

NEW POLYIMIDES BASED ON EPICLON

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Epiclon, as an aliphatic dianhydride and three different aromatic diamines, 1,4-benzenediamine, 4,4'-methylenedianiline 4,4'-oxydianiline, were selected to prepare soluble polyimides, through thermal ring closure of polyamic acids obtained by solution polycondensation in N-methylpyrrolidone. The structures of these polymers were identified by infrared and ¹H-NMR spectroscopy. The polymers were characterized by solution viscometry, solubility and thermal behavior, investigated by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). A good correlation between the polymers structure and their properties has been established.

INTRODUCTION

Polyimides represent an important class of materials because of their applicability which can be attributed to some desirable traits, such as: high thermal stability, chemical and radiation resistance, high glass transition temperature, low dielectric constant, low thermal expansion, long-term stability, and good mechanical properties. Innovative polyimides design has led to their use in aerospace, microelectronics, automotive and packaging industries.¹⁻³ However, deficiencies in the processability, solubility and transparency do not always provide the optimum properties for many special applications. The incorporation of aliphatic segments to form partially aliphatic polyimides, can be used to counteract these shortcomings. Also, it is generally recognized as a successful approach to increase the solubility and processability the introduction into the polymer backbone of bulky and asymmetrical groups, flexible bonds, large pendent or polar substituents⁴⁻⁷

Epiclon is a cycloaliphatic anhydride, with a flexible and asymmetrical chemical structure used, like other tetracarboxylic dianhydrides, as a raw material to perform various polymers⁸⁻¹⁰ with the aim to render new properties. It is expected that the combination in one macromolecule of imide units, aromatic rings, flexible hinge atoms and epiclon

moieties would develop new synthetic polymers offering a favorable balance structure-properties.

Previously, we have synthesized 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 phenylene¹¹. The new partially aliphatic polyimides reported in the present paper were prepared by using polycondensation reaction of 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (Epiclon) and different aromatic diamines. The properties of these polymers with respect to their chemical structure, such as molecular weight, thermal stability and glass transition temperature, solubility, inherent viscosity and film forming ability have been evaluated and compared with those of related compounds.

EXPERIMENTAL PART

1. Starting Materials

Epiclon B-4400 [5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride] and aromatic diamines such as 1,4-benzenediamine, 4,4'-methylenedianiline, 4,4'-oxydianiline, were provided by different commercial sources and used without further purifications. N-methyl-2-pyrrolidinone (NMP) from Merck was dried over phosphorous pentoxide and distilled under reduced pressure.

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2. Measurements

The IR spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrophotometer by using the KBr pellet technique. $^1\text{H-NMR}$ spectra were run on a Jeol 60 MHz $^1\text{H-NMR}$ 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. 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 12 °C/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).

3. Synthesis of the Polymers

Polycondensation of equimolar amounts of epiclon and diamine in NMP, under anhydrous conditions in a nitrogen atmosphere yielded solutions polyimides **PI** (scheme 1). The relative amounts of monomers and DMF 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 3,5 g (18 mmol) of 4,4'-methylenedianiline in 68 mL NMP. The mixture was stirred under nitrogen until complete dissolution. Then, 4,67 g of epiclon (18 mmol) were added at once. The reaction mixture was stirred at room temperature to afford a viscous poly(amic acid) solution after 4 h. The reaction temperature was slowly raised to 180 °C and maintained at this temperature for 5 h to complete imidization. The reaction mixture was cooled and poured into water. The precipitated product was filtered, washed twice with water and then with ethanol under stirring and dried in vacuo at 100 °C for 1 h.

RESULTS AND DISCUSSION

The new polyimides have been synthesized by the classical two-step method involving a polyamic acid (**PAA**) precursor which is subsequently cyclized to form the imide linkage. Polycondensation proceeds by a reversible nucleophilic substitution reaction of a difunctional amine and an aliphatic difunctional anhydride, in a polar aprotic solvent. Imidization was initiated at 70 °C and was performed at 180 °C. Scheme 1 presents the

reactions synthesis of these polymers along with their abbreviations.

