the stability constants of the complexes formed between ligand and metal ions.¹⁰ The complexing ability of polymers is used in nuclear chemistry, electrochemistry, hydrometallurgy, in environmental protection or for gas chromatography.^{9, 10, 11}

The carboxylic functionality can also be conveniently modified by polycondensation reactions. Among a variety of photosensitive materials, azobenzene derivatives demonstrate relatively high values of the induced anisotropy, caused by a high-absorption dichroism in azobenzene units. The well-known *trans-cis-trans* photoisomerization of azobenzenes produces at least three different kinds of motion in the polymer materials to which the azobenzenes are bound. The first is a photoinduced motion of the azobenzene groups only, and they can align in a selected position with respect to the light polarization. The second is a macroscopic motion of huge amounts of polymeric material, producing surface deformation, and the third is a reorganization of smectic domains in liquid crystalline polymers.¹² The materials containing azobenzene derivatives have found applications in optical data storage, holography, photo-switching of optical elements, and alignment of liquid crystals (LC). Also azobenzene moiety has been used as a photochromic mesogen in a variety of systems.^{13, 14, 15}

Various polymeric structures can be also prepared by suspension polymerization technique resulting in the structure diversification of the macroporous crosslinked (co)polymers.¹⁶ The synthesis of ion-exchangers, or adsorbents possessing important selectivity, using aromatic vinyl monomers from which, one with functionality more than two, has been developed and studied.¹⁷

The present paper describes some polymers based on N-(3-acetoxy-4-carboxy-phenyl)-maleimide, a reactive monomer belonging to the salicylic acid family.

EXPERIMENTAL

1. Reagents and materials

Maleic anhydride (Aldrich) was sublimed before use. Acetic anhydride, glacial acetic acid, dioxane, *p*-aminosalicylic acid, *p*-toluenesulfonic acid (PTS), *p*-amino-azobenzene, triethylamine dicyclohexylcarbodiimide (DCC) and benzoyl peroxide were provided by different commercial sources and used as received. Acetone, methanol and chloroform (Chimopar, Romania), dimethylsulfoxide, tetrahydrofuran (Fluka) and dimethylformamide (DMF) were dried before using by standard methods. Copper (II) acetate monohydrate, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, and Cobalt (II) acetate tetrahydrate, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O}$, (all purchased from Chimopar, Romania) were used as received. Divinylbenzene (DVB) was freed from the inhibitor and freshly vacuum distilled. under vacuum.

2. Measurements

¹H NMR spectra were obtained using a JEOL C-60 HL spectrometer. IR absorption spectra were recorded on a SPECORD M80 Carl Zeiss Jena, Germany Spectrophotometer, using KBr pellets. Thermogravimetric measurements were performed by using a MOM Derivatograph (Hungary) at a heating rate of 12 °C/min in air. The gel permeation chromatography (GPC) determinations were performed using a PL-EMD 950 Evaporative Mass Detector equipped with 2xPLgel 5 mm MIXED-C, 300x7.5 mm columns. Wide-angle X-ray diffractograms were obtained at room temperature on a TURM-62 diffractometer.

3. Synthesis of monomers

N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI)

N-(3-acetyl-4-carboxy-phenyl)-maleimide was prepared (Scheme 1) by condensation reaction of maleic anhydride and *p*-aminosalicylic acid.¹⁸ 9.8 g maleic anhydride (0.1 mol) and 15.31 g *p*-aminosalicylic acid (0.1 mol) were dissolved in acetone (200 ml), and then the mixture was stirred at room temperature for 30 min under nitrogen atmosphere. The resulting solution of N-(3-hydroxy-4-carboxy-phenyl)-maleamic acid was treated with 37.72 ml acetic anhydride (0.4 mol), 4 ml triethylamine (0.007 mol.) and 3.7 g sodium acetate (0.04 mol) at 55-60°C for 4 h. The crude product was filtered, washed with water, dried and reprecipitated three times from ether / *n*-hexane; yield 78.5%, mp. 93-94°C.

Elemental analysis (%): Calculated for $\text{C}_{11}\text{H}_9\text{O}_6\text{N}$ (251): C, 52.58; H, 3.58; N, 5.58; Found: C, 52.93; H, 3.02; N, 5.91.

