



*Dedicated to the memory of
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

THERMAL AND ELECTRICAL PROPERTIES OF SOME HYDROXY-CONTAINING IMIDE TYPE POLYMERS

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Two aromatic polyimides have been prepared by solution polycondensation reaction of a fluorinated bis(*o*-aminophenol), namely 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, with aromatic dianhydrides such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis-[4-(3,4-dicarboxyphenoxy)phenyl]isopropane dianhydride. A poly(amide imide) containing hydroxylic groups has been synthesized by using the same fluorinated bis(*o*-aminophenol) and 2,2-bis[N-(4-chloroformylphenyl)phthalimidy]hexafluoropropane. All polymers were soluble in polar organic solvents, such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, as well as in less polar organic solvents, such as tetrahydrofuran. They were amorphous, afforded transparent and flexible films by solution casting, and exhibited good thermal stability. Electrical insulating properties of polymer films were evaluated on the basis of dielectric constant and dielectric loss and their variation with frequency and temperature. The values of the dielectric constant at 10 kHz and 20°C were in the range of 3.41-3.71 for polyimides and 3.93 for poly(amide imide). Two subglass transitions, γ and β , were evidenced by dielectric spectroscopy.

INTRODUCTION

Aromatic polyimides are an important class of high performance polymers widely used in the electronic and space industry because of their combination of properties, including excellent thermal stability, high mechanical strength, good electrical properties and superior chemical resistance.¹ However, the commercial use of these polymers is often limited because of their poor solubility and high softening or melting temperatures. Several approaches to soluble polyimides including the incorporation of flexible linkages or bulky substituents have been developed.^{2,3} The main concept behind of all these approaches is the reduction of the packing force and the increasing of the free volume of the polymers.

The incorporation of hexafluoroisopropylidene (6F) groups into polymer backbones enhances the polymer solubility without sacrificing thermal stability.⁴⁻⁸ Also, the presence of hydroxylic groups on the backbones of aromatic polyimides improves the solubility and enables the modification of these polymers. Soluble hydroxy-containing polyimides are potential materials for photoresist,^{9,10} and nonlinear optical applications.¹¹ It has been demonstrated that aromatic polyimides having hydroxylic groups *ortho* to the imide nitrogen could undergo thermal conversion to polybenzoxazoles upon heating between 350-500°C under nitrogen or vacuum.¹²

Broadband dielectric spectroscopy was used to determine the glass-rubber and subglass transition properties of the polyimide.¹³⁻¹⁵ Typically, three relaxation processes were observed with increasing

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temperature designated γ , β and α , respectively, with α corresponding to the glass-rubber relaxation.

