

Reactions of Compounds Containing Benzoquinone-1,4-diimine Groups with Sulfuric Acid

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Received June 28, 2021; revised June 28, 2021; accepted July 13, 2021

Abstract—The reactions of poly(benzoquinone-1,4-diimine-*N,N'*-diyl-1,4-phenylene) and *N,N'*-di-(4-amino-phenyl)benzoquinone-1,4-diimine with sulfuric acid proceeded as 1,4-addition of sulfuric acid and water to quinonediimine groups. Relative rates of these reactions depend on concentration of sulfuric acid. Electrical conductivities of both synthesized and doped with acids compounds were determined. Maximum value of conductivity 10^{-7} S/cm for doped polymers was achieved in case of doping level approximately 30%.

Keywords: *p*-phenylenediamine, trimer, polymer, *p*-quinonediimine groups, sulfuric acid

DOI: 10.1134/S1070363221090115

Electroactive polymers are easily synthesized by oxidative polymerization of aromatic amines and are applied in various fields of technology. Among them, polyaniline has unique electrophysical properties [1–5]. One of the important properties of polyaniline is the ability of doping-dedoping equilibrium through acid-base reactions. For the first time, conducting polyaniline derivatives with attached acid residues were synthesized, which combining high solubility and electrical conductivity [6, 7], various applications of these polymers are considered. A large number of works are devoted to the study of the synthesis and properties of the obtained polymers [8].

Chemical methods for the preparation of polyaniline derivatives can be divided into two groups: modification of polyaniline and oxidative polymerization of monomeric sulfonic acids. Soluble in weakly alkaline solutions polyaniline with 50% substituted sulfonate groups of aromatic rings was obtained by the reaction of the emeraldine form of polyaniline with fuming sulfuric acid [6]. Polymers with different amounts of sulfonate groups were also obtained by the interaction of polyaniline with 95% sulfuric acid and Ag_2SO_4 [9], with oleum, with chloro- and fluorosulfonic acids [10–14]. Sulfonation of leuco polyaniline yields 75% sulfonated polymer [15]. Sulfonated polyaniline was also synthesized by reaction with sulfurous acid in an aqueous medium [16].

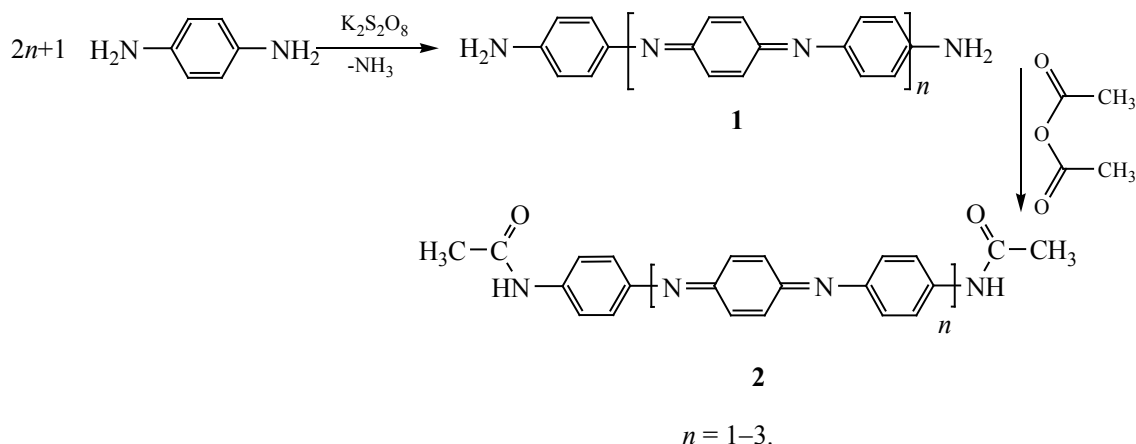
We have showed a method for preparing new polymers with attached sulfate groups, as well as polymers with hydroxyl and sulfate groups in the main chain.

Earlier, on the basis of the literature and experimental data obtained by us, a method was proposed for obtaining a polymer similar in structure to the completely oxidized pernigraniline form of polyaniline, the structure of which consists from successively added 1,4-quinonediimine and 1,4-phenylene groups with terminal NH_2 groups—poly(1,4-benzoquinonediimine-*N,N'*-diyl-1,4-phenylene) **1**. Polymer **2** was obtained by acetylation of the terminal amine groups (Scheme 1).

