

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

## HETEROCYCLIC POLYMERS CONTAINING DIMETHYLSILANE UNITS

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Poly(1,3,4-oxadiazole-imide)s and poly(1,3,4-oxadiazole-imide-amide) have been synthesized by cyclopolycondensation of a diacid chloride which contains preformed imide rings and dimethylsilane unit, namely bis[N-(chlorocarbonylphenyl)phthalimidyl]-dimethylsilane, with aromatic dihydrazides such as terephthalic acid dihydrazide and pyridine-2,5-dicarboxylic acid dihydrazide, or with *p*-aminobenzhydrazide, respectively. A poly(benzoxazinone-imide) containing dimethylsilane unit has been prepared by cyclopolycondensation of the same diacid chloride with 3,3'-dicarboxy-4,4'-diaminodiphenylmethane. The low temperature solution polycondensation technique afforded polyhydrazides, a poly(hydrazide-imide) or a poly(amidic-acid) in the first step, which underwent thermal cyclodehydration in the second step. The cyclization process has been studied by infrared, thermogravimetric and differential scanning calorimetry analyses. The solubility, thermal stability and glass transition temperature of these polymers have been studied and compared with related heterocyclic polymers previously reported.

### INTRODUCTION

Aromatic poly(1,3,4-oxadiazole)s are a class of chemically resistant and thermally stable heterocyclic polymers.<sup>1-4</sup> It has been shown that from the spectral and electronic point of view, the oxadiazole cycle is similar to a *p*-phenylene structure, which is known to be highly thermoresistant<sup>5</sup>. Recently, oxadiazole based polymers have been widely investigated in the field of light-emitting diodes as well as other fields of polymer electronics.<sup>6-11</sup> Also, aromatic polyimides are well known for their outstanding resistance at high temperature, although they are hardly soluble in organic solvents, which creates certain processing problems.<sup>12-14</sup> Aromatic benzoxazinone-type polymers show high thermal resistance and particularly good hydrolytic stability superior to that of the aromatic polyimides.<sup>15,16</sup>

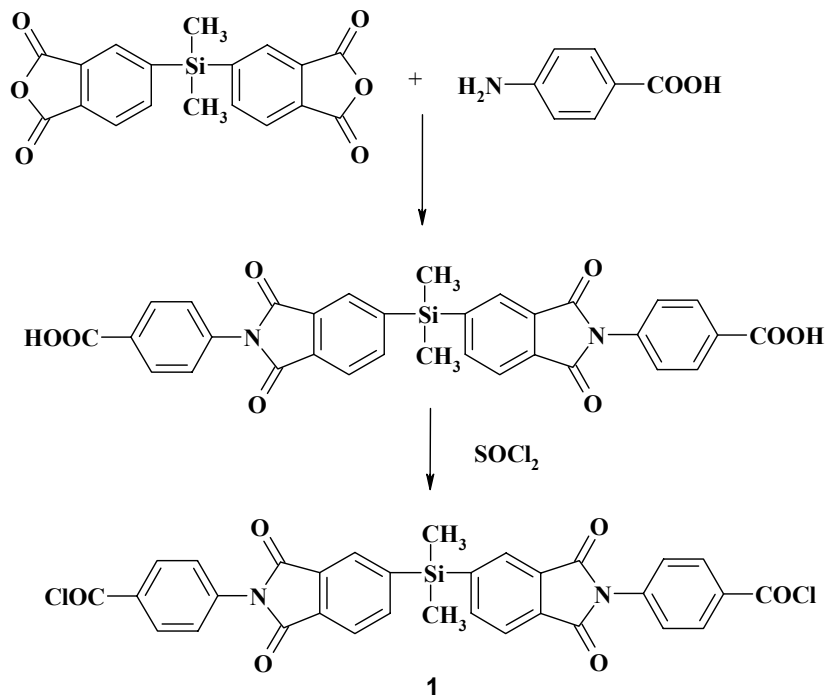
The incorporation of diphenylsilyl groups into the aromatic polymer chains gave soluble products having a remarkable thermal stability and good film-forming ability.<sup>17</sup> More recently, silicon-containing aromatic polymers have attracted much scientific and technological interest because of their potential applications for the production of opto-electronic materials, due to the ability of silicon, when placed among aromatic neighbours, to give a  $\sigma$ - $\pi$  conjugation and thus support the transport of electrons along the macromolecular chain.<sup>18,19</sup>

