# Synthesis and optical properties of copolymers of 4-aminostyrene with the side styrylquinoline chromophore groups

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Successive molecular assembling in polymer chains furnished a series of the comb-shaped copolymers of 4-aminostyrene containing side styrylquinoline chromophore groups. Thermal, thermomechanical, spectroscopic, and luminescent properties of the polymers and low-mo-lecular-weight model chromophores were studied.

**Key words:** copolymers, reactions in chains, side groups, chromophores, styrylquinoline, luminescence.

Styrylquinoline dyes are of special interest among a wide range of organic luminophores, which lately attract attention of researches as a basis for the development of electroluminescent devices.<sup>1-3</sup> The structure of these compounds provides a possibility to widely vary optical characteristics by introduction of substituents in both the styryl fragment and benzene ring of the quinoline system. Styrylquinoline dyes can be used for the preparation of the high-strength optically transparent coatings by vacuum deposition method. Another, no less important method for the preparation of coatings containing the indicated luminophores is the use of polymeric supports with the fragments of styrylquinoline dyes in the main chain or in the side groups.<sup>4</sup>

It should be noted that two types of chromophorecontaining polymeric systems can be distinguished by the method of introduction of chromophores into a polymeric matrix: the systems, in which the chromophore molecules are dispersed in the polymeric matrix, 5-7 and the systems with the chromophore groups covalently incorporated into the main<sup>8,9</sup> or side<sup>10–12</sup> chains of polymers. Polymeric systems of the first type have a number of significant disadvantages, among which first of all are limited compatibility of chromophores with the polymeric matrix and, as a consequence, uneven distribution of the chromophores within the sample; low temperature-time stability of the photophysical properties as a result of the chromophore diffusions and formation of their microcrystals inside the polymeric matrix, as well as low optical quality of the samples and high level of optical losses because of light dispersion on the structural heterogeneities. Polymers with the covalently attached chromophore groups do not have such disadvantages. Synthesis of such polymers, as a rule,

is accompanied by difficulties, for example, by inhibition of the chain growth process with the functional groups of monomer in the case of radical polymerization or difficulties in purification of monomers in the case of polycondensation. One of the most reasonable approaches to the solution of this problem is a successive molecular assembling of chromophore groups using reactions in the polymer chains. We found it interesting to synthesize lowmolecular-weight chromophores of styrylquinoline series and copolymers of styrene with 4-aminostyrene containing side styrylquinoline groups of various structure and study their thermal, spectroscopic, and photoluminescent properties.

## **Results and Discussion**

Due to the specificities of chemical reactions in polymeric chains caused by high viscosity of solutions of polymers, as well as by conformational effects eventually leading to a decrease in the number of functional groups participating in the reaction, it is very difficult to achieve high yields of products in polymer analogous reactions. However, these difficulties can be overcome using catalysts and functional groups with high reactivity. The method of molecular assembling of side chromophore groups in polymers suggested in the present work is based on the reaction between amine and anhydride groups leading to the formation of imide rings with subsequent reaction of the activated methyl group of the quinoline ring with the aldehyde group.

Our choice of chemical structure of polymer was governed by the following suggestions: the polymer should possess linear structure, have active side groups with the

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 2, pp. 288-296, February, 2011.

<sup>1066-5285/11/6002-295 © 2011</sup> Springer Science+Business Media, Inc.

molecular weight of the polymer being high enough for the preparation of a self-supporting film or quality coating. Among widely used materials, functionalized polymers obtained, as a rule, based on traditional polymers, for example, polyalkyl acrylates or polystyrene, with various side functional groups (hydroxy, carboxy, amino groups, *etc.*) are of particular interest. The presence of reactive functional groups in the side chain opens wide prospects for chemical modification of the polymers indicated and development qualitatively new materials on their basis possessing a complex of valuable properties.

The fact that copolymers of styrene are capable of forming thin transparent coatings, 13, 14 makes them promising as optically active polymeric materials. Aminated polystyrene is one of the representatives of this series of polymers, the synthesis of which usually includes three steps: polymerization of styrene, nitration of polystyrene obtained, and subsequent reduction of the incorporated nitro groups to amino groups. Another synthetic approach to the preparation of polystyrene containing amino groups attached to the benzene rings consists in the direct use of the amino-containing monomer, i.e., 4-aminostyrene, in the process of polymerization. However, as it was noted in the literature,<sup>15–18</sup> polymerization of 4-aminostyrene or its copolymerization with styrene gives polymers of very low molecular weight and in very low yield. This fact can be explained by a partial transfer of electron density from the amino group to the vinyl group conjugated with it, that hinders the reaction of the latter with the free radical of initiator or growing polymeric chain.<sup>16</sup>



In this connection, it was suggested to use 4-aminostyrene as a monomer for polymerization, whose amino group is protected by the group readily removable after polymerization, for example, *N-tert*-butoxycarbonyl-4-aminostyrene (Boc-4-aminostyrene),<sup>16</sup> that allowed one to obtain polymers with acceptable characteristics.

