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Bisorthoesters as Polymer Intermediates. IV. Polybenzoxazole Oligomers

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ABSTRACT

Polybenzoxazoles of relatively low molecular weight have been prepared from hexa-n-propylorthoisophthalate in DMSO at 100°C. Unlike the preparation of polybenzimidazoles via the same route which gave high molecular weight linear polybenzimidazoles, condensation of dihydroxy-diaminobiphenyl with bisorthoesters gave only polymers of low molecular weight. It has not been established but it is most likely that the formation of only low molecular weight polymers was caused by the low basicity of the aromatic amino groups. Benzimidazoles of low molecular weight had also been observed when aromatic tetramines of low basicity were used for the condensation with bisorthoesters.

INTRODUCTION

As part of our continuing interest in the use of bisorthoesters as polymer intermediates [1-4], the synthesis of polymers containing benzoxazole rings was investigated.

Orthoesters, a class of reactive carboxylic acid derivatives, have previously been shown to be quite useful in synthetic organic chemistry as cyclization agents for the preparation of aromatic heterocyclic compounds. A wide variety of aromatic heterocycles has been

prepared including oxazoles [5-8], thiazoles [7-9], imidazoles [10-13], oxadiazoles [14, 15], and triazoles [16]. In general, ortho-ester-promoted cyclizations require only short reaction times.

While the utilization of orthoesters has primarily been limited to preparations of low molecular weight cyclic compounds, their use as polymer-forming intermediates or modifiers is now of interest. Linear polymers containing ester groups in the main chain have been prepared by ring-opening polymerization of spiro orthoesters [17] and spiro orthocarbonates [18].

Branched aromatic polycarbonates were made using up to 5 mole % of orthoester as the branching component [19] and low molecular weight poly-1,3,4-oxadiazoles were reported from the polymerization of isophthaloyl dihydrazide and hexaethyl orthosuccinate [20].

Recently, we described a facile method for the preparation of heat-resistant polybenzimidazoles of high molecular weight [1, 2, 4] utilizing aromatic bisorthoesters. The preparation of oligomers containing adenine and hypoxanthine rings was also accomplished by condensing bisorthoesters with aminomalondiamine dihydrochloride or aminomalonamideamidine dihydrochloride [3, 4].

Benzoxazoles are generally formed by the reaction of a carboxylic acid or carboxylic acid derivative with an o-aminophenol [21]. Brinker, Cameron, and Robinson [22] demonstrated that reactions of this type are suitable for the formation of high polymers when they prepared polymers containing benzoxazole rings by the reaction of bis-o-aminophenols with aliphatic dicarboxylic acids and by the self-condensation of ω-o-aminophenol-carboxylic acids. It was subsequently found that the phenyl esters of aromatic dicarboxylic acids are the acid derivatives of choice when polymerizations are conducted in the melt [23]; however, melt polymerizations invariably produced a small fraction of insoluble material.

Polybenzoxazoles of high molecular weight were first prepared in polyphosphoric acid as the solvent and condensing agent by the self-polycondensation of aromatic o-hydroxy-amino acids [24] or the polycondensation of (2,2'-diaminobisphenol) dihydrochlorides with both aliphatic and aromatic dicarboxylic acids [25].

A rigid chain polybenzoxazole, poly(p-phenylene-benzo-bisoxazole) has been prepared in polyphosphoric acid solution [26]. Anisotropic solution properties have been observed for solutions of stiff chain polybenzoxazoles in methanesulfonic or chlorosulfonic acid [27].

Several two-stage reactions have been recently developed to prepare polybenzoxazoles which include a melt polymerization of an aromatic dialdehyde with dihydroxy-diamines [28] and the use of a poly-(ester-oxime), prepared by solution condensation of an aromatic dihydroxy compound with an aromatic bis(carbohydroxamoyl chloride), as an intermediate which could be ring-closed to polybenzoxazole by treatment with toluenesulfonyl chloride [29].

It was the objective of this work to prepare an aromatic polybenzoxazole, poly(2,2'-m-phenylene-bibenzoxazole), by the reaction of hexa-n-propylorthoisophthalate with 3,3'-dihydroxybenzidine in DMSO

and if successful to compare the results from this condensation reaction with the results of other condensation reactions for the synthesis of polybenzoxazoles.

EXPERIMENTAL PART

Materials

Hexa-n-propylorthoisophthalate (HPOI) and trimethylorthobenzoate (TMOB) were prepared and purified according to the procedures described earlier [4]. The absence of a carbonyl absorption in the infrared spectrum of neat HPOI and TMOB in the region 1730 cm^{-1} demonstrated that the normal ester content was below 0.1%.

