Poly(arylene sulphide)s from masked bisthiophenols

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A new approach to the synthesis of poly(arylene sulphide)s using masked bisthiophenols is presented. Bisthiophenols *N*-propylcarbamates can be purified easily by simple recrystallization and polycondensed directly with activated dihalide monomers in *N*-methylpyrrolidone in the presence of potassium bicarbonate.

(Keywords: poly(arylene sulphide)s; bisthiophenols; masked bisthiophenols; carbamates)

Introduction

Poly(arylene ether)s, such as Udel and PEEK, are conventionally synthesized by nucleophilic displacement of bis(4-fluorophenyl) sulphone or 4,4′-difluorobenzophenone with a bisphenol in *N*-methylpyrrolidone (NMP) in the presence of potassium carbonate[1]. Similarly, the sulphide polymers can be prepared from the corresponding bisthiophenols[2]. In general, poly(arylene sulphide)s have better thermal or thermo-oxidative stabilities than the ether analogues. However, they have not been extensively explored, which is partially due to the problems associated with the synthesis and purification of the monomers and polymers. The bisthiophenol monomers, routinely prepared by reduction of the arylsulphonyl chloride, are usually unstable in air and readily oxidize to the disulphide. Thus, care must be taken during purification, storage and polymerization of the bisthiophenol to prevent the oxidation[2]. Recently, we have found that a bisphenol carbamate can be used as a monomer directly for the synthesis of poly(arylene ether)s[3]. In this paper, we report a new method for the synthesis of poly(arylene sulphide)s from bisthiophenol carbamates.

Experimental

Monomer synthesis. To a solution of 1,3-benzenedithiol (5.00 g, 35.2 mmol) in dry ether (10 ml) was added n-propylisocyanate (7.58 ml, 80.9 mmol), followed by a drop of pyridine at 0°C. The solution was allowed to warm up to room temperature gradually in 1 h. The resulting solid was collected by filtration and washed with ether. Recrystallization from toluene gave the desired carbamate as a crystalline solid: 9.97 g (90.8%); m.p. 125–126°C; ^{1}H n.m.r. (200 MHz, $CDCl_3$) 0.880 (t, 6H, CH_3), 1.520 (m, 4H, CH_2CH_3), 3.228 (q, 4H, CH_2NH), 5.552 (br s, 2H, NH), 7.426 (q, 1H, Ar-H_5), 7.583 (m, 2H, Ar-$H_{4,6}$), 7.729 (d, 1H, Ar-H_2).

Model reaction. The mixture of n-propyl benzenethiolcarbamate (1.016 g, 5.20 mmol), bis(4-fluorophenyl) sulphone (0.636 g, 2.50 mmol) and potassium bicarbonate (751 mg, 7.50 mmol) in deoxygenated NMP (8.5 ml) was heated at 150–155°C under argon for 15 min. H.p.l.c. analysis indicated only one product formed along with a residual trace of bis(4-fluorophenyl) sulphone. The reaction mixture was cooled to room temperature and poured into water. After stirring for 30 min, the solid was filtered off, washed with water and dried in air: 0.976 g (90%, 100% pure by h.p.l.c.); m.p. 157–158°C (AcOH); ^{1}H n.m.r. (200 MHz, $CDCl_3$) 7.156 (d, 4H, $J = 8.5$ Hz, Ar-H *meta* to $-SO_2-$), 7.386–7.508 (m, 10H, Ar-H of PhS), 7.710 (d, 4H, $J = 8.5$ Hz, Ar-H *ortho* to $-SO_2-$); m.s. (*m/e*, relative intensity) 434 ($M^{+\bullet}$, 100).

Polymer synthesis. A three-necked flask equipped with a condenser was charged with 1,3-benzenedithiol carbamate (5 mmol), an aryl difluoride (5.0 mmol) and potassium bicarbonate (1.502 g, 0.015 mol) in deoxygenated NMP (10–14 ml). The flask was then immersed in a preheated oil bath at 150–155°C and the reaction was stirred for 2 h while a stream of nitrogen was passed through the flask. The reaction solution was then diluted with NMP (10–15 ml) and poured into a blender or a beaker containing 200 ml of water while being well stirred. The polymer was filtered off and could be purified by dissolving in an appropriate solvent. After filtration and precipitation, the polymer was dried in air and then in a vacuum oven at 70–80°C overnight. The properties of the polymers synthesized are presented in *Table 1*.

