



AROMATIC POLY(AMIDE-IMIDE)S CONTAINING FLEXIBLE LINKAGES

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Aromatic poly(amide-imide)s with flexible linkages have been synthesized by solution polycondensation reaction of two aromatic diamines containing nitrile groups, namely 2,6-bis(*m*-aminophenoxy)benzotrile and 2,6-bis(*p*-aminophenoxy)benzotrile, with trimellitic anhydride chloride. The polymers were easily soluble in polar organic solvents, such as *N*-methyl-pyrrolidinone, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, and dimethylsulfoxide, and exhibited remarkable film forming ability. The thin films prepared by casting polymer solutions onto glass plates were transparent and flexible. The polymers showed high thermal stability, with decomposition temperature being above 400°C. They exhibited a reasonable interval between glass transition and decomposition temperature, which can be advantageous for their processing. The physical properties such as mechanical and dielectric characteristics of these polymers were studied.

INTRODUCTION

Thermostable polymers, particularly polyimides, are used in applications which demand resistance at high temperature maintaining in the same time their structural integrity and a good balance between their chemical, physical and mechanical properties.^{1,2} One of the most important drawbacks of this class of polymers is their difficulty of processing because of the insolubility and infusibility. To overcome these problems, modifications of the polymers structure are often used, including the introduction of flexible linkages or bulky substituents into the macromolecular chains. Aromatic poly(amide-imide)s have been developed as alternative materials which offer a compromise between excellent thermal stability and processability. Poly(amide-imide)s bring together the superior mechanical properties associated with amide units and the high thermal stability determined by the existence of imide rings. Compared with the corresponding polyimides, this class of polymers show good solubility in highly polar solvents, lower glass transition temperatures and a better processability.³⁻⁷

The introduction of the nitrile substituents may lead to the increase of thermooxidative resistance and of dielectric constant comparative to the polymers that do not have this substituent onto the macromolecular chain.⁸⁻¹⁰

Generally, amorphous polymers with side groups exhibit two second order phase transitions T_γ and T_β . Reports show that these transitions can be considered the “activation barrier” for solid-phase reactions, deformation, flow or creep, acoustic damping, physical aging changes, and gas diffusion into polymers.¹¹ Other authors limited the T_γ to very small motions either within the molecule or with bound water. The sub- T_g transitions can sometimes be seen by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA), but they are too weak or too broad for analyzing by these methods. Dynamic-mechanical analysis (DMA) and dielectric spectroscopy analysis (DEA) and similar techniques are usually used.¹²

Most aromatic polyimide and copolyimide films exhibit relaxation phenomena, also called α , β and γ processes, in their dynamic mechanical and dielectric behaviors. At very low temperatures (around -80°C) a γ relaxation process called sub-

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ambient secondary relaxation can be observed in rigid aromatic polymers. This transition is associated with phenyl ring motions and it is influenced by moisture absorption content, aging history and morphology.^{13,14} With the increasing of temperature a sub-glass β relaxation process is observed in the range of 50-250°C during the thermal treatment of polyimides. A α relaxation process attributed to glass transition temperature can be normally observed at high temperatures, above 300°C. Its temperature and magnitude are dependent upon the chain rigidity, order structure, and cooperativity of the segmental motion.¹⁵

