

Synthesis and Characterization of New Copoly(arylene ether)s Containing Naphthalene or Naphthalene/1,3,4-Oxadiazole Units

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Summary

Series of new copoly(arylene ether)s containing naphthalene or naphthalene/1,3,4-oxadiazole units have been obtained by polycondensation in solution starting from the following systems of monomers: 1,5 or 2,6-bis(4-fluorobenzenesulfonyl) naphthalene / 2,6-bis(4-fluorobenzoyl)naphthalene, 1,5 or 2,6-bis(4-fluorobenzenesulfonyl)naphthalene / 2,2'-(oxydi-4,1-phenylene)bis[5-(4-fluorophenyl)-1,3,4-oxadiazole] and 2,6 bis-(4 fluorobenzoyl)naphthalene/2,2'-(oxydi-4,1-phenylene)bis [5-(4-fluorophenyl)-1,3,4-oxadiazole]. Hydroquinone and 4,4'-dihydroxy benzophenone have been used as aromatic dihydroxy compounds. The copolymers, obtained in quantitative yields, possessed inherent viscosities in the range 0.28-0.58 dl g⁻¹, had good thermal stability (10% weight loss temperatures were above 460°C both in nitrogen and air) and high glass transition temperatures (in the range 190-210°C). They have been characterized by infrared analyses, GPC and wide-angle X-ray diffraction. The copolymer property-structure relationships were studied and the properties have been compared with those of the corresponding homopolymers.

Introduction

Poly(arylene ether)s (PAE) are well-recognized high performance engineering thermoplastics possessing an attractive combination of mechanical properties, good environmental resistance and high thermal and thermo-oxidative resistance. They have found wide applications in automobile, precision instruments, electronics, electrical applications and communications. Polymers stable at higher temperatures have become of increasing importance in the last 20 years, particularly for aerospace applications [1-3]. A wide variety of PAEs have so been synthesized and the relationships between their primary structure and polymer properties have been extensively studied [4-9]. The method frequently utilized for their preparation is aromatic nucleophilic substitution polymerization, in which aromatic dihalides activated by strongly electron-attracting groups, as carbonyl or sulfone groups, are generally chosen as partners of bisphenols [10-11].

PAEs containing naphthalene unit [4, 12, 13] or heterocyclic moieties [14] such as benzoxazoles [15, 16], imidazoles [17], 1,3,4-oxadiazoles [4, 18-21] and quinoline [12, 13, 22-24] have been studied for high performance applications. Their most important feature is the increased stiffness of the polymer chains in comparison with those containing benzene ring, resulting in higher T_g s and thermal stability. Moreover a common characteristic of the heterocyclic groups is the activating effect due to their electron-withdrawing character and the presence of a site of unsaturation, which can stabilize the negative charge developed in the displacement reaction. It requires the formation of a Meisenheimer complex, which lowers the activation energy of the displacement reaction.

In previous papers [20, 25], we obtained good results for poly(arylene ether ketone)s synthesized by reaction of 2,6-bis(4-fluorobenzoyl)naphthalene or 2,2'-(oxydi-4,1-phenylene)bis[5-(4-fluorophenyl)-1,3,4-oxadiazole] with hydroquinone and dihydroxybenzophenone: the obtained polymers were crystalline and showed low solubility. On the other hand our recent work on poly(arylene ether sulfone)s containing naphthalene units [25] reports for these polymers good solubility and high T_g s, but no crystallinity. This means that, for use as a composite matrices, the former are difficult and expensive to prepreg but composite structures, when formed, have excellent solvent resistance, while the latter polymers are easy to prepreg from relatively cheap, organic solvent and composite parts based on these amorphous polymers do not have such good solvent resistance. A highly desirable thermoplastic composite matrix would, therefore, be one which combined the ease of prepregging and high T_g of the poly(ether sulfone)s with the semicrystalline and solvent resistant nature of the poly(ether ketone)s. A possible route to achieving this is through copoly(ether ketone sulfone)s. In this paper we present the study carried out preparing copoly(arylene ether)s containing naphthalene or naphthalene/1,3,4-oxadiazole rings bridged by ketone, sulfone and ether groups. We have studied the influence of the contemporary presence of these linking groups on the copolymer thermal properties, solubility and crystallinity. The properties of the synthesized copolymers were compared with those of the corresponding homopolymers.

