Preparation of aromatic polyamidines and their transformation in polybenzimidazoles

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Abstract. Polymers with amidine groups –NH–C(=NH)– in main chain were synthesized by two different approaches. The first strategy consists in polyaddition of dinitriles and diamines in acidic ionic liquids (ILs) which act as catalyst and solvent, while the second approach is based on polycondensation of 4,4′-oxybis(benzoic acid) diamide and diamines in Eaton's reagent (ER). The resulting polyamidines (PADs) with M_w up to 25 000 g/mol possess thermal stability on air up to 288°C, and good solubility in polar organic solvents. Moreover dehydrocyclization of obtained PADs into polybenzimidazoles (PBIs) under the action of various oxidants was also studied in this work. The crosslinked films based on PBI and poly(amino imide) resin (PAIR) possess high mechanical characteristics. It has been proved that the crosslinked films based on PBI matrix are perspective materials for design the phosphoric acid electrolyte membranes for the medium temperature fuel cells.

Keywords: polymer synthesis, polymer blends, polyamidines, polybenzimidazoles, proton exchange membrane fuel cells

1. Introduction

In recent years, considerable researchers' attention has been focused on PADs owing to the wide prospects for their use in optoelectronics, organometallic catalysis, medicine, enzymology, and other fields [1–6]. Although polymers of this class show much promise, they have not been studied to a great extent. In terms of the position of amidine groups in the polymer chain, there are two groups of PADs (Figure 1), among which PADs-I have been most extensively studied [7–10]. PADs with structure II are much less studied compounds. Only a few examples of synthesis of these PADs are known [5, 6, 11–14]. Therefore development of synthetic routs to PADs-II is important problem. In addition to the fundamental importance of PADs-II, they can be used as precursors for the preparation of PBIs. Brand *et al*. [14] outlined possibility of preparing PBIs by oxida-
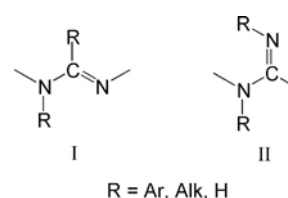

R = Ar, Alk, H

Figure 1. Structures of polyamidines

tive dehydrocyclization of PADs, which were synthesized by polyaddition of dinitriles with diamines in melt. However, the formed polymers had low molecular weights and were incapable to form films and press materials with satisfactory mechanical properties, and therefore they cannot be used in different areas of industry, in particular for proton exchange membrane fuel cells [15].

In this work successful modification of synthesis of aromatic PADs from dinitriles and diamines by using

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acidic ILs as catalyst and solvent is described. Moreover we developed a new method of synthesis of such polymers consisting in polycondensation of 4,4′-oxybis(benzoic acid) diamide and diamines using ER as condensing agent and solvent. The dependence of reaction conditions on molecular weights of the obtained PADs has been investigated in details. Synthesized polymers were characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies, thermogravimetry (TGA) and gel permeation chromatography (GPC). Moreover dehydrocyclization of PADs into PBIs under the action of various oxidants was studied. Also, the mechanical properties and proton conductivity of membranes based on a blend of PBIs and PAIR were also determined.

2. Experimental section

2.1. Materials

1-butyl-3-methylimidazolium chloride ([BMIm]Cl) (99.4%, 4900790100, Merck, Germany), 1-butyl-3-methylimidazolium bromide ([BMIm]Br) (99.8%, 4900870100, Merck, Germany), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF4) (99.9%, 4900490100, Merck, Germany), 1-butyl-2,3-dimethylimidazolium chloride ([BM2Im]Cl) (99.8%, 4900210100, Merck, Germany), 1-Ethyl-3-methylimidazolium chloride ([EMIm]Cl) (99.8%, 4900540100, Merck, Germany), methanesulfonic acid (MSA) ($\geq$99.5%, 471356, Sigma-Aldrich, Germany), terephthalonitrile (99%, 8210760250, Merck, Germany), isophthalonitrile (99%, 8413550100, Merck, Germany), all diamines ($\geq$99%, Sigma-Aldrich, Germany), aluminium chloride (99%, 563919, Sigma-Aldrich, Germany), phosphorus pentoxide ($\geq$98%, 298220, Sigma-Aldrich, Germany), sodium hypochlorite solution (1056142500, Merck, Germany) were used without further purification.

Reagent-grade N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (MP), dimethylsulfoxide (DMSO), chloroform, dichloromethane, methanol were obtained from Sigma-Aldrich (Germany), and were purified by distillation over P_2O_5.

4,4′-oxybis(benzoic acid) diamide was synthesized by low-temperature condensation of 4,4′-oxybis(benzoic acid) dichloride with concentrated aqua ammonia solution as described previously [16]. 4,4′-dicyanodiphenyloxide was obtained by dehydration of 4,4′-oxybis(benzoic acid) diamide using thionyl chloride in DMF solution [17].