Boc-4-aminostyrene 1 was obtained from 4-aminostyrene by the action of di-*tert*-butyl dicarbonate ( $Boc_2O$ ) in dioxane (Scheme 1).

Boc-4-aminostyrene 1 obtained in such a way was used for the synthesis of its copolymer with styrene. The copolymerization was carried out at 75 °C in N,N-dimethylacetamide (DMA) using 2,2'-azobisisobutyronitrile (AIBN) as an initiator (Scheme 2). The starting mixture of monomers consisted of Boc-4-aminostyrene and styrene taken in equimolar amounts.

As it follows from the <sup>1</sup>H NMR spectroscopic data, to be exact, from the comparison of intensities of signals for





the protons of the *tert*-butyl group ( $\delta$  1.5) and the protons of the phenyl ring ( $\delta$  6.2–7.2), the synthesized poly-[(styrene)-co-(*N*-*tert*-butoxycarbonyl-4-aminostyrene)] (**2**) has proportion of the styrene and Boc-4-aminostyrene units virtually unchanged as compared to the starting mixture and equal to 50–52 mol.% of Boc-4-aminostyrene units. This indicates that the reactivity of comonomers is close under conditions of copolymerization chosen. Earlier, it has been shown<sup>16</sup> that Boc-4-aminostyrene **1** possesses a somewhat higher reactivity in copolymerization in toluene as compared to styrene, which results in the fact that even if the content of comonomers in the starting mixture is equimolar, the copolymer is somewhat enriched with Boc-4-aminostyrene units (57 mol.%).

According to the GPC data, copolymer **2** is characterized by the following molecular masses:  $M_n = 33000$ ,  $M_{\rm w} = 71000$ . Provided that the average molecular weight of the monomeric unit is 161.5, this corresponds to the following degrees of polymerization (*N*):  $N_{\rm n} = 204$ ,  $N_{\rm w} = 440$ . The polydispersity index is ~2.15 that is characteristic of polymers obtained by free-radical polymerization.

Removal of the Boc protection was carried out with the solution of trifluoroacetic acid (TFA) in dichloromethane (see Scheme 2).

2-Methyl-3,4-quinolinedicarboxylic acid anhydride has been chosen as a basis for the side chromophore unit, allowing one to obtain a polymer with the styrylquinoline groups in the final step of the synthesis. The former was successfully added to the polymeric chain by the formation of imide rings at the amino groups of copolymer **3**. 2-Methyl-3,4-quinolinedicarboxylic acid (**4**) was synthesized from isatin and ethyl acetoacetate by the Pfitzinger reaction. The anhydride ring closure in the presence of pyridine and acetic anhydride at 60 °C results in the formation of 2-methyl-3,4-quinolinedicarboxylic acid anhydride (**5**) (Scheme 3).

### Scheme 3



In the first step of molecular assembling of side chromophore groups, it was necessary to introduce 2-methylquinoline groups in polymer **3**. To achieve this, anhydride **5** was added to the polymeric chain due to the formation of imide rings at the amino groups of copolymer **3**. In the first step, copolymer containing amic acid fragment was obtained. In the second step, chemical imidization promoted by acetic anhydride and pyridine mixture resulting in poly[(styrene)-co-(4-aminostyrene)-co-(4-(4-methyl-1,3-dioxo-1,3-dihydropyrrolo[3,4-*c*]quinolin-2-yl)styrene)] (**6**) (Scheme 4).



**6:** *n* = 50%, *k* = 10%, *m* = 40%

The <sup>1</sup>H NMR spectral data allowed one to calculate the fraction of units containing 2-methylquinoline groups in polymer **6**. Copolymer **6** contains about 40 mol.% of such units.

It is known that the methyl group at position 2 of the quinoline ring possesses high reactivity and can be involved into different reactions, including reactions with aromatic aldehydes, *i.e.*, the Knoevenagel reaction<sup>19,20</sup> (Scheme 5).

The very process, which is common in the preparation of styrylquinoline chromophores,<sup>21</sup> has been chosen for the formation of side chromophore groups by polymer analogous transformations.

Chemical reactions of aromatic aldehydes with copolymer **6** was carried out on reflux in *o*-dichlorobenzene (*o*-DCB) using piperidine as a catalyst. The synthesized copolymers 7a-d are well soluble in chloroform.



