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New Poly(Imide-Ether-Amide)s Based on Epiclon

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Epiclon, 5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexenyl-1,2-dicarboxylic acid anhydride, reacted with p-aminobenzoic acid to give a dicarboxylic acid containing imide rings. This was further treated with thionyl chloride to give the corresponding diacid chloride having epiclon units and imide rings. New poly(imide-ether-amide)s have been synthesized by a solution polycondensation reaction of this diacid chloride with various aromatic diamines having ether bridges between phenylene rings. These polymers are easily soluble in polar amidic solvents such as N-methylpyrrolidinone or dimethylformamide and can be cast into thin flexible films or coatings from such solutions. They show high thermal stability, with initial decomposition temperature being above 350°C and glass transition temperature in the range of 223°C–238°C.

Keywords poly(imide-ether-amide)s, epiclon, high thermal stability, good solubility

Introduction

Among thermostable heterocyclic polymers, polyimides are well-known for their outstanding resistance at high temperature along with good mechanical and physical properties (1). However, their application is somewhat limited, due to processing difficulties, such as low solubility in organic solvents and high melting or softening temperatures. Therefore, much effort has been made to modify their chemical structure in order to enhance their physical properties with regard to a specific application or to a particular property, and improve the processability. The most widely used method for the synthesis of aromatic polyimides *via* soluble poly(amic-acid) precursors still has certain disadvantages connected with the low stability of the poly(amic-acid) solutions and incomplete cyclization of the poly(amic-acid)s to polyimide structures (2, 3).

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 (4–6). Aromatic poly(imide-amide)s were developed as alternative materials offering a compromise between excellent thermal stability and processability. They bring together the superior mechanical properties associated with amide groups and the high thermal stability determined by imide rings. These polymers show improved solubility in highly

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polar solvents, lower glass transition temperatures and easier processability compared with corresponding polyimides (7, 8).

Also, a cycloaliphatic anhydride named Epiclon, having a flexible chemical structure, is useful, like other tetracarboxylic dianhydrides, as a raw material for the production of polyimide resins. Therefore, epiclon units have been incorporated into various polymers, mainly in aromatic copolyimides and polyesters, with the aim to enhance their solubility and to render new properties (9, 10).

Previously, we have synthesized poly(imide-amide)s by using diacid chlorides containing hexafluoroisopropylidene, methylene or dimethylsilane groups and various aromatic diamines (11–13).

In the present paper, we report the synthesis of new poly(imide-ether-amide)s by using a diacid chloride, having epiclon units and imide groups, which reacted with certain aromatic diamines having ether bridges between phenylene rings. The properties of these polymers such as solubility, film forming ability, inherent viscosity, molecular weight, thermal stability and glass transition temperature have been evaluated with respect to their chemical structure and compared with those of related compounds.

Experimental

Starting Materials

Epiclon B-4400 [5-(2,5-dioxotetrahydrofurfuryl)-3-methyl-3-cyclohexyl-1,2-dicarboxylic acid anhydride], *p*-aminobenzoic acid, glacial acetic acid and pyridine were provided by different commercial sources and used as received. Aromatic diamines containing two ether bridges **I**, such as 1,4-bis(*p*-aminophenoxy)benzene, 4,4'-bis(*p*-aminophenoxy)-biphenyl, 2,2-bis(*p*-aminophenoxy-phenyl)isopropane and 4,4'-bis(*p*-aminophenoxy)-diphenylsulfone, from commercial sources, were used without further purifications. *N*-methyl-2-pyrrolidinone (NMP) from Merck was dried over phosphorous pentoxide and distilled under reduced pressure. Thionyl chloride from Merck was freshly distilled.