Acidic $Al_xHal_y^-$ containing ionic liquids were prepared by the slow addition of the desired amount of $AlHal_3$ to the imidazolium salt. The reaction was left to stir overnight at 0°C for 24 h, in order to allow a perfect homogenization of the resulting acidic ionic liquid [18].

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 P_2O_5 [19]. This mixture was used as a solvent for polycondensation and was prepared just before use.

PAIR was supplied from 'Karbolit' plant (Kemerovo city, Russia) and was used as received.

2.2. Polymer synthesis

2.2.1. Synthesis of polyamidines in ionic liquids

PADs were synthesized in a 50 mL three-necked flask equipped with a stirrer and an inlet and an outlet for argon. The typical procedure is as follows. First, 0.12 g (0.9375 mmol) of terephthalonitrile and 0.1875 g (0.9375 mmol) of 4,4′-diaminodiphenyloxide were added to the clear liquid of [BMIm]Al_2Cl_7. Next, the reaction mixture was placed in a bath, and the temperature was raised up to 190–200°C. After about 15–16 h, viscous solution was poured into a 5% aqueous KOH solution. Finally, precipitate was filtrated, washed several times with water (typically three times) until neutral pH of the washing water, and dried in *vacuo* at 60°C for 24 h. Anal. Calcd for $C_{20}H_{16}N_4O$: C, 73.17%; H, 4.88%; N, 17.07%; O, 4.88%. Found: C, 72.05%; H, 4.72%; N, 18.93%. IR (KBr pellet): 3450 (m), 3000 (m), 2750 (m), 1605 (s, $v_{C=N}$), 1568 (w), 1500 (s), 1368 (w, v_{C-N}), 1200 (s, v_{C-O-C}) cm^{-1}.

2.2.2. 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, $v_{C=N}$), 1540 (w), 1500 (s), 1350 (w, $v_{C–N}$), 1210 (s, $v_{C–O–C}$) cm^{-1}.

2.2.3. Synthesis of polybenzimidazoles

A suspension of 0.5 g of PAD **2a** 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 6 M 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, $v_{C=N}$), 1545 (w), 1450 (s), 1360 (w, $v_{C–N}$), 1110 (s), 1200 (s, $v_{C–O–C}$), 730 (s) cm^{-1}.

2.3. Measurements

Inherent viscosity [η] (IV) was measured with an Ubbelohde-type viscometer at 20°C in DMF or in H_2SO_4. FTIR spectra were recorded on Excalibur FTS 4000 spectrometer (Germany) in the wave number range 4000–400 cm^{-1}. The samples were prepared as KBr pellets. ^{13}C NMR spectra were recorded on a Varian VXR-500S spectrometer (USA) operating at 125 MHz. DMSO-d_6 was used as both solvent and internal standard ($\delta(^{13}C)$ = 39.50 ppm). Dynamic TGA was performed on STA 449 C14/G Jupiter (Netzsch, Germany) 5°C/min. Al_2O_3 was used as a reference. Gel permeation chromatography (GPC) was performed on 'Waters' chromatograph (USA) 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 a 10–15% polymer solution in DMF onto a glass support. PBI–PAIR films of various compositions were prepared by mixing 10–15% solutions of the initial polymers in DMF. The solution distributed on the substrate surface was dried on air at first, and then a crude film was post-dried *in vacuo* at 40–70°C to remove remains of DMF. The films were kept in the extended state under a load of 0.5 kPa in a vacuum oven at 160°C for 48 h. Membranes were obtained by soaking cured films into water solutions of H_3PO_4 with concentrations of 9 M for 5 days. After soaking, the membranes were removed from solutions of H_3PO_4, and acid residues were wiped with a filter paper. The membranes were dried in vacuo at room temperature up to a constant weight. Water content in obtained membranes does not exceed 8–10%.

A proton conductivity of a membrane was measured by van der Pauw four-probe method [20] at current frequency of 500 Hz under dry argon flow and calculated according to Equation (1):

$$\sigma = \frac{I_{12}}{4.53 \cdot h \cdot U_{34}} \tag{1}$$

where σ is a proton conductivity [S/cm]; I_{12} is a current between flank probes of 1 and 2 [A]; U_{34} is a voltage between flank probes of 3 and 4 [V]; h is a thickness of a sample [cm].

3. Results and discussion
3.1. Preparation of polyamidines

The proposed concept to aromatic PADs with an improved molecular weight focuses on two different approaches. The first strategy consists in polyaddition of dinitriles and diamines in ionic liquids, while the second one is based on polycondensation of diamide and diamines in Eaton's reagent.

