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New aromatic polyethers containing phenylquinoxaline and 1,3,4-oxadiazole rings

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Abstract

A series of new heterocyclic polyethers, containing phenylquinoxaline and 1,3,4-oxadiazole rings, was synthesized by polycondensation of bis (4-fluorophenyl)-1,3,4-oxadiazole with a diphenol containing preformed phenylquinoxaline rings. These polymers showed good solubility in chloroform and gave transparent, flexible films, by casting their solutions onto glass plates. They exhibited glass transition temperatures in the range of 225–337°C and were stable when heated up to 420°C, the initial decomposition temperature being in the range of 425–465°C. Solutions of these polymers in chloroform exhibit violet fluorescence, having maximum emission wavelength in the range of 412–425 nm and fluorescence quantum yield in the range of 0.11–0.26. The polymer films displayed a low dielectric constant and tough mechanical properties. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Phenylquinoxaline; 1,3,4-oxadiazole; Polyethers

1. Introduction

One method in the development of high-temperature polymers is the incorporation of heterocyclic units into a poly(aryl ether) system. The interest in poly(arylene ether)s containing heterocyclic rings is due to the heterocycle's tendency to enhance mechanical and adhesive properties as well as glass transition temperatures (T_gs) of the poly (arylene ether) while retaining thermal stability and processability. Some examples of heterocycles introduced into poly(arylene ether)s include imides [1], benzimidazoles [2], benzoxazoles [3], phenylquinoxalines [4], oxadiazoles [5].

Poly(phenylquinoxaline)s are known to possess many desirable properties including excellent thermal stability, low dielectric constant, high T_g and good mechanical properties [6]. Although poly(phenylquinoxaline)s are soluble in selected chlorinated solvents and *m*-cresol, the toxicity of the solvents may limit the use of these polymers in many applications. It has been shown that aryl ethers containing poly(phenylquinoxaline) rings generally show better solubility and melt processing characteristics than their counterparts containing only directly linked aromatic rings.

Aromatic poly(1,3,4-oxadiazole)s are well known due to their high thermal stability in an oxidative atmosphere and specific properties determined by the structure of 1,3,4-oxadiazole ring [7]. Besides their excellent resistance to high temperature, polyoxadiazoles have many desirable characteristics such as good hydrolytic stability, high T_g, low dielectric constant, and tough mechanical properties. Since aromatic poly(1,3,4-oxadiazole)s have limited solubility in common organic solvents, they are generally processed from the soluble polyhydrazide precursor [8,9], somewhat analogous to polyimide formation from the polyamic acid. Improved solubility and processability have been demonstrated by the incorporation of various flexible groups or other ring systems [10].

Poly(oxadiazole-ether)s have been obtained by polycondensation of dicarboxylic acids containing ether groups with hydrazine sulfate in polyphosphoric acid [11], or by polycondensation of diacid chlorides containing ether bridges with aromatic dihydrazides, followed by thermal cyclodehydration of the intermediate poly(hydrazide-ether)s [12]. Another way of introducing aryl ether linkages is via a poly(ether) synthesis in which the generation of aryl ether linkage is the polymer-forming reaction [13–15]. Here the preformed oxadiazole ring may be introduced in the bis(halide) or bis(phenol) monomer and purified prior to polymerization.

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Taking into account the characteristics which phenylquinoxaline and 1,3,4-oxadiazole rings conferred in a polymer, we have designed polymers which incorporate both heterocycles into one macromolecular chain which have led to new polymers having high thermal stability, good solubility in organic solvents, film forming ability, low dielectric constant and tough mechanical properties. The polymers were obtained by the reaction of bis(4-fluorophenyl)-1,3,4-oxadiazole with a bis(hydroxyphenylquinoxaline) or with a mixture of equimolar amounts of bis(hydroxyphenylquinoxaline) and an aromatic bisphenol, using potassium carbonate in *N*-methyl-2-pyrrolidinone.

