

*Dedicated to the memory of
Professor Cristofor I. Simionescu (1920–2007)*

FUNCTIONAL MALEIMIDE-BASED STRUCTURAL POLYMERS*

Camelia HULUBEI

“Petru Poni” Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41 A, 700487 - Iasi, Roumania,
E-mail: hulubei@icmpp.ro

Received January 7, 2008

Two reactive imide type polymers, polymaleimides and addition polyimides have been prepared. Polymaleimides based on N-(4-carboxy-phenyl)maleimide have been synthesized by free radical polymerization, thus resulting the corresponding homopolymer, a linear copolymer with N-vinyl-2-pyrrolidone, and a cross-linked (co)polymer in reaction with trimethylolpropane trimethacrylate. Addition polyimides based on N,N'-4,4'-diphenylether-bismaleimide have been obtained by Michael polyaddition of 5-amino-salicylic acid and 5,5-methylene-bissalicylic acid to the bismaleimide double bond. The chemical structures were identified by IR, and ¹H-NMR spectroscopy. The calculated Q_1 and e_1 parameters for N-(4-carboxy-phenyl)maleimide in copolymerization with N-vinyl-2-pyrrolidone are of 0.035 and 1.013, respectively. The resulting bead-like (co)polymers have porous structures and a diameter in the range of 0.1-1.0 mm. Addition polyimides present inherent viscosities in the 0.28-0.37 dL/g range, and decomposition temperatures above 290 °C.

INTRODUCTION

Maleimides (MI) are monomers of special practical importance in the polymer industry.¹ Maleimides can polymerize either alone or in combination with other suitable monomers, by warming or catalytically.

The free radical polymerization of maleimides yields polyimides, important resins with good properties such as tractability, high thermal stability, high durability, good water, fire and radiation resistance.² On the other hand, bismaleimides (BMI) represent an useful class of thermoset compounds for the microelectronic packaging industry. Bismaleimides are cureble, liable to polymerization, yielding crosslinked resins. In addition, bismaleimides may be homocured in the presence of free radicals or photoinitiators, or combined with other free-radical curing monomers (acrylates, methacrylates, styrenics, vinyl ethers, vinyl esters, allyl monomers, olefins, and the like).

They may be also cured in the presence of comonomers via Diels-Alder, -ene, and Michael addition mechanisms. Bismaleimide-based structural polymers have attracted much attention as linear polymers or matrix resins because of their good adhesive properties, high thermal stability, capability to form network structures without loss of volatiles,³ especially for fiber-reinforced composites, for the electronic industry and aerospace technology.⁴⁻⁶ For practical applications, the use of chain-extended prepolymers is expected to reduce the inherent brittleness of BMIs because of the higher molecular weight between crosslinks.⁵ One such chain-extended copolymerization can develop a Michael addition reaction of a nucleophilic compound to the electrophilic maleimide double bond. BMIs and bis-nucleophiles have been exploited in the synthesis of a variety of linear high-molecular weight polyimides. Bisthiols,⁸⁻¹⁰ bistiohenols¹¹ and diamines¹²⁻¹⁴ are preferred bis-nucleophiles,

* “Chemists do know that the litmus paper changes its colour when shifted from an acid to an alkaline medium. If the sunflower – which quite curiously, in Franch, bears the same name with the above-mentioned paper, tournesol – demonstrates, beyond any doubt, exactly the opposite – namely, the steadfastness of its conduct – is, among others, to show to the humans, in its most dignified and silent way, that they may, – and should ! – live without successive changes in colour, without yielding their conscience and their firm beliefs”. Cristofor I. Simionescu, *Thoughts*, November 3, 1978.

because of their high basicity. In particular, diamines and diols have been used to extend bismaleimides, resulting in polyaspartimides^{15,16} and poly(imido-ether)s¹⁷⁻¹⁹ respectively. This paper presents some results on the versatility of the double bond occurring in the maleimide ring, which is an electron deficient bond, as due to the presence of an electron withdrawing carbonyl group on both sides. The maleimide double bond can be polymerized to give polymaleimides or it can be further polymerized, by addition of nucleophilic difunctional reagents, to give linear polymers.

EXPERIMENTAL

1. Reagents and materials

Maleic anhydride (Aldrich) was sublimed before use. Thionyl chloride was distilled before using. Acetic anhydride, glacial acetic acid, dioxane, N-vinyl-2-pyrrolidone (NVP), *p*-amino-benzoic acid (*p*-ABA), 4,4'-diaminodiphenylether (DDE), 5-aminosalicylic acid (5-ASA), 5,5'-methylene-bissalicylic acid (5,5'-MDSA) and benzoyl peroxide, provided by different commercial sources, were used as received. Solvents such as: acetone, methanol, chloroform, dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF) from different commercial sources, were purified by the usual methods.²⁰ Trimethylolpropane trimethacrylate (TRIM) (from Aldrich) was freed from inhibitor and fresh-vacuum distilled. 2,2'-Azobisisobutyronitrile was recrystallized from methanol several times (m.p. 103°C). Dioxane and toluene were used as diluting agents for the system N-(4-carboxy-phenyl)maleimide (CPMI) /trimethylolpropane trimethacrylate (TRIM); their quantity was expressed as a weight fraction, $f_g = \text{weight of monomers} / \text{total weight of (monomers + solvents)}$.

2. Measurements

The IR spectra were recorded on a Specord M 90 Carl Zeiss Jena Spectrophotometer with KBr pellets. ¹H-NMR spectra were recorded with a JEOL 60 MHz NMR spectrometer in deuterated dimethylsulfoxide (DMSO-*d*₆), without internal reference. DSC (differential scanning calorimetry measurements) were performed with a Mettler DSC 12E, at a heating rate of 10°C·min⁻¹, under nitrogen atmosphere. The thermal gravimetric analysis was carried out in air on a F Paulik Derivatograph, at a heating rate of 12°C·min⁻¹. The number average molecular weights (M_n) and the polydispersity indices (M_w/M_n) of the copolymers were determined by gel permeation chromatography using a PL-EMD 950 Evaporative Mass Detector equipped with 2 x PLgel 5 µm MIXED-C, 300 x 7.5 mm columns.

