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Synthesis, Characterization, and Study of the Thermal Properties of New Poly(arylene ether 1,3,4-oxadiazole)s

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ABSTRACT: A series of new poly(arylene ether 1,3,4-oxadiazole)s has been prepared by nucleophilic displacement of aromatic dihalides with aromatic potassium bisphenates in diphenyl sulfone at elevated temperatures. The polymers, characterized by elemental and infrared analysis, GPC, and wide-angle X-ray diffraction, had inherent viscosity from 0.3 to 0.7 dL/g, were obtained in yields higher than 85%, show good solubility in various organic solvents, and had excellent thermal stability as shown by 10% weight loss temperatures in nitrogen and air (above 445 and 440 °C, respectively) and high glass transition temperatures (in the range of 188−226 °C). The introduction of two 1,3,4-oxadiazole units in the polymer repeat unit determines glass transition temperatures higher than those of similar polymers containing only one oxadiazole group in the repeat unit.

Introduction

The systematic evaluation of new polymer structures with outstanding property profiles dates back to the late 1950s. The driving force for the development of high-performance polymers was the urgent demand from the aerospace industries for new materials. Thermoplastic polymers have a unique combination of chemical, physical, and mechanical properties as well as the potential for low-cost composite fabrication. However, many problems must be resolved before thermoplastics find extensive use in structural aerospace applications.

Poly(arylene ether)s are a class of high-performance polymers that have received considerable attention: they are very processable and sometimes semicrystalline (for solvent resistance and better mechanical strength) and have both moderately high glass transition temperatures (T_gs) (150−200 °C) and operating temperatures; they also possess good thermooxidative integrity.

Polymers that are stable at higher temperatures have become increasingly important over the last 20 years, particularly for aerospace applications.[1−3] A wide variety of aromatic poly(arylene ether)s have so far been synthesized, and the relationship between their primary structures and polymer properties has been studied extensively.[4−17] Heterocyclic units incorporated into the backbone of poly(arylene ether)s generally result in an increase in the T_g and modulus over that of a poly(arylene ether) without heterocyclic units. The degree of increase varies from one system to another. They are often based upon aromatic nitrogen heterocycles such as 1,3,4-oxadiazole,[4,18,19] quinoline,[20−25] phenylquinoxaline,[26,27] pyridine,[25,28] and 1,2,4-triazole.[19] Their synthesis involves a nucleophilic substitution polymerization in which aromatic dihalides activated by strongly electron-attracting groups are generally chosen as partners of bisphenols. Dihalides containing heterocyclic nuclei, such as 1,3,4-oxadiazole, quinoline, phenylquinoxaline, pyridine, and 1,2,4-triazole are activated monomers in this type of reaction; in fact, a common characteristic of these activating groups is their electron-withdrawing character and the presence of a site of unsaturation, which can stabilize the negative charge developed in the displacement through resonance to an electronegative atom. This requires the formation of a Meisenheimer complex, which lowers the activation energy of the displacement reaction.[29] The major advantage of this synthetic approach is the incorporation of greater structural variety in the polymer backbone.

In an effort to obtain poly(arylene ether)s with high thermal stability and T_gs, we synthesized some new polymers containing 1,3,4-oxadiazole units. The synthesis and characterization of the polymers are discussed, and the thermal properties have been compared with those of some other poly(arylene ether)s reported in the literature.

Experimental Section

Materials. *N*-Methylpyrrolidinone (NMP; Aldrich Co) was refluxed in the presence of CaH_2 for 8 h under vacuum and distilled in the same conditions. Toluene was used as the azeotroping solvent and was stirred over calcium hydride for 24 h and distilled in a nitrogen atmosphere. Potassium carbonate [anhydrous grade (Aldrich Co), particle size less than 325 mesh] was dried at 150 °C under reduced pressure before use. 4,4′-Biphenol was purified by crystallization from ethyl alcohol, 4,4′-sulfonyldiphenol from methyl alcohol/water, and 4,4′dihydroxybenzophenone from acetone/water; all of the other dihydroxy monomers and diphenyl sulfone (DPS) were crystallized from toluene. Bisfluoro monomer was synthesized as described elsewhere.[30] Other reagents were commercial materials (Aldrich Co). All reactions were performed under an inert atmosphere of N_2.