Scheme 5

n = 50%, k = 10%, m = 35-15%, s = 5-25%

Copolymers 7a-d are compounds including units of four different types: the fragments of styrene (*n*) and 4-aminostyrene (*k*), units of 4-(4-methyl-1,3-dioxo-1,3-dihydropyrrolo[3,4-*c*]quinolin-2-yl)styrene (*m*), and chromophore-containing units (*s*), *viz.*, 2-phenyl-4-styrylpyrrolo[3,4-*c*]quinoline-1,3-dione derivatives. The ratio of units n : k : m : s in copolymers was determined using <sup>1</sup>H NMR and UV spectroscopy.

Model compounds were synthesized to calculate the molar content of chromophore-containing units in the copolymers. 4-Methyl-2-*p*-tolylpyrrolo[3,4-*c*]quinoline-1,3-dione (8) was obtained first, which was the basis for the synthesis of model compounds 9a-d by the Knoevenagel reaction (Scheme 6).

The absorption maxima and extinction ratios of the main model compound 8 and low-molecular-weight models of units with styrylquinoline chromophores 9a-d synthesized on its basis, as well as copolymers 7a-d are given in Tables 1 and 2, respectively. As it can be seen from the data in Table 1, the long-wave absorption band of compound 8 in the region 355 nm of the UV spectra overlaps with absorption bands of all the models except **9a**, which has  $\lambda_{max1} = 413$  nm. Because of such an overlap, it is impossible to determine the fraction of units with styrylquinoline chromophore groups using only optical density values at  $\lambda_{max}$ . However, separation of extinction ratios of quadruple copolymers at different wavelengths (Fig. 1) to the analogous dependences for copolymer 6and chromophores **9a**–**d** using matrix method allowed us to determine composition of copolymers 7a-d. Results of spectrophotometric measurements allowed us to determine extinction ratios of synthesized copolymers and model chromophores within entire range of wavelengths studied. Using spectra of model chromophores 9a-d and triple copolymer  $\mathbf{6}$  as a basis, we carried out computer separaScheme 6



tion of the spectra of quadruple copolymers, solving the redetermined system of equations of the form:

$$\begin{cases} \varepsilon_{1,1}c_1 + \varepsilon_{1,2}c_2 = D_1 \\ \varepsilon_{2,1}c_1 + \varepsilon_{2,2}c_2 = D_2 \\ \vdots \\ \varepsilon_{n,1}c_1 + \varepsilon_{n,2}c_2 = D_n, \end{cases}$$

Compound	$\lambda_{max}/nm$	$\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$	
8	260	$32000 \pm 1000$	
	324	$3570 \pm 40$	
	355	4250±70	
9a	405-413	39000±3000	
9b	277	$17000 \pm 1000$	
	356	32000±1500	
9c	333	$37700 \pm 600$	
	405	$4700 \pm 200$	
9d	325	$23700 \pm 200$	

 Table 1. Absorption maxima and exctinction coefficients of model compounds 8 and 9a-d

where  $c_1$  and  $c_2$  are the unknown concentrations of the quinoline-containing units and styrylquinoline units in solutions of copolymers **7a**—**d** characterizing its composition;  $\varepsilon_{i,1}$  and  $\varepsilon_{i,2}$  are the extinction ratios of copolymer **6** and model chromophores at the wavelength  $\lambda_i$ ;  $D_i$  is the optical density of solution of the quadruple copolymer at the wavelength  $\lambda_i$ .

This system can be solved by the least squares method,  $^{22}$  whose matrix expression has the form

$$C = [(E^T E)^{-1} E^T] D,$$

where C is the concentration vector  $\{c_1, c_2\}$ , E is the matrix of extinction ratios of the models

$$\begin{cases} \varepsilon_{1,1} & \varepsilon_{1,2} \\ \vdots & \vdots \\ \varepsilon_{n,1} & \varepsilon_{n,2} \end{cases},$$

*D* is the vector of optical densities of quadruple copolymer  $\{D_1...D_n\}$ .

Figure 1 shows an example of expansion of the absorption spectra for copolymer **7b** and low-molecular-weight model **9b** corresponding to it. It is seen that the total spectrum (curve 4) of the triple copolymer **6** and the model obtained with the formula  $D_i = c_1 \varepsilon_{i,1} + c_2 \varepsilon_{i,2}$  satisfactorily

Table 2. Absorption maxima and exctinction coefficients of copolymers 6 and 7a-d

Compound	$\lambda_{max}/nm$	$\epsilon/Lg^{-1}cm^{-1}$
6	259	64±2
	326	8.5±0.3
	353	$8.4{\pm}0.2$
7a	406	45±3
7b	258	44.3±0.5
	353	31.4±0.3
7c	260	65±4
	334	16±2
7d	264	27±1
	323	28±1



Fig. 1. Electronic absorption spectra of copolymer 6(1), model chromophore 9b (2), and copolymer 7b (3) in chloroform, and theoretically calculated total spectrum of model 9b and copolymer 6(4).

agrees with the experimental spectrum of copolymer **7b** (curve 3). Analysis for all the synthesized polymers and determination of their composition were carried out similarly: the results are given in Table 3. The maximum content (28%) of chromophore-containing units (*s*) was found for copolymer **7a**, copolymer **7b** contains 22% of chromophore groups, copolymer **7d** — about 21%. The least fraction of chromophore-containing units (3%) was found in copolymer **7c**.

