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Some aspects of polybenzimidazoles' synthesis in P_2O_5 containing condensation media

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ABSTRACT

The synthesis of various polybenzimidazoles (PBIs) in condensation media such as polyphosphoric acid and Eaton's reagent was accomplished. Molecular weight distribution of the synthesized polymers was examined with respect to the process conditions and the chemical structure of the monomers. It was found that during the synthesis of PBIs a side acylation reaction occurs which leads to the formation of branched macromolecules with M_w up to 2.3×10^6 and higher and even crosslinking, resulting in gelation of the polymers during synthesis. Fraction of the side reaction in the overall process appeared to be dependant on both the chemical structure of the monomers and the condensation media used. The orientation of the acylation reaction was determined by quantum-mechanical calculations.

1. Introduction

Polybenzimidazoles (PBIs) are well known for their excellent thermal and hydrolytic stability and resistance to chemicals [1]. These properties make PBIs so called "high performance polymers" and determine their wide use in many scientific and industrial applications, such as chromatography, ion exchange, membrane separation, catalyst syntheses, heat resistant fiber and performance part production, medicine etc.

Not long ago PBIs gained close attention as materials for high temperature proton exchange membranes for use in fuel cells. Phosphoric acid doped poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] was proposed as a proton exchange membrane material in 1995 [2] and extensively investigated [3–9] and reviewed [10,11] since then. This application imposes on the polymers such requirements as purity, high molecular weight to ensure good mechanical properties and excellent chemical resistance.

The industrial scale synthesis of PBIs is accomplished by melt polycondensation of tetramines with dicarboxylic acid derivatives, mainly phenyl esters [1]. This method seems to be simple but in order to obtain a high molecular weight polymer with good film-forming properties temperatures above 400 °C, use of catalysts and sophisticated equipment are required. Other disadvantages of melt polycondensation include the incomplete cyclization of the polymer and various side reactions. Thermal crosslinking [12] increases the plugging value of the product. The incomplete cyclization facilitates degradation of the material under certain conditions.

A very convenient and simple procedure for obtaining high molecular weight PBIs has been developed by Iwakura and co-workers [13]. The method comprises solution polycondensation of tetramines with carboxylic acids or their derivatives in polyphosphoric acid (PPA). Another polycondensation media – Eaton's reagent (ER) was successfully applied for the synthesis of PBIs and some other polycondensation polymers [14]. ER comprises a solution of phosphorus pentoxide in methanesulfonic acid (1/10 by weight). One of the advantages of ER over PPA is its low viscosity in the whole temperature range. Thus ER can be used to synthesize polymers in more concentrated solutions which in many cases is beneficial in terms of obtaining polymers with higher molecular weight. It is obvious that due to the large quantity of acidic wastewaters solution polycondensation is best suitable only for small-scale production of superior quality PBIs; for example, those needed for fuel cell applications.

In our previous studies we noticed that during the syntheses of some PBIs in both ER and PPA at certain conditions gelation of the reaction mass occurred [15,16]. The current research represents the attempt to carefully investigate the reasons and conditions that led to such phenomenon. We report on the synthesis and properties of some PBIs whose formation in condensation media is most problematic in terms of gelation. The list of PBIs was restricted to those soluble in DMF in order to allow the molecular weight distribution (MWD) characterization by gel-permeation chromatography (GPC).

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2. Experimental section

2.1. Materials

4,4′-Dicarboxydiphenyl ether (DCPE) was obtained from Aldrich and purified by reprecipitation from disodium salt with activated carbon treatment. Isophthalic acid was obtained from Acros and recrystallized from water-ethanol with activated carbon. 3,3′-Diaminobenzidine (DAB) was obtained from Acros and used after drying in vacuum at 55 °C. 3,3′,4,4′-Tetraminodiphenyl ether (TAPE) was recrystallized twice from deoxygenated DI water with activated carbon under argon and dried in vacuum at 55 °C. Extra pure methanesulfonic acid and phosphorus pentoxide were obtained from Acros and used as received. Other reagents were obtained from local suppliers and used with no additional treatment.

