

*Dedicated to the memory of
Professor Cristofor I. Simionescu (1920–2007)*

SYNTHESIS AND CHARACTERIZATION OF SOME POLY(AMIDE-IMIDE)S BY DIRECT POLYCONDENSATION

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Poly(amide-imide)s have been synthesized by direct polycondensation reaction of various aromatic diamines with a dicarboxylic acid containing 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 high thermal stability, with initial decomposition temperature being above 270°C and glass transition temperature in the range of 232–246°C.

INTRODUCTION

The necessity to use heat resistant materials in the electronics industry led to the development of research into different heterocyclic polymers, especially with regard to their application as dielectric films, interlayer dielectrics or passivation coatings in integrated circuits. For this purpose it is desirable to use fully cyclized and soluble heterocyclic polymers for spin coating and casting process. Polyimides are a class of polymers that are highly thermostable and have good chemical resistance and relatively low dielectric constant.¹ However, their application 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.^{2,3} 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.⁴⁻⁶ It is known that the solubility of polymers is often increased when flexible bonds, large pendent groups or polar substituents are incorporated into the polymer backbone.⁷⁻⁹ Thus, we considered that some polymers in which imide rings as well as amide and ether bridges are present in a single polymer chain would have a superior balance of useful properties and processing capability, particularly appropriate for casting into very thin films, which would be useful for various high performance applications.

In the present paper we synthesised and characterized the poly(amide-imide)s obtained by solution polycondensation of a dicarboxylic acid having preformed imide rings with certain aromatic diamines containing different groups between phenylene units. 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.

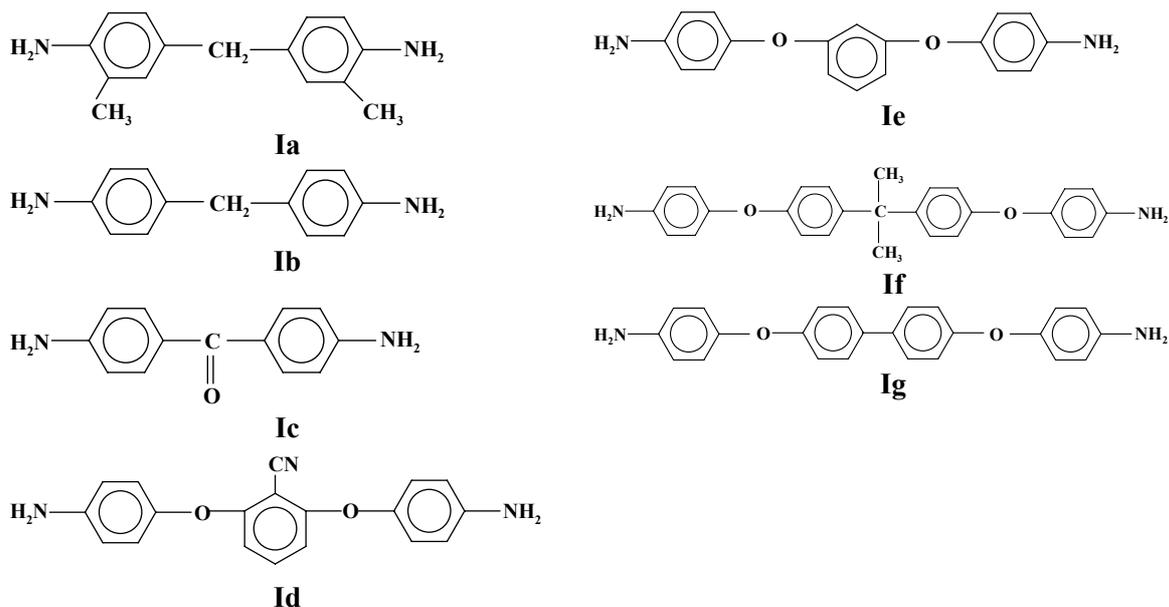
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EXPERIMENTAL