Dimethylsulfoxide (Aldrich Chemical Co.) (DMSO) was fractionally distilled at reduced pressure (bp 83-84°C/15 mm) from calcium hydride and collected over activated 3A Linde molecular sieves.

Pyridine (Aldrich Chemical Co., Gold Label) was distilled from sodium hydroxide pellets onto activated 3A Linde molecular sieves.

Polyphosphoric acid (Matheson, Coleman and Bell) (PPA) was used without additional purification.

3,3'-Dihydroxybenzidine (DHB) (Air Force Materials Laboratory) was purified by first converting it to the dihydrochloride salt, followed by six successive decolorizations and recrystallizations from distilled water. Pure white DHB·2HCl was converted to the free amine just prior to use by dissolving it in water followed by neutralization with aqueous sodium acetate. The latter step was performed under a nitrogen atmosphere in the absence of light. The nearly colorless dihydroxybenzidine was collected by pressure filtration and dried in the absence of light at room temperature and 0.005 mm in a P_2O_5 drying pistol.

o-Aminophenol (Aldrich Chemical Co.) was purified by vacuum sublimation through activated charcoal at 85°C and 0.1 mm.

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 283 double grating spectrophotometer as KBr pellets. Peak assignments were made to the nearest 10 cm^{-1}. Melting points were measured on a Mel-Temp capillary melting point apparatus and are uncorrected.

Solution viscosities ($\eta_{0.2}$) were measured at 30.0°C in a Cannon-Fenske viscometer with conc H_2SO_4 as the solvent.

Elemental analyses were done by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of Model Compounds

2-Phenylbenzoxazole. To a dry 100 mL three-neck round-bottom flask was added 0.60 g (5.5 mmole) o-aminophenol, TMOB (1.0 g, 5.5 mmole), dry DMSO (73 mL), and dry pyridine (7.3 mL). The flask was fitted with a reflux condensor protected by a $CaCl_2$ drying tube, and had a capillary nitrogen inlet. The solution was stirred magnetically under a slow stream of dry nitrogen, then placed in an oil bath at 100°C and heated for 13 hr. The deep red-orange solution was cooled to room temperature and 2-phenylbenzoxazole was precipitated as long gold needles by adding the solution dropwise to 100 mL of chilled distilled water. The crude yield of 2-phenylbenzoxazole was 0.11 g (11%), mp 102-104°C (in Ref. 30, mp 103°C).

2,2'-Diphenyl-6,6'-bibenzoxazole. A dry 6 in. test tube was charged with 0.12 g (0.55 mmole) 3,3'-dihydroxybenzidine (DHB), 0.20 g (1.1 mmole) TMOB, dry DMSO (11 mL), and dry pyridine (1.1 mL). The tube was stoppered with an air-tight rubber septum and immersed in a 100°C oil bath for 16 hr. A gold-brown precipitate formed during heating which was collected by filtration, washed with water and methanol, and dried over P_2O_5 for 24 hr at 100°C and 0.01 mm. The yield of crude product was 0.090 g (42%), mp 245-247.5°C (in Ref. 31, mp 245.5-247.0°C).

2,2'-m-Phenylene-bibenzoxazole from HPOI and o-Aminophenol in DMSO. To a dry 100 mL three-neck round-bottom flask was added 0.48 g (4.4 mmole) o-aminophenol, HPOI (1.0 g, 2.2 mmole), dry DMSO (29 mL), and dry pyridine (2.9 mL). The flask was heated under nitrogen in a 100°C oil bath for 13 hr. Upon cooling to room temperature, small needle-like crystals precipitated from the orange solution. The colorless crystals were isolated by filtration, washed with methanol, dried over P_2O_5 for 24 hr at 100°C and 0.01 mm, and melted at 234.5-236°C (in Ref. 32, mp 227-228°C); the yield was 0.23 g (34%).