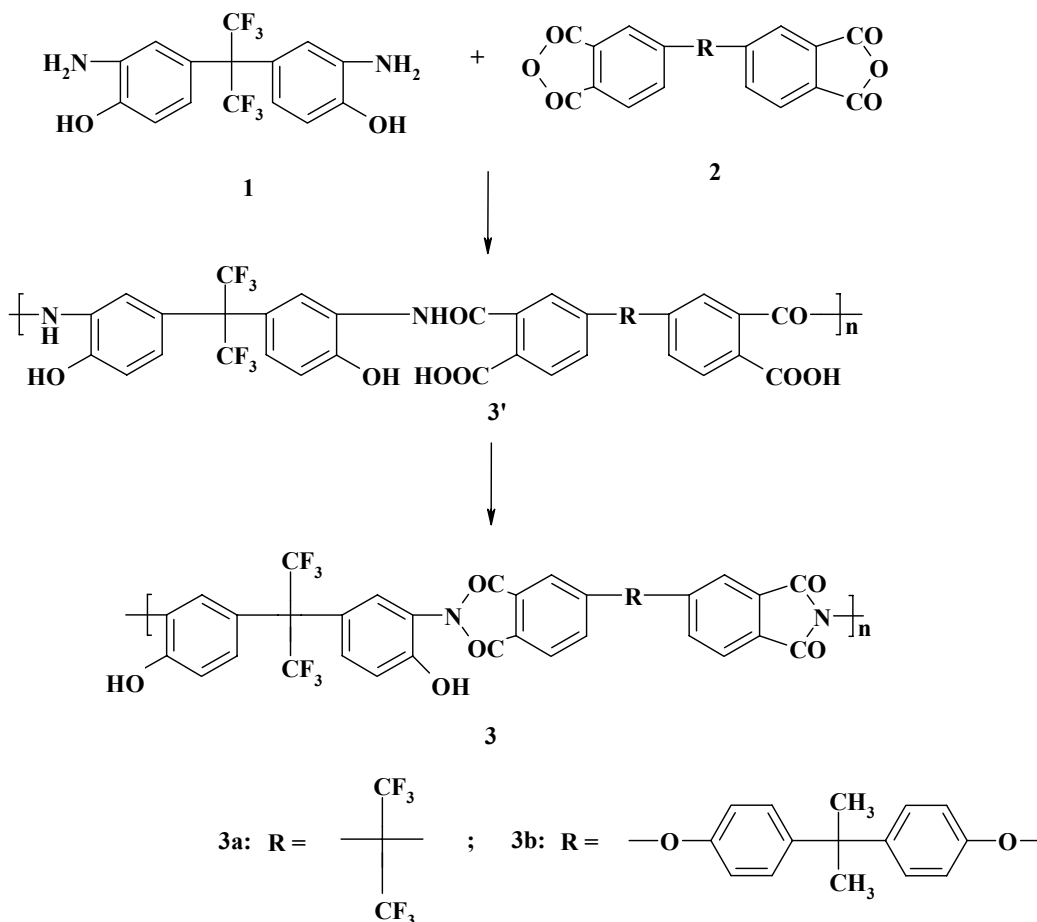
In this article we present the synthesis of two aromatic polyimides and a poly(amide imide) containing hydroxylic groups and hexafluoroisopropylidene units. The properties of these polymers, such as solubility, inherent viscosity, film forming ability, thermal and electrical behaviour have been studied.

RESULTS AND DISCUSSION

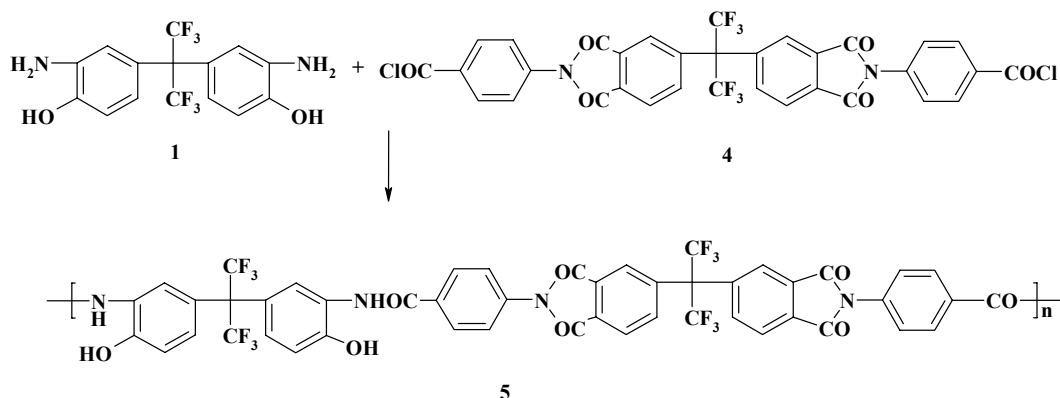
The synthesis of fluorinated polyimides containing hydroxylic groups **3** took place in two steps, in one pot.^{12,16} In the first step, the polycondensation of bis(*o*-aminophenol) **1** with aromatic dianhydrides **2** was performed at room temperature, under nitrogen, leading to the poly(amic acids) **3'** (Scheme 1). In the second step, the resulting solutions of poly(amic-acids) **3'** were heated at 180-185°C, for 4 h, to give the polyimides **3**. The water of imidization was evacuated by a slow stream of nitrogen which was

used as inert medium, at the same time. Polycondensation of equimolar amounts of **1** and diacid chloride **4**, in *N*-methyl-2-pyrrolidinone (NMP), at low temperature, yielded viscous solution of poly(amide imide) **5** (Scheme 2).¹⁷