Synthesis of the monomers

Aromatic diamines **I**, such as 3,3'-dimethyl-4,4'-diaminodiphenyl methane **Ia**, 4,4'-diaminodiphenyl methane **Ib**, 4,4'-diaminobenzophenone, **Ic**, 2,6-bis(*p*-aminophenoxy)benzotrinitril, **Id**, 1,3-bis(*p*-aminophenoxy)benzene, **Ie**, 2,2-bis(*p*-aminophenoxy-phenyl)isopropane, **If**, 4,4'-bis(*p*-aminophenoxy) biphenyl, **Ig**, were used in this paper to synthesized the poly(amide-imide)s. The aromatic diamines **Ib**, **Ic**, **Ie**, **If** and **Ig** 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. 156-157°C; **Ib**: 90-92°C; **Ic**: 243-245°C; **Id**: 210-213°C; **Ie**: 114-116°C; **If**: 126-128°C; **Ig**: 191-193°C. The aromatic diamine **Ia** have been synthesized by a method described in the literature.¹⁰ The diamine **Id**, 2,6-bis(*p*-aminophenoxy)benzotrinitril, was synthesized by the reaction of *p*-aminophenol with 2,6-dichlorobenzotrinitril, in dimethylacetamide (DMAc) with potassium carbonate, according to a published procedure.^{11,12} It was recrystallized from a mixture of dimethylformamide with water. The structures of aromatic diamines are shown in Scheme 1.



Scheme 1 – The structures of aromatic diamines.

Synthesis of bis[N-(3-carboxyphenyl)phthalimidy]benzophenone II

The preparation of dicarboxylic acid **II** was carried out in a round-bottom flask equipped with a condenser, CaCl₂ 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 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 2).

Elemental analysis: calculated for C₃₁H₁₆N₂O₉: 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 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.

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

Synthesis of the polymers

The direct polycondensation reaction of equimolar amounts of diamine and dicarboxylic acid at 105°C, in NMP

as a solvent and in the presence of triphenylphosphite (TPP) and pyridine as condensating agents with CaCl₂ for maintaining the formed polymer in solution, was run for preparation of polymers **III**. Scheme 3 shows the synthesis of the polymers.

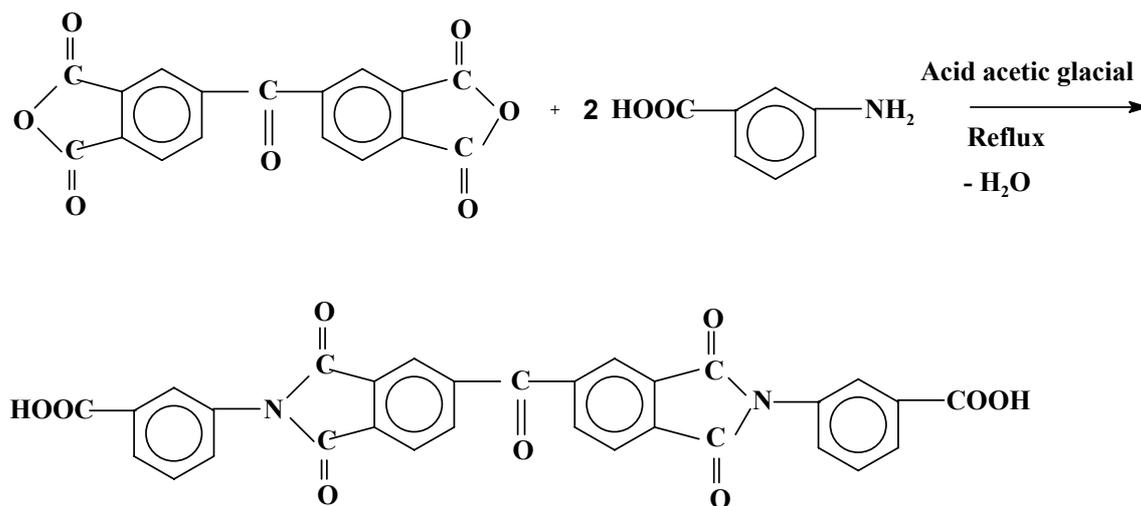
A mixture of 0.834 g (0.0015 mol) of dicarboxylic diacid **II**, 0.4755 g (0.0015 mol) diamine **Id**, 0.5 g calcium chloride, 2 ml triphenyl phosphite, 4 ml of pyridine and 12 ml of N-methylpyrrolidinone was heated with stirring at 105°C for 5 h. After cooling, the reaction mixture was poured into a 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.