Synthesis of the Diacid Chloride **II**

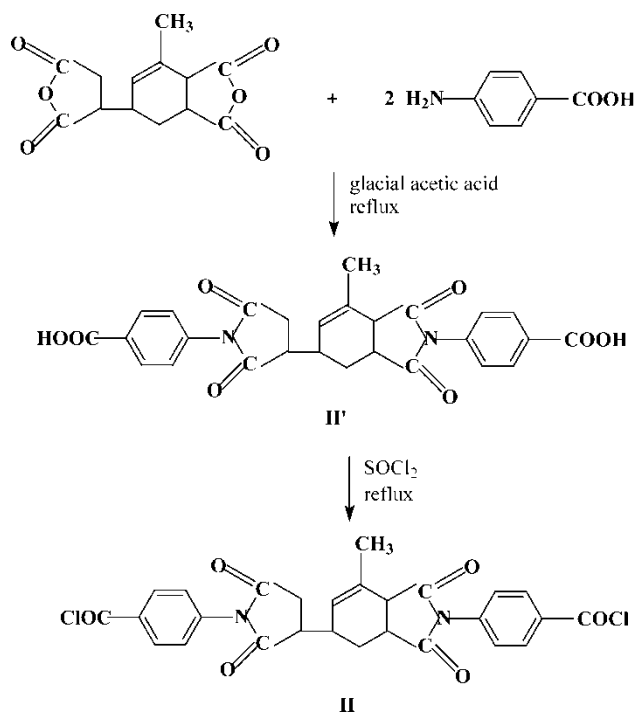
Synthesis of 5-[*N*-(4-carboxyphenyl)succinimido]-3-methyl-[*N*-(4-carboxyphenyl)]-1,2,5,6-tetrahydrophthalimide (Dicarboxylic acid **II'**).

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 17% solids (wt/v) which allowed efficient mixing. 5.48 g (0.04 mol) of aminobenzoic acid and 52 mL of glacial acetic acid were placed in the flask and 5.28 g (0.02 mol) of Epiclon was added with rapid stirring. The reaction mixture was heated at reflux for 10 h. The resulting white product **II'** was filtered, washed with ethanol and dried (yield 65%) (Scheme 1).

Elemental analysis: Calculated for C₂₇H₂₂N₂O₈: C, 64.54%; H, 4.38%; N, 5.57%. Found: C, 64.29%; H, 4.64%; N, 5.22%.

IR spectrum (KBr, cm⁻¹): 3100–2800 (–OH stretching); 1780 (imide carbonyl symmetric stretching); 1720 (imide carbonyl asymmetric stretching and carboxylic C=O); 1390 (C–N stretching); 730 (imide ring) (Figure 1). Melting point: 311–314°C.

¹H-NMR spectrum (60 MHz, DMSO-d₆, TMS, δ, ppm) (Figure 2). 7.42–8.23 (m, 8H), 5.56 (s, 1H), 2.74–3.62 (m, 8H), 1.87 (s, 3H).



Scheme 1. Synthesis of the diacid chloride **II**.

Synthesis of 5-[N-(4-chlorocarbonylphenyl)succinimido]-3-methyl-[N-(4-chlorocarbonylphenyl)]-1,2,5,6-tetrahydrophthalimide (Diacid chloride **II**).

5 g of diacid **II'** was heated at reflux for 3 h with 30 mL of thionyl chloride and using DMF as a catalyst. 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 60 %) (Scheme 1).

Analysis: calculated for $C_{27}H_{20}N_2Cl_2O_6$: Cl, 13.17 %. Found: Cl, 12.9%.

IR spectrum (KBr, cm^{-1}): 1780 (–COCl and imide carbonyl symmetric stretching); 1720 (imide carbonyl asymmetric stretching); 1380 (C–N stretching); 720 (imide ring) (Figure 1). Melting point: 298–302°C.

Synthesis of the Polymers **III**

The polycondensation reaction was run under anhydrous conditions in a nitrogen atmosphere with equimolar amounts of diamine **I** and diacid chloride **II** being used, in NMP as a solvent and with pyridine as an acid acceptor. The relative amounts of monomers and NMP were adjusted to maintain a solid content of 9–12%. A typical reaction was carried out as follows: in a 100 mL three-necked flask, equipped with mechanical stirrer and nitrogen gas inlet and outlet, were placed 1.08 g (0.0025 mol) of 4,4'-bis(*p*-aminophenoxy)-diphenylsulfone, **Id**, 22 mL NMP and 1 mL Py and the mixture was stirred under nitrogen until complete dissolution. The solution was cooled to $-10^{\circ}C$ and 1.3475 g (0.0025 mol) of diacid chloride **II** were added with