3.1.1. Polyamidines from dinitriles and diamines

It is known [21–23] that the reactions of aromatic nitriles with amines are well-catalyzed by protic and aprotic acids. Among many catalysts, the aprotic acids (Lewis acids) have been found to be very useful to provide good yields of desired amidines [21, 22], but in general, the yields are not high enough to consider their use in the formation of high molecular weight polymers. Along with this, acidic ILs on the basis of metal halides can be regarded as an alternative for the traditional heterogeneous and

homogeneous catalysts, in particular aluminium chloride [24]. These ILs were successfully used for different acid-catalyzed reactions, such as Friedel-Crafts alkylation and acylation [24–27], nitrations [24, 25] and halogenations [24, 25, 28].

These data altogether in combination with the ability of ILs to dissolve different organic compounds (in particular, nitriles and amines) and polymers served as the basis for the studying the possibility of synthesis of PADs from aromatic dinitriles and diamines in ionic media (Figure 2). Moreover, the efficacy of ILs in the synthesis of polyheteroarylenes was shown [29–32].

In order to determine the optimal conditions for the reaction, the polyaddition of terephthalonitrile and 4,4′-diaminodiphenyl oxide in [BMIm]Cl/AlCl$_3$ was studied (synthesis of polymer **1a**).

Molar ratio [BMIm]Cl/AlCl3 strongly influences on catalytic activity of IL in acid-catalyzed reactions [24]. Therefore, at first, the effect of amount of aluminium chloride in IL system on [η] of the PAD was examined. It has been found that in the mixtures [BMIm]Cl/AlCl$_3$ containing 0÷1 equivalents of AlCl$_3$, which are, in fact, eutectic mixtures of [BMIm]Cl and [BMIm]AlCl$_4$, only low-molecular weight PADs are formed ([η] = 0.07–0.11 dL/g). Molecular weight of the obtained PAD significantly increases when polymerization was carried out in the systems containing >1 equivalents of AlCl$_3$ (Figure 3). The best results were achieved in IL containing 2 equivalents of AlCl$_3$, i.e. under conditions where strongly acidic IL [BMIm]Al$_2$Cl$_7$, generated
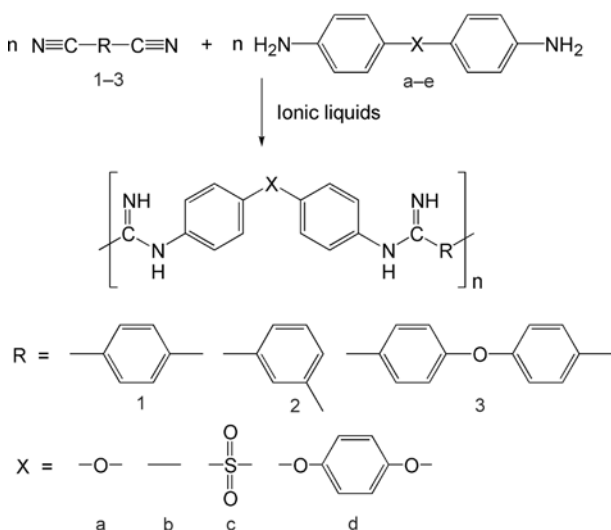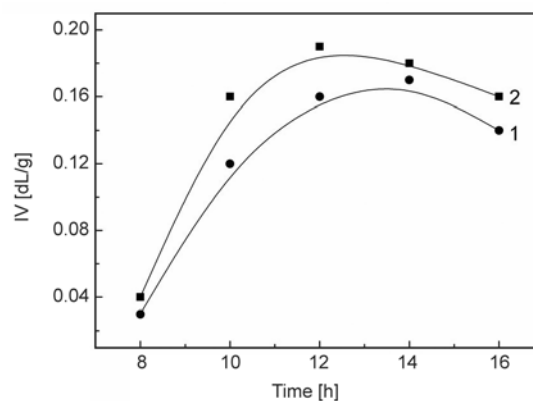

Figure 3. Effect of reaction time on IV of PAD **1a** obtained by the polyaddition in IL: [BMIm]Cl/AlCl$_3$ = 1:1.1 (1), [BMIm]Cl/AlCl$_3$ = 1:2 (2), at 160°C and monomer concentration of 0.6 mol/L

from [BMIm]AlCl$_4$ and AlCl$_3$, serves as the reaction medium [24].

The IV of the synthesized polymer also depends on the temperature and concentration of the initial monomers. The temperature of 190–200°C and the concentration of monomers 1.0 mol/L are optimal (Figure 4). Further increase in the temperature and the concentration of the monomers results in noticeable reduction of the [η] of the PAD.

