Aromatic polybenzimidazoles from diamide and diamines

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Abstract. Aromatic polybenzimidazoles were obtained by oxidative dehydrocyclization of polyamidines, which were originally synthesized through polycondensation of 4,4′-oxybis(benzoic acid) diamide and diamines in Eaton’s reagent. The transformation was performed in solution using hydrogen peroxide or sodium hypochlorite as oxidants. It was found that the degree of conversion was not noticeably influenced by the polymer concentration in solution and by its molecular weight, whereas the oxidant content exerted appreciable influence. Under the optimal reaction conditions degree of cyclization reaches 95%. The viscosity characteristics of polybenzimidazoles suggest that the transformation of polyamidines is not accompanied by a change in their molecular weights.

1. Introduction
In recent years, considerable researchers’ attention has been focused on polybenzimidazoles (PBIs) owing to the wide prospects for their use in airspace constructs, engineering, nuclear energetics, microelectronics and other fields. Moreover, PBI-based compositions are promising materials for creation of 3D-structures using additive manufacturing [1]. Conventional methods of preparation of PBIs are based on polycondensation of tetraamines and dicarboxylic acids or their derivatives. The use of tetrafunctional monomer involves problems with selective polyacylation of amino groups, which can lead to branching and cross-linking. It should also be noted that tetraamines are expensive, unstable and toxic compounds. Therefore, search for alternative environmentally friendly methods for preparing of PBIs from stable, available and nontoxic monomers under mild reaction conditions is a topical problem. In this work we propose an approach to the synthesis of PBIs consisting in dehydrocyclization of polyamidines (PADs) under the action of various oxidants.

2. Materials and Methods
Methanesulfonic acid (MSA) (≥99.5%, Sigma-Aldrich), all diamines (≥99%, Sigma-Aldrich), phosphorus pentoxide (≥98%, Sigma-Aldrich), sodium hypochlorite solution (Merck) were used without further purification. Reagent-grade N,N-dimethylformamide (DMF) and methanol were obtained from Sigma-Aldrich and were purified by distillation over P₂O₅. 4,4′-oxybis(benzoic acid) diamide was synthesized by low-temperature condensation of 4,4′-oxybis(benzoic acid) dichloride with concentrated aqua ammonia solution. For the preparation of Eaton’s reagent (ER) following procedure was used. Phosphorus pentoxide and methanesulfonic acid were placed in a 50 mL round-bottom flask with a magnetic stirrer. The mixture was stirred at 60-70°C until there was complete dissolution of P₂O₅ [2]. This mixture was used as a solvent for polycondensation and was prepared just before use.
2.1. Synthesis of polyamidines in Eaton’s reagent

Typical example of the polycondensation follows. First, 4,4′-oxybis(benzoic acid) diamide 0.768 g (0.003 mol), 4,4′-diaminodiphenyloxide 0.6 g (0.003 mol) were stirred in ER for ~0.5 h at 100°C under argon. After the dissolution of the monomers, the temperature was raised up to 120°C, and the mixture was stirred for 4-5 h at this temperature. The resulted extremely viscous solution was diluted with methanesulfonic acid. This polymer solution was poured into water and neutralized with sodium carbonate solution. The polymer was collected by filtration, washed with hot water and dried in vacuo at 60°C for 24 h. Anal. Calcd for C_{26}H_{20}N_4O_2: C, 74.29%; H, 4.76%; N, 13.33%; O, 7.62%. Found: C, 73.42%; H, 4.84%; N, 14.72%. IR (KBr pellet): 3450 (m), 3010 (m), 2830 (m), 1620 (s, νC=N), 1540 (w), 1500 (s), 1350 (w, νC–N), 1210 (s, νC–O–C) cm⁻¹.

2.2. Synthesis of polybenzimidazoles

A suspension of 0.5 g of PAD in 5 mL of 1 M aqueous HCl and 7 mL of methanol was refluxed with stirring for 30 min. After cooling the resulting solution to room temperature, 2 mL of a hydrogen peroxide solution (40.8%, 35 mmol) was added dropwise. The mixture was stirred for an additional 20 min. Then 15 mL of DMF was added to make the solution fully homogeneous. After adding 6M aqueous KOH (0.6 mL), the mixture was heated at 100°C for 4 h. Then the reaction solution was poured into 300 mL of ice-cold water. The obtained polymer was filtered off and dried in a vacuum oven at 50°C to constant weight. Anal. Calcd for C_{20}H_{12}N_4O: C, 74.08%; H, 3.70%; N, 17.28%; O, 4.94%. Found: C, 73.81%; H, 3.87%; N, 16.93%. IR (KBr pellet): 3450 (m), 3000 (m), 2800 (m), 1630 (s, νC=N), 1545 (w), 1450 (s), 1360 (w, νC=N), 1110 (s), 1200 (s, νC–O–C), 730 (s) cm⁻¹.

