A. A. Berlin and E. F. Razvodovskii

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Abstract

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A. A. Berlin and E. F. Razvodovskii

On the Synthesis of Polymers with Charged Heteroatoms in the Chains of Macromolecules

Onium Polymerization

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Chemistry

The synthesis and study of the properties of polymers with charged heteroatoms in the main chain have until recently not attracted the proper attention of scientists.

At the same time, the development of such work could lead to the creation of a large number of new classes of polymeric substances possessing a very interesting combination of electrical, magnetic, electrochemical, catalytic, and a number of other properties. The basis for developing methods of synthesis of such polymeric substances is provided by data from the chemistry of onium compounds ([1]), as well as by several studies on the preparation of polymers with quaternary ammonium ([2,3]) and pyridinium ([4]) groups. We have investigated the fundamental possibility of obtaining "onium polymers" using the example of the polymerization of 4-chloropyridine—a substance containing a nucleophilic nitrogen atom and a labile halide. When 4-chloropyridine (XII), free from pyridine impurity, is heated at 50-60°, as also when it is kept at 20°, a polymeric product colored yellow-brown is formed. Comparison of the elemental composition of monomeric XII and polychloropyridine shows that in the course of heating or irradiation no cleavage of any atoms or groups is observed (see Table 1). In contrast to monomeric chloropyridine, the polymer contains 90% titratable ionic chlorine of the total amount. The number-average degree of polymerization, determined from terminal chlorine and nitrogen, is 8-14 (M_n = 912–1600). Investigation of the IR spectra of the synthesized products showed a sharp increase in absorption in the region of 802 cm^{-1} in comparison with chlorinated pyridylpyridinium, which indicates the presence of para substitution; the appearance of maxima absent in 4-chloropyridine in the interval 1360–1310 cm^{-1}, corresponding to the presence of −C−N-bonds; and a sharp weakening of the frequencies characteristic of the −C−Cl bond.

Thus the elemental composition, as well as the spectral data, make it possible to regard the product obtained as a polymer containing chloropyridinium units and terminal chlorine and nitrogen atoms. The formation of such polymers apparently proceeds by a stepwise mechanism through a stage of ionized complexes with charge transfer (I) and of a dimer (II). In II the mobility of the terminal halide increases sharply owing to the high electrophilicity of the

positively charged nitrogen. In view of this, further chain development proceeds through migration of the terminal halide to the nitrogen of 4-chloropyridine

$$2\,\mathrm{Cl{-}C_5H_4N} \longrightarrow [\mathrm{Cl{-}C_5H_4N{:}} + \mathrm{C_5H_4N{-}Cl}] \longrightarrow \mathrm{Cl{-}C_5H_4N^+(Cl^-){-}C_5H_4N} \quad \text{(II)}$$

$$\mathrm{N{-}C_5H_4{-}N^+(Cl^-){-}C_5H_4{-}Cl} + n\,\mathrm{N{-}C_5H_4{-}Cl} \longrightarrow \mathrm{N{-}C_5H_4{-}[N^+(Cl^-){-}C_5H_4]_n{-}N^+(Cl^-){-}C_5H_4{-}Cl} \quad \text{(III)}$$

Chain growth is also possible through block polymerization of reactive macromolecules of type III. Such a process leads to the formation of a fraction of higher-molecular-weight products. However, under the experimental conditions adopted, the proportion of such fractions can hardly be high, both because of the lower reactivity of the terminal nitrogens III and because of the cage effect at the high viscosity of the system in the later stages of the reaction.

The observed sharp acceleration of the process upon addition to the monomer of 0.5-2% of compounds containing a mobile chlorine atom (chloranil, polymer XII) speaks in favor of the proposed concept of the polymerization mechanism of XII. Chain scission during the polymerization of XII may occur through interaction of the terminal halide with organic or inorganic bases, or through its inactivation as a result of hydrolysis of the polymeric pyridine salt. Indeed, in the polymerization of 4-chloropyridine in the presence of pyridine, lower-molecular-weight products are formed that do not contain terminal halide (see Table 1).

$$\cdots \mathrm{N^+{-}C_5H_4{-}N^+{-}C_5H_4{-}Cl} + \mathrm{N{-}C_5H_5} \longrightarrow \underset{\mathrm{Cl^-}\quad\mathrm{Cl^-}\quad\mathrm{Cl^-}}{\cdots \mathrm{N^+{-}C_5H_4{-}N^+{-}C_5H_4{-}N^+{-}C_5H_5}}$$

The polymerization product XII, carefully purified from pyridine, has considerable hardness, retains a yellow-brown color on storage, is soluble in water and in water-containing methyl alcohol and pyridine. The polymer does not dissolve in ordinary organic solvents (alcohol, acetone, dioxane, dimethylaniline, hydrocarbons, etc.).

