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Synthesis of fluorinated poly(phenylquinoxaline-amide)s and study of thin films made therefrom

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Abstract

A series of five fluorinated poly(phenylquinoxaline-amide)s were synthesized by a polycondensation reaction of a diacid chloride containing the hexafluoroisopropylidene (6F) group, namely 2,2-bis(*p*-chlorocarbonylphenyl)-hexafluoropropane, with various aromatic diamines incorporating two phenyl-substituted quinoxaline rings. These polymers were easily soluble in polar aprotic solvents such as *N*-methylpyrrolione (NMP), dimethylformamide (DMF), and tetrahydrofurane (THF), and showed a high thermal stability with decomposition temperatures above 400°C and glass transition temperatures in the range of 260–290°C. Polymer solutions in NMP were processed into free-standing films that showed low dielectric constant values, in the range of 3.4–3.9, and good mechanical properties, with tensile strength in the range of 40–80 MPa and elongation to break in the range of 22–55%. Very thin films, in the range of tens of nanometer, which were deposited onto silicon wafers exhibited very smooth surfaces, free of pinholes when studied by atomic force microscopy (AFM). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(phenylquinoxaline-amide)s; Hexafluoroisopropylidene groups; AFM investigations

1. Introduction

Wholly aromatic polyamides have already been noted for their high temperature resistance and excellent mechanical properties. They are also considered as difficult processable materials because of their insolubility in common organic solvents and too high glass transition temperatures (T_g). As such problems restrict the further applications of aromatic polyamides, considerable effort has been made to improve their processing properties by structural modifications. One of the approaches to improving solubility and lowering T_g is the use of selected heterocyclic monomers in the synthesis of aromatic polyamides [1]. Among various heterocyclic units which have been introduced into the main chain of aromatic polyamides, the phenyl-substituted quinoxaline rings proved to be very beneficial [2,3]. Such polymers exhibited an improved solubility in organic solvents and therefore a better capability to be processed from solutions, while maintaining a high thermal resistance. Also, it was shown that the incorporation of hexafluoroisopropylidene groups into the aromatic polymer backbone increases its solubility, lipophilicity, optical transparency and flame resistance, while decreasing its crystallinity, dielectric constant, water absorption and surface energy [4–6]. We considered that some polyamides in which both phenylquinoxaline rings and hexafluoroisopropylidene groups are present in the same polymer chain would have a superior combination of useful properties and processing capability, particularly appropriate for casting into very thin films.

In the present article we report the synthesis of five fluorinated poly(phenylquinoxaline-amide)s by the polycondensation reaction of a fluorinated diacid chloride, namely 2,2-bis(*p*-chlorocarbonylphenyl)-hexafluoropropane or hexafluoroisopropylidene-bis(benzoyl chloride), with certain aromatic diamines having two preformed phenylquinoxaline rings. The thermal stability, glass transition temperature, dielectric constant and the quality of the thin films made from these polymers were investigated and compared with those of the related polymers.

2. Experimental

2.1. Synthesis of the polymers

Fluorinated poly(phenylquinoxaline-amide)s **II** were synthesized by low-temperature solution polycondensation