IR (KBr, cm^{-1}): 3105 (=CH); 2900-3300 (COOH); 1780, 1720 (C=O imide I); 1380, 1410 (C=O imide II); 1165 (C=O imide III); 680-710 (imide IV); 1755, 1265 (C=O ester); 1270, 1070 (C-O-C ester) (Figure 1). ¹H-NMR (DMSO-*d*₆, TMS, ppm): 12.68 (s, 1H, COOH); 7.95-7.10 (m, 3H, Ar-H); 7.03 (s, 2H, vinyl); 2.23 (s, 3H, -CH₃) (Fig. 3).

4. Synthesis polymers

Poly [N-(3-acetoxy-4-carboxy-phenyl)-maleimide] (PACPMI)

PACPMI was obtained by radical polymerization of the corresponding monomer, ACPMI, in tetrahydrofuran (THF), at 60 °C, using N,N'-azobisisobutyronitrile (AIBN) as a radical initiator.¹⁸ The polymer was isolated by precipitation in methanol, purified by

reprecipitation with methanol from dimethylsulfoxide (DMSO), filtered and then dried in vacuum. The composition was determined by elemental analysis (Tab.1).

PACPMI containing azobenzene pendent groups - I

PACPMI was modified into a new polymer with azobenzene pendant group, by direct condensation, at ambient temperature, using DCC as activation agent (Scheme 2). A typical example is the follow: 1.09 g of PACPMI (4 mmol) were placed in a reaction vessel and dissolved in 7mL of dry DMF 0.788 g of *p*-amino-azobenzene (4 mmol) and 0.8232 g of DCC (separately dissolved in a minimum quantity of dry DMF) were added. The reaction was performed under inert atmosphere for 48 h at room temperature. The dicyclohexylurea (DCU) formed in reaction was filtered off. The remaining solution was precipitated in a water/methanol mixture 1/1. To remove the possible DCU traces, the resulting crude product was washed several times with water and methanol, dried, and then it was stirred for an hour with acetic acid, washed with water and dried again. Finally it was extracted with ethanol. Yield: 71%.

Metal Polymer Complexes - II

PACPMI was also used as macromolecular ligand (Scheme 3). PACPMI and metal (II) acetate, in molar ratio 1: 1.12, reported to the functional groups, were separately dissolved in methanol at concentrations of 0.05 mol/L and the solutions were mixed by stirring (Scheme 3). The reaction continued for about 2.5 h at room temperature. Depending of the involved metal, the color of the reaction mixture quickly modified, and a solid product separated. The solid was filtered off, washed with water and methanol and dried first in air stream and then in vacuum at 70 °C.¹⁹

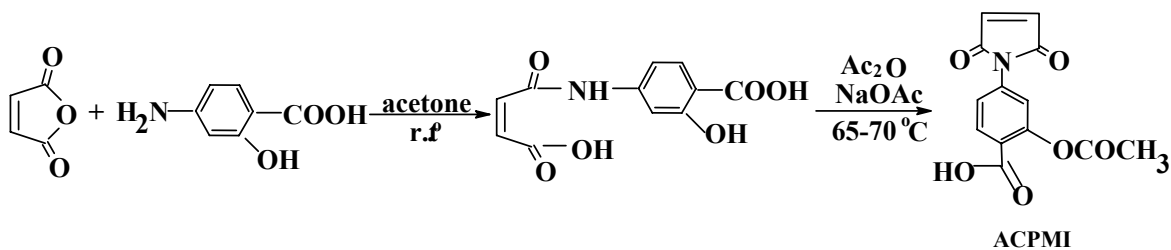
Crosslinked (co)polymers - III

Crosslinked bead-like copolymers from N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI) and divinylbenzene (DVB) have been synthesized by suspension polymerization reaction in dioxane at 80° for 16 h.²⁰ The polymerization mixture - DVB (free of inhibitors), variable quantities of dioxane and initiator (1.0% vs monomer weight) was poured into a flask with water and stabilizers at 60°C. Dioxane was used as solvent for maleimide monomer and was reported as f_g [weight of monomers / total weight (monomers + dioxane)]. The resulting bead fractions (0.10-1.00 mm) were collected, sieved, washed with hot water, dried and then extracted with methanol, in a Soxhlet apparatus. Yield: 89.3 %.

RESULTS AND DISCUSSION

N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI)

ACPMI is a monomer with two functional groups, based on a derivative of the salicylic acid (Scheme 1). This 1,2-ethylene type disubstituted structure determines a good thermal stability and a great structural stiffness of the resulting polymers, as a consequence of the five-member planar ring, that completely hinders the rotation of the imide residues around the chain of the molecule.