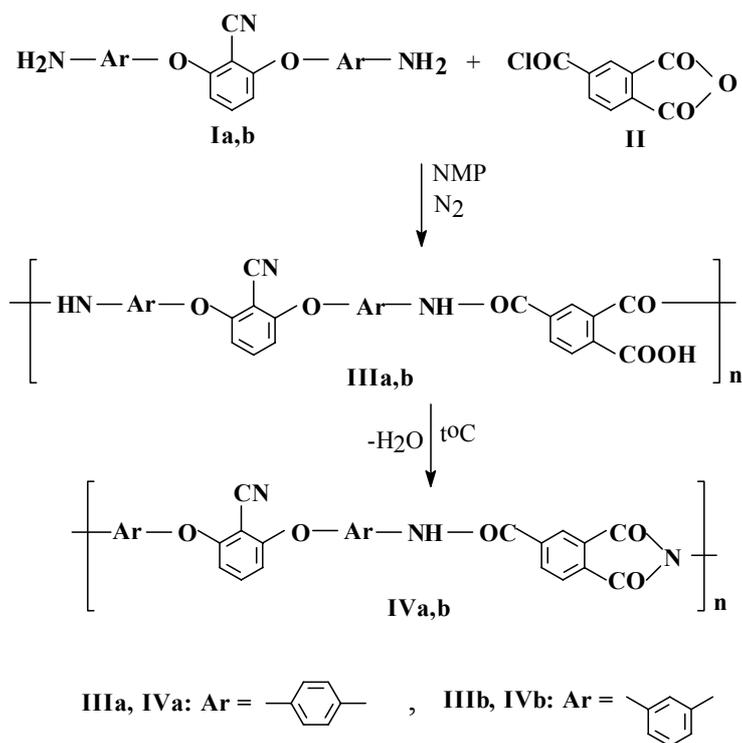
In this paper we present a study of aromatic poly(amide-imide)s incorporating flexible linkages, which were prepared by polycondensation reaction between trimellitic anhydride chloride and two aromatic diamines. The properties of these polymers such as solubility, inherent viscosity, film forming ability and their quality, thermal

stability, and mechanical and dielectric behavior have been investigated and compared.

RESULTS AND DISCUSSION

Aromatic diamines containing cyano groups **Ia** and **Ib**, were prepared by nucleophilic displacement of chloro groups in dichlorobenzonitriles by *p*- or *m*-aminophenoxide using N,N-dimethylacetamide (DMAc) as solvent. The nucleophilic substitution of chloro groups is enabled by cyano substituents which have a strong electron-withdrawing effect.⁸

Polycondensations of equimolecular amounts of diamine **Ia** or **Ib** with trimellitic anhydride chloride **II** in NMP at low temperature, in the first step, gave the intermediate polyamidic acid **III** which underwent cyclodehydration, in the second step, and yielded viscous solutions of poly(amide-imide)s **IV** (Scheme 1).



Scheme 1 – Synthesis of poly(amide-imide)s **IV**.

The structures of polymers were identified by IR spectroscopy. Infrared spectra of all polymers show strong absorptions at 1780, 1718, 1378 and 732 cm^{-1} which are assigned to the imide rings. The amide group from the macromolecular chain was identified at absorption bands at 3363 cm^{-1} characteristic for NH and at 1661 cm^{-1} due to CO. The absorption band at 3076 cm^{-1} was attributed to

C = H aromatic linkage. Sharp peaks were present at 2232 cm^{-1} due to the presence of CN substituent and at 1243 cm^{-1} due to aromatic ether.

The cyclization of polyamidic acids **III** to the corresponding poly(amide-imide) structures **IV** was also evidenced by thermogravimetric analysis (TGA). TGA of the polyamidic acids showed four weight loss steps as follows: at about 100°C due to

the evolution of water; at about 220°C a weight loss due to the removal of solvent; in the range of 220-430°C due to the evolution of water resulting from the thermal cyclization to amide-imide structure; a final weight loss in the range of 450-580°C due to the degradation of the resulting poly(amide-imide) structure.

The polymers were soluble in polar organic solvents such as N-methylpyrrolidinone, N,N-dimethylacetamide, dimethylsulfoxide or N,N-dimethylformamide, at room temperature, and insoluble in less polar solvents like chloroform and tetrahydrofuran. The inherent viscosity of the polymers, in NMP, was in the range of 0.46-0.66 dL/g. This good solubility is due to the relatively high flexibility of macromolecular chains which was obtained by the introduction of ether and amide linkages into the structure of the polymer. These bridges may prevent a dense packing of the chains in tight structures through hydrogen bonding between the amide groups.

