Polymer Bulletin 26, 395–401 (1991)

Polymer Bulletin

Poly(arylene ether sulfones) and poly(arylene ether ketones) derived from dibenzofuran

Synthesis and thermal characterization

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SUMMARY

New polyarylene ether ketones and polyarylene ether sulfones were prepared by polycondensation of various bisphenols with two new dihalide monomers including dibenzofuran structure, respectively 3,6 bis (4-fluorophenylcarbonyl) dibenzofuran and 3,6 bis (4-fluorophenylsulfonyl) dibenzofuran. Most of these thermoplastic polyethers are soluble in NMP and in chlorinated solvents. They exhibit Tgs up to 234°C for the polyetherketones and up to 262°C for the polysulfones, so over 50°C higher than the Tgs of classical available polyethers.

INTRODUCTION

Amorphous polyarylene ethers like polyetherketones and polysulfones are good candidates for high-performance thermoplastic materials. They exhibit good processability, good mechanical properties and high thermostability (1,2,3). They may avantageously be used as matrix for graphite-reinforced composites.

They are usually prepared by polyetherification of bisphenols with appropriate dihalides in a basic medium (4,5). The most common polyethers are prepared by polycondensation of bisphenol A with 4,4'-dichlorodiphenyl sulfone for the polysulfones, and with 4,4'-difluorobenzophenone for the polyetherketones. Glass transition temperatures of these polymers are respectively of 190°C and 165°C.

In this article we report the synthesis of two new dihalides having dibenzofuran structure and containing respectively sulfone and ketone groups.

Polycondensations of these two monomers were performed with various bisphenols and lead to new polyethers. The purpose of this work was to prepare polymers with improved Tg because of the rigid nature of the dibenzofuran structure, in association with a good solubility in most common solvents enhanced by the ether linkage present in the furan ring.

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EXPERIMENTAL

Materials

Dibenzofuran, 4-fluorobenzoylchloride, 4-fluorobenzene sulfonyl chloride were purchased from Aldrich and were used as received. 2,2 Bis (4-hydroxyphenyl) propane (bisphenol A) (Fluka) was recrystallized from toluene. 2,2 Bis (4-hydroxyphenyl) hexafluoropropane (bispherol AF) (Fluka) was recrystallized from a toluene/ethyl acetate (95:5) mixture. 4,4'-Dihydroxybisphenyl (Aldrich) and hydroquinone (Fluka) were recrystallized from acetone. 4,4'-Dihydroxydiphenyl sulfone (Fluka) was used as received. NMP was freshly distilled before use, toluene and o-dichlorobenzene were used without further purifications.

Intrinsic viscosities were determined by using a Schott-Gerate AVS 400 dilution viscosimeter in NMP at 25°C. Differential Scanning Calorimetry (DSC) was performed on a Dupont 990 thermal analyzer in combination with a DSC cell. Thermogravimetric analysis (TGA) were performed on a Dupont 951 thermal analyzer.

Monomers synthesis : the synthesis is illustrated by the Scheme 1.

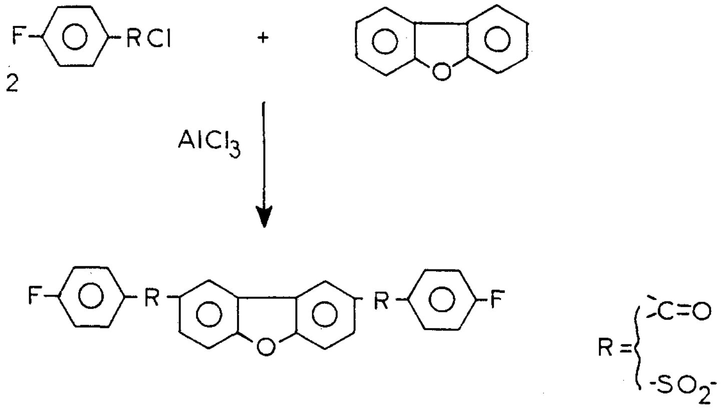
3,6-Bis (4-fluorobenzenecarbonyl) dibenzofuran :

Method A : Into a flask fitted with a nitrogen tube, a condenser and a magnetic stirrer, were introduced 15.35 g (11.5 m.mole) of aluminium trichloride, 5.04 g (30 m.mole) of dibenzofuran in 50 cc of nitrobenzene. The mixture was purged under nitrogen then 14.26 g (90 m.mole) of 4-fluorobenzoylchloride in 30 cc of nitrobenzene was slowly added. The mixture was heated to 100°C and kept at this temperature for 6 hours. After cooling it was poured into 100 cc of a 10 % iced aqueous hydrochloric acid solution. The organic layer was separated, washed twice with water, dried over magnesium sulfate, then nitrobenzene was removed under reduced pressure. The crude product was washed with hot n-hexane and finally recrystallized from glacial acetic acid to afford 10.2 g of crystals.
Yield = 82 % . mp = 192°C.

