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New fluorinated poly(1,3,4-oxadiazole-ether-imide)s

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Abstract

New fluorinated poly(1,3,4-oxadiazole-ether-imide)s have been prepared by solution polycondensation reaction of different aromatic diamines having preformed 1,3,4-oxadiazole ring, such as 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole, 2,5-bis[*p*-(4-aminophenoxy)phenyl]-1,3,4-oxadiazole, 2,5-bis[*p*-(3-aminophenoxy)phenyl]-1,3,4-oxadiazole, 2-(4-dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole and 2-(4-fluorophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole, with an aromatic dianhydride incorporating ether linkages and hexafluoroisopropylidene group, namely 1,1,1,3,3,3-hexafluoro-2,2-bis-[(3,4-dicarboxyphenoxy)phenyl]-propane dianhydride. The polymers were easily soluble in polar organic solvents, such as *N*-methylpyrrolidinone, *N*,*N*-dimethylformamide, and pyridine, as well as in certain low boiling-point organic solvents, such as tetrahydrofuran and chloroform. Very thin coatings deposited onto silicon wafers exhibited smooth, pinhole-free surface in atomic force microscopy. The polymers showed high thermal stability with decomposition temperature being above 410 °C. They exhibited a glass transition in the temperature range of 183–217 °C, with reasonable interval between glass transition and decomposition temperature. Solutions of some polymers in *N*,*N*-dimethylformamide exhibited blue fluorescence, having maximum emission wavelength in the range of 411–424 nm.

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Keywords: Fluorinated poly(1,3,4-oxadiazole-ether-imide)s; Good solubility; High thermal stability

1. Introduction

Aromatic polyimides are a class of polymers known for their high thermal stability, excellent electrical and mechanical properties, and good chemical resistance. Some of these polymers have been widely used in industry as structural materials and as insulating layers in integrated circuits. However, the application of most polyimides is limited due to their insolubility in conventional solvents and extremely high glass transition temperature which make their processing very difficult [1]. Therefore, the processing of the polyimides is generally carried out via soluble poly(amic acid) precursors, which are cast onto various substrates and then they are converted into polyimide films by thermal treatment. This process has severe inherent limitations, like the emission of volatile by-products during curing, and storage instability of the poly(amic acid) intermediates. Polyimides that are soluble in organic solvents may be prepared through the so called one step or single-stage method. In this procedure, the dianhydride and diamine are stirred in a high boiling-point organic solvent at a temperature above 180 °C. Under these conditions, chain growth and imidization essentially occur spontaneously [2].

Various efforts have been made on the synthesis of soluble and processable polyimides without much sacrifice of their excellent thermostability. The introduction of kinks or flexible linkages, noncoplanar units or bulky lateral groups along the backbone was used to improve the solubility of these polymers. The main concept behind all these approaches is the reduction of several types of polymer chain–chain interactions, and the reduction of chain packing and charge transfer electronic polarization interactions [3,4]. It has been generally recognized that aromatic ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. In general, such a structural modification leads to lower glass transition temperature and crystalline melting temperatures as well as significant improvement in solubility and other processing characteristics of the

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polymers without greatly sacrificing other advantageous polymer properties [5,6]. Also, the incorporation of hexafluoroisopropylidene (6F) groups into polymer backbones enhances the polymer solubility without sacrificing thermal stability. The retention of high thermal stability is attributed to the strong C–F bonds. Other effects of the 6F groups are the increased glass transition temperature and flame resistance with a concomitant decreased crystallinity and water absorption. The bulky 6F groups also serve to increase the free volume of the polymers, thus improving its electrical insulating characteristics [7–10]. Different classes of fluorinated thermostable polymers have been developed including heterocyclic polymers such as polyimides [11–15], poly(1,3,4-oxadiazole)s [16,17], polyphenylquinoxalines [18]. These polymers have been largely studied as potential candidates for practical use in microelectronics and related industries.

Recently, fluorinated polyetherimides having high thermal stability, good solubility and excellent electrical properties were reported [19–21].

Poly-1,3,4-oxadiazoles have received considerable interest for the production of high-performance materials due to their high thermal stability in oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring. It has been shown that from the spectral and electronic point of view, the oxadiazole cycle is similar to a *p*-phenylene structure, which is known to be highly thermoresistant. Also, it doesn't contain any hydrogen atoms, it lacks tension, it doesn't have any possibilities of rearrangement, it has structural symmetry, and it is thermally unreactive [22]. More recently, specific properties determined by the electronic structure of oxadiazole ring, especially its electron-withdrawing character, revigourated an intensive research aiming to use such polymers as advanced materials in microelectronics, optoelectronics and other [23].

In continuing our research on the preparation of processable high temperature polymers we report here the synthesis of new fluorinated poly(1,3,4-oxadiazole-ether-imide)s by solution polycondensation of some aromatic diamines containing preformed 1,3,4-oxadiazole rings with a dianhydride having ether linkages and hexafluoroisopropylidene group. The properties of these polymers, such as solubility, inherent viscosity, thermal stability, glass transition temperature, film forming ability and the quality of the thin films made from these polymers as well as their fluorescence ability have been investigated.

