

AROMATIC POLYETHERS CONTAINING 1,3,4-OXADIAZOLE RINGS

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Aromatic polyethers containing 1,3,4-oxadiazole rings were prepared by nucleophilic substitution polymerization technique of 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole with various aromatic bisphenols, such as 4,4'-isopropylidenediphenol, 4,4'-(1,4-phenylene-diisopropylidene)bisphenol, 4,4'-(hexafluoroisopropylidene)diphenol, 4,4'-cyclohexylidene-bisphenol and 4,4'-dihydroxybiphenyl. They showed high thermal stability with decomposition temperature above 400°C and glass transition temperature in the range of 187-211°C. Solutions of some polymers in N,N-dimethylformamide exhibited fluorescence, having maximum emission wavelength in the range of 373-377 nm.

INTRODUCTION

Aromatic polyethers are well recognized as a class of high-performance engineering thermoplastics with the characteristics of good thermo-oxidative stability, high glass transition temperature and excellent mechanical strength. One method in the development of these polymers is the incorporation of heterocyclic units into their macromolecular structure. The interest in aromatic polyethers containing heterocyclic rings is due to the heterocycle's tendency to enhance mechanical and adhesive properties as well as glass transition temperature while retaining thermal stability and processability. Some examples of heterocycles introduced into poly(arylene-ether)s include imide,¹ benzimidazole,² benzoxazole,³ phenylquinoxaline,⁴ pyrimidine.⁵

The introduction of 1,3,4-oxadiazole rings into the macromolecular chains of aromatic polyethers improves the properties of the polymers.⁶⁻¹² The oxadiazole cycle is similar to a *p*-phenylene structure, which is known to be highly thermoresistant. Also, it does not contain any hydrogen atoms, nor any possibilities of rearrangement, it lacks tension, it has structural symmetry, and it is thermally unreactive.¹³ The method frequently utilized for their preparation is the aromatic nucleophilic substitution polymerization, in which an aromatic dihalide activated by strongly electron-attracting 1,3,4-oxadiazole ring is chosen as partner of bisphenols. Polymerization follows a conventional nucleophilic aromatic substitution mechanism *via* a Meisenheimer complex intermediate, the formation of which is the rate-determining step in the polymerization process.¹⁴

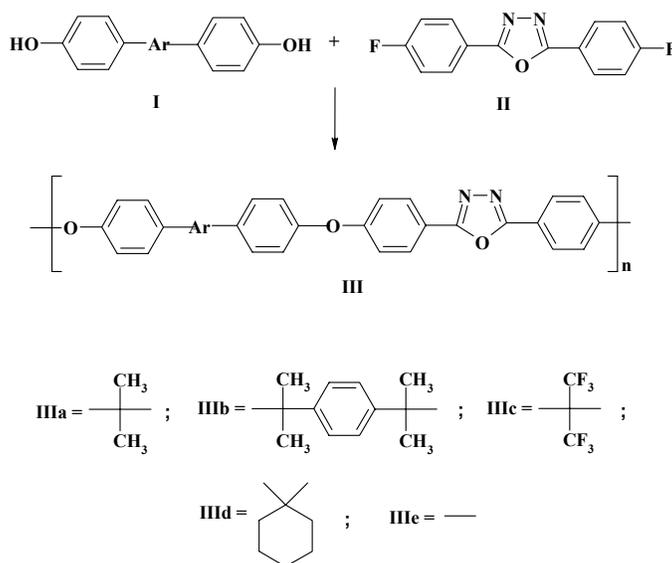
In this paper we describe the synthesis and characterization of various aromatic polyethers containing 1,3,4-oxadiazole rings. They were prepared by reacting an activated aromatic difluoride, 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole, with various aromatic bisphenols. The properties of the polymers, such as solubility, thermal stability, glass transition temperature and fluorescence are described in correlation with their structures.