The present investigation deals with the synthesis and characterization of new poly(1,3,4-oxadiazole-imide)s, poly(1,3,4-oxadiazole-imide-amide) and poly(benzoxazinone-imide) containing dimethylsilane units. The polymers were obtained by the reaction of a diacid chloride containing imide rings and dimethylsilane unit with different aromatic dihydrazides, *p*-aminobenzhydrazide or 3,3'-dicarboxy-4,4'-diaminodiphenylmethane followed by thermal cyclodehydration.

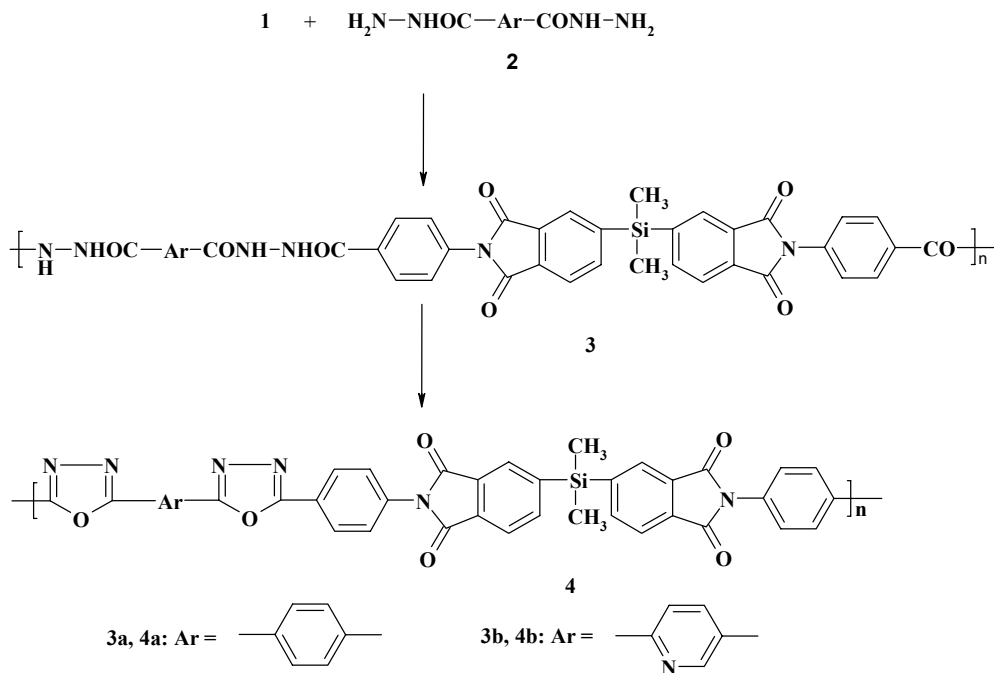
### RESULTS AND DISCUSSION

A diacid chloride containing dimethylsilane groups and imide rings (**1**) was prepared by the reaction of dimethylsilane-bis(phthalic anhydride) with *p*-aminobenzoic acid followed by the reaction of the resulting dicarboxylic imide acid with thionyl chloride, as shown in scheme 1.<sup>20,21</sup>

