Synthesis of poly(pyridazinoquinazolones)

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A model reaction of 2-alkyl-3-aminoquinazolones with α-dicarbonyl compounds benzil and its 4,4′-derivatives, acenaphthenequinone and isatin was studied for the first time. The reaction proceeded in pentafluorophenol and led to the formation of new heterocyclic systems. This approach was used in the synthesis of new thermostable polyheteroarylenes with fluorescent properties, *viz.*, poly(pyridazinoquinazolones).

Key words: polyheteroarylenes, fluorescence, α-diketones, 2-alkyl-3-aminoquinazolones.

Among polymers containing heterocyclic fragments, polyquinazolones (PQ) are noted for flexibility in variation of their chemical structure.[1] First, synthesis of PQ can be based on different diamines, second, it is possible to modify poly(2-alkylquinazolones) by condensation with carbonyl compounds.[2,3] Third, synthesis of PQ can be based on poly(benzoxazinones), in this case chemical structure is varied due to the reactions with different monoamines. In addition, synthesis of polymers consisting of more complex heterocyclic units is possible based on quinazolone and benzoxazinone monomers. This approach was used, for example, in the synthesis of poly(quinazolonoquinolines) obtained by the reaction of bis(2-alkylbenzoxazinones) and bis(*o*-aminobenzophenones).[4] Formation of new heterocyclic system also takes place in the reaction of 2-alkyl-3-aminoquinazolones with α-dicarbonyl compounds. This heterocyclization reaction has been studied not sufficiently and so far has not been considered with respect to polycondensation.

There are literature data[5] on the synthesis of compounds with pyridazinoquinazolone heterocyclic system by the reaction of anthranilic acid and pyridazine derivatives in a mixture of concentrated hydrochloric acid and ethanol in 60—85% yield. A method for the preparation of more complex pyridazinoquinazolone compound based on the 2-methyl-3-aminoquinazolone and 4-bromoacenaphthenequinone derivatives in acetic acid in 65% yield, *i.e.*, according to the scheme more close to that used in the present work, was also described.[6] However, it is obvious that synthesis of polymers using both procedures described above cannot be accomplished under indicated conditions. This is due to both not very high yields and low solubility of more bulky bifunctional monomers and polymers obtained in the solvents used in the works.[5,6] To more objectively estimate the scope of the reaction of 3-amino-2-methylquinazolones, as well as 3-amino-2-benzylquinazolones, with α-dicarbonyl compounds for the synthesis of heterocyclic polymers, more extensive studies of model reactions is required.

Specific solvents are required for carrying out such reactions on polymeric objects possessing considerably lower solubility and absence of fusibility. Various phenols (cresoles, chlorphenols, *etc.*) are frequently used as solvents for the synthesis and modification of polyheteroarylenes. In the case of polyquinazolones, pentafluorophenol (PFP) proved to be an efficient solvent for performing the synthesis and modification of the polymers, since it was found to be able to catalyze various condensation reactions as well.[2,3,7] Small amounts of PFP (from 1 : 1 to 2 : 1 with respect to amounts of the starting compounds) allow one to carry out synthesis of both the model compounds and polymers with high concentrations of reagents in solution. In addition, PFP assists in removal of liberated water from the reaction mixture in the form of azeotrope. This approach to the condensation reactions in the quinazolone series proved more efficient than those described earlier and, therefore, it was used in the present work.

Model compounds

A reaction of 2-methylbenzoxazinone (**1**) with hydrazine hydrate affords 3-amino-2-methylquinazolone (**2**), which reacts with aromatic α-diketones to form pyridazinoquinazolone derivatives **3—5** (Scheme 1).

The reaction proceeds smoothly in PFP used as the solvent, catalyst, and condensation agent at the temperatures of 120—140 °C. The yields of the final products in these reactions were 60—70%, with the reaction time

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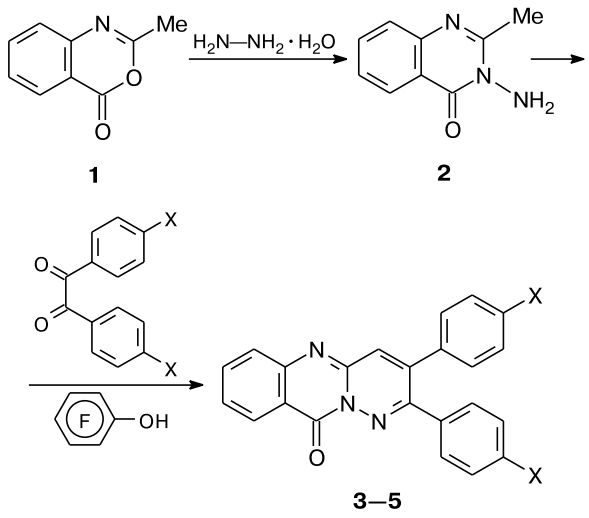
Scheme 1



X = H (**3**), F (**4**), Br (**5**)

being 15 h. The products possess bright green fluorescence in solution and in the solid state, their chemical structures were confirmed by the ^{1}H NMR spectroscopic, mass spectrometric, and elemental analysis data. Isatin and acenaphthenequinone can also be involved into the analogous model reactions (Scheme 2).

The reactions for these compounds are much faster and virtually quantitative yields of the products can be reached upon heating in PFP at 70—80 °C for 1—2 h. The readiness of the reactions can be explained by the fact that the carbonyl groups in isatin and acenaphthenequinone are oriented in the same direction and placed in a plane unlike in benzil and its derivatives, where the carbonyl groups can be turned with respect to the CO—CO bond.

The structure of compound **6** was completely confirmed by the ^{1}H NMR data, whereas two isomers are possible for **7**. However, the ^{1}H NMR spectrum indicates formation of the only reaction product **7**. With allowance for the electron-donating character of the isatin carbonyl groups, formation of pentacycle **7**, rather than **7′**, is more likely. Product **6** possesses bright orange fluorescence in the solid state and in solution, whereas fluorescence of **7** is weaker. UV-visible absorption and fluorescence spectra were recorded for the reaction products of 3-amino-2-methylquinazolone with benzil and acenaphthenequinone (**3** and **6**, respectively) (Figs 1—4).

Comparison of spectra for these two compounds showed that the quantum yield of fluorescence for **6** is higher than for **3**. In addition, the emission maximum is somewhat shifted: the maximum for compound **3** is observed at 520 nm, whereas for **6** at 480 nm. The elec-

