An effective synthesis of polynuclear tetraamines, monomers for polyheteroarylenes

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An effective synthesis of polynuclear tetraamines *via* nucleophilic substitution of chlorine in 2-chloro-5-nitroaniline under ultrasonic irradiation followed by catalytic hydrogenation of dinitrodiaminoarenes in a flow reactor was proposed. A number of monomers, including those not described in the literature, were thus obtained. Two classes of polyheteroarylenes, namely, polynaphthoylenebenzimidazoles and polyphenylquinoxalines were synthesized by the polycyclocondensation in a supercritical carbon dioxide. Incorporation of trifluoromethyl substituents and flexible oxygen bridges into the structure of monomers allowed one to improve the solubility of the polymers. Some properties of synthesized polyheteroarylenes were investigated.

Key words: polynuclear tetraamines, polyheteroarylenes, ultrasonic synthesis, aromatic nucleophilic substitution, catalytic hydrogenation, supercritical carbon dioxide, polynaphthoylenebenzimidazoles, polyphenylquinoxalines.

Polynaphthoylenebenzimidazoles (PNBI) and polyphenylquinoxalines (PPQ) are considered to be promising polyheteroarylenes. They possess a complex of unique properties, namely, thermal, heat, fire, and chemical stabilities, high hydrolytic and radiation resistance, *etc.*[1—4] Recently, various specific physical properties of these polymers, which significantly expands their application in high-technology areas, have been gradually revealed.[5—8]

The main reason that prevents their industrial synthesis and wide application is the lack of a developed monomeric base. That is associated with the low efficiency of the methods for the synthesis of high-purity monomers. This relates primarily to the aromatic tetraamines. The compounds containing a system of aromatic rings linked together by bridging atoms or groups are the most interesting between tetraamines. The presence of such structural elements in polyheteroarylenes increases the flexibility of the polymer chain, improves the solubility and processability of polymers in the wares.[9] The methods for the synthesis of such monomers are multistage and ineffective. In a number of cases, 4-chloronitrobenzene is used as the basic structure.[10] The reaction of 4-chloronitrobenzene with a bisphenol leads to a polynuclear structure. Its further functionalization by reduction and nitration reactions allows the preparation of target tetraamines. Taking into account that the introduction of the nitro group is usually carried out in acidic media, two more steps are added to the synthesis scheme, namely, the acylation of the NH_2-group and the hydrolysis of the C—N bond in the acetamide substituent.

The use of 5-chloro-2-nitroaniline (**1a**) in the synthesis is more attractive. This allows one to reduce significantly the number of synthetic steps. An obstacle to the effective application of this starting compound is its low reactivity in the S_NAr reaction.[11] It was proposed to increase the reactivity of the compound **1a** by converting the amino group to acetamide in order to accelerate the reaction of aromatic nucleophilic substitution.[12] Despite the fact that pure aromatic tetraamines were obtained, for a number of compounds posessing poor solubility carrying out acid hydrolysis required a long time and high temperatures. All this reduced the yield of diaminodinitroarenes.

We have developed an efficient two-stage synthesis of high-purity polynuclear tetraamines in order to obtain new PNBI and PPQ on their basis (Scheme 1). In this case, both known tetraaminoarenes **4a,b** and previously undescribed monomers **4c,d** have been synthesized. Due to a presence of fluorine atoms the latter compounds are of interest for the synthesis of PPQ with low dielectric permittivity.[5]

Results and Discussion

As we have showed earlier,[13] ultrasonic activation significantly accelerates the S_NAr reaction. This approach was used to produce polynuclear diaminodinitroarenes

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N, 17.38. $C_{18}H_{18}N_4O_2$. Calculated (%): C, 67.10; H, 5.57; N, 17.34.

2,2-Bis[4-(3,4-diaminophenoxy)phenyl]hexafluoropropane (4c). Yield 91%, m.p. 154—157 °C. Found: *m/z* 549.1713 $[M + H]^+$. $C_{27}H_{23}F_6N_4O_2$. Calculated: 549.1726. ^{1}H NMR (DMSO-d$_6$), δ: 4.37 (s, 4 H, (4-NH$_2$)$_2$); 4.66 (s, 4 H, (3-NH$_2$)$_2$); 6.14 (d.d, 2 H, H(6´,6´), *J* = 1.6 Hz, *J* = 8.5 Hz); 6.28 (d, 2 H, H(2´,2´), *J* = = 1.5 Hz); 6.51 (d, 2 H, H(5´,5´), *J* = 8.8 Hz); 6.92 (d, 4 H, H(3´,3´,5´,5´), *J* = 8.5 Hz); 7.24 (d, 4 H, H(2´,2´,6´,6´), *J* = 8.4 Hz). ^{19}F NMR (DMSO-d$_6$), δ: –63.49. Found (%): C, 58.94; H, 3.98; N, 10.23. $C_{27}H_{22}F_6N_4O_2$. Calculated (%): C, 59.01; H, 4.01; N, 10.20.

2,2-Bis[4-(4,5-diamino-2- trifluoromethylphenoxy)phenyl] hexafluoropropane (4d). Yield 89%, m.p. 232—235 °C. Found: *m/z* 685.1463 $[M + H]^+$. $C_{29}H_{20}F_{13}N_4O_2$. Calculated: 685.1474. ^{1}H NMR (DMSO-d$_6$), δ: 4.76 (s, 4 H, (4-NH$_2$)$_2$); 5.27 (s, 4 H, (5-NH$_2$)$_2$); 6.29 (s, 2 H, H(6´,6´)); 6.85 (s, 2 H, H(3´,3´)); 6.95 (d, 4 H, H(3´,3´,5´,5´), *J* = 8.5 Hz); 7.29 (d, 4 H, H(2´,2´,6´,6´), *J* = 8.5 Hz). ^{19}F NMR (DMSO-d$_6$), δ: –57.53, –63.46. Found (%): C, 50.76; H, 2.89; N, 8.20. $C_{29}H_{20}F_{12}N_4O_2$. Calculated (%): C, 50.80; H, 2.92; N, 8.18.

Synthesis of polynaphthoylenebenzimidazoles P1, P2 (general procedure). A carefully stirred mixture of dianhydride of 1,3-bis(4,5-dicarboxynaphthalen-1-ylcarbonyl)benzene (**5**), tetradiamine **4a** or **4d**, a mixture of benzimidazole and benzoic acid, taken each 1 mmol, was loaded into high-pressure reactor with volume of 22 mL. The reactor was purged with carbon dioxide to remove water vapors before the synthesis. Then it was heated to a temperature of 90 °C in a thermostat with a programmable temperature controller. Stirring in the reactor was carried out with a magnetic stirrer. The carbon dioxide was fed into the reactor and the necessary pressure of 150 bar was created by means of a piston generator (High Pressure Equipment Company, USA). After the required conditions were created, the reactor was held for 6 h. At the end of the reaction and cooling of the system, stirring was switched off and the system was decompressed. The resulting polymer was dissolved in NMP, then precipitated with water, filtered, washed with ethanol, and dried under vacuum for 10 h at 100 °C.

Synthesis of polyphenylquinoxalines P3, P4 (general procedure). A thoroughly mixed mixture of 1,4-bis(phenylglyoxalyl)-benzene (**6**), tetraamine **4a** or **4d**, taken 1 mmol each, and ethyl or benzyl alcohol (1 mL) was charged into a 22 mL high-pressure stainless steel reactor. The reactor was purged with carbon dioxide to remove water vapor before synthesis, and then heated to 50 °C. After conditioning, the reactor was held for 6 h at this temperature. Formed polyphenylquinoxaline was then treated as described above.

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