Instrumental methods. All melting points of low molecular weight materials were determined on a Buchi 530 capillary melting point apparatus and are uncorrected.

IR spectra (KBr disks) were recorded on a Perkin-Elmer FT-1725-X spectrophotometer.

Elemental analyses were conducted on a Carlo Erba elemental analyzer, model 1106.

Inherent viscosities ($\eta_{inh} = \ln \eta_r/C$ at polymer concentration $C = 0.5$ g dL^{-1}) were measured with an Ubbelohde suspended-

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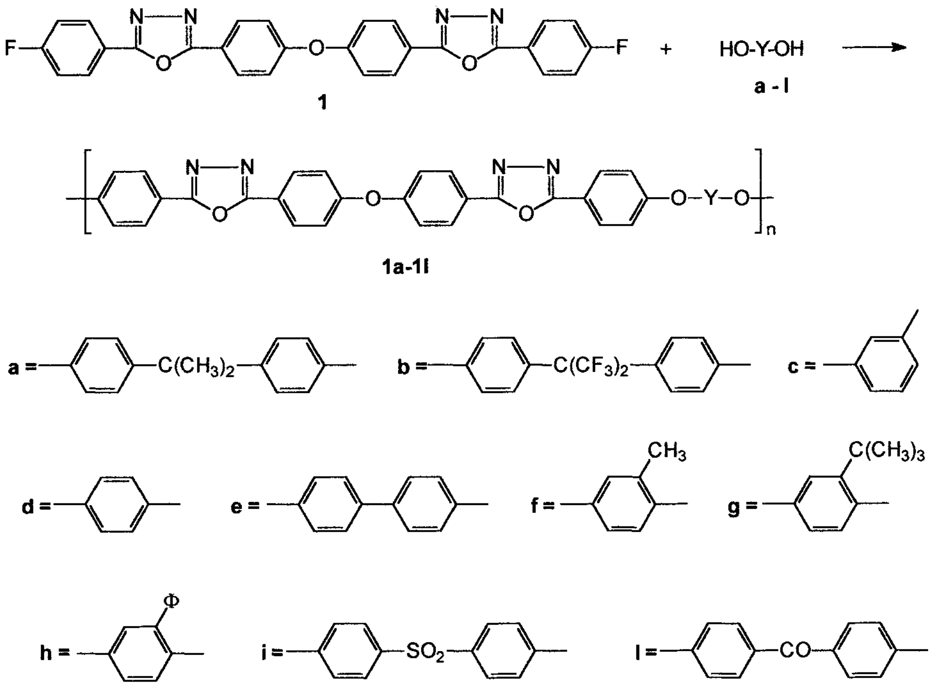
Scheme 1



level viscometer at 30 °C using chloroform, NMP, or sulfuric acid as the solvent.

Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent.

The molecular weight results were generated using an HP 1100 gel permeation chromatography (GPC) instrument operating at 30 or 70 °C, using respectively tetrahydrofuran (THF) or NMP as carrier at a flow rate of 1 mL/min. Separations were accomplished using a PLgel 5 μm mixed-D column from Polymer Labs. Solution concentrations were 2 mg/1 mL in THF or NMP depending on the solubility of the polymer; they were filtered through 0.45 μm PTFE membranes, and samples of 20 μL of the filtered polymer solution were injected into the columns. The results are the average of two injections. Calibration was performed using narrow polydispersity polystyrene standards in weight-average molecular masses in the range 2500 to 400 000 Da.

Thermogravimetric analyses (TG) were performed with a Mettler M3 thermobalance at a heating rate of 10 °C min^{-1} in N_2 flow (25 mL min^{-1}) or in static air. The temperature of 10% weight loss was taken as the decomposition temperature (T_d). Char yields (C_y) were calculated as the percentage of solid residue after heating from room temperature to 700 °C in N_2.

