Synthesis and characterization of polybenzimidazoles carrying additional pyridine and imidazole groups in the main chain

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Six polybenzimidazoles have been prepared by a dispersion polycondensation process using polyphosphoric acid as a dehydrating reagent. Two of these contained an additional pyridine residue in the mainchain, and three of them additional imidazole groups. The molecular structures have been characterized by u.v., i.r. and ^{1}H n.m.r. spectra. Physical characterization has involved solubility measurements, solution viscosity evaluation and thermal stability assessment via thermogravimetric analysis. The latter has confirmed that the inherently high thermo-oxidative stability of polybenzimidazoles is retained in the case of polymers and copolymers with additional nitrogen heterocycles in the mainchain.

(Keywords: synthesis polybenzimidazoles; pyridine- and imidazole-containing polybenzimidazoles)

INTRODUCTION

Polystyrene, polyacrylamide and poly(alkylmethacrylate)-based resins have been used widely and successfully as polymer supports[1-3]. All of these, however, are subject to severe limitations in terms of the temperature at which they can be used. In practice excessive degradation and depolymerization arises above ~150°C. We are now embarked on a research programme aimed at developing porous polymer supports which will be usable at temperatures of 250°C and beyond. In the course of this work we have been expanding the chemistry of polybenzimidazole synthesis[4-7], and, in particular, have been examining the effect of introducing additional pyridine and imidazole groups into the main chain. Earlier reports of the incorporation of a pyridine group[4,8] and an imidazole group[9] do exist although no systematic work has been described. In addition, a variety of other aliphatic[10,11] and aromatic[12] structures have been introduced as constituents of the polybenzimidazole main chain and these include alkene residues, sulphoxide and ketone groups, and dimethylsiloxane and silane groups. In general, however, these functionalities cannot be described as reactive and provide an opportunity neither for direct coordination with metal ion centres, nor for further facile chemical modification. In this work we describe five polybenzimidazoles with additional main chain *N*-containing aromatic groups, and focus on the structural and physico-chemical characterization of these.

EXPERIMENTAL

Materials

Isophthalic acid (IPA), 2,6- and 3,5-pyridine dicarboxylic acid (*o*-PDA and *m*-PDA), 4,5-imidazole dicarboxylic acid (IMA) and 3,3′-diaminobenzidine (DAB) were used as supplied (Aldrich Chemical Co.). Polyphosphoric acid was prepared by dissolving P_2O_5 in orthophosphoric acid. Paraffin oil was used as supplied (A and J Beveridge).

Polymerizations

Polycondensations were carried out via a dispersion polymerization process using paraffin oil as the continuous phase, essentially as described in the literature[13]. Polyphosphoric acid was used as a solvent for the dispersed polymerizing phase, and also as a powerful dehydrating agent[14].

A typical reaction was performed as follows using equimolar quantities of an appropriate diacid (or mixture of diacids) with DAB. A three-necked glass flask equipped with a mechanical stirrer was charged with paraffin oil (20 ml), DAB (2 g) and an equimolar quantity of diacid. To this mixture was added dodecylbenzenesulphonic acid sodium salt (0.5 g) to act as a phase dispersant. The mixture was stirred well under a nitrogen atmosphere and polyphosphoric acid (12 g) added slowly. Stirring was continued at room temperature for 2 h, and then the temperature was raised slowly to 170°C and maintained at this value for 12 h. Finally the temperature was increased to 240°C for 4 h. The colour of the dispersion gradually darkened to brown and then to black as the reaction proceeded. After cooling to room temperature the solid particulate product of various sizes and shapes was washed free of paraffin using n-hexane.

The air dried material was then dissolved in hot concentrated sulphuric acid (98%, 25 ml) and the cooled solution poured into water or methanol (200 ml). The solution was neutralized with solid sodium bicarbonate and the re-precipitated polymer was collected by filtra-

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tion. The polymer was then stirred overnight in aqueous sodium bicarbonate solution (5%, 200 ml). The polymer was again collected by filtration and washed with water, until the washings were neutral. It was then dried in a vacuum oven at 75°C overnight. Finally the polymer was extracted with dichloromethane for 24 h to remove low molecular organics and again vacuum dried at 75°C overnight. Typically the product was a brown-yellow coloured powder and final yields were ~95%. Most losses occurred during the initial dispersion polymerization processes with residues left in the flask and on the stirrer.