2.3. Measurements

Inherent viscosity [η] (IV) was measured with an Ubbelohde-type viscometer at 20°C in DMF. FTIR spectra were recorded on Excalibur FTS 4000 spectrometer in the wave number range 4000-400 cm⁻¹. The samples were prepared as KBr pellets. ¹³C NMR spectra were recorded on a Varian VXR-500S spectrometer operating at 125 MHz. DMSO-d₆ was used as both solvent and internal standard (δ(¹³C) = 39.50 ppm). Dynamic TGA was performed on STA 449 C14/G Jupiter (Netzsch) at 5°C/min. Al₂O₃ was used as a reference. Gel permeation chromatography (GPC) was performed on "Waters" chromatograph at 20°C. Tetrahydrofuran was used as eluent (flow rate – 0.5 mL/min). Weight-average molecular weights (M_w) were calculated relative to polystyrene standards.

Film materials were prepared by casting of a 10-15% polymer solution in DMF onto a glass support. The solution distributed on the substrate surface was dried on air at first, and then a crude film was postdried in vacuo at 40–70°C for 24 h and at 120°C for 24 h to remove remains of DMF.

3. Results and Discussion

3.1. Preparation of polyamidines

Recently, we showed that aromatic PADs could be prepared through the interaction of aromatic dinitriles and diamines in melt or in 1,3-dialkyl-substituted imidazolium ionic liquids. Since dicarboxylic acids amides could transform into dinitriles under the action of dehydrating agents, it was advisable to examine the synthesis of PADs through the “direct polycondensation”, which is based on the interaction of diamines and diamides in a condensing medium. Eaton’s reagent (CH₃SO₃H : P₂O₅ = 10 : 1, wt/wt) was selected as a condensing medium, because it is one of the most effective agents for obtaining of various polyheteroarylenes [3-4].

Aromatic PADs were synthesized according to the Figure 1. The main features of polycondensation were investigated for the interaction of 4,4′-oxybis(benzoic acid) diamide and 4,4′-diaminodiphenyl oxide (synthesis of PAD-1).

The effect of the synthesis temperature on the molecular mass of the PAD-1 was studied in the range of 100–140°C, because the rate of reaction was very low at temperatures below 100°C, whereas decomposition of the main component of Eaton’s reagent, methanesulfonic acid, began at a temperature above 150°C. Polycondensation performed at 120°C and a concentration of initial
monomers of 0.6 mol/L for 10 h yielded the PAD with the highest \([\eta]\) value, 0.20 dL/g. At a temperature of 100–120°C, the polycondensation proceeded with the formation of a transparent light brown solution, whereas at 140°C, after 6–8 h, the reaction solution became dark brown probably owing to the degradation of monomers and/or polymer.

Further study of polycondensation showed that the molecular mass of the formed PAD-1 is strongly affected by the concentration of the initial monomers. It was found that the highest molecular mass PAD is formed at a concentration of monomers of 0.8 mol/L; a further increase in concentration leads to a marked decline in the molecular weight of the PAD.

The molar ratio of phosphorus pentoxide to diamide in case of concentration of monomers of 0.8 mol/L in Eaton’s reagent (\(\text{CH}_3\text{SO}_3\text{H} : \text{P}_2\text{O}_5 = 10 : 1\), wt/wt) was 1.32. Because the polymer prepared under these conditions had the highest \([\eta]\) value, it was advisable to investigate polycondensation at the found optimum ratio, but at higher both monomer concentrations and content of phosphorus pentoxide. As shown in reference [4], the use of additional amounts of \(\text{P}_2\text{O}_5\) leads to a considerable increase in the molecular masses of the polymers. Experiments demonstrated that the addition of \(\text{P}_2\text{O}_5\) during polycondensation resulted in the formation of polymers showing limited solubility in conventional organic solvents, although this reaction occurred under homogeneous conditions. However, if additional amounts of the dehydrating agent were added at the reaction onset (immediately during preparation of the reaction solution) well soluble polymers were formed. It was shown that the highest molecular mass products are formed at a monomer concentration of 1.0 mol/L (\([\eta] = 0.51\) dL/g).

With allowance for the found optimum conditions (\(T = 120°C, t = 4–5\) h, a phosphorus pentoxide to monomer molar ratio of 1.32, and a monomer concentration of 1 mol/L), PAD-2 were also synthesized via scheme presented in Figure 1.

![Figure 1. Synthesis of polyamidines from 4,4'-oxybis(benzoic acid) diamide and diamines.](image)

The polycondensation of 4,4'-oxybis(benzoic acid) diamide and a number of aromatic diamines occurred under homogeneous conditions and produced PADs with high yields and \([\eta] = 0.48–0.51\) dL/g. Thus, high-molecular-mass PADs may be easily prepared via the direct polycondensation of 4,4'-oxybis(benzoic acid) diamide with various diamines in Eaton’s reagent. This approach differs from conventional procedures by a high rate of polymer formation and mild reaction conditions.

