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Synthesis and characterization of new poly(arylene ether 1,3,4-oxadiazole)s based on dihydroxynaphthalene isomers

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Summary

A series of new poly(arylene ether 1,3,4-oxadiazole)s has been obtained starting from a difluorosubstituted monomer containing 1,3,4-oxadiazole rings and some dihydroxynaphthalene isomers. The polymers have been prepared by polycondensation in solution and have been obtained in quantitative yield. They had inherent viscosity from 0.2 to 0.82 dL/g, showed good thermal stability (10% weight loss temperatures in nitrogen and air were above 460 and 450°C, respectively) and high glass transition temperatures (in the range of 197-232°C). The polymers were characterized by elemental and infrared analyses, GPC and wide angle X-ray diffraction.

Introduction

In recent years, high temperature resistant engineering thermoplastic resins have gained acceptance for use as matrices in advanced resin composites for aerospace structural applications, including military aircraft and missiles (1-3). The choice could be directed to composite materials with a polymer matrix, but most of the polymers available do not have the thermal stability required. The main goal of research in this area is the preparation of polymers possessing good thermal and oxidative stability, high glass transition temperature (T_g), tensile strength and moduli. Thus in the synthesis of any thermally stable polymers, a compromise has to be reached between thermo-mechanical properties and processability. Therefore it is very important to study various structure-property relationships in order to predict the effects of structural modification on polymer properties (4-13). In order to produce polymers with high thermal stability and processability, it is necessary to take into account that:

- the introduction of ether linkages can improve the solubility characteristics of rigid polymers (14);
- the incorporation of aromatic rings in the polymer chain not only increases chain stiffness, but also introduces structures which possess good thermal and oxidative stability (15-17);
- the incorporation of heterocyclic units within the backbone of polymers has

Therefore we have designed the incorporation of naphthalene units in the polymer backbone of poly(arylene ether 1,3,4-oxadiazole)s, taking into account that these units would introduce enhanced chain stiffness. The polymers were prepared via the aromatic nucleophilic displacement reaction of an activated bis-fluoro monomer containing 1,3,4-oxadiazole units with various dihydroxynaphthalene isomers. In fact, this method offers distinct advantages over other routes because it includes easier synthesis and more versatility in the chemical structure. In this work, we have studied the influence of the naphthalene unit on the polymer properties and the effect of the position of the two ether bonds (1,6; 2,3 etc.) fixing the naphthalene ring in the chain. The thermal properties of the polymers have been compared with those of other poly(arylene ether 1,3,4-oxadiazole)s.

