

## SILICON-CONTAINING AROMATIC POLY(AMIDE-IMIDE)S

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Silicon-containing poly(amide-imide)s have been synthesized by polycondensation reaction of various aromatic diamines with a dicarboxylic acid or a diacid dichloride containing the dimethylsilylene group and preformed imide cycles. These polymers are easily soluble in polar amidic solvents such as N-methylpyrrolidinone (NMP) or dimethylformamide (DMF) and can be cast into thin flexible films or coatings from such solutions. They show medium to high average molecular weights, high thermal stability, with initial decomposition temperature being above 400°C and glass transition temperature in the range of 220–280°C.

### INTRODUCTION

In the field of heterocyclic polymers, aromatic polyimides are a class of polymers that have unique high temperature stability, excellent mechanical and electrical properties and outstanding chemical resistance. However, because of their chain rigidity and strong interchain interaction, most polyimides are insoluble in common organic solvents and intractable in their imide forms.<sup>1</sup> Therefore much effort has been made to develop structurally modified aromatic polymers having increased solubility with retention of their good thermal stability.<sup>2,3</sup> Aromatic poly(imide-amide)s were developed as alternative materials offering a compromise between excellent thermal stability and processability. These polymers show good solubility in highly polar solvents, lower glass transition temperatures and easier processability compared with corresponding polyimides.<sup>4,5</sup> It is known that the solubility of polymers is often increased when flexible bonds, large pendent groups, polar substituents or rigid but noncoplanar moieties are incorporated into the polymer backbone.<sup>6–9</sup> Also, it was shown that the incorporation of diphenylsilyl groups into the aromatic polymer chain gave soluble products

having a remarkable thermal stability and good film-forming ability.<sup>10,11</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 neighbors, to give a  $\sigma$ - $\pi$  conjugation and thus support the transport of electrons along the macromolecular chain.<sup>12</sup>

In the present paper we compare two series of poly(amide-imide)s, both of them containing silicon in the main chain. One series of polymers has been obtained by direct polycondensation of a silicon-containing dicarboxylic acid having preformed imide cycle with certain aromatic diamines having ether bridges between phenylene rings. The other series of polymers was prepared by solution polycondensation of a silicon-containing diacid chloride having imide rings with the same aromatic diamines. The properties of these polymers such as solubility, inherent viscosity, molecular weight, thermal stability, glass transition temperature and the quality of thin films made from these polymers have been investigated and compared with those of related compounds. Some physical properties of these polymers such as solubility, glass transition temperature and initial

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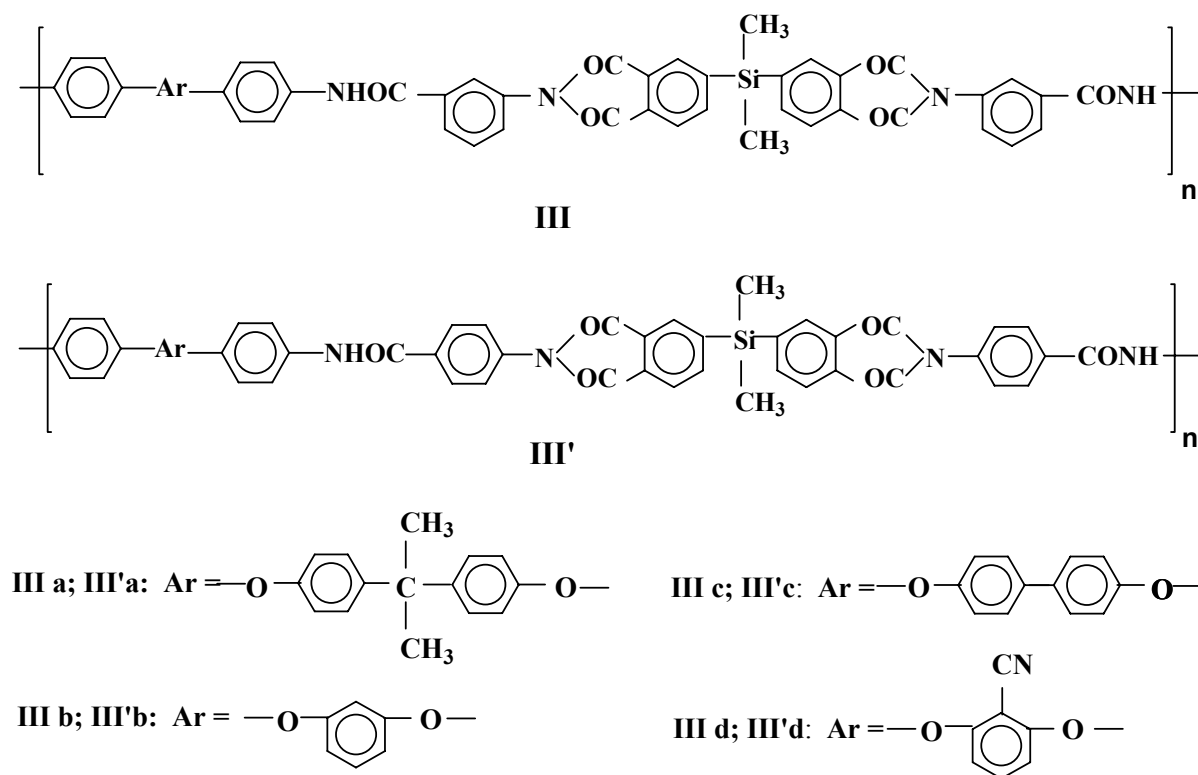
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decomposition temperature have been discussed in relation with the conformational rigidity of their chains and some relationships have been shown.