2. Experimental

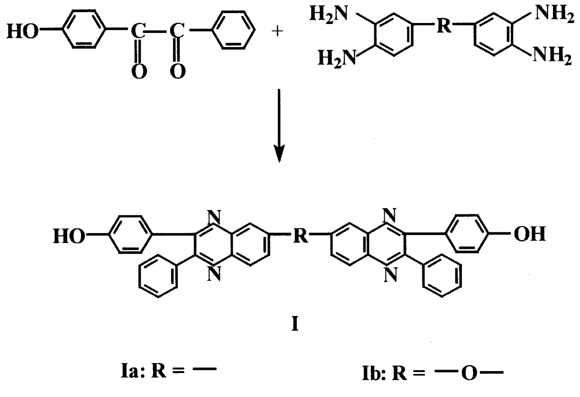
2.1. Starting materials

N-methyl-2-pyrrolidinone (NMP) from Merck was distilled over phosphorous pentoxide under reduced pressure. 4-Fluorobenzoic acid, potassium carbonate, 3,3′-diaminobenzidine, 3,3′,4,4′-tetraaminodiphenylether, 2,2-bis-(4-hydroxyphenyl)-propane, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-dihydroxybiphenyl and 9,9-bis(4-hydroxyphenyl)fluorene were provided by different commercial sources and used as received.

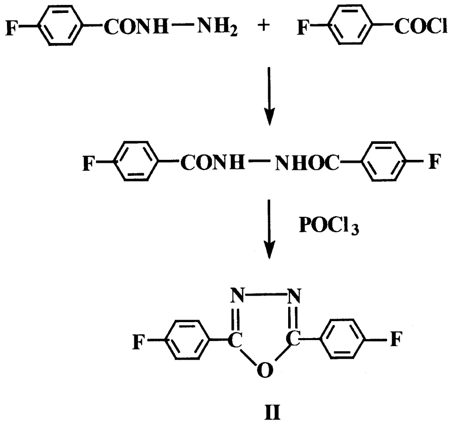
2.2. Synthesis of the monomers

Bis(hydroxyphenylquinoxaline)s **I** were obtained by the reaction of 4-hydroxybenzil with aromatic tetraamines such as 3,3′-diaminobenzidine or 3,3′,4,4′-tetraaminodiphenylether [16], as shown in scheme 1. M.p. **Ia**: 352–354°C; m.p. **Ib**: 184–185°C. Elemental analysis — **Ia**, calculated for $C_{40}H_{24}O_2N_4$: C 81.07%, H 4.08%, N 9.45%; found C 80.85%, H 3.97%, N 9.39%. **Ib**, calculated for $C_{40}H_{24}O_3N_4$: C 78.93%, H 3.97%, N 9.21%; found C 78.70%, H 4.05%, N 9.18%.

2,5-Bis(*p*-fluorophenyl)-1,3,4-oxadiazole, **II**, has been prepared by the reaction of 4-fluorobenzoic acid hydrazide with 4-fluorobenzoyl chloride to give a fluorinated hydrazide which was further dehydrated to oxadiazole structure by treating with $POCl_3$ [17], as shown in Scheme 2. M.p.: 200–202°C. Elemental analysis — calculated for $C_{14}H_8O_1N_2$: C 76.35%, H 3.59%, N 12.72%; found: C 76.21%, H 3.59%, N 12.61%.



Scheme 1.



Scheme 2.

2.3. Synthesis of the polymers **IV** and **V**

A typical synthesis of a poly(phenylquinoxaline-1,3,4-oxadiazole-ether) was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean–Stark trap, and condenser. The flask was charged with bis(hydroxyphenylquinoxaline) **Ia** (2.97 g) and 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole **II** (1.29 g) and 21 ml of NMP and 10 ml toluene. An excess of potassium carbonate (14.7 g) was added. The reaction mixture was heated to reflux and water was removed by azeotropic distillation with toluene for 4–6 h. Then the reaction mixture was heated at 160–170°C for approximately 17 h. After cooling to room temperature, the viscous polymerization mixture was diluted with 20 ml NMP and was added dropwise into water. The fibrous polymer was isolated, washed with water, refluxed with methanol, filtered and vacuum dried. Table 1 lists additional reaction conditions for the preparation of polymers **IV** and **V**.