Characterization of polymers

Elemental microanalyses were performed on a Carlo Erba 1106 Analyser. Fourier transform infra-red spectra and u.v. spectra were recorded on a Nicolet 20SXB *FT*i.r. spectrometer and a Perkin Elmer 402 u.v. spectrophotometer respectively using KBr discs and solutions in 98% H_2SO_4 as appropriate. ^1H nuclear magnetic resonance (n.m.r.) spectra in deutero dimethylsulphoxide (DMSO) or deutero sulphuric acid were obtained on a Bruker WM250 instrument. The solubilities of polymers in various solvent systems were assessed typically using 2–3 mg of each sample in 1 ml of solvent at room temperature. Thermal stabilities were assessed via thermogravimetric analysis using a 990 Du Pont thermogravimetric balance with a constant air flow on the sample. The latter (~50 mg) was in the form of a fine powder and heating was carried out at a constant rate of $5°C\ min^{-1}$. Finally, solution viscosities were measured in 98% H_2SO_4 as solvent at 25°C in the concentration range 0.125–0.5 g per 100 ml. The viscometer employed was an Ubbelohde type.

RESULTS AND DISCUSSION

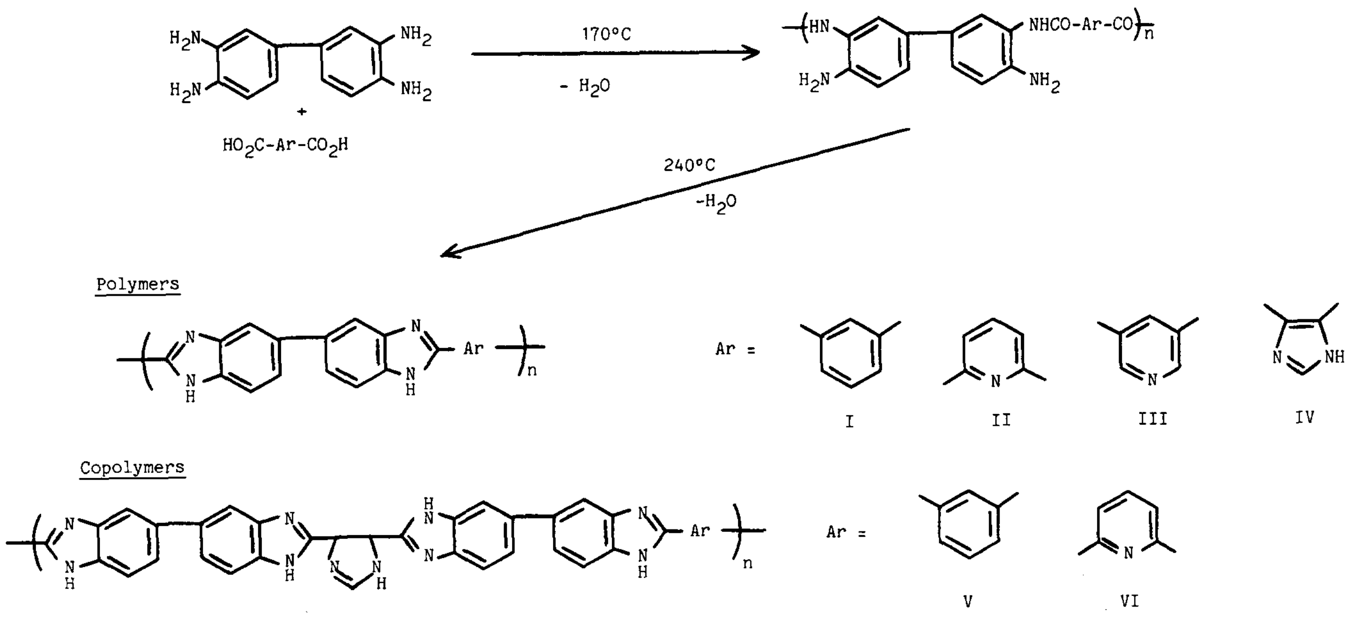
Polymer preparations

The structures of the polymers and copolymers prepared in this work are shown in *Scheme 1*. Details of the reagents used are shown in *Table 1*. Polymer yields were always high, approximately 95%, with the major loss being residues on the reaction vessel and stirrer. This confirms the effectiveness of the use of polyphosphoric acid in these condensations[14]. In contrast, the dispersion technique[13] proved to be totally unsatisfactory, with a broad range of particle size and shape arising in the product, along with considerable aggregation and deposition on the stirrer and reactor walls in some cases. In retrospect the dispersion stabilizer recommended, sodium dodecylbenzene sulphonate, would not be expected to be very effective in the conditions employed and we will report in due course on the advances we have subsequently made in this respect. After isolation and purification good quality powder products were obtained and the relevant elemental nitrogen microanalyses are shown in *Table 1*. In comparison with low molecular weight organic