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LETTERS TO THE EDITOR

Synthesis of Azine Redoxites

L. B. Dzaraeva[a,b], M. I. Gusalova[a], V. Kh. Sabanov[c], R. D. Dzhatieva[c], and A. F. Abaeva[c]

[a] *K.L. Khetagurov North Ossetian State University, Vladikavkaz, North Ossetia-Alania, Russia*

[b] *North Ossetian Medical Academy, ul. Pushkinskaya 40, Vladikavkaz, North Ossetia-Alania, 362025 Russia*
e-mail: miladzaraeva@mail.ru

[c] *Innovation Technological Center of Materials Research, Vladikavkaz, North Ossetia-Alania, Russia*

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Hard-to-get substituted pyridinium redoxites with "inverted" position of the heteroatom are of interest for the preparation of photogenerated luminophores, floculants, emulgators for polymerization of styrene and acrylonitrile, inhibitors of the electrode corrosion in chemical power sources [1,2].

In this paper, in continuation of the studies on the use of pyrilium salts for the synthesis of azine redoxites [3], we have synthesized redoxites on the basis of poly[2,4,6-triphenyl-1-(4-vinylphenylene) pyrilium] and poly[*N*-vinyl-2,4,6-triphenylpyridinium] perchlorates, as well as the polymer charge transfer complex (CTC) on the basis of polyvinyl ester of isonicotinic acid quaternized at the nitrogen atom. The conductivity properties of the synthesized polymers were investigated (resistivity, electric conductivity, specific volume electrical resistivity).

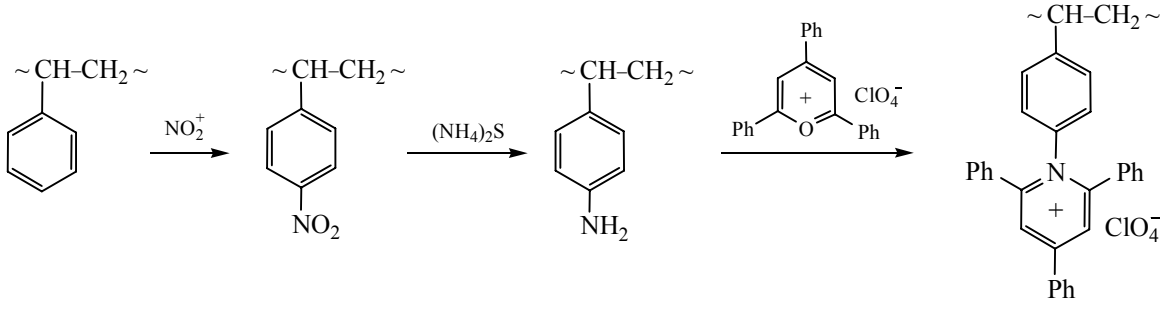
4-(*N*-2,4,6-Triphenylpyridinium) polystyrene perchlorate, which hardly can be synthesized by any alternative method, is formed by the reaction of 2,4,6-triphenylpyrilium perchlorate with 4-aminopolystyrene prepared by nitration of polystyrene **I** [4] and reduction of 4-nitropolystyrene with ammonium sulfide according to Scheme 1.

Formed polymer **III** is a red-brown solid with softening temperature of 243–249°C, practically insoluble in benzene, acetone, methanol, and possessing the properties of electro-exchange resin with the reduction potential E = –0.86 V with respect to the normal calomel electrode (DMF, tetraethylammonium perchlorate).

The reaction of 2,4,6-triphenylpyrilium perchlorate with the commercially available polyvinylamine with molecular mass of 750 proceeds in a similar way (Scheme 2).