2.2. ER preparation

ER was prepared as can be found elsewhere [17] just before use by dissolution of phosphorus pentoxide in methanesulfonic acid (1/10 by wt.) at 70 °C.

2.3. General procedure for PBI synthesis

A 3-necked round bottom flask equipped with an overhead stirrer and a gas inlet/outlet was charged with the monomer(s) and the condensation media. The concentration of the monomer(s) in the reaction mixture in the case of synthesis in ER was 7%, and in the case of PPA – 8%. The flask was purged with dry argon for 30 min. After purging, the flask was placed into an oil bath and the temperature was adjusted according to the schedule presented in Table 1 for each polymer. The reaction was maintained until a certain viscosity of the solution was reached. The reaction mass was poured into DI water as a thin thread. The precipitated polymer was washed with DI water until neutral reaction was obtained, then kept in aqueous ammonia (pH = 10–11) for 1 h and washed until neutral reaction again. The neutralized polymer was dried in air at 100 °C and then in vacuum at 100 °C until constant weight was obtained.

2.4. Gel-permeation chromatography

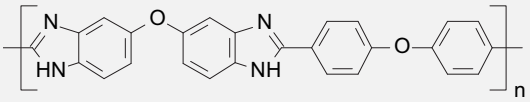
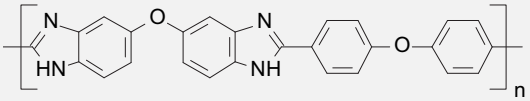
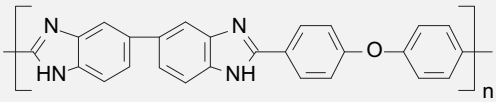
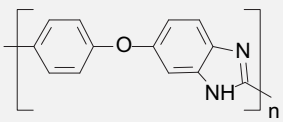
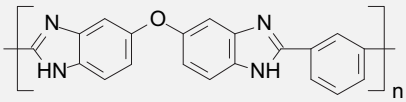
The analysis was performed on an Agilent 1100 chromatograph. The column was filled with spherical sorbent based on hydrolyzed copoly-glycidylmethacrylate-ethylenedimethacrylate [18] using DMF as an eluent with addition of 50 mmol l^{-1} LiCl. Detection was accomplished by a diode array detector at 300 nm. Eluent pumping rate was 0.5 ml min^{-1}. Calibration was performed using polystyrene standard [19].

3. Results and discussion

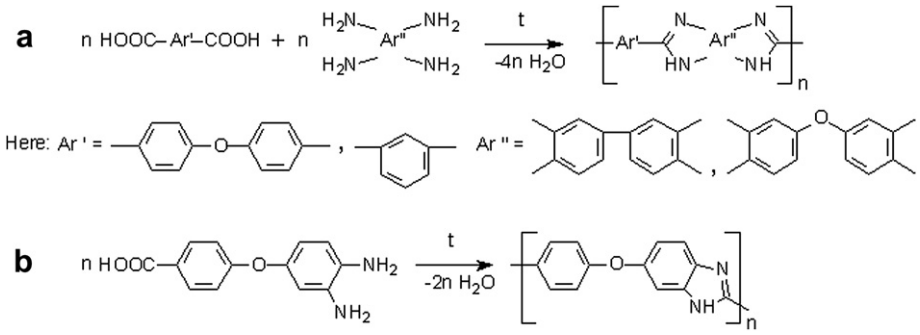
AA-BB PBIs were synthesized in PPA or ER by the interaction of dicarboxylic acids with tetramines according to Scheme 1a. The repeating unit structures and some properties of the synthesized PBIs are presented in Table 1.

