



*Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary*

AROMATIC POLYIMIDES CONTAINING PENDANT CARBOXYLIC GROUPS

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Aromatic polyimides with pendant carboxylic groups were prepared starting from 3,5-diaminobenzoic acid, **DABA**, or equimolar amount of **DABA** and 4,4'-(4,4'-isopropylidenediphenyl-1,1'-diyldioxy)dianiline, and different aromatic dianhydrides. The polymers exhibited high thermal stability with initial decomposition temperature above 430°C and glass transition temperature in the range of 251–302°C. They showed good solubility in polar amidic solvents and some of them in less polar liquids, like chloroform. The polymer solutions could be cast into flexible films. A study of the relation between conformational parameters and properties of these polymers has been carried out by using the Monte Carlo method, and the results were compared with the experimental data and discussed in relation with the rigidity of the chains.

INTRODUCTION

Among heterocyclic polymers widely studied for high performance applications aromatic polyimides have received considerable interest due to their outstanding thermal stability, tough mechanical properties and low dielectric constant.^{1,2} However, the main deficiency of aromatic polyimides is their insolubility in organic solvents and infusibility or extremely high glass transition temperature which makes their processing very difficult. Various efforts have been made on the synthesis of soluble or processable polyimides without much sacrifice of their excellent thermostability. The introduction of flexible linkages, noncoplanar units or bulky lateral groups along the backbone was used to improve the solubility of the polymers.^{3,4} For example the introduction of flexible groups such as ether, isopropylidene, hexafluoroisopropylidene or dimethylsilane groups leads to lower glass transition temperatures and significant improvement in solubility.⁵⁻⁸ A useful approach for reducing the

melting temperature of the polymers and increasing the solubility is the copolymerization of the monomers by which the symmetry of the structure is lowered and lateral packing is disrupted.⁹⁻¹¹

The incorporation of carboxylic groups in the polyimide structure leads to polymers having different potential applications. These polyimides can be further functionalized by reacting the pendant carboxylic groups with different other compounds.¹²⁻¹⁶ Also, they can be used as polymer matrix for composites because the carboxylic groups can improve the attachment of the particles to the macromolecular chains.¹⁷⁻²¹

The present work deals with the synthesis and characterization of some polyimides and copolyimides having functional carboxylic groups and different flexible units. Physical properties of the resulting polymers, such as solubility and glass transition temperature, have been discussed in relation with the conformational rigidity of their chains and some relationships have been shown.

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RESULTS AND DISCUSSION

The monomers used for the preparation of the polyimides containing carboxylic groups, **1** and **2**, were 3,5-diaminobenzoic acid, **DABA**, 4,4'-(4,4'-isopropylidenediphenyl-1,1'-diylidioxy)dianiline, **6HDM**, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride, **6FDA**, 4,4'-(4,4'-isopropylidene-diphenoxy)-bis(phthalic anhydride), **6HDA**, and 4,4'-(dimethylsilane)diphthalic anhydride, **6HSi** (Fig. 1).

The polyimides **1** and **2** were prepared by solution polycondensation reaction in two steps. In the first step poly(amic acid)s were synthesized by

the reaction of **DABA**, or equimolar amounts of **DABA** and **6HDM**, with different aromatic dianhydrides, such as **6FDA**, **6HSi** or **6HDA**, at room temperature, in N-methyl-2-pyrrolidone (NMP) as solvent. The concentration of the reaction mixture was adjusted to 10-15%. The imidization reaction of poly(amic acid)s was performed in solution, in the presence of acetic anhydride and pyridine (2:1), according to a method previously published.²² The chemical structure of polyimides **1** and **2** is illustrated in Fig. 2. Details about the preparation of the polymers are presented in Table 1.