The content of the covalently attached styrylquinoline chromophores in the side chains of copolymers determined using <sup>1</sup>H NMR spectroscopy generally is in good agreement with the results obtained from the UV spectra (see Table. 3).

Polymers meant for the use in optics are frequently exposed to heat (for example, upon laser irradiation or passing the electric current through), therefore, in order to determine the temperature range of operation of new chromophore-containing polymers, it was necessary to

**Table 3.** Composition of copolymers 6 and 7a-d according to the <sup>1</sup>H NMR and UV spectroscopic data

Compound	Proportion of units (mol.%) n: k: m: s		
	<sup>1</sup> H NMR	UV	
6*	2:11:37	58:6:36	
7a	52:11:12:25	58:6:8:28	
7b	52:11:22:15	58:6:14:22	
7c	52:11:34:3	58:6:33:3	
7d	52:11:17:20	58:6:15:21	

\* For copolymer **6** the n : k : m proportion of units is given.

study their general thermal properties: indices of thermal stability and temperature transitions. Method of DSC and TGA were used to solve this problem (Table. 4).

It was shown that the temperature of 383 °C corresponds to the index of thermal stability ( $\tau_5$ ) of the starting copolymer. Introduction of thermally stable imide heterocycles in the side groups does not lead to the increase in thermal stability of copolymer  $\mathbf{6}$  as compared to the starting copolymer 3, rather, it leads to its insignificant decrease. This is due to the fact that thermal stability of carbochain polymers is largely determined by the structure of their main chain, which in the process of polymer analogous transformations remains unchanged. At the same time, general mobility of the system in the process of chemical modification regularly increases because of decrease in density of the hydrogen bonds net, presenting due to the amino groups, and appearance of bulky side substituents hindering intermolecular interactions, that leads to the decrease in thermal stability of the polymer.

It should be noted that introduction of quinolineimide groups in the side chains considerably increased the glass transition temperature from 138.6 °C for the starting copolymer **3** to 197.6 °C for copolymer **6**. For copolymers **7a**-**d** containing styrylquinoline units, the glass transition temperature is within 190–230 °C.

Study of luminescence of coatings prepared from solutions of copolymers synthesized, in particular, showed that copolymer 3 exhibits luminescence in the UV region of the spectrum (Fig. 2, a) with the intensity 250 arb. units at  $\lambda_{exc} = 260$  nm, whereas copolymers 7a-d actively absorb in this region. At the same time, it was found that copolymers **7b**, **d** possess noticeable luminescence in the orange region of the spectrum. The maximum intensity of luminescence in the region 590-600 nm is 105 arb. units at  $\lambda_{\text{exc}} = 352 \text{ nm}$  for copolymer **7b** (Fig. 2, *b*). It is known<sup>23</sup> that for the intensity of luminescence to be high in the visible region of the spectrum, the presence of  $\pi^* - \pi$ -transitions characterizing by high energies is required in the system of conjugated bonds of chromophore groups. In the case of copolymers **7b**,**d**, there are  $\pi^*$ -n-transitions due to the presence of the lone pair of electrons on the nitrogen atom of the quinoline ring, rather than  $\pi^* - \pi$ -

 Table 4. Thermal properties of chromophore-containing copolymers

Copolymer	TGA			DSC
	$\tau_5/^{\circ}C$	$\tau_{10}/^{\circ}C$	Coke (%)	$T_{\rm g}$ /°C
3	383	393	3.0	138.6
6	373	390	37.2	197.6
7a	395	406	36.0	223.0
7b	350	380	18.0	204.3
7c	345	379	23.5	196.4
7d	355	390	34.6	207.5



**Fig. 2.** Luminescence spectra: copolymer **3** at  $\lambda_{\text{exc}} = 260 \text{ nm}(a)$  and copolymers **7b** (1) and **7d** (2) at  $\lambda_{\text{exc}} = 352 \text{ nm}(b)$ .

transitions.<sup>23</sup> Probability of such transitions is low, that is indicated by low extinction ratios in long-wave region of the spectrum (<2000 L mol<sup>-1</sup> cm<sup>-1</sup>), as compared to the  $\pi^*-\pi$ -transitions, for which  $\varepsilon_{max}$  has an order of 10<sup>4</sup>. This explains comparably low intensities of luminescence of copolymers **7b.d** in the visible region.