2,2'-m-Phenylene-bibenzoxazole from HPOI and o-Aminophenol in Polyphosphoric Acid (PPA). Into a dry three-neck flask was weighed polyphosphoric acid (80 g), 0.96 g (8.8 mmole) of o-aminophenol, and 2.0 g (4.4 mmole) of HPOI. The flask was heated under nitrogen in an oil bath to a temperature of 70°C for 90 min, the temperature was then increased from 70 to 200°C over a period of 7 hr, and the dark brown solution was held at this temperature for an additional 7 hr. After cooling, the contents of the flask were poured into 700 mL of distilled water. A finely divided dark brown solid precipitated which was collected by filtration, washed with water and a 5% Na_2CO_3 solution, additional water, and finally dried at 0.1 mm over P_2O_5. The yield of crude product was 1.3 g (98%). Thin-layer chromatography ($CHCl_3$ solvent) revealed the presence of four components; one of the spots was identified as that of 2,2'-m-phenylene-bibenzoxazole. The infrared spectrum (KBr)

showed absorptions at 3055 cm^{-1} (aromatic C–H stretch); 2955-2860 cm^{-1} (aliphatic C–H stretch); a band of weak intensity at 1720 cm^{-1} (carbonyl C=O stretch); 1615, 1550, 1470, and 1450 cm^{-1} (aromatic ring stretch); and 730 cm^{-1} (ortho-substituted aromatic C–H bending).

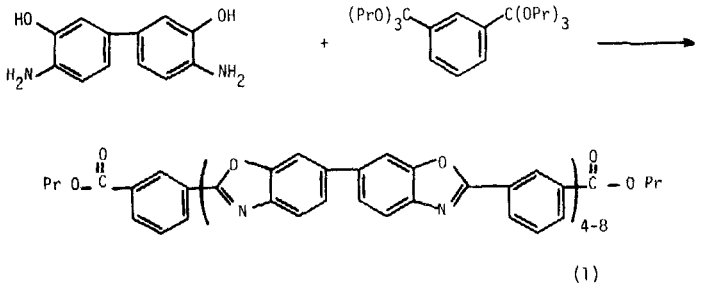
Oligo(2,2'-m-phenylene-6,6'-bibenzoxazole) from HPOI and DHB in DMSO. To a dry 100 mL three-neck round-bottom flask was added DHB (0.70 g, 3.2 mmole), HPOI (1.5 g, 3.2 mmole), dry DMSO (45 mL), and dry pyridine (5 mL). The flask was fitted with a capillary nitrogen inlet, magnetic stirring bar, condenser, and a gas outlet tube connected to a paraffin oil bubbler. For 15 min dry nitrogen (Merriam-Graves pre-purified, minimum 99.995%) was passed through the reaction vessel. The flask was placed in a 100°C oil bath; gradually the reaction solution acquired a bright yellow color. A finely divided yellow solid began to form after 6 hr and the reaction was maintained for an additional 12 hr. After cooling to room temperature, the contents of the flask was poured into 400 mL acetone. The yellow solid was isolated by filtration, washed with fresh acetone, and extracted for 24 hr with acetone in a Soxhlet extractor. The product was dried over P_2O_5 for 24 hr at 100°C and 0.005 mm; yield: 0.87 g (87%); $\eta_{0.2}$ = 0.11 dL/g at 30.0°C in conc H_2SO_4.

Analysis: Calculated for polymer with repeating unit $C_{20}H_{10}N_2O_2$: C, 77.41%; H, 3.25%; N, 9.03%. Calculated for ester-terminated oligomer $C_3H_7OCO(C_{20}H_{10}N_2O_2)_5OCOC_3H_7$: C, 75.99%; H, 3.80%; N, 7.77%. Found: C, 75.66%; H, 4.06%; N, 8.29%. The infrared spectrum (KBr) showed absorptions at 3060 cm^{-1} (aromatic C–H stretch), 2980-2875 cm^{-1} (aliphatic C–H stretch), 1720 cm^{-1} (aromatic ester C=O stretch), 1620 cm^{-1} (–C=N– stretch), and 705 cm^{-1} (ortho-substituted aromatic C–H bending).

RESULTS AND DISCUSSION

Hexa-n-propylorthoisophthalate (HPOI) reacted with 3,3'-dihydroxybenzidine (DHB) and gave a corresponding polybenzoxazole (PBO) in reasonable yield but of low molecular weight. The condensation was carried out at 100°C in a 2% solution of DMSO (containing 10% pyridine). These condensation reactions had produced under most favorable conditions high molecular weight polybenzimidazoles ($\eta_{0.2}$ = 0.8-1.0) in nearly quantitative yields in approximately 10 min but only produced a PBO of inherent viscosity $\eta_{0.2}$ = 0.11 after 18 hr.