The structure of the polymers was confirmed by IR spectroscopy. Strong bands appearing at 1780, 1720, 1380 and 740 cm^{-1} were assigned to imide rings. All the polymers exhibited absorption bands at 1180 and 1210 cm^{-1} due to 6F groups. A broad absorption band at 3380 cm^{-1} confirmed the presence of phenolic hydroxylic groups. The polymer **3b** showed characteristic absorption bands at 2970 cm^{-1} and 2870 cm^{-1} due to methyl group and at 1230 cm^{-1} due to the aromatic ether Ar-O-Ar. In the case of IR spectrum of polymer **5** the wide band which appeared at 3350 cm^{-1} was attributed to phenolic hydroxylic groups and NH stretching vibration in amide groups. Characteristic absorptions appeared at 1660 cm^{-1} due to the carbonyl stretching vibration (amide I), and at 1530 cm^{-1} due to NH deformational vibration (amide II).



Scheme 1 – Synthesis of hydroxy-containing polyimides **3**.



Scheme 2 – Synthesis of hydroxy-containing poly(amide imide) 5.

The inherent viscosities of the polymers were in the range of 0.39-0.68 dL/g (Table 1). The polymers were soluble in polar organic solvents, such as NMP, *N,N*-dimethylformamide, as well as in less polar organic solvents, such as tetrahydrofuran. The good solubility allows the imidization process to be performed in solution so that the final polymers were obtained as imidized products, which is more convenient than using poly(amic acid)s. The improved solubility of these polymers can be explained by the presence of a large number of 6F groups which increased the flexibility of the chains thus enhancing the solubility. Also the introduction of OH units did not allowed a good packing of the macromolecules improving the solubility.

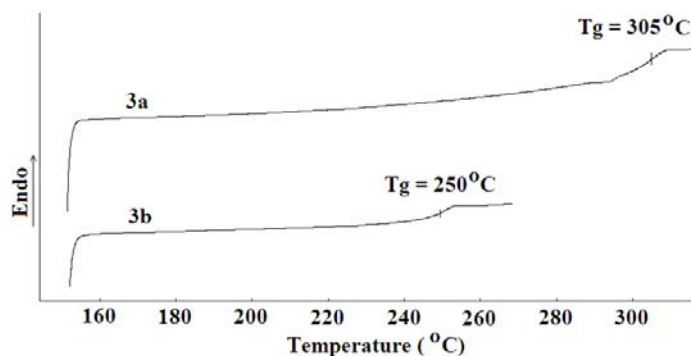
The glass transition temperature (T_g) of the present polyimides **3**, evaluated from DSC curves, was in the range of 250-305°C (Table 1). Figure 1 shows the DSC curves of polymers **3a** and **3b** as an example. Polymer **3a** having two 6F groups in the unit structure exhibited high T_g (305°C). Lower T_g showed polymer **3b** (250°C) containing aromatic ether linkages and isopropylidene groups. These groups increased the flexibility of macromolecular chains thus decreasing the T_g . For polymer **5** was not determined a T_g from DSC curve up to 320°C. The DSC measurements showed no evidence of crystallisation or melting which proves an amorphous morphology.

Table 1

The properties of polymers **3** and **5**

Polymer	η_{inh}^a , dL/g	T_g^b , °C	IDT ^c , °C	T_{10}^d , °C	T_{max1}^e , °C	T_{max2}^f , °C
3a	0.39	305	435	470	515	-
3b	0.52	250	420	465	525	-
5	0.68	-	485	440	325	550

^a Measured at 20°C, in NMP, at a concentration of 0.5 g/100 mL solvent; ^b Glass transition temperature; ^c Initial decomposition temperature = onset temperature, from TGA curve; ^d Temperature of 10% weight loss; ^e Temperature corresponding to the maximum rate of the first degradation step; ^f Temperature corresponding to the maximum rate of the second degradation step.

Fig. 1 – DSC curves of polymers **3a** and **3b**.

The thermal stability of these polymers was studied by thermogravimetric analysis (TGA). The polyimides **3** showed high thermal stability. They began to decompose in the range of 420-435°C in air atmosphere, as indicated by the onset temperature from TGA curves (Table 1). The temperature of 10% weight loss was in the range of 465-470°C. As it can be seen from differential thermogravimetric (DTG) curves of these polymers (Figure 2), the degradation process exhibited one maximum of decomposition. The temperature corresponding to the maximum rate of

decomposition was in the range of 515-525°C. The polymer **5** exhibited two steps of weight loss (Figure 2). The first step, in the range of 270-380°C, was due to the cyclization process to benzoxazole groups.¹⁸ The second step, above 480°C, was due to the destruction of the resulted poly(benzoxazole-imide) polymer. The temperature corresponding to the maximum rate of cyclization to benzoxazole structure was 325°C and temperature of maximum rate of polymer decomposition was 550°C.