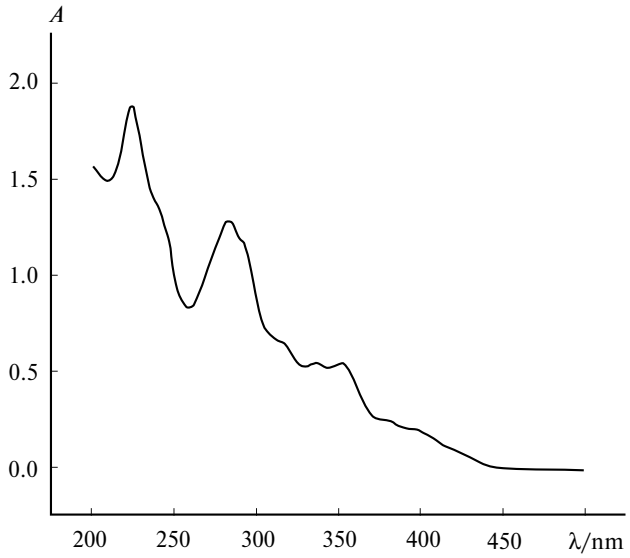
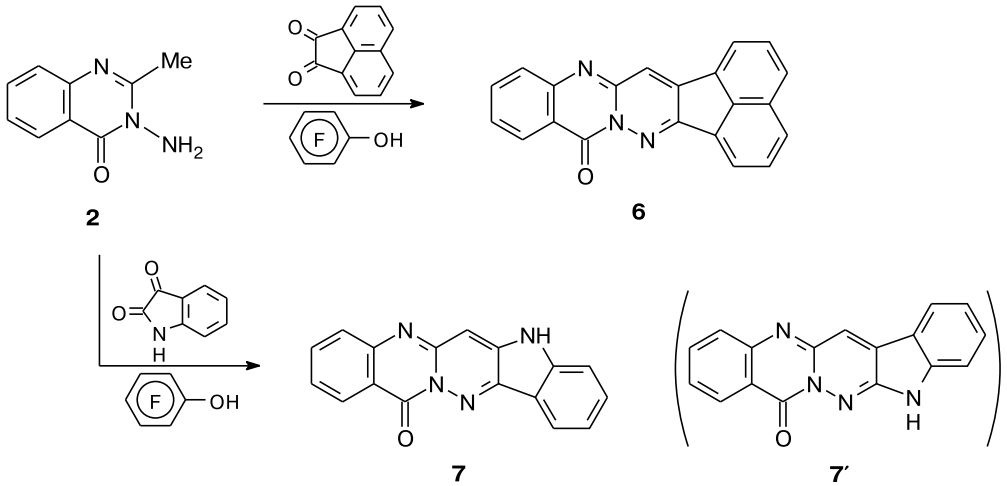


Fig. 1. Absorption spectrum of compound **3** ($1 \cdot 10^{-4}$ *M* solution).

Scheme 2



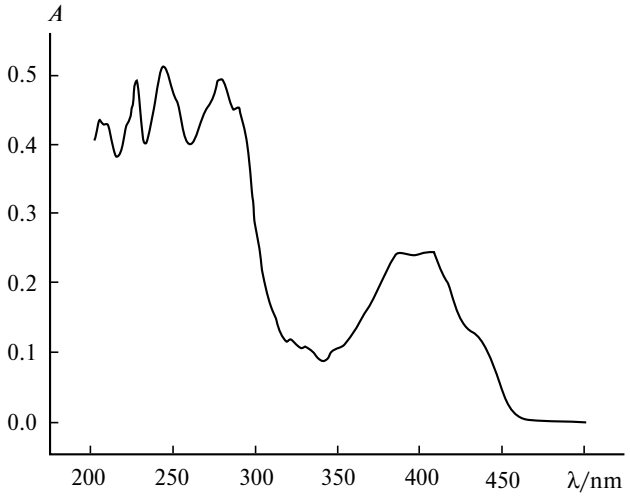


Fig. 2. Absorption spectrum of compound **6** ($2 \cdot 10^{-5}$ *M* solution).

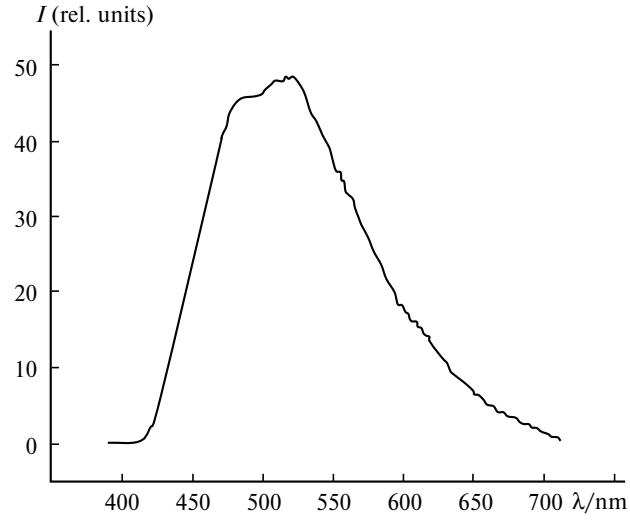


Fig. 3. Fluorescence spectrum of compound **3** ($1 \cdot 10^{-4}$ *M* solution); quantum yield $\varphi = 0.07$.

tron spectra significantly differ as well: the long-wave absorption maximum is shifted from 350 nm for **3** to 410 nm for **6**. It should be noted that the low quantum yield values in this case are compensated by the fact that these compounds fluoresce in the solid state. This is rare for common organic luminophores, since a concentration quenching phenomenon is frequently observed. The differences in the absorption and fluorescence spectra, as well as an increase in quantum yield, can be explained by the differences in spatial structure of the molecules: product **3** is characterized by the turn of the phenyl rings with respect to the plane of pyridazinoquinazolone ring, whereas molecule **6** is planar. Another specific feature of the chromophore system **6** is the presence of an odd nonalternante system, which also significantly contributes to the changes of the chromophore properties.

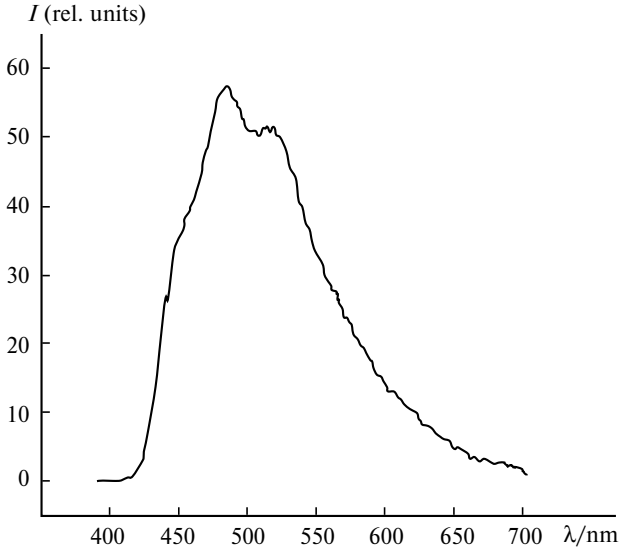
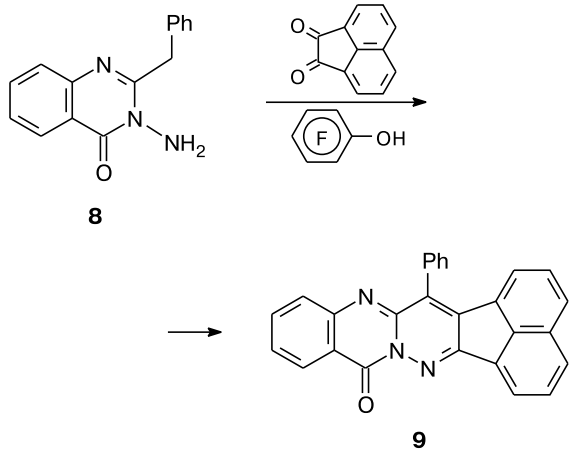


Fig. 4. Fluorescence spectrum of compound **6** ($2 \cdot 10^{-5}$ *M* solution); quantum yield $\varphi = 0.17$.