molecules, the agreement between theoretical and experimental *N*% is rather poor, but it is known that efficient combustion of these aromatic main chain polymers can be very difficult (see thermal stability data later) and the correlation which emerges is in fact not unreasonable. The largest deviation occurs with copolymer V, where the low experimental value for the *N*% might arise as a result of poor incorporation of IMA into the copolymer relative to IPA.

Table 1 Composition of monomers used in polycondensations and resulting elemental N analyses of products

Polymer	Diacid reactant (g)[a]	N% in polymer Found	N% in polymer Calculated
I	IPA (1.40)	17.7	18.2
II	*o*PDA (1.55)	19.9	22.7
III	*m*PDA (1.55)	21.2	22.7
IV	IMA (1.46)	25.5	28.2
V	IPA (0.77); IMA (0.73)	19.0	23.1
VI	*o*PDA (0.77); IMA (0.73)	23.3	25.4

[a] Each with DAB, 2 g, ≈10 mmol. DAB = 3,3′-diaminobenzidine; IPA = isophthalic acid; *o*PDA = 2,6-pyridine dicarboxylic acid; *m*PDA = 3,5-pyridine dicarboxylic acid; IMA = 4,5-imidazole dicarboxylic acid



Scheme 1 Polybenzimidazoles synthesized by polyphosphoric acid catalysed dispersion polycondensation

Spectral characterization of polymers

Table 2 summarizes the u.v. and i.r. spectral data for the polymers. Diagnostically useful i.r. absorption bands have been highlighted before[7,15] and are confirmed in this work: near 800 cm^{-1} (imidazole C–H out-of-plane bending, overlapped by benzene aromatic skeletal absorptions), near 1300 cm^{-1} (imidazole C–N stretching – complicated in these polymers by closely related absorptions associated with the additional N-containing heterocyclic rings in the polymer backbone), near 1450 cm^{-1} (imidazole C–N in-plane vibration, similarly complicated in these macromolecules), and near 1620 and 1510 cm^{-1} (combined C=C and C=N ring vibrations). An important band which is absent is a sharp feature of approximately 1670 cm^{-1}. This corresponds to the carbonyl absorption of an aromatic amide group, and its absence confirms that efficient cyclization of the intermediate amino–amide polymer (*Scheme 1*) to benzimidazole has occurred in each polycondensation. This band is clearly seen in poly(amide-benzimidazole) copolymers[15].