IR (KBr) : 3050/3100 cm^{-1} (C-H, aromatic) ; 1660 cm^{-1} (C=O) ; 1245 cm^{-1} (C-O-C).

Anal calculated for $C_{26}H_{14}F_2O_3$: C, 75.72 % ; H, 3.42 % ; F, 9.17 % . Found : C, 75.92 % ; H, 3.36 % ; F, 8.97 %.

Method B : The same procedure was repeated except that 1.2 dichloroethane was used instead of nitrobenzene. In this case reaction was performed at room temperaure.
Yield : 93 %.



Scheme1 - Synthesis of monomers.

3,6-Bis (4-fluorobenzenesulfonyl) dibenzofuran :

The title compound was prepared according to the procedure described previously (method A), using 4-fluorobenzenesulfonyl chloride instead of 4-fluorobenzoyl chloride.

The crude product was washed with hot n-hexane then recrystallized from chlorobenzene.
Yield = 77 % . mp = 300°C.

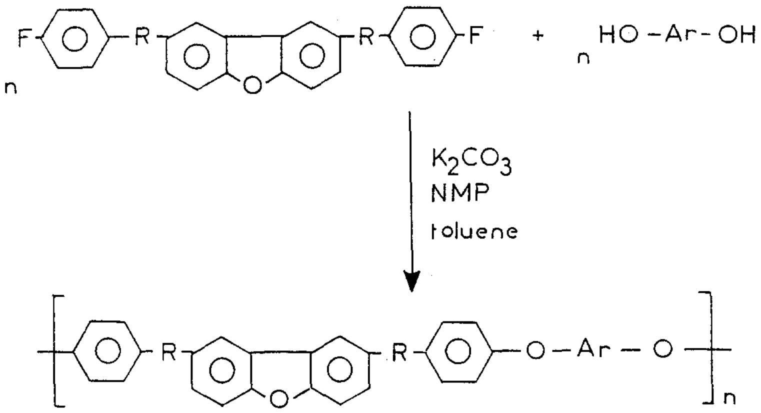
IR (KBr) : 3100 cm^{-1} (C-H, aromatic) ; 1320 cm^{-1} (SO_2); 1245 cm^{-1} (C-O-C).

Anal calculated for $C_{24}H_{14}F_2O_5S_2$: C, 59.50 % ; H, 2.91 % ; F, 7.81 % .
Found : C, 59.53 % ; H, 2.72 % ; F, 7.68 %.

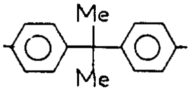
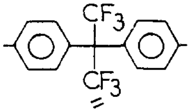
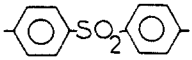
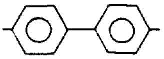
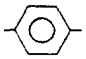
Polyethers synthesis : The synthesis and the different structures are illustrated in the Scheme 2. A typical procedure is given :

Into a flask fitted with a stirrer, a Dean-Stark trap, a condenser and a nitrogen dispersion tube were introduced 40 m.mole of each bisphenol and dihalide considered, 13.4 g (96 m.mole) of well powdered potassium carbonate in 200 cc of N-methylpyrrolidone and 100 cc of toluene. The temperature was raised to 140°C and the refluxing toluene was continuously removed from the trap and replaced by fresh solvent to remove the water. The mixture was maintained at this temperature for 6 hours, then toluene was replaced by o-dichlorobenzene and the temperature was raised to 180°C. The operation was repeated for 6 additionnal hours.

After cooling, the mixture was diluted with NMP, filtered to remove inorganic salts, acidified with acetic acid and coagulated in ten volumes of a methanol/water (50:50) mixture. The precipited polymer was filtered, washed with methanol and dried in a vaccum oven at 80°C for 4 hours.



<u>where</u>

N°	-Ar-	-R-
I a		$>C=O$
I b	=	$-SO_2-$
II a		$>C=O$
II b	=	$-SO_2-$
III a		$>C=O$
III b	=	$-SO_2-$
IV a		$>C=O$
IV b	=	$-SO_2-$
V a		$>C=O$
V b	=	$-SO_2-$

Scheme 2 - Synthesis of polyethers.

RESULTS AND DISCUSSION

The two dihalides are synthesized with good yields and good selectivities by classical Friedel-Crafts acylation and sulfonylation. In the acylation reaction a better yield was obtained at room temperature in 1,2-dichloroethane than in nitrobenzene at 100°C. (An attempt of synthesis at 50°C in nitrobenzene gave only 67 % yield). Sulfonylation reaction was only performed in nitrobenzene.

The monomers were isolated with a high purity witch is required for further polycondensation reactions. Moreover, starting materials are available and non expensive products.