In conclusion, copolymers of 4-aminostyrene with the side styrylquinoline chromophore groups were synthesized by successive molecular assembling, their composition was determined, and spectroscopic and thermal properties were studied. It was shown that some of chromophore-containing copolymers studied possess good luminescent properties.

Based on polymers with styrylquinoline groups, it is possible to obtain metal-polymeric Ir<sup>III</sup> complexes, that allows one to considerably increase their luminescent characteristics.<sup>24</sup> In addition, styrylquinoline chromophores possess high values of molecular quadruple polarizability,<sup>4</sup> therefore, polarized films of such copolymers can demonstrate nonlinear optical properties of the second order. Thus, the synthesized copolymers can be considered as promising optically active materials.

#### **Experimental**

Solvents (DMF and DMA) were dried over calcium hydride and distilled *in vacuo*. Styrene, *o*-DCB, anisaldehyde were purified by vacuum distillation. Pyridine and 1,4-dioxane were dried over potassium hydroxide and purified by simple distillation. Acetic anhydride and piperidine were purified by simple distillation; AIBN was recrystallized from ethanol; isatin, ethyl acetoacetate, Boc<sub>2</sub>O, 4-bromobenzaldehyde, 4-*N*,*N*-dimethylaminobenzaldehyde, benzaldehyde, light petroleum, chloroform, dichloromethane, and TFA were used without additional purification.

<sup>1</sup>H NMR spectra of 1% solutions were recorded on an Avance-400 spectrometer (Bruker, Germany) (400 MHz) using Me<sub>4</sub>Si as an internal standard. Electronic spectra of solutions of chromophore and copolymer models in chloroform were obtained on a SF-2000 spectrophotometer (OKB Spectrum) in the region 250–500 nm with the 1-nm step and range of concentrations  $5 \cdot 10^{-6} - 5 \cdot 10^{-5}$  mol L<sup>-1</sup>. Luminescence spectra were recorded on a LS-100 spectrophotometer (PTI, Canada). The width of in- and outcoming slit was 4 nm. The wavelength of the exciting light was varied from 380 to 230 nm.

Study of copolymers by GPC was carried out on an Agilent 1200 instrument (using DMA-0.05 M LiBr as an eluent, with the rate of elution being 0.7 mL min<sup>-1</sup>, pressure was 67-70 Bar, and temperature was 60 °C) with the UV detection on the wavelength 260 nm and calibration on polystyrene standards in DMA. Elemental analysis was performed on a Vario EL analyzer (Elemental, Germany).

Thermal testing of samples was carried out on the following instruments from Netzsch:

1) a TG 209 F1 thermomicrobalance, measurements were carried out in the range of temperatures from 30 to 500 °C at the rate of heating 10 °C min<sup>-1</sup> under argon atmosphere, argon was passed through the thermomicrobalance at 10 mL min<sup>-1</sup>, the weight of samples was 1-2 mg;

2) a DSC 204 F1 differential scanning calorimeter of thermal flow, tests were carried out in the range of temperatures from 30 to 270 °C at the rate of heating 10 °C min<sup>-1</sup> under argon atmosphere, argon was passed through the sample at 25 mL min<sup>-1</sup>, the measurement cell was purged with argon at 70 mL min<sup>-1</sup>, the weight of samples was 2–3 mg.

Boc-4-aminostyrene (1). A solution of Boc<sub>2</sub>O (2.75 g, 12.6 mmol) in 1,4-dioxane (10 mL) was added dropwise to a solution of 4-aminostyrene (1 g, 8.4 mmol) in 1,4-dioxane (20 mL) at 0 °C with continuous stirring in the flow of argon over 30 min. Then, the cooling was removed and the stirring was continued for 3 h at room temperature. The solvent was evaporated on a rotary evaporator, an oily residue was mixed with ethyl acetate, 10% aqueous KHSO<sub>4</sub> was added to pH 4.5, the mixture obtained was washed with water (3×100 mL), dried with MgSO<sub>4</sub>, and the solvent was evaporated. A precipitate that formed was filtered off, dried, recrystallized from n-hexane to obtain compound 1 (1.35 g, 73%) as white crystals, m.p. 86-87 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 1.51 (s, 9 H, Bu<sup>t</sup>); 5.15 (d, 1 H, =CH<sub>2</sub>, J = 22.0 Hz); 5.64 (d, 1 H, =CH<sub>2</sub>, J = 35.4 Hz); 6.58–6.71 (m, 2 H, CH=, NH); 7.33 (s, 4 H, Ar). Physicochemical and spectroscopic characteristics of Boc-4-aminostyrene 1 agree with those given in the literature.<sup>16</sup>