Experimental

Materials

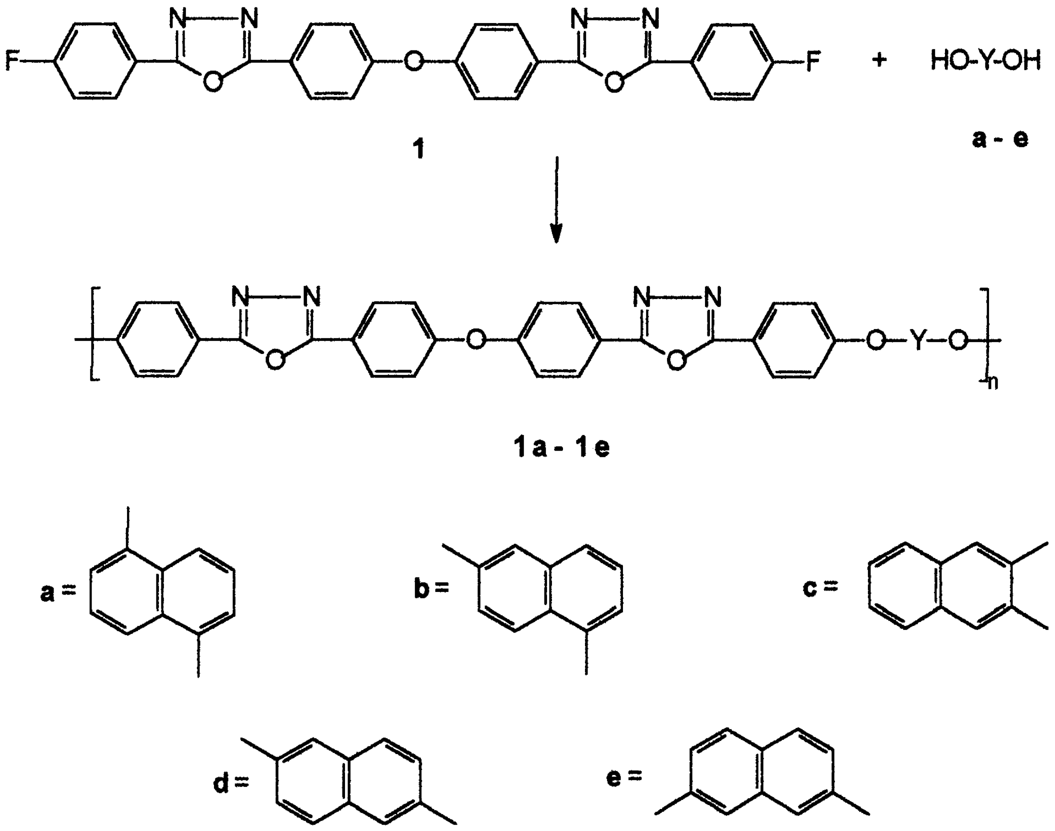
N-Methyl-pyrrolidinone (NMP; Aldrich Co) was refluxed in the presence of CaH_2 for 8 h under vacuum and distilled under the same conditions. Potassium carbonate [anhydrous grade (Aldrich Co), particle size less than 325 mesh] was dried at 150°C under reduced pressure before use. Bis-fluoro monomer **1** was synthesised as described elsewhere (22). Diphenyl sulfone (DPS), 1,6-, 2,3-, 2,6- and 2,7-dihydroxy naphthalene were crystallised from toluene. 1,5-Dihydroxy naphthalene was crystallised from 1,4-dioxane/water. Other reagents were commercial materials (Aldrich Co). All reactions were performed under an inert atmosphere of N_2.

Instrumental

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 Analyser-Mod 1106. Inherent viscosities ($\eta_{inh} = ln\ \eta_r/C$ at polymer concentration C=0.5 g dL^{-1}) were measured with an Ubbelohde suspended-level viscometer at 30°C using NMP or concentrated sulphuric acid as the solvents. The molecular weight values were performed using a HP 1100 gel permeation chromatography (GPC) instrument operated at 70°C using NMP as carrier at a flow rate of 1ml/min. Separations were accomplished using a PLgel 5µm mixed-D column from Polymer Labs., a refractive index detector and toluene as internal standard. Solution concentrations were 2mg/1mL in NMP; they were filtered through 0.45µm PTFE membranes and samples of 20µl 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 weights in the range 2500 to 400000 Da. Thermogravimetric analyses (TG) were performed with a Mettler M3 thermobalance at a heating rate of 10°C min^{-1} in N_2 flow (25ml 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, 50KV) was employed and sample to film distance was set to 7.1 cm. Diffraction patterns were digitised by means of a Fuji Bioimaging Analyser System, mod.BAS-1800.

Polymer synthesis (Scheme 1)

A typical example of polycondensation in solution is as follows: bis-fluoro compound **1** (0.00335 mol) and 1,5-dihydroxynaphthalene (**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 were added and the temperature was increased to 280°C in 3 h. The mixture was then kept for an hour at this temperature and a further quantity of bis-fluoro compound (0.00017 mol) was added 30 minutes before stopping the polymerisation. The mixture was poured onto an aluminium 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 95% and the η_{inh} of the polymer in NMP was 0.38 dL/g. Anal.calcd for $(C_{38}H_{22}N_4O_5)_n$ $(614.62)_n$: C, 74.26; H, 3.61; N, 9.12. Found: C, 74.35 ; H, 3.49; N, 9.25. I.r.: 1607cm^{-1} (C=N), 1243 cm^{-1}(C-O-C) and 1096 cm^{-1} (=C-O-C=).
The other polymers were synthesised by analogous procedures.