Thin films were deposited by spin-coating technique on glass plates using dilute polymer solutions (1% concentration). The quality of these films and the surface topography was studied by

atomic force microscopy (AFM). All the films showed a smooth surface, practically without defects. The root mean square roughness was 1.06 nm for polymer **IVa** and 0.40 nm for polymer **IVb** over an area of 20 x 20 μm^2 . Height profile analysis (inset of Figure 3(c)) along the line shown in Figure 3(a) characterizes the topography of the surface of the film and measures an average height of 0.31 nm. The surface morphology and roughness of the poly(amide-imide) film are due to the characteristics of the polymer chains which govern aggregation and molecular ordering, processes which take place during drying and thermal imidization.¹⁶ A typical AFM image is shown in figure 1.

The thermal stability of the polymers was evidenced by thermogravimetric analysis (TGA). TGA shows that the poly(amide-imide)s are highly thermostable with two maximum decomposition peaks: first ($T_{\text{max}1}$) at 440-460°C due to the degradation of the amidic linkages and the second ($T_{\text{max}2}$) in the range of 510-615°C due to the decomposition of the polymers. For these polymers the expected effect of *meta*-structures on the decrease on thermal stability is very clear (table 1).

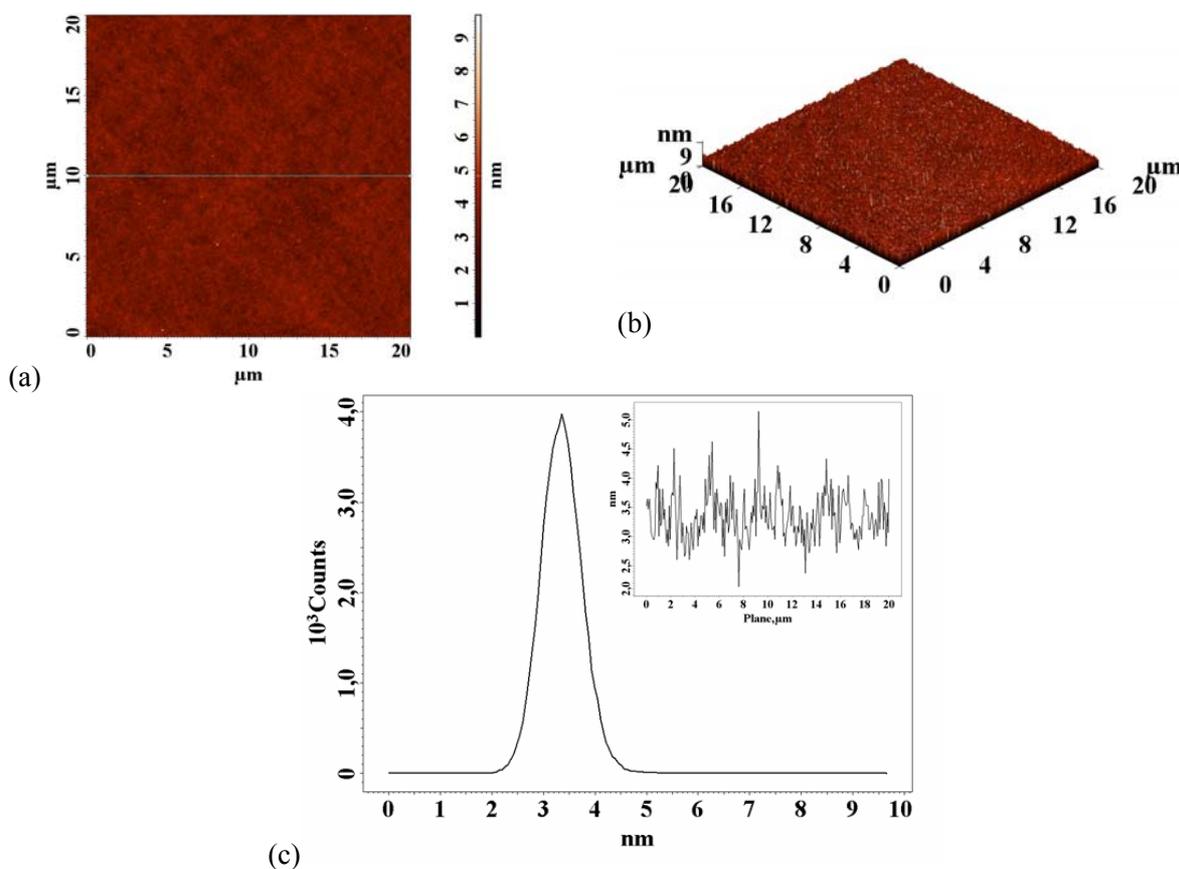


Fig. 1 – AFM images of a polyimide film **IVb** (a) two-dimensional image; (b) three-dimensional image; (c) histogram (the inset shows the surface profile taken along the line in (a)).

Table 1

Thermal properties of poly(amide-imide)s, **IV**

Polymer	T ₅ (°C)	T ₁₀ (°C)	T _{max1} (°C)	T _{max2} (°C)	T _g (°C)
IVa	375	460	460	615	217
IVb	350	440	440	510	227

T₅ = temperature of 5% weight loss; T₁₀ = temperature of 10% weight loss; T_{max1} = temperature of the first maximum speed of decomposition; T_{max2} = temperature of the second maximum speed of decomposition; T_g = glass transition temperature, measured by DSC.