**Poly[(styrene)-co-(***N-tert***-butoxycarbonyl-4-aminostyrene)]** (2). Styrene (1.248 g, 0.012 mol), Boc-4-aminostyrene 1 (2.628 g, 0.012 mol), and a solution of AlBN (0.039 g, 1 wt.%) in DMA (5 mL) were placed into a 15-mL tube. The tube was evacuated at cooling with liquid nitrogen. The sealed tube was kept for 72 h at 75 °C. The copolymer obtained was precipitated in methanol (100 mL), filtered off, and dried for 24 h at 50 °C to obtain copolymer **2** (3 g, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.38 (br.s, 4 H, H(1)); 1.54 (s, 9 H, Bu<sup>t</sup>); 1.86 (br.s, 2 H, H(2)); 6.2–7.2 (br.m, 10 H, H(3)–H(7), NH).

**Poly[(styrene)-co-(4-aminostyrene)] (3).** A solution of copolymer **2** (3 g in a mixture of TFA and dichloromethane (15 mL) was stirred with magnetic stirrer for 3 h at room temperature. The solvent and excess of TFA were evaporated on a rotary evaporator, the residue obtained was dissolved in DMF and precipitated into ethanolic NaOH. A white precipitate that formed was filtered off and dried for 24 h at 40–50 °C to obtain copolymer **3** (1.9 g, 92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.43 (br.s, 4 H, CH<sub>2</sub>); 1.89 (br.s, 2 H, CH); 3.36 (br.s, 2 H, NH<sub>2</sub>); 6.2–7.2 (br.m, 9 H, H(3)–H(7)).

**2-Methylquinoline-3,4-dicarboxylic acid (4)** was obtained according to the known procedure.<sup>25</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 2.9 (s, 3 H, Me); 7.76 (t, 1 H, H(2), J = 7.6 Hz); 7.93 (t, 1 H, H(3), J = 7.6 Hz); 8.19 (d, 1 H, H(4), J = 8.8 Hz); 8.89 (d, 1 H, H(1), J = 9.0 Hz).

**2-Methylquinoline-3,4-dicarboxylic anhydride (5).** Acetic anhydride (16 mL, 0.17 mol)) was added to a mixture of 2-methylquinoline-3,4-dicarboxylic acid (4 g, 17.3 mmol) and anhydrous pyridine (12 mL) at 60–70 °C with continuous stirring. The reaction mixture was heated for 6 h at 60–70 °C, cooled to 8 °C, and kept for 24 h. A precipitate that formed was filtered off, washed with diethyl ether, and dried *in vacuo* at 60 °C to obtain anhydride **5** (2.98 g, 81%) as yellow crystals, m.p. 225–226 °C. Found (%): C, 67.81; H, 3.43; N, 6.35; O, 22.41. C<sub>12</sub>H<sub>7</sub>NO<sub>3</sub>. Calculated (%): C, 67.61; H, 3.31; N, 6.57; O, 22.51.

Poly[(styrene)-co-(4-aminostyrene)-co-(4-(4-methyl-1,3-dioxo-1,3-dihydropyrrolo[3,4-c]quinolin-2-yl)styrene)] (6). Anhydride 5 (1.1 g, 5.16 mmol (3% excess)) was added in one portion to a solution of copolymer 3 (1.2 g) in DMF (22.8 mL), cooled to -10 °C in the flow of argon with stirring. The reaction mixture was stirred for 1 h at -10 °C, then for 6 h at room temperature, and kept for 10 h. Pyridine (0.3 mL) and acetic anhydride (0.6 mL) were added into the reaction mixture, which was stirred for 6 h at room temperature. Then, the reaction mixture was heated to 60 °C and stirred for 1 h. A solution of copolymer was precipitated into 2% aq. Na<sub>2</sub>CO<sub>3</sub> (100 mL). A precipitate that formed was filtered off, washed with water, EtOH, and dried. Copolymer 6 was purified by reprecipitation from the solution in chloroform with light petroleum. The yield was 1.5 g (74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 1.53 (br.s 20 H, H(1)); 1.92 (br.s 10 H, H(2)); 2.55-3.15 (br.m, 12 H, Me), 6.25-7.25 (br.m, 47 H, H(3)-H(8)); 7.35-8.89 (br.m, 16 H, H(9)-H(12)). Intensities of signals were calculated taken n + k + m = 10.