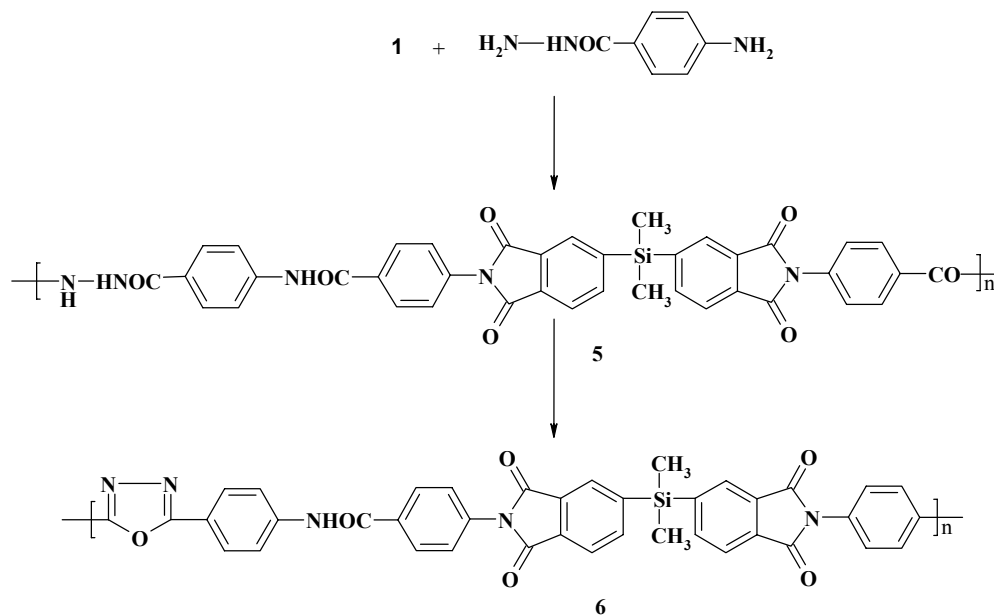
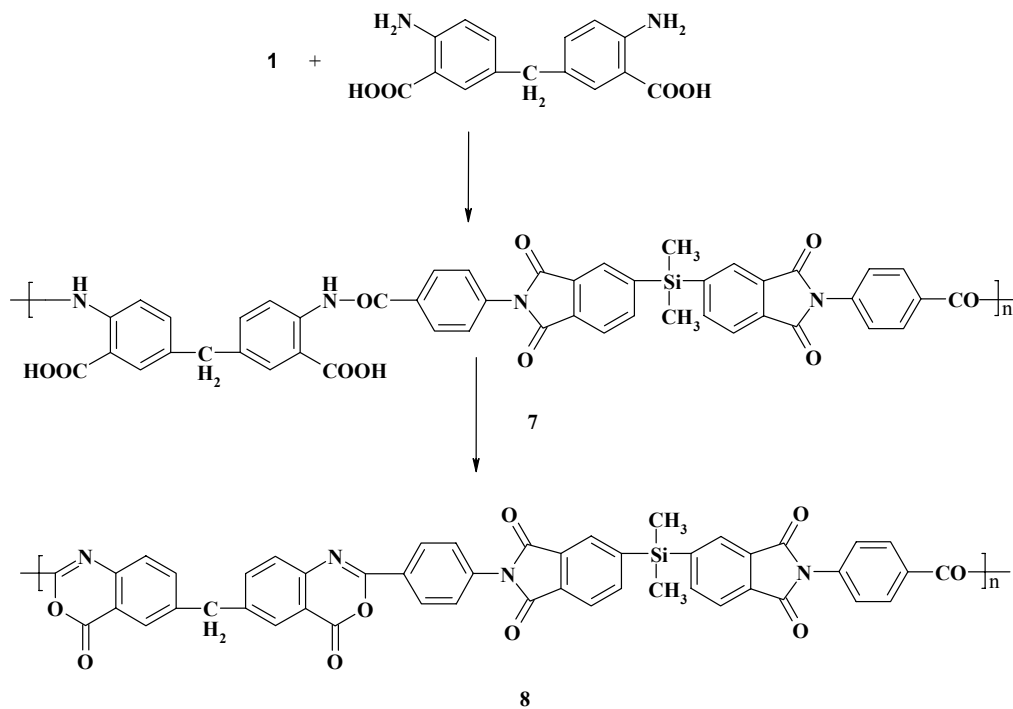
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Scheme 1 – Preparation of imidic diacid chloride **1**.