Under the optimal reaction conditions, the polymerization also occurs in other studied ILs (Table 1). The PAD with the highest molecular weight ([η]) is formed in [BMIm]Al$_2$Br$_7$ and [BMIm]Al$_2$Cl$_7$, while the [η] of PAD obtained in conventional organic solvents (nitrobenzene, sulfolane) and in melt does not exceed 0.13 and 0.28 dL/g, respectively [33].

On the basis of these studies, then, the polyaddition of various dinitriles with diamines was carried out
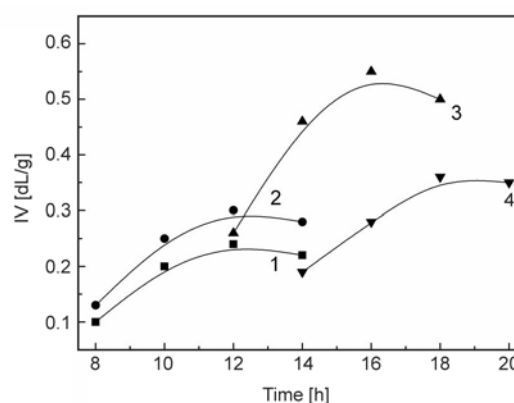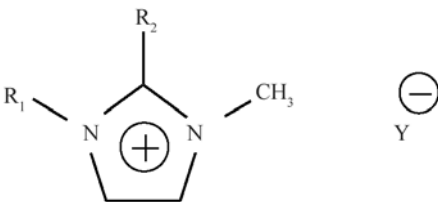

Figure 2. Synthesis of polyamidines from dinitriles and diamines

Figure 4. Effect of reaction time and monomer concentration on IV of PAD **1a** obtained by the polyaddition in [BMIm]Al$_2$Cl$_7$, at 190–200°C and monomer concentration of 0.6 (1), 0.8 (2), 1.0 (3) and 1.2 (4) mol/L

Table 1. Effect of nature of ionic liquids on intrinsic viscosity of polyamidine **1a**

№	IL	R$_1$	R$_2$	Y$^-$	IV^a [dL/g]
1	[BMIm]Cl	C$_4$H$_9$	H	Cl	0.07
2	[BMIm]Al$_2$Cl$_7$	C$_4$H$_9$	H	Al$_2$Cl$_7$	0.55
3	[EMIm]Al$_2$Cl$_7$	C$_2$H$_5$	H	Al$_2$Cl$_7$	0.19
4	[BM$_2$Im]Al$_2$Cl$_7$	C$_4$H$_9$	CH$_3$	Al$_2$Cl$_7$	0.30
5	[BMIm]Al$_2$Br$_7$	C$_4$H$_9$	H	Al$_2$Br$_7$	0.42
6	[BMIm]BF$_4$	C$_4$H$_9$	H	BF$_4$	0.23

^{a}Measured in sulfuric acid at 20°C

under found optimal reaction conditions (Figure 2). The results are shown in the Table 2. The polyaddition proceeded in homogeneous solution and gave quantitative yields of polymers with IV up to 0.55 dL/g.

One of the advantages of ILs is the ability to use them in the recycle. Therefore it was interesting to re-use of [BMIm]Al$_2$Cl$_7$ after polymerization of aromatic dinitriles and diamines. The recycle was performed as follows: first, reaction solution was poured into chloroform or dichloromethane; second, the obtained precipitate was collected by filtration; and finally, mixture of IL and organic solvent was separated by vacuum distillation. It was found that yield of regenerated IL was 60–70%. The reason for the loss of IL could be due to strong complexation of IL

Table 2. Characteristics of polyamidines obtained from dinitriles and diamines in [BMIm]Al$_2$Cl$_7$

№	PAD	IV^a [dL/g]	Decomposition temperature^b [°C]
1	1a	0.55^c	275
2	2a	0.51	272
3	3a	0.32	–
4	1b	0.52	288
5	2b	0.44	278
6	3b	0.27	–
7	1c	0.40	282
8	2c	0.33	–
9	3c	0.22	–
10	1d	0.53	–
11	2d	0.46	–
12	3d	0.29	–

^{a}Measured in sulfuric acid at 20°C
^{b}Temperature of 10% weight loss determined by TGA at a heating rate of 5°C/min
^{c}M_w = 19 000 g/mol, M_w/M_n = 1.62 (GPC). Film properties: tensile strength (σ) = 29.5 MPa, elongation (ε) = 4.2%.

with the formed PAD. Investigation of precipitate obtained after pouring of reaction mixture in chlorinated solvent confirmed this assumption. PAD/IL complexes can be easily hydrolyzed by dissolution in a mixture of 1N aqua HCl and CH$_3$OH (1/1, v/v) and further precipitation of PAD with 5% aqua KOH solution.

So, we not only successfully synthesized aromatic PADs based on dinitriles and diamines in chloroaluminate ILs, but also regenerated ionic solvent.