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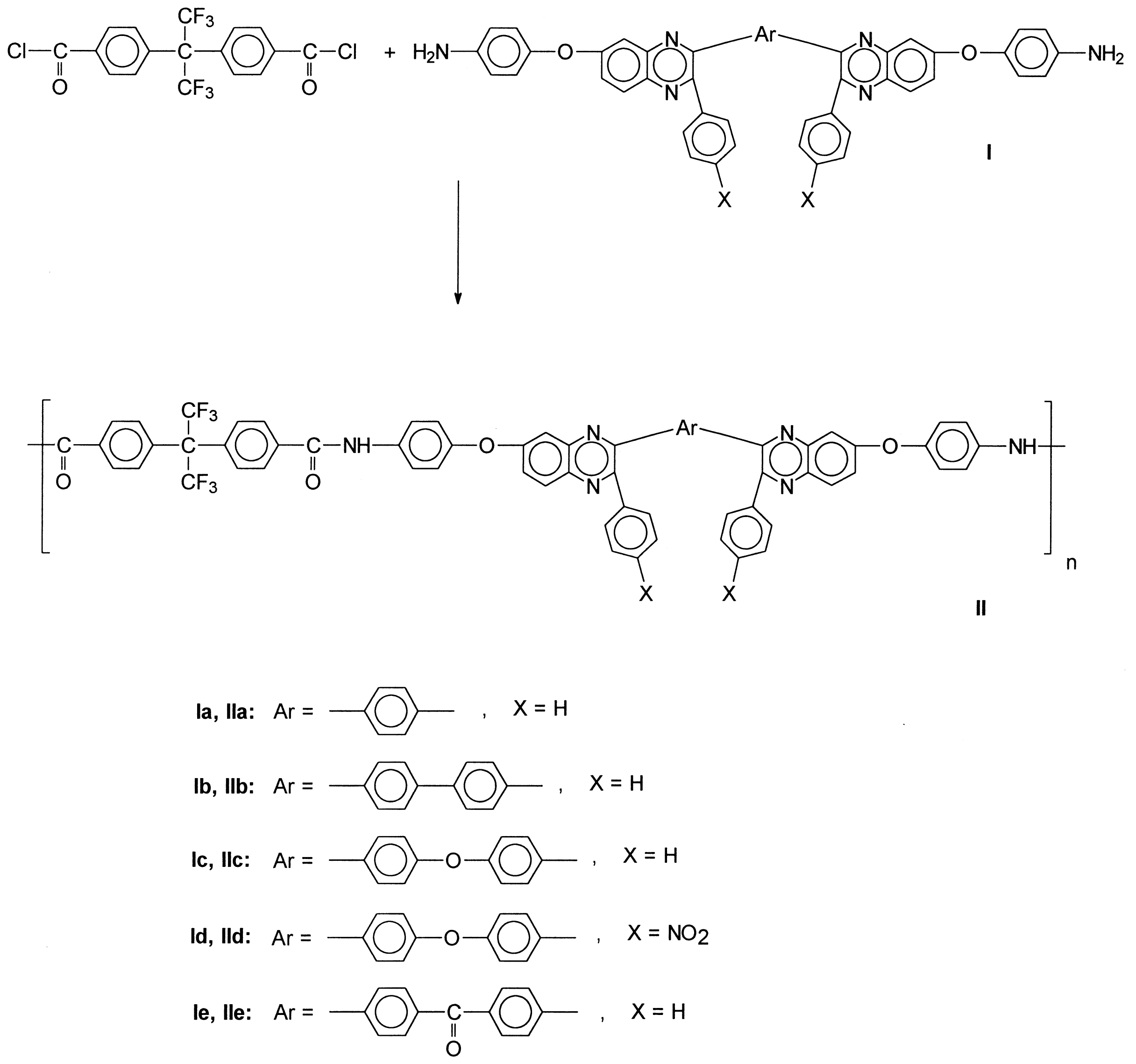

Scheme 1. Synthesis of fluorinated poly(phenylquinoxaline-amide)s **II**.

reaction of equimolar amounts of diaminophenylquinoxalines **I** [7] with 2,2-bis(*p*-chlorocarbonylphenyl)-hexafluoropropane [8], in NMP as a solvent and in the presence of propylene oxide as an acid acceptor (Scheme 1). The relative amount of monomers and NMP were adjusted to maintain a solid content of 10–12%. The resulting viscous polymer solution was used to cast films, or it was poured into water and the precipitated polymer was recovered by filtration followed by repeated washings. The following example illustrates the general procedure.

In a 100 ml three-necked flask fitted with a mechanical stirrer and a nitrogen-inlet and outlet, 1.40 g (0.002 mol) of diamine **Ia**, 20 ml NMP and 0.5 ml propylene oxide were added and the mixture was stirred until complete dissolution occurred. The solution was cooled to −10°C and 0.858 g (0.002 mol) of diacid chloride was added with rapid stirring. The content of the flask was maintained below 0°C for 10 min, then the cooling bath was removed, and the reaction mixture was allowed to reach the room temperature and it was stirred further for 2 h. A part of the resulting viscous solution was poured into water under vigorous stirring and the precipitated fibrous product was filtered, washed thoroughly with water and ethanol under stirring and it was then dried in vacuum at 100°C for 1 h. The precipitated polymer was used for viscosity measurements and thermal analysis.