Scheme 1 – Synthesis of the monomer N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI).

The elemental analysis, IR and ¹H-NMR spectroscopy confirmed the discussed structure.¹⁸ Fig.1 shows the ¹H-NMR spectrum of the ACPMI with details on the position of the different type of proton signals.

Poly[N-(3-acetoxy-4-carboxy-phenyl)-maleimide] (PACPMI)

The homopolymer, PACPMI, has been prepared by radical polymerization of N-(3-acetoxy-4-carboxy-phenyl)-maleimide. The elemental analysis, IR and ¹H-NMR spectroscopy confirmed the expected structure.¹⁸ Some structural characteristics of the resulting polymers are shown in tab. 1.

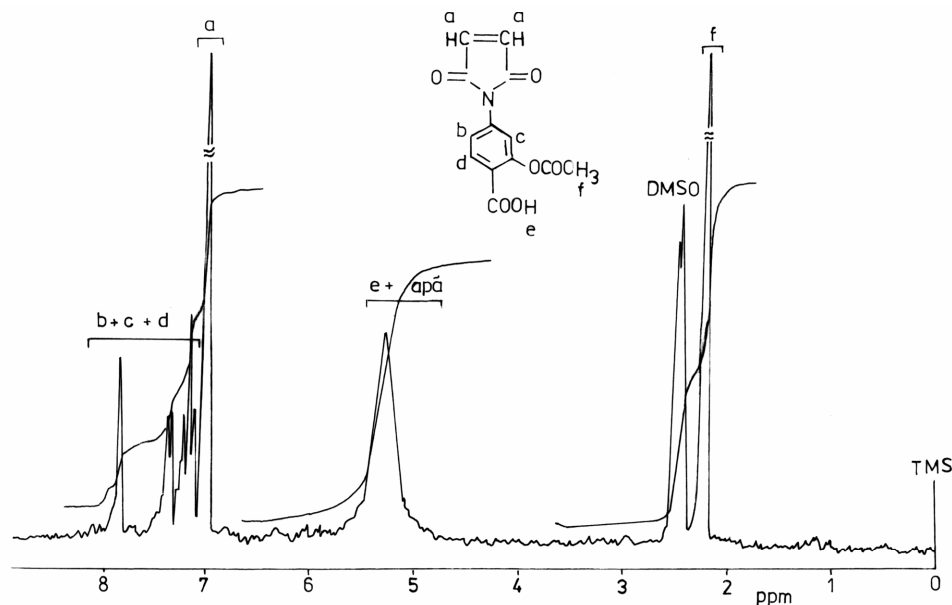


Fig. 1 – The $^1\text{H-NMR}$ spectrum of N-(3-acetyl-4-carboxy-phenyl)-maleimide in DMSO-d_6 .

Table 1

Some characteristics of poly[N-(3-acetoxy-4-carboxy-phenyl)-maleimide]

Reaction conditions ^{a)}			Elemental analysis	Molecular weight distribution ^{b)}		
Solvent (ml)	Temp. °C	Yield %	N %	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n	$\bar{G}P_n$
THF	60	64.8	4.91	5.7	1.60	21

^{a)} [monomer] = 0,236 mol/l; [AIBN] $\times 10^3$ = 2,362 mol/l; time = 168 h.; THF - tetrahydrofuran;

^{b)} By GPC using DMF as eluent.

PACPMI is an amorphous compound (Fig. 2). The X-ray diffraction (XRD) diagram shows the existence of two characteristic diffraction maxima (d_i , d_0).



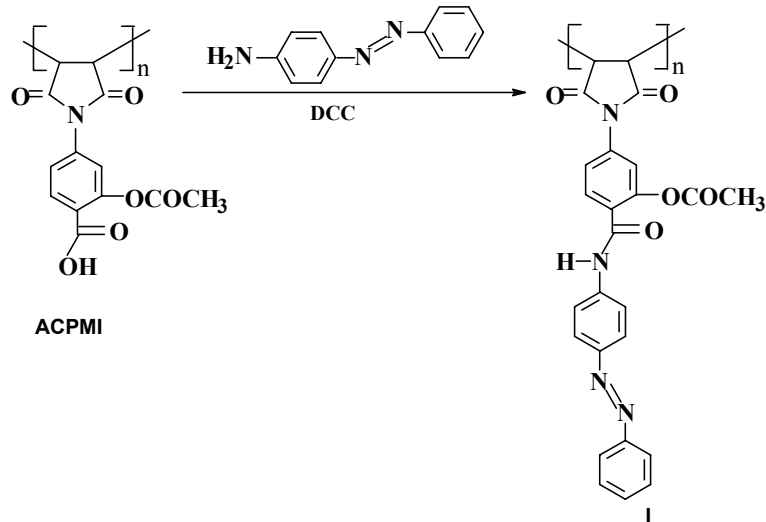
Fig. 2 – X-Ray diffraction diagram of poly[N-(3-acetoxy-4-carboxy-phenyl)-maleimide].