RESULTS AND DISCUSSION

The polyethers **III** were prepared by the reaction of 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole (**I**) with aromatic bisphenols **II**, as shown in Scheme 1. The polycondensations were carried out at elevated temperature in N-methylpyrrolidone (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 obtain

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high performance, high temperature aromatic polyethers. It has been demonstrated that heterocycles can activate aryl halides toward nucleophilic aromatic substitution polymerization, generating high molecular weight polymers containing preformed heterocyclic rings. The oxadiazole moiety in 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole acts as an activating group: it can accept a negative charge and lowers the activating energy for the displacement of the *p*-substituted fluoro group through a Meisenheimer complex, analogously to conventional activating groups such as acyl or sulfonyl functions.



Scheme 1 – Preparation of the polymers **III**.

The structure of polymers **III** was identified by IR and $^1\text{H-NMR}$ spectroscopy. Fig. 1 shows the IR spectrum of **IIIb**, as a typical example. In IR spectra of all polymers, characteristic absorption band for ether linkages appeared at 1240 cm^{-1} . The absorption bands appearing at 1020 cm^{-1} and 980 cm^{-1} were due to the presence of 1,3,4-oxadiazole rings. Characteristic bands at 3060 cm^{-1} were due to aromatic C-H stretching and 1600 cm^{-1} due to aromatic C-C stretching. In the IR spectra of polymers **IIIa** and **IIIb**, characteristic absorption bands of isopropylidene groups appeared at 2980 cm^{-1} and 2880 cm^{-1} . In the IR spectrum of polymer **IIIc** absorption bands appeared at 2920 cm^{-1} and 2850 cm^{-1} due to the presence of CH_2 groups. In the case of polymer **IIIe**, absorption bands of hexafluoroisopropylidene (6F) groups appeared at 1180 cm^{-1} and 1210 cm^{-1} .

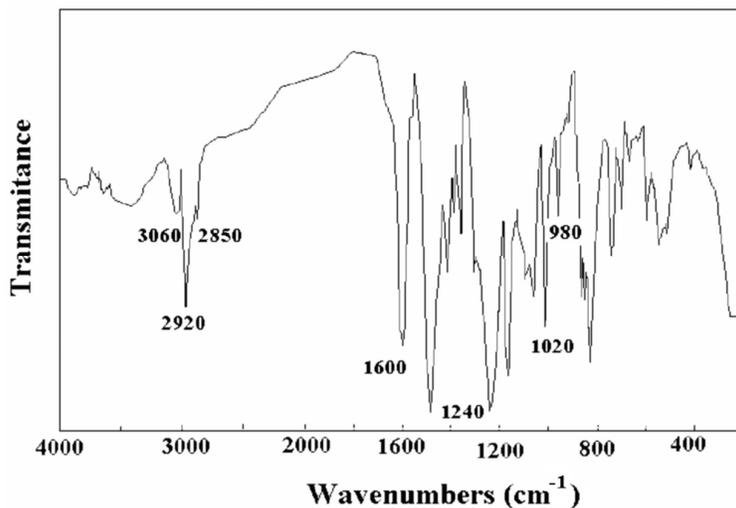


Fig. 1 – IR spectrum of polymer **IIIb**.

Fig. 2 presents the $^1\text{H-NMR}$ spectrum of polymer **IIIb** with the assignment of all protons. The protons H_b were shifted to the downfield region due to the presence in *ortho* position of electron withdrawing of 1,3,4-oxadiazole rings. The protons H_a and H_c were shifted to lower ppm values because of the electron donating properties of aromatic ether. The protons of isopropylidene groups H_f appeared as a singlet at 1.65 ppm.