2.4. Film casting

Dried polymer sample (0.2 g) was dissolved in 4 ml of chloroform to give 5.0% (w/v) solution which was filtered onto a glass plate and carefully spread to the edges. The films were allowed to dry slowly under a Petri dish for 24 h and then dried for 2 h in air at 130°C. The polymer film was released from the glass plates by placing them in water [18].

2.5. Measurements

Melting points of the monomers were measured on a Melt-Temp **II** (Laboratory Devices) apparatus without correction.

Table 1
Preparation of poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V**

Polymer	Bis(hydroxyphenyl quinoxaline)s **I**			2,5-Bis(*p*-fluoro phenyl)-1,3,4-oxadiazole **II**		Bisphenol **III**			K_2CO_3 (g)	NMP (ml)	Reaction time (h)
		(g)	(mol)	(g)	(mol)		(g)	(mol)			
IVa	**Ia**	2.97	0.005	1.29	0.005	–	–	–	14.7	21	17
IVb	**Ib**	3.05	0.005	1.29	0.005	–	–	–	14.7	22	17
Va	**Ia**	1.48	0.0025	1.29	0.005	**IIIa**	0.57	0.0025	14.7	17	17
Vb	**Ia**	1.48	0.0025	1.29	0.005	**IIIb**	0.84	0.0025	14.7	18	18
Vc	**Ia**	1.48	0.0025	1.29	0.005	**IIIc**	0.465	0.0025	14.7	16	20
Vd	**Ia**	1.48	0.0025	1.29	0.005	**IIId**	0.875	0.0025	14.7	18	18

Infrared spectra were recorded with a Specord M 80 Spectrometer by using KBr pellets.

The molecular weight distributions were measured by gel permeation chromatography (GPC), with a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards were used for calibration and dimethylformamide as the mobile phase.

Thermogravimetric analyses (TGA) were performed on Mettler TC 10A at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. The initial decomposition temperature (IDT) is considered the onset on the TGA curve. The temperature of 10% weight loss (T_{10}) and % weight loss at 500°C were also recorded.

Differential scanning calorimetry (DSC) was performed on a DSC II Metler TC 11. The samples were heated at a rate of 10°C min^{-1} under a nitrogen atmosphere to above 300°C. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the T_g. The midpoint of the inflection curve resulting from the typical second heating was assigned as the T_g temperature of the respective polymers.

Fluorescence spectra were recorded by using a home-made photon-counting spectrofluorimeter equipped with a Princeton Applied Research 1140 A/B detection system and using 366 nm excitation wavelength. Fluorescence quantum yields (Φ_f) were measured by comparison with quinine sulfate (in 0.5 mol dm^3 aqueous sulfuric solution) for which $\Phi_f = 0.55$ was taken [19].

Mechanical properties of various materials have been analyzed by cold drawing of solution cast films. Mechanical testing machine Instron 6000 has been used. The samples have been drawn with the rate of 0.5 min^{-1} at room temperature. The stress versus draw ratio dependencies has been recorded.

The analysis of the dielectric properties has been performed in a parallel plate capacitor under a sinusoidal voltage. Solid samples in the form of films having thickness of 25 μm with evaporated golden electrodes (10 mm diameter) have been examined. The frequency analyzer Solartron Schlumberger 1260 ($10^{-1} - 10^6$ Hz) has been used. The complex dielectric permitivity (ε^* given by the equation $\varepsilon^* = \varepsilon' + \varepsilon''$ where ε' is the real component of the dielectric constant and ε'' is the imaginary component of the dielectric constant, has been measured as a function of frequency at constant temperature. The dielectric loss tangent is defined by $\tan\delta = \varepsilon''/\varepsilon'$ and was determined as a function of frequency.