Oxidative condensation of *p*-phenylenediamine proceeds by a stepwise mechanism. At a molar ratio of monomer–oxidant 4 : 1, a trimer—*N,N'*-bis(4-aminophenyl)-1,4-benzoquinone diimine **3** and a pentamer were obtained. Indirect data about the high reactivity of quinonediimine groups were confirmed. These groups easily enter into Michael 1,4-addition reactions, and during the oxidative polymerization of *p*-phenylenediamine with potassium peroxydisulfate in hydrochloric acid, about 7% of the quinonediimine groups add sulfuric acid [17] (Scheme 2).

This gave us the idea of using the reaction of compounds **1** [18] and **2** [19] with sulfuric acid to obtain new polymers and oligomers with acidic sulfate groups.

Scheme 1.



Scheme 2.

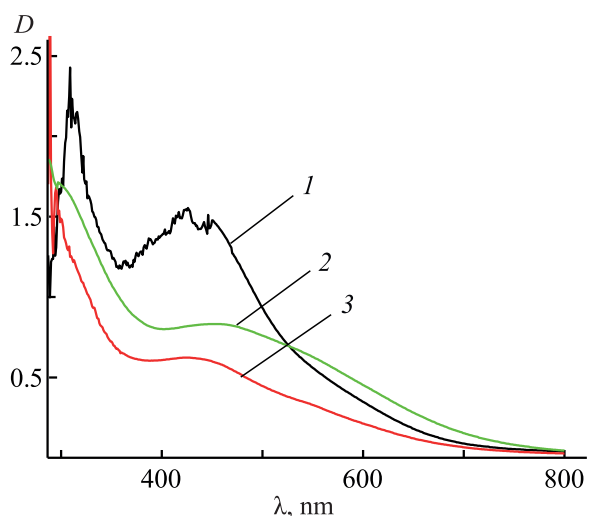
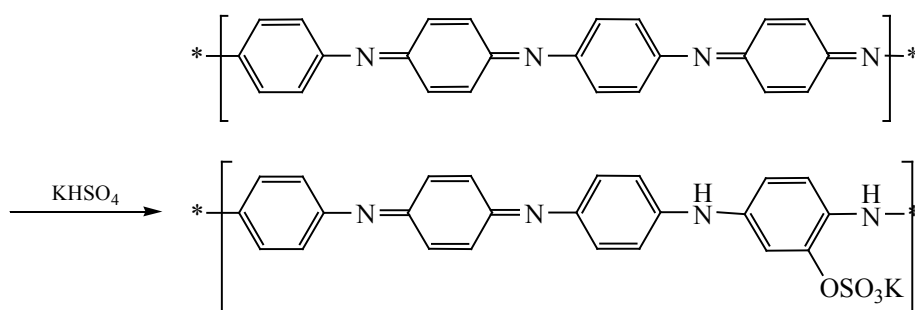
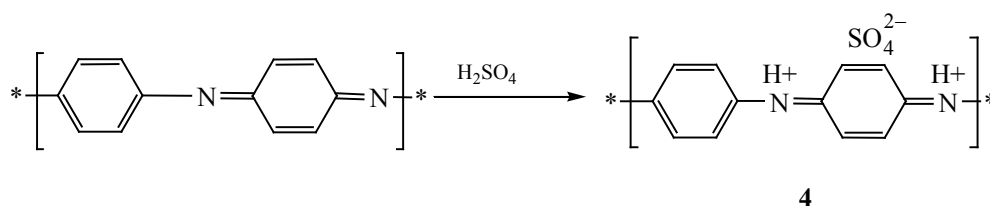


Fig. 1. Electronic spectra of compounds **1**, **4**, **6**. (1) **1**, $\lambda_{1\text{max}}$ 311 nm (D_1 2.155), $\lambda_{2\text{max}}$ 424–452 nm (D_2 1.50 [20]); (2) **4** (DMSO), $\lambda_{1\text{max}}$ 270 nm (D_1 1.95), $\lambda_{2\text{max}}$ 438 nm (D_2 0.83); (3) **6**, $\lambda_{1\text{max}}$ 286.6 nm (D_1 1.5), $\lambda_{2\text{max}}$ 415.5 nm (D_2 0.615).

