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# Pyrylium Salts in the Synthesis of Redoxites

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**Abstract**—Redoxites poly(2,6-diphenyl-4-vinylpyran), poly(2,6-diphenyl-4-vinylpyrylium perchlorate), poly-(2,6-diphenyl-4-vinylpyridine) and poly(2,2',6,6'-tetraphenyl-γ,γ'-dipyridine) were obtained based on pyrylium salts. Poly(2,2',6,6'-tetraphenyl-γ,γ'-dipyridine) was transformed into the polyene to improve its film-forming and conducting properties. Electrochemical properties of polyviologen and conductive properties of the obtained polymers were studied.

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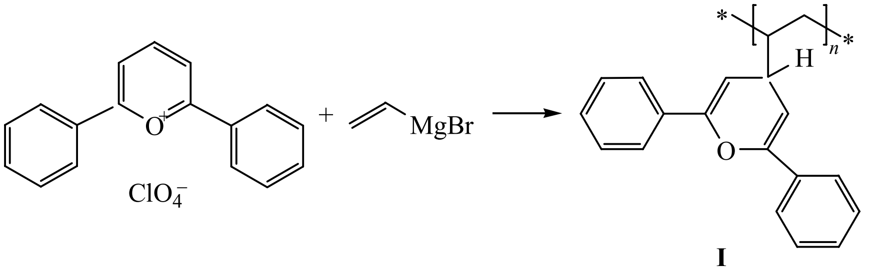
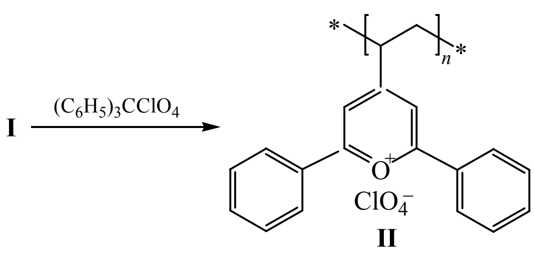
In continuation of our studies on the synthesis of redoxites [1], we obtained some polymers using pyrylium salts as synthons for macromolecules containing pyridinium groups.

Introduction of pyrylium cations into the polymer side chain is of great interest. Firstly, this opens a possibility to obtain redoxites, i. e., substances that can exchange electrons. Secondly, an ease of the replacement of a heteroatom in pyrylium ring makes available a wide range of the polymers containing pyridine, thiapyrylium and other heteroaromatic groups. The obtained pyridinium-containing polymers are of interest for the synthesis of redoxites of azine series, which are conductive materials. This opens the opportunity of synthesizing new nitrogen-containing viologenic polymers. The known preparation methods are unsuitable for them or laborious. Polymers containing γ,γ'-bipyridinium (viologenic) groups are attracting attention as electron-exchange membranes and potential semiconductors. Besides these materials are very promising due to their electrochromic properties.

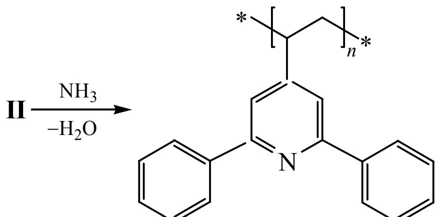
Using the ability of γ-unsubstituted pyrylium salts to react with the active organometallic compounds to form 4*H*-pyrans, we attempted preparation of 4-vinyl-2,6-diphenylpyran with subsequent polymerization. Its appeared, however, according to the film-forming properties and IR spectroscopy data, the polymer was formed at the stage of pyran formation.



Solutions of the obtained oligomer in chloroform and benzene form transparent films after drying. Their softening temperature varies between 120–130°C. The oxidation of poly(2,6-diphenyl-4-vinylpyran) **I** with an excess of trityl perchlorate results in poly(2,6-diphenyl-4-vinylpyrilium perchlorate) **II** identified using IR spectroscopy and elemental analysis data.



The oxygen atom in the pyrylium salt can be replaced by another heteroatom by the action of nucleophilic reagents. The treatment of poly(2,6-diphenyl-4-vinylpyrylium perchlorate) with 25% ammonia solution results in poly(2,6-diphenyl-4-vinylpyridine) **III** identified by IR spectroscopy and elemental analysis data.