## RESULTS AND DISCUSSION

Silicon-containing aromatic poly(amide-imide)s **III** and **III'** have been synthesized with the aim to

obtain highly thermostable, easy soluble and processable products. These polymers were prepared by the polycondensation of different aromatic diamines containing ether linkages **I** with a dicarboxylic acid **II** or a diacid chloride **II'** containing silicon and preformed imide cycle.<sup>13,14</sup> The structure of these polymers is shown in Scheme 1.



Scheme 1 – The general formula of polymers **III** and **III'**.

The structure of polymers **III** and **III'** was identified by IR spectra. Strong bands at  $1780\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$  are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide. The absorption band at  $1375\text{ cm}^{-1}$  is due to C-N stretching in imide ring and the absorption at  $740\text{ cm}^{-1}$  is possibly due to imide ring deformation. The wide bands which appeared at  $3400\text{ cm}^{-1}$  were attributed to N-H stretching vibration in the amide group. Characteristic absorptions appeared at  $1680\text{--}1670\text{ cm}^{-1}$  due to carbonyl stretching vibration (amide I) and at  $1520\text{ cm}^{-1}$  due to N-H deformational vibration (amide II).

All the polymers exhibited IR bands at  $1220$  and  $820\text{ cm}^{-1}$  due to the methyl-silane bonds. The

polymers dissolve easily in polar amidic solvents such as NMP, DMF, dimethylacetamide (DMA) and pyridine. This good solubility is due to the relatively high flexibility of macromolecular chains which was obtained by the introduction of dimethylsilylene and ether linkages into the structure of the polymer. Thus the shape of a macromolecule is far from a linear rigid rod which is characteristic to wholly aromatic insoluble structures. The good solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

The inherent viscosities, measured in NMP solution, were in the range of  $0.3\text{--}0.5\text{ dL/g}$  for polymers **III** and  $0.66\text{--}1.19\text{ dL/g}$  for the polymers **III'** (Table 1).