The glass transition temperature of the poly(amide-imide)s **IV** was determined by dynamic scanning calorimetry and the values are shown in table 1. The polymer containing *meta*-substituted phenylene rings has a higher value of T_g (227°C) than the polymer containing *para*-substituted phenylene rings (217°C respectively).

Table 2 lists the mechanical properties of the poly(amide-imide)s films. These films had tensile stress of 28 MPa and 127 MPa, elongation at break of 1.14% and 7.88%, and tensile modulus of 3.6 GPa and 2.9 GPa, respectively.

Table 2

Mechanical properties of poly(amide-imide)s **IV**

Polymer	Tensile stress (MPa)	Elongation at break (%)	Elastic modulus (GPa)
IVa	27.88 ± 4.50	1.14 ± 0.14	3.59 ± 0.34
IVb	127.01 ± 8.82	7.88 ± 0.67	2.88 ± 0.20

The results indicated that the modulus varies in a narrow range and polymers are quite stiff. The tensile strength changes considerably between the samples. The polymer with higher tensile strength

(>80MPa) **IVb** can be considered as advanced material. Figure 2 presents the stress-strain curves of the poly(amide-imide) **IVb**.

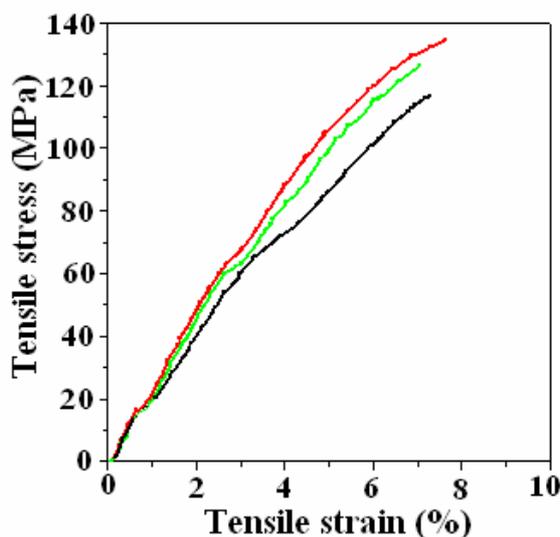
Fig. 2 – Stress-strain curve of the poly(amide-imide) **IVb**.

Figure 3a presents the storage modulus (E') and the loss modulus (E''), and figure 3b presents the loss factor tangent (tan δ) dependences on temperature for films of polyamic acid **IIIa** and of the corresponding poly(amide-imide) **IVa** as registered by dynamic-mechanical analysis. The drops in E' curves and the peaks on E'' and tan δ

indicate the physical transitions which take place in the structure of the polymers. At low temperatures the polymers show a plateau in the E' dependence, above 10⁹Pa, which is typical for the glassy structures, a region where the macromolecules are in the “frozen” state.