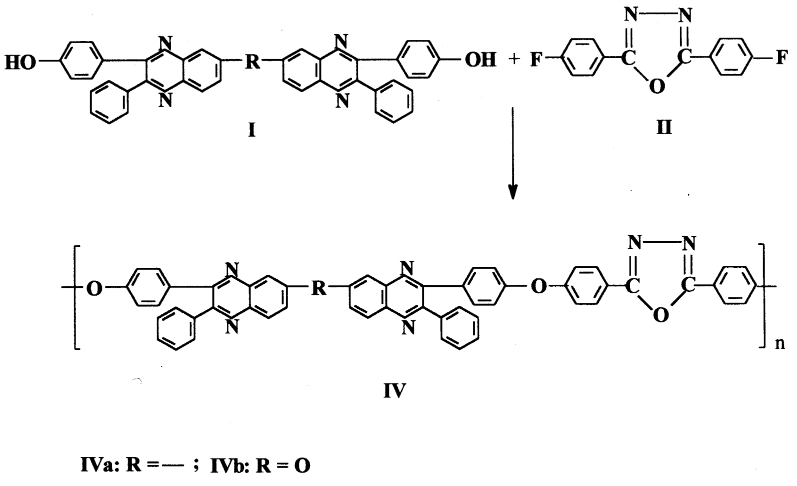
Model molecules for a polymer fragment were obtained by molecular mechanics (MM +) by means of the HYPERCHEM program, Version 4.0 [20].

3. Results and discussion

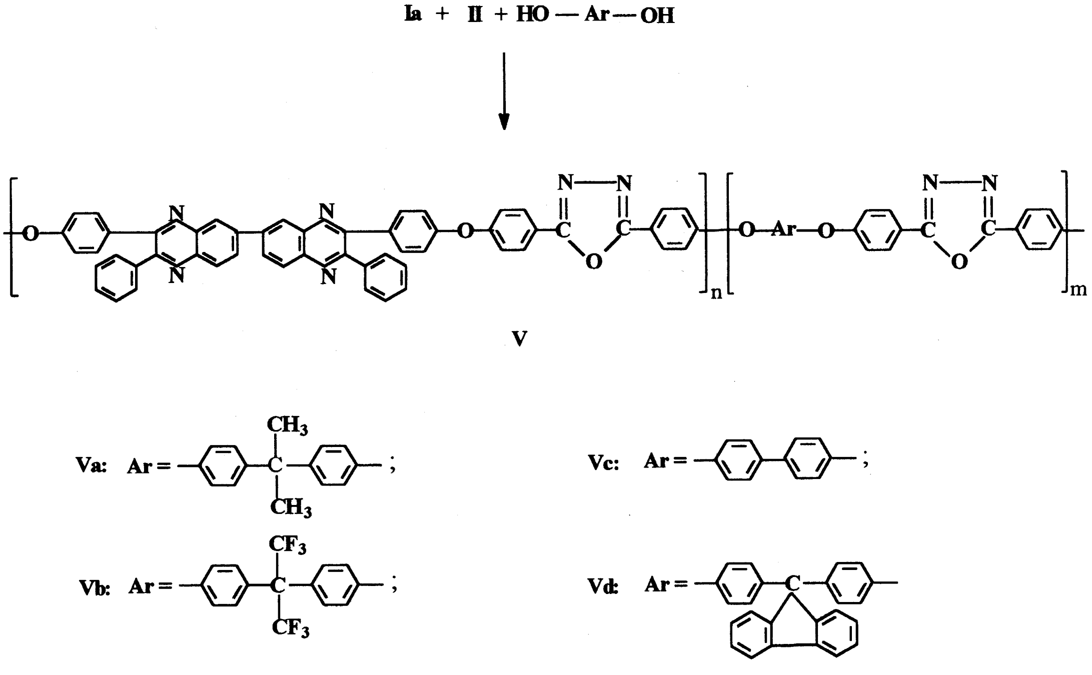
The poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V** were prepared by the conventional aromatic nucleophilic substitution polymerization technique from bis(4-fluorophenyl)-1,3,4-oxadiazole, **II**, with a bis(hydroxyphenylquinoxaline) **I** or with a mixture of equimolar amounts of bis(hydroxyphenylquinoxaline) **I** and an aromatic bisphenol **III** such as 2,2-bis-(4-hydroxyphenyl)-propane, **IIIa**, 4,4′-(hexafluoroisopropylidene)diphenol, **IIIb**, 4,4′-dihydroxybiphenyl, **IIIc**, and 9,9-bis(4-hydroxyphenyl)fluorene, **IIId**, as depicted in Schemes 3 and 4.