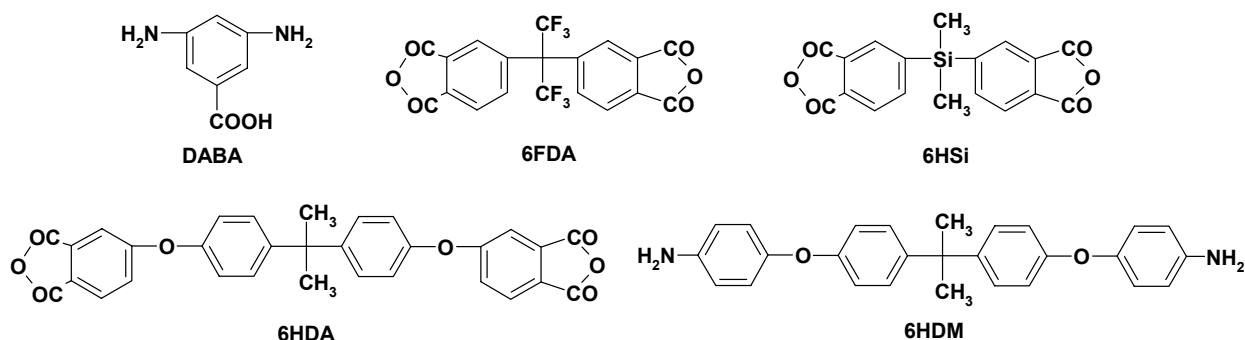


Fig. 1 – The monomers used for the preparation of the polymers **1** and **2**.

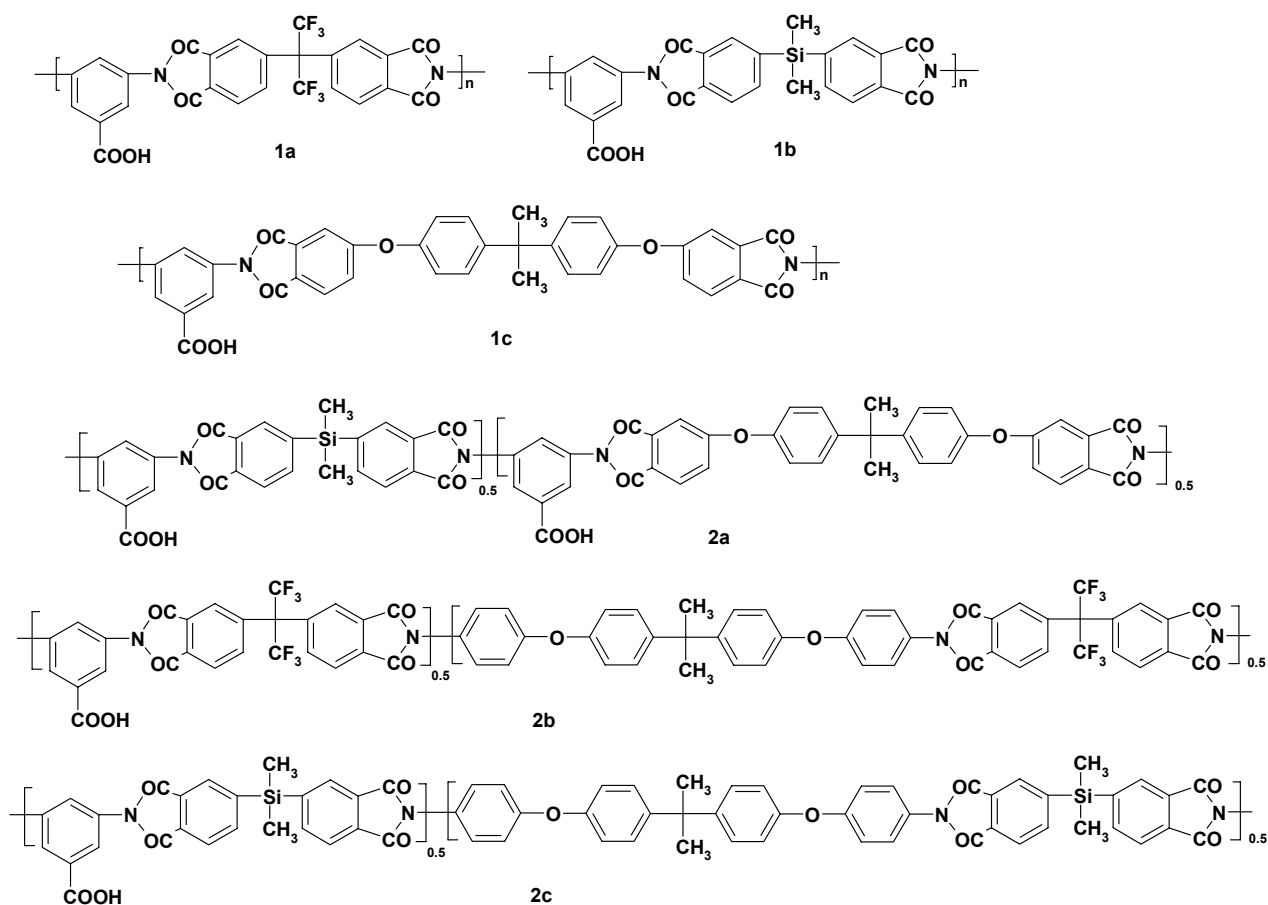


Fig. 2 – The chemical structure of polymers **1** and **2**.