Results and discussion

When thiophenol was treated with a slight excess of n-propylisocyanate in ether, the corresponding carbamate was obtained in high yield. It is a crystalline, odourless solid and easily recrystallized from ethanol. It was found that the carbamate can be cleaved readily upon treatment with potassium bicarbonate or carbonate in NMP at

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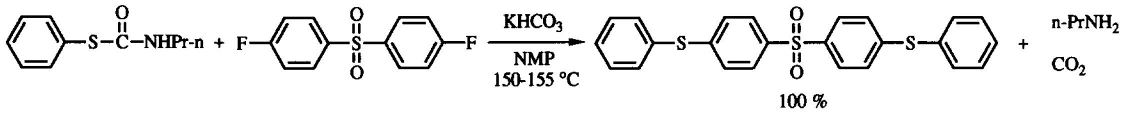
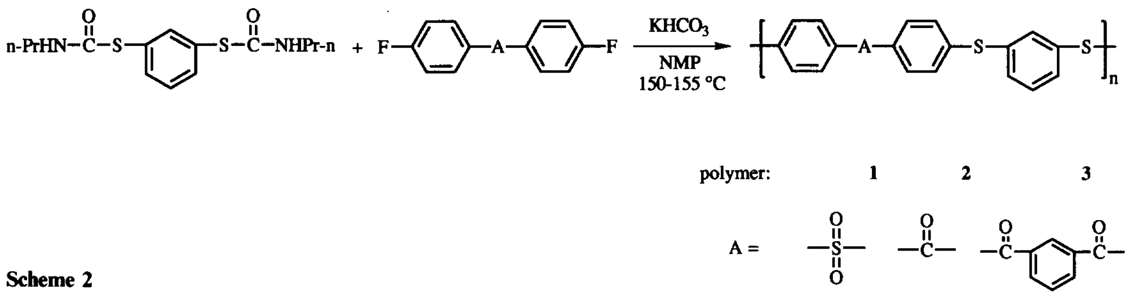
Table 1 Characterization of poly(arylene sulphide)s

Polymer	Yield (%)	η_{inh} [a] (dl g^{-1})	T_g (°C)	T.g.a.[b] (°C)		Solubility[c]	
				Air	N_2	++	+
1	94.4	0.54	150	486	476	$CHCl_3$, TCE NMP, PhCl	DMF, DMSO
2	94.0	0.30	106	515	508	TCE	NMP
3	92.1	0.54	121	473	460	TCE	NMP

[a] 0.5% in s-tetrachloroethane (TCE) at 30°C
[b] 10% weight loss, flow rate: 200 ml min^{-1}
[c] ++, Soluble at room temperature; +, soluble at elevated temperature



Scheme 1



Scheme 2

$\sim$120°C, as evidenced by the formation of gaseous carbon dioxide and n-propylamine (*Scheme 1*). The thiophenoxide, generated *in situ*, then reacted with bis(4-fluorophenyl) sulphone at 150–155°C to form bis(4-thiophenoxyphenyl) sulphone quantitatively in <15 min. Other protecting groups such as acetate and *O*-carbonates gave unsatisfactory results due to competitive reactions between the halide and potassium acetate or alkoxide liberated from the hydrolysis[3].

To demonstrate that the biscarbamates can indeed be used as monomers, 1,3-benzenedithiol was used for the synthesis of poly(arylene sulphide)s. The monomer, recrystallized from toluene as a white crystalline solid, was polymerized with bis(4-fluorophenyl) sulphone, 4,4′-difluorobenzophenone and 1,3-bis(4-fluorobenzoyl) benzene, respectively (*Scheme 2*). All reactants were mixed in NMP and then heated at 150–155°C. High molecular weight polymers were readily formed (*Table 1*) in 2 h and they can be cast into clear, creasable films. In comparison to the conventional two-stage procedure using bisthiophenol as a monomer, which requires a few hours to remove water azeotropically prior to polymerization, this new method offers a simple, rapid, one-stage polymerization.

The sulphone sulphide polymer **1** shows a T_g of 150°C and is soluble in most chlorinated solvents such as chloroform, s-tetrachloroethane and chlorobenzene. Polymers **2** and **3** have T_gs of 106 and 121°C, respectively and are only soluble in s-tetrachloroethane at room temperature. Thermal stabilities of these three polymers were determined by thermogravimetry. It was found that 10% weight loss occurred above 470°C in air, indicating excellent thermal stability.

The method described herein provides an alternative approach to the synthesis of poly(arylene sulphide)s, which eliminates the problems associated with the conventional procedure in handling the unstable bisthiophenol monomers. The synthesis of poly(arylene sulphide)s derived from other aromatic and aliphatic bisthiols using this new methodology is ongoing.

Acknowledgement

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