During the synthesis of PBI-1 in ER at a certain moment, we observed a fast increase of the viscosity of the reaction mass and subsequent gelation, which could not be reversed by addition of extra ER. Polymer precipitated after the beginning of gelation contained large amounts of the insoluble fraction. In order to obtain PBI-1 almost completely soluble in amide solvents and DMSO, it was necessary to carefully monitor the reaction and terminate it at

Table 1
Structure and some properties of the synthesized PBIs.

Abbreviation	Repeating unit	Temperature regime (°C/h)	I. V.[a] (dl/g)	Cond. media	Gel fraction (%)
PBI-1		100/0.5 120/1 140/3	2.05	ER	8.3
PBI-1a		160/0.5 180/1 210/6	1.73	PPA	6.2
PBI-2		100/0.5 120/1 140/5	2.49	ER	–
PBI-3		100/0.5 140/4	0.66	ER	1.5
PBI-4		180/1 210/7	1.44	PPA	–

[a] Inherent viscosity determined for sol-fraction in *N*,*N*-dimethylacetamide at 25 °C.



Scheme 1. Synthetic routes to the considered PBIs.

the point of a very fast viscosity growth prior to gelation. The temperature regimes and the duration of synthesis necessary to obtain soluble PBIs are indicated in Table 1. Preliminary data indicates that decreasing monomer concentration in the reaction mixture from 7% to about 4.5% did not eliminate the problem but rather prolonged the time to reach the gelation point.

The observed gelation was attributed to the side acylation reaction, which could occur in the condensation media. Catalyst free acylation of aromatic compounds by carboxylic acids in ER and PPA has been reported in a number of papers [20–24]. Apparently, acylation also occurs during the synthesis of PBIs in the condensation media and leads to the formation of branched and crosslinked macromolecules (Scheme 2).

Unlike PBI-1, synthesis of PBI-2 was not complicated with the formation of insoluble polymer in the same conditions. It is obvious that the chemical structure of the reacting monomers is the determining factor for the rate of the acylation reaction. In order to investigate the side reaction and its dependence on the structure of the monomers we examined molecular properties of the synthesized PBIs by GPC.

GPC of PBI-2, synthesized in ER revealed that the polymer has a double-mode molecular weight distribution (MWD). The super-high molecular weight ($M_w \approx 1.5 \times 10^6$) fraction of PBI-2 apparently corresponds to the branched macromolecules, which arise from acylation of the linear macromolecules. The other fraction with $M_w = 171\,000$ represents the unbranched linear polymer chains. A multi-modal MWD was also observed for PBI-1. The presence of the low molecular weight fraction in PBI-1 is due to the termination of the reaction at the stage where there is a relatively incomplete conversion of the terminal groups (see above).

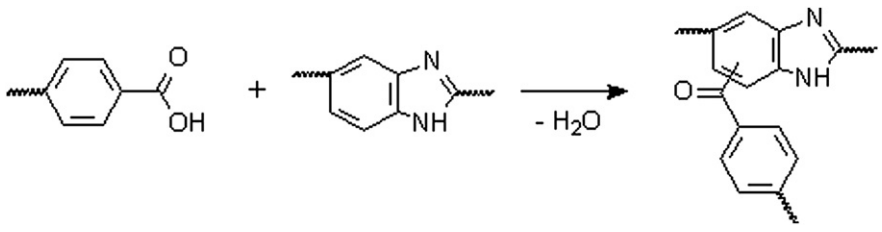
A similar situation took place during homopolycondensation of 3,4-diamino-4′-carboxydiphenyl ether (DACPE) (Scheme 1b) [15] in ER according to Scheme 1b. A portion of the reaction mass was precipitated during the fast viscosity increase phase. The resulting PBI-3 was analyzed by GPC confirming the presence of the considerable fraction of branched macromolecules along with some portion of the low molecular weight fraction. The rest of the reaction mass, left in the reactor, became almost insoluble in less than 5 min.

