Maleimide-containing Polyamides

CAMELIA HULUBEI*
"Petru Poni" Institute of Macromolecular Chemistry, 41A Aleea Grigore Ghica Voda, 700487, Iasi, Romania

Functional polyamides with hydroxyl pendant groups were prepared by the direct polycondensation of 5,5'-methylene-bissalicylic acid, with various diamines (p-phenylenediamine, 4,4'-oxydianiline and 4,4'-methylenedianiline) in N-methyl-2-pyrrolidone, using triphenyl phosphite and pyridine as condensing agents. The resulting polymers were chemically modified with 4-maleimidobenzoyl chloride, resulting in polyamides with maleimide pendant groups. The polymer structures were confirmed by elemental analysis data and spectroscopic (IR, ^{1}H-NMR) characterizations. Their inherent viscosities were in the range of 0.22 to 0.34 dlg^{-1}. The polymers were soluble in dipolar aprotic solvents such as dimethylsulfoxide, dimethylformamide, and were thermally stable up to 314 °C. The chemically modified polyamides exhibited better solubility and thermal stability than their unmodified counterparts.

Keywords: polyamide, maleimide, Yamazaki-Higashi polycondensation, reactive polymers

Aromatic polyamides are considered a class of high-stable resistant engeenering compounds. These thermoplastic polymers possess excellent mechanical properties and thermal stability, but the chain stiffness and intermolecular hydrogen bonding between amide groups [1] limit their solubility and induce high glass transition (Tg) or melt temperatures. The absence of softening or melting behaviour at a convenient processing temperature and the tendency to degrade before or at the softening point [2] make these polymers difficult to process. In order to enhance the solubility and to bring down the Tg or melting temperature, various attempts of structural modifications of the aromatic polyamide backbone have been made either by introducing kinked and flexible bridging units [3–5], by methyl substituted phenylene groups [6,7] or by N-alkyl substitution [8]. Maleimide groups can undergo dimerization and Michael addition reactions under certain conditions. Incorporation of maleimide groups in polymers exhibited effectiveness on the increase of crosslinking density, enhancement of thermal stability, and improvement of flame retardancy [9–13]. The present paper refers to synthesis and characterization of functional polyamides with maleimide pendant groups. The polymers were synthesized by the chemical modification of three reactive polyamides obtained by so-called Yamazaki phosphorylation-polyamidation reaction.

Experimental part

Measurements

Infrared spectra were recorded with a Specord M-80 Spectrophotometer by using KBr pellets. The ^{1}H-NMR spectra were recorded on a JEOL C-60 MHz Spectrometer for polymer solution in deuterated dimethylsulfoxide (DMSO-d_6) using tetramethylsilane (TMS) as internal standard. The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in dimethylformamide (DMF), at 25°C, at a concentration of 0.5 g/dL. Thermogravimetric analyses (TGA) were performed on a MOM derivatograph (Hungary) in air, at a heating rate of 12°C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% wt. loss. The temperature of 10% wt. loss (T_{10}), was also recorded. The glass transition temperatures (Tg) of the polymers were determined with a Mettler differential scanning calorimeter DSC 12E at a heating rate of 10 °C/min under nitrogen atmosphere. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflexion curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymer.

Materials

p-phenylenediamine, 4,4'-oxydianiline, 4,4'-methylene-dianiline, *p*-amino-benzoic acid, 5,5'-methylene-bissalicylic acid, acetic anhydride, triphenyl phosphite and pyridine (Py), from different commercial sources, were used without further purifications. Maleic anhydride (Aldrich) was sublimated before use. Thionyl chloride (Merck) was freshly distilled. Solvents such as acetone, methanol, chloroform and N-Methyl-2-pyrrolidone (NMP) from different commercial sources, were purified by the usual methods [14].