3.2. Preparation of polybenzimidazoles by oxidative dehydrocyclization of polyamidines

The idea of preparing benzimidazole from N-phenyl substituted amidine hydrochloride (proposed by Grenda et al. [5]) consists in generation from the azomethine bond in amidine hydrochloride of an uncharged electron-deficient species, nitrene, which, being extremely reactive, undergoes addition at the \(\alpha\)-position of the benzene ring, thus forming the benzimidazole heterocycle.

In order to investigate the oxidative dehydrocyclization, transformation of PAD-1 was studied in detail. Also, cyclization of PAD-2 was carried out under the optimal reaction conditions.
The transformation was performed in solution using hydrogen peroxide or sodium hypochlorite as oxidants (Figure 2). The PAD was converted to the soluble form using 1 M aqueous HCl and methanol. After vigorous stirring with heating for 30 min, the polymer dissolved virtually fully. Subsequent addition of the oxidant caused formation of a precipitate, which was dissolved by adding a small amount of DMF. To initiate the generation of nitrenes, we added to the reaction mixture 6 M aqueous KOH and heated to 100 °C.

\[ \begin{align*}
\text{NaClO} / \text{H}_2\text{O}_2 & \rightarrow \text{OH} \\
\text{PBI-1: } X = \text{O} & \\
\text{PBI-2: } X = \quad & 
\end{align*} \]

**Figure 2.** Oxidative dehydrocyclization of polyamidines in polybenzimidazoles.

The course of oxidative dehydrocyclization was monitored by IR spectroscopy, namely, by changes in the intensities of the characteristic absorption bands of the N–H (3400 and 3050 cm\(^{-1}\)) and С–N (1360–1365 cm\(^{-1}\)) groups. The other characteristic changes observed in the spectrum are shift of the C=N absorption band at 1610 cm\(^{-1}\) \((\Delta \nu = 20 \text{ cm}^{-1})\), caused by transformation of the acyclic form into the cyclic form, and appearance of a new band at 730 cm\(^{-1}\), corresponding to 1,2-disubstituted benzene ring.

A study of the PAD transformation showed that the degree of conversion was not noticeably influenced by the polymer concentration in solution and by its molecular weight, whereas the oxidant content exerted appreciable influence. For example, when hydrogen peroxide was taken in an equimolar amount relative to PAD repeat unit, only 70% conversion was attained in 8 h, after that the reaction became very slow. Threefold excess of the oxidant led to practically complete conversion in 6 h at 80°C. It is interesting that the rates in both processes in the first hour were similar, but then the kinetics became different, apparently because of hindered diffusion in the polymer solution and limited accessibility of the amidine bond in the polymer chain to the oxidant molecules. With sodium hypochlorite used instead of hydrogen peroxide, the cyclization rate slightly decreased. The maximal rate was attained with increasing temperature to 100°C: the cyclization was complete in 4 h. Further increase in temperature led to considerable deceleration of the reaction, probably because of decomposition of sodium hypochlorite.

The structure of thus obtained PBI-1 was confirmed by IR spectroscopy: characteristic absorption bands of 1,2-disubstituted benzene ring at 730 cm\(^{-1}\) and of C=N (1630 cm\(^{-1}\)) and C–N (1360 cm\(^{-1}\)) bonds are observed. In the \(^{13}\)C NMR spectrum of PBI-1, compared to those of the pristine PAD-1, new signals at 134.6 ppm appear, confirming formation of the \(ω\)-substituted aromatic ring; in addition, the signal of the amidine carbon atom at 158.6 ppm transforms into the signal of the benzimidazole carbon atom at 152.1 ppm.

According to TGA, the temperature of 10% weight loss on air for PBI-1 is 490°C whereas for corresponding PAD this value is 275°C. This fact also indirectly confirms the occurrence of cyclization.
PBI-2 was obtained similar to PBI-1 using sodium hypochlorite as oxidant at 100°C. The viscosity characteristics of PBIs suggest that the transformation of PADs is not accompanied by a change in their molecular weights.

Both obtained PBIs are fully soluble in concentrated sulfuric and formic acids and dissolved in amide solvents at slight heating. By casting 10–15% solutions of PBIs in DMF onto glass supports, we obtained films with tensile strength of 68.0-71.6 MPa and elongation of 2–3%.

4. Conclusion
We showed that aromatic PADs with moderate molecular weights could be prepared by polycondensation of 4,4′-oxybis(benzoic acid) diamide and diamines using ER. Resulted PADs were used as precursors for preparation of aromatic PBIs by oxidative dehydrocyclization. It was found that the degree of conversion was not noticeably influenced by the polymer concentration in solution and by its molecular weight, whereas the oxidant content exerted appreciable influence. Obtained PBIs had high thermal stability (up to 490°C) and good mechanical properties.

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