The structure of the polymers was investigated by IR and ^1H NMR spectroscopy. The IR spectra of the polymers exhibited strong bands at around 1780 and 1720 cm^{-1} which are commonly attributed to the asymmetrical and symmetrical stretching vibrations of carbonyl groups of imide rings; absorption band at 1350 cm^{-1} was due to C–N stretching of imide rings, and that at 740 cm^{-1} was due to imide ring deformation. For all the polymers the characteristic band for carboxylic pendant groups at 1720 cm^{-1} overlaps the absorption

band of carbonyl units of imide groups. In FTIR spectra of polymers **1a** and **2b** absorption bands at 1188 and 1209 cm^{-1} were attributed to 6F groups. Polymers **1c** and **2a-c** exhibited a characteristic absorption band around 1240 cm^{-1} due to aromatic ether linkages. In the case of polyimides **1b**, **2a** and **2c** absorption bands of dimethylsilane units appeared at 1220 and 820 cm^{-1} . The polymers **1b-c** and **2a-c** exhibited characteristic absorption bands at 2970 cm^{-1} due to methyl groups. Fig. 3 presents the IR spectrum of polymer **1c**, as an example.

Table 1

Preparation and some characteristics of polymers 1 and 2

Polymer	Preparation of the polymers					Concentration %	Mn g/mol	Mw g/mol	Mw/Mn
	DABA g	6FDA g	6HSi g	6HDA g	6HDM g				
1a	1.52	4.44	-	-	-	10.65	21000	38800	1.85
1b	1.52	-	3.52	-	-	10.07	8300	15000	1.81
1c	1.52	-	-	5.20	-	14.38	32000	50100	1.57
2a	1.52	-	1.76	2.60	-	10.52	25000	42500	1.70
2b	0.76	4.44	-	-	2.05	12.66	12900	29900	2.32
2c	0.38	-	1.76	-	1.025	13.60	17200	30800	1.79

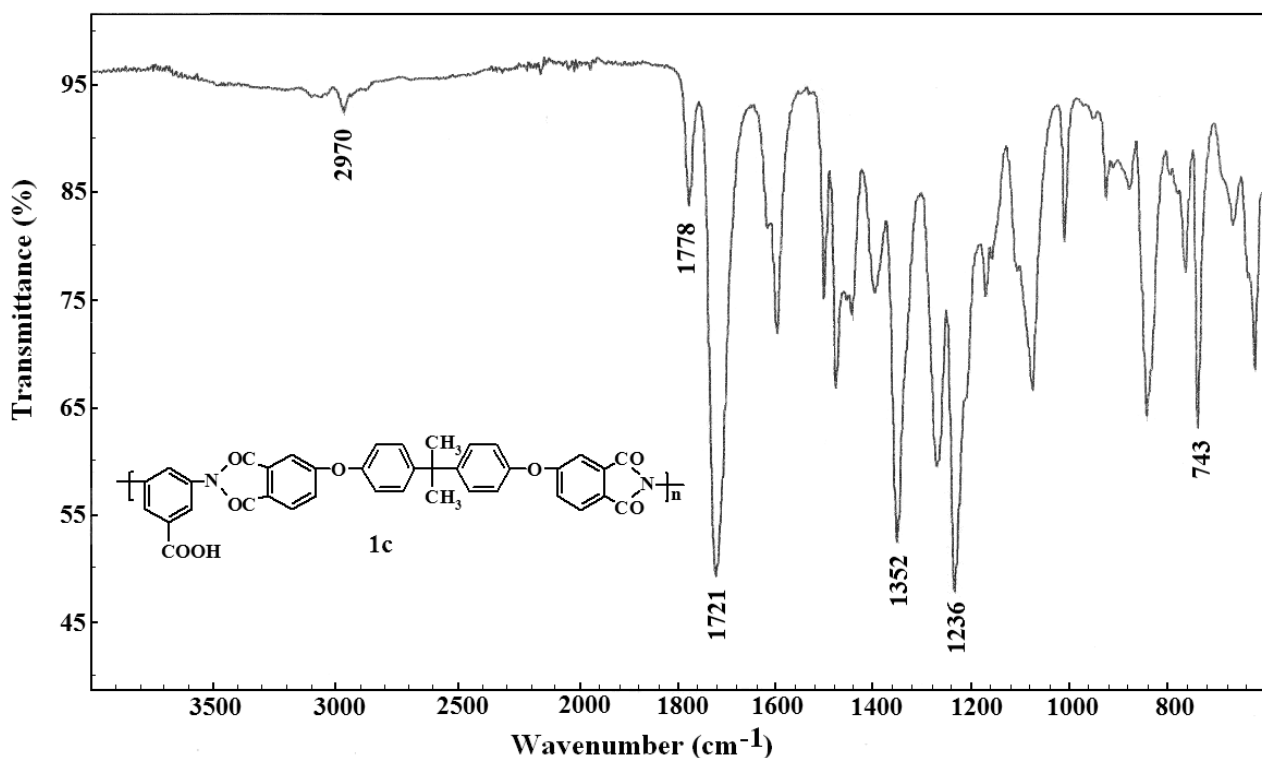
Fig. 3 – IR spectrum of polyimide **1c**.