^{1}H n.m.r. data for the polybenzimidazoles are scarce largely as a result of the limited solubility of these macromolecules, coupled with the tendency for significant line broadening, presumably arising from the variety of chemical environments associated with these relatively rigid macromolecules even in solution. 250 MHz spectra for polymers I–VI dissolved in DMSO and polymer I dissolved in deutero-H_2SO_4 have been obtained. The line broadening observed in DMSO is significantly less than that seen with D_2SO_4. In all cases the chemical shifts lie between $\delta = 7$ and 9 ppm indicating that all the protons are in aromatic environments. No attempt has been made to assign individual resonances in the rather complex multiplets that are observed, but the use of model compounds to achieve this has been reported previously[16]. The spectrum of polymer I is consistent with the most detailed earlier report available[16], and, in general, the spectra become more complex as might be expected as additional aromatic proton resonances are introduced in polymers II–VI. The benzimidazole imino proton in I appears at $\delta = 13.3$ ppm in DMSO and shifts to 11.8 ppm in D_2SO_4. A similar shift has been reported before when deuterated formic acid was used as the solvent for a closely related polymer[16]. In the case of polymers IV–VI containing the additional imidazole group in the main chain, the resonance of the imino proton in DMSO appears to shift to $\delta = 16.0$ ppm. Hydrogen bonding between each imidazole imino proton and the immediate adjacent backbone imidazole tertiary N atom, common to these three polymers, is probably responsible (note: imidazole and benzimidazole imino protons seem equivalent in this context). In the case of copolymer V a resonance at approximately 13.3 ppm is also retained, and a possible explanation of this is that stereo sequences, effectively of polymer I and polymer IV, occur in this copolymer.

Table 2 Ultraviolet and infra-red absorption spectral data for polybenzimidazoles

Polymer	U.v. λ_{max} (nm)[a]	I.r. bands (cm^{-1})[b]				
I	345	1620	1511	1439	1276	797
II	364	1620	1567	1439	1298	797
III	374	1623	1583	1429	1315	800
IV	350	1623	1558	1445	1285	797
V	366	1623	1561	1442	1288	797
VI	368	1627	1561	1445	1285	797

[a] In 98% H_2SO_4
[b] KBr discs

Physical characterization of polymers

The solubilities of the polymers in a selection of solvents (acidic, basic and dipolar aprotic) were assessed and the results are summarized in *Table 3*. Overall H_2SO_4 remains the best solvent, and presumably all the polymers are highly protonated in this medium. DMSO is the most useful of the organic solvents, and perhaps somewhat surprisingly, morpholine has some utility. In general, the incorporation of additional N aromatic heterocycles into the main chain decreases the solubility of the polybenzimidazoles.

The specific viscosities, η_{sp}, of sulphuric acid solutions of polymers were evaluated from the expression:

$$\eta_{sp} = \frac{t - t_0}{ct_0}$$

where t is the flow time for a polymer solution of concentration, c (g 100 ml^{-1}) and t_0 is the flow time of the acid solvent. The results are shown in *Figure 1*. Although no conclusions can be drawn about the absolute molecular weights of the polymers, it is clear that II, IV–VI are most likely of only low molecular weight, whereas I and III are of much higher molecular weight. It must be emphasized, however, that no attempt has been made to optimize molecular weights in this work, because this parameter did not prove to be limiting in the application for which these particular polymers were prepared. There seems little reason to doubt that with appropriate purification of starting materials and appropriate manipulation of polymerization conditions, high molecular weight products could be achieved for all of the polymers I–VI.

Table 3 Solubility of polybenzimidazoles in acidic, basic and dipolar aprotic solvents. S, soluble; PS, partially soluble; SW, swelling only; I, insoluble; DMSO, dimethylsulphoxide; DMF, dimethylformamide; MP, 1-methyl-2-pyrrolidone; M, Morpholine; GA, glacial acetic acid; AA, acetic anhydride

Polymer	H_2SO_4	DMSO	DMF	MP	M	GA	AA
I	S	S	S	S	S	PS	PS
II	S	PS	PS	PS	SW	SW	SW
III	S	S	PS	PS	SW	SW	PS
IV	S	S	SW	PS	PS	PS	PS
V	S	S	SW	PS	I	SW	I
VI	S	PS	PS	PS	S	PS	I

Table 4 Thermal decomposition data for polybenzimidazoles

Polymer	Initial decomposition temperature (°C)	Final decomposition temperature (°C)	Decomposition temperature for % weight loss 10%	20%	30%	40%	IPDT[a] (°C)
I	485	603	490	509	523	532	514
II	476	626	485	500	508	513	534
III	462	626	473	490	499	504	557
IV	452	635	462	490	504	518	562
V	462	631	464	492	506	517	560
VI	438	603	443	476	494	506	550

[a] Integral procedural decomposition temperature (see ref. 17)