Differential scanning calorimetry (DSC) measurements were made using a Mettler DSC 30 with Al pans at a heating rate of 20 °C min^{-1} in N_2.

X-ray diffraction measurements were performed on powder samples with a Philips X-ray diffraction generator equipped with a flat camera and a Fujifilm imaging plate BAS-MS 2025. Cu Kα Ni-filtered radiation (30 ma, 50 kV) was employed, and the sample to film distance was set to 7.1 cm. Diffraction patterns were digitised by means of a Fuji Bioimaging analyzer system, model BAS-1800.

Polymer Synthesis (Scheme 1).

A typical example of solution polymerization is as follows: bisfluoro compound **1** (0.00335 mol) and bishydroxy compound **a** (0.00335 mol) in 12.5 g of diphenyl sulfone were heated to 140 °C under mechanical stirring until the slurry was clear. Then 0.7 g (0.0051 mol) of potassium carbonate was added, and the temperature was increased to 280 °C in 3 h. The mixture was then kept for 1 h at this temperature and a further quantity of the bisfluoro compound (0.00017 mol) was added 30 min before stopping the polymerization. The mixture was poured onto an aluminum tray, crushed, and washed with hot acetone and then with hot water. The polymer was refluxed overnight in methanol, filtered, and dried at 150 °C under vacuum. The yield was 94% and the η_{inh} of the polymer in chloroform was 0.71 dL/g. Anal. Calcd for $(C_{43}H_{30}N_4O_5)_n$ $(682.73)_n$: C, 75.65; H, 4.43; N, 8.21. Found: C, 75.51, H, 4.48; N, 8.19. IR: 1607 (C=N), 1246 (C−O−C), and 1096 cm^{-1} (=C−O−C=). The other polymers were synthesized by analogous procedures.

Results and Discussion

Among the synthetic routes available for the preparation of poly(oxadiazole)s, the cyclodehydration of a poly(diacylhydrazine) thermally or in the presence of a dehydrating agent (e.g., poly(phosphoric acid), phosphorus pentoxide, etc.) to produce poly(1,3,4-oxadiazole) has received the most attention,[31−33] but the conversion by these routes is not always quantitative. Since the aromatic poly(oxadiazole)s have limited solubility in common organic solvents, they are generally processed from the soluble poly(hydrazine) precursor.[34] Another means of introducing aryl ether linkages is via a poly(ether) synthesis in which the generation of the aryl ether linkages is the polymer-forming reaction. Here the preformed oxadiazole heterocyclic linkage may be introduced in the bis(halide) or bis(phenol) monomer and purified prior to polymerization. As reported in the Introduction, facile displacement of the aryl fluorides activated by the heterocyclic moieties was demonstrated with bis(phenol)s generating high molecular weight poly(arylene ether)s with significantly improved solubility and melt processability. This synthetic approach has the major advantage that the incorporation of greater structural variety into the polymer backbone is possible.

Aromatic poly(arylene ether 1,3,4-oxadiazole)s **1a**−**1l** were then synthesized by the aromatic nucleophilic substitution polycondensation of activated aromatic bis fluoro monomer **1** with bis(phenols) **a**−**l** (Scheme 1). An attempt to synthesize polymer **1d** using a mixed solvent system of NMP and toluene in the presence of anhydrous potassium carbonate resulted in a polymer with low η_{inh} (0.22 dL/g in concentrated sulfuric acid), probably due to the high rigidity of this polymer. This

Table 1. Solution Viscosities and Thermal Properties of Polymers 1a−1l

polymer	η_{inh}	T_d (°C)[a]	T_d (°C)[b]	T_g (°C)	T_m (°C)	C_y[c] (%)
1a	0.71[d]	455	445	207		31
1b	0.62[d]	470	460	220		50
1c	0.31[e]	465	440	188		45
1d	0.54[f]	480	470	203[g]	320	48
1e		470	455			56
1f	0.68[e]	450	440	207		58
1g	0.41[e]	470	455	218		46
1h		450	450	226		37
1i	0.35[e]	445	465	225		45
1l	0.51[f]	480	470	198[g]	357	52

[a] Temperature of 10% weight loss determined in nitrogen atmosphere. [b] Temperature of 10% weight loss determined in static air. [c] Char yield (calculated as the percentage of solid residue after heating from room temperature to 700 °C in N_2). [d] Determined in $CHCl_3$. [e] Determined in NMP. [f] Determined in H_2SO_4. [g] Visible only on reheating a quenched sample.