3-Amino-2-benzylquinazolone (**8**) was studied on the possibility to be involved into the heterocyclization reaction as well (Scheme 3).

Scheme 3

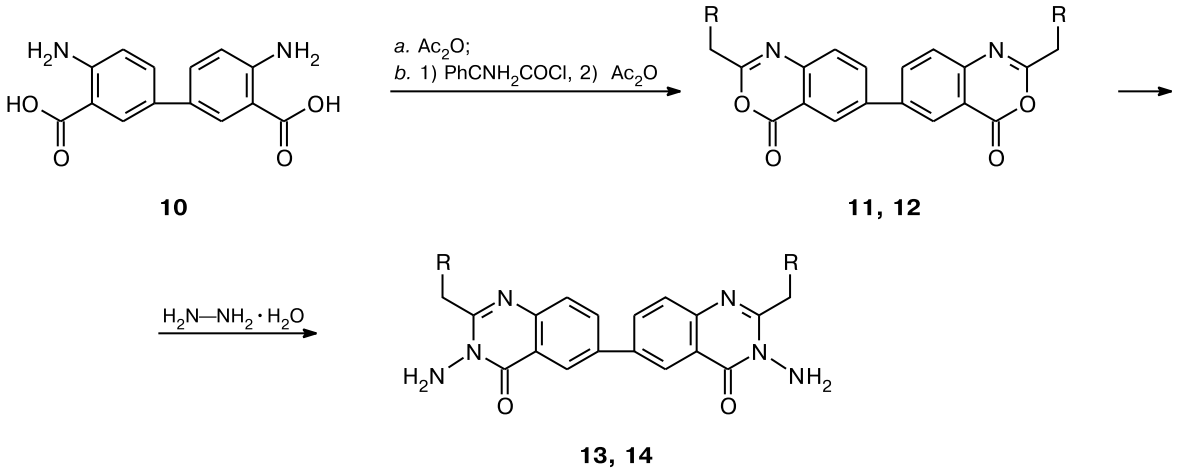


Synthesis of monomers and polymers

Scheme 4 represents the synthesis of bis(2-alkyl-3-aminoquinazolones) **11** and **12**.

The intermediate 6,6′-bis(2-methylbenzoxazinone) (**11**) was obtained from benzidine-3,3′-dicarboxylic acid (**10**) in acetic anhydride without isolation of the intermediately formed product (way *a*), whereas 6,6′-bis-(2-benzylbenzoxazinone) (**12**) by acylation of diaminodicarboxylic acid **10** with phenylacetyl chloride with subsequent cyclization in acetic anhydride (way *b*). The

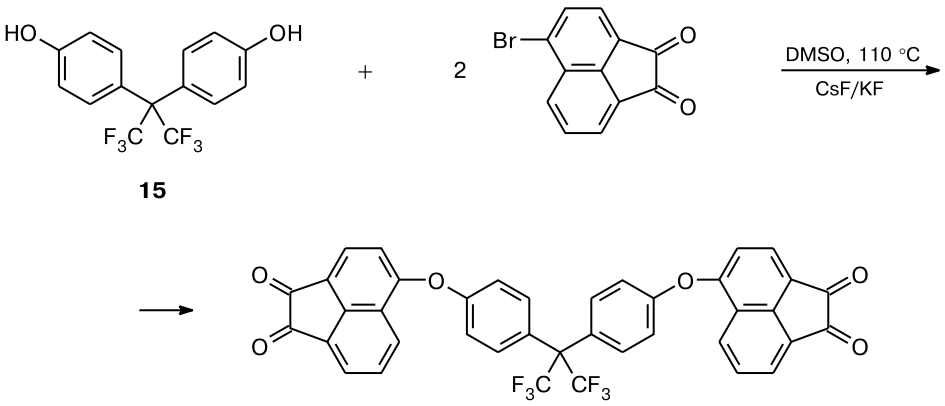
Scheme 4



10 **11, 12** **13, 14**

R = H (**11, 13**), Ph (**12, 14**)

Scheme 5



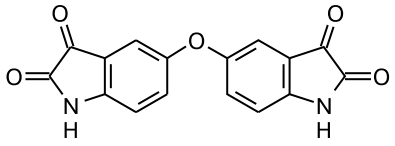
15 **16**

reaction of bis-benzoxazinones with hydrazine hydrate was also carried out differently. The synthesis in the phenol—benzene mixture at 80 °C was optimum for **13**, whereas **14** was obtained at room temperature in THF with an additive of 0.5% aqueous NaOH.

Nucleophilic substitution of bromine in 5-bromoacenaphthenequinone in its reaction with 2,2-bis(4-hydroxyphenyl)hexafluoropropane (**15**) yielded bifunctional acenaphthenequinone monomer **16** (Scheme 5).

5,5′-Bisisatinoxide (**17**) was obtained from 4,4′-diaminodiphenyloxide by the Sandmeyer reaction[8] using 1,4-bis(phenylglyoxalyl)benzene (**18**) as the tetracarbonyl benzil analog.

Based on the monomers described above, new polyheteroarylenes, *viz.*, poly(pyridazinoquinazolones) **19—24**, have been synthesized. The synthesis was carried out in PFP at temperatures of 140—150 °C, in a number of cases in the presence of trifluoroacetic acid as a cosolvent (Scheme 6).



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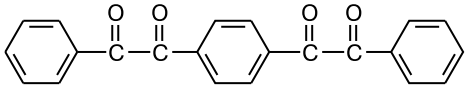

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Reduced viscosities of 0.5 g dL^{-1} of solutions of polymers in H_2SO_4 at 25 °C (η_{red}) and temperatures of 5% mass loss (τ_5) according to the thermogravimetric analysis data (TGA) in air ($\Delta T = 5$ °C min^{-1}) for polymers **19—24** are given in Table 1.

