

NEW IMIDE TYPE POLYMERS BASED ON EPICLON

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Three imide type polymers based on an aliphatic dianhydride, Epiclon, which is 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, have been prepared. Two polyimides were obtained by solution polycondensation of Epiclon with aromatic diamines such as 1,4-benzenediamine or 1,4-bis(*p*-aminophenoxy)benzene. Poly(imide-ester)s and poly(imide-ether-amide)s have been synthesized by using an Epiclon-based diacid, namely 5-[N-(4-carboxyphenyl)succinimido]-3-methyl-[N-(4-carboxyphenyl)]-1,2,5,6-tetrahydrophthalimide in reaction with 4,4'-dihydroxybiphenyl or phenolphthalein, and its corresponding acid chloride in reaction with 1,4-bis(*p*-aminophenoxy)benzene or 4,4-bis(*p*-aminophenoxy)-biphenyl. The resulting products are 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 reasonable thermal stability, with initial decomposition temperature being above 280°C and glass transition temperature in the range of 167-275°C. The correlation between the polymers structure and their properties has been discussed.

INTRODUCTION

Electroactive polymeric materials have been studied extensively during the last two decades due to their high performance properties for applications in electromechanical sensors and actuators, ultrasonic transducers, loudspeakers, sonars, medical devices, prosthetics, artificial muscles, and devices for vibration and noise control.^{1–3} As compared to electroactive ceramics and shape memory alloys, electroactive polymeric materials offer a unique combination of qualities because they are lightweight, conformable, and tough. Recent development of electroactive polymers has offered several new candidates: electrostrictive copolymers, electrostatic elastomers, electrostrictive liquid elastomers, electrostrictive graft elastomers or piezoelectric polyimides containing polar functional groups, for potential use as sensors in high temperature applications.^{4–6}

Electrostrictive materials produce displacement in reaction to an applied electric field. That is,

when an electric field is applied, molecular-level polarization may change the dimensions of the material. Piezoelectric materials, conversely, produce an electrical charge displacement when mechanically strained. This charge displacement is associated with an electric field applied over a specific distance, and thus it results in an electrical potential difference. Most thin film materials used to fabricate microelectromechanical systems (MEMS) devices and actuators are at least several microns thick, and are typically formed using conventional bulk processing methods such as casting, sol-gel technology, or spin coating. Maximizing the piezoelectric response of amorphous polymer materials depends critically on the extent of polarization achieved during the poling procedure and on its retention after the field is removed.⁷ High temperature polyimide polymers are characterized by relative low rotational mobility along the backbone. This is due to the fact that the dipoles in the polymer do not align along the applied electric field efficiently because of limited chain mobility within the imidized closed ring structure.⁸

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Designing an amorphous polymer with a large dielectric relaxation strength and hence piezoelectric response requires the ability to incorporate highly polar groups at high concentrations and cooperative dipole motion. Introduction of aliphatic monomers as comonomers in polyimides seems reasonable to reduce the chain-chain interaction and may disrupt the interactions between aromatic moiety effectively. On the one hand using aliphatic monomers causes enhancement of the flexibility and transparency, improvement of solubility and decrease the dielectric constant.⁹ Soluble and almost entirely colorless imides type polymers synthesized from Epiclone, which is 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, and aromatic diamine and biphenols are presented in this paper. The use of the alicyclic monomers may be a good compromise between processability and thermal properties of the resulting imide type polymers.

EXPERIMENTAL PART

1. Starting Materials

Epiclone B-4400 [5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride], 1,4-diaminobenzene, 1,4-bis(*p*-aminophenoxy)benzene, 4,4'-bis(*p*-aminophenoxy)-biphenyl, 4,4'-dihydroxybiphenyl, phenolphthalein, dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP) and pyridine were provided by different commercial sources and used as received. Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidinone (NMP) were dried before using, by standard methods. The catalyst, 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS), was synthesized according to published data.¹⁰

2. Measurements

The IR spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrophotometer by using the KBr pellet technique. ¹H-NMR spectra were run on a Jeol 60 MHz ¹H-NMR spectrometer at 50 °C in DMSO-*d*₆.