3.1.2. Polyamidines from 4,4′-oxybis(benzoic acid) diamide and diamines

With consideration for the fact that diamides 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. Being one of the most effective agents for obtaining various polyheteroarylenes [34–36], Eaton's reagent (CH$_3$SO$_3$H:P$_2$O$_5$ = 10:1, wt/wt) was selected as a condensing medium. Aromatic PADs were synthesized according to the Figure 5. The main features of polycondensation were investigated for the interaction of 4,4′-oxybis(benzoic acid) diamide and 4,4'-diaminodiphenyl oxide (synthesis of polymer **4a** Figure 5).

The effect of the synthesis temperature on the molecular mass of the PAD 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
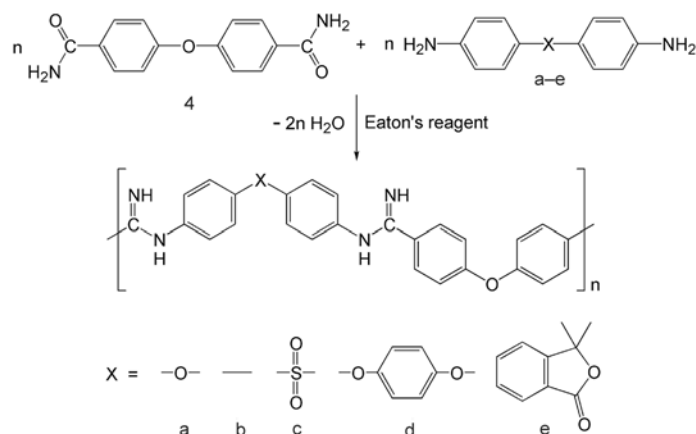
Figure 5. Synthesis of polyamidines from 4,4′-oxybis(benzoic acid) diamide and diamines

10 h yielded the PAD with the highest [η] 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 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 mass of the PAD. The molar ratio of phosphorus pentoxide to diamide for a concentration of monomers of 0.8 mol/L in Eaton's reagent ($CH_3SO_3H:P_2O_5$ = 10:1, wt/wt) was 1.32. Because the polymer prepared under these conditions had the highest [η] 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 [37], the use of additional amounts of P_2O_5 leads to a considerable increase in the molecular masses of the polymers.

Experiments demonstrated that the addition of P_2O_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 (Figure 6) that the highest molecular mass products are formed at a monomer concentration of 1.0 mol/L ([η] = 0.51 dL/g).
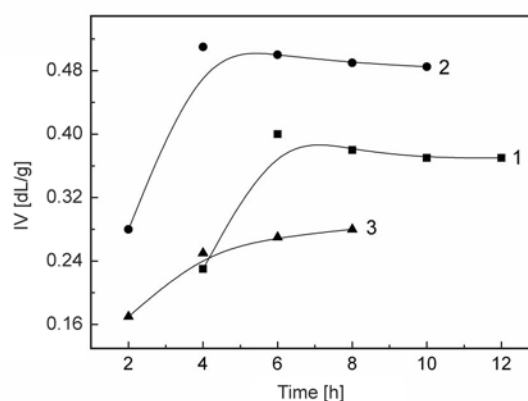

Figure 6. Effect of reaction time and monomer concentration on IV of PAD **4a** obtained by the polycondensation in ER (mole ratio monomer/P_2O_5 = 1/1.32), at 120°C and monomer concentrations of 0.8 (1), 1.0 (2), 1.2 (3) mol/L

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), various PADs were synthesized via the above described Figure 5.

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 [η] = 0.23–0.65 dL/g (Table 3). However, in the case of diamides of iso- and terephthalic acids and diamines, only low-molecular-mass products were obtained. This fact makes it possible to assume that imino carbocations $-C_6H_4-C^+=NH$ serve as active intermediates in polycondensation. In fact, the best results were attained in the case of 4,4′-oxybis(benzoic acid) diamide, which forms an imino carbocation stabilized by an electron-donor ether group. In the case of diamides of iso- and terephthalic acids, the formation of imino carbocations is extremely difficult because of the presence of

Table 3. Characteristics of polyamidines obtained from 4,4′-oxybis(benzoic acid) diamide and diamines in Eaton's regent

№	PAD	IV[a] [dL/g]	Decomposition temperature[b] [°C]
1	4a	0.51[c]	268
2	4b	0.48	280
3	4c	0.44	274
4	4d	0.65[d]	269
5	4e	0.23	246

[a]Measured in DMF at 20°C
[b]Temperature of 10 % weight loss determined by TGA at a heating rate of 5°C/min
[c]M_w = 20 000 g/mol, M_w/M_n = 1.56 (GPC)
[d]M_w = 25 000 g/mol, M_w/M_n = 1.54 (GPC). Film properties: tensile strength (σ) = 32.1 MPa, elongation (ε) = 3.5%.

electron-acceptor groups. Similar relationships were observed in references [34–36] for the synthesis of polybenzazoles and poly(ether ketones) in Eaton's reagent.