2.2. Preparation of the films

A part of the viscous polymer solution, resulting from the polycondensation reaction, was cast onto glass plates which were then heated to evaporate the solvent at 100, 130, 160 and 210°C, for periods of 30 min each. The transparent free standing films were stripped off the glass plates and were

Table 1
Properties of fluorinated poly(phenylquinoxaline-amide)s **II**

Polymer	η_{inh}[a]	IDT[b] (°C)	T_{10}[c] (°C)	T_g[d] (°C)	Tensile strength (MPa)	Elongation to break (%)	Dielectric constant[e]
IIa	0.7	415	504	289	78	55	3.48
IIb	0.55	450	505	292	80	53	3.49
IIc	0.8	461	516	264	59	48	3.61
IId	0.75	380	450	291	37	22	3.93
IIe	0.7	417	524	285	64	34	3.59

[a] Determined for polymer solutions in NMP of concentration 0.5%, at 20°C.
[b] The IDT is the temperature of 5% weight loss, from TGA curves.
[c] Temperature of 10% weight loss, from TGA curves.
[d] Glass transition temperature, from the DSC curves.
[e] Measured at 10 kHz.

used for recording IR spectra and for dielectric measurements. Another part of the polymer solution was diluted with NMP to 1–2% concentration and was used to deposit very thin films, in the range of tens of nanometers, onto silicon wafers by the spin-coating technique, at a rate of 2000–5000 rotations/min. These films, as-deposited, were gradually heated up to 200°C in the same way as described earlier, to remove the solvent and were used for AFM investigations.

2.3. Measurements

The infrared spectra were obtained with a Nicolet Magna FTIR-spectrophotometer by using polymer films of 4–7 μm thickness or by using precipitated polymers ground into potassium pellets.

The inherent viscosities (η_{inh}) were determined at 20°C for polymer solutions of 5 g/l in NMP by using a Ubbelohde viscometer.

The thermogravimetric analysis (TGA) of the precipitated polymers was performed with a Seiko-Robotic TG/DTA 320 equipment, operating at a heating rate of 10°C/min. Samples of 5–7 mg of each polymer were heated in a platinum pan in air at a purge rate of 300 ml/min. Weight loss versus temperature plots were used for calculating the results. The temperature of 5% weight loss was regarded as the initial decomposition temperature (IDT). Also, the temperature of 10% weight loss was calculated from the resulting thermograms.

The glass transition temperatures (T_g's) of the precipitated polymers were determined with a Seiko differential scanning calorimeter DSC 220 C. Samples of 5–7 mg of each polymer were heated in a crimped aluminium pan from an ambient temperature to above 300°C. All heating and cooling ramps were at 10°C/min, under nitrogen, at a purge rate of 50 ml/min. Heat flow versus temperature plots from the second scan were used for reporting the glass transition. The mid-point of the inflection curve resulting from the typical second heating was assigned as the T_g of the respective polymers.

The tensile properties of polymer films were measured with a tensile testing machine, by recording the uniaxial stress–strain curves, with a cross-head speed of 9.0 mm/min, at room temperature. The dumbbell-type specimen was 10 mm wide at the two ends and 4.5 mm wide and 10 mm long at the neck.

The dielectric constant of polymer films having a thickness of 15–20 μm were determined by using the fluid displacement method which was previously described [9]. The capacitance of the films was measured by using circular gold electrodes (diameter 2.54 cm) mounted in a brass dielectric cell held at a constant temperature (25°C) and a Gen Rad Precision LC Digibridge (Model 1688) operating at 10 kHz.

The surfaces of the films were investigated by atomic force microscopy (AFM) by using a SA1/BD2 apparatus (Park Scientific Instruments) in the contact mode, under a constant force, Si_3N_4 pyramidal type, $k_f = 0.032$ N/m.

Model molecules for a polymer fragment were obtained by Molecular Mechanics (MM^+) with the Hyperchem Program, Version 4.0 [10].