The extensive branching of PBI-1, PBI-2 and PBI-3 during the synthesis was attributed to the high reactivity of the corresponding carboxylic acids. These acids are activated in the acylation reaction via electron-donating ether oxygen, which stabilizes acylium cation and favors its formation in the course of the reaction. The acylium ion was considered as an intermediate formed when carboxylic acid was dissolved in Eaton reagent [20,25].

In order to support this conclusion we performed synthesis of PBI-1 in PPA (PBI-1a, Table 2) and PBI-4 and compared MWDs of the obtained polymers. PPA was chosen for this experiment because PBI-4 could not be synthesized in ER [26]. The upper temperature limit of the application of ER, which corresponds to not more than 145 °C due to the decomposition of methanesulfonic acid at higher temperatures, is not enough to promote the interaction with low reactive isophthalic acid. Substitution of DCPE with isophthalic acid led to a lower molecular weight polymer at the same temperature regime (Table 1, 2). Additionally, PBI-4 had a unimodal MWD, indicating the absence of the branched macromolecules.

The introduction of the activating subsistent such as bridging ether oxygen into the molecule of tetramine further promotes the side acylation reaction. The interaction of TAPE with highly reactive DCPE or the homopolycondensation of DACDE, which itself represents a highly reactive acid and activated *o*-diamine leads not only to the intensive formation of the branched macromolecules but also to significant crosslinking of the latter, resulting in a considerable amount of the gel fraction in the polymer. PBI-2 synthesized from less reactive DAB has a large amount of branched fraction but contains no gel.

It was found that the synthesis of PBIs from the highly reactive acids, such as DCPE in ER lead to higher molecular weight polymers compared to those synthesized in PPA. Thus, PBI-1 synthesized from DCPE and TAPE in ER had higher I.V. and molecular weight in comparison to the same polymer (PBI-1a), synthesized in PPA (Tables 1 and 2). Similarly, ER was shown to better promote the side acylation reaction. The branched fraction for PBI-1 has considerably higher molecular weight than that for PBI-1a, plus the gel fraction content is higher for PBI-1 than for PBI-1a.



Scheme 2. Side acylation reaction.

Table 2
Fractional composition and MWD of the synthesized PBIs.

Fraction No.	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	Fraction content (%)
PBI-1				
1	1271	2342	1.8	42.4
2	87	136	1.6	49.8
3	9	12	1.3	7.8
PBI-1a				
1	1149	1650	1.4	56.6
2	79	127	1.6	40.6
3	15	15	1.0	1.1
4	9	9	1.0	1.7
PBI-2				
1	1051	1457	1.4	47.7
2	123	171	1.4	52.3
PBI-3				
1	1266	1389	1.1	42.5
2	43	62	1.4	43.1
3	7	8	1.1	14.4
PBI-4				
1	4	7	1.8	100

In order to determine the orientation of the acylation reaction we calculated effective charges on carbon atoms of the structures, which model the repeating units of the corresponding PBIs. The geometry of the considered substances was modeled with the molecular mechanics method and then improved by the MNDO/PM3 method. The calculation for the energy optimized complexes, their electron characteristics and the effective charge distribution was performed using "Priroda" software [27,28] by DFT-PBE method [29] in 2z-bazis. The results, shown in Fig. 1 reveal that the highest electron density is located in positions 4 and 7 of the benzimidazole cycle of the repeating unit of the considered PBIs. Hence, these sites are the most probable targets for electrophilic substitution.