Table 2. Molar Masses of the Poly(arylene ether oxadiazole)s

polymer	M_n (g mol^{-1})	M_w (g mol^{-1})	M_z (g mol^{-1})	M_w/M_n
1a	10 970	17 990	25 260	1.64
1b	13 070	22 860	35 520	1.75
1c	11 220	21 290	40 890	1.90
1f	12 440	28 000	59 350	2.25
1g	11 360	22 990	45 250	2.02
1i	23 470	47 900	81 550	2.04

rigidity could cause poor solubility, due to the fact that the growing chains crystallize out from the reaction medium, thereby preventing the formation of high molecular weight polymer chains. For this reason we preferred to use the DPS/K_2CO_3 system as described in the Experimental Section: by this procedure it was possible to reach higher temperatures (280−300 °C) with a subsequently higher solubility of the growing chains. Polymer **1d** obtained in this way showed a η_{inh} of 0.54 dL/g determined in sulfuric acid. Because end groups could affect the thermal stability of the polymers, to ensure that most of the chains were fluorine terminated an excess of 5 mol % of the bisfluoro monomer was added 30 min before stopping the polymerization. The cleanup of the polymers was carefully carried out to ensure that all the DPS and the inorganic salts were removed. The yields of the polymers were always higher than 85% and the η_{inh} were between 0.31 and 0.71 dL/g as measured in chloroform, NMP, or concentrated sulfuric acid, depending on the solubility of the polymers (Table 1). The η_{inh} of polymers **1a** and **1b** were determined in chloroform because the presence of $-C(CH_3)_2-$ and $-C(CF_3)_2-$ groups in these polymers increased the solubility. Polymers **1e** and **1h** were insoluble in all solvents due to the rigid structure of the bisphenol monomers.

The elemental analysis values for carbon, hydrogen, sulfur, and nitrogen were in agreement with the calculated values for all polymers.

IR spectra exhibit bands characteristic of the oxadiazole ring at 1096 cm^{-1}(=C−O−C=) and 1607 cm^{-1}(C=N); other characteristic vibrations include the C−O−C stretching of the aryl ether group at 1246 cm^{-1}.

Size exclusion chromatography was used to determine the molecular weight of the polymers soluble in THF or NMP and the results are listed in Table 2. The molecular weight distributions were essentially unimodal with no evidence of oligomeric or unreacted species. The reported values are polystyrene equivalent weights. In any case, these values have to be taken as being only indicative, 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.[35]

Table 3. Solubility of Polymers 1a−1l[a]

polymer	H_2SO_4	NMP	DMAc	DMF	THF	$CHCl_3$
1a	++	++	++	+	++	++
1b	++	++	++	++	++	++
1c	++	++	±	+	−	+
1d	++	−	−	−	−	−
1e	−	−	−	−	−	−
1f	++	+	±	±	−	+
1g	++	++	+	+	±	++
1h	−	−	−	−	−	−
1i	++	+	+	±	−	±
1l	++	−	−	−	−	−

[a] Key: ++, soluble; +, soluble on heating; ±,partially soluble on heating; −, insoluble; NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N*,*N*-dimethylacetamide; DMF, dimethylformamide; THF, tetrahydrofuran; $CHCl_3$, chloroform.

The thermal behavior of the polymers was investigated by TG and DSC. The polymers were stable up to 445 and 440 °C in nitrogen and air atmospheres respectively (Table 1). In the polymer **1b** thermal degradation occurs in a two-stage process because the scission of the $-CF_3$ groups may occur after the cleavage of the bonds in the oxadiazole ring.[34]

The high thermal stability of these polymers was confirmed by the high C_y reported in Table 1.