Scheme 6

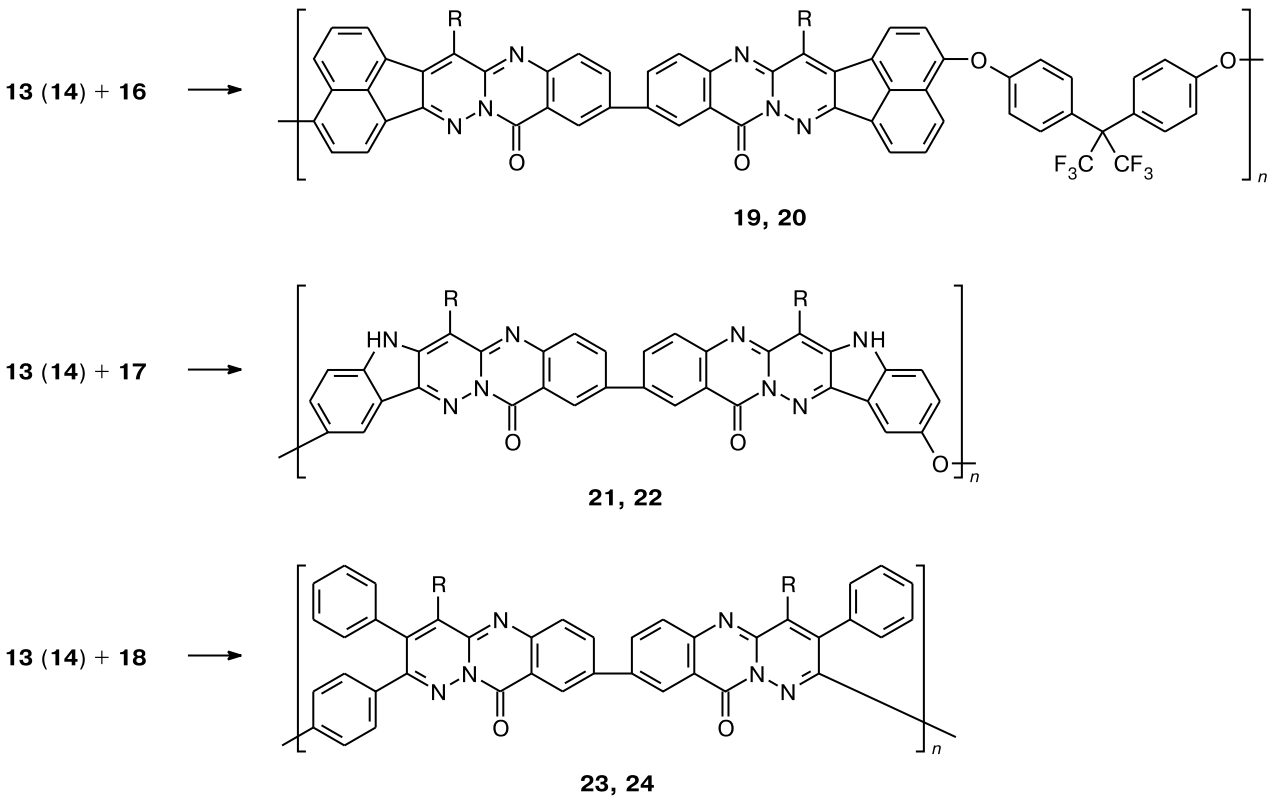


Table 1. Viscosimetric and thermogravimetric characteristics of polymers **19—24**

Polymer	η_{red} /g dL^{-1}	τ_5 /°C	Polymer	η_{red} /g dL^{-1}	τ_5 /°C
19	0.29	440	**22**	0.39	421
20	0.47	475	**23**	0.17	410
21	0.51	380	**24**	0.09	452

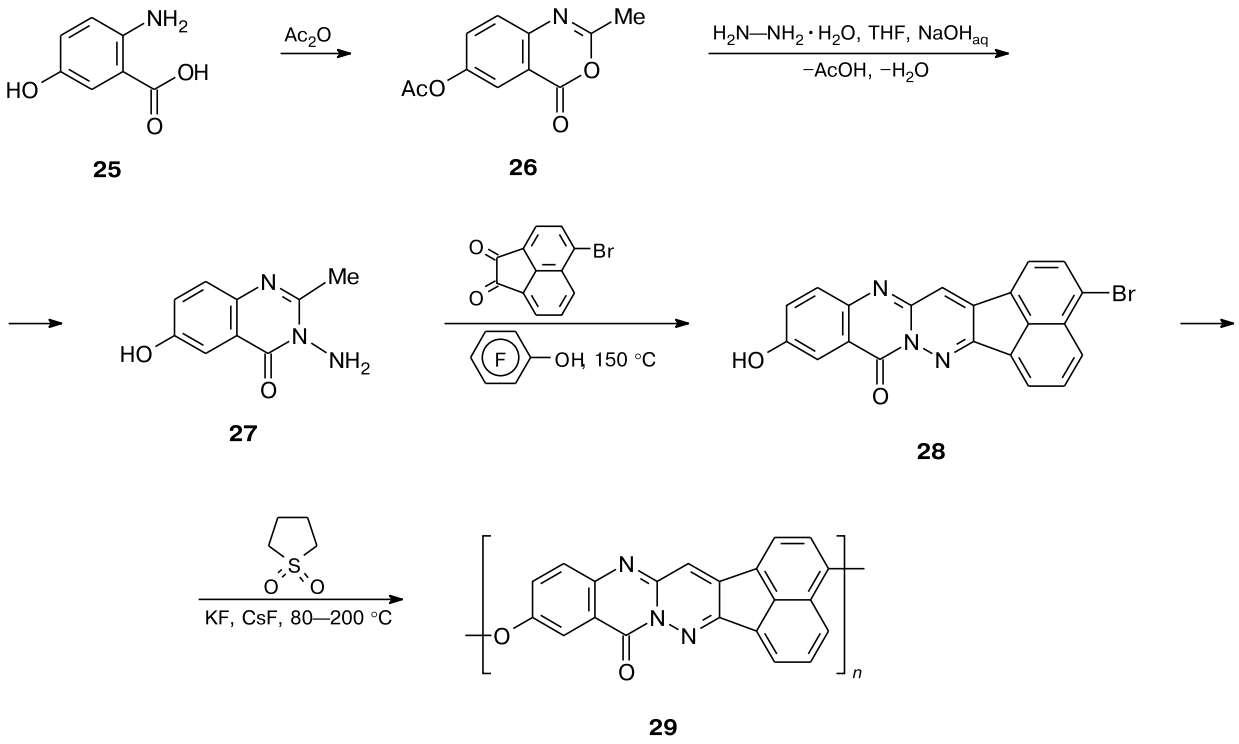
The polymers obtained are soluble in sulfuric, formic, and trifluoroacetic acids, whereas polymers **23** and **24** are soluble in chloroform as well. The polymers exhibit abilities to form films. The TGA data allow one to draw conclusion on the high thermostability of the polymers with R = Ph, *i.e.*, **20**, **22**, and **24**. Polymers **23** and **24** possess especially bright yellowish green fluorescence in both solution and the solid state.

Synthesis through the AB-monomer was studied in the present work as an alternative approach to the preparation of poly(pyridazinoquinazolones) (Scheme 7). 5-Hydroxyanthranilic acid **25** was the starting compound in this case, reflux of which in acetic anhydride gave 6-acetoxy-2-methylbenzoxazinone (**26**). Further, 3-amino-6-hydroxy-2-methylquinazolone (**27**) was obtained and, finally, cyclocondensation of the latter with 4-bromoacenaphthenequinone in PFP afforded monomer **28**. Polycondensation of **28** in sulfolane in the presence of potassium and cesium fluorides by nucleophilic substitution furnished poly(pyridazinoquinazolone) **29**.

However, the η_{red} of the polymer **29** samples synthesized did not exceed 0.12 g dL^{-1} (a solution in H_2SO_4, 0.5 g dL^{-1}, 25 °C), which is considerably lower than η_{red} of polymers **19** and **20** containing analogous units in the chain, but obtained based on two bifunctional monomers. From this, a conclusion can be drawn that in the synthesis of such poly(pyridazinoquinazolones), more "difficult" nucleophilic substitution reaction should be preferably used in the step for the monomer synthesis, whereas the heterocyclization reaction, proceeding with participation of acenaphthenequinone derivatives at high rate, in the polycondensation step.

In conclusion, in the present work a model reaction of 2-alkyl-3-aminoquinazolones with aromatic α-dicarbonyl compounds was studied for the first time, based on which a new class of poly(pyridazinoquinazolones) was synthesized.