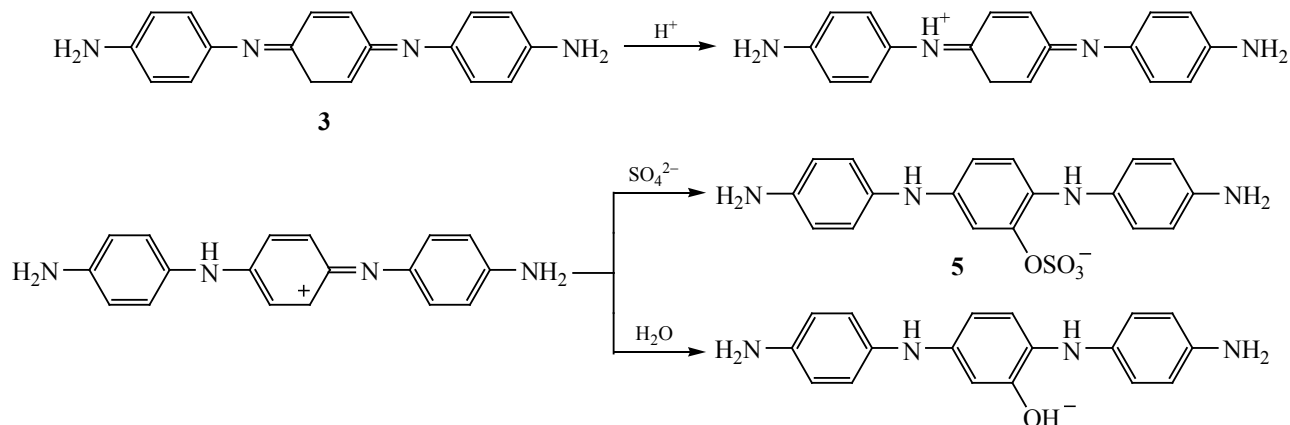
The effect of the concentration of sulfuric acid on the structure and properties of the obtained compounds was investigated. Since in the reaction of sulfuric acid with compound **1**, other than the Michael addition reaction, the salt formation reaction also proceeds (Scheme 3), the reaction product was treated with an aqueous solution of sodium carbonate.

According to literature data, pernigraniline reacts with 1 N hydrochloric acid during mixing [20]. It was this concentration that was chosen as the initial one for the reaction with sulfuric acid and we obtained compound **4**. According to elemental analysis data, 12.5–12.8% of quinonediimine groups reacted with sulfuric acid. The calculation was carried out taking into account the fact that the obtained compound contains only the initial groups and groups that have reacted with sulfuric acid. However, according to the electronic spectra of the starting compound **1** and the resulting compound **4** (Fig. 1), about 40% of the quinonediimine groups

Scheme 3.



Scheme 4.



underwent transformation. The conversion degree was calculated from a comparison of the absorption intensities of the quinonediimine groups of compounds **1** and **4** in the range 424–452 nm.

To obtain additional data, the same reaction with model compound **3** was studied. By comparing the intensities of chemical shifts of OH groups at 9 ppm (intensity 0.3) with the intensity of one proton of amino groups (0.5), it can be calculated that 60% of aromatic rings of compound **3** reacted with water. Based on the chemical shifts of the others protons at 5.7–8.6 ppm (intensity $6.7/0.5 = 13.44$) and taking into account the fact that 60% of the cycles reacted with water, as well as the fact that sulfate groups contain one crystal hydrate molecule, it is possible to calculate that 28% of aromatic rings of compound **3** reacted with sulfuric acid ($13.44 - 12.6 = 0.84$; $0.84/3 = 0.28$) (Scheme 4).

The comparison of the electronic spectra (Fig. 2) of compound **3** and the product of its interaction with 1 N sulfuric acid shows a decrease in the relative absorption intensity of quinonediimine groups at $\lambda_{3\text{max}}$ 496 nm in the spectrum of compound **3** due to their reaction with water. The dependence of the amount of sulfate and

hydroxyl groups on the concentration of sulfuric acid has been investigated. When carrying out the reaction of compound **3** with 0.5 N sulfuric acid solution, based on spectral data, it was calculated that 79% of quinonediimine groups reacted with water, and 15% one with sulfuric acid (according to elemental analysis of sulfur, 16.18%).

According to ^1H NMR data, there is no proton shift of hydroxyl groups in the spectrum of the reaction product **3** with 95% (35.52 N) sulfuric acid. Therefore, the reaction with water does not take place. Chemical shifts at 4.6–5.4 ppm correspond to NH_2 groups (the intensity of one proton is $2.5/4 = 0.63$), aromatic protons are recorded at 5.4–6.8 ppm (the intensity of one proton is $7.4/11 = 0.67$). The intensity of one proton, calculated from the total intensity of aromatic and amino groups, is $9.9/15 = 0.66$. Chemical shifts at 6.7–8.4 ppm, the shift of the protons of the NH groups and crystalline H_2O (intensity $2.7/4 = 0.67$) prove that after the precipitate is washed with methanol, the individual sodium salt of 2,5-di(4-aminophenylamino)phenyl sulfate **5** left.