The geometry of the maleimidic monomer unit plays an important role regarding the stereospecificity of this polymer. *Cis* enchainments are not very probable and require a *trans*-opening of the double bonds.²¹ The third maximum, that can be observed as a shoulder on the outer peak, suggests a possible formation of a helix chain sequences in polymer. But the different orientations of the substituents on the phenyl ring

together with the possible intercalation of di-syndiotactic and atactic chain polymer sections, can affect the symmetry of the helix sequences.

PACPMI containing azobenzene groups in the side chain (PACPMI-Az) – I

The carboxylic reactive groups of the PACPMI can be directly modified by chemical reactions on the polymer. Scheme 2 outlines the synthetic route to prepare the polymer with azobenzene groups in the side chain.



Scheme 2 – Synthesis of the polymer I.

Fig. 3 shows the IR spectra of the monomer ACPMI, homopolymer PACPMI and the new polymer with azobenzene pendent groups, I.

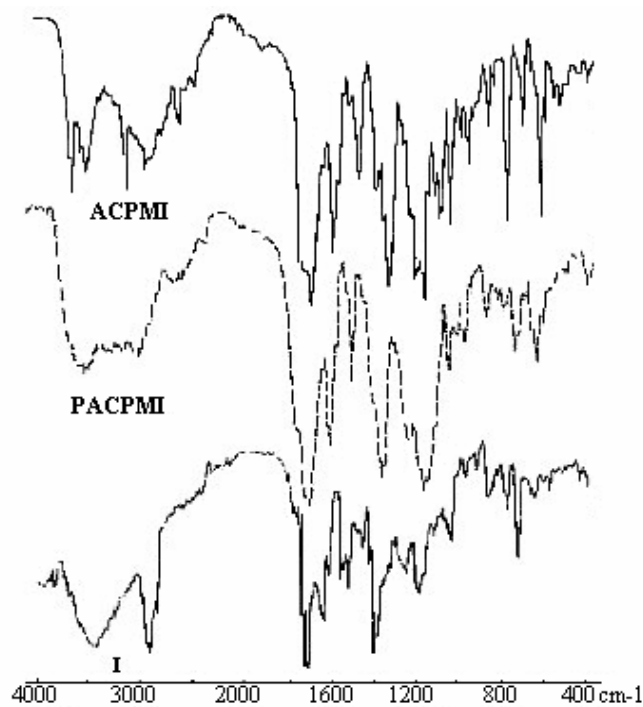


Fig. 3 – The IR spectra of the monomer (ACPMI), homopolymer (PACPMI) and the polymer I.

The absorptions bands at 1780 cm^{-1} , 1720 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide ring (imide I). The absorptions at 1380 cm^{-1} are due to C-N stretching in imide ring (imide II) and the bands at 1150 cm^{-1} (imide III) and at $760\text{-}750\text{ cm}^{-1}$ are assigned to imide ring deformation. A characteristic band for the newly formed HN-CO linkage at 1640 cm^{-1} was also registered (Fig. 3 polymer I).

The $^1\text{H-NMR}$ spectrum confirmed the expected structure for the polymer I (Fig. 4). The chemical shift of the amidic protons was identified at 10.67 ppm . The protons resonances of the succinimidic ring appear as a broad signal in the range of $3.5\text{ - }4.1\text{ ppm}$, while those of the acetoxy group appear at 2.3 ppm . as sharp singlet. Between $7.23\text{ - }8.56\text{ ppm}$ there is a broad peak assigned to the aromatic proton resonances. Another signal, corresponding to the proton resonance of the carboxylic acid appears at 12.7 ppm , which proves that the chemical modification reaction was not complete.

