COMPARED PROPERTIES OF SOME POLY(AMIDE-IMIDE)S OBTAINED BY DIRECT POLYCONDENSATION

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Abstract: *Two series of poly(amide-imide)s have been synthesized by direct polycondensation reaction of dicarboxylic acids containing dimethylsilylene or carbonyl group and preformed imides cycles with various aromatic diamines. These polymers show high thermal stability, with initial decomposition temperature being above 300 °C and glass transition temperature in the range of 220-270 °C. Very thin polymer films deposited by spin-coating technique onto silicon wafers showed a smooth, pinhole-free surface in atomic force microscopy investigations.*

Key words: *poly(amide-imide)s, direct polycondensation, dimethylsilylene, high thermal stability, thin films.*

1. Introduction

Polyimides are high-performance polymer materials which have been widely used in microelectronic industries and other advanced fields because of their outstanding properties, such as high thermal stability, mechanical properties, chemical resistance, dielectric properties and excellent tensile strength and modulus [18]. The application of these kind of polymers is somewhat limited due to processing difficulties, such as insolubility in conventional solvents and extremely high glass transition temperatures. Therefore much effort has been made to develop structurally modified aromatic polymers having increased solubility with retention of their good thermal stability [1], [10]. Aromatic poly(amide-imide)s were developed as alternative materials offering a compromise between thermal stability and processability when compared with polyamides or polyimides of analogous structures. They bring together the superior mechanical properties associated with amide groups and the high thermal stability determined by imide rings. These polymers show good solubility in highly polar solvents, lower glass transition temperatures and easier processability compared with corresponding polyimides [4], [5], [14]. The incorporation of flexible bonds, large pendent groups or polar substituents into the polymer backbone often increased the solubility of the polymers [3], [6], [11]. The presence of diphenylsilylene groups into the aromatic polymer chains gave soluble products having a remarkable thermal stability and good film-forming ability [7], [8], [12], [17].

The present paper compare poly(amide-imide)s obtained by direct polycondensation reaction of dicarboxylic acids containing dimethylsilylene or carbonyl group and preformed imide rings with certain aromatic diamines containing different groups between phenylene units. The properties of these polymers such as

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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.

2. Experimental

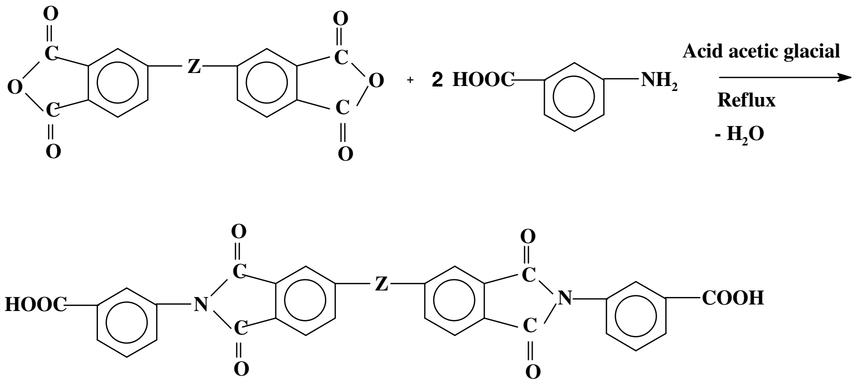
• Synthesis of the monomers

Aromatic diamines ***I***, such as 2,2-bis(*p*-aminophenoxy-phenyl)isopropane, **Ia,** 1,3-bis(*p*-aminophenoxy)benzene **Ib,** 2,6-bis(*p*-aminophenoxy)benzonitril, **Ic,** 4,4'-bis(*p*-aminophenoxy)biphenyl, **Id,** 4,4'-diaminobenzophenone, **Ie,** were used in this paper to synthesized the poly(amide-imide)s. The aromatic diamines **Ia, Ib, Id** and **Ie** have been provided by different commercial sources and purified by recrystallization from ethanol or from a mixture of ethanol with water. Melting point (M. p.) **Ia**: M.p. 126-128 °C; **Ib**: 114-116 °C; **Ic**: 210-213 °C; **Id**: 191-193 °C; **Ie**: 243-245 °C. The diamine **Ic,** 2,6-bis(*p*-aminophenoxy)benzonitril, was synthesized by the reaction of *p*-aminophenol with 2,6-dichlorobenzonitril, in dimethylacetamide (DMAc) with potassium carbonate, according to a published procedure [2], [16]. It was recrystallized from a mixture of dimethylformamide with water.