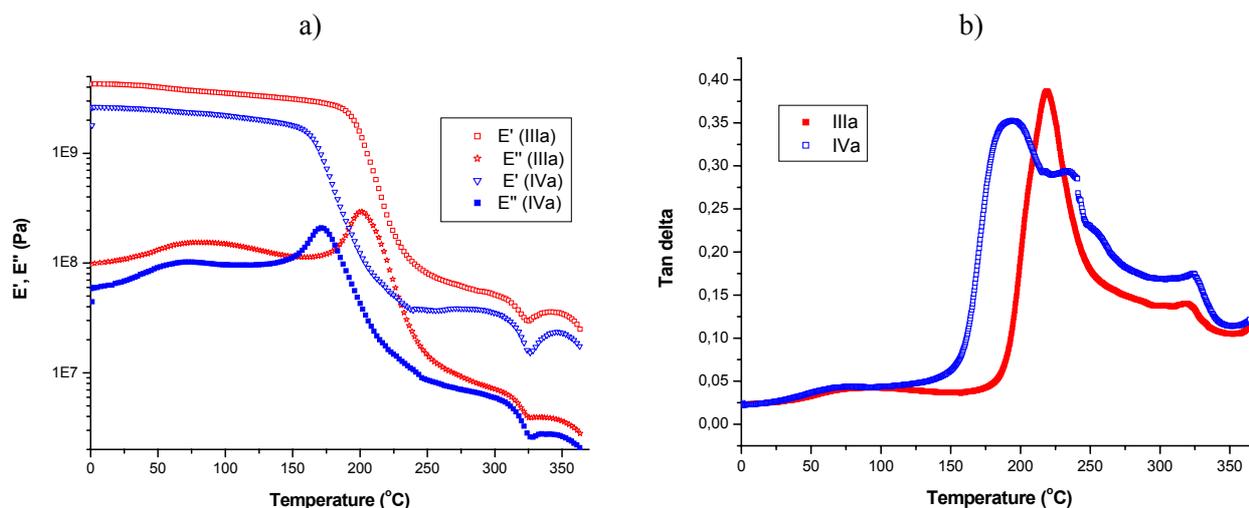


Fig. 3 – DMA curves of poly(amic acid) **IIIa** and of corresponding poly(amide-imide) **IVa**.

The value of the storage modulus, E' , in the glassy region, of the poly(amide-imide) **IVa** is lower than that of the corresponding polyamidic acid **IIIa**, which demonstrates that the chains gain more flexibility through the imidization process: in polyamidic acid **IIIa**, there are more interactions between macromolecular chains, due to carboxylic and amidic groups, which make the polymer more rigid, while in polyimide **IVa** such interactions disappear and consequently this polymer becomes more flexible.

The maximum peak on E'' curve of polyamidic acid **IIIa** has a value of about 205°C showing the beginning of glass transition temperature (T_g). This value can be also found on $\tan \delta$ curve (figure 3b). The glass transition temperature of the poly(amide-imide) **IVa** (175°C) structure is lower than that of polyamidic acid **IIIa** (205°C); these value can also be found in the E' and $\tan \delta$ curves. The lower value of T_g and $\tan \delta$ of PAI films is characteristic for a structure with a higher molecular flexibility than its corresponding precursor form.¹⁷

The precise measurement of T_g of the polyamidic acid is difficult because of the concurrent imidization reaction, which takes place simultaneously in the DMA experiment. Therefore the thermal cyclization of adjacent carboxylic and amide groups takes place during analysis, and it is reflected in the variation of modulus.

The magnitude of $\tan \delta$ at T_g is a measure of the energy-damping characteristics of a material, and it is related with the impact strength of a material. The flexibility of the polymers increases with the increase of $\tan \delta$ value at T_g . The results indicate that the introduction of flexible moieties into the main chain of the polymer would lead to the increase of the polyimide flexibility.