The reaction of DHB with HPOI was much slower and a solid began to precipitate after 6 hr even in low concentrations (Eq. 1); under similar conditions, polybenzimidazole remained in solution up to a 4% solid concentration. PBO of low molecular weight was isolated by filtration and showed the characteristic infrared absorptions expected from a compound of this nature (Fig. 1a). In addition, infrared absorptions at 2980-2875, 1720, and 1070 cm^{-1} were observed and are



(1)

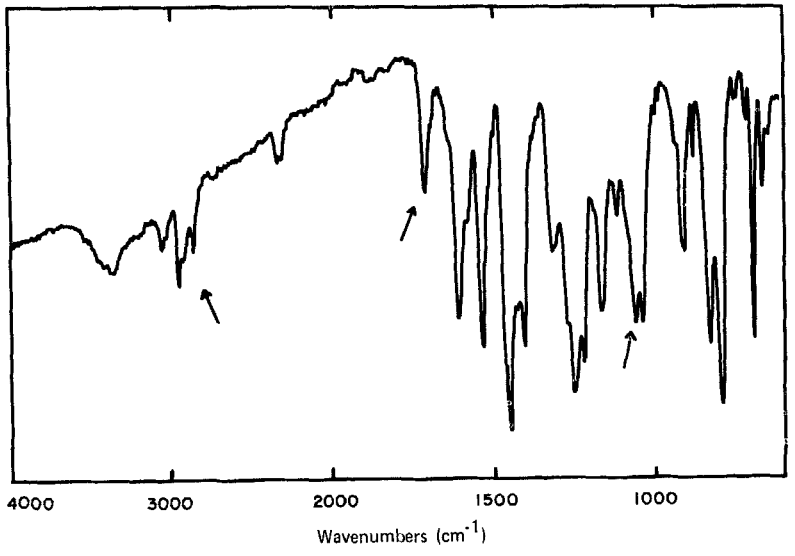


FIG. 1a. Infrared spectrum (KBr) of oligo(2,2'-m-phenylene-6,6'-bibenzoxazole) from HPOI and DHB in DMSO.

characteristic bands of the n-propyl ester group (for comparison see Fig. 1b, infrared spectrum of a high molecular weight PBO). Several modifications of the reaction were subsequently carried out without success of improving the molecular weight of the PBO. Extensive purification of the reactants and a model compound study were undertaken. At the same time the same starting materials were used to prepare polybenzoxazole by established synthetic routes that are known to give high molecular weight polymers.

To obtain a better understanding of the details for the preparation of PBO from bisorthoesters, a careful study of the synthesis of

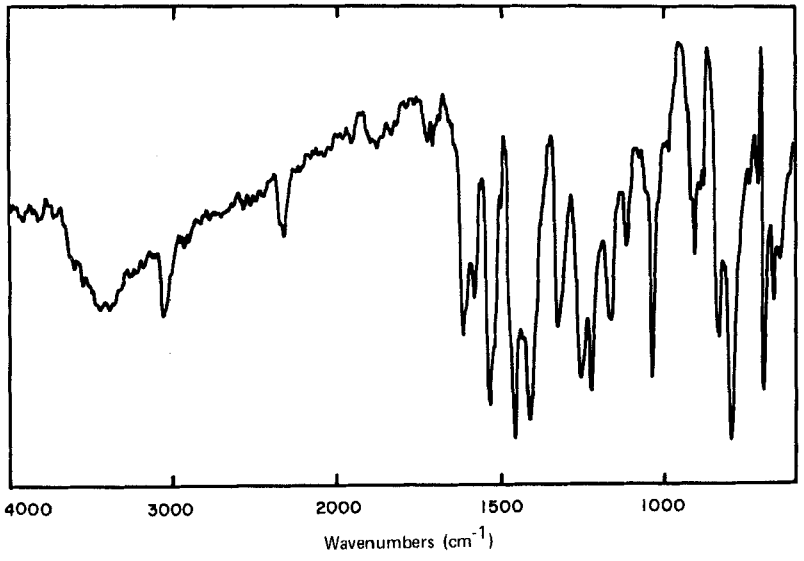
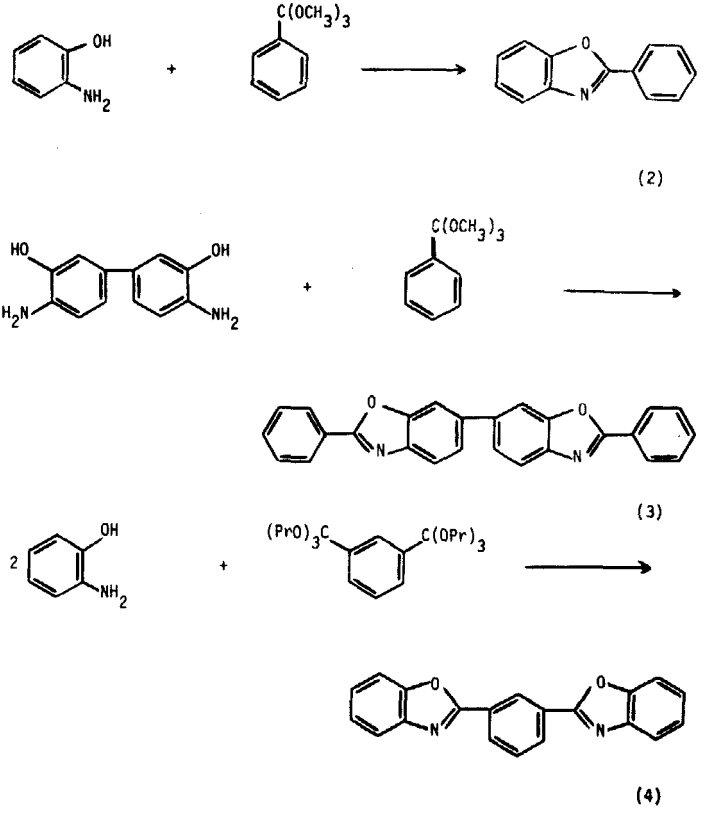