Experimental

Materials

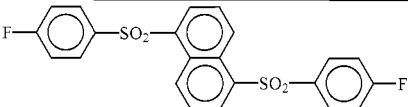
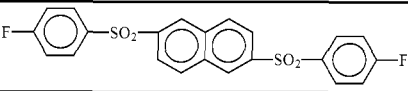
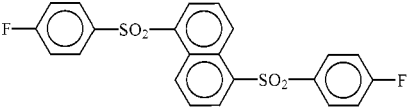
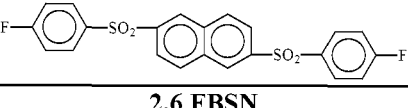
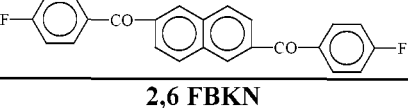
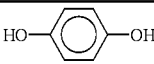
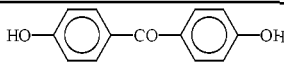
N-Methyl-pyrrolidinone (NMP; Aldrich Co) was refluxed in the presence of CaH_2 for 8 h under vacuum and distilled in the same conditions. Potassium carbonate [anhydrous grade (Aldrich Co), particle size less than 325 mesh] was dried at 150°C under reduced pressure before use. Diphenyl sulfone (DPS) and hydroquinone (HQ) were crystallised from toluene, 4,4'-dihydroxybenzophenone (DHBP) was purified by crystallization from acetone/water, 1,5 and 2,6-bis(4-fluorobenzenesulfonyl)naphthalene (1,5-FBSN and 2,6-FBSN) [26], 2,6-bis(4-fluorobenzoyl)naphthalene (2,6-FBKN) [12] and 2,2'-(oxydi-4,1-phenylene)bis[5-(4-fluorophenyl)-1,3,4-Oxadiazole] (FBOXA) [20] were synthesized as described according to the literature. Other reagents were commercial materials (Aldrich Co). All reactions were performed under an inert atmosphere of N_2 .

Instrumental measurements

IR spectra were recorded on a Perkin Elmer FT-1725-X spectrophotometer and are the result of 10 scans. The data were acquired in the transmission mode using KBr disks. Inherent viscosities ($\eta_{inh} = \ln \eta_r/C$ at polymer concentration $C=0.5 \text{ g dl}^{-1}$) were measured using an Ubbelohde suspended-level viscometer at 30°C using NMP or concentrated sulfuric acid as solvents. Quantitative solubility was determined using 0.05 g of the polymer in 1 ml of solvent. Molecular weight distributions were determined using an HP 1100 gel permeation chromatography (GPC) instrument operating at 70°C , using NMP as carrier at a flow rate of 1 ml min^{-1} . Separations were accomplished using a PLgel $5 \mu\text{m}$ mixed-D column connected with a PLgel $5 \mu\text{m}$ 500 \AA column (Polymer Labs). The measurement utilized a refractive index detector and toluene as internal standard. The polymer samples were dissolved in NMP at concentration of 2 mg ml^{-1} ; they were filtered through $0.45 \mu\text{m}$ PTFE membranes and injected in $20 \mu\text{l}$ aliquots. The results are the average of two injections. Narrow molecular weight polystyrene standards in the range 2500 to 400000 Da were used for calibration. Thermal gravimetric analysis (TG) was carried out with a Mettler M3 thermobalance at a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 flow (20 ml min^{-1}) or in static air. Decomposition temperatures (T_d) were taken as the temperatures of 2, 5 and 10% weight loss. 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) data were obtained from 4-6 mg samples in a nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$ using a Mettler DSC 30. 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-K_α Ni-filtered radiation (20 mA, 40 KV) was employed and sample to film distance was set to 90 mm. Diffraction patterns were digitized by means of a Fuji Bio-imaging Analyser System, mod. BAS-1800.

