

Preparation and properties of polybenzimidazoles containing dibenzothiophenediyl or 5,5-dioxodibenzothiophenediyl units

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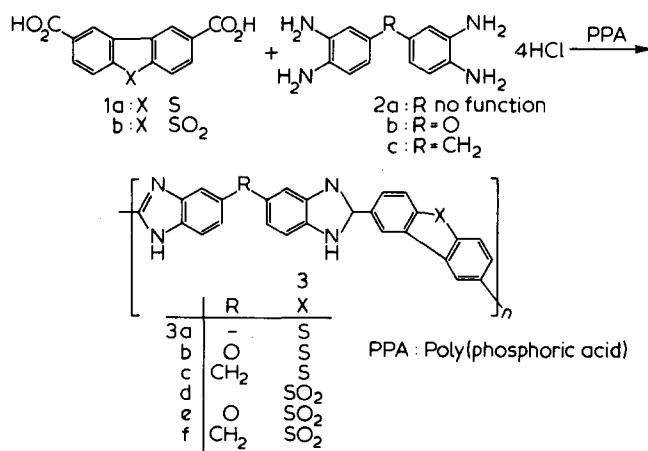
INTRODUCTION

In the past, investigations concerning the thermally stable polybenzimidazoles have been widely carried out¹. The thermal stability of these polymers depends on the nature of chemical features of the rings and of the connecting groups. A fully aromatic polybenzimidazole shows good thermal stability, which can be increased by introducing double-strand heterocyclic units. We have demonstrated earlier that polybenzimidazoles containing a phenoxathine unit have superior stability compared with the open-chain diphenylether linked polymers². In this report we describe the preparation of polybenzimidazoles containing dibenzothiophene units wherein a sulphur network replaces an open-chain diphenyl linkage. The objective of the present study was to improve the thermal stability of the polymers and evaluate the effect of the introduced heterocyclic unit on the resulting polymer properties. Recently polyamides containing dibenzothiophene units were reported by us³.

EXPERIMENTAL

The infra-red spectra was recorded in a Perkin-Elmer 257 spectrometer (KBr pellets). The density measurements were made in a small pycnometer with hexane at 30°C. The inherent viscosities were measured in an Ostwald viscometer in *N,N*-dimethylformamide (DMF) at 30°C ($\eta = 0.5$ g/dl). Those polymers which are insoluble in DMF were dissolved in concentrated sulphuric acid. The thermogravimetric analysis were carried out in a Stanton thermobalance at a heating rate of 10°C/min in air.

3,3'-Diaminobenzidine⁴, bis(3,4-diaminophenyl)ether⁵ and bis(3,4-diaminophenyl)methane⁶ were prepared from the corresponding diamines using the literature procedures.



Dibenzothiophene was prepared⁷ in a 30% yield from diphenyl sulphur and aluminium chloride. 2,8-Diacetyldibenzothiophene was prepared by the procedure of Albrecht *et al.*⁸.

2,8-Dibenzothiophenedicarboxylic acid (1a): To a suspension of 2,8-diacetyldibenzothiophene (2.68 g, 0.01 mol) in pyridine (40 cm³), was added with stirring to 5% aqueous sodium hypochlorite (60 cm³) at room temperature, dropwise over a 2 h period. The mixture was then stirred for 8 h at 40°C. After this period the excess sodiumhypochlorite was destroyed by the addition of sodium bisulphite (0.5 g). The solution was filtered and acidified with 11 M HCl. The precipitated acid was filtered, purified by dissolution in aqueous sodium bicarbonate and subsequent reprecipitation. It was a light yellow powder, yield 2.9 g (50%) m.p. 394°C. Composition found: C, 61.76%; H, 2.94%; C₁₄H₈O₄S requires C, 61.69%; H, 2.92%. IR (K Br): 3600 (OH); 1690 cm⁻¹ (C=O).

2,8-Dibenzothiophenedicarboxylic acid 5,5-dioxide (1b): To 5% aqueous sodium hypochlorite (250 cm³) heated to 90°C, was added 2,8-dibenzothiophenediacetyl (3.0 g, 0.01 mol) with stirring. The solution was then refluxed for 12 h. Excess hypochlorite was destroyed by the addition of sodium bisulphite (0.5 g). The solution was acidified with hydrochloric acid. The acid was filtered, dissolved in sodium bicarbonate and reprecipitated with acid. Yellow powder, yield 2.8 g (70%); m.p. 342°C. Composition found: C, 55.26%; H, 2.63%. C₁₄H₈O₆S requires C, 55.18%; H, 2.59%. IR (KBr): 3600 (OH); 1680 (C=O); 1310 and 1170 cm⁻¹ (SO₂).

2,8-Bis(2-benzimidazolyl)dibenzothiophene (4): 2.16 g (0.02 mol) of *o*-phenylenediamine (2.16 g, 0.01 mol) and 2,8-dibenzothiophenedicarboxylic acid (2.72 g, 0.01 mol) were added to poly(phosphoric acid). The mixture was heated to 170°C with stirring. After 8 h the mixture was poured into excess water. The precipitate was filtered, washed with hot methanol and recrystallized from a DMF-methanol mixture. Yield: 3.82 g (68%); m.p. 420°C (from d.t.a.). Composition found: C, 75.0%; H, 3.58%; N, 13.46%. C₂₆H₁₆N₄S required C, 75.2%; H, 3.79%; N, 13.44%. i.r. (K Br): 3320 (NH); 1610 (C=N), 1260 and 810 cm⁻¹ (imidazole).