**Preparation of modified polymers 7a-d (general procedure).** A mixture of copolymer **6** (0.35 g, 0.7 mmol on the Me groups of the quinoline ring), *o*-DCB (9.5 mL) and the corresponding aldehyde (1.05 mmol) was heated to boiling, piperidine (1 drop) was added, and the mixture was refluxed for 4 h. The solution was cooled and poured into EtOH (100 mL), a precipitate that formed was filtered off, washed with EtOH, and dried. Copolymers **7a-d** obtained were repricipitated from solutions in chloroform into light petroleum. In the <sup>1</sup>H NMR spectra of copolymers **7a-d**, signals related to the units *n*, *k*, and *m* are identical to the corresponding signals of copolymer **6**. Signals for the protons of units s are given below.

Poly[(styrene)-co-(4-aminostyrene)-co-(4-(4-(4-dimethylaminostyryl)-1,3-dioxo-1,3-dihydropyrrolo[3,4-*c*]quinolin-2yl)styrene)] (7a). The yield was 47%. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.53 (br.s 2 H, H(1)); 1.92 (br.s 1 H, H(2)), 2.91 (br.s 6 H, NMe<sub>2</sub>); 6.25–7.25 (br.m, 4 H, H(3)–H(6)); 7.31–8.89 (br.m, 10 H, H(9)–H(12), H(14), H(15), H(1')–H(4')).

Poly[(styrene)-co-(4-aminostyrene)-co-(4-(4-(4-methoxystyryl)-1,3-dioxo-1,3-dihydropyrrolo[3,4-*c*]quinolin-2-yl)styrene)] (7b). The yield was 62%. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.53 (br.s 2 H, H(1)); 1.92 (br.s 1 H, H(2)); 3.76 (br.s 3 H, OMe); 6.25–7.25 (br.m, 6 H, H(3)–H(6), H(1'), H(3')); 7.31–8.89 (br.m, 8 H, H(9)–H(12), H(14), H(15), H(2'), H(4')).

Poly[(styrene)-co-(4-aminostyrene)-co-(4-(4-(4-bromostyryl)-1,3-dioxo-1,3-dihydropyrrolo[3,4-*c*]quinolin-2-yl)styrene)] (7c). The yield was 49%. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.53 (br.s 2 H, H(1)); 1.92 (br.s 1 H, H(2)); 6.25–7.25 (br.m, 4 H, H(3)–H(6)); 7.31–8.89 (br.m, 10 H, H(9)–H(12), H(14), H(15), H(1')–H(4')).

Poly[(styrene)-co-(4-aminostyrene)-co-(4-(1,3-dioxo-4styryl-1,3-dihydropyrrolo[3,4-*c*]quinolin-2-yl)styrene)] (7d). The yield was 53%. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.53 (br.s 2 H, H(1)); 1.92 (br.s 1 H, H(2)); 6.25–7.45 (br.m, 6 H, H(3)–H(6), H(1')–H(3')); 7.45–8.89 (br.m, 9 H, H(9)–H(12), H(14), H(15), H (2'), H(4'), H(5')).

4-Methyl-2-(4-methylphenyl)pyrrolo[3,4-c]quinoline-1,3-dione (8). A solution of anhydride 5 (2.24 g, 0.01 mol) in DMF (20 mL) (pre-prepared by stirring on a magnetic stirrer over 1 h) was added to a solution of p-toluidine (1.125 g, 0.01 mol) in DMF (8.5 mL) cooled to -5 °C with stirring in the flow of argon, maintaining temperature below 10 °C. The reaction mixture was stirred for 1 h at 5 °C, then for 6 h at room temperature, and kept for 10 h. Pyridine (0.55 mL) and acetic anhydride (1.1 mL) were added to the reaction mixture, which was refluxed for 6 h, excess of the solvent was evaporated in vacuo. A precipitate that formed was filtered off, washed with EtOH, and dried. Recrystallization from the 1,4-dioxane-water solvent mixture yielded compound 8 (2.0 g, 63%) as light yellow crystals, m.p. 188 °C. <sup>1</sup>H NMR (CDCl<sub>2</sub>), δ: 2.45 (s, 3 H, H(1)); 3.1 (s, 3 H, Me); 7.35 (s, 4 H, H(2)-H(5)); 7.76 (t, 1 H, H(7), J = 7.6 Hz); 7.93 (t, 1 H, H(8), J = 7.6 Hz); 8.19 (d, 1 H, H(9), J = 8.8 Hz); 8.89 (d, 1 H, H(6), J = 9.0 Hz). Found (%): C, 75.11; H, 5.18; N, 8.76; O, 10.95. C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>. Calculated (%): C, 75.50; H, 4.63; N, 9.27; O, 10.60.

Synthesis of model compounds 9a-d (general procedure). A mixture of compound 8 (0.17 g, 0.56 mmol), o-DCB (5.3 mL) and the corresponding aldehyde (0.84 mmol) was heated to boiling, piperidine (1 drop) was added followed by reflux for 4 h. After cooling, excess of o-DCB was evaporated *in vacuo*. A precipitate that formed was filtered off, dried, and recrystallized from the 1,4-dioxane-water mixture.