As was noticed from the GPC of the synthesized polymers (see above) the introduction of bridging oxygen into the tetramine molecule further promotes the acylation reaction. Additional electron density on benzene ring of benzimidazole in the repeating

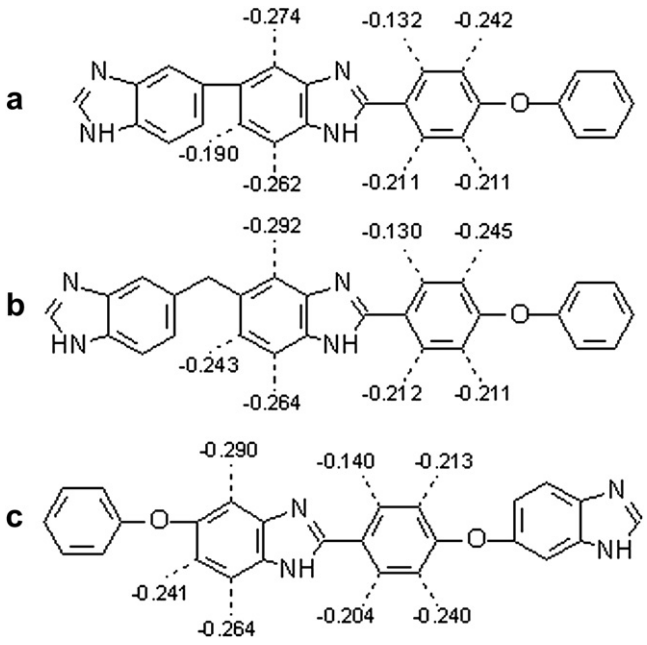


Fig. 1. Distribution of the effective charges in the structures, modeling PBI repeat units.

units of PBI-1 (Fig. 1b) and PBI-3 (Fig. 1c) compared to PBI-2 (Fig. 1a) can be clearly seen from the quantum-mechanical calculations.

4,4′-Diphenyl ether fragment in the repeating unit of PBI-1 and PBI-2 or 4-phenoxy fragment in the unit of PBI-3 are also activated by ether oxygen. However, these fragments are less favorable for acylation due to the deactivating influence of benzimidazol-2-yl units. The electron-withdrawing effect of benzimidazolyl groups was proved with the enhanced reactivity of 2-(4-fluorophenyl)-5(6)-hydroxybenzimidazole in comparison with 5(6)-fluoro-2-(3-hydroxyphenyl)benzimidazole in the reaction of self-polymerization of the substances via nucleophilic substitution [30].

One of the theoretically possible products of the side reaction could be *N*-acylated benzimidazole units. In order to examine the synthesized PBIs for the presence of such moieties we have subjected polymer samples to a treatment with an ethanol-water (1/4) solution of NaOH (10%) at the boiling temperature for 6 h. Ethanol was added to the solution to promote swelling of the polymer and fast distribution of alkali in the polymer matrix. The thoroughly washed and dried polymers were analyzed by GPC. The change in MWD of the polymers after treatment was less than 7%, which stands for the absence of a noticeable amount of either the *N*-acylated product or the uncyclized moieties, both susceptible to hydrolysis.

The small difference in the MWDs of the pristine and alkali treated PBIs indirectly proves, that the super-high molecular weights of fractions of the polymers do not result from the association of macromolecules during analysis. For example, one of the possible mechanisms for such association could be salt formation between terminal carboxyls and benzimidazole units. The carboxy-groups treated with NaOH are converted to sodium salt and lose their ability to interact with benzimidazole units.

4. Conclusions

During the synthesis of PBIs from dicarboxylic acids and tetramines in ER and PPA or from the A-B type monomers, containing both functionalities, the side acylation reaction occurs which leads to the formation of branched macromolecules. The portion of the side reaction in the overall process mainly depends on the reactivity of the carboxylic acid. The reactivity of the acid increases when electron-donating substituents are placed adjacent to carboxy-groups. The introduction of activating bridging ether oxygen into the molecule of nucleophile promotes the acylation reaction and leads to the intensive gelation of the polymer during synthesis. The side acylation reaction most probably proceeds into positions 4 or 7 of the benzimidazole ring of the repeating unit of PBI.

ER better promotes both the target polycyclocondensation reaction and the side acylation reaction in comparison with PPA.

Neither *N*-acylated benzimidazole rings nor uncyclized fragments were found in the precipitated PBIs, synthesized in ER and PPA.

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