Table 1

Properties of the polymers

Polymer	$\eta_{inh}$ dL/g	T <sub>g</sub> <sup>a</sup> (°C)	IDT <sup>b</sup> (°C)	T <sub>10</sub> <sup>c</sup> (°C)	l <sub>0</sub> (Å°)	A (Å°)	p	Mw (g/mol)	Mn (g/mol)	Mw/ Mn
<b>IIIa</b> <b>III'a</b>	<u>0.37</u> 0.86	<u>219</u> 263	<u>437</u> 411	<u>480</u> 432	<u>45.88</u> 41.12	<u>23.24</u> 39.63	<u>4.12</u> 6.75	<u>72000</u> 197000	<u>32000</u> 79000	<u>2.25</u> 2.5
<b>IIIb</b> <b>III'b</b>	<u>0.38</u> 0.66	<u>220</u> 251	<u>428</u> 433	<u>480</u> 470	<u>40.60</u> 41.40	<u>21.71</u> 32.46	<u>3.75</u> 5.49	<u>72500</u> 195000	<u>41600</u> 88000	<u>1.74</u> 2.2
<b>IIIc</b> <b>III'c</b>	<u>0.44</u> 1.06	<u>239</u> 275	<u>407</u> 420	<u>471</u> 454	<u>44.23</u> 45.04	<u>28.71</u> 43.69	<u>5.19</u> 7.76	<u>84000</u> 211000	<u>48000</u> 92000	<u>1.74</u> 2.3
<b>III d</b> <b>III'd</b>	<u>0.54</u> 1.19	<u>255</u> 281	<u>464</u> 425	<u>500</u> 450	<u>40.60</u> 41.40	<u>28.72</u> 49.46	<u>4.95</u> 8.38	<u>106000</u> 239000	<u>53800</u> 114000	<u>1.97</u> 2.1

<sup>a</sup> Glass transition temperature; <sup>b</sup> Initial decomposition temperature = temperature of 5% weight loss; <sup>c</sup> Temperature of 10% weight loss; l<sub>0</sub>, contour length over repeating structural unit; A, Kuhn segment; p, conformational rigidity parameter.

The molecular weight of the polymers was determined by gel permeation chromatography (GPC). The values of weight-average molecular weight Mw are in the range of 72000-106000, the number-average molecular weight Mn values are in the range of 32000-53800 and the polydispersity Mw/Mn is in the range of 1.7-2.25 for polymers **III**. For polymers **III'** the values of weight-average molecular weight Mw are in the range of 195000-239000, the number-average molecular weight Mn values are in the range of 79000-114000 and the polydispersity Mw/Mn is in the range of 2.1-2.5. As can be seen from the table 1 the values of number-average molecular weight Mn and the weight-average molecular weight Mw values of the polymers **III'** which were obtained from diacid chloride and aromatic diamines, are higher than the values of the polymers **III** which were synthesized by direct polycondensation reaction. In the same time the polymers which were prepared by direct polycondensation reaction have presented the narrow polydispersity 1.7-2.25 than the polymers **III'** which showed polydispersity values of 2.1-2.5.

All these polymers possess good film-forming ability due to their good solubility and were processed into thin films by casting their solution onto glass plates. Their solutions in NMP having a concentration of about 10% were cast onto glass substrates and dried to yield thin transparent free-standing films having a thickness of tens of micrometers. The films were tough, flexible and creasable. Very thin coatings having a thickness in the range of tens of nanometers have been prepared from diluted NMP-solutions (concentration 2%) by spin-coating onto silicon wafers. The quality of such films as-deposited on substrates was studied by atomic force microscopy (AFM). The films exhibited smooth surfaces; the values of root mean

square roughness calculated from the AFM data are in the range of 2-5 Å being of the same order of magnitude as that of the highly polished silicon wafers which were used as substrates. This means that the deposited films are smooth and homogeneous. They do not show any pinholes or cracks and are practically defectless.

The thermal stability was evaluated by thermogravimetric analysis (TGA). The initial decomposition temperature of the polymers **III** is in the range of 407–464°C and the temperature of 10% wt. loss (T<sub>10</sub>) is in the range of 470–500°C. The polymers **III'** begin to decompose in the range of 420–450°C and have a 10% weight loss in the range of 450–485°C, in air atmosphere (Table 1). By comparing these aromatic poly(amide-imide)s containing dimethylsilane linkages with related poly(amide-imide)s<sup>15</sup> that have been synthesized from the same diamines but with a monomer which does not contain silicon, it can be seen that their decomposition temperatures are in the same range. This shows that the presence of dimethylsilane groups preserves the high thermal stability while improving the solubility. In the same time by comparing the thermostability of the present polymers **III** and **III'** it can be seen that the thermal stability of the first polymers is slightly higher than the thermal stability of the polymers **III'** (Table 1). In the same time the glass transition temperature (T<sub>g</sub>) of the silicon-containing poly(amide-imide)s **III** was in the range of 219-255 °C (table 1) being slightly lower than the T<sub>g</sub> of the polymers **III'** which presented T<sub>g</sub> in the range of 251-281°C. It can be noticed that there is a large interval between T<sub>g</sub> and the decomposition temperature, which could be advantageous in the processing of these polymers by a thermoforming technique.