2. Experimental

2.1. Synthesis of the monomers

The diamines which were used in the synthesis of the polymers are shown in Scheme 1. They were prepared as follows: 2,5-bis(*p*-aminophenyl)-1,3,4-oxadiazole, **1a**, was prepared by the reaction of *p*-aminobenzoic acid with hydrazine hydrate in polyphosphoric acid (PPA) [24]; mp 260–262 °C. 2,5-Bis[*p*-(4-aminophenoxy)phenyl]-1,3,4-oxadiazole, **1b**, and 2,5-bis[*p*-(3-aminophenoxy)phenyl]-1,3,4-oxadiazole, **1c**, were synthesized starting from *p*-fluorobenzoic acid (2 mol) and hydrazine hydrate (1 mol) which reacted in PPA to produce 2,5-bis-(*p*-fluorophenyl)-1,3,4-oxadiazole. The reaction of the latter (1 mol) with 4-aminophenol or 3-aminophenol (2 mol) and K_2CO_3 in *N*-methylpyrrolidinone (NMP) at 150 °C gave the diamines **1b** and **1c**, respectively [25]; mp of **1b**: 225–227 °C; mp of **1c**: 189–192 °C. 2-(4-Dimethylaminophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole, **1d**, has been synthesized by a multistep procedure, starting from *p*-dimethylamino-benzhydrazide and 3,5-dinitrobenzoyl chloride, according to a published method [26]; mp 203–205 °C.

2-(4-Fluorophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole, **1e**, was prepared by starting from 3,5-dinitrobenzoyl chloride and *p*-fluorobenzhydrazide, through a sequence of reactions, as shown in Scheme 2.

A detailed description of preparation for diamine **1e** is as follows.

2.1.1. *N*-(3,5-Dinitrobenzoyl)-*N*′-(4-fluorobenzoyl)-hydrazine (**1′e**)

4-Fluorobenzhydrazide (6.391 g, 41.5 mmol), NMP (60 ml) and pyridine (3.5 ml) were placed in a 100 ml three-necked flask equipped with mechanical stirrer, and the mixture was stirred until complete dissolution was achieved. The solution was cooled to 0 °C, and 3,5-dinitrobenzoyl chloride (9.565 g, 41.5 mmol) was added under stirring. The flask content was kept at 0 °C for 1 h and at room temperature for 6 h. The reaction mixture was precipitated into water and the resulting precipitate was filtered, washed with water and dried.

Yield: 13.3 g (92.1%); mp 268–270 °C. Elem. Anal. Calcd for $C_{14}H_9FN_4O_6$ (348.05 g mol^{-1}) (%): C, 48.29; H, 2.60; N, 16.09. Found (%): C, 48.19; H, 2.75; N, 15.91.

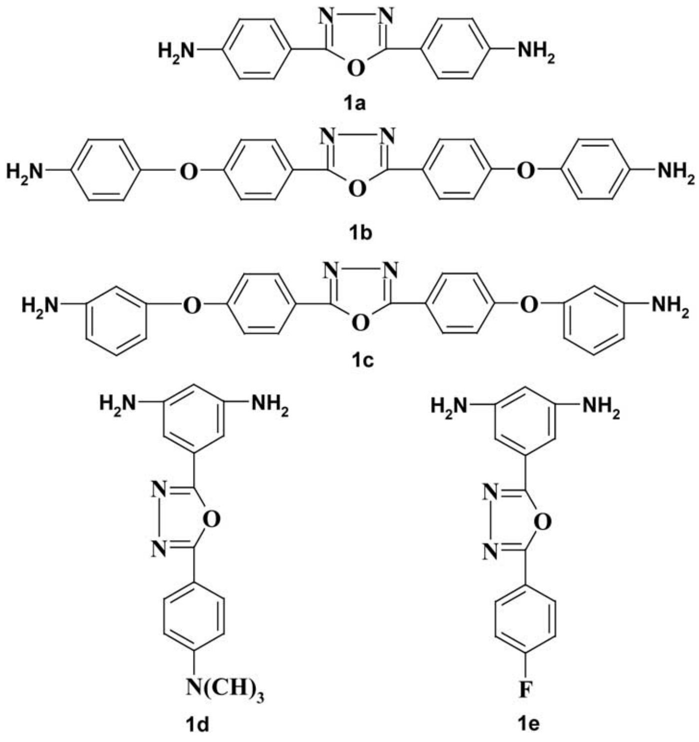
IR (KBr, cm^{-1}): 3260 (NH), 3100 (C–H aromatic), 1710 and 1650 (C=O), 1550 and 1385 (NO_2 groups).

^{1}H NMR (DMSO-d_6, 250 MHz, ppm): $\delta = 11.3$ (NH), 10.8 (NH), 9.10 (2H, H_b), 9.03 (1H, H_a), 8.02 (2H, H_c), 7.43 (2H, H_d).

^{13}C NMR (DMSO-d_6, 250 MHz, ppm): $\delta = 167.0$, 165.2 (C^9), 165.0, 162.0 (C^5, $C^{5'}$), 148.5 (C^2), 135.0 (C^4), 130.5 (C^7), 129.0 (C^6), 128.0 (C^3), 122.0 (C^1), 116.0 (C^8).