Polymer solubilities were determined at room temperature at a concentration of 1% (w/v). 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 distributions 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 as the mobile phase. Thermogravimetric analyses (TGA) were performed on a MOM derivatograph (Hungary) in air, at a heating rate of 12 °C/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.

Differential scanning calorimetry (DSC) measurements were done by using a Mettler TA instrument DSC 12E at a

heating rate of 12 °C/min under nitrogen atmosphere, with the glass transition temperature (T_g) taken as the inflection point of the heat capacity versus temperature.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM⁺) by means of the Hyperchem program, version 4.0¹¹

Synthesis of monomers

Synthesis of dicarboxylic acid (I)

The dicarboxylic acid, 5-[*N*-(4-carboxyphenyl)succinimido]-3-methyl-[*N*-(4-carboxyphenyl)]-1,2,5,6-tetrahydrophthalimide, was synthesized according to a published procedure.¹² Yield 65%; m.p. 311-314 °C. 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). ¹H-NMR spectrum (60 MHz, DMSO-*d*₆, 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).

Synthesis of diacid chloride (II)

The diacid chloride of 5-[*N*-(4-chlorocarbonylphenyl)succinimido]-3-methyl-[*N*-(4-chlorocarbonylphenyl)]-1,2,5,6-tetrahydrophthalimide was synthesized according to the literature.¹² Yield 60%; m.p.: 298-302°C. Analysis: calculated for C₂₇H₂₀N₂Cl₂O₆: 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).

Synthesis of polymers

Synthesis of polyimides (PI)

Polycondensation of equimolar amounts of Epiclone and diamine in NMP, under anhydrous conditions in a nitrogen atmosphere yielded solutions of polyimides **PI** (scheme 1). 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 inlet and outlet, were placed 5.26 g (0.018 mmol) of 1,4-bis(*p*-aminophenoxy)benzene in 68 mL NMP. The mixture was stirred under nitrogen until complete dissolution. Then 4.76 g (0.018 mmol) of Epiclone were added at once. After stirring for 4 h at room temperature, a viscous poly(amic acid) solution was obtained. In the next step, the reaction temperature was slowly raised to 180 °C and it was maintained for 5 h for imidization process. The reaction mixture was cooled and poured into water, filtered, washed twice with water and ethanol under stirring and dried for 1 h in vacuo at 100 °C.

Synthesis of poly(imide-ester)s (PIE)

The poly(imide-ester)s were prepared by direct solution polycondensation, at ambient temperature. A typical example: 0.7035 g of diacid **I** (0.0014 mmol) were placed in a reaction vessel and dissolved in 5 mL of dry DMF. Then, 0.4456 g of phenolphthalein (0.0014 mmol) and 0.7828 g of DCC, separately dissolved in a minimum quantity of dry DMF, were added. The catalyst, DPTS, 0.0847g (0.288mmol), was introduced at the end. The reaction mixture was stirred at room temperature, under inert atmosphere, for 96 hours. The dicyclohexylurea (DCU) formed in reaction was filtered off, and the remained solution was poured into a water/methanol

mixture 1/1. The resulting crude product was washed several times with water and methanol, and dried. To remove the remained DCU traces, the product was stirred with acetic acid for an hour, washed with water, dried and extracted with ethanol. Yield: 71%.

Synthesis of poly(imide- ether-amide)s (PIEA)

The reactions were run under anhydrous conditions in a nitrogen atmosphere with equimolar amounts of diamine and diacid chloride **II**. NMP and pyridine were used as solvent and acid acceptor, respectively. A typical reaction was carried out as follows (solid content of monomers in NMP, 9-12 %): in a 100 mL three-necked flask, equipped with mechanical stirrer and nitrogen gas inlet and outlet, were placed 0.73 g (0.0025 mol) of 1,4-bis(*p*-aminophenoxy)benzene, 22 mL NMP and 1 mL Py. The reaction mixture was stirred under nitrogen until complete dissolution; after that it was cooled to -10°C and 1.3475 g (0.0025 mol) of diacid chloride were added with rapid stirring. The temperature was kept below 0°C for 15 min and after that reaction mixture was stirred for 4 h at room temperature. 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. The remained polymer solution was diluted to about 6% by addition of more NMP and the polymer was precipitated by pouring into water. The resulting product was filtered, washed twice with water and then with ethanol under stirring and dried under vacuum at 100°C for 1 h.