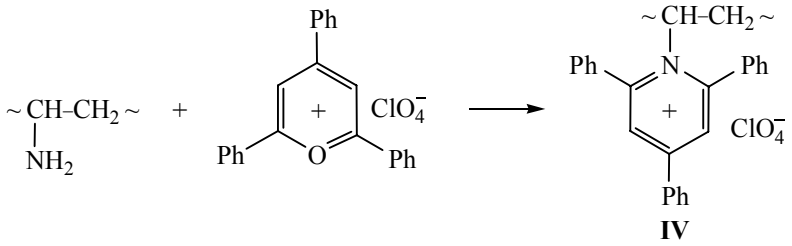
Polymer **IV** with the softening temperature of 180–190°C is readily soluble in acetone, toluene, acetonitrile, DMF. Polymers **III** and **IV** are reversibly

Scheme 1.



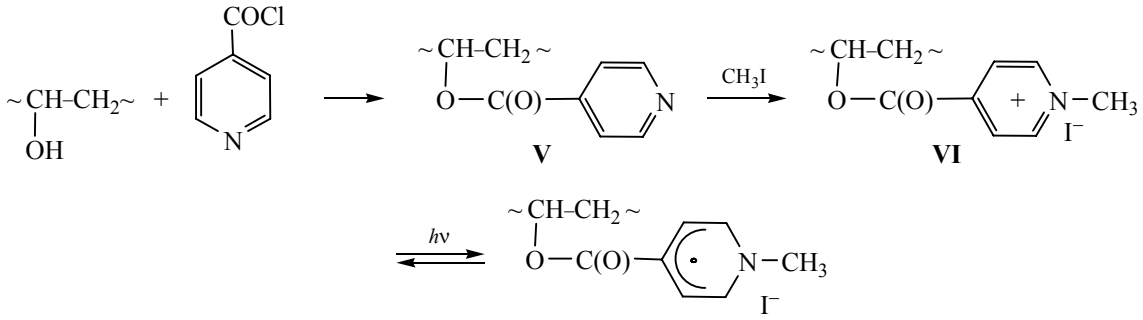
I **II** **III**

Scheme 2.



IV

Scheme 3.



reduced to the corresponding pyridinium polyradicals electrochemically or by the action of zinc powder.

Esters of isonicotinic acid quaternized at the nitrogen atom are CTCs and under the action of light are reversibly transformed into the radical pair due to the electron transfer from the anion to the cation [5]. This fact made it possible to prepare light-sensitive polymers containing similar groups by esterification of polyvinyl alcohol with isonicotinic acid chloride followed by quaternization of the reaction product with methyl iodide (Scheme 3).

In the electronic spectra of the prepared polymer a band is observed at 360 nm corresponding to CTC formation. The reduction of the cation-containing polymer leads to the pyridinyl polyradical stable under anaerobic conditions, showing a typical absorption in the UV region (320 nm). The obtained poly-CTC is an effective inhibitor of corrosion of aluminum metal in alkaline medium.

Conductive properties of the obtained polymers are as follows: Specific volume electrical resistivity (Ω cm) = 5.7×10^4, resistivity (cm/Ω) = 4.2×10^{-3}, electric conductivity $(\Omega\ \text{cm})^{-1} = 1.4 \times 10^{-5}$ for **III**; 5.9×10^5, 4.1×10^{-4}, 1.6×10^{-4} for **IV**, and 6.2×10^4, 3.9×10^{-4}, 1.5×10^{-3} for **V**. These values have been determined at constant voltage according to GOST 6433.2-71 on the samples in the form of discs of 10 mm diameter.

Comparison of the obtained parameters with those for electroconductive materials allows a conclusion that the synthesized polymers are semiconductors.

4-Nitropolystyrene (I) was prepared by the procedure [2]. White solid with soft.p. 150–160°C. IR spectrum, ν, cm^{-1}: 2850 (CH, CH_2), 1630 (aromatic ring), 1520, 1340 (NO_2).

4-Aminopolystyrene (II) was prepared by shaking 4-nitropolystyrene with aqueous solution of ammonium sulfide for 5 h until complete reduction. The precipitate was filtered off, washed with water, alcohol, and dried to obtain light-brown solid with soft.p. 200–210°C. IR spectrum 850 cm^{-1} (C–N).