2.1.2. 2-(4-Fluorophenyl)-5-(3,5-dinitrophenyl)-1,3,4-oxadiazole (**1″e**)

N-(3,5-dinitrobenzoyl)-*N*′-(4-fluorobenzoyl)-hydrazine **1′e** (11 g) and $POCl_3$ (150 ml) were introduced in a flask equipped with magnetic stirrer, and refluxed for 2 h. After cooling to room temperature, the reaction mixture was poured in an ice–water mixture, and the resulting precipitate was filtered, washed several times with water and dried.



Scheme 1. Structure of the diamines **1**.

Yield: 10.1 g (95.8%); mp 234–235 °C. Elem. Anal. Calcd for $C_{14}H_7FN_4O_5$ (330.04 g mol^{-1}) (%): C, 50.92; H, 2.14; N, 16.97. Found (%): C, 50.75; H, 2.21; N, 16.81.

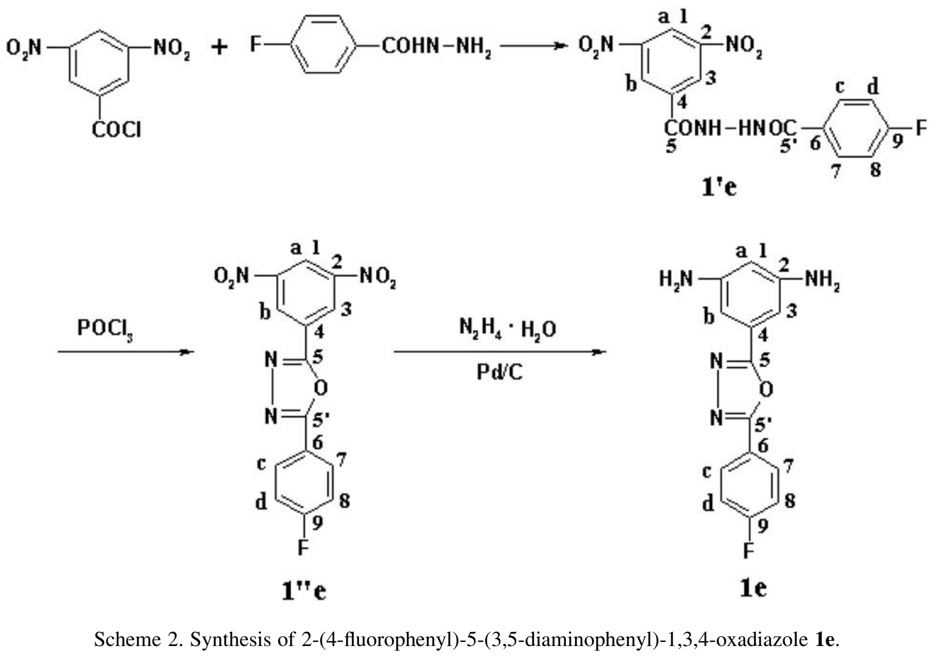
IR (KBr, cm^{-1}): 3100 (C–H aromatic), 1610 (aromatic), 1020, 980 (1,3,4-oxadiazole ring).

^{1}H NMR (DMF-d_7, 250 MHz, ppm): $\delta = 9.31$ (2H, H_b), 9.15 (1H, H_a), 8.40 (2H, H_c), 7.57 (2H, H_d).

^{13}C NMR (DMF-d_7, 250 MHz, ppm): $\delta = 166.8$, 162.7 (C^9), 165.1, 162.2 (C^5, $C^{5'}$), 148.7 (C^2), 135.2 (C^4), 130.6 (C^7), 129.0 (C^6), 128.0 (C^3), 121.8 (C^1), 116.0 (C^8).

*2.1.3. 2-(4-Fluorophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole (**1e**)*

The dinitrocompound **1″e** (3 g) and 10% Pd/C catalyst (0.05 g) were suspended in ethanol (80 ml). The suspension was heated to reflux, and hydrazine monohydrate (25 ml)



Scheme 2. Synthesis of 2-(4-fluorophenyl)-5-(3,5-diaminophenyl)-1,3,4-oxadiazole **1e**.

was added dropwise. The reflux was continued for about 10 h. The catalyst was removed by hot filtration. The precipitate was recrystallized twice from ethanol.

Yield: 1.41 g (61%); mp 248–250 °C. Elem. Anal. Calcd for $C_{14}H_{11}FN_4O$ (270.09 g mol^{-1}) (%): C, 62,22; H, 4.10; N, 20.73. Found (%): C, 62.15; H, 4.22; N, 20.66.

IR (KBr, cm^{-1}): 3415, 3320 and 3225 (NH-amine), 1020 and 980 (1,3,4-oxadiazole ring).

^{1}H NMR (DMSO-d_6, 250 MHz, ppm): $\delta = 8.34$ (2H, H_c), 7.70 (2H, H_d), 6.81 (2H, H_b), 6.28 (1H, H_a), 5.30 (NH).

^{13}C NMR (DMSO-d_6, 250 MHz, ppm): $\delta = 166.5$, 162.5 (C^9), 165.5, 163.0 (C^5, $C^{5'}$), 150.5 (C^2), 129.7 (C^7), 124.0, 120.5 (C^4, C^6), 117.0 (C^8), 103.0 (C^1), 101.0 (C^3).