RESULTS AND DISCUSSION

Epiclone is a cycloaliphatic anhydride with a flexible and asymmetrical chemical structure, used, like other tetracarboxylic dianhydrides, as a raw material to perform various polymers¹³⁻¹⁵ with the aim to render new properties. It is generally recognized as a successful approach to increase the solubility and processability, the incorporation into the polymer backbone of aliphatic segments, bulky and asymmetrical groups, flexible bonds, large pendent or polar substituents.¹⁶⁻¹⁹ It is expected that the combination in one macromolecule of imide units, aromatic rings, flexible hinge atoms and epiclone moieties would develop new synthetic polymers offering a favorable balance structure-properties.

The partially aliphatic polyimides (**PI**) were prepared by using classical solution polycondensation. Imidization was initiated at 70°C and it was performed at 180°C .

The poly(imide-ester)s (**PIE**) were synthesized by using direct polycondensation reaction of the Epiclone-based diacid with two biphenols. The reactions were performed at ambient temperature, with dicyclohexylcarbodiimide (DCC), as an activating agent, and 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS) as catalyst.

The poly(imide-ether-amide)s (**PIEA**) were obtained by using the Epiclone-based diacid chloride containing imide groups which reacted with aromatic diamines having ether bridges between phenylene rings.

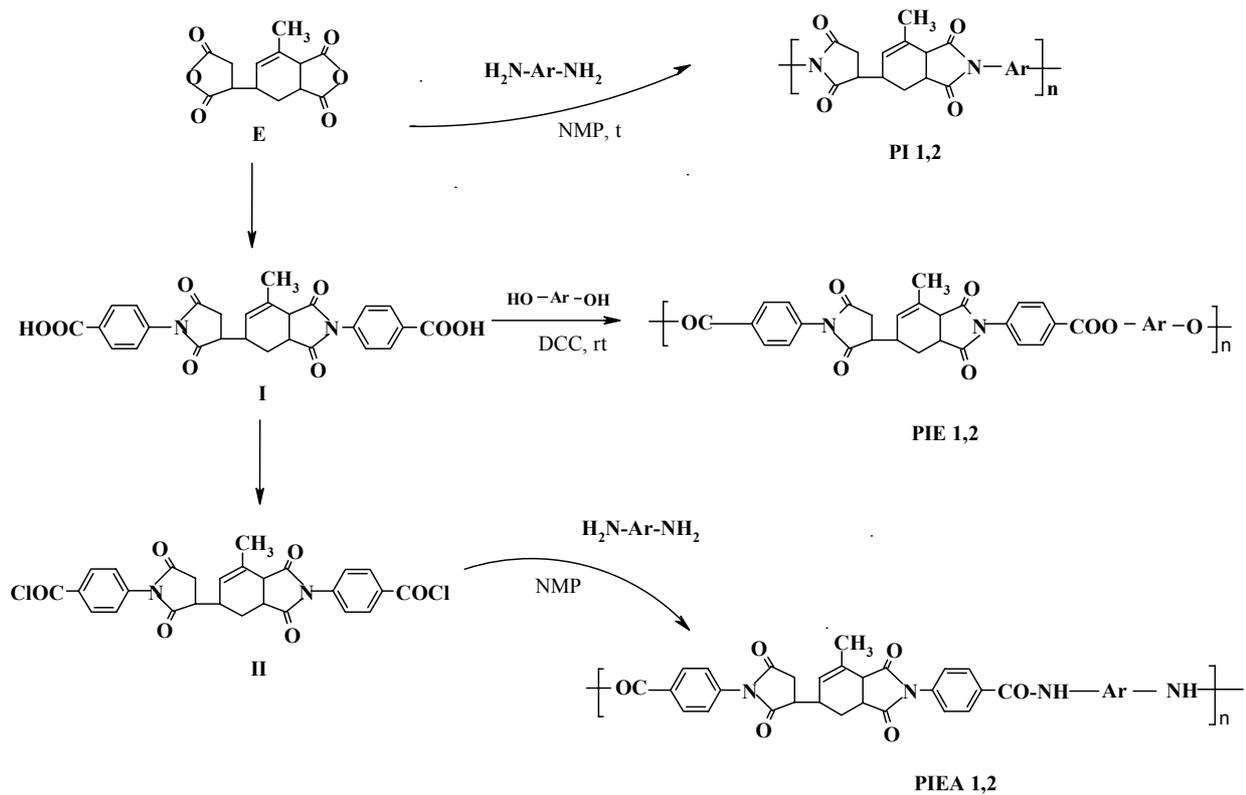
The properties of these polymers with respect to their chemical stability and glass transition temperature, solubility, inherent viscosity and film forming ability have been evaluated. The synthetic chemistry for the synthesized polymers is outlined in Scheme 1.