Low temperature solution polycondensation of aromatic dihydrazides **2** or *p*-aminobenzhydrazide with the diacid chloride **1** gave poly(hydrazide-imide)s **3** (Scheme 2) and poly(hydrazide-imide-amide) **5**, respectively (Scheme 3).

Scheme 2 – Preparation of poly(hydrazide-imide)s **3** and poly(1,3,4-oxadiazole-imide)s **4**.

The same polycondensation technique of the diacid chloride **1** with 3,3'-dicarboxy-4,4'-diaminodiphenylmethane gave a poly(amidic-acid) **7** (Scheme 4).

Scheme 3 – Preparation of poly(hydrazide-imide-amide) **5** and poly(1,3,4-oxadiazole-imide-amide) **6**.Scheme 4 – Preparation of poly(amidic-acid) **7** and poly(benzoxazinone-imide) **8**.

All the polycondensation reactions took place in *N*-methylpyrrolidone (NMP) as solvent, at low temperature (0°C), for 1 h, and at room temperature, for further 8 h.

The structure of the polymers was confirmed by infrared and <sup>1</sup>H-NMR spectroscopy. In the IR spectra of polymers **3**, **5** and **7** absorption bands appeared at 3300–3400 cm<sup>-1</sup> and at 1650 cm<sup>-1</sup> due to NH and C=O stretching vibrations in the amide groups, respectively. Characteristic absorption bands of imide groups appeared at 1785 cm<sup>-1</sup> and 1720 cm<sup>-1</sup> due to imide carbonyl (symmetric and asymmetric stretching) and at 1100 cm<sup>-1</sup> and 720 cm<sup>-1</sup> due to imide rings. Absorption bands for dimethylsilane units appeared at 1220 cm<sup>-1</sup> and 820 cm<sup>-1</sup>.

In the  $^1\text{H-NMR}$  spectra of the polymers **3**, **5** and **7**, the absorption signals of the aromatic protons appeared in the region of 6.8-8.3 ppm. The peak corresponding to  $\text{CH}_3$  resonance from dimethylsilane units appeared at 0.8 ppm. In the case of the polymers **3** and **5**, the peak corresponding to NH resonance from the hydrazide groups was observed around 10.5 ppm.

The inherent viscosity of the polymers **3**, **5** and **7** was in the range of 0.39-0.61 dL/g (Table 1).

All the poly(hydrazide-imide) **3**, poly(hydrazide-imide-amide) **5** and poly(amidic-acid) **7** were easily soluble in polar amidic solvents such as NMP and N, N-dimethylformamide (DMF). The polymers were also soluble in concentrated sulfuric acid and insoluble in chloroform or tetrahydrofuran.

Thermogravimetric analysis (TGA) of polymers **3** and **5** shows a first weight loss at about  $100^\circ\text{C}$  due to the evolution of absorbed water, a second weight loss in the range of  $275\text{-}370^\circ\text{C}$  which was attributed to the evolution of water resulting from the thermal cyclization of hydrazide groups and a third weight loss above  $400^\circ\text{C}$  due to the degradation of the resulted poly(1,3,4-oxadiazole) (Figure 1). The total weight loss at  $450^\circ\text{C}$  was in the range of 20-42%. The differential scanning calorimetry (DSC) curves of the polymers present a broad endotherm at about  $100^\circ\text{C}$  due to the evolution of absorbed water (Figure 2). All the samples show an endotherm just above  $300^\circ\text{C}$ . According to thermogravimetric analyses, the polyhydrazides underwent thermal cyclization in the same range of the DSC endotherm. The maximum temperature and the temperature range of the process of cyclization are listed in Table 1.