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, at 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

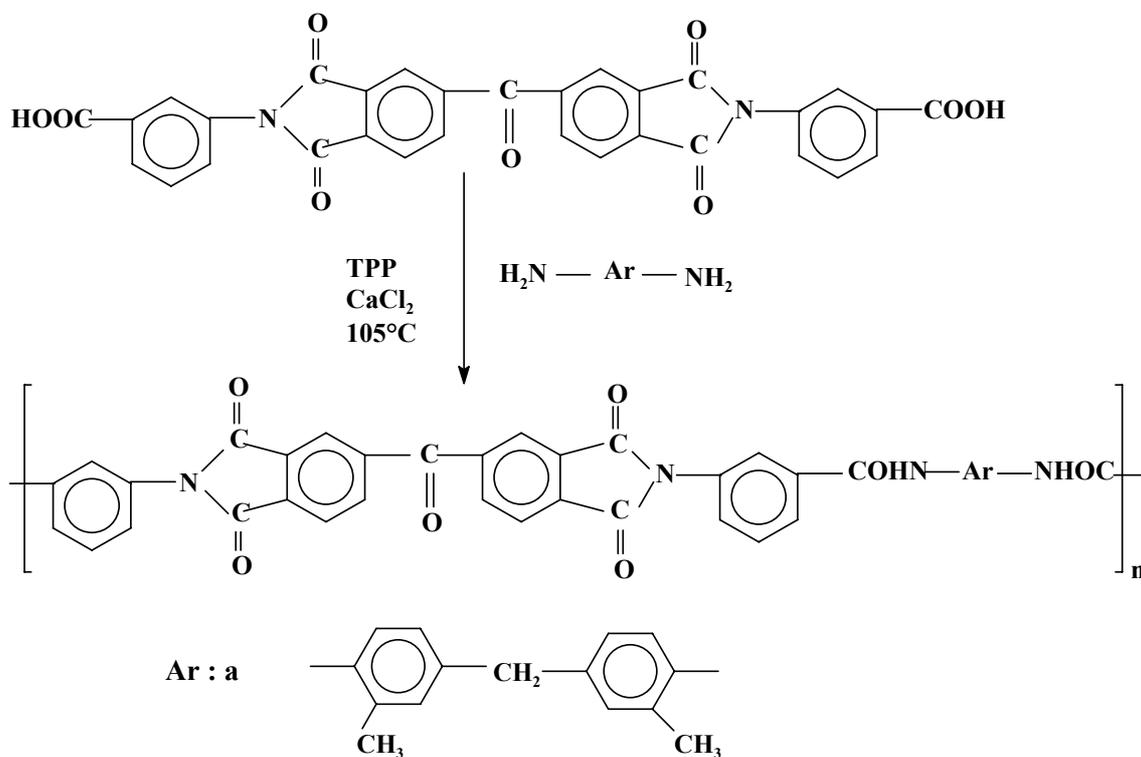
in DMF containing 0.1 M NaNO₃ and by using DMF with 0.1 M NaNO₃ as eluent. Polystyrene standards of known molecular weight were used for calibration. Thermogravimetric analyses (TGA) were performed on a MOM derivatograph made in Budapest, Hungary, at a heating rate of 12°C/min in air. The initial decomposition 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 (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