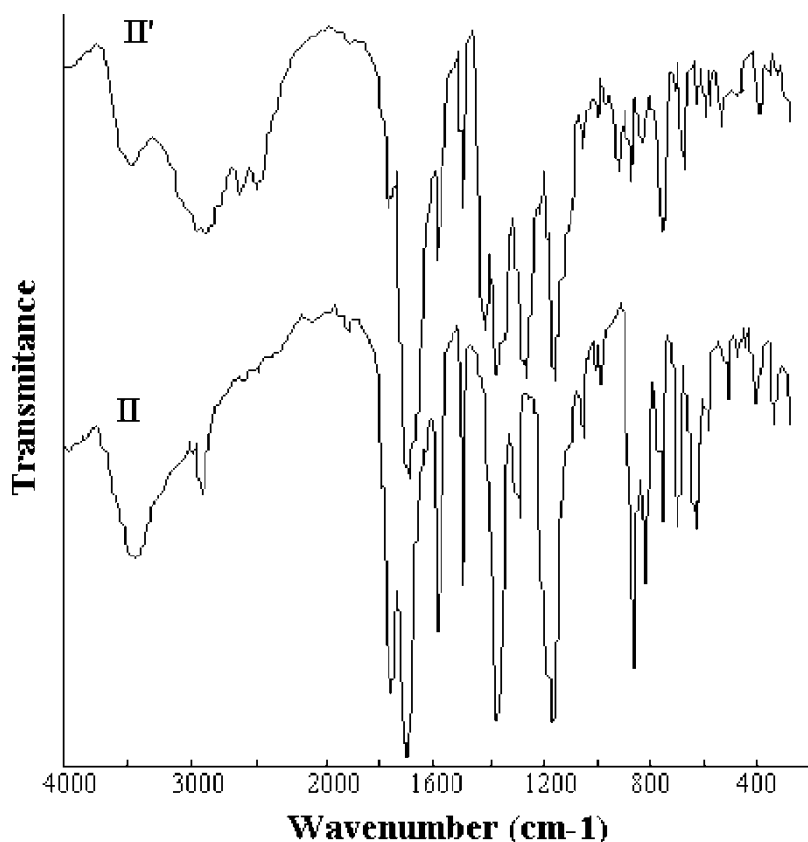


Figure 1. IR spectra of the dicarboxylic acid, 5-[N-(4-chlorocarbonyl)succinimido]-3-methyl-[N-(4-chlorocarbonylphenyl)]-1,2,5,6-tetrahydrophthalimide **II'**, and of the diacid chloride, 5-[N-(4-carboxyphenyl)succinimido]-3-methyl-[N-(4-carboxyphenyl)]-1,2,5,6-tetrahydrophthalimide **II**.

rapid stirring. The content of the flask was kept below 0°C for 15 min. The cooling bath was then 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 1 h, a flexible transparent film was obtained which was stripped off the plate by immersion in hot water for 2 h. It was 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 100°C for 1 h. Details for the preparation of the polymers are given in Table 1.

Measurements

Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices) apparatus without correction.

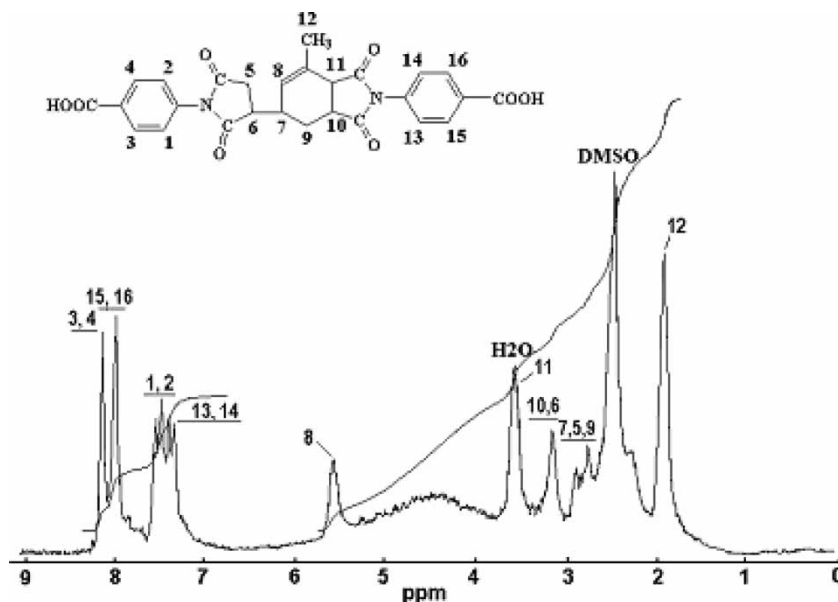


Figure 2. $^1\text{H-NMR}$ spectrum of the dicarboxylic acid, 5-[N-(4-chlorocarbonyl)succinimido]-3-methyl-[N-(4-chlorocarbonylphenyl)]-1,2,5,6-tetrahydrophthal **II'**, in DMSO-d_6 at room temperature.