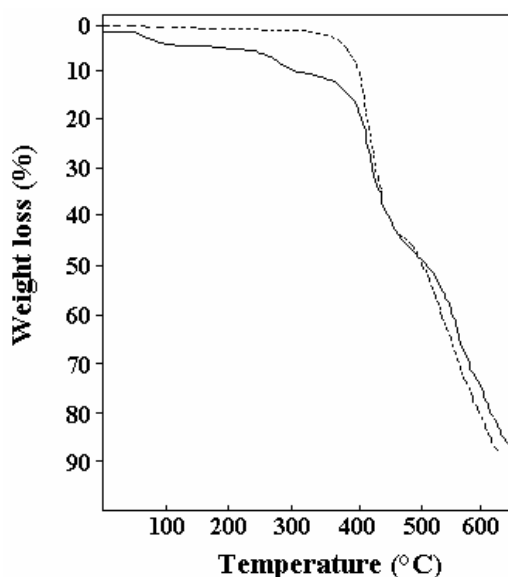


Fig. 1 – TGA curves of poly(hydrazide-imide) **3a** (solid line) and corresponding poly(1,3,4-oxadiazole-imide) **4a** (dashed line).

Table 1

Properties of polymers **3**, **5** and **7**

Polymer	$\eta_{\text{inh}}^{\text{a}}$ (dL/g)	$T_{\text{max}}^{\text{b}}$ ( $^\circ\text{C}$ )	$T_{\text{c}}^{\text{c}}$ ( $^\circ\text{C}$ )	Weight loss at $450^\circ\text{C}$ (%)
<b>3a</b>	0.48	330	285-360	35
<b>3b</b>	0.39	325	275-355	42
<b>5</b>	0.61	361	290-370	20
<b>7</b>	0.55	282	220-300	20

<sup>a</sup> Measured at  $20^\circ\text{C}$  with solutions of 0.5% conc in NMP.

<sup>b</sup> Temperature of cyclization determined from maximum endotherm of DSC curves.

<sup>c</sup> Temperature range of cyclization from TG curves.

Thermogravimetric analysis of poly(amidic-acid) **7** shows two distinct steps of weight loss (Table 1, Figure 3). The first one, in the range of  $180\text{-}250^\circ\text{C}$ , represents the loss of water caused by cyclodehydration reaction to the benzoxazinone rings and the second one, in the range of  $300\text{-}400^\circ\text{C}$ , represents the loss of

volatiles caused by the degradation of the polymers. The cyclization process was also seen in DSC curve which showed a strong endotherm above 200°C (Figure 4).

Fig. 2 – DSC curves of poly(hydrazide-imide) **3a** (1) and corresponding poly(1,3,4-oxadiazole-imide) **4a** (2).

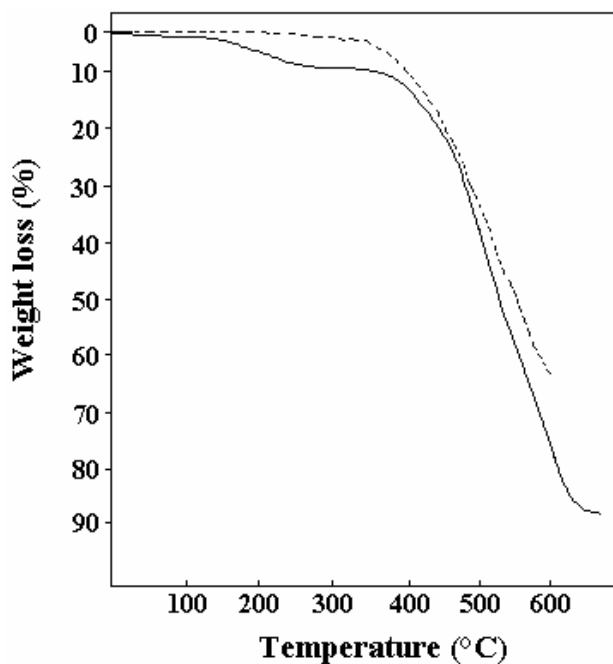
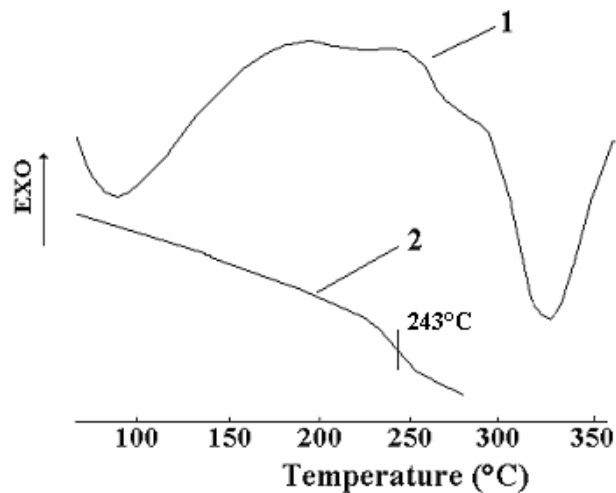