1,1,1,3,3,3-Hexafluoro-2,2-bis-[(3,4-dicarboxyphenoxy) phenyl]-propane dianhydride, **2**, has been prepared according to [27]; mp 229–231 °C.

2.2. Synthesis of the polymers

Fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3** were prepared by solution polycondensation reaction of equimolar amounts of aromatic diamines containing 1,3,4-oxadiazole ring **1** with 1,1,1,3,3,3-hexafluoro-2,2-bis-[(3,4-dicarboxyphenoxy)phenyl]-propane dianhydride, **2**, in NMP as a solvent. A typical polycondensation was run as shown in the following example: In a 100 ml three-necked flask equipped with mechanical stirrer and nitrogen-inlet and outlet were introduced diamine **1a** (0.378 g, 1.5 mmol) and NMP (11 ml). The mixture was stirred under nitrogen to complete dissolution. Then the dianhydride **2** (0.942 g, 1.5 mmol) was added to the resulting solution and stirring was continued for 6 h. The solution became viscous. It was then heated at 180–185 °C for 4 h, under a nitrogen stream, to perform the cyclization of the polyamic acid **3′a** to the corresponding polyimide structure **3a**. The water evolved during imidization was removed from the reaction mixture with the slow stream of nitrogen which was used as inert medium. 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 under stirring and it was then dried at 120 °C.

2.3. Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). 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. Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 300 instruments, by using solutions in deuterated dimethylsulfoxide (DMSO-d_6), *N*,*N*-dimethylformamide (DMF-d_7) or chloroform ($CDCl_3$). UV spectra of polymer solutions in DMF were recorded on a Perkin–Elmer Lambda 15 spectrometer. The fluorescence spectra of polymer solutions in DMF were obtained with a SPEX fluorolog II (212) spectrometer. The molecular weight was determined by gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. Measurements were carried out with polymer solutions of 2% concentration in DMF containing 0.1 M $NaNO_3$ and by using DMF with 0.1 M $NaNO_3$ as eluent. Polystyrene standards of known molecular weight were used for calibration. Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 12 °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. The surfaces of the very thin films as-deposited on silicon wafers were studied by atomic force microscopy (AFM) with a SA1/BD2 apparatus (Park Scientific Instruments) in contact mode, under a constant force, with a pyramidal type tip.

3. Results and discussion

The diamines containing 1,3,4-oxadiazole ring **1a**, **1b**, **1c** and **1d** (Scheme 1) have been synthesized by using reported procedures. The diamine **1e** has been prepared through a sequence of reactions, as shown in Scheme 2. 3,5-Dinitrobenzoyl chloride reacted with *p*-fluorobenzhydrazide in NMP as solvent to give *N*-(3,5-dinitrobenzoyl)-*N′*-(4-fluorobenzoyl)-hydrazine **1′e**. The cyclodehydration of **1′e** with phosphorous oxychloride gave the corresponding dinitro-1,3,4-oxadiazole derivative **1″e**. Finally, the reduction of the latter with hydrazine hydrate in the presence of Pd/C catalyst, in ethanol, afforded the diamino-1,3,4-oxadiazole derivative **1e**.

The structures of dinitro-compounds **1′e**, **1″e** and diamine **1e** were confirmed by elemental analyses as well as IR and NMR spectroscopy. The spectra are in good agreement with the proposed molecular structures. In the IR spectrum of **1′e** absorption bands at 1550 and 1385 cm^{-1} were due to nitro groups and the strong absorption bands that appeared at 3260, 1710, and 1650 cm^{-1} were attributed to NHCO groups. In the IR spectrum of **1″e** the absorption bands for amide groups disappeared and new absorption bands appeared at 980 and 1020 cm^{-1} due to =C–O–C= stretching vibration in oxadiazole ring. The absorption bands at 3415, 3320, and 3225 cm^{-1} in the IR spectrum of compound **1e** were attributed to the aromatic primary amine groups. In the ^{1}H NMR spectrum of cyclized dinitrocompound **1″e**, the aromatic protons (H_b) in the *ortho* position to the nitro group have the largest chemical shift (9.31 ppm) due to the effect of nitro group. In the ^{1}H NMR spectrum of diamine **1e**, the chemical shift at 9.31 ppm was absent indicating that the dinitro compound **1″e** was quantitatively reduced to the diamine structure; the protons in *ortho* position to the amine groups (H_b) appeared at 6.81 ppm and the primary aromatic amine protons appeared at 5.30 ppm. In the ^{13}C NMR spectra, the compounds **1′e**, **1″e** and **1e** showed 11 signals which resonate in the region of 167.0–116.0, 166.8–116.0 and 166.5–101.0 ppm, respectively.

The solution polycondensation reaction to prepare fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3** took place in two steps, in one pot. In the first step a poly(amic acid) **3′** was synthesized by the reaction of an aromatic diamine **1** which contains preformed 1,3,4-oxadiazole ring with 1,1,1,3,3,3-hexafluoro-2,2-bis-[(3,4-dicarboxyphenoxy)phenyl]-propane dianhydride, **2**, at room temperature, in NMP as solvent (Scheme 3). The concentration of the reaction mixture was adjusted to 10–15% wt/v, except for polymer **3a**. In the case of polymer **3a** it was necessary to have a lower concentration of the monomers in NMP (6.5% w/v) in order to keep it in solution. In the second step the resulting solution of polyamic acid is heated, under a nitrogen stream, at 180–185 °C, for 4 h. The water of imidization was evacuated by a slow stream of nitrogen which was used as inert medium, at the same time. The same approach of removing the imidization water was reported by other authors too [28]. All the polymers **3** were soluble in NMP at the end of the reaction.