Infrared spectra were recorded with a Specord M 80 spectrometer in transmission mode, at 4 cm^{-1} resolution, by using monomers or precipitated polymers ground in potassium bromide pellets.

The $^1\text{H-NMR}$ spectra were recorded on a JEOL 60 MHz spectrometer for polymer solution in dimethylsulfoxide- d_6 (DMSO-d_6) using tetramethylsilane (TMS) as internal standard.

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 .

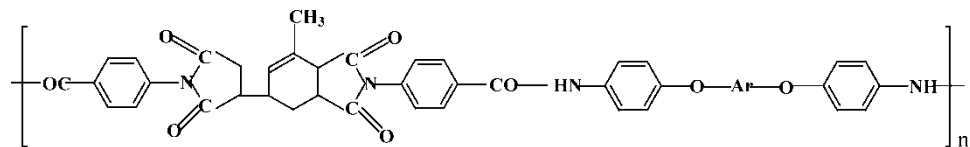
The molecular weight were determined by gel permeation chromatography (GPC) using a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards of known molecular weight were used for calibration and dimethylformamide (DMF) as the mobile phase.

Thermogravimetric analyses (TGA) were performed on a MOM derivatograph (Hungary) in air, at a heating rate of $12^\circ\text{C}/\text{min}$. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% wt loss. The temperature of 10% wt 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 samples were heated from ambient temperature to above 300°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen. Heat flow vs. 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.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM^+) by means of the Hyperchem program, version 4.0 (14).

Table 1
Preparation of the polymers **III** general formula



III

Polymer	Ar	η_{inh}^a (dL/g)	Diamine (g)	Diacid chloride (g)	NMP (mL)	Conc. (%)	Reaction time (h)
IIIa		0.26	0.4380	0.8085	12.5	9.5	5
IIIb		0.31	0.9200	1.3475	17	12	4
IIIc		0.35	0.6157	0.8085	10.5	12	5
IIIId		0.28	1.0800	1.3475	22	10	4

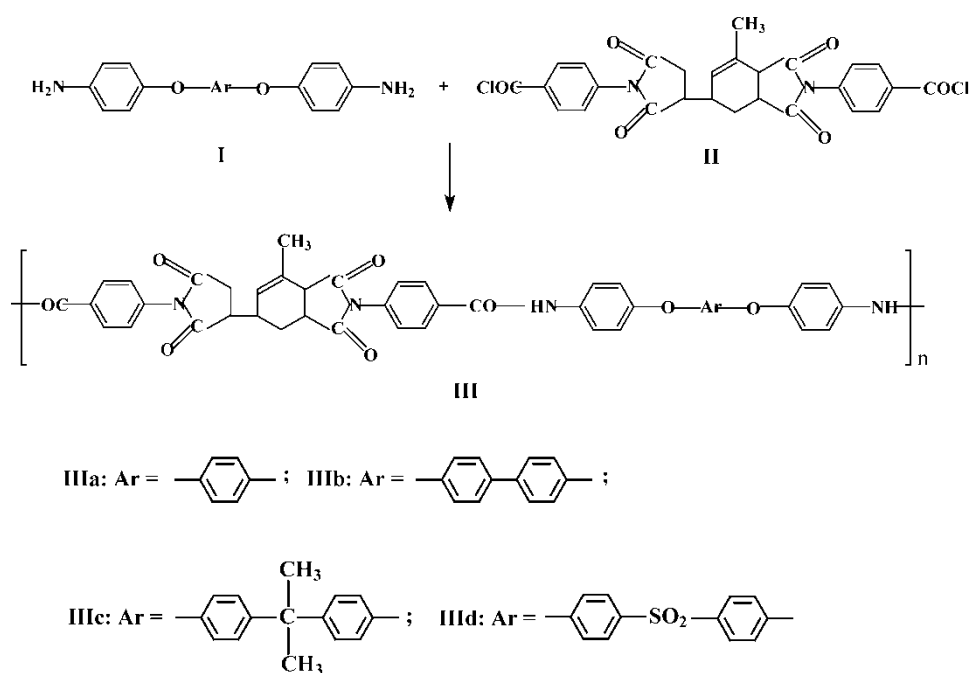
^aDetermined in NMP at 20°C, at a concentration of 0.5 g/dL.