Spectral characterization

Methods such as infrared and proton resonance spectroscopy have been used to identify the resulting polymers. A number of structural changes occurs during polyamic acid formation and subsequent imidization. Characteristic infrared absorptions attributable to the imide structure are identified for all the compounds. Strong bands at 1780 cm^{-1} and 1720 cm^{-1} commonly attributed to the symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide can be observed for all the samples. There are also absorptions at 1380 cm^{-1} , due to C–N stretching in imide ring and at 760–750 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. The polymer PI-3 showed special bands at 1225–1220 cm^{-1} due to the ether bonds. Figure 1 shows the IR spectra for the epiclon and two resulting polymers, PI-2 and PI-3.

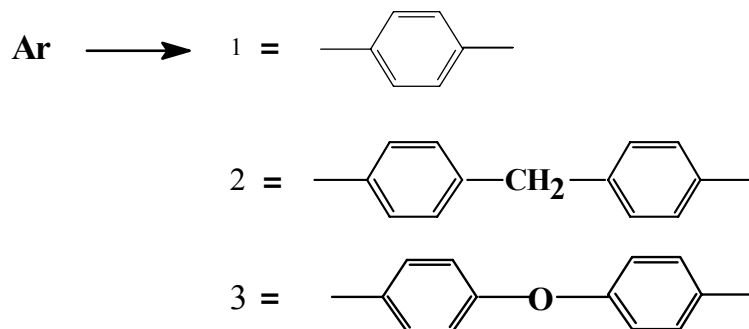
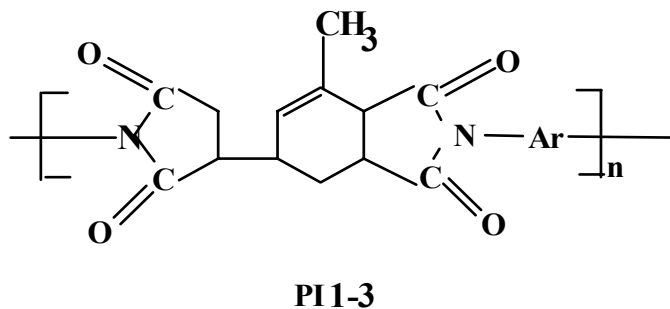
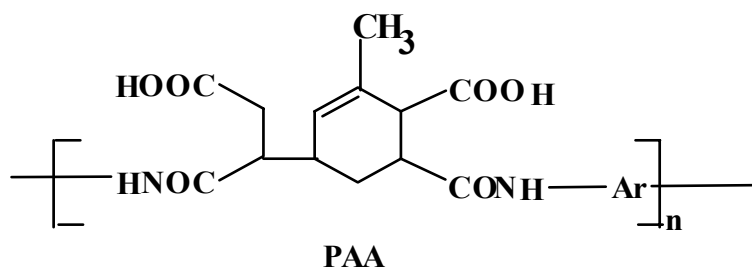
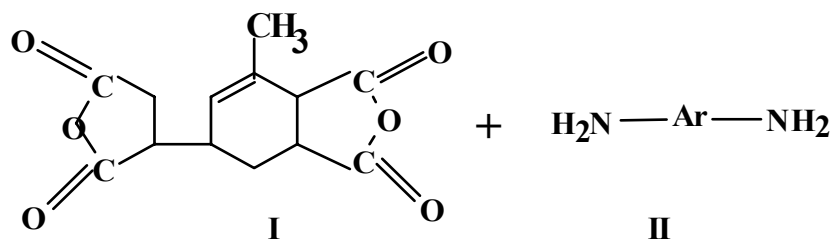
The $^1\text{H-NMR}$ spectra also confirm the expected structures. Figure 2 presents the $^1\text{H-NMR}$ spectrum of the polymer **PI-1** which contains the signals characteristic to the both corresponding monomers. The peaks in the field of 1.97–3.62 ppm, (overlapped by the solvent and water proton signals) were associated with the resonance values of the methyl, methylene and methine protons in aliphatic and succinimide rings of the structure. The peaks in a relative downfield spectrum region at about 7.23–7.85 ppm were assigned to the aromatic protons. The signals at about 10.2 ppm and at 12.3 ppm respectively, are due to the –NH–CO– and –COOH protons resonances, corresponding to the uncyclized poly(amic acid) sequences.