Fig. 4 illustrates the ^1H NMR spectrum of polymer **1a** with the assignments of all the protons. The protons H_2 closed to the electron-withdrawing carboxylic groups and imide rings appeared at the farthest downfield region of the spectrum. Also, the protons coming from dianhydride segment appeared at high ppm values due to the electron properties of imide rings. Fig. 5 presents the ^1H NMR spectrum of the copolymer **2b**, derived from dianhydride **6FDA** and equimolar amount of diamines **DABA** and **6HDM**. The aromatic protons coming from **DABA** and **6FDA** units

appeared at higher ppm values due to the presence of imide rings and carboxylic groups. The protons H_6 , H_7 , H_8 and H_9 coming from the diamine **6HDM** appeared as doublets at lower ppm values due to isopropylidene linkage and electron-donating properties of aromatic ether units. Aliphatic protons H_{10} of isopropylidene groups appeared as a singlet at 1.6 ppm. From the ^1H NMR spectra it was found that the composition of the polymers was similar with the composition of the reactants used for the synthesis.

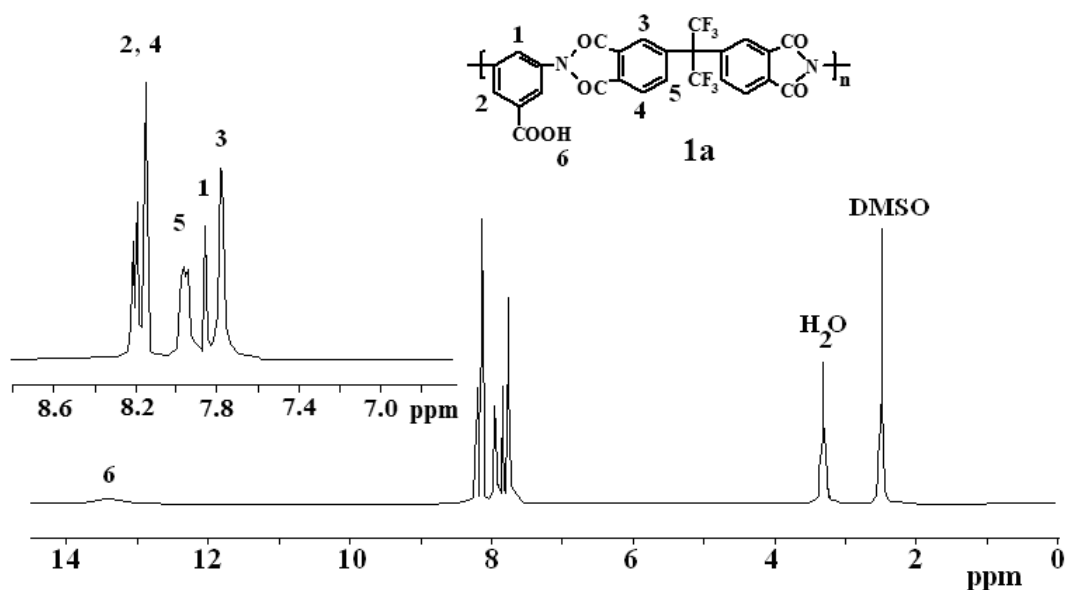


Fig. 4 – ^1H NMR spectrum of polyimide **1a**.