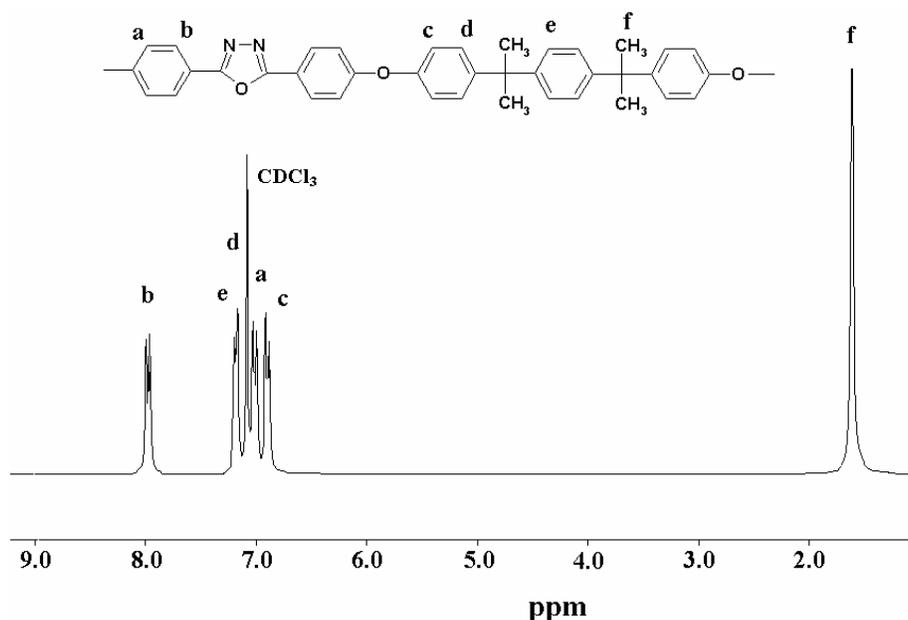


Fig. 2 – $^1\text{H-NMR}$ spectrum of polymer **IIIb**.

The solubility of polymers **III** is presented in Table 1. The polymers **IIIa**, **IIIb** and **IIIc** were soluble in polar organic solvents such as NMP, N,N-dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF). Polymer **IIIc** had higher solubility in such solvents when compared with polymers **IIIa** and **IIIb**. The polymers **IIIa** and **IIIb** were also soluble in low-boiling solvents like chloroform and dichloroethane. Polymers **IIIb** and **IIIc** were not soluble in any organic solvent due to the high rigidity of the macromolecular chains. The good solubility of the polymers **IIIa**, **IIIb** and **IIIc** can be explained by the presence of isopropylidene or 6F groups which increase the flexibility of the macromolecular chains and consequently make the shape of the macromolecules to be far from a “rigid rod”, as evidenced by molecular modeling (Fig. 3). Also, the bulky 6F groups, in the case of the polymer **IIIc**, produced sterical hindrance and did not allow a strong packing of the macromolecular chains; thus the molecules of solvents can penetrate easier through the macromolecular chains improving the solubility.

Table 1

Solubility of polymers **III**

Polymer	Solvent				
	NMP	DMAc	DMF	chloroform	dichloroethane
IIIa	+	+	+	+	+
IIIb	+	+	+	+	+
IIIc	+	+	+	-+	-+
IIIb	-+	-	-	-	-
IIIc	-+	-+	-+	-	-

NMP = N-methylpyrrolidone; DMAc = dimethylacetamide; DMF = N,N-dimethylformamide.
+ soluble; -+ partial soluble; - insoluble.

The inherent viscosity of the polymers **IIIa**, **IIIb** and **IIIc** was in the range of 0.58-0.73 dL/g (Table 2). For polymers **IIIa** and **IIIb** it was determined in chloroform, while for polymer **IIIc** it was measured in NMP.