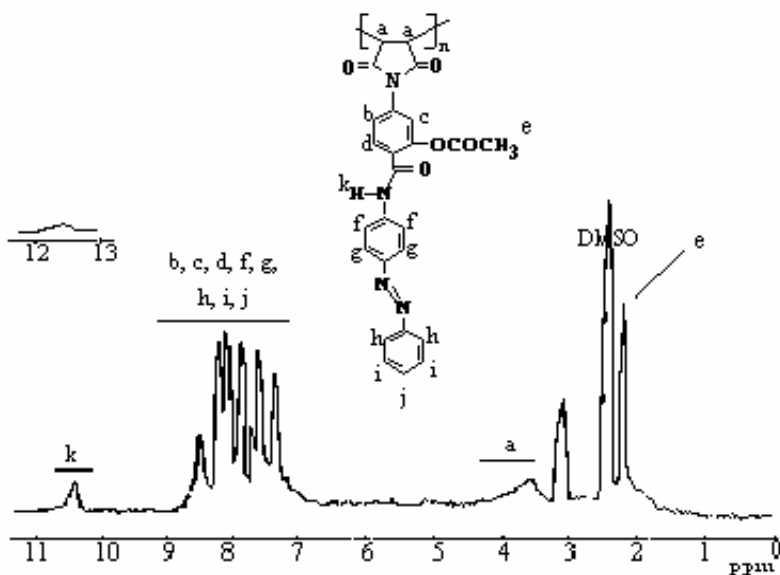


Fig. 4 – $^1\text{H-NMR}$ spectrum of the polymer I, in DMSO-d_6 , at room temperature.

The UV-vis spectrum of the polymer I is presented in Fig. 5. The sample exhibited an absorption maximum around 364 nm , due to the $n\text{-}\pi^*$ transitions of the azobenzene chromophore.

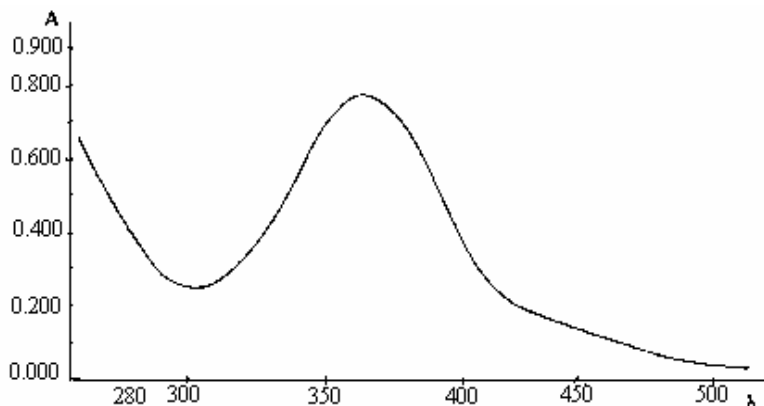
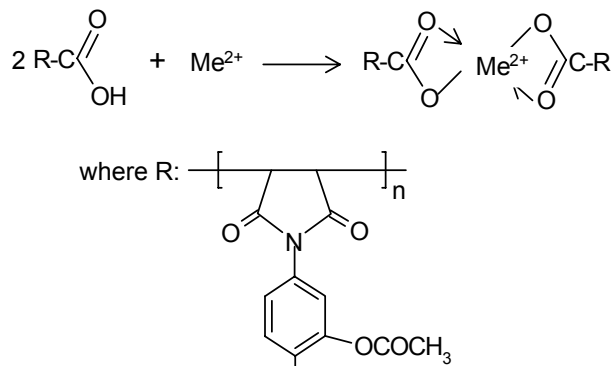


Fig. 5 – The UV-vis spectrum of the polymer I.

The new polymer dissolve easily in electro-donating organic solvent such as DMF, NMP, DMAc, DMSO and THF. This good solubility is due to the introduction of the large pendent groups which induce steric hindrance and prevent a dense packing of the chains.

Metal complex polymer, II

Poly[N-(3-acetoxy-4-carboxy-phenyl)-maleimide] (PACPMI) contains carboxylic acid and ester groups which can act as coordinating groups (Scheme 3).



Scheme 3 – Synthesis of the metal complex polymer, II.