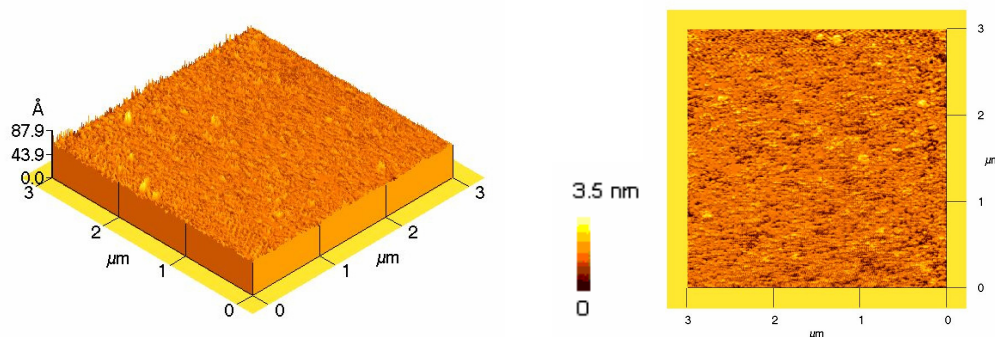


Fig. 1 – AFM pictures of the film made from polymer **IIIa** (left: side view; right: top view).

We have studied some physical properties of poly(imide-amide)s **III** such as solubility, glass transition temperature ( $T_g$ ), initial decomposition temperature (IDT), and we have made some correlations with their conformational rigidity. A correlation between a physical property of a polymer and the conformational rigidity of its chain shows that the contribution of the conformational rigidity to this polymer property is significant.<sup>16</sup>

The conformational rigidity of a polymer can be estimated using the Kuhn segment value  $A$  and the number of aromatic rings in the Kuhn segment,  $p$ , which were calculated by using the Monte Carlo method as shown in the literature.<sup>17,18</sup>

Conformational rigidity characterizes the degree of macromolecular coiling and it is governed by chain geometry: lengths of virtual bonds, angles between them, and the allowed rotations of these bonds. The term “virtual bonds” is used to indicate a rigid section of a chain approximated by a straight line about which rotation is possible. In a particular case, it can be an ordinary valence bond; more generally, it can contain rings as well.

For polyheteroarylenes where a macromolecule unit contains virtual bonds of various lengths arranged at various angles, the contour length ( $l_0$ ) is taken to be the length of a broken line connecting the centers of these bonds. In this case,  $l_0$  does not depend on the chain conformation and can serve as a measure of the length of the macromolecule.

Since many physical properties such as glass transition temperature of polyheteroarylenes are determined by the presence of aromatic rings or heterocycles in the polymer backbone, the introduction of this parameter is very useful for comparison of polymers with different structures but containing the same heterocycles.<sup>19</sup>

As shown earlier the present polymers dissolve easily in polar solvents such as NMP or dimethylformamide. The good solubility of these polymers is due to the high flexibility of the macromolecular chains, which is in agreement with relatively low values of the Kuhn segment  $A$  being in the range of 21.71–28.71 Å for the polymers **III** and in the range of 32.46–49.46 Å for polymers **III'**. As can be seen the values for the polymers which contain *meta* linkages are slight lower than the values from the polymers which contains the *para* linkages in the diacid component (Table 1). This behavior can be explained by the presence of more flexible units and by the presence of bulky dimethylsilane units, which introduce a factor of asymmetry that prevents dense packing of the chains.

The dependence of the  $T_g$  as determined from DSC curves, on the parameter of conformational rigidity  $p$  is shown in Fig. 2 and 3.