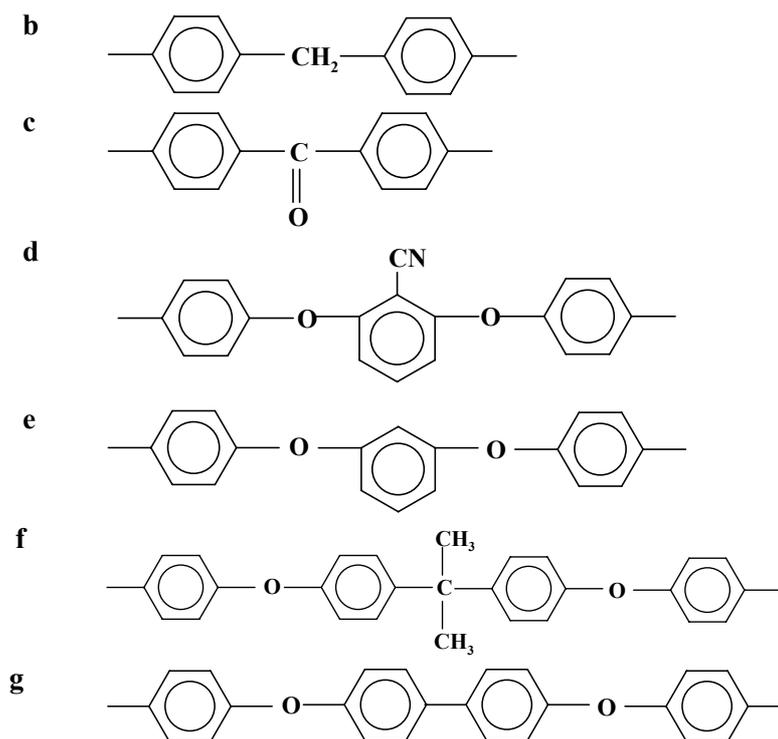
rate of 10°C/min under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflection curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers. 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 7.5.¹³



II

Scheme 2 – Synthesis of dicarboxylic diacid containing preformed imide cycle.



Scheme 3 – Preparation of the polymers **III**.

RESULTS AND DISCUSSION

The synthesis of the dicarboxylic acid containing carbonyl group and imide rings, namely bis[N-(3-carboxyphenyl)phthalimidyl]benzophenone **II**, was performed in the same manner as described in the literature for similar compounds.^{14,15} 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^{16,17} 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.

The polymers **III**, were synthesized according to Scheme 3. All the polycondensation reactions readily proceeded in homogenous solution. Tough and stringy precipitates formed when the viscous polymer solutions were trickled into the stirring methanol. Yields over 96.5% 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 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 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 **III**d at 2230 cm⁻¹. FTIR spectrum of the poly(amide-imide) **III**d is presented in Fig. 1.

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 **III**a and **III**d is shown in Fig. 2. 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.