Polymerization

Poly(phosphoric acid) was freshly prepared from phosphorous pentoxide and orthophosphoric acid for each condensation. To this 3,3'-diaminobenzidinetetrahydrochloride (3.94 g, 0.01 mol) was added and nitrogen was bubbled through the mixture to remove HCl. 2,8-Dibenzothiophenedicarboxylic acid (2.72 g, 0.01 mol) was

Table 1 Result of the Condensation Polymerizations^a

Polymer	Yield %	inh ^b dl/g	Density g/cc	Temperature at various % decomposition ^d			IPDT
				10	30	50	
3a	62	0.82	1.218	410	490	565	502
3b	60	0.90	1.208	418	493	558	498
3c	63	0.92	1.236	427	482	561	482
3d	52	0.73 ^c	1.018	420	533	582	512
3e	60	0.68 ^c	1.131	415	510	570	508
3f	58	0.73 ^c	1.124	422	523	568	504

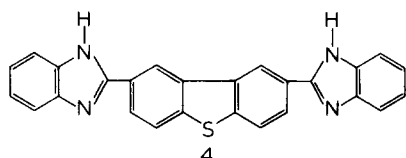
^a Mol ratio 1 : 1 in poly(phosphoric acid)^b In DMF: c = 0.5 g/dl^c In H₂SO₄^d Rate of heating, 10° C/min

added to it and the mixture heated to 170°C with stirring for 12 h. The polymer was isolated by pouring into excess water filtered and washed with dilute sodium carbonate solution, water and methanol. It was then dried at 110°C for 4 h. Dark brown solid, yield: 3.2 g (62%). The other polymers 3b-f were prepared analogously.

RESULTS AND DISCUSSION

Polybenzimidazoles containing dibenzothiophene units have been prepared. The tetramines were prepared according to known literature procedure. The method of Imai *et al.*⁹ for the hypochlorite oxidation of the diacetyl compound was employed with modification for preparation of the dicarboxylic acids.

The reaction of *o*-phenylenediamine with 2,8-dibenzothiophenedicarboxylic acid was studied as a model reaction. The bisimidazole was isolated as a 60% yield and it was characterized by its i.r. spectrum and elemental analysis.



The i.r. spectrum for the polymers showed the following peaks at 3330 (NH), 1610 C=N, 1260 and 750 cm⁻¹ (imidazole). The absence of any other functional groups like the carbonyl group indicate that the cyclization has gone to the maximum extent. The properties of the polymers are given in Table 1. The polymerization was found to proceed smoothly to give polymers whose viscosities ranged from 0.6 dl/g to 0.9 dl/g. The solubilities of the polymers are shown in Table 2. A 10% solution (w/w) was arbitrarily taken as a measure of the solubility. It was found that the introduction of a rigid and bulky dibenzothiophene group does not influence the solubility while that of the 5,5-dioxodibenzothiophene unit does. Those polymers containing dibenzothiophene groups were soluble in polar aprotic solvents like DMF, Dimethyl acetamide, while 5,5-dioxodibenzothiophene containing polymers were insoluble. However all the polymers were soluble in concentrated sulphuric acid. Since the two oxygen atoms in the 5,5-dioxodibenzothiophene ring lie out of the plane of the conjugated ring system, polymers containing the sulphone ring will be less densely packed. The X-ray diffraction studies of poly-

Table 2 Polymer solubility

Solvent	Polybenzimidazole					
	3a	3b	3c	3d	3e	3f
Concentrated sulphuric acid	S	S	S	S	S	S
<i>N,N</i> -Dimethylformamide	S	S	S	I	I	I
Dimethylacetamide	S	S	S	I	I	I
<i>m</i> -Cresol	S	I	S.S	I	S.S	I
Pyridine	S.S	I	I	S.S	I	I

S = soluble; S.S = slightly soluble; I = insoluble

amides containing 5,5-dioxodibenzothiophene units shows that the polymers were, to a large extent, amorphous³. The density measurements of the polybenzimidazoles containing the dioxodibenzothiophene ring shows a lower value than the dibenzothiophene containing polymers. The thermal stabilities of the polymers were determined by thermogravimetric analysis in air. All the polymers are stable in air up to 400°C, and a 10% weight loss was observed for the polymers at 400°-420°C. In order to get a semiquantitative data on the decomposition the integral procedural decomposition temperature¹⁰ (IPDT) of the polymers were calculated. The IPDT values for the polymers containing the dibenzothiophene 5,5-dioxide were higher than the dibenzothiophene containing polymers even though the initial decompositions are similar. Accordingly these results suggest that the polymers containing double-strand heterocyclic dibenzothiophene units are much more stable than the conventionally prepared open-chain diphenyl linked polymers.

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