Monomer synthesis

4-Maleimidobenzoic acid (MBA)

The monomer MBA was obtained by the reaction between maleic anhydride and *p*-amino-benzoic acid, in dried acetone, at ambient temperature, followed by chemical cyclodehydration with sodium acetate and acetic anhydride (scheme 1), according to the method reported by Searle [15]. 9.8 g maleic anhydride (0.1 mole) and 13.71 g *p*-amino-benzoic acid (0.1 mole) were dissolved in acetone and the mixture was stirred at room temperature for 4 h under nitrogen atmosphere. The resulting N-(4-carboxyphenyl)maleamic acid was treated with 37.72 mL. acetic anhydride (0.4 mole), 4 mL triethyl amine (0.0007 mole) and 3.7 g sodium acetate (0.04 mole), at 55-60 °C, and stirred for 4 h. The reaction mixture was poured into a large amount of water to give the crude 4-maleimido-benzoic acid, which was filtered, washed with water, dried and recrystallized from methanol-water (6:1) mixture solution. Yield 76%: m.p. 241°C (lit. 244 °C [16]).

Elemental analysis (%): Calculated for $C_{11}H_7NO_4$ (217.17): C, 60.83; H, 3.25; N, 6.45. Found: C, 60.48; H, 2.84; N, 5.97.

IR (KBr) cm^{-1}: 3600-2700 (broad O-H), 1777 (C=O free imide I), 1710 (imide I), 1600, 1510 (C=C, aromatic), 1390 (imide II), 1215 (C-O, COOH), 1145 (imide III), 820 (1,4-phenylene ring), 690 (imide IV). ^{1}H-NMR (DMSO-d_6, ppm),

* *email: hulubei@icmpp.ro; Tel.: 0232 260 332 260 334*

δ: 12.36 (s, 1H, COOH), 7.93 (d, 2H, ortho to COOH), 7.49 (d, 2H, ortho to -N<), 7.15 (s, 2H, olefinic).

4-Maleimidobenzoyl chloride (MBC)

The acid chloride monomer was prepared using thionyl chloride [17] (scheme 1). Yield 81%; m.p. 168-170 °C (lit. m.p. 170 °C [17])

Elemental analysis (%): Calculated for $C_{11}H_6ClNO_3$ (235.63): C, 56.07; H, 2.57; N, 5.94; Cl, 15.05. Found: C, 56.51; H, 2.79; N, 6.34; Cl, 15.63. IR (KBr) cm^{-1}: 3120 (w, olefin C-H), 3080 (w, aromatic C-H), 1780 (s, acyl chloride C=O), 1718 (s, imide C=O); 1390 (imide II), 1145 (imide III), 890 (COCl), 845, 830 (1,4-phenylene ring), 720 (imide IV). ^{1}H-NMR (DMSO-d_6, ppm), δ: 8.12 (d, 2H, ortho to COCl), 7.49 (d, 2H, ortho to -N<), 7.20 (s, 2H, olefinic).

Polymer Synthesis

Polyamides with hydroxyl pendant groups (**3**)

Polymers **3a**-**3c** were prepared by direct polycondensation according to a reported method by Yamazaky-Higashi [18]. In a typical experiment, a mixture of 2.5 mmol of an aromatic dicarboxylic acid, 2.5 mmol of a diamine, 5 mmol of triphenyl phosphite, 40 mL NMP and 20 ml pyridine already containing 0.75 g of dissolved LiCl was heated with stirring at 100°C for 3h under nitrogen. After cooling to room temperature, the reaction mixture was poured into a large excess of methanol. The precipitate was filtered, washed with methanol and hot water. The polymer formed was vacuum dried for 8h.

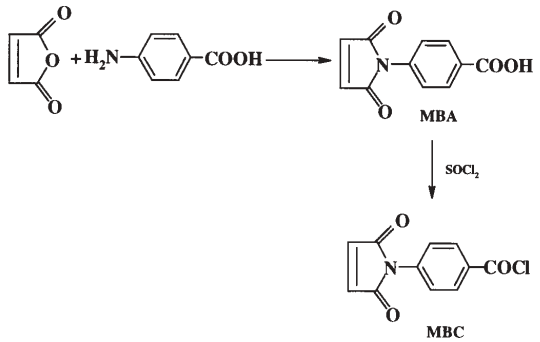
Polyamides with maleimide pendant groups (**3**)