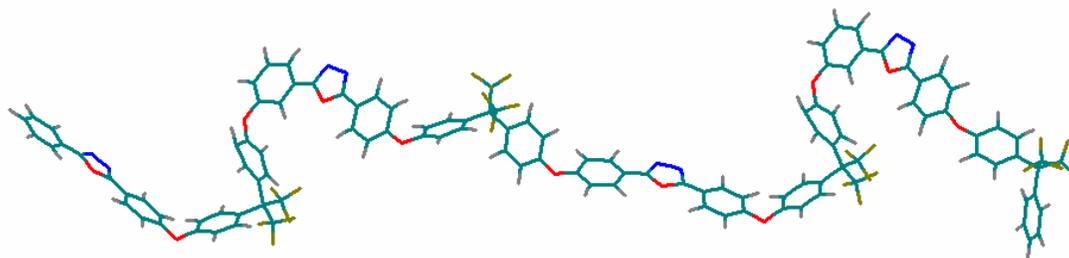
Fig. 3 – Model molecules (four repeating units) of polymer **IIIc**.

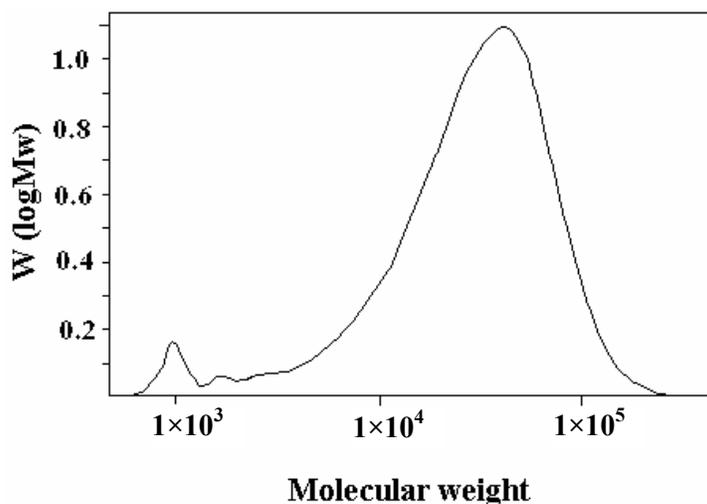
Table 2

Properties of polymers **III**

Polymer	η_{inh} (dL/g)	Mn (g/mol)	M _w (g/mol)	M _w /Mn	λ_{abs}^a (nm)	λ_{em}^b (nm)
IIIa	0.61	12 500	27 000	2.2	305	377
IIIb	0.73	17 000	40 000	2.4	304	376
IIIc	0.58	14 000	37 000	2.6	300	373

^a Maximum absorption wavelength.^b Maximum emission wavelength.

The molecular weight of polymers **IIIa**, **IIIb** and **IIIc** was determined by gel permeation chromatography (GPC). The values of weight-average molecular weight (M_w) and number-average molecular weight (Mn) were in the range of 27000-40000 g/mol and 12000-17000 g/mol, respectively. The polydispersity M_w/Mn was in the range of 2.2-2.6 (Table 2). The GPC curves showed narrow molecular weight distribution and low quantity of oligomers. The molecular weight distribution of polymer **IIIb** is shown in Fig. 4, as a typical example. The molecular weight of the oligomers was an order of magnitude lower than that of the chain unit of the polymer.

Fig. 4 – GPC curve of polymer **IIIb**.

The UV-VIS absorption spectra of the polymers **IIIa**, **IIIb** and **IIIc** in DMF solution were investigated. The polymer solutions exhibited absorption maxima in the range of 300-305 nm (Table 2). Fluorescence emission and excitation spectra in DMF solution were also recorded. Fig. 5 presents the fluorescence emission and excitation spectra of polymer **IIIc**. The emission of these polymers was nearly UV having maxima emission wavelength around 373-375 nm (Table 2). All the emission spectra were relatively broad due to the distribution of the diphenyl-1,3,4-oxadiazole units in the polymer matrix .