• Synthesis of diacid chlorides containing preformed imide rings II

The preparation of dicarboxylic acid **IIa** and **IIb** was carried out in a round-bottom flask equipped with a condenser, $CaCl_2$ drying tube, magnetic stirrer and heating source. The concentration of reactants used in this synthesis was 10% solids (w/v) which allowed efficient mixing. 150 mL of glacial acetic acid and 6.85 g (0.05 mol) of *m*-aminobenzoic acid were placed in the flask and 8.05 g (0.025 mol) of benzophenontetracarboxylic dianhydride (or 8.8 g (0.025 mol) of bis(3,4-dicarboxyphenyl)dimethylsilane dianhydride) was added with rapid stirring. The reaction mixture was heated at reflux temperature for 16-20 h. The resulting white product **II** was filtered, washed with ethanol and dried (yield 90%) (Scheme 1).

Elemental analysis (**IIa**): calculated for $C_{31}H_{16}N_2O_9$: C, 66.42%; H, 2.88%; N, 5%. Found: C, 66.36%; H, 2.83%; N, 4.57%. IR spectrum (KBr, cm^{-1}): 3200-2800 (-OH stretching); 1780 (imide carbonyl symmetric



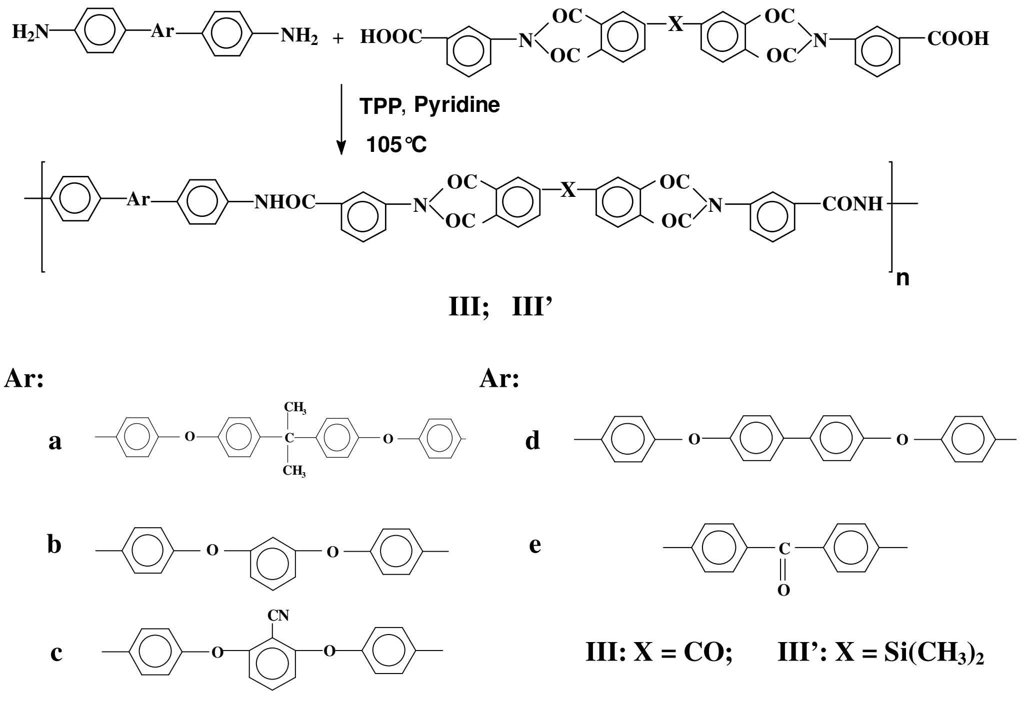
IIa: Z = CO; **IIb: Z = Si $(CH_3)_2$**

Scheme 1. *Synthesis of dicarboxylic diacid containing preformed imide cycle* stretching); 1730 (imide carbonyl asymmetric stretching and carboxylic C=O); 1375 (C-N stretching); 740 (imide ring) and 1640 due to the carbonyl group from benzophenone. Melting point: > 350 °C.