Polyamides **3** were obtained by a polymer analogous reaction on the polymers **3** (scheme 2). In a flask equipped with a mechanical stirrer and a condenser were placed 0.77g (2 mmol) polymer **3a** in 15 mL of dry DMF, and 0.165 ml (2 mmol) pyridine at 10°C . To this solution, 0.94 g (4 mmol) of 4-maleimidobenzoyl chloride in 5 mL of dry DMF, was added dropwise, with continuous stirring. The reaction mixture was heated to 60°C and kept at this temperature for 6 h. The obtained product was precipitated into acidified water, washed and dried for 4 h in a vacuum oven.

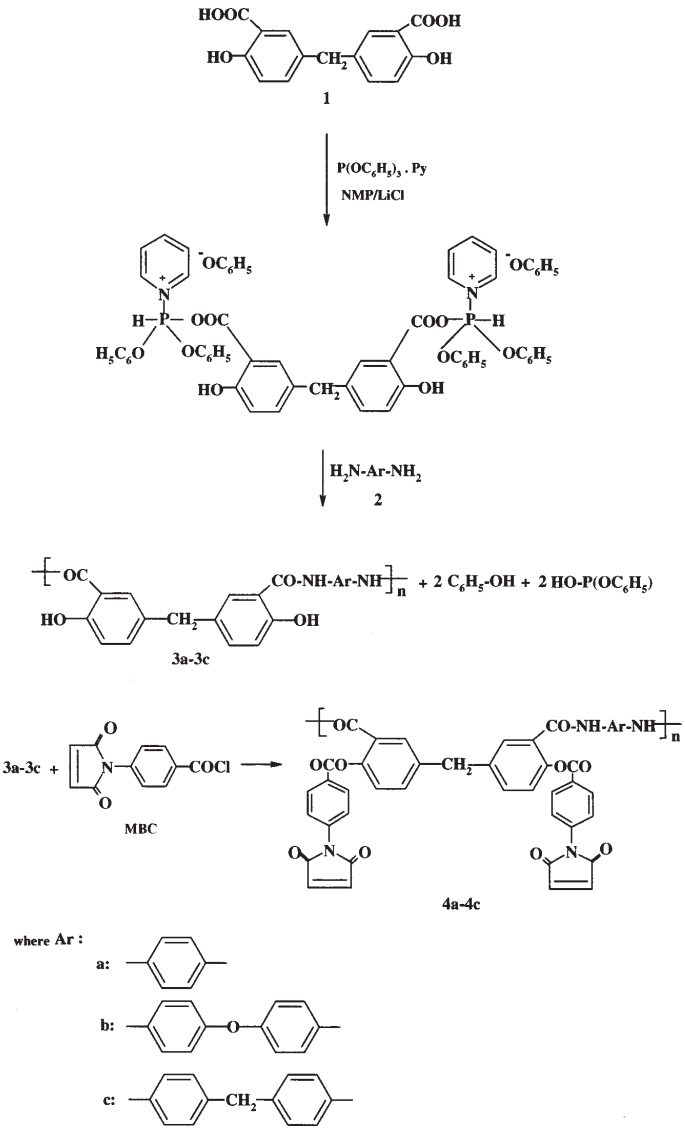
Results and Discussions

For the purpose of incorporating maleimide units into polyamides chains, 4-Maleimidobenzoyl chloride was synthesized as scheme 1describes .

The polyamides **3a**-**3c** have been obtained by so-called Yamazaki-Higashi phosphorylation-polyamidation reaction of the 5,5'-methylene-bissalicylic acid with three aromatic diamines. The chemical modified polymers, **4a-4c,** have been obtained by a Schotten-Baumann method, using 4-maleimidobenzoic acid, *via* its acid chloride. Scheme 2 shows the preparation of the polyamides with maleimide pendant groups in the side chain.