Generally,  $T_g$  increases with increasing chain rigidity. The polymer **IIIb** containing *meta*-phenylene ring in the segment coming from diamine monomer has the lowest value of the conformational rigidity parameter  $p$ , 3.75 and consequently, a lower value of  $T_g$  (220°C) when compared with polymer **III'b** having a similar structure but having *para*-phenylene rings in diacid dichloride component and which have the value of  $p$  5.48 and a  $T_g$  of 251°C. When a CN substituent is present on the phenylene ring, which is the case of the polymer **III'd**, the  $T_g$  value increased compared with the related structure **IIIb**, without CN. Thus, the polymer **III'd** having the highest  $p$  value (8.38) has the highest  $T_g$  (281°C). This is associated with increasing chain rigidity due to CN groups, which is in agreement with the literature concerning the effect of side substituents, located on the phenyl ring, on the conformational rigidity.<sup>20-23</sup>

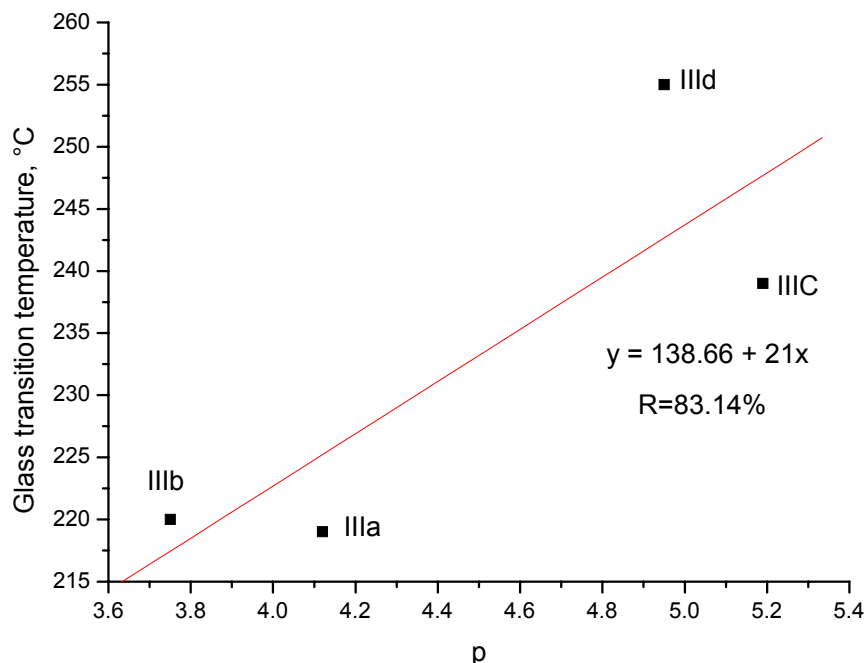


Fig. 2 – The dependence of glass transition temperature of polymers **III** on conformational rigidity parameter **p**.