Elemental analysis (**IIb**): calculated for $C_{32}H_{22}N_2SiO_8$: C, 65.08%; H, 3.73%; N, 4.74%. Found: C, 64.76%; H, 3.83%; N, 4.57%. IR spectrum (KBr, cm^{-1}): 3200-2800 (-OH stretching); 1780 (imide carbonyl symmetric stretching); 1730 (imide carbonyl asymmetric stretching and carboxylic C=O); 1375 (C-N stretching); 740 (imide ring) and 1230 and 830 due to the methylsilane bonds. Melting point 329-331 °C.

• Synthesis of the polymers

The direct polycondensation reaction of equimolar amounts of diamine and dicarboxylic acid at 105 °C, in N-methyl-2-pyrrolidinone (NMP) as a solvent and in the presence of triphenylphosphite (TPP) and pyridine as condensating agents with $CaCl_2$ for maintaining the formed polymer in solution, was run for preparation of polymers **III** and **III'**. Scheme 2 shows the synthesis of the polymers.



Scheme 2. *Preparation of the polymers **III** and **III'***

A mixture of 0.834 g (0.0015 mol) of dicarboxylic diacid **IIa**, 0.4755 g (0.0015 mol) diamine **Ic**, 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 0.72 dL/g, measured at a concentration of 0.5 g/dL at 20 °C. This general procedure was used for all the polymers.

• Measurements

FTIR spectra were recorded with a FT-IR VERTEX 70 (Bruker Optics Company), with a resolution of 0.5 cm^{-1}. The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in NMP, at 20 °C, and a concentration of 0.5 g/dL. The molecular weight 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 $NaNO_3$ and by using DMF with 0.1 M $NaNO_3$ 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 glass transition temperatures (T_g) of the precipitated polymers were determined with a Mettler differential scanning calorimeter DSC 12E. The samples were heated from ambient temperature to above 300 °C at a heating rate of 10 °C/min under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. 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. Model molecules for a polymer fragment were obtained by molecular mechanics MM+) by means of the Hyperchem program, Version 7.5 [20].