Scheme 1. Synthesis of 4-maleimidobenzoic (**MBA**) acid and its acid chloride (**MBC**)



Scheme 2. Synthesis of the polyamides **3** and **4**

The polyamidation carried out with the *in situ* activation of the dicarboxylic acid (scheme 2). The reaction took place at 100°C, in a mixed Py / NMP solvent, containing triphenyl phosphite as condensing agent, and lithium chloride. The inorganic salt was used in order to preserve the solubility of polymer during the condensation reaction. The positive influence of 3-4% lithium chloride in the synthesis of aromatic polyamides is well known [19]. All the polycondensation reactions proceeded homogenously in solution, without precipitation and gave quantitative yields of polymers.

The chemical structures of the obtained polymers were supported with the analytical results of IR and ^{1}H-NMR spectroscopy. The IR data for all the polyamides showed characteristic amide absorptions around 3400cm^{-1} attributed to N–H stretching vibration. Other amide absorptions appeared between 1670-1645 cm^{-1}, due to C=O stretching vibration (amide I) and at about 1520 cm^{-1}, due to N–H deformational vibration (amide II). Polyamides **3** presented special absorption bands for unassociated phenol –OH group, at about 3100-3500 cm^{-1}. The IR spectra of the chemical modified polymers **4,** showed characteristic absorptions of imide bands at about 1780 cm^{-1} (asymmetric C=O stretching of imide ring), 1720 cm^{-1} (symmetrical C=O stretching of imide ring), 1385 cm^{-1} (C–N), and 695-705 cm^{-1} (imide ring deformation). Other characteristic absorptions include aryl ether stretching near

1242 cm^{-1} (**3b**, **4b**). Figure 1 presents the IR spectra for the pair of polyamides **3b** and **4b.**

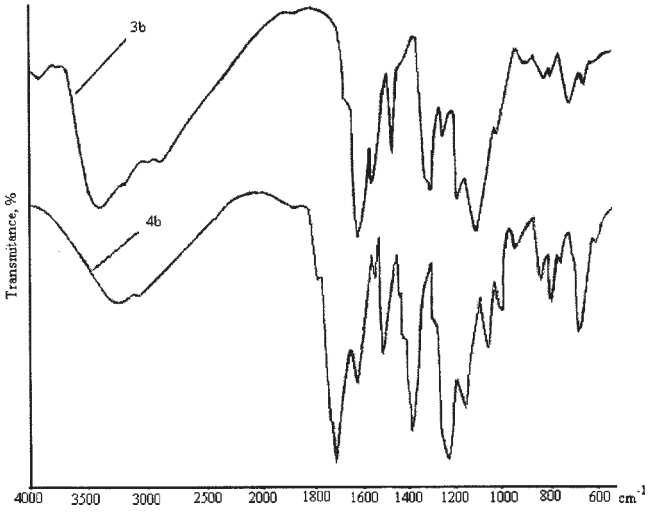


Fig. 1. IR spectra of the polymers **3b** and **4b**

The ^{1}H-NMR spectra of the polyamides, in DMSO-d_6 solution, displayed signals characteristic to the corresponding monomers and the maleimide group respectively. The majority of peaks, in a relative downfield spectrum region, are assigned to the resonances of the -NH-CO- proton at about 10.50 ppm, the aromatic protons, in the field of 6.70 - 8.03 ppm, and additionally, to the vinyl protons of the maleimide ring, at about 7.2 ppm (**4a**-**4c**).

Nitrogen content, from elemental analysis data is in good agreement with the calculated values (table 1).

All the products were soluble in electro-donating organic solvents such as DMSO, DMF, NMP, and they were insoluble in the others (table 2). Room temperature solubility tests were performed using the following solvents: DMSO, NMP, DMF, THF, $CHCl_3$, acetone, methanol, toluene, benzene. The solubility is explained by the presence of flexible bridges, such as ether, and the pendant groups, which induce asymmetry and steric hindrance which prevented a dense packing of the polymer chains and make the shape of the respective macromolecules to be far from a linear rigid rod.