Scheme 7



Experimental

Melting points were determined on a Boetus heating stage and did not corrected. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AMX-400 (400.13 MHz) and Bruker AV-300 (282.40 MHz) spectrometers in DMSO-d_6. The δ values were calculated from the residual proton signals of the deuterated solvent used as a reference (^{1}H) and $CFCl_3$ as an external standard (^{19}F). Absorption and fluorescence spectra were recorded on a Shimadzu RF-5301 spectrometer at 293 K for solutions in acetonitrile in 9.97-mm thick cuvettes. The reaction course and purity of the isolated products were monitored by TLC on Silufol UV-254 plates, with the toluene—acetone solvent mixture (2 : 1, v/v) used as an eluent. Reduced viscosity of polymers were measured on a Ubbelode capillary viscosimeter for solutions of polymers (0.5 g dL^{-1}) in 98% sulfuric acid at 25 °C. Dynamic TGA was performed on a MOM Q-1000 derivatograph.

Anthranilic acid (Aldrich, 98%, m.p. 144—148 °C) and 5-hydroxyanthranilic acid (Aldrich, 99%, m.p. 247 °C) were used as purchased. Hydrazine hydrate was purified by azeotropic distillation with toluene in the flow of argon, collecting a fraction with b.p. 115—120 °C. Benzil (Aldrich, 98%, m.p. 94—95 °C), 4,4′-dibromobenzil (Acros Organics, 98%, m.p. 227—228 °C), 4,4′-difluorobenzil (Acros Organics, 99%, m.p. 120—122 °C), isatin (Aldrich, 98%, m.p. 193—195 °C), and acenaphthenequinone (pure grade, m.p. 249—252 °C) were used as purchased. 4,4′-Benzidine-3,3′-dicarboxylic acid was synthesized according to the known procedure,[9] m.p. > 300 °C (decomp.). 4-Bromoacenaphthenequinone was obtained by bromination of acenaphthenequinone with a 10-fold excess of bromine, purified by crystallization from acetone. m.p. 235—238 °C (*cf.* Ref. 10: m.p. 231—232 °C). 1,4-Bis(phenylglyoxalyl)benzene was obtained according to the known procedure,[9] m.p. 123 °C (*cf.* Ref. 9: m.p. 122—124 °C). 2,2-Bis(4-hydroxyphenyl)hexafluoropropane was purified by sublimation *in vacuo* at 150—160 °C, m.p. 160—161 °C. Pentafluorophenol (pure for analysis grade, m.p. 34—36 °C) was used as purchased.

2-Methyl-4*H*-3,1-benzoxazin-4-one (1). Anthranilic acid (8 g, 58 mmol) was refluxed for 4 h in Ac_2O (20 mL) using a condenser equipped with a calcium chloride drying tube. Excess Ac_2O was evaporated. Crystals obtained were sublimed at 75—100 °C (0.01 Torr). The yield was 8.30 g (88%), m.p. 80—82 °C (*cf.* Ref. 11: m.p. 86—87 °C).

2-Benzyl-4*H*-3,1-benzoxazin-4-one. Anthranilic acid (4.11 g, 30 mmol) was dissolved in dimethylacetamide (10 mL), followed by a dropwise addition of phenylacetyl chloride (5.10 g, 33 mmol) with stirring and cooling in an ice-water bath. After all the chloride was added, the reaction mixture was stirred for another 20 min, then poured into water (100 g). The suspension obtained was filtered, a precipitate was washed with water and dried. The yield of *N*-(phenylacetyl)anthranilic acid was 7 g (92%), m.p. 186—190 °C. Then, the product was placed into Ac_2O (20 mL) and refluxed for 4 h using a condenser equipped with a calcium chloride drying tube. Excess Ac_2O was evaporated. Crystals obtained were sublimed at 100—150 °C (0.01 Torr). The yield was 5.12 g (72%), m.p. 82—86 °C (*cf.* Ref. 12: m.p. 90.5 °C).

6-Acetoxy-2-methyl-4*H*-3,1-benzoxazin-4-one (26). 5-Hydroxyanthranilic acid (3.06 g, 20 mmol) was refluxed for

4 h in Ac_2O (8 mL) using a condenser equipped with a calcium chloride drying tube, then heating was stopped, and the reaction mixture was kept for ~14 h. Then, the solution was triturated with a glass rod in a glass flask, the crystalline mass obtained was diluted with diethyl ether (30 mL), a precipitate was filtered off and washed with diethyl ether. The yield was 3.04 g (70%), m.p. 115 °C (*cf.* Ref. 13: m.p. 116.5—117.5 °C).

3-Amino-2-methylquinazolone (2). 2-Methylbenzoxazinone (**1**) (3.22 g, 20 mmol) was dissolved in THF (12 mL) and added to hydrazine hydrate in excess amount (4 mL, 80 mmol) with stirring. Formation of white precipitate (acetimidinium salt) was observed. After addition of 0.5% aq. NaOH (10 mL), formation of purple emulsion was observed, which was heated until the color disappeared. The reaction mixture was diluted with water (20 mL) and a white precipitate formed was filtered off, washed with water, and dried. The yield was 1.75 g (99%), m.p. 149—150 °C (*cf.* Ref. 14: m.p. 149.3 °C). ^{1}H NMR ($CDCl_3$), δ: 2.70 (s, 3 H, Me); 4.89 (s, 2 H, NH_2); 7.43 (t, 1 H, J = 7.6 Hz); 7.62 (d, 1 H, J = 8.4 Hz); 7.71 (t, 1 H, J = 7.8 Hz); 8.21 (d, 1 H, J = 8.0 Hz).

3-Amino-2-benzylquinazolone (8) was obtained similarly to compound **2** by the reaction of 2-benzylbenzoxazinone (4.75 g, 20 mmol) with hydrazine hydrate. The yield was 4.08 g (81%), m.p. 160—165 °C (*cf.* Ref. 15: m.p. 164 °C). ^{1}H NMR ($CDCl_3$), δ: 4.38 (s, 2 H, $—CH_2—$); 4.78 (s, 2 H, NH_2); 7.15—7.50 (m, 6 H); 7.74 (s, 2 H); 8.21 (d, 1 H, J = 7.2 Hz).

3-Amino-6-hydroxy-2-methylquinazolone (27). 6-Acetoxy-2-methylbenzoxazinone (**26**) (3.03 g, 14 mmol) was dissolved in THF (16 mL) and added to hydrazine hydrate in excess amount (4 mL, 80 mmol) with stirring. Sequential formation of a beige emulsion, exothermic reaction with the formation of solution with shade of pink, and then formation of white precipitate (acetimidinium salt) were observed. A 0.5% aq. NaOH (20 mL) was added to the reaction mixture and the suspension was stirred for 1 h, then a precipitate was filtered off and washed with water. The yield was 2.36 g (96%), m.p. 337 °C (with decomp.). ^{1}H NMR (DMSO-d_6), δ: 2.53 (s, 3 H, Me); 5.76 (s, 2 H, NH_2); 7.24 (q, 1 H, J_1 = 8.9 Hz, J_2 = 2.8 Hz); 7.37 (d, 1 H, J = 2.8 Hz); 7.47 (d, 1 H, J = 8.7 Hz). Found (%): C, 56.50; H, 4.77; N, 22.05. $C_9H_9N_3O_2$. Calculated (%): C, 56.54; H, 4.74; N, 21.98.