3. Synthesis of monomers

N-(4-carboxyphenyl)maleimide (CPMI) was obtained by the reaction of maleic anhydride with *p*-amino-benzoic acid, in dried acetone, at ambient temperature, followed by cyclodehydration with sodium acetate and acetic anhydride. Yield 82 %, mp: 242-243 °C (m.p. 244 °C according to literature data²¹).

Elemental analysis (%): Calculated for C₁₁H₇NO₄ (217): C, 60.83; H, 3.25; N, 6.45. Found: C, 60.48; H, 3.04; N, 5.97. IR (cm⁻¹): 3150, 2980, 2300, 1770, 1700, 1640, 1600, 1390, 1370, 1200, 820, 690. (Fig. 1) ¹H-NMR (ppm): 13.45-12.78 (s, 1H, COOH), 8.03 (d, 2H, aromatic), 7.49 (d, 2H, aromatic), 7.22 (s, 2H, olefinic).

4-Maleimido-benzoyl chloride (CPMIC) was synthesized by the reaction of CPMI with thionyl chloride, according to the procedure reported by Liu²². Yield 78 %, m.p. 166-167 °C (m.p. 168-169 °C according to literature data²²).

N,N'-4,4'-diphenylether-bismaleimide (BMI) was synthesized following the literature²³: m.p. 180-181°C. Yield: 82.5% Elemental analysis (%): Calculated for C₂₀H₁₂N₂O₅ (360.32). N (%) calcd/ found: 7.78/7.52; IR spectrum (KBr disc): 3140 (C=C), 1735, 730 (imide ring), 1510 (aromatic ring), 1420 (C-N stretching), 1265 (C-O-C); ¹H-NMR (DMSO-*d*₆) : δ (ppm): 7.3-7.96 (aromatic ring), 7.16 (vinyl group)

4. Synthesis of polymers

Polymaleimides. Homopolymerization of N-(4-carboxyphenyl) maleimide (CPMI) and its copolymerization with N-vinyl-2-pyrrolidone (NVP) were performed at 90 °C in sealed glass tubes with a radical initiator (AIBN 0.3 mol%) in dry DMF, under nitrogen atmosphere (Scheme 1). The resulting polymers, poly(N-(4-carboxyphenyl)maleimide [I] and poly(N-(4-carboxyphenyl) maleimide-co-N-vinyl-2-pyrrolidone) [II], respectively, were isolated by precipitation in methanol and water, and dried under vacuum at room temperature. The feeding compositions and the experimental conditions are given in Table 1.

Cross-linked polymer networks. Porous poly(CPMI-co-TRIM)s [III] (Scheme 1) were obtained by suspension copolymerization of CPMI and TRIM, in the presence of a diluting agent (dioxane, or dioxane-toluene mixture). The polymerization mixture, composed of monomers and variable amounts of diluents (Table 3, Co= abbreviation of copolymer) was poured into a flask containing water and stabilizers, at 45°C. The organic:water phase ratio was 1:5. Polymerizations were performed at 80 °C for 12 hours. A mixture consisting of the ammonium salt of styrene-maleic anhydride copolymer (0.40% vs. water), gelatine (0.2% vs. water) and NaCl (3% vs. water) was used in order to stabilise the droplets of the organic liquids. The resulting bead-like (co)polymers evidencing a porous structure, are separated, sieved and washed with warm water, and fraction 0.10-1.00 mm was collected. After filtration, the copolymer beads were extracted with methanol to remove the diluting agents. All samples were vacuum-dried at 50 °C for 48 h. The yields of cross-linked (co)polymers were 71.60 – 76.50% .

Poly(imido-eter)s. The reaction involves Michael polyaddition of a nucleophilic monomer (5-amino-salicylic acid or 5,5'-methylene-bissalicylic acid respectively) to N,N'-4,4'-diphenylether-bismaleimide, in an 1:1 molar ratio. (Scheme 1). The syntheses were performed under nitrogen atmosphere, in a dry NMP solvent (40% monomer concentration solution), at 95-105 °C, for 20-36 h, after which the reaction mixture was poured into water. The polymers were separated by filtration and washed several times with water and methanol. Products [IV and V] were dried at 50 °C for 8 h in a vacuum oven.

RESULTS AND DISCUSSION

Polymaleimides I and II. In spite of the fact that homopolymerization of maleimide is

extremely difficult, it copolymerizes quite readily with several vinyl monomers. The peculiar homo- and copolymerization characteristics of the electron-deficient maleimide group make it an attractive monomer for designing special vinyl polymers. Equally, it is known to form alternating copolymers with electron-rich monomers.²⁴ Apart from enhancing the thermal stability and glass transition temperature of the resultant copolymers, the maleimide group can effectively serve as a vehicle for many functional groups for their predefined distribution in a vinyl polymer backbone, through free radical copolymerization. Copolymerization is a method for improving polymer properties to meet specific requirements. Knowledge of the copolymerization process is also of considerable interest to evaluate the reactivity ratios of comonomers. The radical copolymerization

of CPMI (monomer 1) with NVP (monomer 2) was performed in an aprotic dipolar solvent, dimethylformamide (DMF), at 90°C, using 2,2'-azobisisobutyronitrile (AIBN) as initiator (Scheme 1). The structures were confirmed by IR and ¹H-NMR spectroscopy. Fig. 1 presents the IR spectrum of the CPMI monomer, with characteristic absorptions at: 3100-3070 cm⁻¹ (=CH of phenyl group), 2900-2850 cm⁻¹ (symmetrical and asymmetrical stretching vibrations of the aliphatic groups), 1780 cm⁻¹ (ν_{C=O} in plane), 1710-1730 cm⁻¹ (ν_{C=O} out of plane), 1400-1380 (ν_{C-N-C}), 740-700 cm⁻¹ (ν_{O=C-N}), as due to imide rings. The large band between 2900-3300 cm⁻¹ and the absorption peaks at about 1660 cm⁻¹ and 1200 cm⁻¹, respectively, are ascribed to the carboxylic pendant groups.²⁵