The polymers solubility was tested in various organic solvents. It was found that all the polymers were soluble in polar solvents such as NMP, DMSO, DMF, dioxane, DMAc and THF. They were partially soluble in chloroform and insoluble in methanol, benzene, toluene, n-hexane and other hydrocarbons solvents. Improvement in polymer solubility is due to chain flexibility promoted by linking groups with greater rotational freedom, such as, –O–, –CH₂– and the introduction of bulky groups such as the epiclon unit, which decrease the entropy energy of internal rotation, thereby

decreasing close packing.¹² The solvent can diffuse easily among macromolecules and thus facilitates the solubilization.

Molecular modeling showed that the shapes of the macromolecular chains are flexible in

comparison with the wholly aromatic polyimides, usually rigid linear polymers. Model molecule for a fragment of the polymer **PI-1** is shown in Figure 3 and was obtained by means of the Hyperchem program, version 4.0 (14).¹³



Scheme 1 – Preparation of the polymers **PI 1-3**.

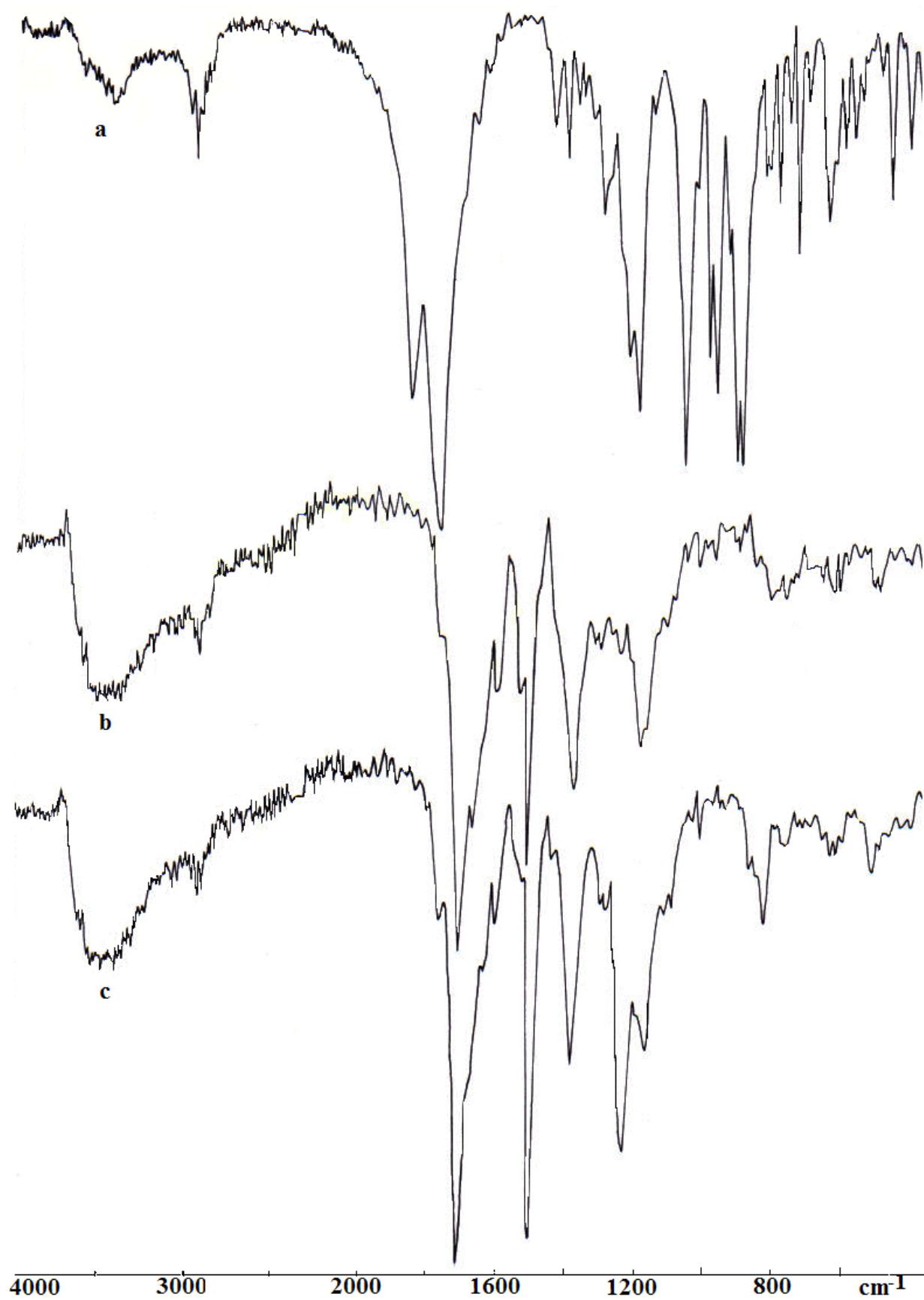


Fig. 1 – IR spectra of the **Epiclon** (a) , **PI-2** (b) and **PI-3** (c).