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.

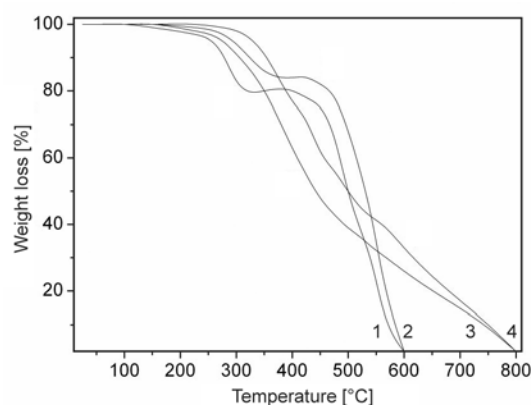### 3.1.3. Characterization of polyamidines

The structures of PADs were investigated by a combination of elemental analysis, IR investigation, and ^{13}C NMR spectroscopy. The chemical shift of the amidine carbon atom is observed in the ^{13}C NMR spectrum at ≈158 ppm. Typical NMR spectrum of PAD **4b** is presented in Figure 7. Elemental analysis data are in a good agreement with the calculated values. The IR spectra of the polymers show characteristic absorption bands at 1608–1615 (C=N), 1360–1370 (C–N), and 3500–2500 (N–H, C_{Ar}–H)
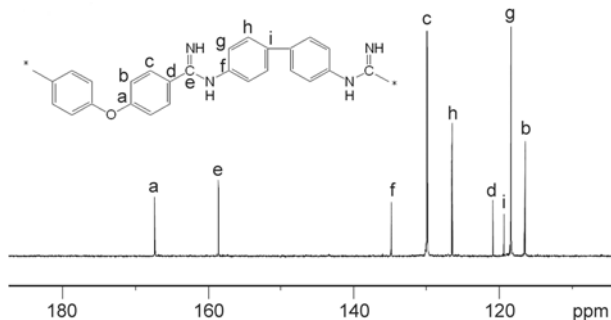
Figure 7. NMR ^{13}C spectrum of PAD **4b**

cm^{-1}, thereby indicating the formation of amidine functional groups [38].

The thermal properties of PADs were evaluated via TGA in the air and argon atmospheres and the data are summarized in Tables 2 and 3. All the samples used for studying the TGA were subjected to exhaustive drying in a vacuum oven at 60°C. Typical TG curves of PADs **4b** and **1b** are shown in Figure 8. For all the samples two distinct different weight losses on TG curves on air are observed. We believe that oxidative dehydrocyclization of PAD in more thermally stable PBI under the action of oxygen occurs during TG experiment on air. In argon atmosphere one-step degradation of PADs is observed, which indirectly indicates the formation of benzimidazole rings during TGA in the presence of oxygen. These assumptions, however, need to be further examined with more effective characterization techniques. The 10% weight loss temperatures both in air and argon were at around 246–288°C.

The polymers are fully soluble in concentrated sulfuric acid, concentrated formic acid and in polar organic solvents (DMF, DMAA, MP, THF, etc.) at room temperature or under slight heating. Moreover, all of the synthesized polymers are soluble in a mixture of 1N aqua HCl/methanol (1/1, v/v). Solubility of polymers in conventional organic solvents allowed to determine their molecular masses by GPC. As noted in Tables 2 and 3 the PADs have moderate molecular masses (M_w) up to 25 000 g/mol. Films prepared by casting of polymer solutions in DMF had tensile strength of 29.5–32.1 MPa and elongation of 3.5–4.2%.

Figure 8. TG curves of PADs **4b** (1, 3) and **1b** (2, 4) in air and argon atmosphere, respectively

3.2. Preparation of polybenzimidazoles by oxidative dehydrocyclization of polyamidines

Practical importance of synthesized PADs increases if they can be used as precursors for the preparation of high-performance PBIs. Therefore, it seemed appropriate to study oxidative dehydrocyclization of these PADs in detail (Figure 9) and to analyze the operation characteristics of PBI membranes prepared by this procedure.

The idea of preparing benzimidazole from N-aryl substituted amidine hydrochloride (proposed by Grenda *et. al.* [39]) consist in generation from the azomethine bond in amidine hydrochloride of an uncharged electron-deficient species, nitrene, which, being extremely reactive, undergoes addition at the *o*-position of the benzene ring, thus closing the benzimidazole heterocycle.

In order to investigate the oxidative dehydrocyclization, transformation of PAD **2a** was studied in detail. Also cyclization of PAD **4d** was carried out under the optimal reaction conditions.