FIG. 1b. Infrared spectrum (KBr) of poly(2,2'-m-phenylene-6,6'-bibenzoxazole) from IPA and DHB.2HCl in PPA.

phenylbenzoxazoles in DMSO (10% pyridine) was undertaken. 2-Phenylbenzoxazole was prepared from TMOB and o-aminophenol but was only obtained in 11% yield (Eq. 2). Condensation of DHB with TMOB gave a 42% yield of 2,2'-diphenyl-6,6'-bibenzoxazole (Eq. 3), and condensation of HPOI and o-aminophenol in DMSO gave 2,2'-m-phenylene-bibenzoxazole in 34% yield (Eq. 4).

In order to be able to compare the route of bisorthoesters in DMSO with the synthesis utilizing the free dicarboxylic acid in PPA, a study of the preparation of PBO in PPA was investigated under conditions which could be compared with the bisorthoester route. It was shown that polycondensation of isophthalic acid and DHB-2HCl in PPA gave the desired PBO as described in the literature as a yellow solid in 100% yield and of an η_{inh} of 1.0. When attempts were made to prepare the same polymer from HPOI and DHB-2HCl in PPA it was found that under the conditions used, HPOI decomposed vigorously at these (higher) reaction temperatures. A very dark brown solid was formed which could not be purified. Model compound studies in PPA with bisorthoesters as reactants gave some indication of the complicated nature of the reaction of HPOI in PPA.

Condensation of HPOI and o-aminophenol in PPA gave, after a slow increase of the reaction temperature from 70 to 200°C over periods of several hours, a finely divided dark brown solid in nearly 100% recovery which consisted of four components in about equal amounts.



(2)

(3)

(4)

One of the components was identified by thin-layer chromatography as being the desired 2,2'-m-phenylene-bibenzoxazole. It was consequently concluded from these model compound studies that HPOI or other bisorthoesters could not be used as intermediates for the condensation in PPA.

Our oligomeric PBO obtained by the condensation of HPOI and DHB was found to contain terminal normal ester groups and it is therefore of interest to look at the possibility of using these ester endgroups for the preparation of copolyesters containing heat-resistant blocks. Recently Marvel and co-workers [33] described a method for the preparation of oligomeric benzimidazoles with reactive nitrile and carboxy endgroups. We have consequently carried out the condensation polymerization of HPOI and DHB in DMSO using a 10% excess of the bisorthoester in an attempt to prepare PBO oligomers with a controlled amount of ester endgroups. It was found that the condensation proceeded smoothly and PBO was obtained with ester endgroups; in addition, the molecular weight of the oligomers, as judged by the

inherent viscosity, was not significantly different from the PBO obtained by condensation of equal molar quantities of HPOI and DHB. This result suggested that the limitation of our molecular weight in the condensation of HPOI and DHB was primarily caused by the fact that the orthoester groups of the bisorthoester HPOI degraded to some extent thermally to the normal ester groups prior to their condensation with the o-aminophenol groups, and the normal ester group is not capable of forming further condensation products with the o-aminophenol to produce high molecular weight polymers.

These results are similar to those of a molecular-weight-limiting reaction that was observed in the preparation of purine containing polymers from orthoesters and aminomalondiamidine [3] or from tetra-amino aromatic compounds other than tetra-aminobiphenyl with bisorthotere- and isophthalates for the preparation of polybenzimidazoles [2].

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