The conversion of poly(amic acid) to the fully cyclized polyimide was confirmed by IR and ^{1}H NMR spectroscopy. The complete conversion of *o*-carboxy-amide groups to the imide rings was confirmed by the disappearance of the absorption bands at 1660–1670 cm^{-1} and 2500–3000 cm^{-1}. In all IR spectra of polymers **3** strong bands appearing at 1780–1770 cm^{-1} and 1730–1720 cm^{-1} were attributed to symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide rings, and absorption band at 740 cm^{-1} was due to imide ring deformation. All the polymers exhibited absorption bands at 1180 and 1210 cm^{-1} due to 6F groups. The absorption bands appearing at 1020 and 970 cm^{-1} were characteristic of =C–O–C= stretching in 1,3,4-oxadiazole rings. Characteristic absorption band for ether linkages appeared at 1240 cm^{-1}. The imidization of the poly(amic acid) was also confirmed by the fact that ^{1}H NMR spectra of polymers **3** showed no residual resonance in the region 9–11 ppm indicating the absence of amide NH protons. Fig. 1 shows the IR and ^{1}H NMR spectra of polymer **3e**, as an example.

The polymers were easily soluble in organic solvents such as *N*-methylpyrrolidinone, dimethylformamide, pyridine and some of them were also soluble in chloroform or tetrahydrofuran (Table 1). Polymers derived from more flexible diamines, such as **1b** and **1c**, displayed a higher solubility than those obtained from more rigid components like **1a**. Polymer **3e** containing fluorine substituent in the diamine segment was soluble in chloroform while the polymer **3d** containing $N(CH_3)_2$ group in the diamine segment was not soluble in such solvent.

Their good solubility allows the imidazition process to be performed in solution so that the final polymers were obtained as imidized products, which is more convenient than using polyamidic acids. The improved solubility of these polymers can be explained by the presence of a large number of ether linkages and 6F groups which increased the flexibility of the macromolecular chains thus enhancing the solubility. The higher solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

The inherent viscosity of the polymers was in the range of 0.21–0.61 dl/g (Table 1).

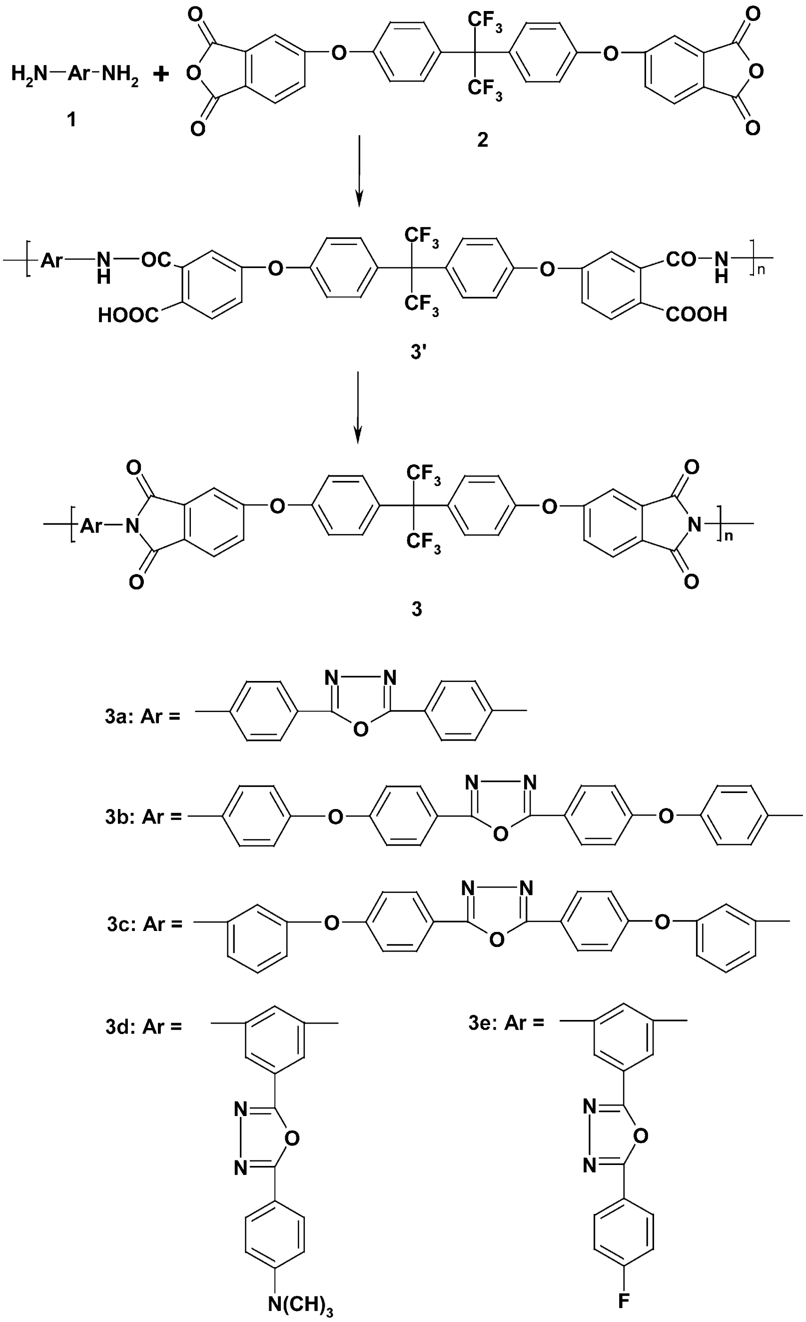
The molecular weight of the polymers was determined by gel permeation chromatography. The values of weight-average molecular weight (M_w) were in the range of 20,000–76,000 g/mol, the number-average molecular weight (M_n) were in the range of 16,000–45,000 g/mol and the polydispersity M_w/M_n was in the range of 1.25–1.70 (Table 2). The polymers **3a**, **3d** and **3e** had lower inherent viscosities and lower number-average molecular weights than the other polymers, **3b** and **3c**, probably due to the lower reactivity of the diamines **1a**, **1d** and **1e**.