The transformation was performed in solution using hydrogen peroxide or sodium hypochlorite as oxidants. 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.

The course of oxidative dehydrocyclization was monitored by IR spectroscopy (Figure 10), namely, by changes in the intensities of the characteristic absorption bands of the N–H (3400 and 3050 cm^{-1}) and C–N (1360–1365 cm^{-1}) groups. The other char-
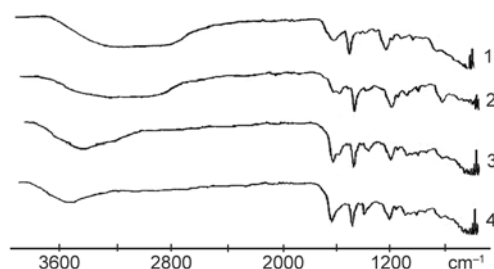

Figure 10. Evolution of the FTIR spectrum of PAD in the course of its transformation into PBI: PAD (1), intermediate states (2, 3), and PBI (4)

acteristic changes observed in the spectrum are shift of the C=N absorption band at 1610 cm^{-1} ($\Delta v = 20$ 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 (Figure 11, curve 4), after that the reaction became very slow. Threefold excess of the oxidant led to practically complete conversion in 6 h at 80°C (Figure 11, curve 2). 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 (Figure 11, curve 3), the cyclization rate slightly decreased. The maximal rate was attained with increasing temperature to 100°C: the cyclization was complete in 4 h (Figure 11, curve 1). Further increase
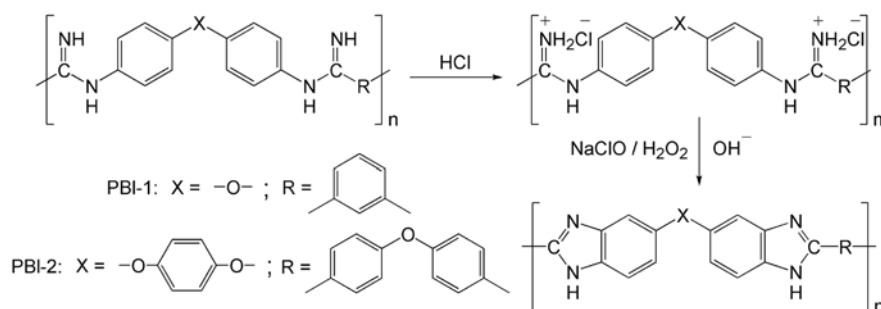

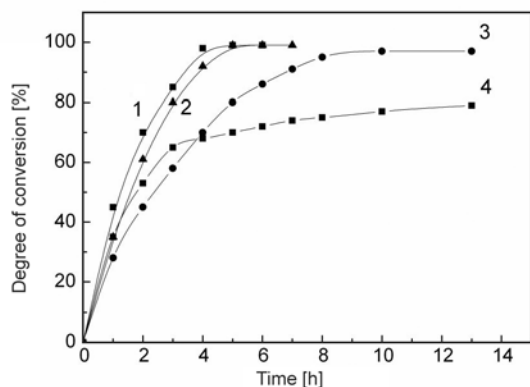**Figure 9.** Oxidative dehydrocyclization of polyamidines in polybenzimidazoles

Figure 11. Degree of conversion γ of PAD into PBI as a function of time τ: [NaClO]/[PAD] = 3, 100°C (1); [H$_2$O$_2$]/[PAD] = 3, 80°C (2); [NaClO]/[PAD] = 3, 80°C (3) and [H$_2$O$_2$]/[PAD] = 1, 80°C (4)

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 (Figure 10): 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, new signals at 134.6 ppm appear, confirming formation of the *o*-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 dissolve 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%.

One of the most practically important properties of membranes based on PBI is ionic conductivity, allowing their use in fuel cells. However, doping the PBI-1 with orthophosphoric acid drastically decreased the strength of the membrane, making it practically unsuitable for use. For example, tensile strength of

membrane decreased by 67.5%, becoming as low as 23.27 MPa. Therefore, to improve the strength characteristics of film materials, we performed structuring of PBI with three-dimensional PAIR prepared from N,N′-(4,4′-diphenylmethane) bis-maleimide and 4,4′-diaminodiphenylmethane. For this purpose, we mixed solutions of PBI and PAIR, prepared film materials, and heat-treated them at 230°C for 7 h. Opening of the unsaturated bond of the terminal maleimide ring led to the formation of a 3D network in which PBI was retained owing to mechanical interweaving of macromolecular chains. It should be noted, however, that intermolecular interaction of the C=C bonds of the resin with secondary amino groups of the benzimidazole ring of PBI, with the formation of a graft copolymer, can occur along with PAIR polymerization. Correspondingly, we observed in the IR spectra a low-frequency shift of the absorption band of the carbonyl groups, caused by formation of the less strained succinimide ring. Thus, we prepared film materials with satisfactory strength characteristics from the PBI–PAIR blends of various compositions (Figure 12).