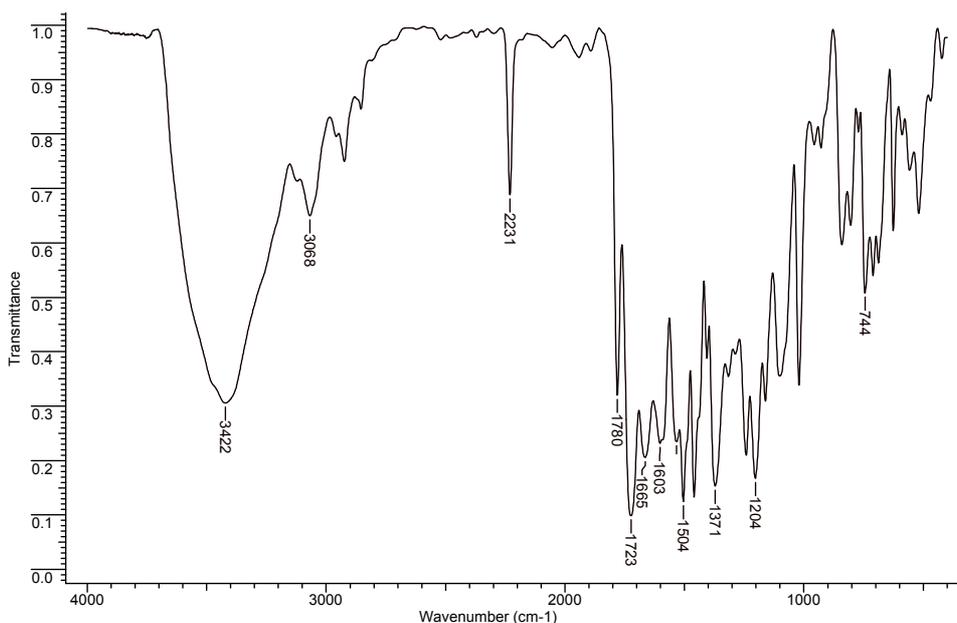


Fig. 1 – FTIR spectrum of poly(amide-imide)s **III d**.

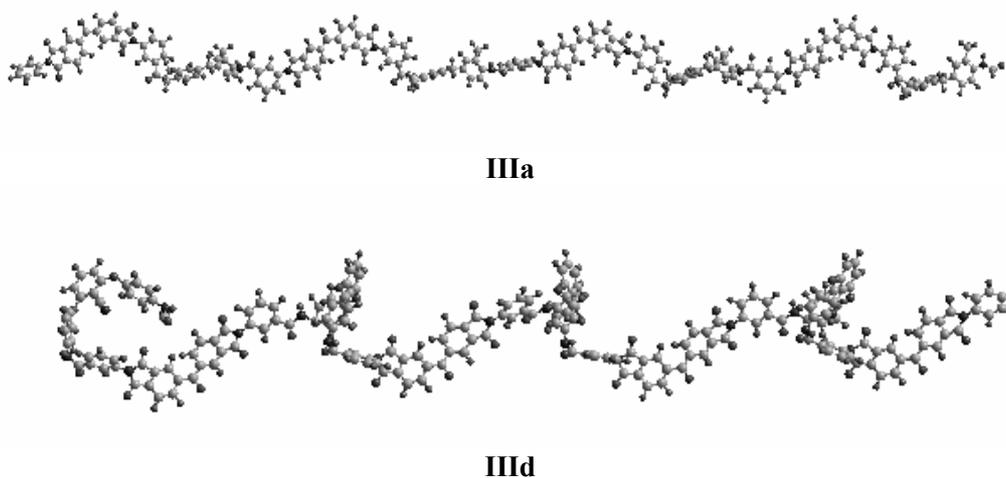


Fig. 2 – Model of a fragment incorporating 4 repeating units of the polymer **III a** and **III d**.

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 defectless. A typical AFM image is shown in Fig. 3.

The inherent viscosities, measured in NMP solution, were in the range of 0.47-0.72 dL/g (Table 1).

The molecular weight of the polymers was determined by gel permeation chromatography (GPC). The values of number-average molecular weight M_n are in the range of 51000-70000, the

weight-average molecular weight M_w values are in the range of 98000-154500 and the polydispersity M_w/M_n is in the range of 1.93-2.4 (Table 1). These values have to be taken as indicative only,

since calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the studied polymers deviate strongly from those of polystyrene.