3. Results and discussion

The structures of fluorinated poly(phenylquinoxaline-amide)s **II** were identified by elemental analysis, IR and ^{1}H NMR spectra. All IR spectra exhibited broad absorption bands at 3430 cm^{-1} characteristic for N–H and at 1680 cm^{-1} because C=O in amide groups. Absorption peaks at 1348 and 1315 cm^{-1} were attributed to quinoxaline rings. All the polymers showed IR bands at 1174 and 1210 cm^{-1} which were assigned to the hexafluoroisopropylidene groups. Absorption bands which were found at 1244 cm^{-1} were attributed to aromatic ether Ar–O–Ar. Aromatic C–H absorptions were found at 3065 cm^{-1}, while aromatic C=C bonds appeared at 1610 and 1510 cm^{-1}. The ^{1}H NMR spectra show the N–H peak of the amide bond at 10.58 ppm and the related aromatic proton resonances.

All the polyamides **II** are soluble in polar aprotic solvents

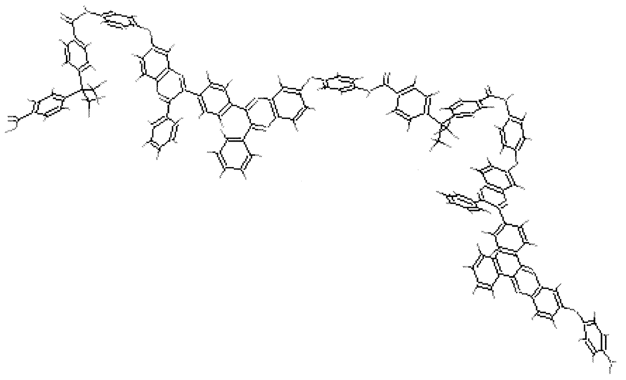

Fig. 1. Model of a fragment incorporating two repeating units of the polymer **IIa**.

such as NMP or DMF, and even in less polar liquids such as tetrahydrofuran (THF). The inherent viscosities of the polymers are in the range of 0.55–0.8 dl/g (Table 1). The improved solubility of the present polyamides compared with the traditional aromatic polyamides is explained by the presence of the voluminous phenylquinoxaline units and flexible 6F groups which determine a less efficient intermolecular packing through hydrogen bonds between amide groups and thus facilitate the penetration of solvent molecules among the polymer chains. The shape of a macromolecule fragment can be visualized by molecular modeling (Fig. 1), being far from a linear rigid rod shape of a classical aromatic polyamide.

All these products gave transparent free-standing films by casting from 10–12% polymer solutions. The films were flexible and creasable. Very thin films having a thickness in the range of 20–50 nm were deposited by the spin-coating technique onto silicon wafers, by using diluted polymer solutions (concentration 1–2%). The homogeneity of film surfaces was studied by AFM. All the films exhibited a very smooth surface, without any defects or pinholes, over large scanning ranges (1–100 μm), as can be seen in Table 2 and Fig. 2(a) and (b). In Table 2 we only give the scanning range of 3–30 μm which represents the typical conditions to evaluate the root mean square (RMS) roughness. The RMS value of 5–16 Å which is shown in Table 2 is in the same range as that of the highly polished silicon wafers which were used as substrates, which means that the deposited films are very smooth.

Table 2
Surface roughness of polymer films

Polymer	Scan field (μm)	RMS[a] (Å)
IIa	3 × 3	5.4
	10 × 10	5.6
	30 × 30	8.5
IIb	10 × 10	9.8
	30 × 30	11
IIc	3 × 3	5.4
	10 × 10	5.9
	30 × 30	6.9
IId	3 × 3	11.7
	10 × 10	12.4
	30 × 30	12.9
IIe	10 × 10	16.3
	30 × 30	14.6

[a] Root mean square roughness, determined from typical AFM images.

The thermal stability of the polymers was studied by TGA. A typical thermogram is shown in Fig. 3. These polymers do not show a significant weight loss up to 400°C. The IDT (5% weight loss) is in the range of 415–465°C and the 10% weight loss is in the temperature range of 500–525°C, except for the polymer **IId** whose values are 380 and 450°C, respectively (Table 1). The overall thermal behavior of these polymers is very similar to that of the related poly(phenylquinoxaline-amide)s which do not contain 6F groups [11] and to aromatic polyamides [1]. Knowing that the degradation of aromatic polyphenylquinoxalines does not take place below 500°C [11], it can be stated that the decomposition of the present polymers begins with the rupture of amide groups. Therefore, the thermal stability of all these polymers is mainly determined by the amide bridges. In the case of the polymer **IId** the slightly lower IDT (380°C) could be explained by the presence of nitro groups which are more sensitive to thermal degradation. Also, the temperature of 10% weight loss of this polymer **IId** is 450°C, while that of the others (**IIa**, **IIb**, **IIc**, **IIe**) is above 500°C. A similar thermal behavior was shown by previously reported poly(amide–imide)s [12] and polyamides [13–15], both containing the *p*-nitro-phenyl substituted quinoxaline rings, which were prepared by using the same diamine **Id** but with other diacid chlorides. The lower decomposition temperature of the polymer **IId** also can be due to the loss of residual NMP which could have been retained by the polar nitro groups.