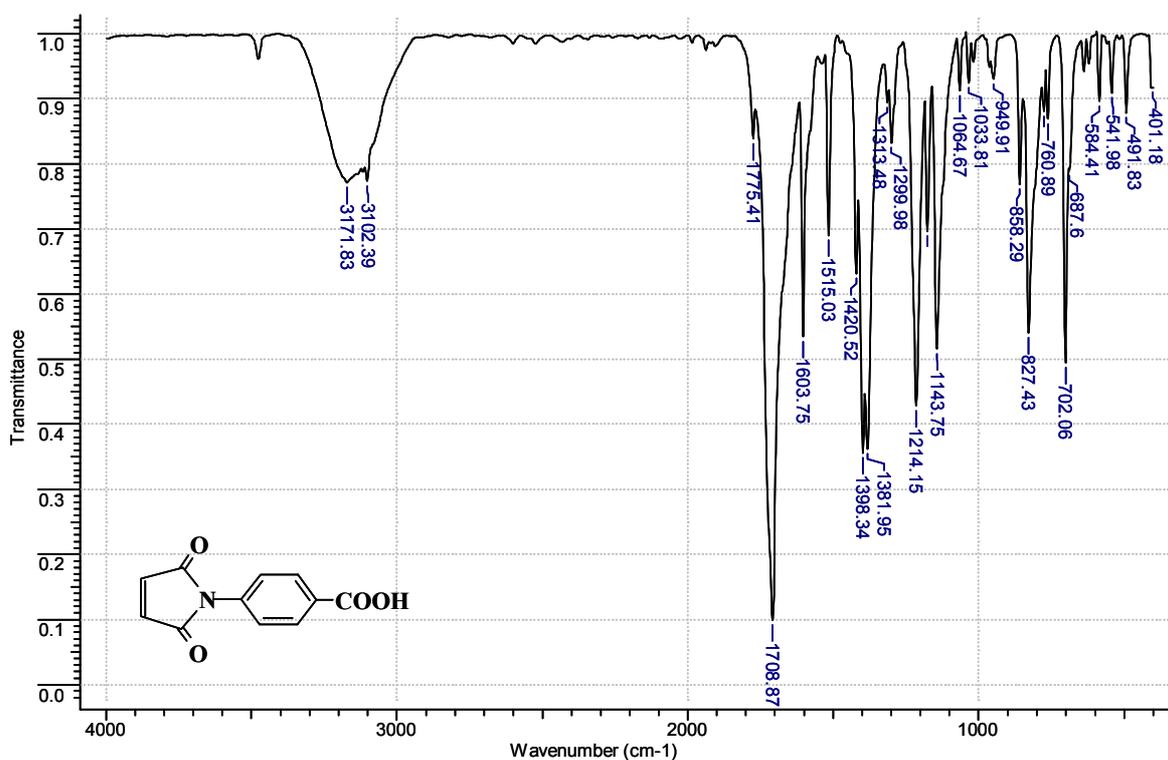
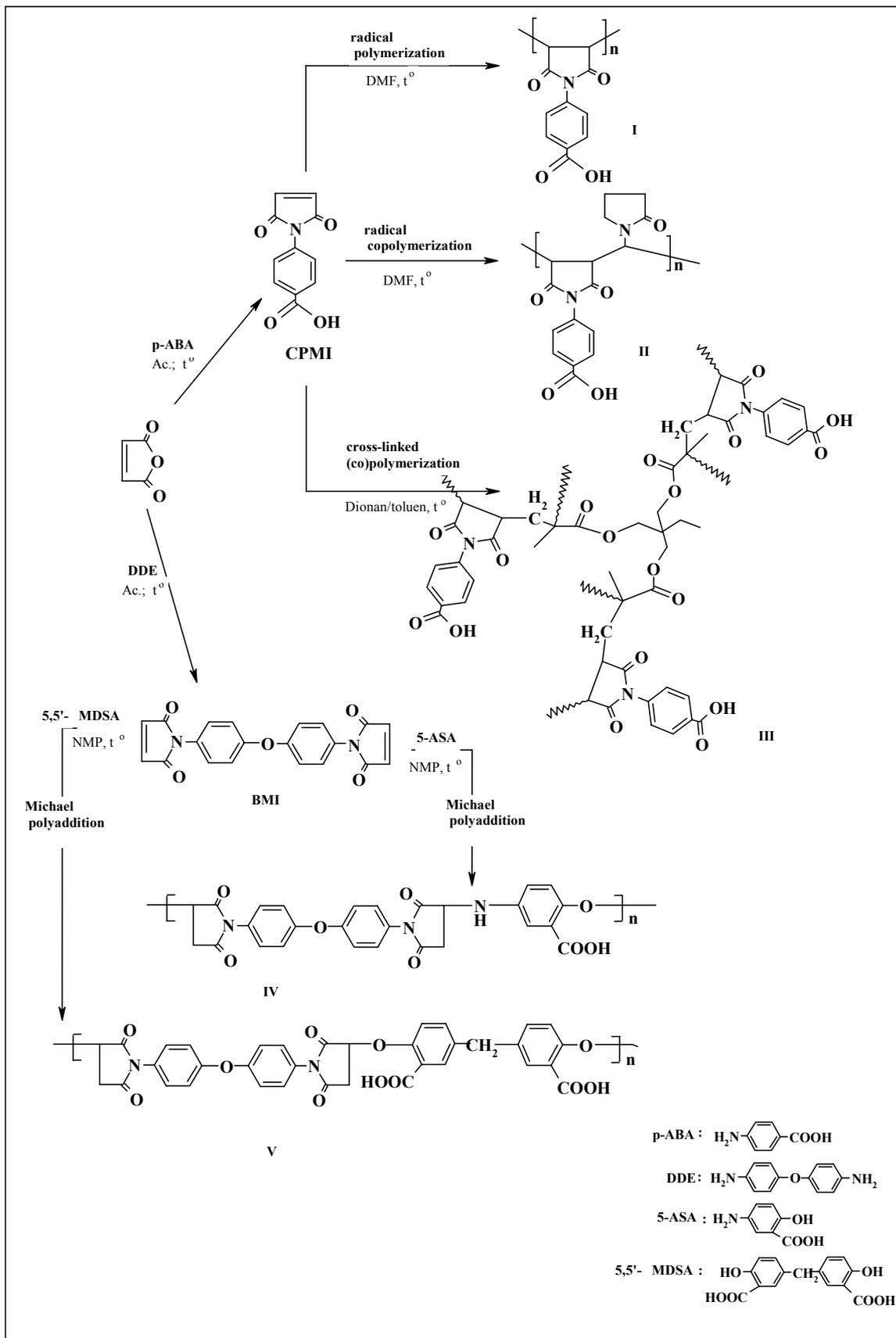