According to the equation below, $\tan \delta$ is the ratio of the loss modulus (E'') and storage modulus (E') for a test sample deformed under frequency f , at time t and temperature T :

$$\tan \delta(f, t, T) = \frac{E''(f, t, T)}{E'(f, t, T)}$$

When $\tan \delta > 1$, the sample exhibits viscoelastic liquid-like behavior; and when $\tan \delta < 1$, the sample exhibits viscoelastic solid-like behavior. It has been reported that polymer with $\tan \delta$ values > 1 are relatively easy to thermoplastically mold into well consolidated composites; those with $\tan \delta < 1$ were difficult to process.¹⁸ The maximum value of $\tan \delta$ of these samples was considered as glass transition temperature T_g . For the poly(amide-imidic) acid the value $\tan \delta$ is smaller than 1, meaning that the films exhibit viscoelastic solid-like behavior at their respective T_g s. The higher value T_g is attributed to its stiff molecular structure.

The dielectric spectroscopy analysis (DEA) over a large interval of temperature for polyimide **IVa** is presented in figure 4. Three relaxation processes can be observed, designated in descending order, from high to low temperature, as γ , β and α according to the common convention.¹⁹ The strength of these secondary transitions is related to how strongly a polymer responds to those processes. These sub- T_g transitions are associated with materials properties in the glassy state. It is important to note that the temperature peak for the transitions shifts to higher temperatures as the frequency increases. When the applied stress is faster, the macromolecules have

less time to react and it is necessary a higher temperature to stimulate the long-range coordinated molecular movements characteristic for these transitions.^{20,21}

The dielectric constant of polymers decreased gradually with increasing frequency because the response of the electronic, atomic and dipolar polarizable units vary with frequency. This behavior can be attributed to the frequency dependence of the polarization mechanism. The magnitude of the dielectric constant is dependent upon the ability of the polarizable units to orient fast enough to keep up with the oscillation of the alternative electric field.²²

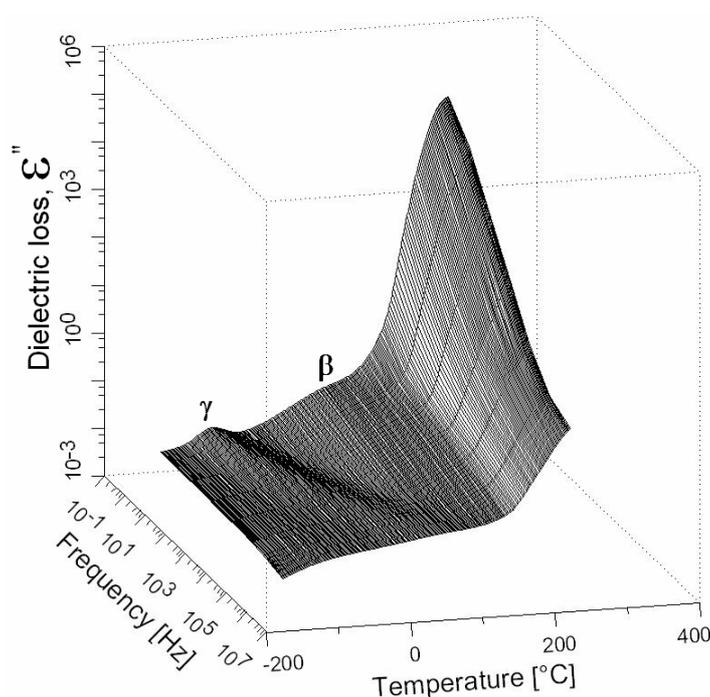


Fig. 4 – DEA plot for poly(amid-imide) **IVb**.