2,3-Diphenyl-10*H*-pyridazino[6,1-*b*]quinazolin-10-one (3). 3-Amino-2-methylquinazolone (**2**) (0.35 g, 2 mmol) and benzil (0.42 g, 2 mmol) were heated for 15 h in PFP (0.8 g) at 140 °C. TLC: R_f = 0.6, a fluorescing spot. The reaction mixture was cooled and precipitated with methanol (10 mL), a precipitate was filtered off, dried, and then sublimed at 180 °C and residual pressure of 0.01 Torr. The yield was 0.42 g (60%), m.p. 189—190 °C (*cf.* Ref. 5: m.p. 189—190 °C). ^{1}H NMR (DMSO-d_6), δ: 7.25—7.45 (m, 10 H, Ph); 7.60 (t, 1 H, J = 6.7 Hz); 7.82 (d, 1 H, J = 7.7 Hz); 7.88 (s, 1 H, —CH=); 7.95 (t, 1 H, J = 6.7 Hz); 8.37 (d, 1 H, J = 6.7 Hz). Found (%): C, 79.16; H, 4.22; N, 11.97. $C_{23}H_{15}N_3O$. Calculated (%): C, 79.07; H, 4.33; N, 12.03.

2,3-Bis(4-fluorophenyl)-10*H*-pyridazino[6,1-*b*]quinazolin-10-one (4) was obtained similarly to compound **3** by the reaction of compound **2** with 4,4′-difluorobenzil (0.49 g, 2 mmol). The yield was 0.50 g (62%), m.p. 186—223 °C (amphoteric compound). ^{1}H NMR (DMSO-d_6), δ: 7.12—7.41 (m, 4 H); 7.31—7.36 (m, 2 H); 7.38—7.43 (m, 2 H); 7.59 (t, 1 H, J = 6.5 Hz); 7.80 (d, 1 H, J = 6.5 Hz); 7.85 (s, 1 H, —CH=); 7.98 (t, 1 H, J = 6.5 Hz); 8.35 (d, 1 H, J = 6.6 Hz). Found (%): C, 71.62; H, 3.30; F, 9.80; N, 10.95. $C_{23}H_{13}F_2N_3O$. Calculated (%): C, 71.68; H, 3.44; F, 9.86; N, 10.90.

2,3-Bis(4-bromophenyl)-10*H*-pyridazino[6,1-*b*]quinazolin-10-one (5) was obtained similarly to compound **3** by the reaction of compound **2** with 4,4′-dibromobenzil (0.74 g, 2 mmol). The yield was 0.70 g (62%), m.p. 193—196 °C. ^{1}H NMR (DMSO-d_6), δ: 6.98 (d, 2 H, J = 7.1 Hz); 7.18 (d, 2 H, J = 7.9 Hz); 7.32—7.49 (m, 4 H); 7.56 (d, 1 H, J = 7.0 Hz); 7.62 (s, 1 H, —CH=); 7.68—7.78 (m, 2 H); 8.44 (d, 1 H, J = 7.3 Hz). Found (%): C, 54.52; H, 2.50; Br, 31.56; N, 8.34. $C_{23}H_{13}Br_2N_3O$. Calculated (%): C, 54.47; H, 2.58; Br, 31.51; N, 8.29.

9*H*-Acenaphtho[1′,2′:3,4]pyridazino[6,1-*b*]quinazolin-9-one (6). 3-Amino-2-methylquinazolone (**2**) (0.184 g, 1 mmol) and acenaphthenequinone (0.182 g, 1 mmol) in PFP (0.3 g) were heated for 1.5 h at 70 °C. Gradual formation of a precipitate was observed. The reaction mixture was diluted with ethanol (10 mL), an orange precipitate was filtered off, washed with acetone, and dried. The yield was 0.28 g (87%), m.p. >350 °C. TLC: R_f = 0.4, a fluorescing spot. ^{1}H NMR (CF_3COOD), δ: 7.30—8.52 (m, 4 H); 8.69 (t, 1 H, J = 7.8 Hz); 8.82 (d, 1 H, J = 8.0 Hz); 8.88 (d, 1 H, J = 8.0 Hz); 9.01 (d, 1 H, J = 7.2 Hz); 9.91 (d, 1 H, J = 6.8 Hz); 9.14 (s, 1 H, —CH=); 9.21 (d, 1 H, J = 8.4 Hz). Found (%): C, 78.52; H, 3.49; N, 13.01. $C_{21}H_{11}N_3O$. Calculated (%): C, 78.49; H, 3.45; N, 13.08.

Indolo[3′,2′:3,4]pyridazino[6,1-*b*]quinazolin-7(14*H*)-one (7). 3-Amino-2-methylquinazolone (**2**) (0.184 g, 1 mmol) and isatin (0.147 g, 1 mmol) in PFP (0.4 g) were heated for 2 h at 80 °C. Gradual formation of a precipitate was observed. The reaction mixture was diluted with acetone (10 mL), an orange precipitate was filtered off, washed with acetone, and dried. The yield was 0.33 g (100%), m.p. > 350 °C. TLC: R_f = 0.3, a fluorescing spot. ^{1}H NMR (CF_3COOD), δ: 7.54 (t, 1 H, J = 7.6 Hz); 7.76 (d, 1 H, J = 8.4 Hz); 7.88—8.00 (m, 3 H); 8.26 (t, 1 H, J = 7.6 Hz); 8.36 (d, 1 H, J = 8.0 Hz); 8.74 (d, 1 H, J = 8.4 Hz); 8.84 (s, 1 H, —CH=). Found (%): C, 71.36; H, 3.58; N, 19.61. $C_{17}H_{10}N_4O$. Calculated (%): C, 71.32; H, 3.52; N, 19.57.

15-Phenyl-9*H*-acenaphtho[1′,2′:3,4]pyridazino[6,1-*b*]-quinazolin-9-one (9) was obtained similarly to **6** by the reaction of 3-amino-2-benzylquinazolone (**8**) (0.251 g, 1 mmol) with acenaphthenequinone (0.182 g, 1 mmol). The yield was 0.38 g (96%), m.p. > 350 °C. ^{1}H NMR ($CDCl_3$), δ: 7.11 (d, 1 H, J = 6.8 Hz); 7.25 (s, 1 H); 7.43—7.53 (m, 2 H); 7.62—7.84 (m, 7 H); 7.93 (d, 1 H, J = 8.0 Hz); 8.03 (d, 1 H, J = 8.0 Hz); 9.01 (d, 1 H, J = 7.2 Hz); 8.50 (d, 1 H, J = 6.8 Hz); 8.54 (d, 1 H, J = 7.6 Hz). Found (%): C, 81.57; H, 3.75; N, 10.63. $C_{27}H_{15}N_3O$. Calculated (%): C, 81.60; H, 3.80; N, 10.57.

7-Bromo-3-hydroxy-9*H*-acenaphtho[1′,2′:3,4]pyridazino-[6,1-*b*]quinazolin-9-one (28) (AB-monomer) was obtained similarly to **6** by the reaction of sodium salt of 3-amino-6-hydroxy-2-methylquinazolone (**27**) (0.640 g, 3 mmol) with 4-bromoacenaphthenequinone (0.783 g, 3 mmol). The yield was 1.21 g (96%), m.p. > 350 °C. ^{1}H NMR (CF_3COOD), δ: 7.30—8.52 (m, 3 H); 8.81 (d, 1 H, J = 8.0 Hz); 8.82 (d, 1 H, J = 8.4 Hz); 9.01 (d, 1 H, J = 7.6 Hz); 9.91 (s, 1 H); 9.14 (s, 1 H, —CH=); 9.21 (d, 1 H, J = 8.4 Hz). Found (%): C, 60.64; H, 2.47; Br, 19.25; N, 10.15. $C_{21}H_{10}BrN_3O_2$. Calculated (%): C, 60.60; H, 2.42; Br, 19.20; N, 10.10.