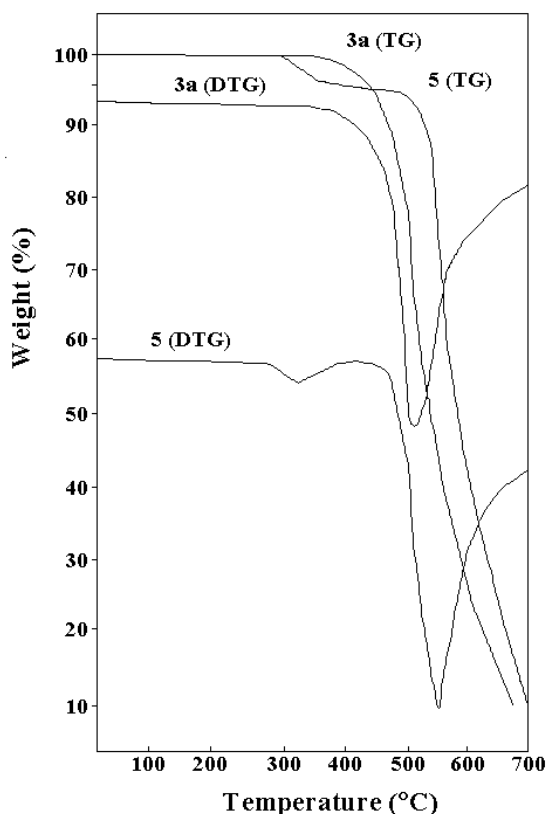


Fig. 2 – TG and DTG curves of polymers **3a** and **5**.

Electrical insulating properties of polymer films **3** and **5** were evaluated on the basis of dielectric constant and dielectric loss, and their variation with frequency and temperature. The dielectric permittivity of a material is, in general, a complex quantity, when measured in the frequency domain. Its real part (ϵ') is called the “dielectric constant” and decreases with increasing frequency with characteristic steps. Its imaginary part (ϵ'') is usually called the “dielectric loss” and may show the maxima on the diagrams vs. frequency (or vs. temperature). The maxima on dielectric loss diagrams and “steps” on dielectric constant diagrams correspond to different molecular

relaxation phenomena. Figure 3 presents the dependence of real and imaginary parts of complex permittivity on frequency, for polymers **3** and **5**, at three chosen temperatures.

It can be seen that ϵ' slightly decreased with increasing frequency. The ϵ' of polymers decreased gradually with increasing frequency because the response of the electronic, atomic and dipolar polarizable units varies with frequency. The ϵ' values at 100 Hz, 10 kHz and 1 MHz are listed in table 2. By comparing with polymer **3a**, the polymer **3b** showed lower ϵ' over the entire interval of frequency, at room temperature, probably due to a lower content/unit structure of

OH groups and imide rings. The ϵ' values of both polymer films **3a** and **3b** at 10 kHz (3.71 and 3.41, respectively) are comparable with that of “H Film”, a polyimide which is prepared from pyromellitic dianhydride and 4,4'-diaminodiphenylether and which is one of the most

preferred high performance dielectrics in microelectronic applications having a dielectric constant of 3.5.¹⁹ Poly(amide imide) **5** exhibited higher ϵ' values than polyimides **3** due to the presence of highly polarized carbonyl in amide groups and higher humidity absorption.