Copolymer synthesis

Copoly(arylene ether)s **1a-5b** were prepared according to *Scheme 1* by reaction of bis-fluoro monomer mixtures **1-5** (50/50 mol % ratios) and bis-hydroxy compounds **a-b**. A typical example of solution polymerization is as follows: 1,5-FBSN (0.001675 mol), 2,6-FBKN (0.001675 mol) and hydroquinone (0.00335 mol) in 10 g of diphenyl sulfone were heated to 140°C under mechanical stirring until the slurry was clear. Then 0.70 g (0.0051 mol) of potassium carbonate were added and the temperature was increased to 280°C in 3 hour time. The mixture was then kept for one hour at this temperature and a further quantity of 2,6-FBKN (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 of copolymer **1a** was 95%, the η_{inh} , determined in NMP was 0.35 dl g^{-1} and i.r. spectra exhibited bands at 1651 (C=O), 1304 (as SO_2), 1229 (as COC) and 1136 cm^{-1} (s SO_2). The other copolymers were synthesized by analogous procedures and the characterization was presented in *Table 1*.

Bis-fluoro monomer mixtures (50/50 mol % ratios)		+	HO—Ar—OH	→	Copoly(arylene ether)
1-5			a, b		1a - 5b
Monomer mixtures					
1					
	1,5 FBSN				2,6 FBKN
2					
	2,6 FBSN				2,6 FBKN
3					
	1,5 FBSN				FBOOXa
4					
	2,6 FBSN				FBOOXa
5					
	2,6 FBKN				FBOOXa
Bis-hydroxy compounds					
					
	a				b

Scheme 1. Copolymerization of monomer mixtures (**1-5**) with bis-hydroxy compounds (**a-b**)

Results and discussion

Aromatic copoly(arylene ether)s **1a-5b** were synthesized by the aromatic nucleophilic substitution polycondensation of bis-fluoro monomer mixtures **1-5** (50/50 mol %

ratios) with bis-hydroxy compounds **a-b** using the DPS/K₂CO₃ system as described in the Experimental Procedures (*Scheme 1*). By this procedure it was possible to reach high temperatures (280°C) with a subsequent higher solubility of growing chains. The clean-up of the polymers was carefully carried out to ensure that all the DPS and the inorganic salts were removed. The yields of the copolymers were always higher than 95% and the η_{inh} values were between 0.28 and 0.58 dl g⁻¹ as measured in NMP or sulfuric acid, depending on the solubility of the polymers (*Table 1*). The i.r. spectra for polymers **1a-2b** exhibited bands characteristic of the sulfone groups at ~ 1310 and ~1140 cm⁻¹, and the one of the ether group at ~1230 cm⁻¹. The i.r. spectra for polymers **3a-4b** showed bands characteristic at ~ 1600 (C=N), ~1310 (as SO₂), ~1235 (as COC), ~ 1148 (s SO₂) and 1090 cm⁻¹ (=C-O-C=). Copolymers **5a** and **5b** exhibited bands characteristic of the oxadiazole ring at ~ 1590 (C=N) and ~1100 cm⁻¹ (=C-O-C=), the band of the ketone group was at ~ 1651 cm⁻¹, while the C-O-C stretching of the ether group was at ~ 1234 cm⁻¹. Solubility of the copolymers was reported in *Table 1*: copolymers **1a-4b** were soluble on heating in NMP and DMAc and partially soluble in DMF. It was due to the presence, in the polymer backbone, of two sulfone groups that were active in disrupting polymer chain planarity due to different bond angles (105° for Ar-SO₂-Ar with respect to 124° for Ar-O-Ar), resulting in a lower interaction between the chains and so increasing the solubility [27]. Copolymers **5a** and **5b**, were insoluble in all solvents except in H₂SO₄ where the observed partial solubility made possible to determine their solution viscosity. This behaviour was determined by their semicrystalline character confirmed by DSC and wide angle X-ray diffraction.