As shown in figure 4 the γ relaxation was sensitive to frequency change. With frequency increase the γ relaxation temperature moved towards higher temperature in accordance with Arrhenius law, which can be used in describing the temperature dependence for many thermal analysis systems. The Arrhenius equation can calculate the activation energy Ea of this relaxation from peak temperatures at different frequencies.

$$f = A \exp(-Ea/RT)$$

where A is the preexponential factor, R is the gas constant, T is the relaxation peak temperature and Ea is the activation energy. Former reports stated that this equation is appropriate to be used for non-

cooperate processes (sub-glass relaxions).²³ The magnitude of the activation energy (Ea) of a relaxation depends on rotation potential energy barriers, internal friction, and the volume and environment of the moving repeat units. The activation energy of a relaxation calculated from dielectric data is generally lower than the activation energy calculated for the same relaxation from mechanical data.²⁴

The γ relaxation Ea of 50.33 kJ/mol calculated for poly(amide-imide) **IVb** (figure 5) agrees reasonably well with the value of 43 kJ/mol reported for Matrimid polyimide.²⁵

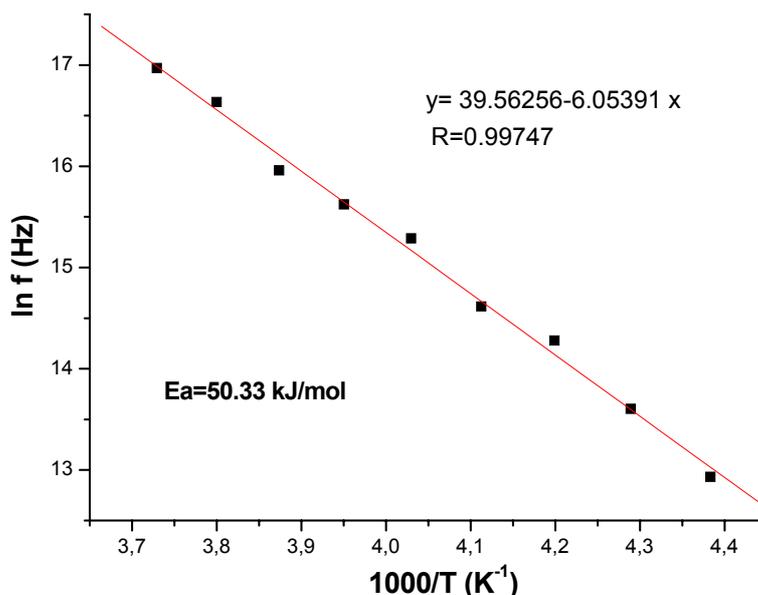


Fig. 5 – γ relaxation activation energy for poly(amide-imide) **IVb**.

EXPERIMENTAL

Synthesis of the monomers

Aromatic diamines 2,6-bis(*p*-aminophenoxy)benzotrile (**Ia**) and 2,6-bis(*m*-aminophenoxy) benzotrile (**Ib**) were prepared by the reaction of *p*- or *m*- aminophenol and 2,6-dichlorbenzotrile in *N,N*-dimethylacetamide (DMAc) with potassium carbonate, according to a method described earlier.^{26,27} They were recrystallized from a mixture of ethanol with water. M.p.(**Ia**) = 136-138°C, m.p.(**Ib**) = 211-213°C. The diamines structure was confirmed by IR and ¹H NMR spectroscopy. Trimellitic anhydride chloride (**II**) was prepared by treating the trimellitic anhydride with thionyl chloride at reflux. The excess solvent was removed under vacuum and the residue was thoroughly washed with ether. M. p. (**II**) = 165-168°C.

Synthesis of the polymers

Low temperature solution polycondensation of equimolecular amounts of diamine and trimellitic anhydride was carried out in *N*-methyl pyrrolidinone to give the poly(amide-imide)s (**IV**) (scheme 1).