The polycondensations were carried out at elevated temperature in NMP, in the presence of anhydrous potassium carbonate. The nucleophilic aromatic substitution of an aryl halide with a phenoxide is the most common route to high-performance, high-temperature poly(aryl ether)s [13]. It has been demonstrated that heterocycles can activate aryl halides toward nucleophilic aromatic substitution polymerization generating high molecular weight poly(aryl ether)s containing preformed heterocyclic rings [21]. The oxadiazole moiety in bis(4-fluorophenyl)-1,3,4-oxadiazole acts as an activating group: it can accept a negative charge and lower the activating energy for the displacement of the *p*-substituted fluoro group through a Meisenheimer complex, analogous to conventional activating groups such as ketone or sulfone.

The structure of the polymers was identified by infrared spectra and elemental analysis. The absorption band at 1240 cm^{-1} was assigned to ether linkages. Absorptions were found near 1020 and 950 cm^{-1} that are characteristic of =C–O–C= stretching in oxadiazole rings. Absorption peaks at 1348 and 1315 cm^{-1} were attributed to quinoxaline



Scheme 3.



Scheme 4.

rings [22]. Elemental analyses data for C, H and N are in good agreement with the calculated values (Table 2).

The poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V** were soluble in chloroform due to the presence of flexible ether linkages and bulky phenylquinoxaline units which create a distance between the macromolecular chains, as evidenced by molecular modeling. The disturbed packing of macromolecular chains facilitates the diffusion of small molecules of solvent, which leads to better solubility. The higher solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes. However, the polymer **Vc** after isolation

Table 2
Elemental analysis data of poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V**

Polymer	C %		H %		N %	
	Calculated	Found	Calculated	Found	Calculated	Found
IVa	79.79	79.91	3.97	3.57	10.34	10.10
IVb	78.25	78.72	3.89	4.09	10.14	10.46
Va	79.16	79.73	4.32	4.25	8.90	9.12
Vb	72.91	72.38	3.54	3.31	8.20	7.98
Vc	78.93	79.72	3.97	3.78	9.21	9.42
Vd	80.85	81.70	4.09	4.10	8.11	8.30

Table 3
GPC analysis of poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V**

Polymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n
IVa	23,000	63,000	2.7
IVb	14,000	33,000	2.3
Va	24,000	69,000	2.9
Vb	9000	59,000	6.8

from the NMP reaction mixture was not soluble in common organic solvents, probably due to increased rigidity produced by the presence of diphenylene units into the chains. The free-standing films prepared from all the other polymers were transparent, flexible and creasable. The films having a thickness of 3–7 μm were prepared for use in recording the infrared spectra, while somewhat thicker films (20–30 μm) were produced for mechanical and dielectric measurements.

The molecular weight of polymers was determined by GPC. The molecular weight values M_n are in the range of 9000–24,000, M_w in the range of 33,000–69,000, and M_w/M_n in the range of 2.3–6.5 (Table 3). In any case these values have to be taken as indicative only, since calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the polymers studied deviate strongly from those of polystyrene.

The inherent viscosity of polymers, determined in chloroform, is in the range of 0.30–0.47 dl g^{-1} (Table 4).