All these polymers possess film-forming ability. Their solutions in NMP having a concentration of about 10% were cast onto glass substrates and dried to yield thin films having a thickness of 20–30 μm. Free standing flexible films were obtained in the case of polymers **3b**, **3c** and **3e**. The films made from polymers **3a** and **3d** were brittle, probably due to their high rigidity.

Very thin coatings have been prepared from diluted-NMP solutions (concentration 2%) by spin coating onto silicon wafers. These coatings showed a very strong adhesion to the silicon support. The quality of such films as deposited on substrates was studied by atomic force microscopy (AFM). A typical AFM image for a film made from polymer **3b** is shown in Fig. 2: the scanning range of 10×10 μm was used to evaluate the root mean square (RMS) roughness; the RMS value of polymer film determined from AFM image was 3 Å. The deposited film did not show any pinholes or cracks and were practically without defects. Such qualities are required when such films are used in microelectronic devices.

The thermal stability was investigated by thermogravimetric analysis (TGA). All polymers exhibited high thermal stability, with insignificant weight loss up to 400 °C. They lost 5% weight in the range of 410–480 °C and the temperature of 10% weight loss (T_{10}) was in the range of 460–506 °C (Table 2). Polymer **3d** had the lowest values of T_5 and T_{10}, probably due to the presence of methyl substituents in the diamine segment.

The glass transition temperature (T_g) of the present



Scheme 3. Preparation of fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3**.

Table 1
Solubility and inherent viscosity of fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3**

Polymer	η_{inh}[a] (dL/g)	DMF	NMP	Py	THF	Chloroform
3a	0.31	+	+	+	−+	−
3b	0.61	+	+	+	+	+
3c	0.34	+	+	+	+	+
3d	0.21	+	+	+	−+	−
3e	0.29	+	+	+	−+	+

DMF, dimethylformamide; NMP, *N*-methylpyrrolidinone; Py, pyridine; THF, tetrahydrofuran; +, soluble; −+, partial soluble; −, insoluble.

[a] Measured at a concentration of 0.5 g polymer in 100 ml of NMP, at 20 °C.