Figure 1 presents the IR spectra of the monomers **I** and **II**.

The $^1\text{H-NMR}$ spectrum confirms the structure of the obtained Epiclone-containing diacid. The peak at about 5.6 ppm was assigned to the vinylic proton, and the multiplet at about 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 (Figure 2).

All the synthesized polymers show characteristic infrared absorption bands attributable to the imide structure at 1780 cm^{-1} and 1720 cm^{-1} , assigned to the symmetrical and asymmetrical stretching vibrations of the carbonyl in imide rings. Other typical absorptions can be observed at 1380 cm^{-1} , due to C–N stretching in imide ring and at $760\text{--}750\text{ cm}^{-1}$, possibly associated to imide ring deformation. All the polymers presented strong infrared absorptions at 1520 cm^{-1} attributable to the =CH in aromatic rings. Special bands due to the ether bonds are present in the polymers **PI** and **PIEA** at $1225\text{--}1220\text{ cm}^{-1}$. Polymers **PIE** show a characteristic peak at 1755 cm^{-1} associated with the carbonyl in the ester bonds. Figure 3 shows the IR spectra for the Epiclone and the polymers **PIE-1** and **PI-2**.

$^1\text{H-NMR}$ spectra confirmed the proposed structures. The $^1\text{H-NMR}$ spectrum of the polymer **PIE 2** (figure 4) contains the signals characteristic to the diacid monomer and the corresponding biphenols. The majority of peaks in a relative downfield spectrum region are assigned to the aromatic protons, at about 7.20 – 8.30 ppm. A characteristic peak was registered at about 5.7 ppm due to vinylic proton of the Epiclone moiety. The peaks in the field of 1.97-4.2 ppm, (overlapped by the solvent and water proton signals) were associated with the resonance values of the methyl, methylene and methine protons in the aliphatic and succinimide rings of the structure.



Scheme 1. Synthesis of the imide type polymers.

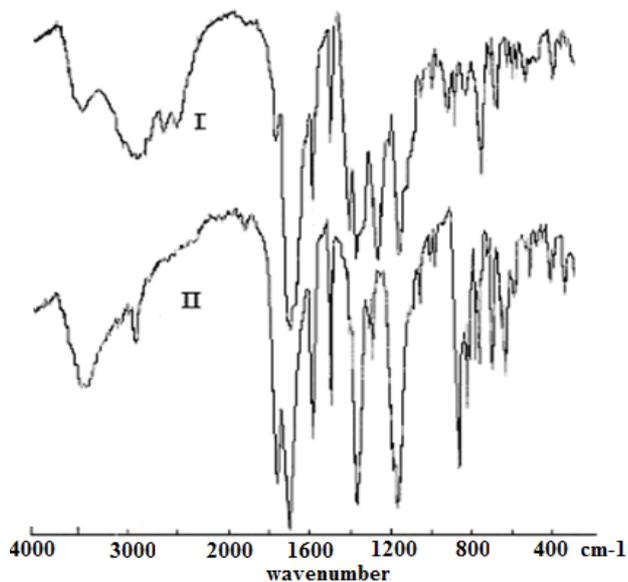


Fig. 1 – IR spectra of the dicarboxylic acid (I) and the diacid chloride (II).