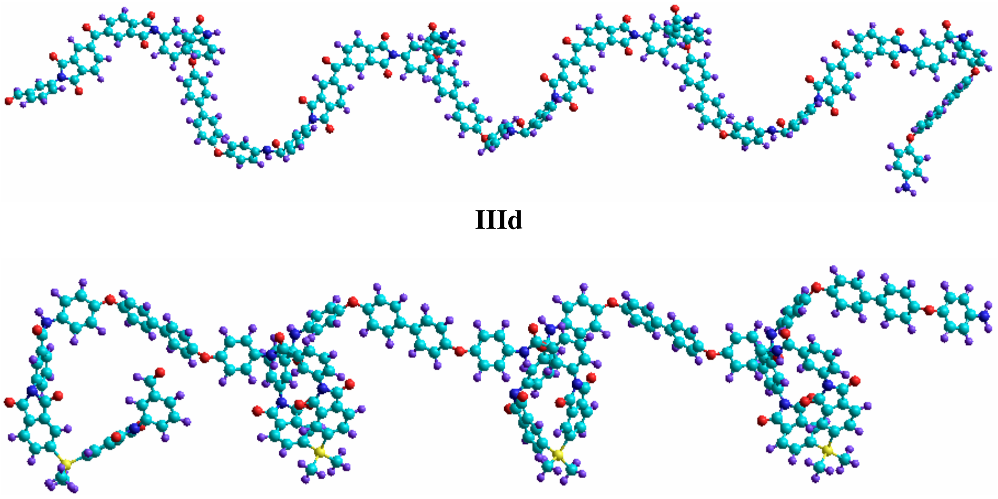
3. Results and Discussion

The synthesis of the dicarboxylic acids containing carbonyl or dimethylsilylene group and preformed imide rings, ***(bis[N-(3-carboxyphenyl)phthalimidyl]benzophenone IIa** and **bis[N-(3-carboxyphenyl) phthalimidyl]-dimethylsilane IIb)*** was described earlier [13], [15]. Direct polycondensation of dicarboxylic acids with aromatic diamines by using triphenyl phosphite and pyridine as condensating agents has been known as a convenient preparative method for aromatic polyamides. This method, the so-called Yamazaki-Higashi method [9], [19] requires the use of an aprotic polar solvent and a basic co-solvent, such as pyridine, at a moderate temperature (ca 100 °C), generally in the presence of inorganic salts such as calcium chloride or lithium chloride or their mixture.

All the polycondensation reactions readily proceeded in homogeneous solution. Tough and stringy precipitates formed when the viscous polymer solutions were trickled into the stirring methanol. Yields over 96% were always achieved.

The structure of polymers **III** was identified by FTIR spectra. Strong bands at 1780 cm^{-1} and 1720 cm^{-1} are commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide. The absorption band at 1370-1375 cm^{-1} is due to C-N stretching in imide ring and the absorption at 740 cm^{-1} is possibly due to imide ring deformation. The wide bands which appeared at 3400-3420 cm^{-1} were attributed to N-H stretching vibration in the amide group. Characteristic absorptions appeared at 1670-1660 cm^{-1} due to carbonyl stretching vibration (amide I overlapping with carbonyl from benzophenone) and at 1520 cm^{-1} due to N-H deformational vibration (amide II). The CN group from benzonitril appears in polymer **IIIc** and **III'c** at 2230 cm^{-1}. The polymers **III'** exhibited IR bands at 1220 and 820 cm^{-1} due to the methyl-silane bonds.

The polymers dissolve easily in polar amidic solvents such as NMP, DMF, dimethylacetamide (DMA) and partially soluble in pyridine. This good solubility is due to the relatively high flexibility of macromolecular chains which was obtained by the introduction of ether linkages together with *m*-catenation 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. A model molecule of a polymer **IIId** and **III'd** is shown in Figure 1. Due to such a shape, the dense packing of the chains is disturbed, the diffusion of small molecules of solvents between the polymer chains is facilitated and that leads to better solubility.



IIId

III'd

Fig. 1. *Model of a fragment incorporating 4 repeating units of the polymers* ***IIId*** *and* ***III'd***

All these polymers possess good film-forming ability due to their solubility and were processed into thin films by casting their solution onto glass plates. Their solutions in NMP having a concentration of between 5-8% 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. The films exhibited smooth surfaces; the values of root mean square (rms) roughness calculated from the AFM data are in the range of 5-8 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 deffectless. A typical AFM image is shown in Figure 2. The inherent viscosities, measured in NMP solution, were in the range of 0.47-0.72 dL/g for the polymers III and in the range of 0.37-0.54 for the polymers III' (Table 1).

The molecular weight of the polymers was determined by gel permeation chromatography (GPC). The values of number-average molecular weight Mn are in the range of 51000-70000 for the polymers III and in the range of 32000-53800 for the polymers III', the weight-average molecular weight Mw values are in the range of 98000-154500 for the polymers **III** and in the range of 72000-106000 for the polymers **III'** and the polydispersity Mw/Mn is in the range of 1.93-2.4 for the polymers **III** and in the range of 1.74-2.25 for the polymers **III'** (Table 1).

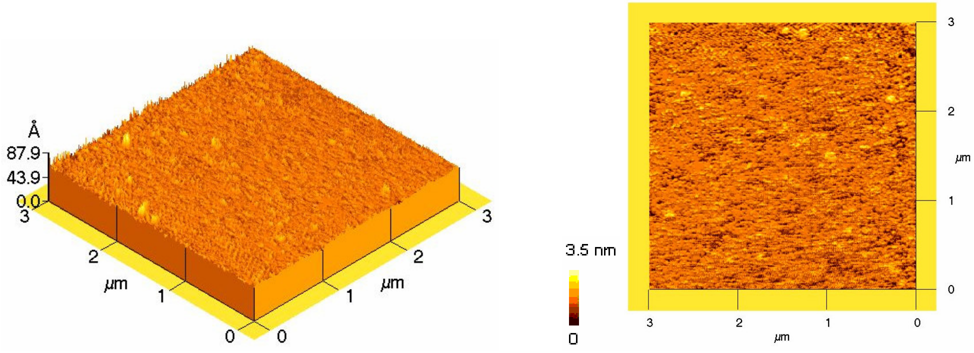


Fig. 2. *AFM pictures of the film made from polymer **III'a***
(left: side view; right: top view)