As seen from the obtained data, addition of 10 wt% PAIR to PBI results in a sharp increase in the tensile strength. Further increase in the amount of the resin in a blend with both PBIs leads to a decrease in the film strength. Obviously, the 90:10 weight ratio of PBI and PAIR in the blend is optimal. The 90:10 PBI-1–PAIR membrane was doped with 9M orthophosphoric acid to constant weight. After that, the strength characteristics decreased by only 10–15%, and the ionic conductivity of the membrane was 1.15·10^{-3} S/cm. With an increase in temperature, the membrane conductivity also increased with the activation energy of 28±2 kJ/mol, reaching 3·10^{-2} S/cm
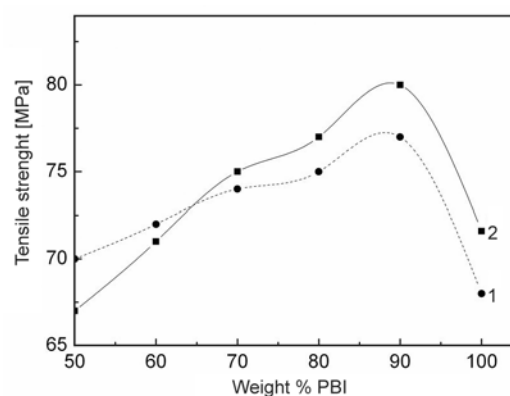

Figure 12. Tensile strength as a function of composition of PBI–PAIR blends. PBI-1 (1) and PBI-2 (2)
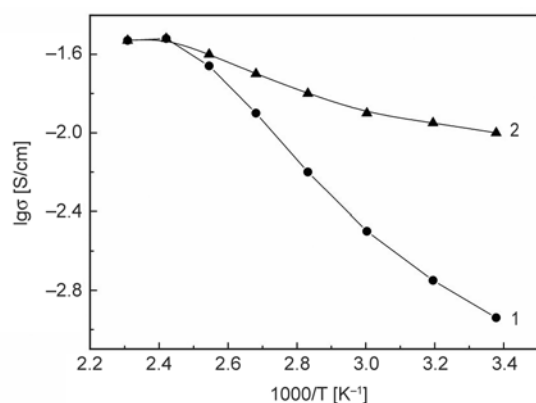
Figure 13. Temperature dependence of the ionic conductivity σ of the 90:10 PBI–PAIR membrane doped with phosphoric acid (1) and of the same membrane additionally modified with acidic zirconium phosphate (2)

at 160°C (Figure 13, curve 1). These values are similar to the conductivity of conventional membranes based on PBIs. However mechanical properties of doped blend membrane of PBI and PAIR are considerably higher than those of common membranes on the base of PBIs [15].

It is interesting that additional treatment of the doped membrane with acidic zirconium phosphate leads to an increase in the conductivity at low temperatures by almost an order of magnitude ($1.0 \cdot 10^{-2}$ S/cm at 23°C) and to a decrease in the activation energy to 8.5±0.5 kJ/mol. However, further increase in temperature leads to only a slight increase in the conductivity, and already at 120°C the conductivities of the doped membrane and membrane treated with zirconium phosphate become virtually equal, varying synchronously on further heating (Figure 13, curve 2). Presumably, an increase in the low-temperature ionic conductivity of the membranes modified with acidic zirconium phosphate is due to the high intrinsic ionic conductivity of finely dispersed $Zr(HPO_4)_2 \cdot nH_2O$ [40] and to sorption processes occurring at the boundary of the organic and inorganic phases [41].

4. Conclusions

We showed that aromatic PADs with moderate molecular weights could be prepared by polyaddition of dinitriles and diamines in acidic ILs. It has been shown that nature of ionic solvent influences on inherent viscosities of resulting polymers. Also we were able to regenerate ionic solvent after polyaddition. Moreover we developed new method of synthesis of such polymers consisting in polycondensation of 4,4′-oxybis(benzoic acid) diamide and diamines using ER. Molecular weights of synthesized polymers reached 25 000 g/mol, and 10% weight losses were up to 288°C, films prepared by casting of PADs solutions in DMF had satisfactory mechanical properties. 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. After doping with phosphoric acid, the ionic conductivity of blend membrane of PBI and PAIR reaches $3 \cdot 10^{-2}$ S/cm at 160°C. Additional treatment of the doped membrane with acidic zirconium phosphate leads to an increase in the conductivity at low temperatures by almost an order of magnitude ($1.0 \cdot 10^{-2}$ S/cm at 23°C) and to a decrease in the activation energy to 8.5±0.5 kJ/mol.

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