6,6′-Bis(2-methylbenzoxazinone) (11). Benzidine-3,3′-dicarboxylic acid (14.32 g, 50 mmol) was refluxed for 4 h in Ac_2O (50 mL) using a condenser equipped with a calcium chloride

drying tube. Excess of Ac_2O was evaporated, a residual suspension was diluted with diethyl ether and filtered off the precipitate, which was sublimed at 270 °C (0.01 Torr). The yield was 11.6 g (73%), m.p. 310—312 °C (*cf.* Ref. 14: m.p. 313 °C).

6,6′-Bis(2-benzylbenzoxazinone) (12). Benzidine-3,3′-dicarboxylic acid (8.2 g, 30 mmol) was dissolved in DMA and added dropwise to phenylacetyl chloride (10.2 g, 66 mmol) with stirring and cooling with icy water, the mixture was stirred for another 20 min, poured into water (100 g). A suspension obtained was filtered, a precipitate was washed with water and dried. Then, the product was placed in Ac_2O (60 mL) and refluxed for 4 h using a condenser equipped with a calcium chloride drying tube, a precipitate was filtered off, washed with diethyl ether, and dried. The yield was 9.9 g (70%), m.p. 225—237 °C. Found (%): C, 76.20; H, 4.32; N, 5.87. $C_{30}H_{20}N_2O_4$. Calculated (%): C, 76.26; H, 4.27; N, 5.93.

6,6′-Bis(3-amino-2-methylquinazolone) (13). A mixture of phenol (15 g), benzene (3 mL), and hydrazine hydrate (3 mL, 60 mmol) was heated for 1 h at 100 °C, then 4,4′-bis-(2-methylbenzoxazinone) (**11**) (4.8 g, 15 mmol) was added to it. A suspension obtained was heated with stirring for 10 h in the flow of argon and diluted with water. A precipitate formed was filtered off, placed in 5% aq. K_2CO_3 (100 mL), and refluxed for 30 min, then filtered and washed with water. A paste-like product was dried at 100 °C. The yield was 3.7 g (71%), m.p. >300 °C (with decomp.). ^{1}H NMR ($CDCl_3$), δ: 2.62 (s, 6 H, Me); 5.77 (s, 4 H, NH_2); 7.70 (d, 2 H, J = 8.4 Hz); 8.13 (d, 1 H, J = 8.4 Hz); 8.40 (s, 2 H). Found (%): C, 62.01; H, 4.69; N, 24.18. $C_{18}H_{16}N_6O_2$. Calculated (%): C, 62.06; H, 4.63; N, 24.12.

6,6′-Bis(3-amino-2-benzylquinazolone) (14). A suspension of 6,6′-bis(2-benzylbenzoxazinone) (**12**) (7 g, 15 mmol) in THF (40 mL) was gradually added to hydrazine hydrate (5 mL, 0.1 mol). Dissolution of the precipitate and exothermic reaction were observed. The reaction mixture was kept for ~14 h, then 0.5% aq. NaOH (50 mL) was added to the suspension obtained, the mixture was stirred for 1 h. A precipitate was filtered off, washed with water and ethanol, dried, and placed in DMSO (20 mL), followed by stirring for 1 h. The product was filtered off, washed with water and methanol, and dried. The yield was 5 g (70%), m.p. 320—325 °C. ^{1}H NMR (CF_3COOD), δ: 5.52 (s, 4 H, —CH_2—); 8.10—8.18 (m, 10 H, Ph); 8.62 (d, 2 H, J = 11.7 Hz); 9.06 (d, 1 H, J = 8.5 Hz); 9.47 (s, 2 H). Found (%): C, 72.03; H, 4.80; N, 16.70. $C_{30}H_{24}N_6O_2$. Calculated(%): C, 71.99; H, 4.83; N, 16.79.

2,2-Bis[4-(1,2-dioxoacenaphthene-5-yloxy)phenyl]hexafluoropropane (16). Bromoacenaphthenequinone (2.87 g, 11 mmol), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (1.68 g, 5 mmol) and CsF (1.52 g, 10 mmol) and KF (0.58 g, 10 mmol) pre-heated at 150 °C *in vacuo* were heated for 10 h in anhydrous DMSO (15 mL) in the flow of argon at 90—110 °C. The reaction mixture was diluted with the methanol—water mixture (1 : 1, v/v, 30 mL) and the yellow precipitate was filtered off. The yield was 2.72 g (78%), m.p. > 350 °C. ^{1}H NMR (DMSO-d_6), δ: 7.26 (d, 2 H, J = 7.8 Hz); 7.45 (d, 4 H, J = 9.0 Hz); 7.57 (d, 4 H, J = 8.6 Hz); 7.96 (t, 2 H, J = 7.7 Hz); 8.10 (d, 2 H, J = 7.8 Hz); 8.15 (d, 2 H, J = 6.5 Hz); 8.51 (d, 2 H, J = 7.8 Hz). ^{19}F NMR (DMSO-d_6), δ: −141.84 (6 F, —CF_3). Found (%): C, 67.28; H, 2.63; F, 16.42. $C_{39}H_{18}F_6O_6$. Calculated (%): C, 67.25; H, 2.60; F, 16.37.

Poly{oxy-[3,3″-bis(9-oxo-9*H*-acenaphtho[1′,2′:3,4]pyridazino[6,1-*b*]quinazoline)-7,7″-diyl]oxy-1,4-phenylene-2,2′-hexafluoropropylene-1,4-phenylene} (19). 6,6′-Bis(3-amino-2-methylquinazolone) (**13**) (0.34836 g, 1 mmol) and compound **16** (0.73139 g, 1.05 mol) were heated in PFP (2 g) with additive of chloroform (1 mL) with stirring at 100 °C for 30 min in the flow of argon. Then CF_3COOH (1 mL) was added, during which dissolution of the monomers was observed. The temperature was elevated step-wise to 150 °C and the synthesis was carried out for another 8 h. Then, the polymer was dispersed in ethanol (100 mL), an orange precipitate was filtered off, and extracted for 2 h in the Soxhlet apparatus with the methanol—acetone (1 : 1, v/v) mixture, and dried. The yield was 0.842 g (86%), η_{red} = 0.29 g dL^{-1}. Found (%): C, 70.27; H, 2.72; F, 11.65. $C_{57}H_{26}F_6N_6O_4$. Calculated (%): C, 70.37; H, 2.69; F, 11.72.