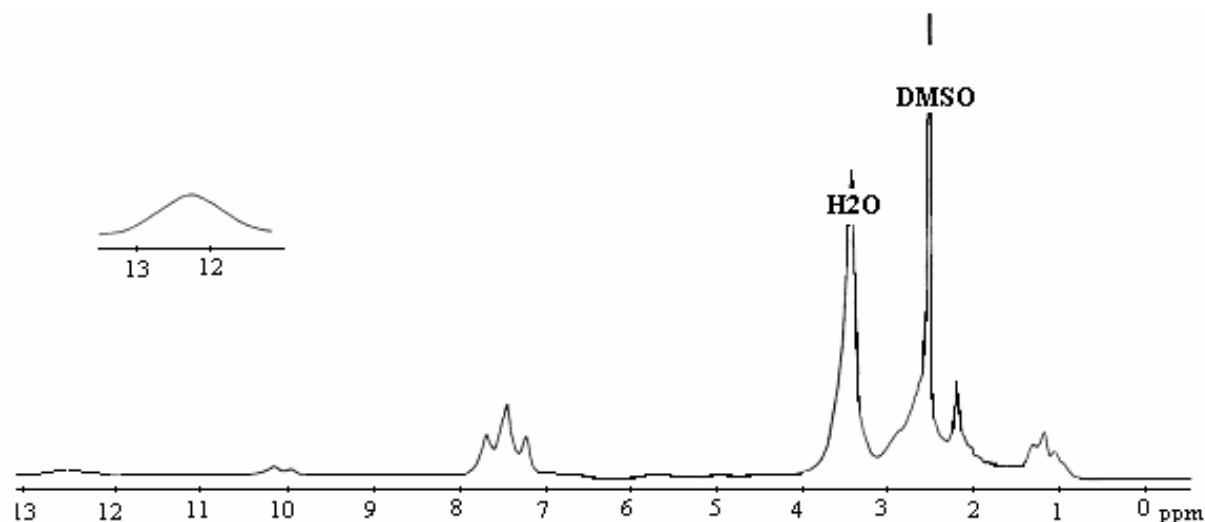


Fig. 2 – $^1\text{H-NMR}$ spectrum of the polymer **PI-1** in DMSO-d_6 .

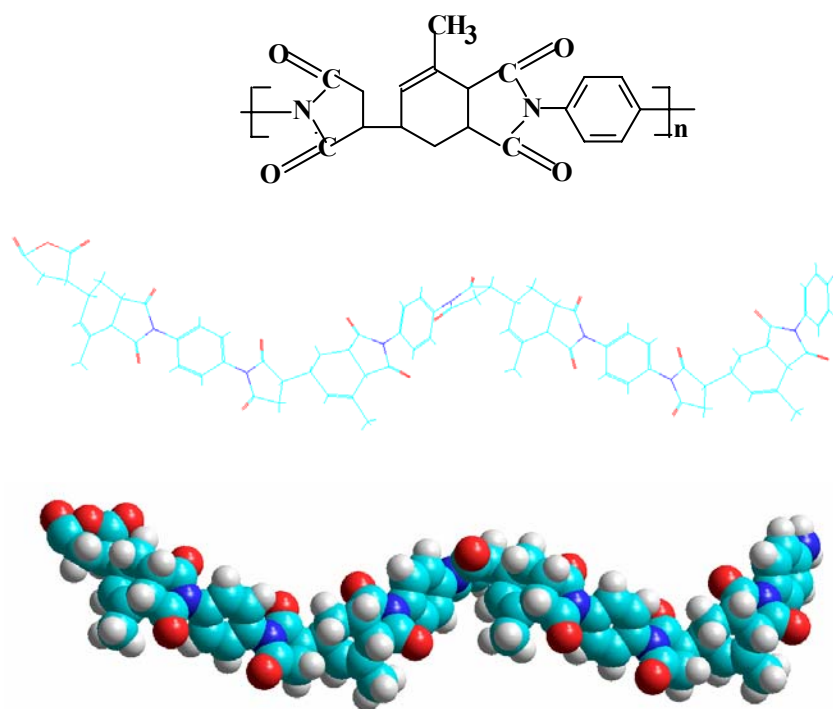


Fig. 3 – Model molecule of the polymer **PI-1**.