Fig. 1 – IR spectrum of N-(4-carboxyphenyl)maleimide (CPMI).

Copolymerization of CPMI with NVP was studied over a wide composition interval, with mole fractions of maleimide, ranging from 0.10 to 0.90 in the monomer feeding (Table 1).

If copolymerization of N-phenylmaleimide with styrene gives exactly an alternating copolymer for different monomers ratios in the feeding, in the copolymerization of N-(*p*-carboxyphenyl) maleimide with styrene the alternating character decreases,²⁶

also observed in the copolymerization of N-(carboxyphenyl)maleimide with N-vinyl-2-pyrrolidone. Fig. 2 plots the copolymerization diagram of the resulting copolymer, poly(CPMI-*co*-NVP). The curve suggests a copolymerization with a tendency towards an alternating structure, to be ascribed to the well-known system derived from the electron deficient maleimide and electron-rich styrene, or from N-vinyl-2-pyrrolidone monomers.²⁷



Scheme 1 – Chemical structures of monomer CPMI, polymaleimides **I** and **II**, cross-linked network **III** and poly(imido-eter)s **IV** and **V**.

Table 1

Copolymerization of CPMI (monomer 1) with NVP in solution at 90 °C

Sample	Monomer 1	Feed M ₁ (mole fraction)	Conv. ^b (wt %)	C ^c	Copolymer m ₁ (mole fraction)	\overline{M}_n^d × 10 ⁻³	$\frac{\overline{M}_w^d}{\overline{M}_n}$	IDT ^e (°C)
II-1	CPMI ^a	0.10	31.40	0.84	0.1740	25.50	1.3	248
II-2		0.30	47.10	2.16	0.3510	18.50	1.2	258
II-3		0.50	55.00	3.13	0.4390	8.70	1.4	263
II-4		0.70	41.80	4.00	0.5000	4.30	1.2	265
II-5		0.90	10.90	5.42	0.5750	4.10	1.4	268

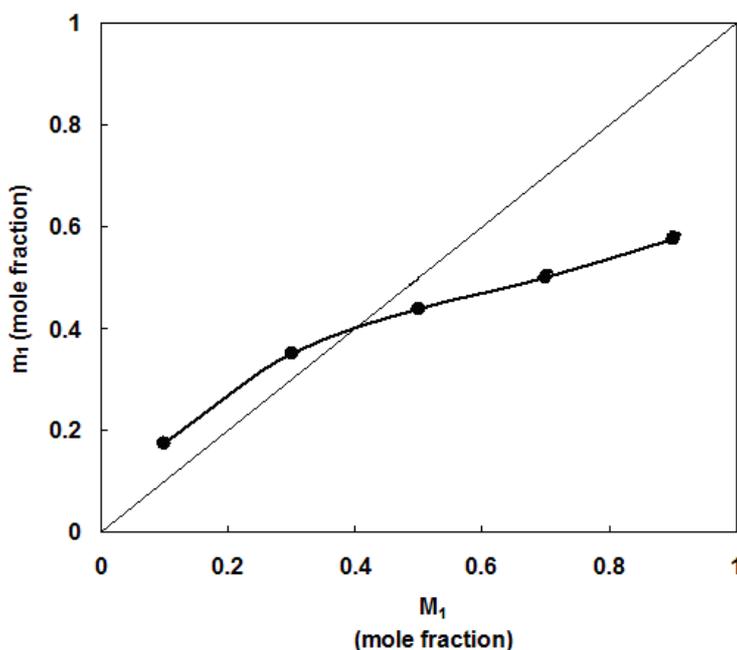
^a Solvent: DMF = 5 ml; [AIBN] = 0.3 mol% (with respect to the monomers mixture);Wt_{M1} + Wt_{M2} = 1 g; polymerization time = 1.5 h.^b Polymer insoluble in methanol.^c C = I_{Ar} / I_{CH(NVP)}; I_{Ar} and I_{CH(NVP)} are the intensities of the aromatic protons from RMI and of methine proton from NVP, used in the calculation of the mol fractions of m₁ and of m₂.^d Estimated by GPC.^e Initial decomposition temperature.

Fig. 2 – Monomer-copolymer composition curve for the copolymerization of CPMI with NVP.