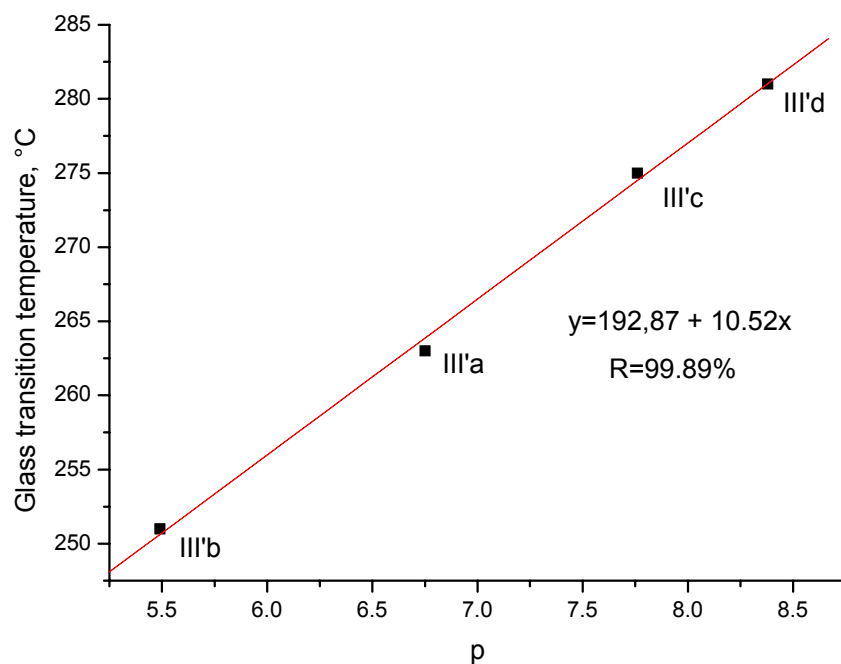


Fig. 3 – The dependence of glass transition temperature of polymers **III'** on conformational rigidity parameter **p**.

The introduction of isopropylidene groups in the polymer **III'a** results in a decrease in its Tg, 263°C, compared to the corresponding polymer **III'd** whose Tg is 281°C. This fact is due to the higher flexibility of the polymer **III'a** ( $p = 6.75$ ) by comparing with polymer **III'd** ( $p = 8.38$ ). In the same time it can be seen that the values of

conformational rigidity parameters of polymers **III** are lower than the values of conformational rigidity parameters of polymers **III'**. This fact can be explained by the presence of more *meta*-incatenations in the polymers **III** which introduce much more flexibility and consequently the rigidity of these polymers is slightly lower than the rigidity

of polymers **III'**. For this reason the dependence of glass transition temperature on conformational rigidity parameter can be described by a linear equation. The factor of convergence for polymers **III** and **III'** is 83% and 99.89%, respectively. That means that the *meta*-incatenation introduce a large factor of asymmetry and the linear dependence is perturbed.

The decomposition temperature of these polymers did not exhibit a significant dependence on the chain rigidity. This fact is due to the presence of amide units, which are more sensitive to thermal degradation and begin to decompose at a lower temperature. A similar behavior was reported for other heterocyclic polymers containing amide groups.<sup>24,25</sup>

## EXPERIMENTAL

### Monomers

*Aromatic diamines containing two ether bridges I*, such as 2,2-bis(*p*-aminophenoxy-phenyl)isopropane, **Ia**, 1,3-bis(*p*-aminophenoxy)benzene, **Ib** and 4,4'-bis(*p*-aminophenoxy)biphenyl, **Ic**, have been provided by different commercial sources and purified by recrystallization from ethanol or from a mixture of ethanol with water. M. p. **Ia**: 126-128°C; **Ib**: 114-116°C; **Ic**: 197-199°C. The diamine **Id**, 2,6-bis(*p*-aminophenoxy)benzotrinitril, was synthesized by the reaction of *p*-aminophenol with 2,6-dichlorobenzotrinitril, in dimethylacetamide (DMAc) in the presence of potassium carbonate, according to a published procedure.<sup>26</sup> It was recrystallized from a mixture of dimethylformamide with water. M. p. of **Id**: 210-213°C.

*Synthesis of bis[N-(3-carboxyphenyl) phthalimidyl] dimethylsilane IIa and of bis[N-(4-carboxyphenyl)phthalimidyl] dimethylsilane IIb*

The preparation of dicarboxylic acids **II** was carried out by the reaction of *para* or *meta*-aminobenzoic acid and bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride<sup>27</sup> in glacial acetic acid at 10% concentration at reflux temperature for 16 h. The resulting white products **II** were filtered, washed with ethanol and dried (yield around 90%). Melting point **IIa**: 329-331°C; **IIb**: 349-351°C.<sup>13,14</sup>

*Synthesis of bis[N-(3-chlorocarbonylphenyl)phthalimidyl]-dimethylsilane II'a*. We have tried to prepare the diacid chloride corresponding, by the reaction of the dicarboxylic acid **IIa** with conventional chlorinated agents such as thionyl chloride, phosphorus pentachloride or oxalyl chloride, but we were not successful. The resulting diacid chloride did not have the required purity as to be used further in polycondensation reaction. In all cases a viscous, almost colorless oil resulted which was identified by means of IR as impure bis[N-(3-chlorocarbonylphenyl) phthalimidyl] dimethylsilane.