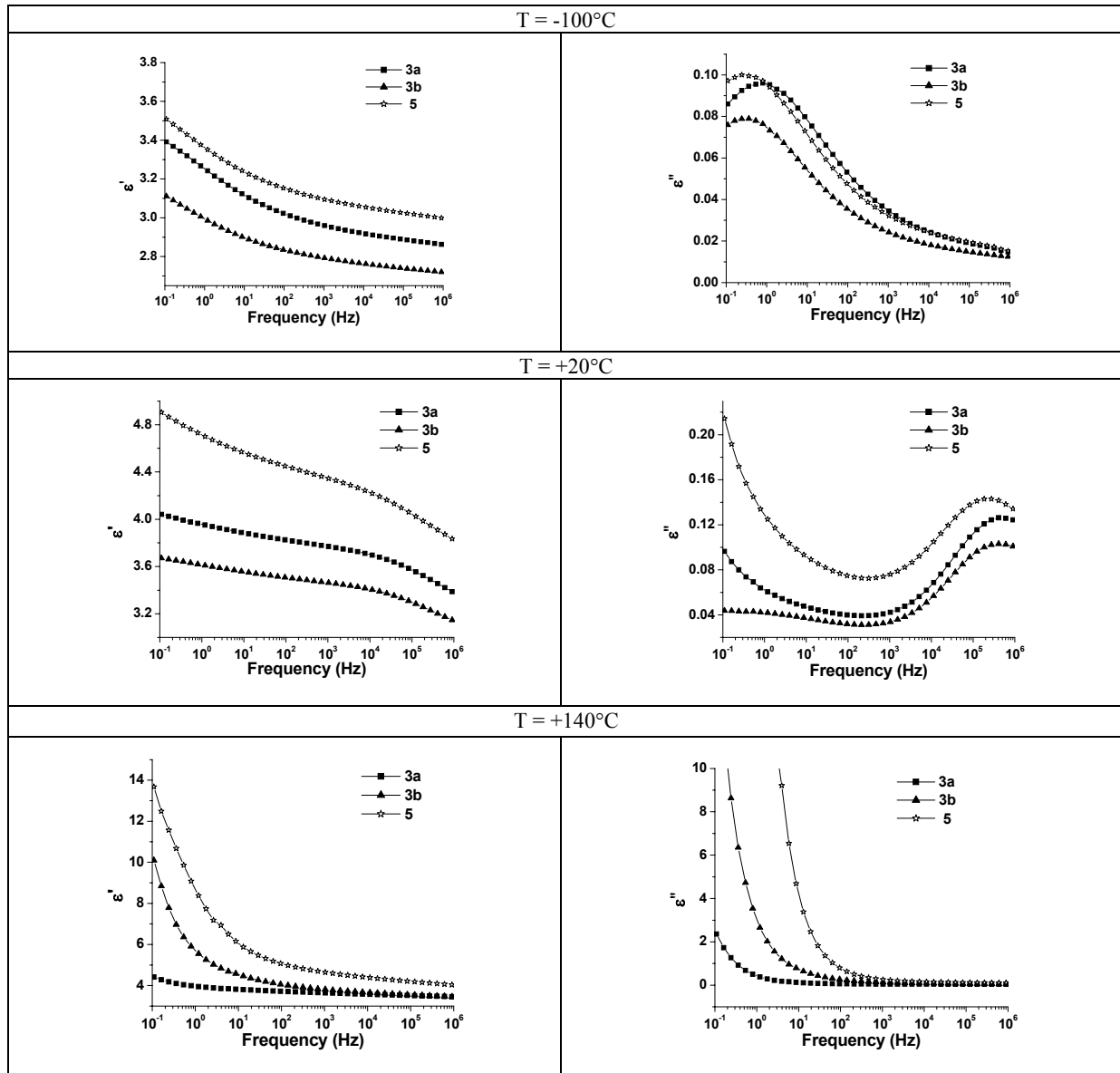


Fig. 3 – Dependences of ϵ' and ϵ'' versus frequency, at different temperatures, for polymers **3** and **5**.

Table 2

Dielectric constant at selected frequency, at 20°C, and activation energies of relaxation phenomena calculated from $\epsilon''(f)$ dependencies, for polymers **3** and **5**

Polymer	Dielectric constant at			E_a of γ relaxation (kJ/mol)	E_a of β relaxation (kJ/mol)
	100 Hz	10 kHz	1 MHz		
3a	3.86	3.71	3.38	52.6	84.1
3b	3.50	3.41	3.14	52.8	104.9
5	4.12	3.93	3.53	52.9	91.2

The ε'' for polymer film **3b** at different temperatures taken in the range from -100°C to 140°C is shown in figure 4. Two secondary γ and β relaxation processes, connected with local movements of polymer chain, appeared. Then the conductivity process arises and masks the primary relaxation connected with glass transition, which should have place at higher temperature. These two relaxation processes appeared at similar temperature in all samples and shifted to higher frequencies with increasing temperature. Also, the values of ε'' for poly(amide imide) **5** were higher than corresponding values for polyimides **3**.

