

## Polyaroylenebenzimidazoles Based on 2,3-Di(3,4-diaminophenyl)quinoxaline

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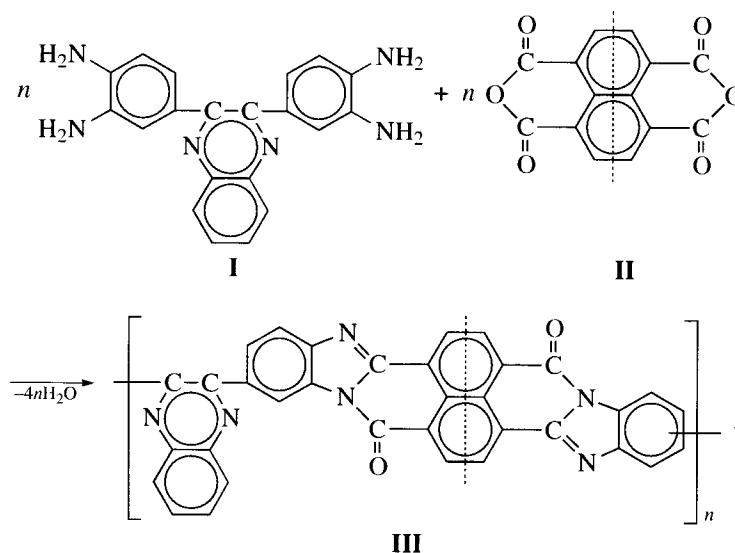
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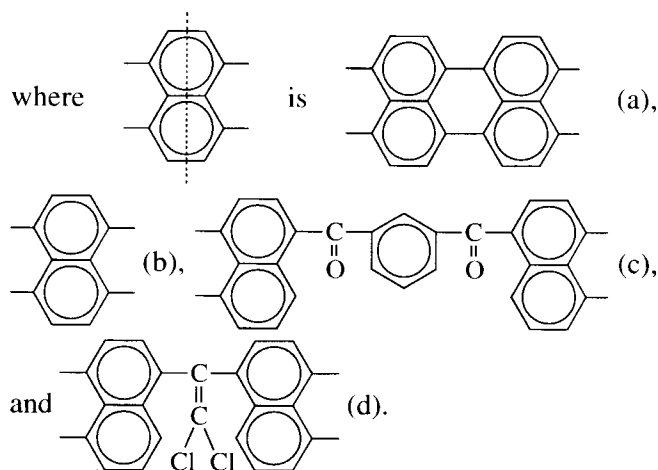
**Abstract**—Polyaroylenebenzimidazoles containing quinoxal-2,3-diyl groups are synthesized by interaction of 2,3-di(3,4-diaminophenyl)quinoxaline with dianhydrides of 3,4,9,10-perylenetetracarboxylic, 1,4,5,8-naphthalenetetracarboxylic, and some bisnaphthalic acids. It is shown that polyaroylenebenzimidazoles thus obtained combine solubility in phenolic solvents with high thermal stability and heat resistance.

The introduction of quinoxal-2,3-diyl groups into polyheteroarylenes (PHAs) provides an efficient way of improving their solubility with thermal characteristics maintained unchanged. For example, this approach was used to advantage for improvement of the behavior of polyimides [1–3], polybenzimidazoles [3], and polyphenylquinoxalines [4–6]. As a continuation of earlier studies [1–6], we made an attempt to modify properties, in particular, to improve the solubility of polyaroylenebenzimidazoles (PABIs) with a

partial ladder structure [7] via incorporation of quinoxal-2,3-diyl groups. This goal was attained by interaction of 2,3-di(3,4-diaminophenyl)quinoxaline (**I**) (a derivative of DDT [4, 5]) with dianhydrides of 3,4,9,10-perylenetetracarboxylic (**IIa**), 1,4,5,8-naphthalenetetracarboxylic (**IIb**), and isophthaloylbisnaphthalic (**IIc**) acids [8], and 1,1-dichloro-2,2-[di(4,5-dicarboxy)naphth-1-yl] (**IId**) [9]. The synthesis of PABIs containing quinoxal-2,3-diyl groups was carried out by the following scheme:



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The synthesis of PABIs was performed as described in [10] in *m*-cresol at 180–200°C for 5 h using benzoic acid as a catalyst. The concentration of each monomer was equal to 0.15 mol/l, whereas the optimum concentration of benzoic acid was as high as 0.35 mol/l, which is related to a reduced basicity of compound **I** due to the electron-acceptor nature of quinoxal-2,3-diyl groups [11].

All reactions of PABI synthesis proceeds under homogeneous conditions to produce quantitative yields of polymers. As is evident from IR measurements, the polymers thus prepared are free of noncyclized fragments. The IR spectra of all PABIs exhibit absorption bands at 1710 cm<sup>-1</sup> due to carbonyl groups of polyaroylenebenzimidazole cycles [12] and at 1640 cm<sup>-1</sup>, corresponding to C=N groups of quinoxal-2,3-diyl fragments [13]. Moreover, the IR spectrum of polymer **IIIc** displays absorption maxima at 1680 cm<sup>-1</sup> due to carbonyl groups of diarylketone fragments [14], and the IR spectrum of polymer **IIIb** shows absorption bands at 840 and 960 cm<sup>-1</sup> attributed to 1,1-dichloroethylene groups [15].

The X-ray diffraction analysis showed that all PABIs under examination are amorphous, which is associated with the isomeric chemical heterogeneity of PABIs, that is, with the presence of a wide variety of

isomers [16], and the presence of nonsymmetric quinoxal-2,3-diyl substituents.

The amorphous structure of PABIs in combination with their peculiar chemical structure determines the solubility of the polymers obtained in organic solvents. Specifically, all PABIs are soluble in phenolic solvents (*m*-cresol, a tetrachloroethane–phenol mixture, and *p*-chlorophenol). However, it should be noted that **IIIa** and **IIIb** PABIs are highly soluble in the aforementioned solvents under heating, whereas **IIIc** and **IIIb** polymers dissolve at room temperature. Moreover, **IIIb** shows high solubility in *N*-methylpyrrolidone. The reduced viscosities of PABIs under consideration comprised 0.45–1.20 dl/g (*m*-cresol, 25°C). Films with strength parameters listed in the table were cast from polymer solutions in *m*-cresol with the maximum viscosity characteristics.

According to thermomechanical-analysis data, the softening temperatures of PABIs range from 415 to 460°C.

The thermal stability of the PABIs synthesized was studied by dynamic TGA in air; polymer samples were heated at a rate of 4.5 K/min.

According to the dynamic TGA of PABIs, a 10% weight loss was observed in the range 480–530°C; for polymer **IIIa**, the temperatures of softening and 10% weight loss were found to be very close. A rather low temperature of 10% weight loss for polymer **IIIb** can be attributed to the occurrence of intramolecular dehydrochlorination of 1,1-dichloro-2,2-bisphenyl groups.

Analyzing the experimental data of this work, one can conclude that the introduction of quinoxal-2,3-diyl groups into PABIs macromolecules is accompanied by improvement of their solubility, while retaining their high softening temperatures. This indicates that there is a similarity between quinoxal-2,3-diyl groups and cardo fragments [17–19].

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Some characteristics of PABIs

Polymer	$\eta_{\text{red}}$ ( <i>m</i> -cresol, 25°C), dl/g	Temperature, °C		Film characteristics at 25°C	
		softening	10% weight loss	$\sigma$ , MPa	$\epsilon$ , %
<b>IIIa</b>	0.45	460	480	–	–
<b>IIIb</b>	0.68	430	550	–	–
<b>IIIc</b>	0.94	415	490	79	8
<b>IIIb</b>	1.20	400	530	98	12

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