The thermal stability of the polymers was studied by TGA. All polymers are highly thermostable. They begin to decompose in the range of 425–465°C and the temperature of 10% weight loss is in the range of 465–520°C. The weight loss at 500°C is in the range of 7.5–17.5% (Table 4). The bisphenol components in the polymer chain significantly influence the thermal stability. The polymer **Va** based on 2,2-bis-(4-hydroxyphenyl)propane exhibited lower decomposition temperature than the other polymers. This is due to the presence of isopropylidene units, which are more sensitive to thermal degradation. In the case of polymer **Vb**, by using hexafluoroisopropylidene units instead of isopropylidene units, an increase of decomposition temperature was observed when compared with that of polymer **Va**. The DSC measurements showed no evidence of crystallization or melting, which proves amorphous morphology. The T_gs , as shown by DSC analysis, are in the range of 225–337°C (Table 4) being higher than those of related polymers which do not contain phenylquinoxaline rings [5]. The polymer **IVa** containing two flexible ether linkages in the repeating unit showed a higher T_g than that of polymer **IVb** which contains an additional ether linkage coming from bis(hydroxy-phenylquinoxaline) monomer **Ib** (321 and 248°C, respectively). The polymers **Va**, **Vb** and **Vc** showed a lower T_g (255, 260 and 225°C, respectively), than the polymer **IVa** (321°C). This behavior could be explained by the decreased number of phenylquinoxaline units in the repeating unit of polymers **Va**, **Vb** and **Vc** compared with polymer **IVa**. The polymer **Vd** having fluorene units exhibited the highest T_g (336°C). This is due to the introduction of voluminous fluorene units, which make the chains more rigid, and therefore determines a higher T_g. It can be also noticed that there is a large interval between T_g and decomposition temperature of all these polymers which could be advantageous in their processing by thermoforming techniques.

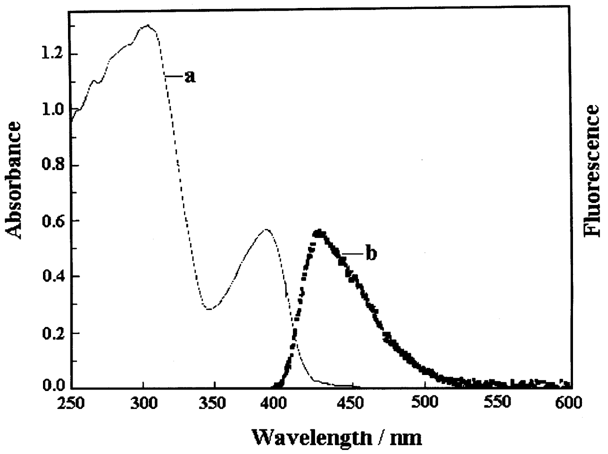


Fig. 1. Absorption (a) and emission spectra (b) of the poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **Vd** in a chloroform solution.

Table 4
Properties of poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V**

Polymer	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	IDT[c] (°C)	T_{10}[d] (°C)	Weight loss at 500°C (%)
IVa	0.45	321	450	500	10
IVb	0.33	248	465	520	7.5
Va	0.47	255	425	465	17.5
Vb	0.42	260	460	495	11.5
Vc	–[e]	225	455	505	9
Vd	0.3	337	450	485	12.5

[a] Determined in NMP at 20°C, at a concentration of 0.5 g dl^{-1}.
[b] Glass transition temperature.
[c] Initial decomposition temperature = onset of the TG curve.
[d] Temperature of 10% weight loss.
[e] Insoluble in chloroform.

Table 5
Fluorescence properties of poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V** in chloroform (Φ_f = fluorescence quantum yield)

Polymer	λ_{abs1}[a] (nm)	λ_{abs2}[b] (nm)	E (kcal/mol)	λ_{em}[c] (nm)	Φ_f
IVa	300	385	70.3	425	0.26
IVb	300	370	72.9	412	0.11
Va	302	380	70.5	424	0.26
Vb	303	383	70.4	424	0.26
Vd	304	385	70.3	424	0.24

[a] First maximum absorption wavelength.
[b] Second maximum absorption wavelength.
[c] Maximum emission wavelength.