Scheme 1. Polymerization of monomer **1** with dihydroxynaphthalene isomers **a-e**.

Results and discussion

Synthesis of polymers

Aromatic poly(arylene ether 1,3,4-oxadiazole)s **1a-1e** were synthesized by the aromatic nucleophilic substitution polycondensation of bis-fluoro compound **1** with dihydroxy **a-e** using the DPS/K_2CO_3 system according to Scheme 1. By this procedure it was possible to reach high temperatures (280°C) with a subsequent higher solubility of growing chains. Because end-groups could affect the thermal stability of the polymers, in order to ensure that most of the chains were fluorine terminated, an excess of 5 mol % of bis-fluoro monomer was added 30 min before stopping the polymerisation. The clean-up of the polymers was carefully done to ensure that all the DPS and the inorganic salts were removed. The yields of the polymers were always higher than 94% and the η_{inh} values were between 0.20 and 0.82 dLg^{-1} as measured in concentrated sulphuric acid or NMP (Table 1), depending on the solubility of the polymers. The elemental analysis values for carbon, hydrogen and nitrogen were in close agreement with the calculated values for all polymers. I.r. spectra exhibit bands characteristic of the oxadiazole ring at 1096 (=C-O-C=) and 1607 cm^{-1} (C=N); other characteristic vibrations include the =C-O-C= stretching of the diarylether groups at $\approx$1240 cm^{-1}.

Size exclusion chromatography was used to determine the molecular weight only of the polymers soluble in NMP and the results are listed in Table 1. The molecular weight distributions were essentially unimodal with no evidence of oligomeric or unreacted species. The reported values have to be taken as indicative only, since calibration with polystyrene standards may lead to questionable results as the polarity and stiffness of the polymers studied deviate strongly from those of polystyrene.

According to X-ray diffraction and thermal analysis, all the polymers were amorphous. The fact that the polymers were amorphous, even after annealing at temperatures higher than the glass transition temperatures, was not surprising considering that the non-linear shape of monomers inhibits molecular packing.

Table 1. Viscosities, thermal properties and molar masses of poly(arylene ether)s **1a-1e**.

Polymer	η_{inh} (dLg^{-1})	$T_d{}^a$ (°C)	$T_d{}^b$ (°C)	T_g (°C)	$C_y{}^c$ (%)	M_n (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n
1a	0.38[e]	470	460	212	53	12820	22670	1.77
1b	0.65[d]	480	475	228	61			
1c	0.20[e]	480	475	197	55	6010	8130	1.35
1d	Ins.	480	450	230	54			
1e	0.82[d]	460	462	232	45			

[a]temperature of 10% weight loss determined in nitrogen atmosphere; [b]temperature of 10% weight loss determined in static air; [c]char yield; [d]determined in H_2SO_4; [e]determined in NMP.

Thermal properties of the polymers

The thermal behaviour of the polymers was investigated by TG and DSC. The polymers were stable up to 460 and 450°C in nitrogen and air atmospheres respectively (Table 1) and the high thermal stability was confirmed by the C_y values that were in the range 48-61% for all polymers (Figure 1).

The T_g values were in the range 197-232°C depending on the structure of the dihydroxy monomers used in the synthesis (Table 1). In a previous work (23), we studied how the introduction of a naphthalene unit and the location of the naphthalene-ether bond affected the thermal properties in polymers such as poly(arylene ether ketone)s and poly(arylene ether sulfone)s. For these classes of polymers, the properties seemed be modulated as a function of the position of the two ether bonds (1,6; 2,3 etc.) fixing the naphthalene ring in the chain. Also for the polymers synthesised in this work, the position of the naphthalene-ether bond appears to affect the polymer properties, in fact, the T_g values were in the range 197-232°C. T_g is known to depend on several factors (chain symmetry, polar groups, cross-linking, intermolecular forces etc.), but it primarily depends on the rigidity of the polymer chain. In fact, the increase of the rigidity of the polymer backbones increases the energy barrier for segmental motion, the mobility is hindered and hence T_g increases. Therefore, the higher thermal stability and T_g value of polymer **1d** with respect to polymer **1a** could be related to the higher rigidity and symmetry of the 2,6-naphthalene moiety with respect to the 1,5 one as already reported for polymers containing these units (24). Instead, in polymer **1c**, containing the 2,3-naphthalene unit, the presence of pendant groups probably inhibited the close packing of polymer chains, determining a lower value of T_g.

