New routes to poly(benzylenebenzimidazoles)

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Reaction of 3,3'-diaminobenzidine with either 3,3,7,7-tetraphenyltetrathiopyromellitide or α,α'-dibromo-2,5-dicyano-*p*-xylene produced new polymers which are stable up to 350°C. In the latter case, the solution polymerization was completed in 24 h at reflux temperature in quantitative yields with inherent viscosity of 0.66 dl g^{-1}; the dark coloured polymer would dissolve only in formic or sulphuric acid. In the former case, however, an orange coloured solid having inherent viscosity of 0.09 dl g^{-1} was obtained in quantitative yields; this polymer was soluble in a number of solvents such as chloroform, ethanol, benzene and DMF.

(Keywords: thermally stable polymer; ladder polymer; poly(benzylenebenzimidazole); synthesis)

INTRODUCTION

Because of the facile reaction between phthaladehyde and *o*-phenylene diamine to form benzylenebenzimidazole[1], several unpublished attempts have been made to use this reaction to produce a ladder polymer. The downfall has been that the synthesis of pyromellitaldehyde, although published[2], has not been possible, even though it has been attempted by several researchers.

Work on polyimidines[3] led to other possible routes to polymers of benzylenebenzimidazole when it was recognized that the bisphthalide monomer used for polyimidines is, indeed, a cyclized isomer of the needed tetraaldehyde. The possibility then arose of condensing aromatic tetraamines with bisphthalides to produce this new aromatic ladder polyheterocycle.

EXPERIMENTAL

General

All chemicals and solvents used in the experiments were commercially available except those specified. The solvents were purified by vacuum distillation and dried over Linde 411 molecular sieves. *o*-Phenylenediamine was purified by sublimation.

Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Combustion elemental analyses were performed at Southwest Texas State University on a Perkin–Elmer 240 C Elemental Analyzer. The infra-red spectra in KBr matrix were obtained with a Beckman IR-9 and a Perkin–Elmer IR-363. Inherent viscosities were measured using a Cannon–Fenske number 100 viscometer tube with chloroform or formic acid as solvent.

MODEL REACTIONS

Benzylenebenzimidazole (I)

This compound was synthesized by two routes:

Route 1. Phthalide (1.08 g, 0.01 mole) and 1.34 g (0.01 mole) of *o*-phenylenediamine were heated at 190°C for 24 h, under positive nitrogen pressure. Recrystallization of the molten mass from 95% ethanol with a small amount of decolourizing charcoal gave 1.4 g (68%) of colourless crystals, m.p. 212°C–213°C (ref. 4, m.p. 212°C).

Route 2. N-Bromosuccinimide (NBS) (35.6 g, 0.2 mole) and 2 g (0.008 mole) of benzoyl peroxide were added to a solution of 23.4 g (0.2 mole) of *o*-tolunitrile in dry carbon tetrachloride (200 ml). The mixture was heated at reflux for 2 h and filtered hot. The solution was concentrated to 50 ml and cooled in an ice-bath. The resulting precipitate was suction filtered and recrystallized from absolute ethanol to give 25 g (63%) of α-bromo-*o*-tolunitrile, m.p. 74°C (ref. 5, m.p. 74°C). This compound (1.5 g, 0.008 mole) was then mixed with excess (1.8 g, 0.017 mole) *o*-phenylenediamine in *N,N*-dimethylformamide (DMF) (10 ml) and heated to 150°C in a beaker and cooled. The contents were poured into 100 ml of water, suction filtered and the product was recrystallized from 95% ethanol to give 1.0 g (48%) of colourless crystals, m.p. 212°C–213°C.

Diphenylbenzylenebenzimidazole (II)

A mixture containing 3.2 g (0.01 mole) of 3,3-diphenyl-1,2-dithiophthalide[6] and excess (5 g) of *o*-phenylenediamine in 50 ml of mixed xylenes was heated at reflux under nitrogen atmosphere for 24 h. Solvent was removed by rotary evaporation and the resulting oil was dissolved in ethanol. The desired product was precipitated by the slow addition of water, filtered and recrystallized from absolute alcohol to give 3 g (84%) of

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colourless crystals which melted at 219°C–220°C.

Anal. Calcd. for $C_{26}H_{18}N_2$: C, 87.12%; H, 5.02%; N, 7.82%; Found: C, 87.22%; H, 5.58%; N, 7.81%.

MONOMER SYNTHESIS

*α,α′-Dibromo-2,5-dicyano-*p*-xylene* (VI)

A mixture containing 20 g (0.13 mole) of 2,5-dicyano-*p*-xylene in 1 litre of dry carbon tetrachloride was heated with vigorous stirring until all the crystals dissolved. To this, a mixture of 45.6 g (0.256 mole) of NBS and 4 g of dibenzoyl peroxide was added and the reaction vessel was illuminated with 100 watt u.v. light source, and heated at reflux for 2 h until the succinimide floated to the top. The mixture was filtered hot and concentrated to 500 ml using a rotary evaporator. The solution was then chilled in an ice-bath and the resulting crystals filtered and recrystallized from absolute ethanol to give 3 g (7%) of white, fluffy crystals which melted at 160°C–161°C (ref. 7, 163°C).