Table 2

Reactivity ratios calculated by different methods for the copolymerization of CPMI (monomer 1) with NVP (monomer 2)

Monomer 1	Method	r ₁	r ₂
CPMI	ext K-T	0.027 ± 0.010	0.347 ± 0.021
	M-H	0.029 ± 0.006	0.347 ± 0.013
	Average:	0.028	0.347

Notes: ext K-T - extended Kelen-Tüdös method; M-H - Mao-Huglin method.

The calculated average reactivity ratio of NVP is of 0.347 for the copolymerization with CPMI. It can be seen that the reactivities of the growing radicals (regardless of their ends) are higher

towards the other monomer than towards themselves. The r₁·r₂ value is closer to zero, indicating a greater tendency towards alternation (e.g., of 0.0097 for the CPMI / NVP system). The

calculated Q_1 and e_1 parameters are of 0.035 and 1.013, respectively, for CPMI. The values of $Q_2 = 0.14$ and $e_2 = -1.14$ for NVP are taken over from the literature.²⁸ The obtained positive e values indicate that the maleimide monomer has an electron-poor double bond. The reactivity ratios and the Q and e values obtained for CPMI agree with the existing literature data.²⁹ The thermal behavior of the resulting polymaleimides was evaluated by thermogravimetric analysis (TGA). The initial decomposition temperatures (IDT) are above 250 °C. No T_g s were observed for either poly(CPMI) or poly(CPMI-co-NVP)s below their decomposition temperatures, which may be the result of the strong polarity of the carboxylic function located at the *para* position of the aromatic ring side group, and of the whole macromolecular chain as well. In this case, the contribution of the intra- or intermolecular polar interactions between the COOH groups in the neighboring units of a determined macromolecule or between the COOH groups in different polymer chains, should be also considered.³⁰ The resulting polymers are soluble in aprotic dipolar solvents such as: *N*-methylpyrrolidone, dimethylformamide, dimethylsulfoxide and tetrahydrofuran, their good solubility being due to the pendant groups which reduce the tight packing of the macromolecules. The disturbed packing facilitates the diffusion of small molecules of solvents and, by consequently, assures a better solubility.

Cross-linked network (co)polymers, III.

New cross-linked bead-like (co)polymers based on *N-p*-carboxyphenyl-maleimide (CPMI) and trimethylolpropane trimethacrylate (TRIM) were prepared with dioxane and toluene as porogens, by suspension polymerization (polymer III Scheme 1). Polymers with a good spherical geometry (Fig. 3) were obtained from different amounts of diluting agents (dioxane/toluene) as porogens, at a

constant molar ratio of the polyunsaturated crosslinking agent (TRIM) and of the monofunctional compound containing the maleimide polymerizable group (CPMI).



Fig. 3 – Spherical beads of cross-linked (co)polymer III-2.

The characterization of the network edifice was performed from the swelling values at equilibrium. The structures of the resulting copolymers depend on the synthesis parameters. Strong influence of the thermodynamic quality (δ_d =solubility parameter) and of the quantity of diluent used as porogen [f_g = weight of monomers/total weight of (monomers + diluents)] is manifested on the discontinuous phase (holes) which forms the porous macroreticular networks (Table 3). These parameters do not affect the continuous phase which forms the network structure.³¹

Vacuum-dried samples (48 hours at 50 °C) were analyzed to measure the values of specific density (ρ_p), apparent density (ρ_{ap}), and porosity (%P), according to the methods presented elsewhere.³²

The IR spectra illustrate the complex structure of the crosslinked copolymers. Typical absorption bands characteristic for both comonomers used (Fig. 4), yet wider, can be observed at about 3300-2900 cm^{-1} (-OH stretching), 1780 cm^{-1} (imide carbonyl symmetric stretching), 1720 cm^{-1} (imide carbonyl asymmetric stretching and carboxylic C=O), 1390 cm^{-1} (C-N stretching) and 730 cm^{-1} (imide ring).

Table 3

Initial composition of diluents mixture used in synthesis ^{a)}

Sample	Diluent		
	Nature of diluent	f_g ^{b)}	δ_d ^{c)} (J/m^3) ^{1/2} /mol
III-1	Dioxane	0.26	16.16
III-2	Dioxane:toluene=1:1	0.26	17.21

^{a)} The initial monomers composition, for all synthesized samples are CPMI : TRIM = 0.15 : 0.85 mol/mol

^{b)} The quantity of diluent f_g = weight of monomers/total weight of (monomers + diluents)

^{c)} δ_d (solubility parameter of the diluent):
$$\delta_d = \frac{X_1V_1\delta_1 + X_2V_2\delta_2}{X_1V_1 + X_2V_2}$$

where: X_1 , V_1 , δ_1 and X_2 , V_2 , δ_2 are volume fraction, molar volume and the solubility parameter of dioxane and toluene, respectively.

Table 4

Morphological characteristics of the resulting porous copolymers III

Sample	$\Delta\delta^{1)}$ (J/m^3) ^{1/2} /mol	$\rho_{\text{ap}}^{2)}$	$\rho_{\text{sp}}^{3)}$	P% ⁴⁾
III-1	2.38	1.3169	1.5646	15.83
III-2	1.33	0.8125	1.4290	43.14

¹⁾ $\Delta\delta^2 = \Delta\delta_d^2 - \Delta\delta_p^2$, where $\delta_p = 18.54$ (J/m^3)^{1/2}/mol. (solubility parameter of the polymer);

$\delta_s = 18.22$ (J/m^3)^{1/2}/mol. (solubility parameter of the swelling solvent)