Table 1. Solution viscosities, solubility and molar masses of copolymers **1a-5b**

Polymer	η_{inh} (dl g ⁻¹) ^a	Solubility ^b				Molar masses		
		NMP	DMAc	DMF	H ₂ SO ₄	M _n (g mol ⁻¹)	M _w (g mol ⁻¹)	M _w /M _n
1a	0.35	+	+	+	+++	20500	38800	1.89
1b	0.48	+	+	±	+++	15800	29600	1.87
2a	0.58	+	+	+	+++	26600	50700	1.90
2b	0.45	+	+	±	+++	19800	35200	1.78
3a	0.28	+	+	+	+++	7200	12700	1.76
3b	0.34	+	+	±	+++	13700	25500	1.86
4a	0.30	+	+	+	+++	11400	21500	1.88
4b	0.26	+	+	+	+++	10500	18450	1.75
5a	0.28 ^c	-	-	-	++	-	-	-
5b	0.53 ^c	-	-	-	++	-	-	-

^a Measured in NMP; ^b +++ soluble, ++ partially soluble, + soluble on heating, ± partially soluble on heating, - insoluble; ^c Measured in H₂SO₄

Gel permeation chromatography was used to determine the molecular weight of the polymers soluble in NMP and the results were listed in *Table 1*. GPC is related to hydrodynamic radius of the polymers in solution, so the molar masses have to be taken as being only indicative. Calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the polymers studied deviate strongly from those of polystyrene [11]. The molecular weight distribution for polymers **1a-4b** was essentially unimodal with no evidence of unreacted species. The

molar masses of these copolymers were in the range 7200-26600 (M_n) and 12700-50700 (M_w). No determination was possible for copolymers **5a** and **5b** due to their insolubility in NMP.

Table 2. Thermal characterization of copolymers **1a-5b**

Polymer	T_d^a	T_d^b	T_d^c	T_d^d	T_d^e	T_d^f	T_g (°C)	T_m (°C)	C_y^g
1a	280	420	460	260	425	475	195		43
1b	360	435	480	325	435	485	190		51
2a	330	460	480	280	445	510	208		53
2b	390	450	495	365	450	505	190		56
3a	270	415	455	310	430	465	200		46
3b	375	440	475	375	445	470	195		50
4a	310	405	445	305	400	450	210		46
4b	415	460	490	375	465	490	191		52
5a	410	455	475	370	445	475	180 ^h	250 ^h 320	52
5b	425	450	470	405	440	465	195 ^h	260 ^h 370	54

^a Temperature of 2% weight loss determined in nitrogen atmosphere; ^b Temperature of 5% weight loss determined in nitrogen atmosphere; ^c Temperature of 10% weight loss determined in nitrogen atmosphere; ^d Temperature of 2% weight loss determined in static air; ^e Temperature of 5% weight loss determined in static air; ^f Temperature of 10% weight loss determined in static air; ^g Char yield calculated as the percentage of solid residue after heating from room temperature to 700°C under nitrogen; ^h Visible on reheating a sample annealed at 250°C for 30 minutes

The thermal behaviour of the polymers was investigated by TG and DSC and the T_d , T_g , T_m and C_y were summarized in *Table 2*. The T_d s of polymers **1a-5b**, determined under N_2 , were in the range 270-425°C (2% weight loss), 405-460°C (5% weight loss) and 455-495°C (10% weight loss) while the ones determined in static air were in the range 260-405°C (2% weight loss), 400-465°C (5% weight loss) and 450-510°C (10% weight loss). The copolymers obtained by reaction of the monomers **1-4** with DHBP showed higher T_d values (especially for the temperature of 2% weight loss) than those of the copolymers obtained by reaction of the same monomers with HQ. The high thermal stability of these polymers was confirmed also by the high C_y values, that were in the range 43-56% (*Table 2*). The T_g s of the copolymers were in the range 190-210°C: in every series, they were higher for polymers obtained by reaction with hydroquinone. Polymer **5a** showed, “as made”, a T_m at 330°C and, on reheating the sample annealed at 250°C for 30 minutes, a T_g at 180°C and two endothermic transitions at 250 and 320°C. Polymer **5b** showed, “as made”, a T_m at 370°C and, on reheating the sample annealed at 250°C for 30 minutes, a T_g at 195°C and two endothermic transitions at 260 and 360°C. Wide angle X-ray diffraction were obtained on sample pellets and diffraction patterns were shown in *Figure 1*. The sharp and diffuse pattern for copolymers **5a** and **5b** were characteristic of semicrystalline structures. The peaks became sharper in polymer **5b** compared to ones of polymer **5a**: it might be due to the increase of ketone content (coming from DHBP) in **5b**.