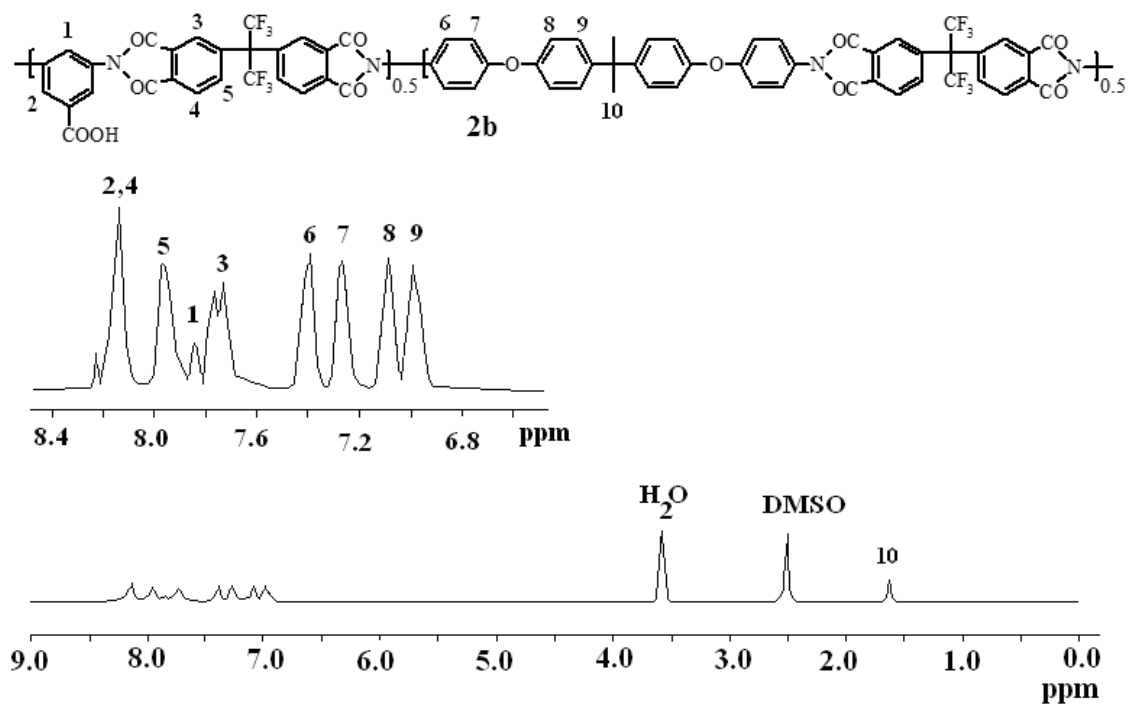


Fig. 5 – ^1H NMR spectrum of copolyimide **2b**.

The molecular weight of the polymers was determined by gel permeation chromatography. The values of weight-average molecular weight (M_w) were in the range of 15000-50100 g/mol, the number-average molecular weight (M_n) were in the range of 8300-32000 g/mol and the polydispersity M_w/M_n was in the range of 1.57-2.32 (Table 1).

Physical properties of polymers such as solubility and glass transition temperature (T_g) were studied, and some correlations with the conformational rigidity were made. A correlation between a physical property of a polymer and the conformational rigidity of its chain shows that the contribution of the conformational rigidity to this polymer property is significant.^{23,24} The Kuhn segment (A) and the characteristic ratio (C_∞) were chosen as the conformational parameters.

As is known, the Kuhn statistical segment under the assumption of free rotation can be written as:

$$A = \lim_{n \rightarrow \infty} \left(\frac{\langle R^2 \rangle}{nl_0} \right)$$

where ($\langle R^2 \rangle/nl_0$) is the ratio of the average square end-to-end distance of a chain to its contour length; n is the number of repeat units; l_0 is the contour length of a repeat unit. Conformational rigidity characterizes the degree of macromolecular coiling and it is governed by chain geometry: lengths of virtual bonds, angles between them and the allowed rotations about these bonds. The Kuhn segment was calculated by using the Monte Carlo method as shown in the literature.²⁵ Another conformational parameter is the characteristic ratio (C_∞) that can be evaluated by the relation:

$$C_\infty = A/l_0$$

Table 2 presents the calculated conformational parameters of polymers **1** and **2**. The solubility of the polymers **1** and **2** correlated well with their conformational rigidity. All the polymers were soluble in polar solvents like NMP and N,N-dimethylacetamide, and in less polar solvents like tetrahydrofuran. The good solubility was due to the high flexibility of the macromolecular chains, which is in agreement with relatively low values of the Kuhn segment being in the range of 19.28-21.11 Å. By decreasing the **DABA** content, an increase of the solubility appeared. Thus, the polymers **2b** and **2c** were easily soluble even in chloroform, while **1a-c** and **2a**, having a high concentration in COOH groups, were not soluble in this solvent. The improved solubility of the polymers **1** and **2** can be explained by the presence of large number of flexible ether linkages, isopropylidene, hexafluoroisopropylidene and dimethylsilane groups which increased the flexibility of the macromolecular chains thus enhancing the solubility. Also, in the case of copolyimides **2**, the solubility increased due to the effect of copolymerization.

The polymer solutions in NMP having a concentration of about 10% were cast onto glass substrates and dried to yield thin films with a thickness of 20-30 µm. Free standing flexible films were obtained in the case of all polymers, except **1a** and **1b**. These films were brittle, probably due to their high rigidity and a higher concentration of pendant carboxylic groups.

Table 2

Thermogravimetric analyses and conformational rigidity parameters of polymers **1** and **2**

Polymer	T_g^1 (°C)	T_5^2 (°C)	T_{10}^3 (°C)	T_{max1}^4 (°C)	T_{max2}^5 (°C)	l_0^6 (Å)	A^7 (Å)	C_∞^8
1a	302	450	480	460	530	17.19	20.45	1.189
1b	301	440	470	465	610	17.68	20.94	1.184
1c	254	445	470	450	575	27.10	19.28	0.711
2a	275	440	465	460	580	22.39	20.33	0.907
2b	251	440	480	440	530	24.55	20.85	0.849
2c	257	430	460	449	575	25.03	21.11	0.843

¹ Glass transition temperature, determined from DSC curves; ² Initial decomposition temperature = the temperature of 5% weight loss; ³ Temperature of 10% weight loss; ⁴ First maximum polymer decomposition temperature; ⁵ Second maximum polymer decomposition temperature; ⁶ The contour length over repeating structural unit; ⁷ The value of Kuhn statistical segment; ⁸ The characteristic ratio parameter of conformational rigidity.

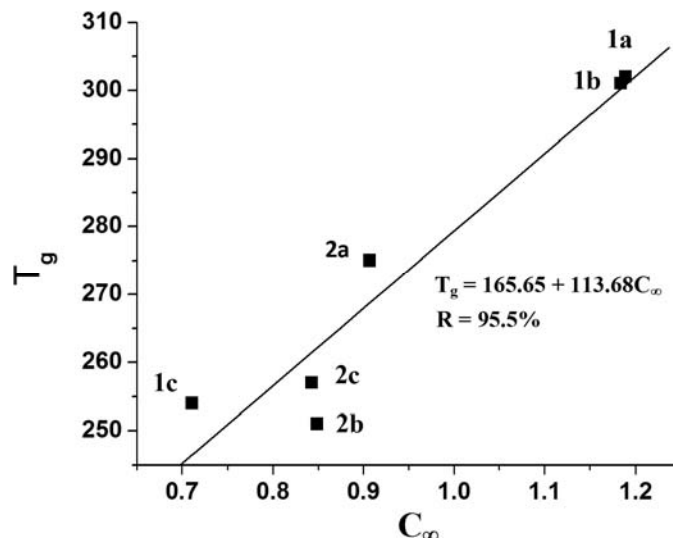


Fig. 6 – The dependence of T_g of polymers **1** and **2** on conformational rigidity parameter C_{∞} .

The thermooxidative stability of the polymers was studied by thermogravimetric analysis (TGA), effectuated in air atmosphere. The main thermal parameters are summarized in Table 2. The polymers began to decompose in the range of 430-450 °C, as indicated by the temperature of 5% weight loss in TG thermograms. The temperature of 10% weight loss was in the range of 460-480°C. The degradation process exhibited two maxima of decomposition. The first (T_{max1}) is in the domain of 440-465 °C and corresponds to the degradation of the carboxylic groups. The second maximum of decomposition (T_{max2}) is in the domain of 530-610 °C and can be associated to the generalized polymer degradation.