T_g values were in the range 188−226 °C depending on the bis(phenol) used in the synthesis. T_g is known to depend on several factors such as chain symmetry and intermolecular forces, but it primarily depends on the rigidity of the main polymer chain.[36] Polymer **1b** exhibits a higher T_g with respect to polymer **1a** because of the stronger interchain interactions due to the polar $-CF_3$ groups which partially balance their flexibilizing effect. No T_g was detected for polymer **1e**. Polymers **1d** and **1l** were semicrystalline, showing T_g at 203 and 198 °C respectively, determined in both of them only after quenching, and T_m at 320 and 357 °C, respectively. The difference in T_g values between polymer **1d** and polymers **1f** and **1g** can be ascribed to the hindrance effect of the chain rotation in the methyl-substituted polymers.[37] In polymer **1g,** the incorporation of a bulky pendent group imparted a significant increase in both T_g and thermooxidative stability by restricting segmental mobility, while providing good solubility due to decreased packing and crystallinity.[38] As expected, polymer **1i**, containing a sulfone group, shows a T_g value higher than the ones shown from the other polymers because the introduction of this unit results in a lower interaction between the chains due to the bond angles of 105 °C and to disruption of the polymer chain planarity.[39]

Solubilities of the polymers are reported in Table 3. The high solubility of polymer **1b** was probably due to the nonplanar structure and low cohesive energies caused by the $-CF_3$ groups. The introduction of methyl groups was highly effective and gave soluble polymers; thus polymer **1f** was soluble on heating in NMP and $CHCl_3$ and partially soluble in DMAc and DMF, and polymer **1g** was soluble in NMP and $CHCl_3$ and on heating in DMAc and DMF, while the unsubstituted polymer **1d** was insoluble in the aforementioned solvents.

As reported in the Introduction, heterocyclic units incorporated into the backbone of poly(arylene ether)s

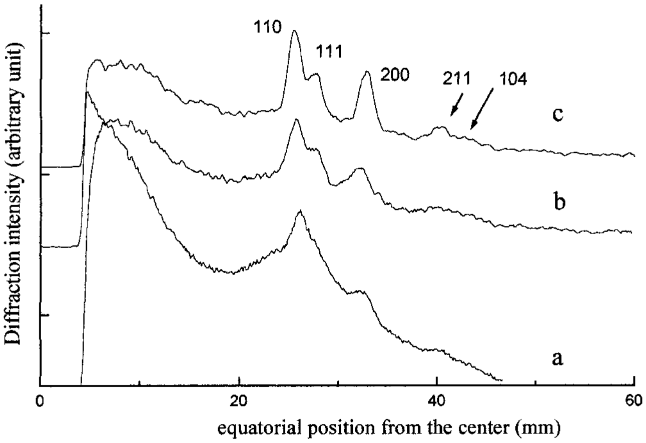


Figure 1. X-ray diffraction intensity, from radial scan of the diffraction pattern: scan for **1e** (a), **1d** (b), and **1l** (c).

generally result in an increase in the T_g, but the degree of increase varies from one system to another and also depends on the number of heterocyclic units introduced in the repeat unit. The influence of the presence of two 1,3,4-oxadiazole unit in the polymer backbone could be evaluated by comparison of the thermal properties of our polymers with analogues reported in the literature. In fact, by comparing polymers **1a** and **1b** with the corresponding polymers obtained by reaction of 2,5-bis-(fluorophenyl)-1,3,4-oxadiazole and 4,4′-isopropylidenediphenol **a** (T_g = 201 °C)[40] or 4,4′-hexafluoroisopropylidenediphenol **b** (T_g = 210 °C;[40] T_g = 192 °C[41]), our polymers showed higher T_g values. The T_g of the polymers obtained starting from 2,5-bis(fluorophenyl)-1,3,4-oxadiazole and 4,4′-sulfonyldiphenol **i** and 4,4′-dihydroxybenzophenone **l** are respectively 226 and 205 °C[19] and are comparable with those of our polymers **1i** and **1l**. In this case, the lower effect of the second oxadiazole unit is only apparent in fact the polymers reported in the literature have higher viscosities (η_{inh} = 1.02 and η_{inh} = 1.57) with respect to those of polymers **1i** and **1l**, and it is known that T_g increases with the molecular weight of the polymers. The effects of the presence of two oxadiazole units in the repeat unit of the polymer can be rationalized considering the greater positive effect on chain polarity of the 1,3,4-oxadiazole connecting groups and the fact that the oxadiazole ring introduces a catenation angle of 134° into the backbone.[35] Thus, the oxadiazole rings result in a more extended chain conformation (more rodlike structure), which causes more rigid chains and hence high T_gs.