Results and Discussion

The reactions presented in Scheme 1 show the method applied for the synthesis of diacid chloride **II** by treating the corresponding dicarboxylic acid **I'** with thionyl chloride which resulted from the reaction of Epiclon with *p*-aminobenzoic acid by using glacial acetic acid as solvent. Glacial acetic acid has been proven to be an effective solvent in the synthesis of imide containing monomers, allowing the recovery of a relatively pure dicarboxylic acid monomer, when compared to those prepared in an amide solvent (15). Figure 2 shows the $^1\text{H-NMR}$ spectrum of the dicarboxylic acid **I'**. The peak at about 5.6 ppm was assigned to the vinylic proton, while the multiplet at 2.74–3.62 ppm was associated with the resonance values of the methylene and methine protons in the succinimide and the unsaturated rings of the structure. The chemical shift of the carboxylic acid protons are difficult to see, being very close to the water protons.

Polycondensation of equimolar amounts of diamine **I** and diacid chloride **II** in NMP, at low temperature, yielded viscous solutions of poly(imide-ether-amide)s **III** (Scheme 2).

The structure of polymers was identified by IR and $^1\text{H-NMR}$ spectroscopy. 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 1380 cm^{-1} is due to C–N stretching in imide ring and the absorption at $760\text{--}750\text{ cm}^{-1}$ is possibly due to imide ring deformation. The wide bands, which appeared at 3400 cm^{-1} were attributed to N–H stretching vibration in amide group. Characteristic absorptions appeared at $1670\text{--}1660\text{ cm}^{-1}$ due to carbonyl stretching vibration (amide I) and at 1520 cm^{-1} due to N–H deformational vibration (amide II). All the polymers exhibited IR bands at $1225\text{--}1220\text{ cm}^{-1}$ due to the ether bonds.



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

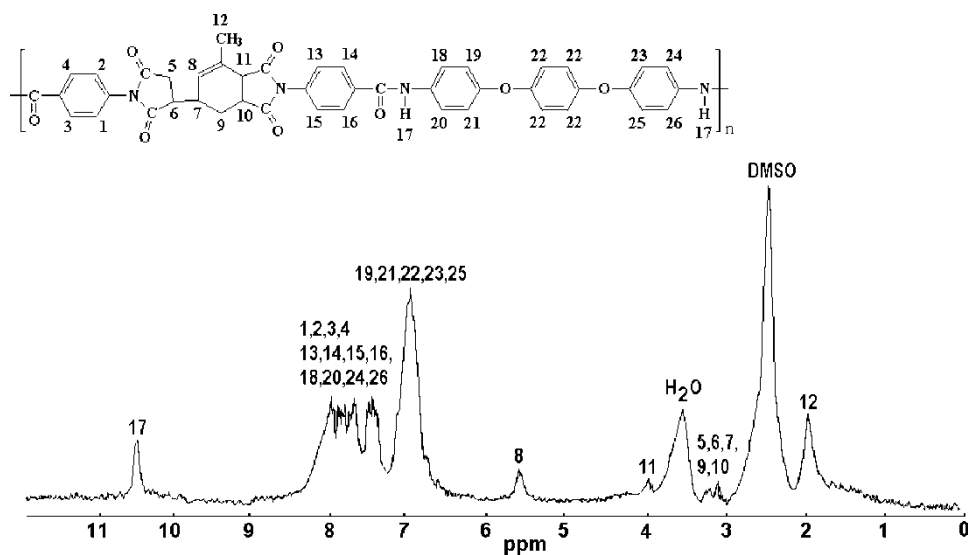


Figure 3. $^1\text{H-NMR}$ spectrum of the polymer **IIIa** in DMSO-d_6 at room temperature.

$^1\text{H-NMR}$ spectra confirmed the proposed structures. The $^1\text{H-NMR}$ spectrum of the polymer **IIIa** (Figure 3) contains the signals characteristic to the diacid monomer and to the corresponding diamine. The majority of peaks in a relative downfield spectrum region are assigned to the $-\text{NH}-\text{CO}-$ proton resonance values at 10.45 ppm and to the aromatic protons at about 6.83–8.25 ppm.