The activation map is the best way for a comparison of all samples and it is also necessary for the calculation of activation energy. Relaxation times (τ) of the secondary relaxation processes at the various temperatures have been determined from maxima position of ε'' at frequency scale. The activation plots are shown in figure 5. The magnitude of the activation energy of relaxations depends on rotational potential energy barriers, internal frictions, and the volume and environment

of the moving repeat units. The activation energy for γ and β relaxations was calculated by applying the Arrhenius equation:²⁰

$$f = A \exp(-E_a/RT) \quad (1)$$

where f is frequency, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the peak-maximum temperature. The γ relaxation is assigned to the small scale, local oscillations of imide rings.²¹ The values of activation energy of γ relaxation for the polymers **3** and **5** were in the range of 52.6-52.9 kJ/mol (Table 2) suggesting the existence of the same process for this transition. The β relaxation occurs below the T_g and is associated with local bond rotations and molecular segment motions along the polymer backbone. The magnitude of this relaxation is proportional to the concentration of segments contributing to the relaxation. The activation energy of β relaxation was in the range of 84.1-104.9 kJ/mol for polymers **3** and 91.2 kJ/mol for polymer **5**.

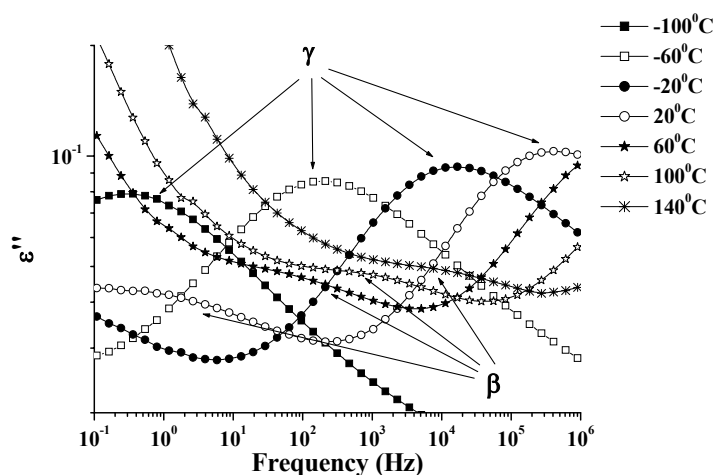


Fig. 4 – Dependence of ε'' versus frequency, at different temperatures, for polymer **3b**.

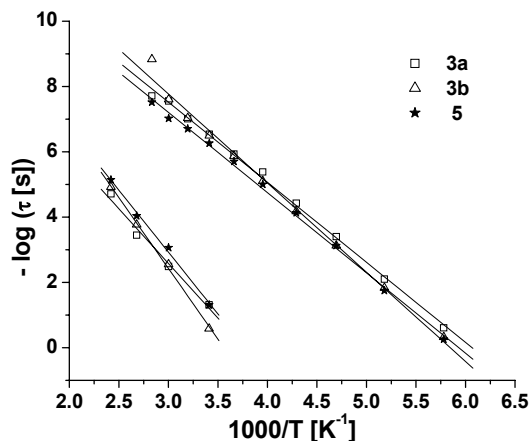


Fig. 5 – Activation map for polymers **3** and **5**.

EXPERIMENTAL

Monomers. The monomers bis(*o*-aminophenol) **1**, and dianhydrides **2a**, and **2b**, have been obtained from commercial sources and used as received. The diacid chloride **4** was obtained by treating with thionyl chloride the corresponding dicarboxylic acid resulting from the condensation reaction of dianhydride **2a** with *p*-aminobenzoic acid, glacial acetic acid being used as solvent and dehydrating reagent, at reflux;²² mp: 311-313°C. IR (KBr, cm⁻¹): 1780 (C=O of imide ring and COCl), 1720 (C=O of imide ring), 1600 (aromatic), 1390 (C-N), 1210 and 1180 (6F), 1100 and 720 (imide ring). ¹H NMR (DMSO-d₆, ppm): δ = 8.22 (2H, d), 8.11 (4H, d), 7.91 (2H, d), 7.73 (2H, s), 7.61 (4H, d).