Poly[2,4,6-triphenyl-1-(4-vinylphenylene)pyridinium] perchlorate (III). A mixture of 1.19 g (0.01 mol) of 4-aminopolystyrene and 4.87 g (0.01 mol) of 2,4,6-triphenylpyrilium perchlorate in 30 mL of acetic acid was refluxed for 2 h, cooled, the precipitate was filtered off, washed with water and alcohol to obtain red-brown solid with soft.p. 210–220°C, moderately soluble in acetonitrile. Yield 4.5 g (85%). IR spectrum, ν, cm^{-1}: 850 (C–N). ^{1}H NMR spectrum, $CDCl_3$, δ, ppm: 8.98 s (5H, C_6H_5), 8.90 s (CH), 8.51 d (CH), 8.41 d (CH), 6.82 d (CH), 7.79 m (4H); 3.50 s (CH); 1.30 s (CH).

Poly[1-vinyl-2,4,6-triphenylpyridinium] perchlorate (IV). 0.44 g (0.01 mol) of polyvinylamine and 4 g

(0.01 mol) of 2,4,6-triphenylpyrilium perchlorate was dissolved in DMF, refluxed for 2 h, the formed precipitate filtered, washed with water, alcohol and dried to obtain light-brown solid with soft.p. 180–190°C, yield 4 g (92%). IR spectrum, ν, cm^{-1}: 1350 (C–N), 1100 (ClO_4^-).

Poly[4-carboxyvinylpyridine] (V). Mixture of 2.5 g (0.02 mol) of isonicotinic acid and 6 g of thionyl chloride was refluxed until complete dissolution of isonicotinic acid. The excess of thionyl chloride was distilled off, and to the residue the solution of 0.9 g (0.02 mol) of polyvinyl alcohol in pyridine was gradually added at cooling and vigorous stirring. The formed precipitate was filtered off, washed with water and alcohol. The dried product was a white solid with soft. p. 300°C. Yield 2 g (90%). IR spectrum, ν, cm^{-1} : 2860–2990 (CH, CH_2), 1735 (C=O), 1350 (C–N), 1620, 770 (pyridine ring).

Poly[4-carboxyvinyl-1-methylpyridinium] iodide (VI). 1 g of 4-carboxyvinylpyridinium and 5 g of methyl iodide were sealed in an ampule and heated on a boiling water bath until dissolution of the precipitate. The reaction product was sedimented with hexane, the precipitate was filtered off and dried in air to give a red-orange compound with soft.p. 190–200°C. Yield 1.2 g (80%). IR spectrum, ν, cm^{-1}: 2855 (CH, CH_2), 1735–1680 (C=O), 1650 (C=N). UV spectrum: λ_{max} = 320 nm (CTC).

IR spectra were registered on a Magna IR 750 Calybrum Fourier spectrometer. ^1H NMR spectra were taken on a Bruker BioSpin spectrometer at 400 MHz; residual signals of chloroform were used as an internal reference.

REFERENCES

1. Kruchinina, N.E., Timasheva, N.A., Ivantsova, N.A., and Alekseeva, M.A., *Voda i Ekologiya: Problemy i Resheniya*, 2013, no. 4 (56), p. 36.
2. Letuta, S.N., *Opt. Spektroskop*., 1990, vol. 68, no. 2, p. 344.
3. Dzaraeva, L.B., Sabanov, V.Kh., Dzhatieva, R.D., and Abaeva, A.F., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 8, p. 1526. DOI: 10.1134/S1070363213080094.
4. Japan Patent 49-15957, 1970, *C. A.*, 1974, vol. 24, p. 225.
5. Kosower, E., *Molecular Biochemistry*, New York: McGraw-Hill, 1962. Translated under the title *Molekulyarnaya biokhimiya,* Moscow: Mir, 1964, p. 201.