The polymers dissolve easily in polar amidic solvents such as NMP and DMF. This good solubility is due to the relatively high flexibility of macromolecular chains, which was obtained by the introduction of epiclone units and ether linkages into the structure of the polymer. Molecular modeling showed that the shapes of the macromolecular chains are far from the rigid linear ones, which are usually characteristic to wholly

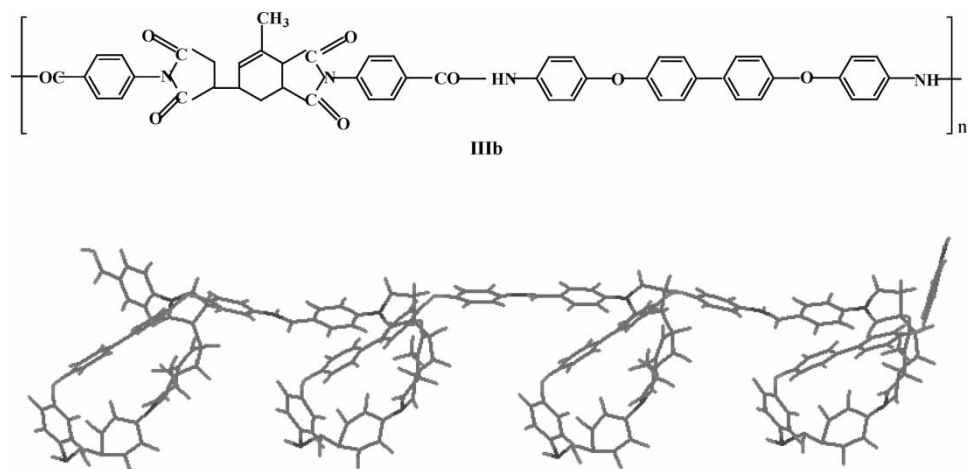
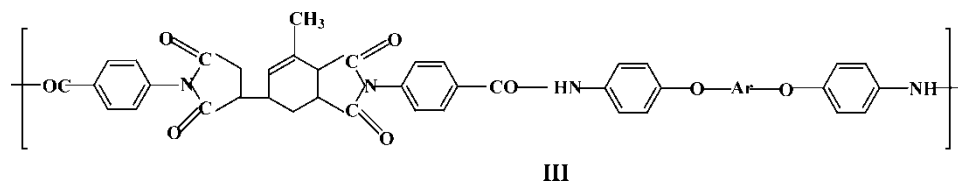


Figure 4. Model molecule of the polymer **IIIb**.

Table 2
GPC data and thermal properties of the polymers **III** general formula



Polymer	Ar	Mw (g/mol)	Mn (g/mol)	Mw/Mn	IDT ^a (°C)	T ₁₀ ^b (°C)	T _g ^c (°C)
IIIa		53,300	33,100	1.61	350	400	238
IIIb		66,000	41,500	1.59	370	415	223
IIIc		50,000	31,500	1.59	370	410	234
III d		48,600	29,200	1.66	380	420	226

^aInitial decomposition temperature = the temperature of 5% wt loss.

^bTemperature of 10% wt loss.

^cGlass transition temperature.

aromatic polyimides. Due to such shapes of the present polymers, the packing of their chains is disturbed and the solvent can diffuse easily among macromolecules and thus facilitates the solubilization. A model molecule of a polymer **III** is shown in Figure 4.

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 0.3–0.4 dL/g (Table 1).

The molecular weight of polymers was determined by gel permeation chromatography (GPC). The values of weight-average molecular weight M_w are in the range of 48600–66000 g/mol, the number-average molecular weight M_n in the range of 29200–41500 g/mol, and the polydispersity M_w/M_n in the range of 1.59–1.66 (Table 2).

All these polymers possess film-forming ability. 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 and flexible.

The thermal stability was evaluated by thermogravimetric analysis (TGA). These polymers do not show significant weight loss below 350°C. They begin to decompose in the range of 350°C–380°C and show 10% wt loss in the range of 400°C–420°C (Table 2). A typical TGA curve is shown in Figure 5.