The absorption at 420–489 nm in the electronic spectrum (Fig. 2) is probably the result of the reaction of sodium sulfate groups with the secondary amino groups

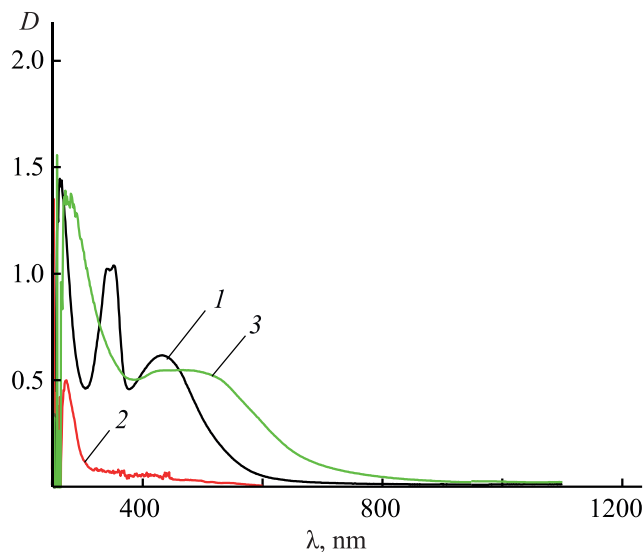


Fig. 2. Electronic spectra of compounds **3**, **5**. (1) **3**, $\lambda_{1\max}$ 260 nm (D_1 1.470), $\lambda_{2\max}$ 341 nm (D_2 1.454), $\lambda_{3\max}$ 496 nm (D_3 0.946 [19]); (2) reaction product of compound **3** with 1 N sulfuric acid solution, $\lambda_{1\max}$ 274 nm (D_1 0.47), $\lambda_{2\max}$ 370 nm (D_2 0.052); (3) **5** (DMF), $\lambda_{1\max}$ 276 nm (D_1 1.34), $\lambda_{2\max}$ 420–488 nm (D_2 0.71).

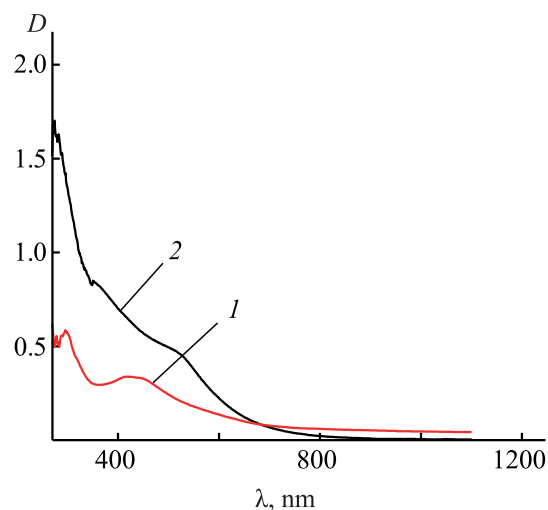


Fig. 3. Electronic spectra of compounds **2** and **7** (DMF). (1) **2**, λ_{\max} 292 nm (D_1 0.606), $\lambda_{2\max}$ 418–434 nm (D_2 0.323 [18]); (2) **7**, $\lambda_{1\max}$ 274 nm (D_1 1.64), $\lambda_{2\max}$ 353 nm (D_2 0.85), $\lambda_{3\max}$ 482 nm (D_3 0.51).

of compound **5**. The spectrum of poly(2-methoxy-5-sulfoxyaniline) has strong absorption at 452 nm [21], and poly(4-aminodiphenylamine-2-sulfonic acid) absorbs at 440 nm [22]. The solubility of compound **5** in water is 0.0015 g in 0.3 mL, 0.5 g in 100 mL.

The reaction of polymer **1** with 0.5 N and with 95% sulfuric acid has also been investigated. According to the results of elemental analysis, 8.4% of quinonediimine groups reacted with 0.5 N sulfuric acid with the formation of the reaction product **6**. This is also confirmed by the data of the electronic spectrum (Fig. 1). When polymer **1** interacts with 95% sulfuric acid in the mass without

solvent, the reaction proceeds very slowly, and in DMF medium it is slightly faster at 20°C (Table 1).