²⁾ ρ_{ap} = apparent density; ³⁾ ρ_{sp} = specific density; ⁴⁾ % P = porosity

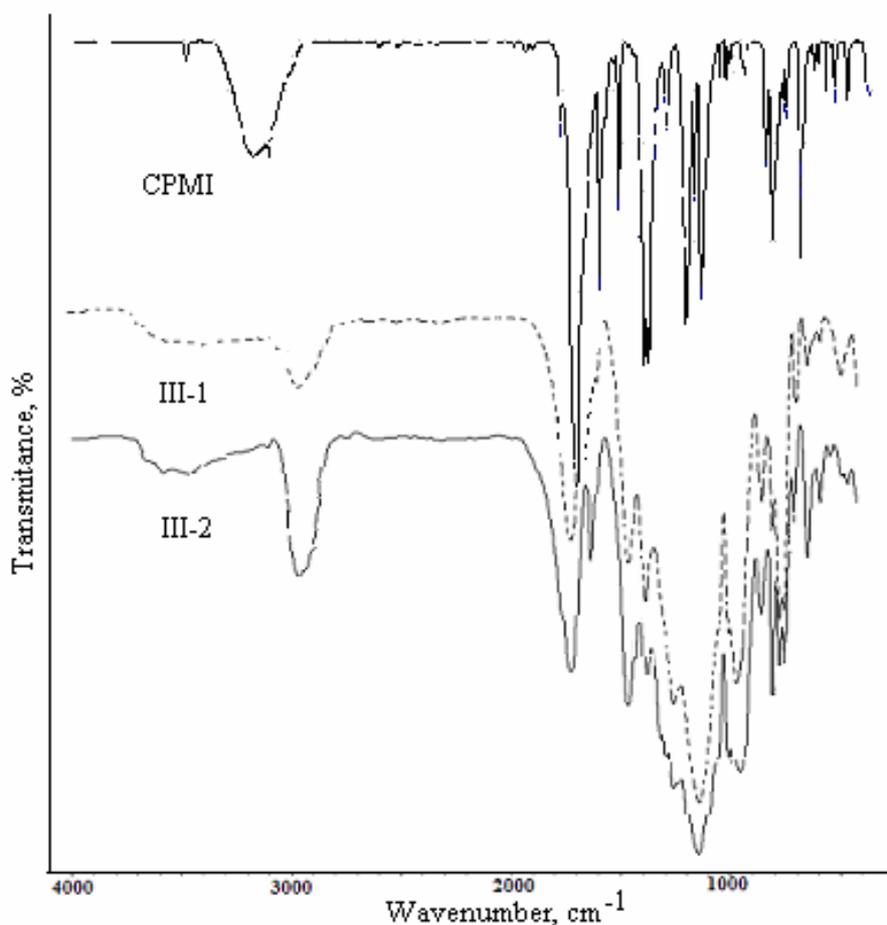


Fig. 4 – IR spectra of CPMI monomer and the cross-linked (co)polymers: III-1 and III-2.

The absorbance values recorded at 1630 cm^{-1} and 1330 cm^{-1} correspond to the carbon-carbon double bonds, while those at 2970 cm^{-1} and at 750 cm^{-1} are assigned to the aliphatic group of the polymer main chain. The polymers also show a large band between $2900\text{--}3300\text{ cm}^{-1}$, and others in the $1200\text{--}1300\text{ cm}^{-1}$ range, all ascribed to the carboxylic pendant groups. The copolymers exhibited a reasonable stability, with a 5% weight loss above $240\text{ }^\circ\text{C}$. Their thermal behaviour depends on the thermodynamic synthesis parameters, the chemical structure of the crosslinked copolymers and solubility parameter of the diluent.

Addition polyimides IV and V. The Michael addition reaction is a versatile synthetic method for an efficient coupling of electron poor olefins to a vast array of nucleophiles. The Michael addition benefits from mild reaction conditions, high functional group tolerance, a large host of polymerizable monomers and functional precursors, as well as high conversions and favorable reaction rates⁷. An outstanding property of the maleimide compounds is their susceptibility to a variety of chemical reactions, as a result of the electron withdrawing effect of the two adjacent carbonyl groups in the maleimide ring, which

creates a very electron-deficient double bond. This double bond is highly reactive. As a result, the maleimide type compounds are susceptible to a facile attack of a great number of nucleophilic agents (Michael reaction). Reactions between *N,N'*-4,4'-diphenylether-bismaleimide and salicylic acid derivatives were carried out in dry NMP, by mixing and heating an equimolar mixture of reagents. Polymerization occurred in solution,

through the addition of the nucleophilic groups NH_2 and OH respectively, to the $\text{C}=\text{C}$ double bond of the maleimide rings. The obtained structures (polymers **IV** and **V** Scheme 1) were confirmed by elemental analysis, IR, $^1\text{H-NMR}$, and characterized by molecular weights, thermogravimetric analysis and solution viscometry. Some data on the resulting polymers are listed in Table 5.

Table 5

Reaction between *N,N'*-4,4'-diphenylether-bismaleimide and salicylic acid derivatives*