Solutions of the PACPMI and metal acetates were mixed at room temperature and gave complexes (Tab. 2) which suddenly separated as fine powders from the reaction medium (methanol) Based on the insolubility of the complexes, it can be assumed that intermolecular-bridged polymer-metal complexes are formed. While the macromolecular ligand is soluble in a large range of solvents (DMF, DMSO, dioxane, THF, methanol) the complexes are insoluble in the common solvents.¹⁹

Table 2

Some characteristics of the metal-polymer complexes

Sample Code	Metal	Yield, ^a %	Aspect, color	Elemental analysis, % N Found /calcd ^b
IIa	Co	85.1	Pink powder	4.0 / 4.6
IIb	Cu	81.3	Light blue-greenish fine powder	4.2 / 4.6

^a Expressed as insoluble part; ^b Calculated for the structural unit.

It is difficult to verify the participation of the ester groups of the ACPMI and PACPMI in metal coordination by IR spectroscopy (Fig. 6). Firstly: the characteristic band of ester group in the range of 1680-1780 cm^{-1} is overlapped by the imide bands and no significant displacements of the other C=O (1190 cm^{-1}) and C-O-C (1090 cm^{-1}) ester groups are visible.

Secondly: the IR broad band in 2900-3300 cm^{-1} range, assigned to $\nu_{\text{O-H}}$ of the H-bonded carboxylic groups in PACPMI disappeared in the complexes, IIa, due to their consumption in the metal salt formation and, based on the insolubility of the reaction product, we can assume that the formation of the chelate polymer of salt type is favored.

The absorption band in the range of 3300-3500 cm^{-1} can be assigned to the water presence, either as lattice or in coordination sphere.

Fig. 7 presents the TGA curves. They show the weight losses in the range of 100-200 °C assigned both to the loss of crystallization (100-150 °C) and coordination water (150-200 °C).²²

This explains the differences which appear between the found and calculated elemental analysis values. Based on the values found for nitrogen content it can be appreciated that a chelate unit contains about three water molecules (Tab.2). As a proof for the presence of the metal in these polymer networks is the high char residue in TGA analysis of the chelate which represent the quantity of metal oxides formed during the thermooxidative decomposition and remained as residues up to 25% related to the initial molecular weight.

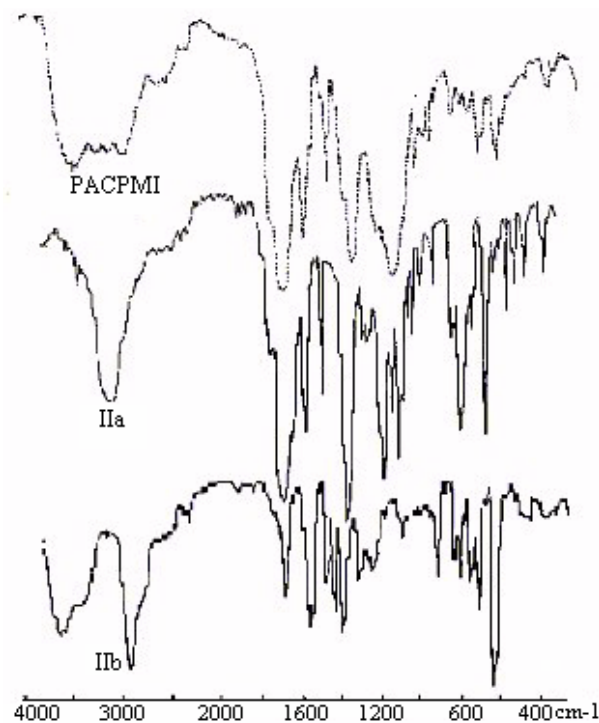
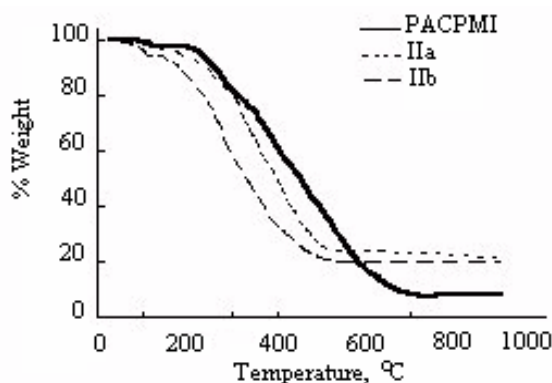


Fig. 6 – The IR spectra of the homopolymer **PACPMI** and the metal complexes **IIa** and **IIb**.

Fig. 7 – Thermal behavior of the homopolymer **PACPMI** and the metal complexes **IIa** and **IIb**.