The glass transition temperatures, as shown by the DSC analysis, are in the range of 268–295°C (Table 1). A typical DSC curve is shown in Fig. 4. It can be observed that there is a large interval between glass transition and decomposition temperature for all these polymers which can be advantageous for their processing by thermoforming techniques.

The tensile properties of the polymer films are summarized in Table 1. The films have tensile strengths in the range of 37–80 MPa and elongation to break in the range of 22–55%. These values are comparable to those of the related aromatic polyamides [16].

Electroinsulating properties of these polymers have been evaluated on the basis of dielectric constant values. The dielectric constant of polymer films is in the range of 3.4–3.9, as shown in Table 1. The slightly higher dielectric constant (3.9) of the polymer **IId** compared with polymers **IIa**, **IIb**, **IIc**, **IIe** is attributed to the high polarizability of the nitro groups which are pendent along the macromolecules. A similar influence of the nitro groups on the dielectric constant was observed in the case of previously reported poly(amide–imide)s containing the *p*-nitro-phenyl

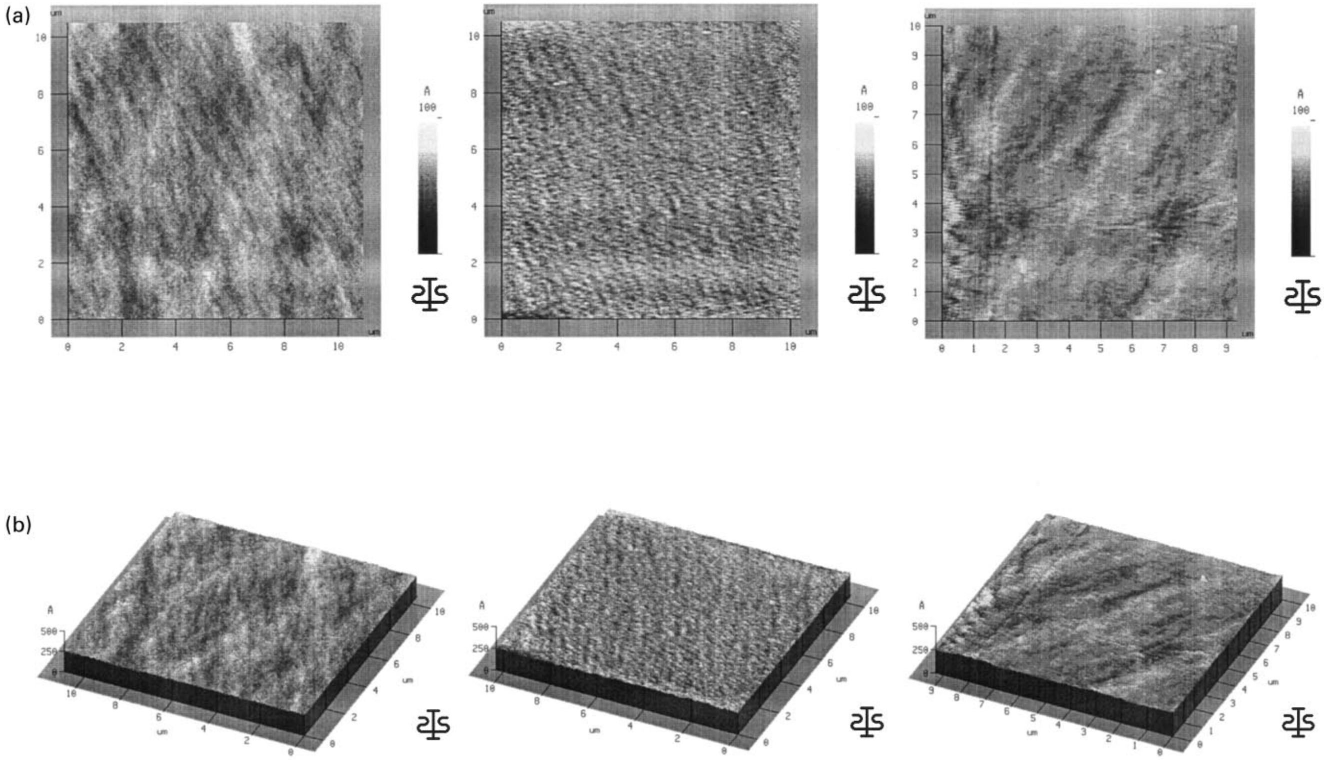

Fig. 2(a). Top-view AFM images of the polymer films **IIa**, **IIb**, **IIe**; 2(b) side-view AFM images of the polymer films **IIa**, **IIb**, **IIe**.

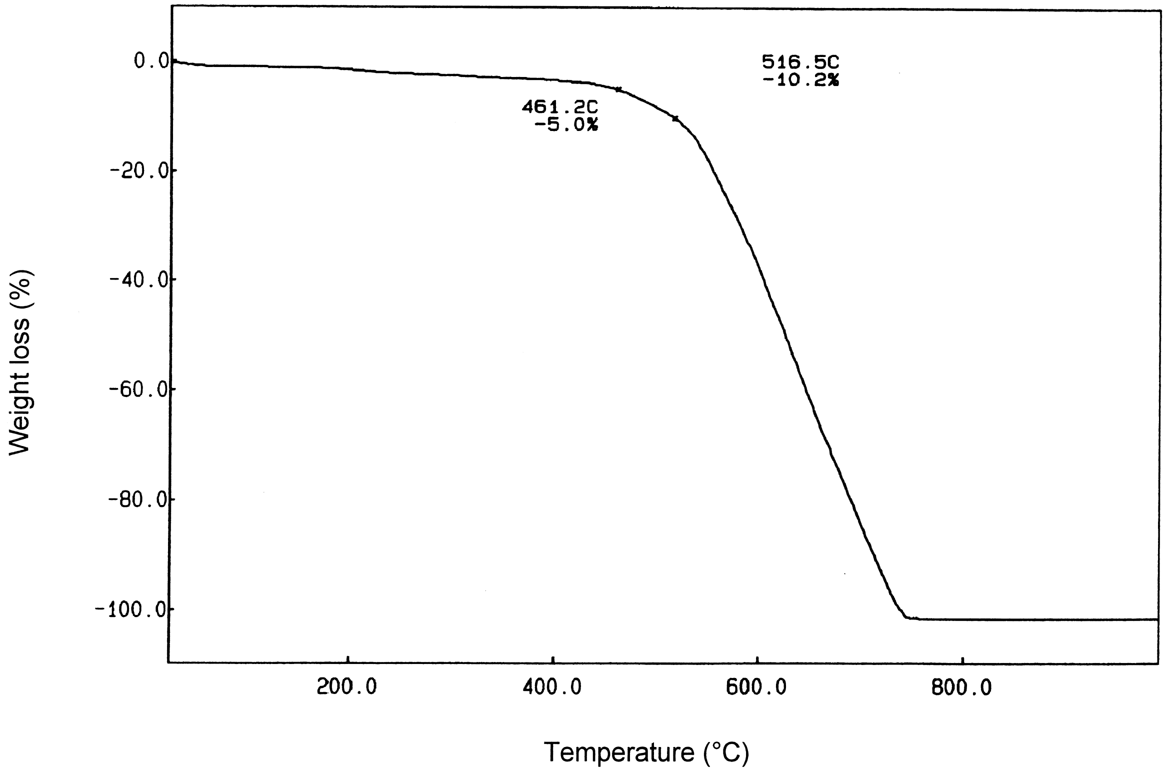

Fig. 3. The TGA curve of the polymer **IIc**.