According to X-ray diffraction and thermal analysis, all polymers are amorphous at room temperature excepted for **1d** and **1l**, which are partially crystalline with a similar diffraction pattern. The fact that the other polymers are amorphous, even after annealing at temperatures higher than the glass transition temperature, is not surprising considering that the nonlinear shape of monomers, except for the biphenol unit (monomer **1e**), inhibits molecular packing. Indeed, two weak and broad Debye–Scherrer rings are detectable in the diffraction pattern of the **1e** annealed (220 °C, for 3 h) sample (Figure 1). We do not have an explanation for the low crystallinity of **1e** compared to that of **1d**, but the high axial length of the monomer probably decreases the molecular mobility too much thus inhibiting crystallinity.

As concerns the crystalline phase, it is difficult to evaluate lattice parameters for **1d** and **1l** because we were unable to prepare oriented samples of polymers, thus taking advantage of more structural information from their polarized diffraction patterns. To make any attempt more difficult, only few reflections are observed in the diffraction patterns. Notwithstanding, some interesting similarities with poly(ether–ether–ketone) (PEEK)[42,43] and phase I of poly(*p*-hydroxy benzoate) (PHBA)[44,45] diffraction patterns provide us with a plausible unit cell for both **1d** and **1l**. In fact, in Table 4, the observed integrated intensity of Bragg reflections and the correspondent lattice spacings of **1d** and **1l** are compared with those of PEEK and PHBA taken from refs 43 and 45, respectively. In the case of **1l** the weak 100 reflection is also observed, similar to the case of PHBA. Thus, the same Bragg indices of PHBA, phase I, and PEEK are assigned to the observed Debye–Scherrer rings of **1d** and **1l**. Cell parameters are evaluated accordingly and are given in Table 5.

Table 4. X-ray Diffraction Data for Polymers 1d, 1e, and 1l

PHBA[a]			PEEK[b]			**1d**			**1l**		
d	*hkl*	Int	*d*	*hkl*	Int	*d*	*hkl*	Int	*d*	*hkl*	Int
7.44	100	1							7.22	100	<1
4.52	110	100	4.70	110	100	4.50	110	100	4.50	110	100
4.26	111	19	4.25	111	25	4.13	111	27	4.20	111	59
3.71	200	50	3.89	200	50	3.66	200	57	3.61	200	78
3.03	211	13	3.09	211	20	3.00	211	23	3.04	211	50
									2.88	104	2

[a] Data taken from ref 45. [b] Data taken from ref 43

Table 5. X-ray Diffraction Data for Polymers 1d, 1e, and 1l

polymer	*a* (Å)	*b* (Å)	*c* (Å)	space group
PHBA (phase I)	7.42	5.70	12.45	$Pbc2_1$
PEEK	7.77	5.90	9.99	*Pbcn*
1d	7.32	5.71		
1l	7.22	5.75		

Conclusions

Poly(aryl ether oxadiazole)s containing two oxadiazole groups in the repeat unit have been prepared by nucleophilic aromatic substitution generating aryl ether linkages as the polymer-forming reaction and structural variety has been introduced through the use of different bis(phenol)s. The obtained polymers show good solubility in various organic solvents and high thermal stability. Their glass transition temperatures are higher with respect to those of similar polymers containing only one oxadiazole unit in the repeat unit. All polymers are amorphous except for polymer **1d** and **1l**, which are partially crystalline. The overall properties of these new polymers make them promising as high performance materials.

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