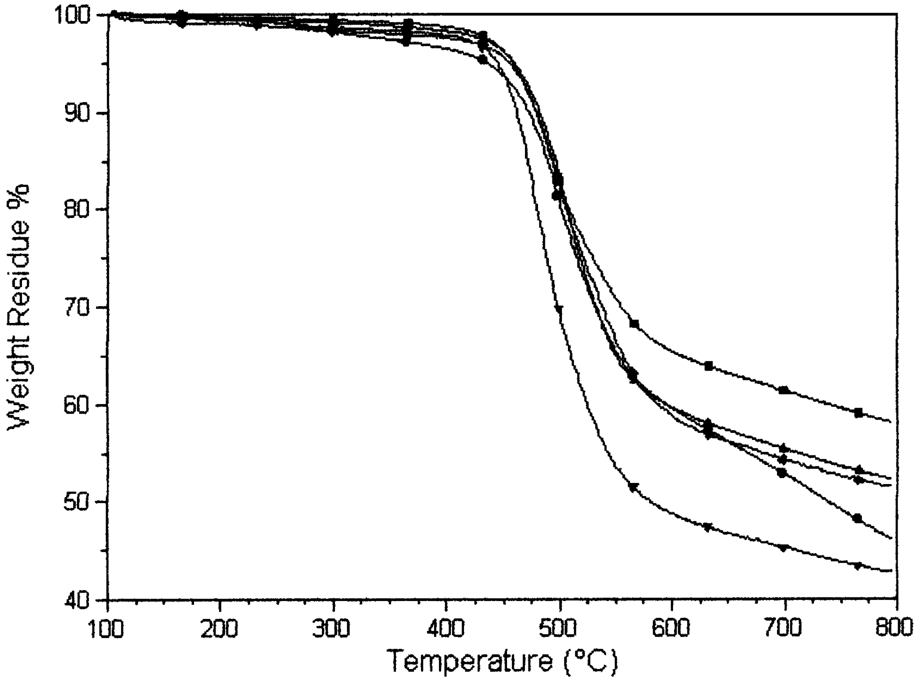


Figure 1. TG curves obtained in N_2 atmosphere of polymers **1a(●)**, **1b(■)**, **1c(▲)**, **1d(◆)**, and **1e(▼)**.

The influence of the presence of naphthalene moieties in the polymer backbone could be evaluated by comparison of the thermal properties of the obtained polymers **1a-1e** with analogues containing other rigid structures. The T_d values of the polymers containing naphthalene units were always higher with respect to those of polymers where the naphthalene unit has been substituted with a phenyl ring, showing T_ds under N_2 and in static air respectively at 455 and 445°C (25). These results confirmed that the introduction of a naphthalene ring into the polymer main chain leads to an increase in thermal stability in comparison with the benzene ring, because of the contribution from the more rigid structure of the former. This effect was also confirmed by comparing the T_g values: except for polymer

1c, they were always higher with respect to those of the polymer containing the phenyl ring, showing a T_g at 203°C and were comparable with those of the polymers obtained starting from monomer **1** and 4,4'-(hexafluoroisopropylidene)diphenol (T_g=220°C), *t*-butylhydroquinone ((T_g=218°C), phenylhydroquinone (T_g=226°C) and 4,4'-sulfonyldiphenol (T_g=225°C) (25). Instead, the T_g of polymer **1c**, containing the 2,3 naphthalene unit, is comparable with that of the polymer obtained by the reaction of monomer **1** and resorcinol (T_g=188°C) (25).

In conclusion, poly(arylene ether)s incorporating 1,3,4-oxadiazole and naphthalene groups in the repeating unit showed good thermal properties and high T_g values. All the polymers resulted in amorphous materials and some of them were soluble in aprotic solvents. These properties seem to be modulated as a function of the location of the naphthalene-ether bond present in the chain.

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