Polypyridinium chloride, synthesized from 4-chloropyridine and pyridine (4:1 by volume), in addition to water and pyridine, is soluble in methyl alcohol and somewhat less readily in ethyl alcohol. Storage of this polymer in the light causes a change in color from brown to dark green. At 160-165° polymer XII begins to decompose. A freshly obtained polymer purified from monomer, as well as a polymer stored in the absence of moisture, shows narrow electron-paramagnetic-resonance signals analogous to those established for macromolecules with a system of conjugated bonds ([5],[6]). The content of paramagnetic particles in such

polymers of 4-chloropyridine is $3.8 \cdot 10^{18}$ per 1 g, the g-factor is 2.00, and the signal width is 6 oersteds. The paramagnetism of polypyridinium chloride is apparently due to high-molecular-weight fractions containing stable macroradicals ([6]). The formation of such paramagnetic particles is all the more probable since the presence in the conjugation chain of positively charged nitrogen atoms facilitates pairing of π-electrons and their delocalization along the macromolecular chain. It should be noted that for polymers stored in aqueous solution and then precipitated from it with acetone, no EPR signal is detected. Such polymers contain substantially smaller amounts of titratable chlorine. Under these conditions hydrolysis takes place both of the terminal halide and of the salt bonds, which leads to the formation, at the chain end, of units of (4-pyridyl)-4-pyridone (4), and within the chain, of a pyridine base. Such rearrangement of the molecule ultimately leads to the transition from macroradical structures to valence-saturated diamagnetic compounds:

$$\mathrm{Cl{-}C_5H_4N^+{=}C_5H_4N^+{=}\cdots{=}C_5H_4N^+{=}C_5H_4N} \xrightarrow{\mathrm{HOH}} \mathrm{O{=}C_5H_4N{-}C_5H_4N^+{=}\cdots{=}C_5H_4N^+{-}C_5H_4N}$$
$$\mathrm{Cl^-\quad Cl^-\quad Cl^-}$$

The principle of onium polymerization can also be used to obtain various copolymers. An example of "onium copolymerization" may be the synthesis carried out by us of copolymers through the interaction of γ,γ'-dipyridyl with chloranil. This process was carried out both in solution (toluene) and in the melt at 130°. The product formed in this way, colored dark brown, is partially soluble in methyl alcohol,

pyridine and in water, with the proportion of soluble fractions being higher for the bulk product. When the polymer is dissolved in conc. H_2SO_4, HCl is liberated. Silver chloride is precipitated from the soluble fractions. The polymer shows a symmetrical EPR signal corresponding to $5 \cdot 10^{18}$ paramagnetic particles per 1 g, has a g-factor of 2.00 and a signal width of 8 Oe. The elemental-analysis data (Table 1) allow one to assume that, under the experimental conditions adopted, mainly three reactive halogens react. This is also indicated by the fact that an insoluble fraction is formed both in solution and in bulk. The data from the investigation of IR spectra confirm the above, since it was found that the IR spectra retain the frequencies characteristic of quinone carbonyls, and the intensity of the C–Cl bond lines decreases.

Table 1

Composition of polychloropyridine, γ,γ'-dipyridyl, and chloranil

Substance	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.	Cl, % found	Cl, % calc.	Cl, % ionic
4-Chloropyridine	53.01	52.86	3.50	3.52	12.31	12.33	31.04	31.27	—
Polychloropyridine	52.77	52.86	3.72	3.52	12.13	12.33	31.10	31.27	28.40
Polypyridinium chloride with 20% pyridine	53.07		4.19		13.52		25.72		25.69
Polymer of γ,γ'-dipyridyl and chloranil (in solution)*	54.38	55.93	3.40	2.87	9.68	10.09	22.47	25.42	

* The calculation was made on the assumption that the polymer unit has the following formula:
$C_{26}H_{16} \times O_2N_4Cl_4$.

Table 2

Electrical conductivity of polychloropyridine and of the copolymer of dipyridyl and chloranil in comparison with the perchlorate of 4-pyridylpyridinium chloride

Type of compound	δ_0	δ_{300}	E, kcal/mol
Perchlorate of 4-pyridylpyridinium chloride	$3 \cdot 10^{11}$	$3 \cdot 10^{-15}$	35.8
Polychloropyridine	10^5	10^{-7}	18.2

Type of compound	δ_0	δ_{300}	E, kcal/mol
Copolymer of dipyridyl with chloranil (from solution)	10^5	10^{-9}	21.7

Note. The samples were not evacuated before the determination of electrical conductivity.

The synthesized onium polymers possess increased electrical conductivity, which rises sharply with increasing temperature (see Table 2).

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Note: Figure translations are in progress. See original paper for figures.