The resulting polymers presented inherent viscosities in the range of 0.28-0.34 dL/g indicative of moderate molecular weights. No considerable differences in the η_{inh} values of modified and unmodified polyamides were observed.

Thermal stability was evaluated by TGA analysis. The polymers began to decompose in the range of 314-342 °C and the temperature of 10% weight loss (T_{10}) was in the range of 347-392 °C (table 3).

The higher stability of the polymer **3a** might be attributed to the restricted molecular mobility in the main chain arising from the stiffness of the aromatic diamine skeleton structure. It has been recognized that aromatic ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. In general, such a structural modification leads to lower glass transition temperature and crystalline melting temperatures as well as improvement of solubility and other processing characteristics of the polymers without greatly sacrificing other advantageous polymer properties [20, 21]. Based on the similar structures one can assume that the degradation process could begin in the aliphatic

Table 1
ANALITICAL DATA AND SPECTROSCOPIC PROPERTIES OF POLYAMIDES **3** AND **4**

Polymer	Empirical formula/ formula weight	N%* Found (calcd.)	IR (KBr) ν, cm^{-1}	^{1}H-NMR δ, ppm
3a	$(C_{21}H_{14}N_2O_4)_n$/ $(358)_n$	7.09 (7.82)	1640, 1525 (C=0 amide I, II)	10.55 (s, 2H, NH,) 4.01 (s, 2H, CH_2) 6.72-7.67 (m, 10H aromatic)
3b	$(C_{27}H_{18}N_2O_5)_n$/ $(450)_n$	5.41 (6.22)	1645, 1510 (C=0 amide I, II)	10.45 (s, NH, 2H) 3.98 (s, 2H, CH_2) 6.70-7.57 (m, 14H aromatic)
3c	$(C_{28}H_{20}N_2O_4)_n$/ $(448)_n$	5.78 (6.25)	1645, 1520 (C=0 amide I, II)	10.50 (s, NH, 2H) 4.05, 4.30 (s, 2H, CH_2) 6.78-7.61(m, 14H aromatic)
4a	$(C_{43}H_{26}N_4O_{10})_n$/ $(756)_n$	7.97 (7.40)	1645, 1525 (C=0 amide I, II) 1780, 1720,1387, 1145, 698 (imide structure)	10. 59 (s, NH, 2H) 4.05, (s, 2H, CH_2) 7.05-8.30 (m, 22H aromatic, and vinyl)
4b	$(C_{49}H_{30}N_4O_{11})_n$/ $(848)_n$	6.03 (6.60)	1647, 1510 (C=0 amide I, II) 1777, 1725,1387, 1150, 703 (imide structure)	10.48 (s, NH, 2H) 4.10 (s, 2H, CH_2) 6.90-8.25 (m, 26H aromatic and vinyl)
4c	$(C_{50}H_{32}N_4O_{10})_n$/ $(846)_n$	5.84 (6.62)	1650, 1525 (C=0 amide I, II) 1775, 1715,1405, 1143, 695 (imide structure)	10.55 (s, NH, 2H) 4.10, 4.30 (s, 2H, CH_2) 6.95-8.30 (m, 26H aromatic and vinyl)

Table 2
SOLUBILITY OF POLYAMIDES [a] **3** AND **4**

Polymer	DMSO	DMF	NMP	THF	1,4 Dioxane	m-Cresol	$CHCl_3$
3a	++	++	++	-	-	-	-
3b	++	++	++	-	+-	-	-
3c	++	++	++	-	-	-	-
4a	++	++	++	+-	-	-	-
4b	++	++	++	++	++	+-	-
4c	++	++	++	++	+-	-	-

[a]Solubility: (++) soluble at room temperature; (+-) partial soluble; (-) insoluble

Table 3
PROPERTIES OF POLYAMIDES **3** AND **4**

Polymer	η_{inh} [a] (dL/g)	T_g [b]	IDT[c] (°C)	T_{10} [d] (°C)
3a	0.34	-	335	368
3b	0.28	251	323	355
3c	0.31	-	314	347
4a	0.32	-	350	392
4b	0.26	257	342	385
4c	0.29	263	327	373

[a]Measured at the concentration of 0.5 g/dL in DMF at 25 °C.
[b]Glass transition temperature determined from DSC curve
[c]Temperature of initial weight
[d]Temperature of 10% weight loss

segment of the backbone and then propagates to the entire structure [22]. It can be observed that the incorporation of the maleimide pendant group along the polymer backbone, did not influence the glass transition temperature. A possible explanation could be the polar nature of the maleimide ring, which contributes to a high density of the hydrogen bridges, fact that overcome the effect of asymmetry and irregularity introduced by the pendant group which should decrease the Tg.