It is interesting to compare the properties of the new synthesized copolymers **1a-5b** with those of the polymers obtained starting from 1,5-FBSN, 2,6-FBSN, 2,6-FBKN or FBOXA with HQ or DHBP [20, 25]. About the thermal properties, the copolymers

maintained high T_d values comparable with those of all the homopolymers, instead the T_g s of copolymers **1a-4b** were lower than those of the polymers obtained starting from 1,5 and 2,6-FBSN. In polymers **1a-2b**, this effect was due to contemporaneous presence in the copolymer backbone of sulfone and ketone bridging units: in fact it is known that the glass transition temperatures of polymers depend on both chain rigidity and polarity. In poly(arylene ether sulfone)s the sulfone groups exhibit strong electronegative characteristics which lead to a delocalisation of π -electrons from the aromatic rings. The resulting double-bond character of the C-S link restricts rotation and consequently enhances chain rigidity, leading to an increase in T_g .

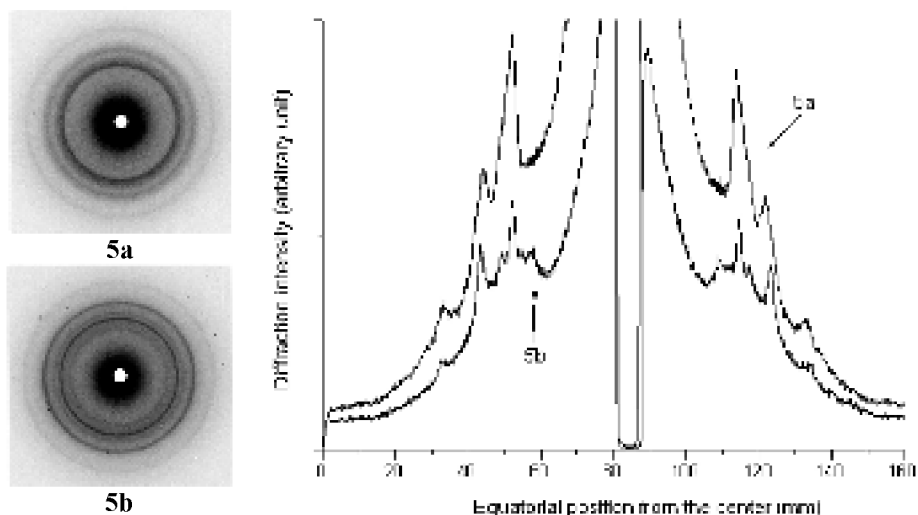


Figure 1. WAXD and X-ray diffraction patterns of copolymers **5a** and **5b**

The ketone linkage also induces an electron-withdrawing effect leading to a chain rigidification by electron delocalization, however, because of its lower electronegativity, its efficiency is less than that of the sulfone group [27]. So the T_g s of the copolymers **1a-2b**, obtained changing a sulfone group to a ketone linking group, were lower than those of the homopolymers obtained from 1,5 and 2,6-FBSN containing only sulfone linkages. In copolymers **3a-4b**, the decrease in the T_g s values were probably due to the presence of the ether group bridging the oxadiazole units, in fact the two O-C links on both side of the ether group are fully not-rigid and the rotation around these links is free. Copolymers **5a** and **5b** showed good values of T_g : they were higher than those coming from homopolymers obtained starting from the 2,6-FBKN monomer and near to those of the homopolymers synthesized from FBOOXA. Moreover, copolymers **5a** and **5b** showed crystalline domains as the corresponding homopolymers. About the solubility, we could observe an improvement especially respect to homopolymers obtained starting from 2,6-FBKN and FBOOXA, in fact while they were completely insoluble in aprotic solvents, copolymers **1a-4b**, in which also sulfone units were present, resulted soluble on heating in NMP and DMAc and partially soluble on heating in DMF.

In conclusion, as expected, the properties of the new synthesized copolymers were function both of the contemporary presence and number of naphthalene or oxadiazole units bridged by ether, ketone and/or sulfone groups. The new copolymers showed

improved properties with respect to those of the respective homopolymers but, nevertheless, the optimum balance of properties necessary to obtain highly desirable thermoplastic composite matrix was not yet achieved. Works are in progress to study the properties of copolymers obtained varying the ratio of naphthalene to oxadiazole units, or ketone to sulfone groups and exploiting the possibility of synthesizing block copolymers.

Acknowledgements

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