Polycondensation was performed by fluoro displacement in the dihalide with phenol in potassium carbonate/N-methylpyrrolidone medium (6,7). In this reaction substitution of the fluoro group is activated by the carbonyl or the sulfonyl electron withdrawing group leading to an ether linkage through a Meisenheimer complex.

Reactions are conducted according to a well known procedure using toluene then o-dichlorobenzene as cosolvent to remove continuously the in-situ generated water by azeotropic distillation.

Stoichiometry, time and temperature of reaction were suited to ensure completion of the polycondensation in order to obtain high - molecular weight polymers.

Each of the two dihalides was reacted with five representative bisphenols. High - molecular weight polyethers were obtained as indicated by the intensic viscosities reported in the Table 1. The good solubility in hot NMP prevents premature precipitation of the polymers before completion of the chain growing. Yields of polycondensation are high as shown in Table 1. The polymers are white to beige fibrous materials.

Most of the polymers exhibit solubility at room temperature in NMP and in chlorinated solvents like chloroform or dichloromethane. The results are summarized in Table 1. Polyethers containing ketone linkages are less soluble than those containing sulfone ones. Bisphenol AF or bisphenol A structure in the main chain improves the solubility. Polyether ketone derived from hydroquinone is insoluble in the considered solvents. Its eventual cristalline nature would be specified in a future work.

Thermal behaviors were investigated by DSC at 20°C/min. Tgs were pointed at the baseline deflection in the second run. All polymers exhibit glass transition temperatures. The results are summarized in Table 1.

Tgs of polyetherketones are from 205°C to 234°C, that is from 40°C to 69°C more than for a standard bisphenol-A polyetherketone. Higher Tg were noticed when diphenylsulfone or biphenyl units are present in the macromolecular chain.

In the same way, Tgs of the polysulfones presented herein are from 244°C to 262°C, that is about 54°C to 72°C higher than for a classical polysulfone. The influence of the bisphenol nature upon the Tg is identical with that for the previous polyetherketones. These improved Tgs could be attributed to the rigid structure of the dibenzofuran group.

Thermal stability was evaluated by thermogravimetric analysis on polymers Ia and Ib. Results are illustrated in the Figure 1. Both polyethers exhibit excellent thermal stability in air with initial weight loss at 430°C for the polyetherketone and at 400°C for the polysulfone.

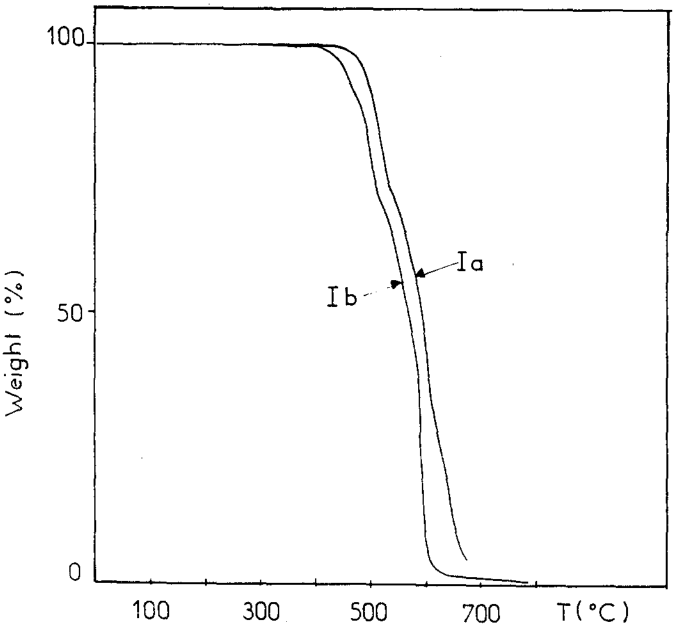
In conclusion, the two new monomers presented herein lead to polyetherketones and polysulfones with improved Tg of about 50°C more than Tg of the usual available polyether of each category, in association with a good solubility and an excellent thermostability. Further investigations will included morphological and mechanical data.

These structures could be used also for the synthesis of ethynyl or amine end-capped polyethers, in the field of thermosetting thermoplastics and polyimide synthesis.

N°	Yield (%)	(a) $[\eta]$ (dL/g)	Solubility (b)		(c) Tg (°C)
			NMP	$CHCl_3$	
I a	96	1.05	+	+	205
II a	86	0.96	+	+	223
III a	90	1.12	+	—	233
IV a	93	0.87	+	—	234
V a	89		—	—	220
I b	86	0.89	+	+	254
II b	79	0.71	+	+	244
III b	89	1.07	+	—	262
IV b	87	0.94	+	—	247
V b	83	1.03	+	+	250

a) intrinsic viscosity in NMP at 25°C.
b) + sol , - insol at room temperature.
c) DSC at 20°C/min.

Table 1 - Characteristics of polyethers.



Heating rate : 10°C/min.
Atmosphere : air.

Figure 1- Thermogravimetric analysis of some polyethers.

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Accepted April 9, 1991 C