Conclusions

Polyamides bearing maleimide pendants were synthesized by a chemical modified reaction of some functional polyamides obtained by the Yamazaki- Higashi method. The polymers were soluble in electron-donating organic solvents. They showed reasonable thermal stability with decomposition temperatures in the range of 314-342 °C and glass transition temperatures in the range of 251-263°C. The incorporation of maleimide pendant groups in the polyamides **4** brought about an increase of the solubility and thermal stability in comparison with their unmodified counterparts. Functionalization with maleimides might induce more chemical versatility to the polymers and extend their fields of application.

References

1. PRESTON, J., DOBINSON, F., J. Polym. Sci. B, **2**, 1964, p.1171
2. BIER, G., Adv. Chem. Ser., **91**, 1969, p. 612.
3. HSIAO, S.H., HUANG, P.C., J. Polym. Sci., Polym. Chem. Ed., **35**, 1997, p. 2421
4. CHIRIAC, C., STILLE, J.K., Macromolecules, **10**, 1977, p.712
5. YANG, C.P., LIN, J.H., J. Polym. Sci., Polym. Chem., **31**, 1993, p. 2153
6. TAKATSUKA, R., UNO, K., FTODA, J., IWAKURA, Y., J. Polym. Sci., Polym. Chem. Ed., **15**, 1977, p. 1905
7. KORSHAK, V.V., J. Polym. Sci., A-1, **9**, 1971, p. 1027
8. GREENWOOD, T.D., KAHLEY, R.A., WOLFE, J.F., J. Polym. Sci., Polym. Chem. Ed., **18**,1980, p.1047
9. HULUBEI, C., Mat. Plast., **39**, nr. 2, 2002, p. 120
10. HULUBEI, C., COZAN, V., High. Perform. Polym., **16**, 2004, p. 149
11. HULUBEI, C., Mat. Plast., **43**, nr. 2,2006, p. 123
12. LIU, Y.L., CHEN, Y.J., WEI, W.L., Polymer, **44**, 2003, p. 6465
13. LIU, Y.L., WANG, Y.H., J. Polym. Sci. Part A: Polym. Chem. Ed., **42**, 2004, p. 3178
14. PERRIN, D.D., ARMAREGO, W.L.F., (eds) "Purification of Laboratory Chemicals", 3rd edition, Pergamon Press, New York, 1988.
15. SEARLE, N.E., U.S. Pat. 2 444 536 , 1948; C.A.,42,7340 d , 1948
16. MIKROYANNIDIS, J.A., J. Polym. Sci., Part. A: Polym. Chem., **28**, 1990, p. 679
17. HOYT, A.E., BENICEWICZ, B.C., J. Polym. Sci. A: Polym. Chem., **28**, 1990, p. 3403
18. YAMAZAKI, N., HIGASHI, F., KAWABATA, J., J. Polym. Sci. Part A, **12**, 1974, p. 2149
19 CHIRIAC, C., STILLE, K. J., Macromolecules, **10**, 1977, p. 710
20 HAMCIUC, E., LUNGU, R., HULUBEI, C., BRUMA, M., J. Macromol. Sci., **43**, 2006, p. 1
21 YANG, C. P., HSIAO, S., HYANG, C.C., J. Polym. Research, **10**, 2003, p. 181
22 HULUBEI, C., CAZACU, M., MORARIU, S., High. Perform. Polym., **18**, 2006, p. 101

Manuscript received: 14.03.2008