Crosslinked (co)polymers – III

The copolymerization of polyunsaturated monomers is the most suitable method to perform heterogeneous crosslinked structures. New types of macromolecular architectures by free-radical crosslinking copolymerization of N-(3-acetoxy-4-carboxy-phenyl)-maleimide (ACPMI) and divinylbenzene (DVB) are obtained. Using the suspension polymerization technique and different ratio of ACPMI and DVB, several crosslinked polymers as beads with a good spherical geometry have been prepared. A possible architecture of the resulting polymers are shown in Fig. 8.

The characterization of the network edifice was performed by IR spectroscopy, thermal analysis, ion exchanger capacities and the swelling values at equilibrium. Practical and theoretical average molecular weight between crosslinks and crosslinking density were measured and calculated.²⁰

Since the crosslinking in a network has a random distribution, the characteristics of the copolymer structure are closely related to the average molecular weight between two crosslinks, M_c . The values of M_c for the studied copolymers were calculated from the swelling data at equilibrium. The M_c values (Fig. 9a, 9b) show that the synthesized structures via free-radical crosslinking copolymerization are sensitively dependent on the synthesis conditions.

Fig. 8 – A possible of the crosslinked copolymers III.

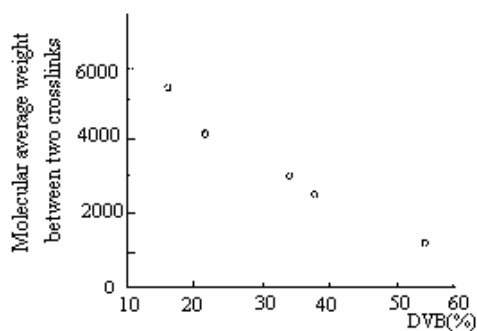
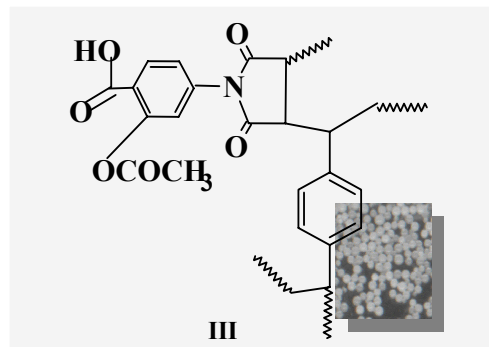
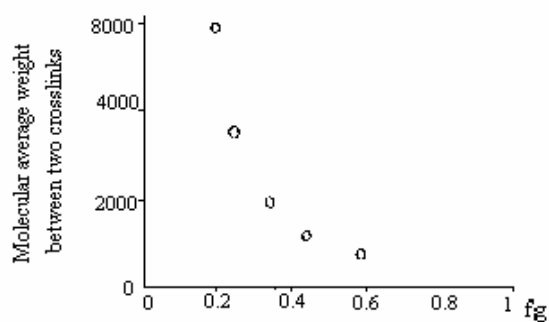


Fig. 9a – Variation of the average molecular weight between crosslinks vs. DVB quantity used in the polymer syntheses.

Fig. 9b – Variation of the average molecular weight between crosslinks vs. f_g used in the polymer syntheses.

From a macroradical-end evolution point of view if one double bonds is attached to a growing polymer chain, the next double bond added must belong to another molecule. The polymer chains first formed have pendant double bonds. By polymerization of pendant groups and by copolymerization, newly formed radical will attach to a previously formed polymer molecule, with propagation along that chain. Based on previous studies on crosslinked architectures, the possible reactions of the discussed macroradical-end are: 1) polymerization (with ACPMI or DVB); 2) crosslinking (with linear, branched or crosslinked polymer); and 3) cyclization. Finally, when multilayer structures join to form a network, the macroscopic structure is obtained.²³

CONCLUSIONS

New polymers based on N-(3- acetoxy- 4-carboxy-phenyl)maleimide have been prepared and their properties have been studied. All of these polymers exhibit fairly high thermal stability, with decomposition temperatures above 260 °C. The homopolymer based on N-(3- acetoxy- 4-carboxy-phenyl)maleimide was used as ligand for transition metals such Cu and Co. The crosslinked (co)polymers based on N-(3- acetoxy- 4-carboxy-phenyl)maleimide and divinylbenzene show a good spherical geometry and are promising candidates for use as ion exchangers.

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