The UV–vis absorption and the emission spectra in chloroform solution were investigated. Fig. 1 presents the absorption and emission spectra of polymer **Vd**. The absorption spectra of these polymers showed two maxima at 300–304 and 370–385 nm. The emission spectra displayed a maximum in the range of 412–425 nm (Table 5). The shape of the fluorescence spectra is structureless and symmetric with the lowest energy absorption band with moderate Stokes shift in all polymers. These bands belong probably to a transition due to a charge transfer on the aryl substituted quinoxaline unit. The different polymers show similar photophysical properties and high fluorescence quantum yield, of about 0.25, except **IVb**, where the singlet energy is higher, in accordance with the expectations, considering that the ether linkages between quinoxaline moieties decrease the electron acceptor character of the heteroaryl group. The decrease of the fluorescence quantum yield of **IVb** compared to the others, can be explained from the increase of the singlet energy that may involve a higher thermally enhanced nonradiative process by the proximity effect, as is often observed in the case of heteroaromatic molecules.

The tensile properties of some polymer films are summarized in Table 6. The meaning of the parameters determined is illustrated in Fig. 2. Elastic modulus (E) and the coordinates of the yield point (ε_Y, σ_Y) as well as of the point of fracture (λ_B, σ_B) have been determined as averages of three to five independent drawing experiments.

All materials have showed similar type of behavior with the elastic deformation range at small strains up to $\lambda = 1.03$, with the yield point indicating the beginning of plastic flow range and finally with a ductile fracture in some cases after weak strain hardening. The values of elastic modulus are in the range of 1.24–1.84 GPa and the values of yield stress vary in the range of 43.2–66.5 MPa, which shows that these polymers have tough mechanical properties.

Table 6
Parameters describing mechanical properties of polymer films of poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V** (E is modulus, σ_y is yield stress, ε_y is yield strain, σ_B is tensile strength, and λ_B is draw ratio at break)

Sample	E (GPa)	σ_y (MPa)	$\varepsilon_y = \lambda_y - 1$	σ_B (MPa)	λ_B
IVa	1.24	43.2	0.0577	44.1	1.16
IVb	1.47	60.0	0.0635	51.9	1.11
Va	1.37	51.8	0.0573	51.6	1.40
Vb	1.52	57.3	0.0615	59.9	1.45
Vd	1.84	66.5	0.0617	63.3	1.09

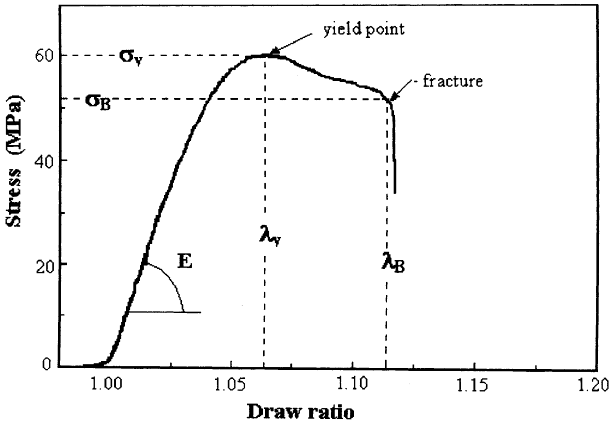


Fig. 2. Schematic stress–strain dependence with the parameters characterizing the elasticity at small deformation as well as the yield and the break points.