POLYMER SYNTHESES

Poly(tetraphenyl-bis-benzylenebenzimidazole)

A mixture of 3,3′-diaminobenzidine (0.428 g, 0.002 mole) and 3,3,7,7,-tetraphenyltetrathiopyromellitide (0.985 g, 0.002 mole) in DMF (25 ml) was flushed with argon and evacuated three times and then heated to reflux for 48 h, under positive argon atmosphere. After 12 h, the solution turned dark purple and then dark brown. A small amount of declolourizing charcoal was added and the mixture filtered. The filtrate was poured into 250 ml of water to precipitate the solid. After filtration, the solid was dissolved in DMF and precipitated into water three times to afford 0.69 g (63%) of orange-coloured polymer, which did not melt below 350°C (slight decomposition occurs above 310°C). After postcuring at 300°C for 24 h, in a closed tube under argon, and purifying by the same precipitation method as described above, a 0.46 g of the orange solid polymer was obtained. The inherent viscosity of the polymer in chloroform at 23.5°C was 0.09 dl g^{-1}.

Anal. Calc. for $C_{46}H_{28}N_4$: C, 86.79%, H, 4.40%; N, 8.81%. Found (before postcure): C, 72.49%; H, 4.44%; N, 8.22%. Found (after postcure): C, 80.81%; H, 4.63%; N, 6.87%.

Poly(bis-benzylenebenzimidazole)

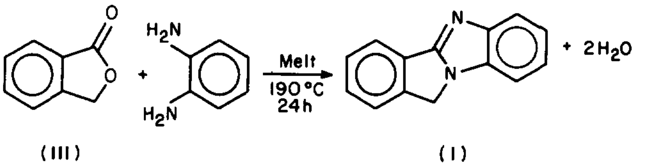
A solution of 0.68 g (0.003 mole) of 3,3′-diaminobenzidene in DMF (15 ml) was placed in a three-necked, round-bottomed flask fitted with a condenser and a dropping funnel. The system was purged with argon and brought to reflux under positive argon atmosphere. A solution of α,α′-dibromo-2,5-dicyano-*p*-xylene (1.0 g, 0.003 mole) in DMF (10 ml) was added slowly to the solution through the dropping funnel over a period of 30 min and heated at reflux for 24 h. The dark solid was suction filtered, washed several times with acetone, dissolved in concentrated formic acid and precipitated from water to give 1.02 g (96%) of the polymer, which did not melt below 350°C. The inherent viscosity in formic acid at 26.5°C was 0.66 dl g^{-1}.

Anal. Calcd. for $C_{22}H_{12}N_4$: C, 79.52%; H, 3.61%; N, 16.87%. Found: C, 57.43%; H, 3.75%; N, 13.12%; Br, 0.25%.

RESULTS AND DISCUSSION

Model reactions and monomers

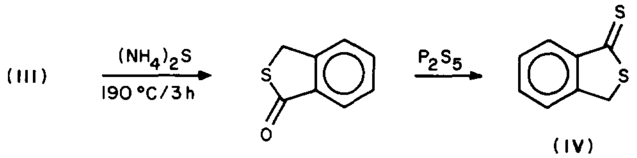
Benzylenebenzimidazole (I). Although benzylenebenzimidazole (I) has been synthesized earlier[4] from a reaction of *o*-phenylenediamine dihydrochloride with phthalide (III), no attempt to synthesize it from phthalide and the free diamine has been reported.



(III) (I)

After successful repetition of the former, several attempts using the free diamine were tried with melt synthesis being the only successful one.

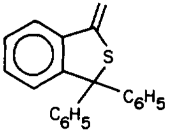
Diphenylbenzylenebenzimidazole (II). Several attempts to thionate both oxygens of the unphenylated lactone (III) with P_2S_5 were unsuccessful; P_2S_5 seemed to thionate only the carbonyl position of (III). Even the rearrangement reactions as reported by Prey and coworkers[8–10] were attempted without success. However, the reaction of phthalide (III) with $(NH_4)_2S$ did yield 2-thiophthalide, which upon further reaction with P_2S_5 gave 1,2-dithiophthalide (IV). This compound melted at 59°C–60°C, although the literature[8–10] gives the melting point of dithiophthalide as 67°C; the compound was further confirmed by i.r. and elemental analysis.



(IV)

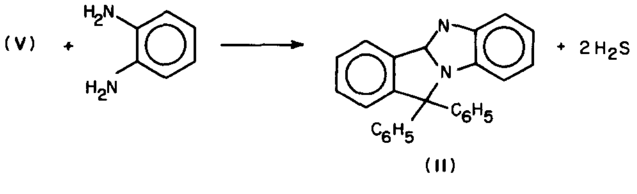
Purification of (IV), even by the use of a wide range of solvents, proved to be very difficult and recrystallization often resulted in an unworkable red–black oil. At other times, a red powder, which melted above 200°C, was isolated. This substance could possibly be the dimer of dithiophthalide as mentioned by Gabriel[11,12]. The compound (IV), when stored in air for 24 h, decomposed into a black tarry substance.