Poly{oxy-[3,3″-bis(15-phenyl-9-oxo-9*H*-acenaphtho[1′,2′:3,4]pyridazino[6,1-*b*]quinazoline)-7,7″-diyl]oxy-1,4-phenylene-2,2′-hexafluoropropylene-1,4-phenylene} (20). 6,6′-Bis(3-amino-2-benzylquinazolone) (**14**) (0.7508 g, 1.5 mmol) and compound **16** (1.0448 g, 1.5 mmol) were heated in PFP (2 g) with an additive of CF_3COOH (0.5 mL) with stirring at 90 °C for 1 h in the flow of argon. Gradual dissolution of the monomers was observed. The temperature was elevated stepwise to 150 °C and the synthesis was carried out for another 20 h. Then, the polymer was diluted with CF_3COOH (10 mL), dispersed in methanol (60 mL), a red precipitate was filtered off, extracted for 2 h in the Soxhlet apparatus with the methanol—acetone (1 : 1, v/v) mixture, and dried. The yield was 0.89 g (77%), η_{red} = 0.47 g dL^{-1}. Found (%): C, 73.65; H, 3.02; F, 10.16; N, 7.43. $C_{69}H_{34}F_6N_6O_4$. Calculated (%): C, 73.66; H, 3.05; F, 10.13; N, 7.47.

Poly{oxy-[9,9″-bis(7-oxo-14*H*-indolo[3′,2′:3,4]pyridazino[6,1-*b*]quinazoline)-3,3′′-diyl]} (21). 6,6′-Bis(3-amino-2-methylquinazolone) (**13**) (0.34836 g, 1 mmol) and 5,5′-bisisatin oxide (**17**) (0.30825 g, 1 mmol) were heated in PFP (1.5 g) with an additive of CF_3COOH (1.5 mL) with stirring at 100 °C for 1 h in the flow of argon. Visible changes of the reaction mixture were observed: an orange suspension turned a dark red solution. Then, the temperature was elevated stepwise to 140 °C and the synthesis was carried out for another 8 h. To reduce viscosity of the reaction mixture during the synthesis, additional amount of PFP (1.5 g) was added portion-wise. In a number of cases, formation of a gel-fraction was observed, which, however, could be separated from solution of the polymer by filtration. The reaction mixture was diluted with CF_3COOH (10 mL) and dispersed in methanol (100 mL), a red precipitate was filtered off, extracted in the Soxhlet apparatus for 2 h with the methanol—acetone (1 : 1, v/v) mixture, and dried. The yield was 0.523 g (89%), η_{red} = 0.51 g dL^{-1}. Found (%): C, 69.77; H, 2.88; N, 19.11. $C_{34}H_{16}N_8O_3$. Calculated (%): C, 69.86; H, 2.76; N, 19.17.

Poly{oxy-[9,9″-bis(7-oxo-13-phenyl-14*H*-indolo[3′,2′:3,4]pyridazino[6,1-*b*]quinazolin-7(14*H*)-one)-3,3″-diyl]} (22). 6,6′-Bis(3-amino-2-benzylquinazolone) (**14**) (0.7659 g, 1.53 mmol) and 5,5′-bisisatin oxide (**17**) (0.4624 g, 1.5 mmol) were heated in PFP (2 g) with an additive of CF_3COOH (0.5 mL) and chloroform (1 mL) with stirring at 100 °C for 1 h in the flow of argon. Then, the temperature was elevated stepwise to 140 °C, complete dissolution of the monomers was observed and heating was continued for 6 h. As in the case of polymer (**21**), it is possible formation of the gel-fraction. Then, the reaction mixture was diluted with CF_3COOH (20 mL), dispersed in methanol (100 mL), a red precipitate was filtered off, extracted in the Soxhlet apparatus for 2 h with the methanol—acetone

(1 : 1, v/v) mixture, and dried. The yield was 0.89 g (77%), η_{red} = 0.39 g dL^{-1}. Found (%): C, 74.89; H, 3.25; N, 15.16. $C_{46}H_{24}N_8O_3$. Calculated (%): C, 74.99; H, 3.28; N, 15.21.

Poly{[8,8´-bis(10-oxo-4-phenyl-10*H*-pyridazino[6,1-*b*]-quinazoline)-2,2´-diyl]-1,4-phenylene} (23). 6,6´-Bis-(3-amino-2-methylquinazolone) (**13**) (0.34836 g, 1 mmol) and 1,4-bis-(phenylglyoxalyl)benzene (**18**) (0.34233 g, 1 mmol) were heated in PFP (1 g) with stirring at 100 °C for 1 h in the flow of argon. Then, the temperature was elevated stepwise to 150 °C, P_2O_5 (0.2 g) was added as an additional condensation agent and the heating was continued for another 20 h. To reduce viscosity of the reaction mixture during the synthesis, PFP (1.5 g) was added in portions. Then, the polymer was dispersed in methanol (100 mL), an orange precipitate was filtered off, extracted for 2 h in the Soxhlet apparatus with the methanol—acetone mixture (1 : 1, v/v), and dried. The yield was 0.556 g (90%), η_{red} = 0.17 g dL^{-1}. Found (%): C, 77.57; H, 3.50; N, 13.51. $C_{40}H_{22}N_6O_2$. Calculated (%): C, 77.66; H, 3.58; N, 13.58.

Poly{[8,8´-bis(10-oxo-3,4-diphenyl-10*H*-pyridazino[6,1-*b*]-quinazoline)-2,2´-diyl]-1,4-phenylene} (24). 6,6´-Bis-(3-amino-2-benzylquinazolone) (**14**) (0.50056 g, 1 mmol) and 1,4-bis-(phenylglyoxalyl)benzene (**18**) (0.34233 g, 1 mmol) were heated in PFP (2 g) with an additive of CF_3COOH (0.5 mL) with stirring at 80 °C for 1 h in the flow of argon. The temperature was elevated stepwise to 150 °C and the synthesis was carried out for another 10 h. Then, the polymer was diluted with CF_3COOH (20 mL), dispersed in methanol (100 mL), a yellow fluorescing precipitate was filtered off, extracted for 2 h in the Soxhlet apparatus with the methanol—acetone (1 : 1, v/v) mixture, and dried. The yield was 0.89 g (77%), η_{red} = 0.09 g dL^{-1}. Found (%): C, 80.97; H, 3.99; N, 11.01. $C_{52}H_{30}N_6O_2$. Calculated (%): C, 81.02; H, 3.92; N, 10.90.

Poly[oxy-(9-oxo-9*H*-acenaphtho[1´,2´:3,4]pyridazino-[6,1-*b*]quinazoline-3,11-diyl)] (29). 7-Bromo-3-hydroxy-9*H*-acenaphtho[1´,2´:3,4]pyridazino[6,1-*b*]quinazolin-9-one (**28**) (0.624 g, 1.5 mmol) with CsF (0.30 g, 2 mmol) and KF (0.12 g, 2 mmol) pre-dried at 150 °C *in vacuo* were heated for 1 h in sulfolane (1 g) at 80—100 °C in the flow of argon. Dissolution of the monomer with subsequent precipitation of the polymer were observed. Then, the reaction was carried out in suspension at 160—200 °C for 20 h. The reaction mixture was precipitated with ethanol and a dark precipitate was filtered off, extracted for 2 h in the Soxhlet apparatus with the methanol—acetone (1 : 1, v/v) mixture, and dried. The yield was 0.49 g (98%), η_{red} = 0.11 g dL^{-1}. Found (%): C, 74.47; H, 2.69; N, 12.41. $C_{21}H_9N_3O_2$. Calculated (%): C, 75.22; H, 2.71; N, 12.53.

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