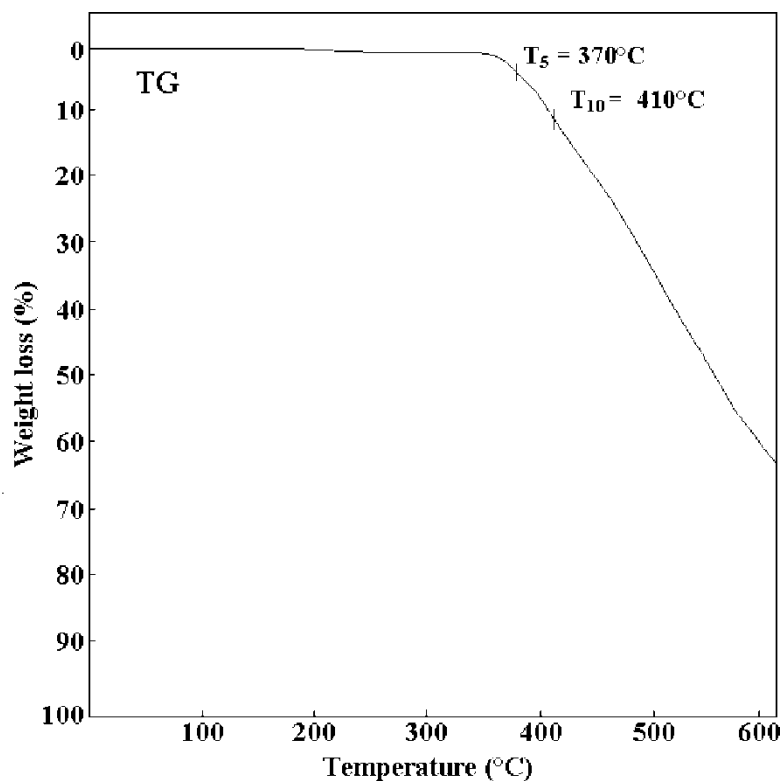


Figure 5. TGA curve of the polymer **IIIc**.

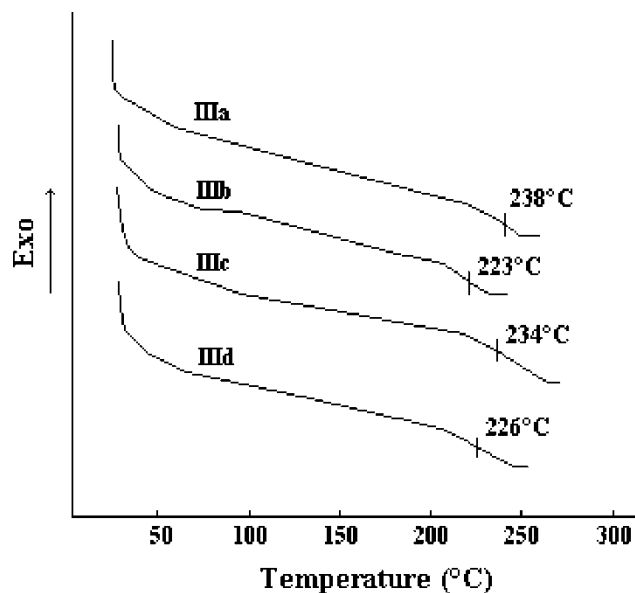


Figure 6. DSC curves of the polymers III.

By comparing the present poly(imide-ether-amide)s based on Epiclon with related polymers that have been synthesized from the same aromatic diamines but with another diacid chloride, based on hexafluoroisopropylidene-diphthalic dianhydride and *p*-aminobenzoic acid, (11) it can be seen that the present polymers exhibit slightly lower thermal stability: they begin to decompose above 350°C, while the corresponding polymers containing hexafluoroisopropylidene groups begin to decompose above 400°C.

The glass transition temperature (T_g) of the poly(imide-ether-amide)s III were in the range of 223°C–238°C (Table 2, Figure 6). It can also be noticed that there is a large interval between T_g and the decomposition temperature, which could be advantageous in the processing of these polymers by a thermoforming technique.

Conclusions

The incorporation of epiclon units together with ether linkages into the main chain of poly(imide-ether-amide)s gave products with substantially improved solubility in polar amidic solvents. These polymers maintain high thermal stability, with the decomposition temperature being above 350°C and a glass transition in the range of 223°C–238°C. The large interval between glass transition and decomposition temperature may be advantageous for their processing by a thermoforming technique. The polymers can also be processed from solutions into flexible thin films. All these properties, associated with an easy processability, make the present polymers potential candidates for practical applications in microelectronics or related advanced fields.

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