Polycondensations were run by adding the trimellitic anhydride chloride to a solution of diamines in NMP with stirring under nitrogen at -15°C. After addition of the chloride the concentration of the solution was 11% solids. The reaction mixture was kept under stirring at -15°C and nitrogen stream for 2 h. Few mL of propylene oxide were added to capture the hydrochloric acid formed during the reaction. Then the reaction mixture was allowed to reach the room temperature and it was stirred for additional 2 h to give the polyamidic acid (**III**). Approximately 4 mL from this solution were precipitated into 50 mL of water. A fibrous product resulted which was thoroughly washed with 100 mL water, filtered and dried under vacuum. The rest of polymer solution was heated at 185-190°C for 5 h, under a nitrogen stream, to perform the cyclization of the poly(amidic-acid) to the corresponding poly(amide-imide) (**IV**). The water evolved during imidization was removed from the reaction mixture with the slow stream

of nitrogen which was used as inert medium. The solution was cooled-down to room temperature and small parts of it have been cast onto glass plates to check the film forming ability. The rest of solution was poured into water to precipitate the polymer. The solid product was filtered, washed with water under stirring and dried at 120°C for 2 h.

Measurements

Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices) apparatus with no correction. Inherent viscosities were determined at 20°C for solutions of polymers (0.5 g/dL) in NMP, using an Ubbelohde viscometer. IR spectra were recorded on a Perkin-Elmer spectrometer using KBr pellets. ¹H NMR spectra were recorded on a Varian EM-390 Spectrometer, at 90 MHz, for solutions in deuterated dimethylsulfoxide (DMSO-d₆). Thermogravimetric analysis (TGA) was performed on a MOM-type Derivatograph made in Budapest, Hungary, operating in air at a heating rate of 12°C/min. The glass transition temperature (*T*_g) was measured on a Mettler DSC 12E apparatus in nitrogen with a heating rate of 20°C/min. The mid-point of the inflection curve resulting from the typical second heating cycle was considered as the *T*_g of polymers. The quality of the films was investigated by AFM. The images were taken in air, on a SPM SOLVER Pro-M instrument. Mechanical properties of the polymer films were analysed by tensile testing using an Instron 5566 apparatus. The samples were used in the form of strips having the thickness of 0.03 mm, gauge length of 25 mm and width of 15 mm. Stiffness, tensile strength and elongation-at-break were determined at 10 mm/min cross-head speed. The tensile stress (MPa) versus tensile strain (%) dependencies was recorded. Dynamic mechanical analysis (DMA) was performed with a Perkin Elmer Diamond apparatus equipped with a standard tension attachment. The experiments were run on film samples with dimensions 10 x 10 x 0.04 mm by heating from 0°C up to beyond the temperature of the glass transition, with a heating rate of 2°C/min. The film samples were longitudinally deformed by a small sinusoidal stress at a frequency of 1 Hz and the resulting strain was measured. The variations of the storage modulus *E*',

loss modulus E'' and tension loss tangent $\tan \delta$ ($\tan \delta = E''/E'$) as functions of temperature were obtained. Dielectric spectroscopy measurements of the polymer films at various temperatures in the range of 173–423 K and in the frequency range of 10^{-1} – 10^6 Hz have been performed using a Novocontrol Dielectric Spectrometer (GmbH Germany), CONCEPT 40. Polymer films were placed in a flat parallel plate capacitor arrangement having gold plated electrodes with 20 mm diameter. The thickness of the films was in the range of 0.04–0.07 mm. The amplitude of AC applied voltage was 1 V.

CONCLUSIONS

Aromatic poly(amide-imide)s with flexible ether linkages in the main chain were prepared by polycondensation reaction of trimellitic anhydride chloride with aromatic diamines having cyano substituents and ether bridges. These polymers are soluble in polar aprotic solvents, and can be cast into thin films from such solutions giving smooth films with no defects. The poly(amide-imide)s show high thermal stability with decomposition temperature of about 350°C and glass transition in the range of 217–227°C. The polymer containing *meta* catenation exhibited higher tensile strength (>80MPa) than the one having *para* catenation and can be considered as advanced material. Dielectric spectroscopy evidenced the sub-glass transitions of the polymers and allowed the calculation of the activation energy of such transitions.

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