Fig. 3 – TGA curves of poly(amidic-acid) **7** (solid line) and corresponding poly(benzoxazinone-imide) **8** (dashed line).

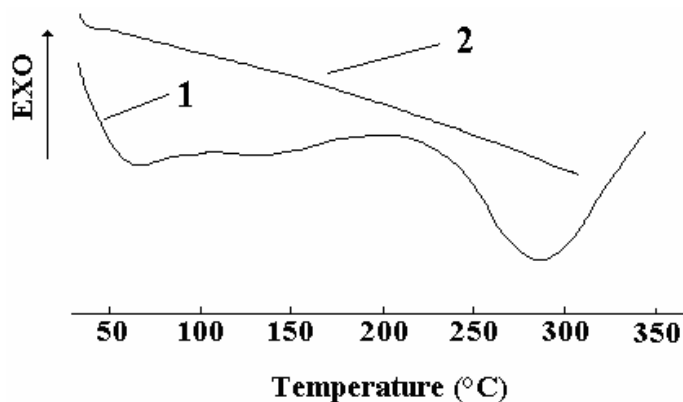


Fig. 4 – DSC curves of poly(amidic-acid) **7** (1) and corresponding poly(benzoxazinone-imide) **8** (2).

Poly(hydrazide-imide)s **3** and poly(hydrazide-imide-amide) **5** were converted to the corresponding poly(1,3,4-oxadiazole-imide)s **4** and poly(1,3,4-oxadiazole-imide-amide) **6**, respectively, by thermal cyclodehydration in bulk by heating the polymers at 270°C for 24 h (Scheme 2 and Scheme 3). The poly(amidic-acid) **7** was converted to poly(benzoxazinone-imide) **8** by thermal cyclodehydration in bulk, too, by heating the polymer at 200°C, 250°C and 300°C, each for 1 h (Scheme 4).

The thermal cyclodehydration of poly(hydrazide-imide)s **3** and poly(hydrazide-imide-amide) **5** was confirmed by infrared spectroscopy. Thus the infrared spectra of polymers **4** do not show the characteristic absorptions of NH stretching and carbonyl functions in the hydrazide groups. Also, in the case of polymer **6** a decrease of the intensity of the absorption characteristic of C=O from amide groups at 1650 cm<sup>-1</sup> can be observed. All the IR spectra present weak absorption bands at 1020 cm<sup>-1</sup> and 980 cm<sup>-1</sup> due to =C-O-C= stretching of 1,3,4-oxadiazole rings.

The cyclization of poly(amidic-acid) **7** to poly(benzoxazinone-imide) **8** was also confirmed by IR spectroscopy. In the IR spectrum of polymer **8** the absorption band at 3400-3100 cm<sup>-1</sup> (due to NH and OH stretching vibrations) and at 1650 cm<sup>-1</sup> (due to NHCO groups) disappeared; new bands appeared at 1240 cm<sup>-1</sup> and 1060 cm<sup>-1</sup> which are characteristic for benzoxazinone rings. The 1780-1760 cm<sup>-1</sup> should represent two carbonyl peaks due to the imide carbonyl (symmetric stretching) and lactone carbonyl of the benzoxazinone rings. However, the two carbonyls individually are so strong that they become inseparable and the overall absorption is seen at 1780 cm<sup>-1</sup>.

The thin films were prepared from polymers **5** and **7** by casting their solutions onto a glass plate and heating at temperatures of 120°C, 140°C and 180°C, each for 1 h; these films were flexible and maintained their shape after repeated bendings.