**4-(4-Dimethylaminostyryl)-2-**(*p*-tolyl)**pyrrolo**[**3**,**4**-*c*]**quino-line-1,3-dione (9a).** Dark brown crystals. The yield was 61%, m.p. 262–264 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 2.47 (s, 3 H, H(1)); 3.07 (s, 6 H, NMe<sub>2</sub>); 6.74 (d, 2 H, H(14), H(15), *J* = 9.0 Hz); 7.38 (s, 4 H, H(2)–H(5)); 7.63–7.69 (m, 3 H, H(7), H(12), H(13)); 7.88 (t, 1 H, H(8), *J* = 7.9 Hz); 8.15–8.21 (m, 2 H, H(9), H(11)); 8.27 (d, 1 H, H(10), *J*=15.9 Hz); 8.83 (d, 1 H, *J*=7.6 Hz). Found (%): C, 76.87; H, 5.98; N, 9.14; O, 8.01. C<sub>28</sub>H<sub>23</sub>N<sub>3</sub>O<sub>2</sub>. Calculated (%): C, 77.60; H, 5.31; N, 9.70; O, 7.39.

**4-(4-Methoxystyryl)-2-**(*p*-tolyl)pyrrolo[3,4-*c*]quinoline-1,3dione (9b). Yellow crystals. The yield was 69%, m.p. 247–249 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 2.45 (s, 3 H, H(1)); 3.78 (s, 3 H, OMe); 7.06 (d, 2 H, H(12), H(13), J = 8.7 Hz); 7.35 (s, 4 H, H(2)–H(5)); 7.72 (d, 2 H, H(14), H(15), J = 8.6 Hz); 7.83 (t, 1 H, H(7), J = 8.0 Hz); 8.01 (t, 1 H, H(8), J = 8.0 Hz); 8.15–8.23 (m, 3 H, H(9)–H(11)); 8.74 (d, 1 H, H(6), J = 8.2 Hz). Found (%): C, 76.15; H, 5.28; N, 6.03; O, 12.54. C<sub>27</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>. Calculated (%): C, 77.14; H, 4.76; N, 6.67; O, 11.43.

**4-(4-Bromostyryl)-2-(***p***-tolyl)pyrrolo**[**3**,**4**-*c*]**quinoline-1**,**3dione (9c).** Light yellow crystals. The yield was 73%, m.p. 246 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 2.47 (s, 3 H, H(1)); 7.38 (s, 4 H, H(2)-H(5)); 7.55 (d, 2 H, H(12), H(13), J = 8.5 Hz); 7.62 (d, 2 H, H(14), H(15), J = 8.5 Hz); 7.74 (t, 1 H, H(7), J = 7.7 Hz); 7.93 (t, 1 H, H(8), J = 7.7 Hz); 8.22 (m, 2 H, H(9), H(11)); 8.38 (d, 1 H, H(10), J = 15.8 Hz); 8.87 (d, 1 H, H(6), J = 8.3 Hz). Found (%): C, 65.44; H, 4.13; N, 5.77; O, 7.87. C<sub>26</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>Br. Calculated (%): C, 66.52; H, 3.62; N, 5.97; O, 6.82.

**4-Styryl-2-**(*p*-tolyl)pyrrolo[3,4-*c*]quinoline-1,3-dione (9d). Greenish yellow crystals. The yield was 56%, m.p. 250–252 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 2.47 (s, 3 H, H(1)); 7.28–7.45 (m, 7 H, H(2)–H(5), H(14), H(15), H(16)); 7.70 (t, 1 H, H(7), *J* = 7.2 Hz); 7.76 (d, 2 H, H(12), H(13), *J* = 7.2 Hz); 7.91 (t, 1 H, H(8), *J* = 7.2 Hz); 8.21 (d, 1 H, H(9), *J* = 8.7 Hz); 8.28 (d, 1 H, H(11), *J* = 15.9 Hz); 8.38 (d, 1 H, H(10), *J* = 15.7 Hz); 8.84 (d, 1 H, H(6), *J* = 8.3 Hz). Found (%): C, 79.22; H, 5.16; N, 6.93; O, 8.69. C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>. Calculated (%): C, 80.00; H, 4.62; N, 7.18; O, 8.20.

The authors are grateful to Marietta Böhm, Dipl.-Ing., University of Bayreuth (Germany), Chair of Macromolecular Chemistry 2, for the study of copolymers by GPC.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 09-03-00408-a and  $N_{0} 09-03-12173$ -ofi\_m).

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Received April 20, 2010; in revised form November 16, 2010