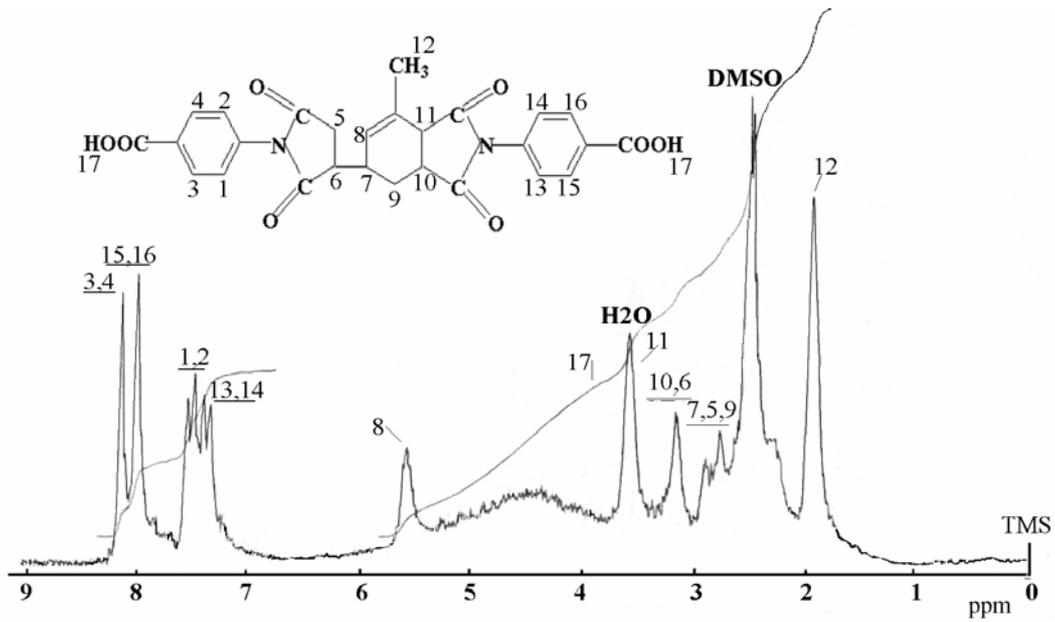


Fig. 2 – $^1\text{H-NMR}$ spectrum of the dicarboxylic acid **I**, in DMSO-d_6 at room temperature.