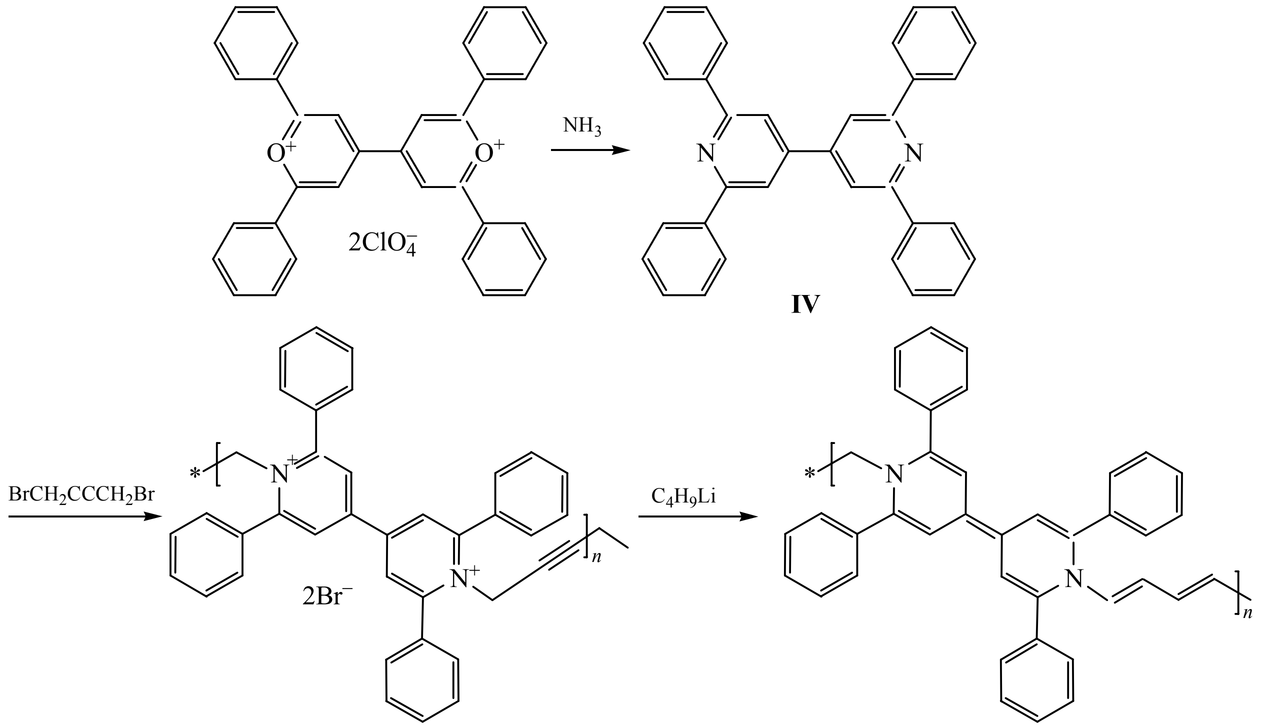


**III**

After drying, a solution of poly(2,6-diphenyl-4-vinylpyridine) **III** in acetonitrile gives a transparent film.

Treating of readily 2,2',6,6'-tetraphenyldipyrylium diperchlorate with ammonium acetate in acetic acid [2] results in γ,γ'-dipyridine **IV**, starting from which we obtained substituted azine polymer **V** of viologen type.

In order to improve the film-forming and conductive properties the polymer **V** was transformed into the polyene **VI** by treatment with butyllithium.



It is difficult to obtain polymers containing the substituted dipyridinium salts in the main chain (substituted polyviologens) by any other methods. These polymers are brown powders melting at 310 and 285°C, respectively. They are soluble in DMF, moderately soluble in acetonitrile and acetic acid, and the second one, also in toluene. The resulting polymers have the pronounced electron-exchange properties.

Electrochemical properties of polyviologen **V** were studied by cyclic voltammetry ($E_{\text{p}K}$ –0.80, –1.27 V, DMF, 0.1 M NaClO$_4$ vs saturated mercury chloride electrode, on platinum electrodes). By cyclic voltammetry data, the reduction of polycation involves two reversible one-electron (relative to each unit) wave corresponding to stable poly(radical-cation) and then to the completely reduced quinoid structure. Polymers of this type have the properties of active electron donors: they reduce triphenylpyrylium and phenyldiazonium cations and sterically hindered *o*-quinones.

The application of heteroaromatic polymer redoxites as acceptor components of photosensitive compositions of the information recording or film forming bases for electrochromic devices is based on easy one-electron transfer. Polymeric redoxites are

The conductive properties of polymers **I**–**VI**

| Comp. no. | Volume resistivity, $\Omega$ cm | Electrical resistivity, cm $\Omega^{-1}$ | Electrical conductivity, $\Omega^{-1}$ cm$^{-1}$ |
|---|---|---|---|
| **I** | $5.8\times10^{4}$ | $4.2\times10^{-3}$ | $1.4\times10^{-4}$ |
| **II** | $6.3\times10^{3}$ | $4.0\times10^{-4}$ | $2.0\times10^{-4}$ |
| **III** | $6.2\times10^{4}$ | $3.9\times10^{-4}$ | $1.5\times10^{-3}$ |
| **V** | $5.9\times10^{4}$ | $4.2\times10^{-5}$ | $1.4\times10^{-5}$ |
| **VI** | $6.3\times10^{7}$ | $3.6\times10^{-4}$ | $2.0\times10^{-4}$ |

also highly effective inhibitors of corrosion of aluminum electrodes in electrochemical cells.