For comparison, polymers **7** with different amounts of sulfate groups (52 and 23%) were obtained by reaction of compound **2** with 95% sulfuric acid. Electronic spectra (DMF) of compound **7** (52 and 23% sulfate groups) are very similar (Fig. 3). Comparison with the spectrum of compound **2** [18] shows that a reaction of sulfate groups with phenylenediamine groups have occurred.

The electrical conductivities of compounds **4** (2.8×10^{-9}) and **7** (52% conversion)— 2.5×10^{-9} S/cm were determined. The initial polymers have an electrical

Table 1. Reaction of polymers **1** and **2** with sulfuric acid

no.	Polymer		DMF, mL	Sulfuric acid			Stirring time, h/ reaction time, days	Yield, g	Conversion degree, %
	m , g	x , mmol		c	V , mL	x , mmol			
1	0.0515	0.286	1.5	0.5 H.	6.8	1.72	43.5/9	0.04595	8.4
1	0.1022	0.567	—	1 H.	6.8	3.4	35.5/8	0.0944	13.8
2	0.2	1.111	20	95%	0.36	6.315	27/4	0.0876	23
1	0.13235	0.73	—	95%	1.09	19.7	20.5/4	0.123	22
2	0.15155	0.842	15	95%	0.36	6.88	33.5/8	0.25	52

conductivity of $<10^{-11}$ S/cm, and with the appearance of sodium sulfate groups in the polymer structure, the electrical conductivity increases by more than three orders of magnitude. Treatment of the last compound with 95% sulfuric and 3 N hydrochloric acids led to approximately the same values of electrical conductivity— 2.6×10^{-7} and 2.2×10^{-7} S/cm, respectively.

New polymers have been obtained containing hydroxyl and sulfate, as well as only sulfate groups attached to iminophenylene structural units of the polymer chain. Polymers have semiconducting properties, however, the electrical conductivity is low compared to other polymers with a similar structure. When doping of pernigraniline with 1 N hydrochloric acid, 50% of quinonediimine units react with hydrochloric acid [20], and the resulting polymer has an electrical conductivity of ~ 0.1 S/cm. This conductivity cannot be considered the conductivity of the salt form of pernigraniline, since the addition of hydrogen chloride to quinonediimine units leads to the chlorine-substituted form of emeraldine and, accordingly, the salt form of the latter is obtained. At 52% conversion of polymer **2** with sulfuric acid, similar results could be expected, but the obtained values of electrical conductivity are much lower.

EXPERIMENTAL

Compounds **1** and **2** were synthesized according to the procedure [18], as well as compound **3** [19]. Electronic spectra were performed on a Specord 65 spectrophotometer. IR spectra were recorded on a Nicolet/Nexus FT IR spectrometer. NMR spectra were recorded on a Mercury 300 Varian NMR spectrometer. To measure the electrical conductivity, polymer powders were pressed into tablets under a pressure of 30 kg/cm². Conductivity was measured using an AT512 Precision Resistance Meter device.

Reaction of polymers **1** and **2** with sulfuric acid.

Sulfuric acid was added to polymer **1** or to a mixture of polymer **2** and DMF and stirred for several hours at 20°C. In the intervals, the reaction mixture was kept at 20°C. The reaction time was several days (see Table 1). After interacting with 1 N and 0.5 N sulfuric acid solutions, the reaction mixture was filtered off, the precipitate was washed with cold distilled water to pH 7. The precipitate was stirred for several hours with a 15% sodium carbonate solution at 0–2°C (1.2 mol of Na₂CO₃ was added per 1 mol of polymer). During reaction with 95% sulfuric acid, 1.1 mol of a 15% sodium carbonate solution was added

to the reaction mixture per 1 mol of acid at 0–2°C, after which the mixture was stirred for 6 h. The mixture was filtered, the precipitate was washed with cold distilled water until neutral medium and the absence of sulfate ions, washed with alcohol, and dried in vacuum over P₂O₅ (0.2 kPa).

Polymer (4). IR spectrum, ν , cm⁻¹: 3423, 3339 (NH, NH₂), 3211 (CO–H), 2921 (C–H), 2852, 1629 (NH, NH₂), 1608 (C=C, benzene ring), 1512 (C=C, benzene ring), 1412 (SO₄), 1384 (CH), 1351 (SO₄), 1309 (NH), 1289 (OH), 1175 (SO₄), 1086 (OH), 1175, 1135 и 949 (1,2,4-trisubstituted benzene ring), 831 (C–H, 1,4-disubstituted benzene ring), 619 (SO₄).