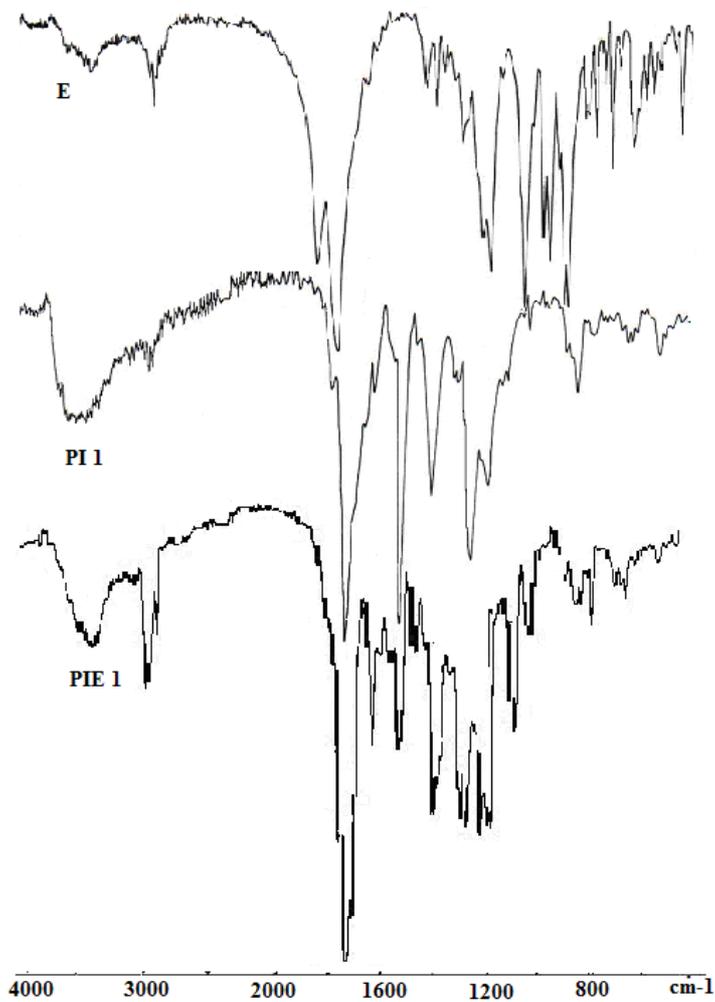


Fig. 3 – The IR spectra of the Epiclon (**E**), polyimide **PI 1** and the poly(imide-ester) **PIE 1**.

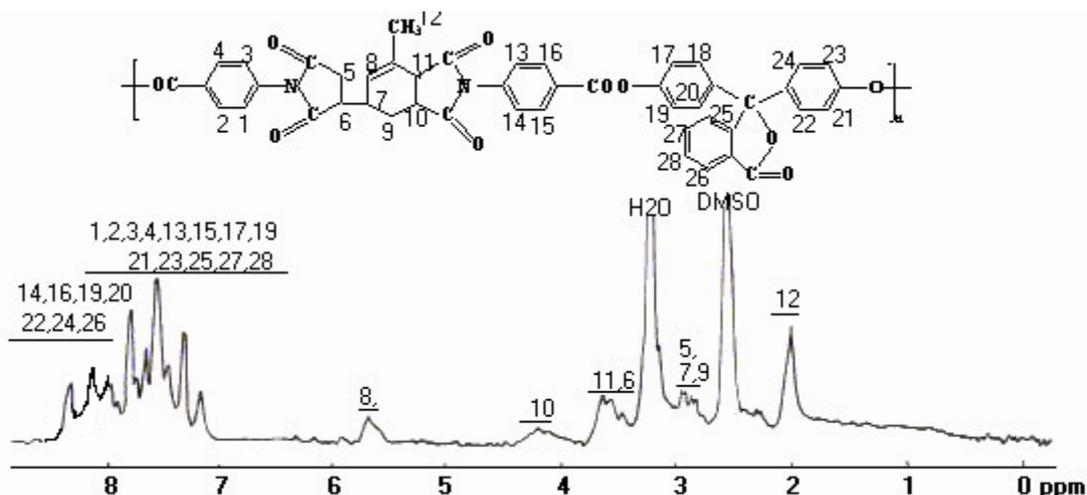


Fig. 4 – The $^1\text{H-NMR}$ spectrum of the poly(imide-ester) **PIE 2** in DMSO-d_6 at room temperature.

The new compounds dissolve easily in polar organic solvent, such as DMF, NMP, DMAc, DMSO, and THF. Some of them were partially soluble in chloroform and insoluble in methanol, benzene, toluene, n-hexane and other hydrocarbons solvents. The introduction of bulky groups, such as the Epiclone and phenolphthalein units, decrease close packing by decreasing of the entropy energy of internal rotation.²⁰ Improvement in polymer solubility is also due to chain flexibility promoted by ether linking groups with greater rotational freedom. Thus, it is facilitated an easier diffusion of the solvent among macromolecules, increasing the solubilization. The good solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

Model molecule for a fragment of the polymer **PI-2** is shown in Figure 5 and it was obtained by means of the Hyperchem program, version 4.0 (14).¹¹ Molecular modeling showed that the shapes of these macromolecular chains are flexible in comparison with the wholly aromatic polyimides, usually rigid linear polymers.