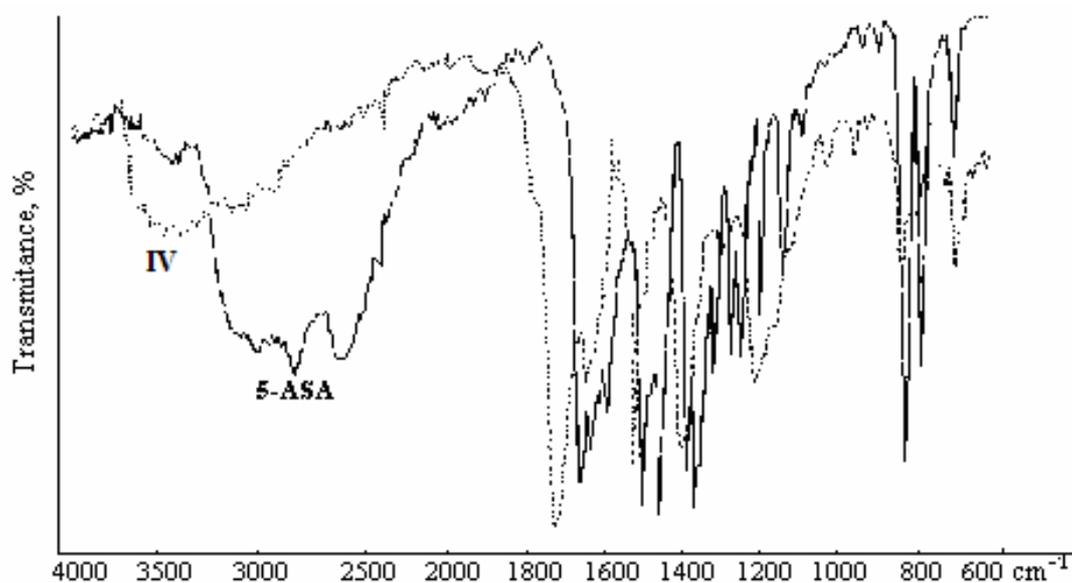
Polymer	N % Calc. / Found	η_{inh}^a (dL/g)	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_w / \overline{M}_n$	IDT ($^{\circ}\text{C}$)
IV	8.18 / 9.02	0.28	23.9	2,34	290
V	4.32 / 3.61	0.37	44.4	3.69	340

*Scheme 1 (**IV** - polymer based on 5-ASA; **V** - polymer based on 5,5'-MDSA)^aInherent viscosity measured at a concentration of 0.5 g/dL in DMF at 25 $^{\circ}\text{C}$.

According to the bands assignment reported in literature for the maleimide ring, the strong absorption at about 3100 cm^{-1} is associated with ν_{CH} , while that at 1150 cm^{-1} (imide III) with $\nu_{\text{C-N-C}}$.³³ By infra-red absorption spectroscopy, the disappearance of the characteristic band for the maleimide ring could be followed, together with the appearance of the succinimide ring formed during polyaddition as typical bands at 2900 cm^{-1} , 2850 cm^{-1} (ν_{CH_2}), and 1180 cm^{-1} ($\nu_{\text{C-N-C}}$) (Fig. 5). There are also signals for the newly-formed ether bridge¹⁸ at $1230\text{--}1270\text{ cm}^{-1}$ and for the NH-CH bond¹⁵ at $3380\text{--}3360\text{ cm}^{-1}$. The products show a

large band between $2900\text{--}3300\text{ cm}^{-1}$ and other special bands at about 1660 and 1200 cm^{-1} , respectively, all ascribed to the carboxylic pendant groups.

The $^1\text{H-NMR}$ spectra in DMSO-d_6 confirm the expected structures. Fig. 6 shows the $^1\text{H-NMR}$ spectrum of polymer **IV**, with peaks for the aromatic protons at $6.83\text{--}7.78\text{ ppm}$, as well as for the newly formed -NH bond, at about $5.58\text{--}5.72\text{ ppm}$. A multiplet in the $4.45\text{--}4.71\text{ ppm}$ region has been assigned to the methine protons from the succinimide ring, produced by the chain elongation reaction.

Fig. 5 – IR spectra of 5-amino-salicylic acid (5- ASA) and the polymer **IV**.

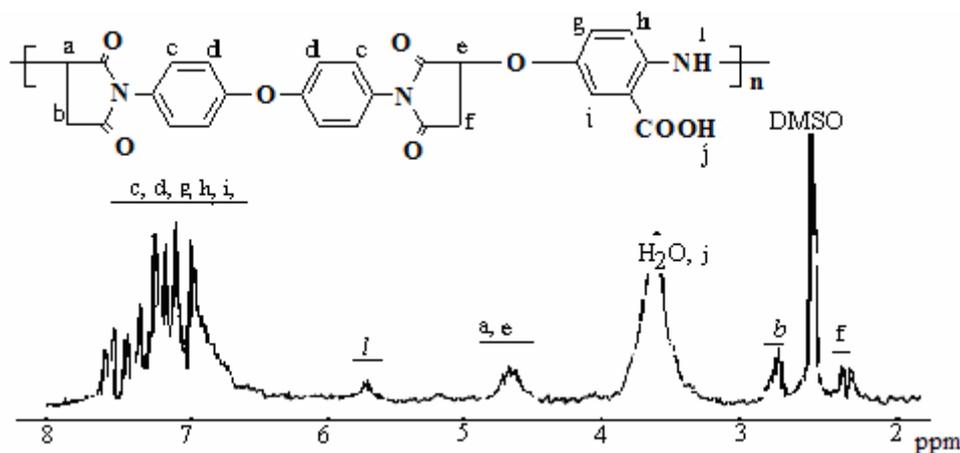


Fig. 6 – $^1\text{H-NMR}$ spectrum of the polymer **IV** in DMSO d-6.

The polymers begin to decompose in the 290–340 °C range. Solubility tests were determined at a concentration of 1%(w/v) at room temperature for different common solvents such as: dimethyl sulfoxide, dimethylformamide, 1-methyl-2-pyrrolidone, tetrahydrofurane, dichlorethan, chloroform and acetone. All products are soluble in electro-donating organic solvents such as NMP, DMF, DMSO and THF; and insoluble in the others.