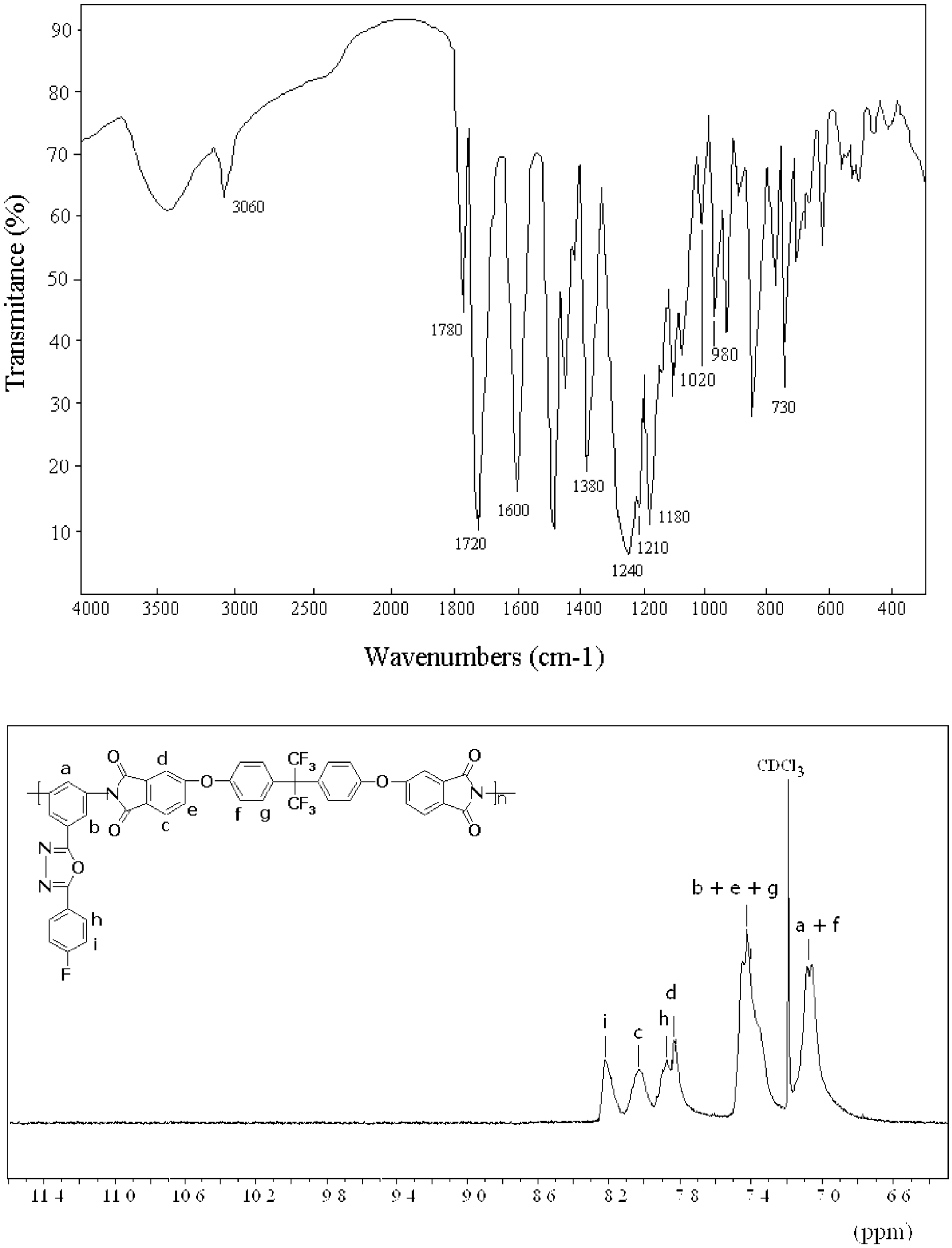


Fig. 1. Typical IR (KBr pellets) (top) and ^{1}H NMR (bottom) spectra (in $CDCl_3$) of fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3e**.

Table 2
The properties of fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3**

Polymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g[a] (°C)	T_5[b] (°C)	T_{10}[c] (°C)
3a	29,000	46,000	1.58	210	455	490
3b	45,000	76,000	1.68	215	480	506
3c	34,000	58,000	1.70	183	455	490
3d	16,000	20,000	1.25	193	410	460
3e	32,000	54,000	1.68	217	460	490

[a] Glass transition temperature.

[b] Temperature of 5% weight loss.

[c] Temperature of 10% weight loss.

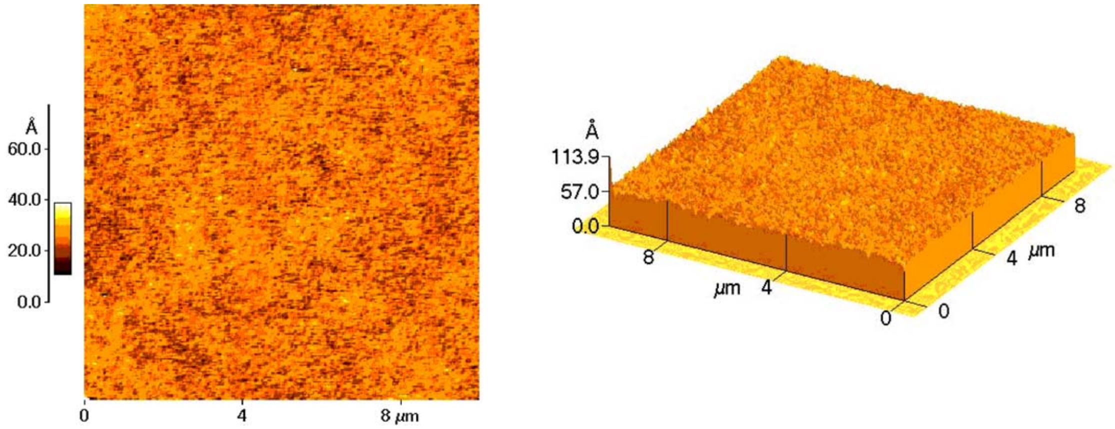


Fig. 2. AFM images of a film made from polymer **3b** (left: top view, right: side view): polymer solution in NMP, 2% concentration; 500 rpm for 30 s and 1500 rpm for 30 s; heating from 80 to 200 °C to drive off the solvent.

polymers, evaluated from DSC curves, was in the range of 183–217 °C (Table 2). The DSC measurements showed no evidence of crystallisation or melting which proves an amorphous morphology. The polymer **3b** containing only *para*-phenylene rings into the diamine segment had higher T_g (215 °C) when compared with that of polymer **3c** (183 °C) which contains two *meta*-phenylene rings in the diamine segment. The introduction of the pendent oxadiazole groups in the case of polymers **3d** and **3e** resulted in small changes in the T_g values. The polymer **3e** having fluorine substituent on the pendent groups had higher T_g (217 °C) when compared with the polymer **3d** having $N(CH_3)_2$ as substituents ($T_g = 193$ °C). It can be noticed that there is a large interval between the glass transition and decomposition temperature which makes these polymers attractive for thermoforming processing, as well.