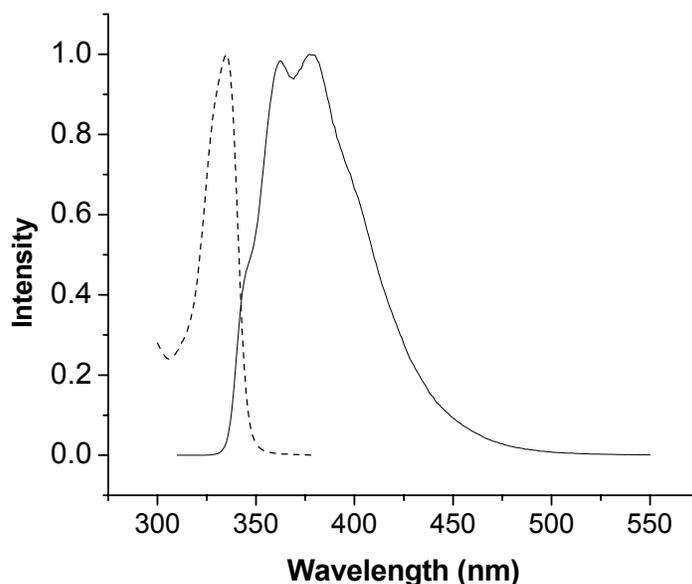


Fig. 5 – Excitation (dash line) and emission (solid line) spectra of polymer **IIIc** in a DMF solution.

The thermal stability of these polymers was studied by thermogravimetric analysis (TGA) (Table 3). All polymers exhibited high thermal stability. They began to decompose in the range of 398-432°C in the air atmosphere, as indicated by the temperature of 5% weight loss (IDT) in TGA thermograms. The temperature of 10% weight loss was in the range of 409-452°C. A typical TGA curve is shown in Fig. 6. The degradation process exhibited one maximum of decomposition, as can be seen from the differential thermogravimetric (DTG) curves of these polymers. The maximum polymer decomposition temperature T_{max} was in the range of 438-491°C. The polymer containing 6F groups, **IIIc**, exhibited slightly higher thermal stability (IDT=432°C) when compared with polymers having isopropylidene groups, **IIIa** and **IIIb** (whose IDT were 418°C and 420°C, respectively), due to the higher thermal resistance of 6F groups. Polymer **IIIe** exhibited the lowest IDT (398°C) due to the presence of cyclohexylidene units which were more sensitive to thermal degradation.

Table 3

Thermal properties of polymers **III**

Polymer	T_g^a (°C)	IDT ^b (°C)	T_{10}^c (°C)	T_{max}^d (°C)
IIIa	190	418	438	471
IIIb	187	420	434	449
IIIc	211	432	452	491
IIIe	195	398	409	438
IIIe	ND	416	431	460

^a Glass transition temperature.

^b Initial decomposition temperature = the temperature of 5% weight loss.

^c Temperature of 10% weight loss.

^d Maximum polymer decomposition temperature.

ND = not detected.

The glass transition temperature (T_g) of the present polymers, evaluated from DSC curves, was in the range of 187-211°C (Table 3). The DSC measurements showed no evidence of crystallization or melting which proves an amorphous morphology (Fig. 7). As expected, the polymer **IIIc** containing 6F groups exhibited higher T_g (211°C) when compared with polymers **IIIa** and **IIIb** having isopropylidene groups (whose T_g were 190 and 187°C, respectively). T_g is known to depend on the rigidity of the polymer main chain, the increase of the rigidity of the polymer backbone increases the energy barrier and hence T_g

increases. Polymer **IIIe** did not exhibit a glass transition temperature when heated up to 300°C because the biphenyl unit seems to hinder the mobility. For polymers **IIIa-d** 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.