The determined conductivity, electrical conductivity, volume resistivity of the polymers obtained are given in the table.

The measurement of volume resistivity was carried out at a constant voltage according to GOST 6433.2-71 using samples as discs of 10 mm in diameter and also in powder form.

Comparing the data obtained with the values of these parameters for the electrically conductive materials, it can be concluded that these compounds are semiconductors.

## EXPERIMENTAL

**Poly(4-vinyl-2,6-diphenyl-4*H*-pyran) (I).** To 0.6 g of magnesium in 20 ml of anhydrous tetrahydrofuran under argon was added 3 ml of vinyl bromide (activation with bromine), maintaining the temperature in the range of 40–50°C. The resulting vinyl magnesium bromide was filtered off under argon. To an obtained solution was added dropwise a suspension of 2,6-diphenylpyrylium perchlorate in THF. The mixture was stirred for 1 h, and then treated with saturated solution of $NH_4Cl$. The organic layer was separated and water layer extracted with diethyl ether. Combined extract was dried over $CaCl_2$ and the solvent was distilled off in a vacuum. The residue was dissolved in acetonitrile and treated with a double excess of tritylperchlorate. Yellow-green powder was obtained, softening point 140–150°C. IR spectrum, ν, cm$^{-1}$: 1100 ($ClO_4^-$), 1650 (pyrylium ring), 2900–2850 (CH, $CH_2$). Found, %: C 62.03; H 3.81; Cl 9.66. $[C_{19}H_{15}ClO_4]_n$. Calculated, %: C 63.59; N 4.18; Cl 9.90.

**Poly(4-vinyl-2,6-diphenylpyridine) (III).** A sample of 1 g of poly(2,6-diphenyl-4-vinylpyrylium perchlorate) was kept in 25 ml of 25% ammonia solution for 24 h. The precipitate was filtered off, washed with water, and dried. Yield 0.6 g. IR spectrum, ν, cm$^{-1}$: 1200 (pyridine ring), 1620 (C=N bond in the pyridine ring), the band at 1100 ($ClO_4^-$) is absent.

**2,2',6,6'-Tetraphenyldipyridine (IV).** A mixture of 0.01 mol (6.31 g) of 2,2',6,6'-tetraphenylbispyrylium diperhlorate and 0.2 mol of ammonium acetate (15 g) in 50 ml of acetic acid was refluxed for 1 h, and then was cooled and poured into water. The obtained 2,2',6,6'-tetraphenyldipyridine was filtered off, washed with water, and dried. Yield 4.14 g (90%), colorless crystalline solid, mp 247°C (ethanol). IR spectrum, ν, cm$^{-1}$: 1620 (C=N, pyridine). Found, %: C 86.5; H 4.95; N 5.01. $C_{34}H_{24}N_2$. Calculated, %: C 88.7; H 5.22; N 6.09.

**Poly[*N*,*N*'-1,4-but-2-ynediyl-(2,2',6,6'-diphenyl-γ,γ'-dipyridinium dibromide)] (V).** A mixture of 0.02 mol (9.2 g) of 2,2',6,6'-tetraphenyldipyridine and 0.01 mol (2.32 g) of 1,4-dibromobut-2-yne was heated in 59 ml of dimethylformamide for 2 h. The reaction mixture was poured into water. The precipitate was filtered off, washed with water, and dried. Yield 5.51 g (82%), red-brown powder, softening point 310°C. IR spectrum, ν, cm$^{-1}$: 2230 (C≡C), 2550, 1620. Found, %: C 67.86; H 4.17; N 4.17; Br 23.80. $C_{38}H_{28}N_2Br_2$. Calculated, %: C 66.13; H 4.35; N 3.76; Br 21.86.

**Polyene VI.** A mixture of 0.01 mol (6.68 g) of salt **IV** and an excess of butyllithium solution was kept in an inert atmosphere for 12 h. Then the resulting polyene was filtered off, washed with water, with alcohol, and dried. Yield 4.05 g (80%), brown powder, softening point 285°C. IR spectrum, ν, cm$^{-1}$: 3035 (C–H), 1650 (C=C). Found, %: C 88.10; H 4.35; N 4.12. $C_{38}H_{28}N_2$. Calculated, %: C 89.06; H 5.47; N 5.47.

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