CONCLUSIONS

A reactive monomer, namely *N*-(4-carboxyphenyl)maleimide (CPMI), has been homopolymerized, copolymerized (with *N*-vinyl-2-pyrrolidone) and cross-linked (co)polymerized (with trimethylolpropane trimethacrylate) respectively. The linear copolymer **II**, poly(CPMI-co-NVP), evidences a marked tendency towards alternation. The average reactivity ratios were found to be $r_1=0.028$, $r_2=0.347$ for the CPMI/NVP system. Both Q and e parameters under estimation confirmed *N*-(4-carboxyphenyl)maleimide as a monomer with an electron-poor double bond. No T_g s were observed for either poly(CPMI), **I**, and poly(CPMI-co-NVP)s, **II**, below their decomposition temperatures, which may be the result of the strong polarity of the carboxylic function located at the *para* position of the aromatic ring side group. The porous cross-linked (co)polymers, **III**, poly(CPMI-co-TRIM), were prepared by suspension polymerization technique, as spherical beads with a diameter in the range of 0.1–1.0 mm. The quantity of diluent used as a porogen, strongly influences the discontinuous phase (holes), which gives the porous structure of polymers. The continuous phase forming the

network structure is not affected by the quantity and thermodynamic quality of the porogen. Addition polyimides, **IV** and **V**, based on *N,N'*-4,4'-diphenylether-bismaleimide and salicylic acid derivatives, have an inherent viscosity in the 0.28–0.37 dL/g range, reasonable thermal stability (with initial decomposition temperatures above 290 °C) and good solubilities in electro-donating organic solvents such as NMP, DMF, DMSO, and THF. The presence of the carboxyl reactive groups permit chemical modification reactions in these media. The resulting structures may be used for hybride composite materials or as polymer matrix for novel separation materials.

REFERENCES

1. D. J. T. Hill, L. Y. Shao, P. J. Pomery and A. K. Whittaker, *Polymer*, **2001**, *42*, 4791–4802.
2. Y. L. Zhao, H. M. Li and P. S. Liu, *J. Appl. Polym. Sci.*, **2000**, *77*, 805–814.
3. H. D. Stenzenberger, “Addition Polyimides”, 1994 In: Hergenrother PM(ed) *Advances in polymer science, High performance polymers*. Springer, Berlin Heidelberg New York, vol. 117, p. 163.
4. S.C. Lin and E. M. Pearce, “High-performance thermosets: chemistry, properties, applications”, Hanser Munich, 1994.
5. R. Chandra and L. Rajabi, *J. Macromol. Sci., Rev. Macromol Chem Phys.*, **1997**, *C37*:61–69.
6. P. Mison and B. Sillion, *Advances in Polymer Science*, **1998**, *140*, 137–179.
7. B. D. Mather, K. Viswanathan, K. M. Miller and T. E. Long, *Prog. Polym. Sci.*, **2006**, *31* 487–531
8. J. V. Crivello, *J. Polym. Sci. A: Polym. Chem.*, **1976**, *14*, 159–182.
9. A. J. White and Scaia M D, *Polymer*, **1984**, *25*, 850–857.
10. A. J. White, A. D. Snider and M. D. Scaia, *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*, 589–587.
11. J. W. Connel, P. M. Hergenrother and S. I. Havens, *High Perform. Polym.*, **1989**, *1*, 119.

12. J. V. Crivello, *J. Polym. Sci. Polym. Chem. Ed.*, **1973**, *11*, 1185-1200.
13. M. R. Patel, H. S. Patel and J. D. Patel, *Eur. Polym. J.*, **1983**, *19*, 101.
14. A. J. White, M. D. Scaia, and A. D. Snider, *J. Appl. Polym. Sci.*, **1984**, *29*, 891-902.
15. L. V. Bell and R. P. Young, *J. Polym. Sci. Part. A. Polym. Chem.*, **1986**, *24*, 2647.
16. M. Sava and C. V. Grigoras, *J. Macromol. Sci., Part. A*, **2005**, *42*, 1095-1108.
17. A. Renner, I. Fargo, W. Hofmann and K. Ramsteiner, *Helv. Chim. Acta*, **1978**, *61*, 1443-1449.
18. C. Hulubei, C. Cojocariu, S. Pecincu and F. Popescu, *J. Macromol. Sci.-Pure Appl. Chem.*, **1997**, *A 34*, 1085-1095.
19. C. Hulubei and V. Cozan, *High Perform. Polym.*, **2004**, *16*, 149-158.
20. D. D. Perrin and W. L. F. Armarego (Eds) "Purification of Laboratory Chemicals", 3rd edition, Pergamon Press, New York, 1988.
21. J. A. Mikroyannidis, *Polym. Sci. A*, **1990**, *28*, 679-685.
22. F. J. Liu, S. Munukutia, K. Leven and G. Tesoro, *J. Polym. Sci., Part A, Polym. Chem.*, **1992**, *30*, 157-162.
23. C. Hulubei, V. Cozan and M. Bruma, *High Perform. Polym.*, **2004**, *16*, 405-418.
24. T. Oishi, K. Sase and H. Tsutsumi, *J. Polym. Sci., Part A: Polym. Chem.*, **1998**, *36*, 2001-2012.
25. S. Morariu and C. Hulubei, *High Perform. Polym.*, **2006**, *18*, 185-198.
26. C. P. R. Nair, D. Mathew and K. N. Ninan, *Eur. Polym. J.*, **1999**, *35*, 1829-1840.
27. C. Hulubei and S. Morariu, *Rev. Roum. Chim.*, **2006**, *51*, 425-433.
28. L. J. Young, *J. Polym. Sci.*, **1961**, *54*, 411-455.
29. K. Ito and Y. Yamashita, *J. Polym. Sci.*, **1965**, *A-1*, 2165-2187.
30. T. Oishi, M. Iwahara and M. Fujimoto, *Polym. J.*, **1991**, *23*, 1409-1417.
31. C. D. Vlad and C. Hulubei, *High Perform. Polym.*, **2002**, *14*, 31-40.
32. C. Viklund, E. Ponten, B. Glad, K. Irgum, P. Horstedt and F. Svec, *Chem. Mater.*, **1997**, *9*, 463-471.
33. M. F. Grenier-Loustalot and Da Cunha, *High Perform. Polym.*, **1998**, *10*, 285-308.