The polymers **4a** and **8** were not soluble in polar amidic solvents. They were soluble only in concentrated sulfuric acid. Polymers **4b**, containing pyridine units, and polymer **6**, having amide groups, were soluble in polar organic solvents like NMP, DMF or N, N-dimethylacetamide. A slight decrease in the inherent viscosity of the polymers **4b** and **6** is observed by comparing them with the corresponding polyhydrazide precursors (Table 2).

Table 2  
Properties of polymers **4**, **6** and **8**

Polymer	$\eta_{inh}^a$ (dL/g)	$T_g^b$ (°C)	$T_5^c$ (°C)	$T_{10}^d$ (°C)	$T_{max1}^e$ (°C)	$T_{max2}^f$ (°C)
<b>4a</b>	-	243	390	410	420	540
<b>4b</b>	0.29	234	390	405	430	540
<b>6</b>	0.45	280	406	420	430	560
<b>8</b>	-	ND	410	425	515	-

<sup>a</sup>) Measured at 20°C with solutions of 0.5% conc in NMP.

<sup>b</sup>) Glass transition temperature determined from DSC curves.

<sup>c</sup>) Temperature of 5% weight loss in TGA curves.

<sup>d</sup>) Temperature of 10% weight loss in TGA curves.

<sup>e</sup>) Temperature of the first maximum decomposition rate in TGA curves.

<sup>f</sup>) Temperature of the second maximum decomposition rate in TGA curves.

The thermal behavior of the polymers **4**, **6** and **8** was evaluated from TGA and DSC analyses (Figures 1 - 4). All the polymers exhibited high thermal stability with insignificant weight loss up to 380°C. They lost 5% weight in the range of 390-410°C and the temperature of 10% weight loss ( $T_{10}$ ) was in the range of 410-425°C. The polymers **4** and **6** exhibited two maxima of decomposition: the first one ( $T_{max1}$ ) was in the range of 420-430°C and the second one ( $T_{max2}$ ) was in the range of 540-560°C. Polymer **8** exhibited only one maximum of decomposition at 515°C (Table 2). When comparing the thermostability of polymers **4a** and **4b** with that of related poly(1,3,4-oxadiazole-imide)s<sup>22</sup> that have been synthesized from the same dihydrazides but with diacid chlorides which do not contain silicon it can be seen that the thermal stability of the former is lower than that of the latter (by about 60°C), probably due to the presence of methyl-silane groups that are more sensitive to thermal destruction.

The glass transition temperature ( $T_g$ ) of the polymers **4** and **6**, evaluated from DSC curves, was in the range of 234–280°C (Table 2). Polymer **8** did not exhibit any  $T_g$  up to the temperature when the degradation process appeared. The DSC measurements showed no evidence of crystallization or melting which proves amorphous morphology (Figure 2 and Figure 4).

## EXPERIMENTAL

### Synthesis of the monomers

4,4'-Diaminodiphenylmethane-3,3'-dicarboxylic acid was prepared by benzidine rearrangement of methylene-dianthranilic acid which has been obtained from anthranilic acid and 40% formaldehyde solution in absolute ethanol, according to the literature.<sup>23</sup>

Bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride was prepared by a multistep reaction, following a published method<sup>24</sup>.

Bis[N-(chlorocarbonylphenyl)phthalimidy]dimethylsilane **1** was synthesized by treating with excess thionyl chloride the corresponding dicarboxylic acid which was resulted from the reaction of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride (1 mol) with *p*-aminobenzoic acid (2 mol), in glacial acetic acid as solvent and dehydrating agent (Scheme 1)<sup>20,21</sup> IR spectrum (KBr,  $\text{cm}^{-1}$ ): 1780 (–COCl and imide carbonyl symmetric stretching); 1730 (imide carbonyl asymmetric stretching); 1375 (C–N stretching); 740 (imide ring) and 1220 and 820 due to methyl-silane bonds. Melting point: 218–222°C. <sup>1</sup>H-NMR (DMSO- $d_6$ , 250 MHz, ppm): 8.21 (2H, d), 8.10 (4H, d), 7.95 (2H, d), 7.76 (2H, s), 7.62 (4H, d)