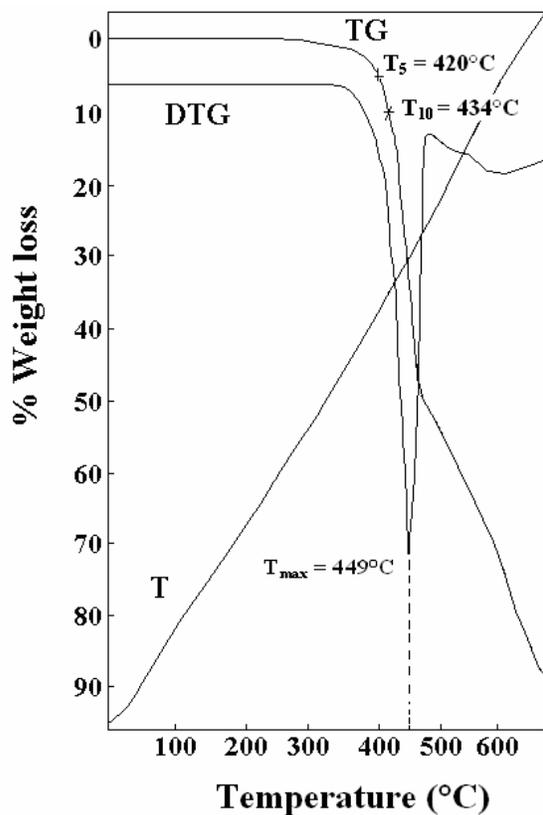
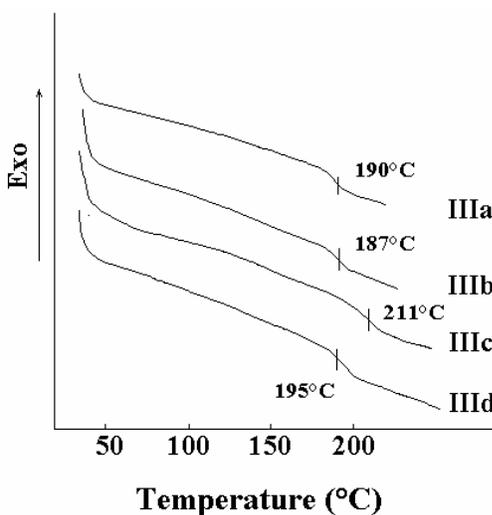


Fig. 6 – TGA curve of polymer **IIIb**.

Fig. 7 – DSC curves of polymers **III**.



EXPERIMENTAL

2,5-Bis(*p*-fluorophenyl)-1,3,4-oxadiazole (**II**) has been prepared by the reaction of 4-fluorobenzoic acid with hydrazine hydrate, in polyphosphoric acid.¹⁵ M.p.: 200-202°C.

Synthesis of the polymers III

A typical synthesis of a poly(1,3,4-oxadiazole-ether) was conducted in a three-neck flask equipped with a nitrogen inlet, mechanical stirrer, Dean-Stark trap and a condenser. The flask was charged with 4,4'-isopropylidenediphenol (0.684 g, 0.003 mol), 2,5-bis(*p*-fluorophenyl)-1,3,4-oxadiazole (0.774 g, 0.003 mol), NMP (14 mL) and toluene (10 mL). An excess of potassium carbonate (0.7 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 20 h. After cooling to room temperature, the viscous polymerization mixture was diluted with NMP (10 mL) and then it was added dropwise into water. The fibrous polymer was isolated, washed with water, refluxed with methanol, filtered and vacuum dried.

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 chloroform or 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. ¹H-NMR spectra were recorded on a Bruker AC 300 instrument, using solutions in deuterated chloroform or deuterated DMF. 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. Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in the air, at a heating rate of 10°C/min. The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss (T_{10}) was also 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. Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 4.0.¹⁶

CONCLUSIONS

Aromatic poly(1,3,4-oxadiazole-ether)s were prepared by nucleophilic substitution polymerization of a difluorinated compound incorporating 1,3,4-oxadiazole ring with various bisphenols. The presence of isopropylidene and hexafluoroisopropylidene units increased the solubility of the resulting polymers. The polymers containing diphenyl or diphenylcyclohexylidene units exhibited low solubility in organic solvents. All polymers exhibited high thermal stability and a glass transition temperature in the range of 187-211°C. Due to the presence of the diphenyl 1,3,4-oxadiazole units, solutions of the polymers exhibited fluorescence having maximum emission wavelength in the range of 373-377 nm.

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