The optical properties of polymers **3** were also investigated. The UV–vis absorption spectra of polymers **3** in DMF solution are shown in Fig. 3. The peak absorption wavelengths are shown in Table 3. The UV–vis spectra showed maxima in the range of 300–352 nm. The UV–vis spectrum of polymer **3e** did not exhibit a maximum in that range.

Fig. 3 gives also the fluorescence spectra of polymers **3** (excitation wavelength at the absorption maximum), in DMF solution at a concentration of 10^{-4} M; the peak wavelengths are shown in Table 3. The emitting wavelengths of the polymers depended on the structure. The

Table 3
The absorption and fluorescence maxima of fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3** in DMF solutions, at a concentration of 10^{-4} M (excitation wavelength at the absorption maximum)

Polymer	Absorption (nm)	Fluorescence (nm)	Stokes shift (nm)
3a	308	411	103
3b	304	375	71
3c	300	372	72
3d	352	424	70

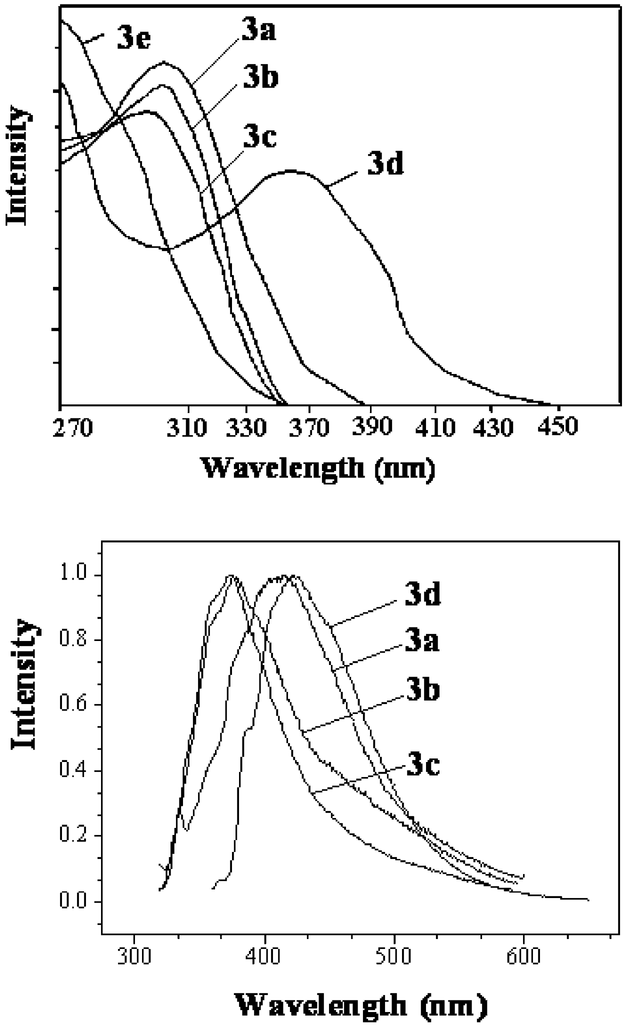


Fig. 3. UV–vis absorption (top) and emission (bottom) spectra of fluorinated poly(1,3,4-oxadiazole-ether-imide)s **3** in DMF solution, at a concentration of 10^{-4} M (excitation wavelength at the absorption maximum).

fluorescence peaks of polymers **3b** and **3c** were nearly in the near-UV, at 375 and 372 nm, respectively, whereas the fluorescence bands of polymers **3a** and **3d** were in the blue range of the visible spectrum, at 411 and 424 nm, respectively. The introduction of the ether linkages into the macromolecular chains produced, in the case of polymers **3b** and **3c**, a shift of the emission maxima towards the UV region.

From previous investigations [25] it was concluded that the polymers containing dimethylamino-substituent in the *para* position of the pendent diphenyl-1,3,4-oxadiazole unit are the most promising candidates for emissive materials in light-emitting devices. Here, the polymer **3d** containing the *p*-dimethylamino substituent on oxadiazole rings showed clear blue emission with the maximum of 424 nm. Polymer **3e**, containing fluoro-substituent in the *para* position of the diphenyl-1,3,4-oxadiazole did not exhibit fluorescence.

In Table 3, the Stokes shift is the difference between fluorescence and UV–vis peaks. If the Stokes-shift is too small, the emission and absorption spectra will overlap more. Then the emitting light will be self-absorbed and the luminescence efficiency will decrease in the devices [29]. The highest value for Stokes shift was obtained for polymer **3a**. Polymers **3b**, **3c**, and **3d** exhibited moderate Stokes shift values.

4. Conclusions

The incorporation of hexafluoroisopropylidene groups into the macromolecular chain of poly(1,3,4-oxadiazole-ether-imide)s resulted in soluble polymers that retain a high thermal stability. The polymers did exhibit a glass transition, with a large interval between the glass transition and decomposition temperature, which may be advantageous for their processing by thermoforming technique. The polymers can be also processed from solution into thin flexible films having the thickness in the range of tens of micrometers by using casting technique or into very thin coatings having the thickness in the range of tens of nanometres by using spin-coating technique. Such films were smooth, homogeneous, practically without defects, when studied by atomic force microscopy. Two polymers showed blue fluorescence in DMF solution. All these properties, associated with an easy processability make the present polymers potential candidates for high-performance applications.

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