The inherent viscosity values, measured in DMF, are in the range of 0.20–0.34 dL/g. Table 1 presents some data concerning the molecular weight of polymers (determined by gel permeation chromatography) and their thermal stability.

The solutions of polymers 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 of polyimides and poly(imide-ester)s were tough and brittle, while those of poly(imide-ether-amide)s were tough and flexible.

The thermal stability was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymers begin to decompose in the range of 280–370 °C and show 10% wt loss in the range of 341–415 °C (Table 1). Chemical moieties that decrease the thermal stability of polyimides may be aliphatic C–H bonds in the Epiclone moieties.

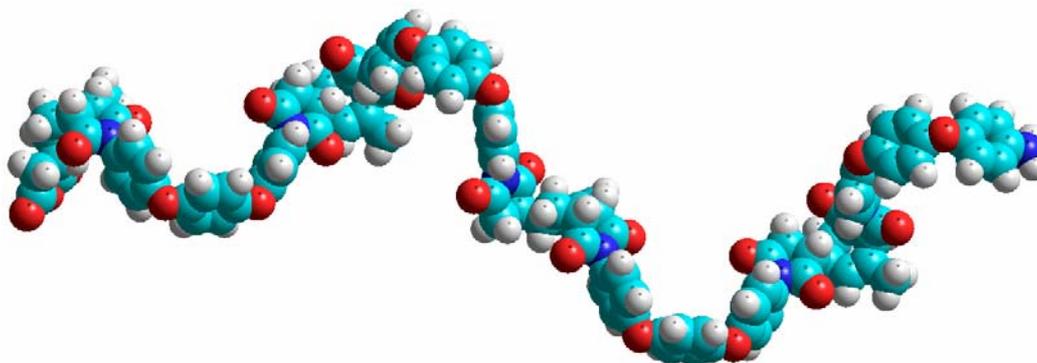
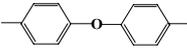
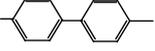
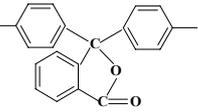
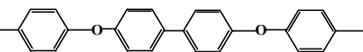


Fig. 5 – Model molecule of the polyimide **PI 2**.

Table 1
GPC data and thermal properties of the resulting polymers

Polymer	Ar	Mn (g/mol)	IDT ^a (°C)	T ₁₀ ^b (°C)	T _g ^c (°C)
PI 1		48200	281	341	275
PI 2		75000	280	368	230
PIE 1		24400	335	370	201
PIE 2		17000	330	355	167
PIEA 1		33000	350	400	238
PIEA 2		41500	370	415	223

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

^b Temperature of 10% weight loss.

^c Glass transition temperature.

Differential scanning calorimetry (DSC) was used to probe the T_g of polymers by monitoring the heat capacity as a function of temperature. The T_g is a second order endothermic transition. The glass transition temperature (T_g) could be considered as the temperature at which a polymer undergoes extensive cooperative segmental motion along the backbone. The flexible linkages decrease the energy of internal rotation, lowering the T_g²¹. Different intra- and intermolecular interactions including hydrogen bonding, electrostatic and ionic forces, chain packing efficiency and chain stiffness affect the T_g. Table 1 presents the T_g's of the resulting polymers.

The synthesized polymers exhibited glass transition temperatures between 167 - 275 °C, depending on their chemical structures. The imide type polymers which have the ability to form flexible films are under investigation as matrix systems for insertion of micro- and nanoparticles, in order to obtain magnetopolymeric membranes for microactuation. These studies will be discussed in a future presentation.

CONCLUSION

The cycloaliphatic units of Epiclon incorporated into the main chain of the synthesized polyimides together with different kind of flexible linkages gave products with a reasonable thermal stability

and substantially improved solubility in polar solvents. The polymers presented decomposition temperature between 280-370 °C and a glass transition in the range of 167-275 °C.

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