Measurements. Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). The inherent viscosity of the polymers was determined with an Ubbelohde viscometer, by using polymer solution in NMP, at 20°C, at a concentration of 0.5 g/dL. Infrared spectra were recorded with a Specord M80 spectrometer. ¹H NMR spectra were recorded on a Bruker Avance DRX 400, by using solutions in deuterated dimethylsulfoxide (DMSO-d₆). Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 12°C/min. The initial decomposition temperature was considered the onset on the TGA curve. The temperature of 10% weight loss was also recorded. The glass transition temperature (*T_g*) of the precipitated polymers was determined with a Mettler-Toledo differential scanning calorimeter DSC 12E, 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 *T_g*. The dielectric measurements were carried out using a Novocontrol system composed from an Alpha frequency response analyzer and Quattro temperature controller. The samples were prepared in the form of films with thickness of 20 - 40 μm with gold electrodes evaporated in vacuum. The samples were sandwiched between two copper electrodes of diameter 20 mm and placed inside temperature controlled sample cell. The complex permittivity: $\epsilon^*(f) = \epsilon'(f) - i\epsilon''(f)$ has been determined in the frequency (*f*) range from 10⁻¹ Hz to 10⁶ Hz and at temperature range from -100°C to 140°C. The AC voltage applied to the capacitor was equal to 1.5 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C. The points used for the activation maps, *i.e.* the relaxation times (τ) at a given temperature *T*, were determined by WinFIT software using the Havriliak-Negami function fitting.

Preparation of polyimides 3. A typical polycondensation was run as shown in the following example.²³ In a 100 mL three-necked flask equipped with mechanical stirrer and nitrogen-inlet and outlet were introduced 0.728 g (0.002 mol) of **1** and 10 mL of NMP. The mixture was stirred under nitrogen to complete dissolution. Then 0.888 g (0.002 mol) of the dianhydride **2a** was added to the resulting solution and stirring was continued for 6 h. The solution became viscous. A part of the resulting solution was then heated at 180-190°C for 4 h, under a nitrogen stream, to perform the cyclization of the poly(amic acid) **3a'** to the corresponding polyimide structure **3a**. The flask was cooled down to room temperature and the resulting polymer solution was poured into water to precipitate the polymer. The solid product was filtered, washed three times with water and then dried at 120°C for 6 h. The other

part of the solution containing the poly(amic acid) **3a'** was cast onto a glass plate and dried gradually at 80°C, 120°C, 160°C, 180°C, and 220°C, each for 1 h. The resulting flexible transparent film was stripped off the plates by immersion in hot water for 2 h and was dried at 120°C for 6 h.

Synthesis of poly(amide imide) 5. The polycondensation reaction was run under anhydrous conditions, in a nitrogen atmosphere, with equimolar amounts of diamine and diacid chloride being used, in NMP as a solvent and with pyridine as the acid acceptor. A typical reaction was carried out as follows: in a 100 mL three necked flask equipped with a mechanical stirrer and a N₂ inlet and outlet, were placed 0.728 g (0.002 mol) of **1**, 16 mL NMP and 0.4 mL pyridine, and the mixture was stirred until complete dissolution. The solution was cooled to -10°C and 1.438 g (0.002 mol) of **4** were added with 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 a further 4 h. Half of the resulting viscous solution was cast onto a glass plate and after evaporating the solvent at 80°C, 120°C, 160°C, 180°C, and 220°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 dried at 120°C for 6 h and used for different measurements. The other half of the polymer solution was diluted to about 4% by addition of more NMP and the polymer was precipitated by pouring into water. The precipitated product was filtered, washed twice with ethanol under stirring and dried under vacuum at 80°C for 1 h.

CONCLUSIONS

Two fluorinated polyimides and a poly(amide imide) containing hydroxylic groups were synthesized by polycondensation reaction of a bis(*o*-aminophenol) with aromatic dianhydrides and a diacid chloride having preformed imide rings, respectively. The polymers were soluble in organic solvents, and possessed good film forming capacity thus being appropriate for processing into transparent films from solutions. They exhibited good thermal stability and high glass transition temperature. The presence of hydroxylic groups slightly increased the dielectric constant values of the polymers. At low and moderate temperature the samples studied by dielectric spectroscopy showed two secondary relaxation processes connected with local movements of polymer chains.

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