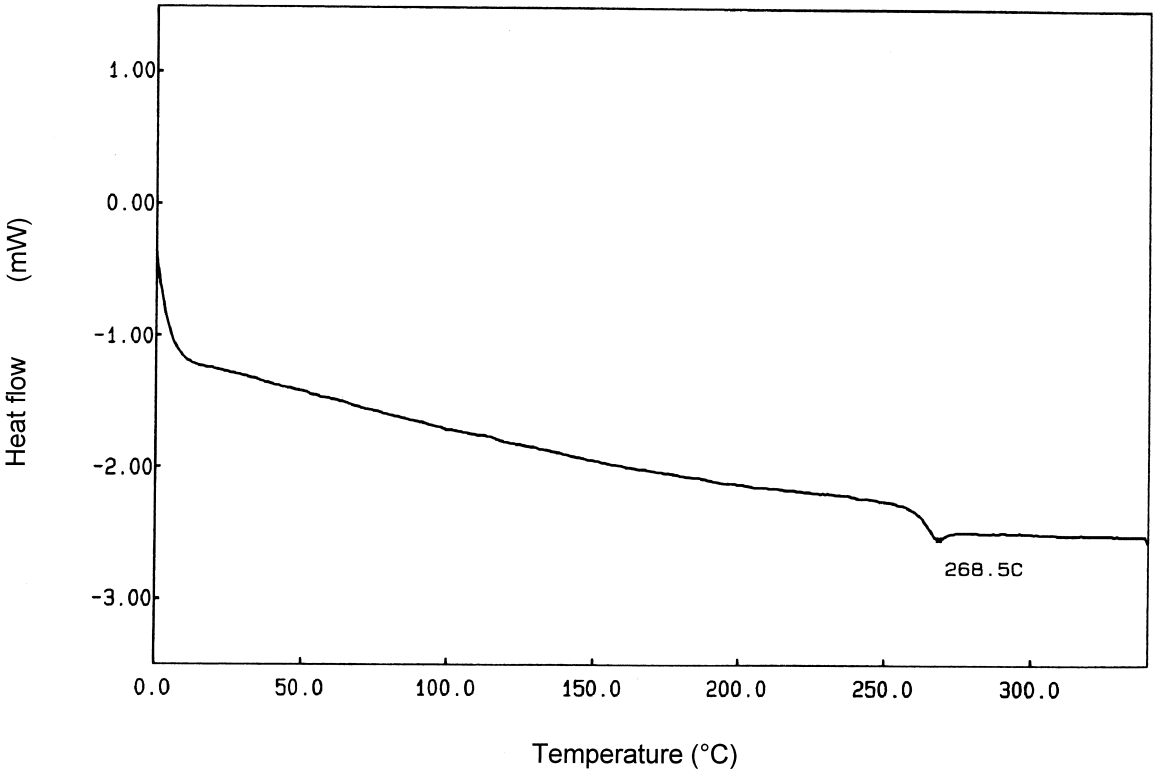

Fig. 4. The DSC curve of the polymer **IIc**.

substituted quinoxaline rings [17]. The dielectric constant values of the present polymers are comparable with that of other high performance dielectrics such as fully aromatic polyimides, whose value is 3.5 [18]. They are also comparable with previously reported poly(phenylquinoxaline-imide–amide)s without 6F groups, whose dielectric constant is in the range of 3.2–3.7 [19] and with other heterocyclic polyamides which do not contain 6F groups, whose dielectric constant is in the range of 3.3–4.0 [20,21]. These facts show that the dielectric constants are mainly influenced by the highly polarized carbonyl groups in all these types of polymers [22]. Thus, the introduction of 6F groups into the chain of poly(phenylquinoxaline-amide)s did not influence substantially the dielectric constant of these polymers. The most important advantage of the 6F groups being introduced into these polymers is the remarkable solubility and easy processability into high quality thin films. The potential use of such thin films in microsensor devices is under investigation.

4. Conclusions

A series of polyamides containing phenylquinoxaline rings and hexafluoro-isopropylidene bridges in the main chain were prepared and compared with classical aromatic polyamides or with other heterocyclic polyamides which do not have 6F groups. Incorporation of 6F moities along with phenylquinoxaline rings into an aromatic polyamide backbone gave easily soluble and processable compounds while maintaining a high thermal stability and a large window between glass transition and decomposition temperature. These polymers exhibit an outstanding capability to be processed from solution into thin and ultrathin films having very smooth and defectless surface, low dielectric constant and good mechanical properties. Potential applications in microelectronics or related advanced fields are foreseen.

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