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. Therefore much effort has been made to develop structurally modified aromatic polymers having increased solubility with retention of their good thermal stability. 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. 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. 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. 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 σ-π conjugation and thus support the transport of electrons along the macromolecular chain.

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
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.\textsuperscript{13,14} The structure of these polymers is shown in Scheme 1.

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

All the polymers exhibited IR bands at 1220 and 820 cm\textsuperscript{-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 0.3-0.5 dL/g for polymers III and 0.66-1.19 dL/g for the polymers III' (Table 1).
processed into thin films by casting their solutionability due to their good solubility and wereexhibited smooth surfaces; the values of root meanby atomic force microscopy (AFM). The films such films as-deposited on substrates was studiedspin-coating onto silicon wafers. The quality offilms were tough, flexible andcreasable. Very thin coatings having a thickness inthe range of tens of nanometers have been preparedfrom diluted NMP-solutions (concentration 2%) byconcentration of about 10% were cast onto glassplates. Their solutions in NMP having apolydispersity Mw/Mn is in the range of 2.1-2.5values  are in the range of 79000-114000 and thenumber-average molecular weight Mn values are inthe range of 2-5 Å being of the same order ofmagnitude as that of the highly polished siliconwafersthe deposited films are smooth andhomogeneous. They do not show any pinholes orcracks and are practically defectless.

The thermal stability was evaluated bythermogravimetric analysis (TGA). The initialdecomposition temperature of the polymers III is inthe range of 407–464°C the temperature of 10%weight loss (T10) is in the range of 470–500°C. Thepolydispersity of 450–485°C,420–450°C and have a 10% weight loss in the rangeof 450–485°C, in air atmosphere (Table 1). Bycomparing these aromatic poly(amide-imide)scontaining dimethylsilane linkages with relatedpoly(amide-imide)s that have been synthesizedfrom the same diamines but with a monomer whichdoes not contain silicon, it can be seen that theirdecomposition temperatures are in the same range.This shows that the presence of dimethylsilane groupspreserves the high thermal stability whileimproving the solubility. In the same time bycomparing the thermostability of the presentpolymers III and III’ it can be seen that the thermalstability of the first polymers is slightly higher thanthe thermal stability of the polymers III’ (Table 1).

All these polymers possess good film-formingability due to their good solubility and wereprocessed into thin films by casting their solutiononto glass plates. Their solutions in NMP having aconcentration of about 10% were cast onto glasssubstrates and dried to yield thin transparent freestanding films having a thickness of tens ofmicrometers. The films were tough, flexible andcreasable. Very thin coatings having a thickness inthe range of tens of nanometers have been preparedfrom diluted NMP-solutions (concentration 2%) byspin-coating onto silicon wafers. The quality ofsuch films as-deposited on substrates was studiedby atomic force microscopy (AFM). The filmsexhibited smooth surfaces; the values of root mean

<table>
<thead>
<tr>
<th>Polymer</th>
<th>ηinh (dL/g)</th>
<th>Tg (°C)</th>
<th>IDT (°C)</th>
<th>T10 (°C)</th>
<th>l0 (Å)</th>
<th>A (Å²)</th>
<th>p</th>
<th>Mw (g/mol)</th>
<th>Mn (g/mol)</th>
<th>Mw/Mn</th>
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</thead>
<tbody>
<tr>
<td>IIIa</td>
<td>0.37</td>
<td>219</td>
<td>437</td>
<td>480</td>
<td>45.88</td>
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<td>4.12</td>
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<td>32000</td>
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<tr>
<td>III’a</td>
<td>0.86</td>
<td>263</td>
<td>411</td>
<td>432</td>
<td>41.12</td>
<td>39.63</td>
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<td>79000</td>
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<tr>
<td>IIIb</td>
<td>0.38</td>
<td>220</td>
<td>428</td>
<td>470</td>
<td>41.40</td>
<td>21.71</td>
<td>3.75</td>
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<td>41600</td>
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<td>0.66</td>
<td>251</td>
<td>433</td>
<td>475</td>
<td>41.40</td>
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<td>88000</td>
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<tr>
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<td>0.44</td>
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<td>471</td>
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<tr>
<td>III’d</td>
<td>1.19</td>
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<td>450</td>
<td>41.40</td>
<td>49.46</td>
<td>8.38</td>
<td>239000</td>
<td>114000</td>
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</tr>
</tbody>
</table>

* Glass transition temperature; b Initial decomposition temperature = temperature of 5% weight loss; c Temperature of 10%weight loss; l0, contour length over repeating structural unit; A, Kuhn segment; p, conformational rigidity parameter.
We have studied some physical properties of poly(amide-imide) III such as solubility, glass transition temperature (Tg), 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.16

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.17,18

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.19

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 slightly 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 dimethysilane units, which introduce a factor of asymmetry that prevents dense packing of the chains.

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

Generally, Tg 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 Tg (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 Tg of 251°C. When a CN substituent is present on the phenylene ring, which is the case of the polymer III'd, the Tg 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 Tg (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.20,23
The introduction of isopropylidene groups in the polymer \( \text{III}'a \) results in a decrease in its \( T_g \), 263°C, compared to the corresponding polymer \( \text{III}'d \) whose \( T_g \) is 281°C. This fact is due to the higher flexibility of the polymer \( \text{III}'a \) (\( p = 6.75 \)) by comparing with polymer \( \text{III}'d \) (\( p = 8.38 \)). In the same time it can be seen that the values of conformational rigidity parameters of polymers \( \text{III} \) are lower than the values of conformational rigidity parameters of polymers \( \text{III}' \). This fact can be explained by the presence of more meta-incatenations in the polymers \( \text{III} \) 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-incatentation 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.24,25

**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. of Ia: 126-128°C; Ib: 114-116°C; Ic: 197-199°C. The diamine Id, 2,6-bis(p-aminophenoxy)benzonitril, was synthesized by the reaction of p-aminophenol with 2,6-dichlorobenzonitril, in dimethylacetamide (DMAc) in the presence of potassium carbonate, according to a published procedure.26 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 dianhydride27 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.13,14

**Synthesis of bis[N-(3-chlorocarboxyphenyl)phthalimidyl]-dimethylsilane II'a.** We have tried to prepare the dicarboxilic acid II'a with conventional chlorinated agents such as thionyl chloride, phosphorus pentachloride or oxalyl chloride, but we were not successful. The resulting dicarboxylic acid II'a with conventional chlorinated agents such as thionyl chloride, phosphorus pentachloride or oxalyl chloride, but we were not successful. The resulting dicarboxylic acid II'a 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-chlorocarboxyphenyl)] phthalimidyl] dimethylsilane.

**Synthesis of bis[N-(4-chlorocarboxyphenyl)phthalimidyl]-dimethylsilane II'b** was performed by heating of dicarboxilic acid II'b 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 I. The polymers III were synthesized by direct polycondensation reaction 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 phosphate, 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 dicarboxylic 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 (ηinh) 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 NaNO3 and by using DMF with 0.1 M NaNO3 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 (T10) was also recorded. The glass transition temperatures (Tg) 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/B2 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 than 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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