*Synthesis of bis[N-(4-chlorocarbonylphenyl)phthalimidyl]-dimethylsilane II'b* was performed by heating of diacid **IIb** at reflux temperature in excess of thionyl chloride for 6 h. A part of thionyl chloride was distilled and the remaining solution was cooled. A white product crystallized. It was filtered,

washed with hexane and dried (yield 75%). Melting point: 218-222°C.

N-methyl-2-pyrrolidinone (NMP) from Merck was dried over phosphorous pentoxide and distilled under reduced pressure.

**Polymerization procedure.** The general structure of polymers **III** and **III'** is presented in Scheme 1. The polymers **III** were synthesized by direct polycondensation reaction<sup>28</sup> of aromatic diamines **I** with dicarboxylic acid **IIa**. A mixture of 0.615 g (0.0015 mol) of diamine **Ia**, 0.885 g (0.0015 mol) of dicarboxylic diacid **IIa**, 0.5 g calcium chloride, 2 ml triphenyl phosphite, 4 ml of pyridine and 12 ml of N-methylpyrrolidinone was heated with stirring at 105°C for 5 h. After cooling, the reaction mixture was poured into a large amount of methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 105°C for two days. The inherent viscosity of the polymer in NMP was 0.370 dL/g, measured at a concentration of 0.5 g/dL at 20°C.

The polycondensation reaction with equimolar amounts of diamine **I** and diacid chloride **II'b** at low temperature under anhydrous conditions, in a nitrogen atmosphere, in NMP as a solvent and with pyridine as an acid acceptor was run for preparation of polymers **III'**. The relative amounts of monomers and NMP were adjusted to maintain a solid content of 8-10%. The content of the flask was kept below 0°C for 15 min and then the cooling bath was removed and the reaction mixture was allowed to reach room temperature after which it was stirred for another 4 h. Half of the resulting viscous polymer solution was cast onto a glass plate and after evaporating the solvent at 120°C, 160°C, 180°C and 210°C, each for 1h, a flexible transparent film was obtained which was stripped off the plate by immersion in hot water for 2 h and used for different measurements. The other half of the polymer solution was diluted to about 6% by addition of more NMP and the polymer was precipitated by pouring into water. The precipitated product was filtered, washed twice with water and then with ethanol under stirring and dried under vacuum at 105°C for 24 h.

### Measurements

Infrared spectra were recorded with a Specord M 80 spectrometer in transmission mode by using KBr pellets. The inherent viscosities ( $\eta_{inh}$ ) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20°C, at a concentration of 0.5 g/dL. The molecular weights were determined by gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. Measurements were carried out with polymer solutions of 0.2% concentration in DMF containing 0.1 M NaNO<sub>3</sub> and by using DMF with 0.1 M NaNO<sub>3</sub> as eluent. Polystyrene standards of known molecular weight were used for calibration. Thermogravimetric analyses (TGA) were performed on a MOM derivatograph made in Budapest, Hungary, at a heating rate of 12°C/min in air. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves 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. The surfaces of the very thin films as-deposited on silicon wafers were studied by atomic force microscopy (AFM) with a SA1/BD2 apparatus (Park Scientific Instruments) in contact mode, under a constant force, with a pyramidal type tip.

## CONCLUSIONS

Two series of poly (amide-imide)s have been synthesized and compared. The polymers which have been obtained by direct polycondensation, from dicarboxylic acid which contains a phenyl ring in meta position, have a lower glass transition temperature with about 30°C then the polymers which have been prepared by the reaction of diacid dichloride and which contain a phenyl ring in para position, probably due to the presence of meta phenylene rings in the macromolecular chain of the first polymers. In the same time the average molecular weights of the first polymers are lower than the average molecular weights of the other polymers, and the decomposition temperatures are slightly higher. Very thin polymer films deposited by spin-coating technique onto silicon wafers showed a smooth, pinhole-free surface in Atomic Force Microscopy investigations for the both series of polymers. The conformational rigidity parameters values of the polymers correlates well with their solubility and glass transition temperatures.