Polymer (6). IR spectrum, ν , cm⁻¹: 3423, 3351 (NH, NH₂), 3230 (O–H), 2962, 2925, 2852 (C–H), 1629 (NH), 1608 и 1512 (C=C, benzene ring), 1412 (SO₄), 1384 (=NC), 1351 (SO₄), 1309 (NH), 1290 (OH), 1176 (SO₄), 1136, 1085, 958 (1,2,4-trisubstituted benzene ring), 831 (C–H, 1,4-disubstituted benzene ring), 619 (SO₄).

Polymer (7) (52% conversion). IR spectrum, ν , cm⁻¹: 3458, 3323, 3203 (N–H), 3051, 2917, 2848 (C–H), 1602 (C=C, benzene ring), 1508 (C=C, benzene ring), 1412 (SO₄), 1385 (=N–C), 1369 (SO₄), 1309 (NH), 1255 (NH–C), 1174 (SO₄), 1099, 1022 (1,2,4-trisubstituted benzene ring), 827 (C–H, 1,4-disubstituted benzene ring), 659, 619 (SO₄).

Compound (5). 0.204 g (2.08 mmol) of pre-cooled 95% sulfuric acid was added to 0.1 g (0.3472 mmol) of compound **3** with cooling. The reaction mixture was kept at room temperature for 8 days, and then the reaction was carried out with sodium carbonate as described above. The reaction mixture was stirred at 0–5°C for 6.5 h, and then filtered. The precipitate was washed with methanol until the absence of trimer **3**. The insoluble part was dried in vacuum over P₂O₅ (0.2 kPa). Yield 0.078 g (56%). IR spectrum, ν , cm⁻¹: 3419, 3342, 3219 (NH₂, NH), 2926 (CH), 1629, 1618 (NH₂, NH), 1607 (C=C, benzene ring), 1514 (C=C, benzene ring), 1439 (SO₄), 1384, 1350 (NH, SO₄), 1290 (NH), 1174, 1132 (1,2,4-trisubstituted benzene ring), 832 (C–H, 1,4-disubstituted benzene ring), 622 (SO₄). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 4.6–5.4 m (4H, NH₂), 5.4–6.8 m (11H_{Ar}), 6.7–8.4 m (4H, NH, H₂O).

Reaction of compound **3 with 1 N sulfuric acid solution (1 : 12 eq).** The experiment was carried out similarly to the above. 4.2 mL of 1 N H₂SO₄ solution was added to 0.1 g (0.347 mmol) of aniline trimer **3**, and kept at room temperature for 2 days, then reacted with

sodium carbonate as described above, stirred at 0–5°C for 6.5 h. The precipitate was washed with methanol until the absence of trimer **3**. Yield of methanol-insoluble residue 0.026 g, mp >290°C. ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 5–5.5 m (4H, NH₂), 5.7–8.6 m (15H, H_{Ar}, NH, H₂O), 9–9.2 m (1H, OH).

Reaction of trimer 3 with 0.5 N sulfuric acid solution (1 : 12 eq.). To 0.099 g (0.34 mmol) of compound **3**, 8.3 mL of 0.5 N sulfuric acid solution was added and stirred at 20–25°C for 24 h, then made alkaline with 0.25 g of 10% sodium carbonate solution and stirred at 0–4°C for 6 h. The precipitate was filtered off, washed with cold water and treated with methanol 2 times. Methanol-soluble part—0.01 g. The methanol-insoluble residue (0.088 g) was dried in vacuum over P₂O₅ (0.2 kPa). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 5–5.4 m (4H, NH₂), 5.7–8.6 m (15H, H_{Ar}, NH, H₂O), 9.0 s (1H, OH). Found S, %: 16.3.

Treatment with hydrochloric acid. To 0.05 g of a finely ground polymer, 1.9 mL of 3 N sodium hydroxide solution was added hydrochloric acid, and kept for 7 days at room temperature. The precipitate was filtered off, washed with small amount of ethanol and dried to constant weight in a vacuum in a desiccator over P₂O₅ (2 kPa). Treatment with 95% sulfuric acid solution was carried out as described above, but 1 mL of acid was taken per 1 g of polymer.

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FUNDING

This study was financially supported by the Enterprise Incubator Foundation (EIF) and PMI Science.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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