The dielectric constant ε' and dielectric loss tangent of polymers **IV** and **V** are displayed from 10^{-1} to 10^6 Hz. Fig. 3 presents the dependence of real dielectric constant values (ε') on frequency. Fig. 4 presents the dependence of dielectric loss tangent (tan δ) on frequency. The frequency dependencies are typical for all the polymers. By increasing the frequency a small monotonic decrease in ε' appeared. The dielectric loss tangent values are very small due to the very small values of ε'' of complex permittivity. The dielectric constants for all the polymers at 100 Hz, 10 KHz and 1 MHz

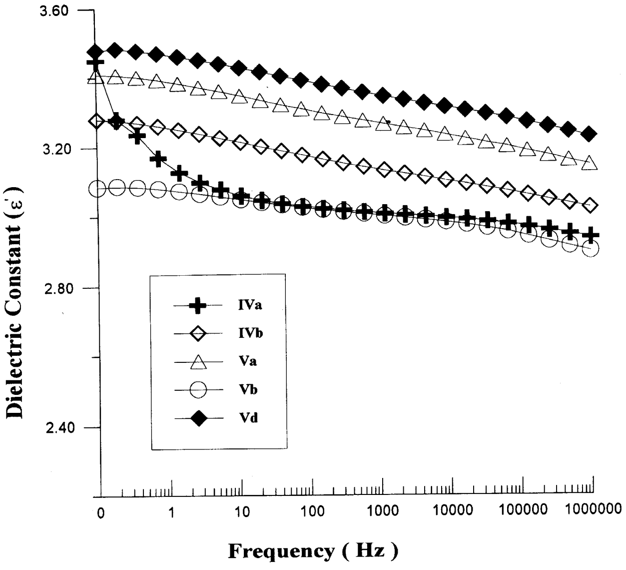


Fig. 3. Dielectric analysis plot showing the real dielectric constant versus frequency for poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V**.

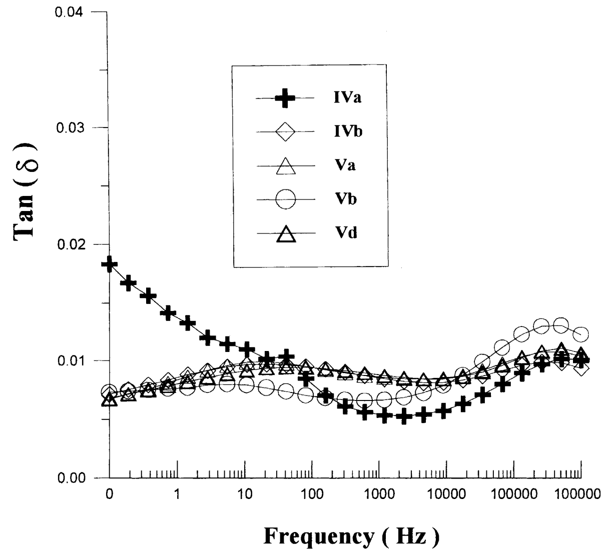


Fig. 4. Dielectric analysis plot showing the loss tangent versus frequency for poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V**.

Table 7
Dielectric constant at selected frequencies for poly(phenylquinoxaline-1,3,4-oxadiazole-ether)s **IV** and **V**

Polymer	Dielectric constant at		
	100 Hz	10 kHz	1 MHz
IVa	3.03	3.00	2.95
IVb	3.18	3.10	3.04
Va	3.32	3.25	3.16
Vb	3.01	2.97	2.92
Vd	3.38	3.33	3.24

are listed in Table 7. The values at 1 MHz were in the 2.92–3.24 range. These low values of the dielectric constant are very similar to those reported for related polyphenylquinoxalines [6] and are even lower than 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 [23]. That makes the present polymers potential candidates for use in high-temperature processing of high-speed integrated circuits.

4. Conclusions

The introduction of phenylquinoxaline and 1,3,4-oxadiazole rings into the main chain of aromatic poly(ether)s gave polymers with good solubility. These polymers exhibit high thermal stability, with decomposition temperature being above 420°C and a large interval between glass transition and decomposition temperature, which is advantageous for thermoforming processing. The polymers can also be processed from solutions into thin flexible films, which exhibited low dielectric constant and tough mechanical properties. The solutions of these polymers in chloroform exhibited violet fluorescence. All these properties make the present polymers potential candidates for practical applications in microelectronics or related advanced fields.

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