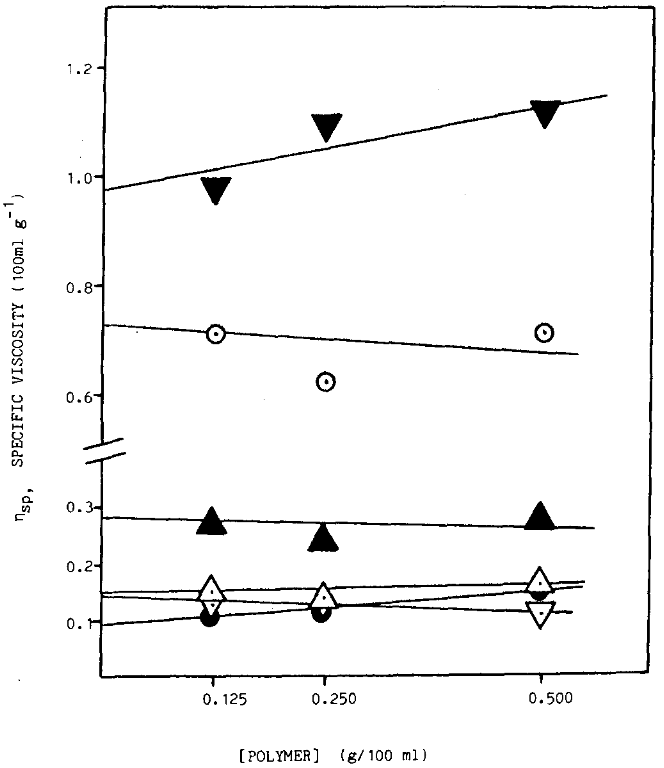


Figure 1 Sulphuric acid solution viscosities of polybenzimidazoles at 30°C: I ○; II ▲; III ▼; IV ●; V △; VI ▽

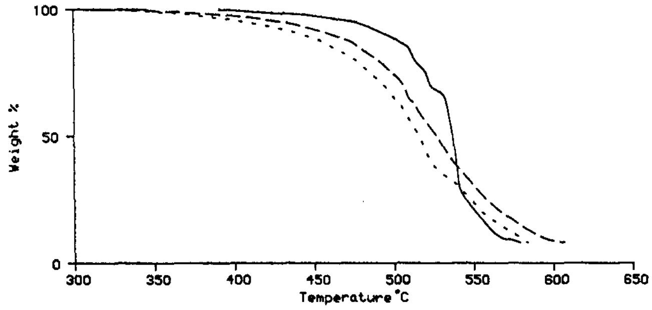


Figure 2 Thermogravimetric analysis traces for polybenzimidazoles in air heated at 5°C min^{-1}: I ———; IV ——; VI -----

One of the most important parameters in terms of our own interest in polybenzimidazoles is their intrinsically high thermo-oxidative stability. Thermogravimetric analysis (t.g.a.) curves for polymers I, IV and VI are shown in *Figure 2*. Analogous curves for the other polymers fell within the envelope described by the curves for polymers I and VI, and are not reproduced here to avoid over-complicating *Figure 2*. Clearly all the polymers are stable up to 400°C in the presence of air and thereafter progressive oxidative degradation starts. The integral procedure decomposition temperature, IPDT, of each polymer was calculated according to the method of Doyle[17]. The IPDT values are shown in *Table 4*, together with quantitative decomposition data for all the polymers. The major conclusion is that incorporation of additional N heterocyclic residues into the polymer chain does not alter radically the inherent thermo-oxidative stability of polybenzimidazoles. In general the temperature at which the onset of oxidation occurs is reduced marginally, but the final temperature of decomposition is correspondingly increased in all cases except copolymer VI. It is also important to realize that these trends seem to be essentially molecular weight independent, although in the case of copolymer VI the final temperature of decomposition may be indicative of the low molecular weight of this particular product.

CONCLUSIONS AND FUTURE WORK

Polybenzimidazoles with additional pyridine and imidazole groups in the main chain have been prepared by a dispersion polycondensation process. The materials have been shown to retain the inherent thermo-oxidative stability of simple polybenzimidazoles. Currently a much improved dispersion procedure is in development, and the present materials are being used as polymer supports for transition metal complex oxidation catalysts.

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