The thermal stability was evaluated by thermogravimetric analysis (TGA). All the polymers show good thermal stability. The decomposition begins at about 300 °C, as indicating by the temperature of 5% weight loss in TGA thermograms for polymers III and at around 400 °C for polymers III' (Table 1). As can be seen the thermal stability of the polymers III' is higher than that of polymers III probably due to the presence of

*Compared properties of the polymers **III** and **III'*** Table 1

Polym.	Inh. Viscosity[a]	Mn	Mw	Mw/Mn	IDT[b] [°C]	T_{10}[c] [°C]	Tg[d] [°C]
IIIa	0.45	59500	119000	2.0	280	420	232
III'a	0.37	32000	72000	2.25	437	480	219
IIIb	0.52	51000	98000	1.93	400	468	240
III'b	0.38	41600	72500	1.74	428	480	220
IIIc	0.72	64500	143000	2.22	320	460	ND
III'c	0.54	53800	106000	1.97	464	500	255
IIId	0.47	57500	120000	2.09	280	435	ND
III'd	0.44	48000	84000	1.74	407	471	239
IIIe	0.65	62000	128000	2.05	350	460	ND
III'e	0.40	41600	77000	1.85	404	447	260

[a] Measured in NMP at 0.5 g/dL; [b] Initial decomposition temperature = temperature of 5% weight loss; [c] Temperature of 10% weight loss; [d] Glass transition temperature.

dimethylsilane linkages which preserve the high thermostability of the polymers.

The glass transition temperature (*Tg*) of the poly(amide-imide)s **III** were in the range of 232-240 °C (Table 1). As can be seen from the Table 1 only the polyamide-imide **IIIa** and **IIIb** show *Tg* and the other polymers do not show *Tg* until 350 °C. This can be explain by the influence of the isopropylidene linkage in the case of polymer **IIIa** or by the introduction of much more *meta*-incatenation in the case of **IIIb.**

On the other hand, the absence of ether linkages in the case of polymers **IIIe,** the presence of CN or biphenyl groups in the case of poly(amide-imide)s **IIIc** and **IIId** led to more rigid macromolecular chains and these polymers do not show any glass transition until 350 °C.

The glass transition temperature (*Tg*) of the silicon-containing poly(amide-imide)s **III'** were in the range of 219-260 °C (Table 1). It can be seen that the *Tg* values of these polymers is about 30 °C lower than that of the similar polymers which contain only the *para*-catenation [13]. The lower values of *Tg* can be explained by the presence of *meta*-catenation in the macromolecular chains of present polymer. As can be seen from the Table 1 the *Tg* of the polyamide-imides which contain dimethylsilylene group show a lower *Tg* in comparison with polymers which contain carbonyl group due to probably the higher flexibility of the macromolecular chains of the polymers with dimethylsilylene units.

4. Conclusions

The incorporation of dimethylsilylene or carbonyl groups together with *meta*-catenated phenylene rings into the main chain of aromatic poly(amide-imide)s gave products with substantially improved solubility in polar amidic solvents. These polymers maintain high thermal stability, with decomposition temperature being above 300 °C for polymers which contain carbonyl group and above 400 °C for polymers with dimethylsilane units. The polymers which contain carbonyl group have higher glass transition temperature than that of dimethylsilylene containing poly(amide-imide)s and in the same time the initial decomposition of the latter are higher, probably due to the higher stability of the silylene units. The polymers can also be processed from solutions into flexible thin and ultrathin, pinhole-free films having good adhesion to silicon wafers. The poly(amide-imide)s have a fairly high molecular weight with Mn being in the range of 32000-64500 and polydispersity of 1.74-2.25.

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