It has been shown earlier[6] that reaction of the lactone with phosphorus pentasulphide following Prey and Kondler's method[9] gave 3,3-diphenyldithiophthalide (V), as orange platelets.



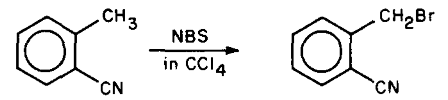
(V)

Condensation of 3,3-diphenyldithiophthalide with *o*-phenylenediamine in xylene resulted in a product (II) which melted at 219°C–220°C.

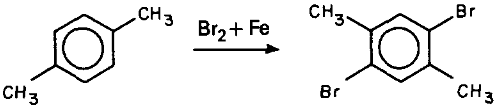


(II)

*α-Bromo-*o*-tolunitrile.* Following the method of Tcheou[5], α-bromo-*o*-tolunitrile was obtained in 30–40% yields. However, better yields were obtained when a high intensity u.v. source was used.

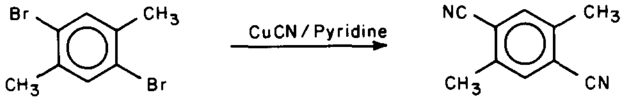


*2,5-Dibromo-*p*-xylene.* 2,5-Dibromo-*p*-xylene was prepared by direct halogenation of *p*-xylene with liquid bromine and elemental iron in an electrophilic aromatic bromination.

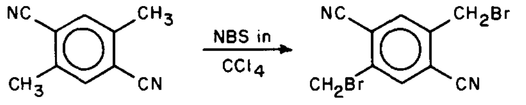


All reactions were run in carbon tetrachloride to achieve 60–70% yields. A small amount of by-product (20–30%) obtained was identified as 2-bromo-*p*-xylene. It was then immediately brominated to form the dibromo derivative.

*2,5-Dicyano-*p*-xylene.* This compound was prepared in 80% yield by the method of Cachia and Wahl[13]. 2,5-Dibromo-*p*-xylene was reacted with a copper cyanide pyridine complex in a melt synthesis.

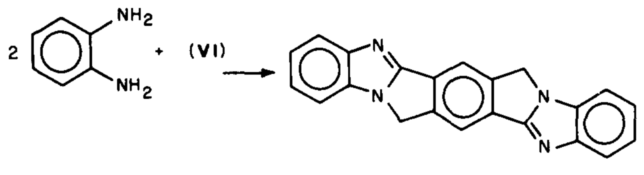


*α,α′-Dibromo-2,5-dicyano-*p*-xylene.* Synthesis of this compound by the method of Diesbach[7] resulted only in the isolation of the α,α,α′,α′-tetrabromo product. However, bromination of 2,5-dicyano-*p*-xylene with NBS was successful, although yields were consistently low (~8%).



(VI)

Reaction of the monomer (VI) with two moles of *o*-phenylenediamine in DMF under nitrogen afforded a pink, powdery substance which did not melt below 350°C and was not soluble in any of the common solvents. Even the expected reaction, namely



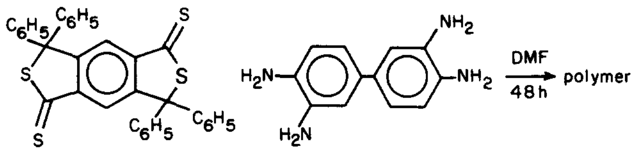
did not occur neatly.

Anal. Calcd. for $C_{22}H_{14}N_4$: C, 79.04%; H, 4.19%; N, 16.77%. Found: C, 78.13% H, 4.19%; N, 16.53%.

The inconsistency of these values may be due to incomplete cyclization of the ring system or polymerization.

Polymers

Polymerization of 3,3,7,7-tetraphenyltetrathiopyromellitide. The polymerization of 3,3,7,7-tetraphenyltetrathiopyromelliitide (*trans*) was carried out with 3,3′-diaminobenzidine in DMF. The orange-coloured polymer was soluble in a number of solvents such as chloroform, ethanol, benzene and DMF, even after post-cure. As a result, the polymer was precipitated from DMF/H_2O mixture. Elemental analysis on the polymer before post-cure indicated incomplete cyclization.



*Polymerization of α,α′-dibromo-2,5-dicyano-*p*-xylene.* Early attempts to polymerize this monomer with 3,3′-diaminobenzidine resulted in a crosslinked polymer which was insoluble in any solvent. The addition of the monomer to a boiling tetraamine–DMF solution improved the results somewhat. However, the polymer would dissolve only in formic and sulphuric acid. Elemental analyses do not support the proposed polymer structure.

Anal. Calcd. for $C_{22}H_{12}O_4$: C, 79.52%; H, 3.61%; N, 16.87%. Found: C, 57.43%; H, 7.74%; N, 13.12%; Br. 0.25%.

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