The glass transition temperature (T_g), evaluated from DSC curves, was in the range of 251-302 °C (Table 2). The DSC measurements showed no evidence of crystallisation or melting which proves an amorphous morphology. The dependence of T_g on the parameter of conformational rigidity C_{∞} is shown in Fig. 6. T_g increased with increasing chain rigidity. Thus, the polymers **1a** and **1b** having the highest value of C_{∞} (1.189 and 1.184, respectively) exhibited the highest value of T_g (302 °C and 301 °C, respectively). The introduction of flexible ether linkages, isopropylidene, hexafluoroisopropylidene and dimethylsilane groups, in the case of polymers **1c** and **2a-c**, reduced the values of C_{∞} in the interval 0.711-0.907, suggesting higher flexibility of the macromolecular chains. The decrease of the rigidity of the polymer backbone limits the rotational energy barrier and hence T_g exhibits lower values. Using the least-squares method, the dependence of the T_g on the conformational parameter C_{∞} can be described by a linear equation.

The factor of convergence R was high (95.5%), as shown in Fig. 6. The polymer **2b** goes out from common dependence, probably because its higher polydispersity than other polymers. As mentioned in the literature,²⁶ if the dependence is linear with a good factor of convergence, this equation can be used for the theoretical estimation of T_g for polymers having similar structures. It can be noticed that there is a large interval between T_g and decomposition temperature which makes these polymers more attractive for thermoforming processing.

EXPERIMENTAL

Monomers. The monomers **DABA**, **6HDM**, **6FDA** and **6HDA** were provided from Aldrich and purified before use. Dianhydride **6HSi** was synthesized as it was previously described.²⁷ **DABA** was recrystallized from water. The dianhydrides **6FDA**, **6HSi** and **6HDA** were recrystallized from acetic anhydride. NMP from Aldrich was distilled over P_2O_5 .

Measurements. Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices). Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets. 1H NMR (400 MHz) spectra were performed at room temperature on a Bruker Avance DRX 400 spectrometer, using $DMSO-d_6$ as solvent. The molecular weights were determined by means of gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and Shodex MZ Column. Measurements were carried out with polymer solutions of 2% concentration in DMF, and by using DMF as eluent. Standard polystyrene of known molecular weight was used for calibration. Thermogravimetric analysis was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10°C/min. The temperature at which the samples achieve a 5% weight loss (T_5) and the temperature of 10% weight loss (T_{10}) were recorded. The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler 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 reporting the glass transition temperature. The mid-point of the inflexion curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers.

Preparation of polymers 1 and 2. A typical polycondensation reaction was run as shown in the following example for polyimide **1a**: In a 100 mL three-necked flask, equipped with mechanical stirrer and nitrogen inlet and outlet, were introduced diamine **DABA** (1.52 g, 0.01 mol) and 50 mL of NMP. The mixture was stirred under nitrogen to complete dissolution. Then dianhydride **6FDA** (4.44 g, 0.01 mol) was added to the solution, under stirring at room temperature. The mixture became clear rapidly with a slight exothermic effect. The resulting colorless solution was maintained under stirring and nitrogen stream for 8 h to yield a viscous solution of poly(amic acid). Then, a mixture of acetic anhydride/pyridine (6 mL/3 mL) was added and the solution was stirred overnight at room temperature, and 1.5 h at 80 °C. The solution was poured into water and the precipitate that formed was washed several times with water and ethanol. The final polyimide was dried in a vacuum oven at 120 °C for 12 h. Polyimides **1b** and **1c** were synthesized according to the above procedure, using dianhydride **6HSi** or dianhydride **6HDA** instead of **6FDA**, while copolyimide **2a** was prepared from **DABA** and equimolar amount of dianhydrides **6HSi** and **6HDA**. Copolyimides **2b** and **2c** were prepared from equimolar amount of **DABA** and **6HDM** with dianhydrides **6FDA** or **6HSi**, respectively (Table 1).

CONCLUSIONS

Aromatic polyimides and copolyimides containing pendant carboxylic groups were synthesized and characterized. Some of the physical properties such as solubility and glass transition temperature were studied and correlated with the conformational rigidity of their macromolecular chains. The introduction of flexible groups such as isopropylidene, hexafluoroisopropylidene, dimethylsilane or aromatic ether units, led to polymers with high solubility, good film forming ability, while maintaining a good thermal stability. The solubility of the polymers correlated well with the Kuhn segment values. Also, the glass transition temperature increased with the increase of conformational rigidity parameters.

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