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## REFERENCES

1. C. E. Sroog, *Prog. Polym. Sci.*, **1991**, *16*, 561-694.
2. S. J. Huang and A. E Hoyt, *Trends Polym. Sci.*, **1995**, *3*, 262-271.
3. J. de Abajo and J. G. de la Campa, *Adv. Polym. Sci.*, **1999**, *140*, 23-59.
4. J. L. Hedrick and R. Twieg, *Macromolecules*, **1992**, *25*, 2021-2025.
5. C. D. Diakoumakos and J. A. Mikroyannidis, *Polymer*, **1994**, *35*, 1986-1990.
6. E. Hamciuc, C. Hamciuc, I. Sava and M. Bruma, *Eur. Polym. J.*, **2001**, *37*, 287-293.
7. A. S. Jadhav, N. N. Maldar, B. M. Shinde and S. P. Vernekar, *J. Polym. Sci. Part A: Polym. Chem.*, Vol. **1991**, *29*, 147-153.
8. M. Bruma and B. Schulz, *J. Macromol. Sci.-Polym. Rev. C*, **2001**, *41*, 1-40.
9. D. J. Liaw, F. C. Chang, M. K. Leung, M. Y. Chou and K. Muellen, *Macromolecules*, **2005**, *31*, 4024-4029.
10. E. Hamciuc, B. Schulz, T. Köpnick, Y. Kaminorz and M. Bruma, *High Perform. Polym.*, **2002**, *14*, 63-75.
11. S. Janietz and B. Schulz, *Eur. Polym. J.*, **1996**, *32*, 465-474.
12. B. Schulz, Y. Kaminorz and L. Brehmer, *Synth. Met.*, **1997**, *84*, 449-450.
13. E. Hamciuc, M. Bruma, B. Schulz and T. Köpnick, *High Perform. Polym.*, **2003**, *15*, 347-359.
14. I. Sava, M. Bruma, B. Schulz and T. Köpnick, *High Perform. Polym.*, **2005**, *17*, 483-495.
15. C. Hamciuc, M. Bruma, F. W. Mercer, T. Köpnick and B. Schulz, *Macromol. Mater. Eng.*, **2000**, *276/277*, 38-43.
16. I. A. Ronova and S. A. Pavlova, *High Perform. Polym.*, **1988**, *10*, 309-329.
17. S. A. Pavlova, G. I. Timofeeva, I. A. Ronova and L.A. Pankratova, *J. Polym. Sci. Polym. Phys. Ed.*, **1980**, *18*, 1-18.
18. I. A. Ronova, A. N. Vasilyuk, C. Gaina and V. Gaina, *High Perform. Polym.*, **2002**, *14*, 195-208.
19. I. A. Ronova, L. B. Eylshina, A. N. Vasilyuk, A. L. Rusanov and E.G. Bulycheva, *Russ. Chem. Bull. Int. Ed.*, **2002**, *51*, 820-824.
20. C. Hamciuc, I. A. Ronova, E. Hamciuc and M. Bruma, *Angew. Makromol. Chem.*, **1998**, *254*, 67-74.
21. C. Hamciuc, E. Hamciuc, M. Bruma and I. A. Ronova, *J. Macromol. Sci.*, **2005**, *42*, 61-68.
22. I. Sava, *Rev. Roum. Chim.*, **2006**, *51*, 753-758.
23. I. Sava and C. Hamciuc, *Rev. Roum. Chim.*, **2006**, *51*, 759-764.
24. C. Hamciuc, E. Hamciuc, I. A. Ronova and M. Bruma, *High Perform. Polym.*, **1997**, *9*, 177-188.
25. M. D. Iosip, M. Bruma, I. A. Ronova, M. Szesztay and P. Müller, *Eur. Polym. J.*, **2003**, *39*, 2011-2021.
26. M. Bruma, B. Schulz and F. W. Mercer, *J. Macromol. Sci., Pure Appl. Chem. A*, **1995**, *32*, 259-286.
27. J. R. Pratt and S. F. Thames, *J. Org. Chem.*, **1973**, *38*, 4271-4274.
28. F. Higashi, S. Ogata and Y. Aoki, *J. Polym. Sci. Polym. Chem. Ed.*, **1982**, *20*, 2081-2087.