### Synthesis of the polymers

Poly(hydrazide-imide)s **3** and poly(hydrazide-imide-amide) **5** have been prepared by polycondensation of equimolar amounts of diacid chloride **1** with aromatic dihydrazides **2** or with *p*-aminobenzhydrazide, respectively (Scheme 2 and Scheme 3). The poly(amidic-acid) **7** was prepared by polycondensation of equimolar amount of the same diacid chloride **2** with 3,3'-dicarboxy-4,4'-diaminodiphenylmethane (Scheme 3). A typical polycondensation was run as follows: Terephthaloyl dihydrazide (0.97 g, 0.005 mol) and NMP (35 ml) were placed in a 100 ml three necked flask equipped with mechanical stirrer and nitrogen stream. It was cooled at 0°C and diacid chloride **1** (3.135 g, 0.005 mol) was added under rapid stirring. The flask was kept at 0°C for 1 h, then the cooling bath was removed and the reaction mixture was stirred at room temperature for further 8 h. Half of the polymer solution was cast onto a glass plate and dried at 100°C, 140°C and 180°C, each for 1 h resulting in a transparent film. The other half of the polymer solution was poured slowly into methanol and the precipitate was washed with methanol and water, collected by filtration and dried to give quantitative yields of the polymer.

### Cyclodehydration of the poly(hydrazide-imide)s **3**, poly(hydrazide-imide-amide) **5** and poly(amidic-acid) **7**

Polymers **3** and **5**, in bulk form, were cyclodehydrated to the corresponding oxadiazole structure **4** and **6** following a previously reported procedure<sup>25</sup>, by heating in an oven from room temperature to 270°C over 3 h and keeping them isothermally at 270°C for a total time of 24 h.

The thermal cyclization of poly(amidic-acid) **7** to the benzoxazinone structure **8** was performed as earlier reported<sup>26</sup>, by heating the polymer, in bulk form, in an oven from room temperature to 200°C within 1 h and keeping at 200°C, 250°C and 300°C for 1 h each.

### Measurements

The inherent viscosities of the polymers were determined in NMP at 20°C, at a concentration of 0.5 g/dL, by using an Ubbelohde viscometer.

Infrared spectra were recorded with a Specord M-80 Spectrophotometer by using KBr pellets or polymer films with a thickness of 2–5  $\mu\text{m}$ .

Thermogravimetric analyses (TGA) were performed on a MOM Derivatograph (Budapest, Hungary) in air, at a heating rate of 10°C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss ( $T_{10}$ ) was also recorded.

The glass transition temperatures ( $T_g$ ) of the precipitated polymers were determined with a Mettler differential scanning calorimeter DSC 12E by using a heating rate of 10°C/min, under nitrogen. The samples were heated from ambient temperature to above 300°C under nitrogen. 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 inflection curve resulting from the typical second heating was assigned as the  $T_g$  temperature of the respective polymers.

## CONCLUSIONS

Silicon containing poly(hydrazide-imide)s, poly(hydrazide-imide-amide) and a poly(amidic-acid) were prepared by low temperature solution polycondensation of an aromatic diacid chloride incorporating dimethylsilane unit and imide rings with aromatic dihydrazides, *p*-aminobenzhydrazide or 3,3'-4,4'-dicarboxydiphenylmethane, respectively. These polymers were soluble in polar organic solvents and gave

thin flexible films. Thermal cyclization of these polymers gave silicon containing poly(1,3,4-oxadiazole-imide)s, poly(1,3,4-oxadiazole-imide-amide) and poly(benzoxazinone-imide). The cyclized polymers exhibited high thermal stability; they began to decompose at about 390°C. The glass transition temperature of some of the polymers was in the range of 234-280°C, with a large interval between glass transition and decomposition temperature which may be advantageous for their processing.

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