The inherent viscosity values, measured in DMF, are in the range of 0.2–0.34 dL/g and vary based on the rigidity of the polymer chain. Table 1 presents some data concerning to 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 were tough and brittle. It is

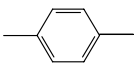
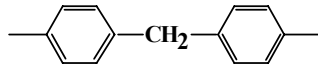
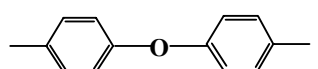
generally argued that the film-forming property of a polymer is a function of its structural characteristics: flexibility of the backbone chain, relative lower cohesive energy and lower degree of microstructural defects¹⁴. A high cohesive energy, induced by crystallization, strong polar-polar interaction and secondary valence bonds formation, generally decreases the film forming property. By comparing with related poly(imide-ether-amide)s¹¹ it can be observed that the capacity to form flexible films of the present partial aliphatic polyimides is virtually

absent. This behavior may be explained by a too low cohesive energy that could cause a dimensional

instability of the polymer film.

Table 1

GPC data and thermal properties of polyimides (PI)

Polymer	Ar	M _n (g/mol)	IDT (°C)	T ₁₀ (°C)	T _g (°C)
PI-1		57100	270	352	-
PI-2		50000	273	330	255
PI-3		48200	281	341	235

Thermal studies

The thermal stability was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymers begin to decompose in the range of 270-281 °C and show 10% wt loss in the range of 340-352 °C (Table 1). Chemical moieties that decrease the thermal stability of polyimides may be aliphatic C-H bonds in the epiclone moieties.

Differential scanning calorimetry (DSC) was used to probe the T_g of polymers by monitoring the heat capacity as a function of temperature. 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 T_g is a second order endothermic transition. 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 resulting polyimides that differ in diamine structure. In particular, the chain stiffness has been found to have an important influence on the T_g value. The T_g increases with chain stiffness which is a function of the diamine bridging unit. The lack of T_g for the polymer **PI-1** is in accordance with the chain rigidity of this structure and could be related to aryl groups.

The presence of flexible linkage increased the polymer chain flexibility by decreasing the energy of internal rotation, thereby lowering the T_g as is evident from table 1, showing that the flexible ether-linked diamine lead to the lowest T_g of 235 °C (**PI-3**).¹⁵

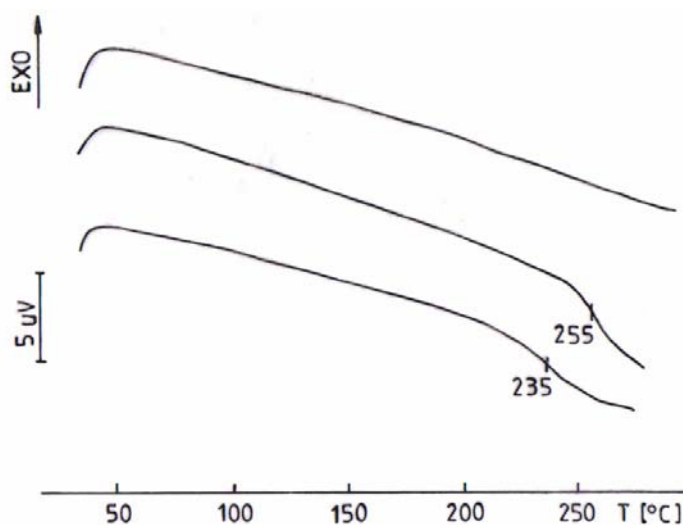


Fig. 4 – The glass transition temperature (T_g) of the polyimides **PI 1-3**.

The resulting polyimides **PI 2**, **PI 3** presented glass transition temperatures at 255 °C and 235 °C respectively, in accordance with their chemical structures (Table 1, Figure 4).

CONCLUSION

The incorporation of epichlorohydrin units together with flexible linkages into the main chain of polyimides gave products with substantially improved solubility in polar solvents. The polymers maintain a reasonable thermal stability, with the decomposition temperature being above 270 °C- 281 °C and a glass transition in the range of 235 °C–255 °C.

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