rms (region) ~1 (0,3) nm, p/v 100 (20) nm
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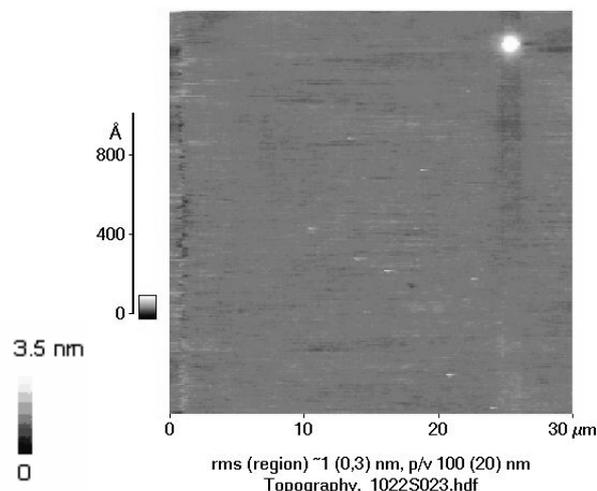
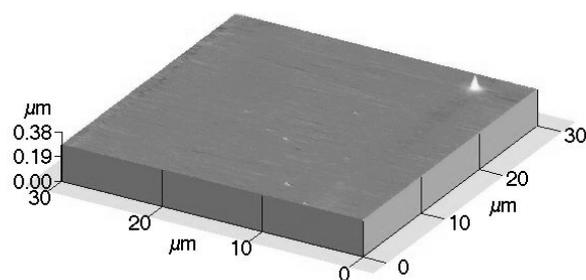


Fig. 3 – AFM pictures of the film made from polymer **III**d (left: side view; right: top view).

Table 1

Characterization of the polymers **III**

Polymer	IDT ^a (°C)	T ₁₀ ^b (°C)	T ^c max °C	T _g ^d (°C)	Inh. Viscosity ^e	M _n	M _w	M _w /M _n
III a	270	420	560	246	0.68	70250	140500	2
III b	290	435	565	ND	0.70	64000	154500	2.4
III c	350	460	565	ND	0.65	62000	128000	2.05
III d	320	460	560	ND	0.72	64500	143000	2.22
III e	400	468	562	240	0.52	51000	98000	1.93
III f	280	420	555	232	0.45	59500	119000	2.0
III g	280	435	554	ND	0.47	57500	120000	2.09

^a Initial decomposition temperature = temperature of 5% weight loss.

^b Temperature of 10% weight loss.

^c Temperature of maximum rate of decomposition

^d Glass transition temperature.

^e Measured in NMP at 0.5 g/dL

The thermal stability was evaluated by thermogravimetric analysis (TGA). These polymers do not show significant weight loss below 250°C. They begin to decompose in the range of 270-400°C; they show 10% weight loss in the range of 420-470°C (Table 1). The maximum rate of decomposition is around 560°C for all the investigated polymers. By comparing the present aromatic poly(amide-imide)s containing carbonyl group between two phenylene rings with poly(amide-imide)s which contain dimethylsilane linkages obtained by the same method¹⁵ it can be seen that their decomposition temperatures are slightly lower. In the same time by comparing the thermostability of the present polymers and the

polymers obtained from the same diamines and bis[N-4-chlorocarbonylphenyl]phthalimidyl-dimethylsilane,¹⁴ it can be seen that the thermal stability is slightly lower (Table 1). This fact can be explain by the more vulnerability of the carbonyl group in comparison with dimethylsilane units.

The glass transition temperature (T_g) of the poly(amide-imide)s **III** were in the range of 232-246 °C (table 1). As can be seen from the table 1 only the polyamide-imide **III**a, **III**e, and **III**f show T_g and the other polymers do not show T_g until 350°C. This can be explain by the influence of the substituents methyl in the case of polymer **III**a or by the introduction of much more *meta*-intercatenation in the case of **III**e or by presence of

isopropylidene linkage in the case of polymer **III**f. On the other hand, the absence of ether linkages in the case of polymers **III**b and **III**c, the presence of CN or biphenyl groups in the case of poly(amide-imide)s **III**d and **III**g led to more rigid macromolecular chains and these polymers do not show any glass transition until 350°C.

CONCLUSIONS

The incorporation of imide cycle together with amide groups and ether linkages 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 and a glass transition in the range of 232-246°C. 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 51000-70000 and polydispersity of 1.93-2.4.

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