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Abstract

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Synthesis of New Nitrogen- and Oxygen-Containing Polymers with Conjugated Bonds from Sodium Carbonate and Ammonium Chloride

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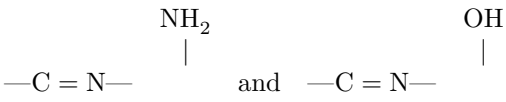
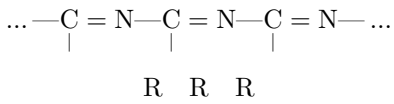
Polymers with a system of conjugated bonds are of considerable interest, since in a number of cases they exhibit semiconductor properties. In our work, high-molecular compounds containing the following repeating structural units were obtained for the first time:

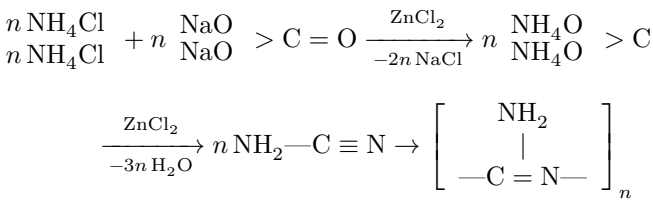


The first polymeric compounds containing a system of conjugated bonds



were obtained by V. A. Kargin, V. A. Kabanov, and others ([1]), who used the principle of ordered arrangement of the monomer molecules of various nitriles.

In our work, polycyanamide and polycyanic acid were obtained from ammonium chloride, sodium carbonate, and sodium bicarbonate. The reaction proceeds according to the equations:



(1)

$$n\,NH_4Cl + n\ \begin{matrix}NaO\\HO\end{matrix} > C=O \xrightarrow[-n\,NaCl]{ZnCl_2} n\ \begin{matrix}NH_4O\\HO\end{matrix} > C=O \rightarrow$$

$$\xrightarrow[-2n\,H_2O]{ZnCl_2} n\,HO{-}C\equiv N \rightarrow \left[\begin{matrix}OH\\|\\-C=N-\end{matrix}\right]_n \qquad (2)$$

The reaction was carried out between solid salts upon heating them in autoclaves to 250—300°, in the absence of atmospheric oxygen, under pressure in

Table 1

Characteristics of nitrogen- and oxygen-containing polymers

No.	Starting substances	Products obtained	$ZnCl_2$, mol. number	Duration of experiment, hours	Yield of polymer, theoretical, %	Characteristic viscosity in formamide
1	$2NH_4Cl + Na_2CO_3$	$\left[\begin{matrix}NH_2\\|\\-C=N-\end{matrix}\right]_n$	5	25	48	0.10
2	$2NH_4Cl + Na_2CO_3$	$\left[\begin{matrix}NH_2\\|\\-C=N-\end{matrix}\right]_n$	5	30	87	0.14
3	$NH_4Cl + NaHCO_3$	$\left[\begin{matrix}OH\\|\\-C=N-\end{matrix}\right]_n$	3	25	51	0.13
4	$NH_4Cl + NaHCO_3$	$\left[\begin{matrix}OH\\|\\-C=N-\end{matrix}\right]_n$	3	30	83	0.175

20-25 atm. The duration of the experiments was 5-30 h. Under identical conditions, 2-3 parallel experiments were carried out. After completion of the reaction, the products were ground and washed with warm water and then with ammoniacal water to remove zinc chloride completely and the monomers that had not entered into the reaction. The polymers obtained in amounts of about 8 g were dried under vacuum over calcium chloride to constant weight, after which the following determinations were made: yield relative to the theoretical value, melting point or decomposition point (if the polymers did not melt), elemental composition, solubility in various solvents, the heat effect of dissolution in acids; the intrinsic viscosity of polymer solutions was studied; the infrared spectrum was recorded (the samples were pressed into tablets with KBr); electron paramagnetic resonance was determined. The results obtained for some samples are given in Table 1.

Figure 1

Figure 1: Figure 1

Fig. 1. Dependence of the reduced viscosity of samples of polycyanamide *(1, 2)* and polycyanic acid *(3, 4)*, obtained under different conditions, on the concentration of the solutions. Polymerization temperature 300°; polymerization time, h: *1*–$\tau = 25$, *2*–$\tau = 30$, *3*–$\tau = 25$, *4*–$\tau = 30$.

The polymers of polycyanamide obtained are finely crystalline powders of brown color, from light to dark shades (depending on the duration of the experiment).

These are infusible substances, which begin to decompose at temperatures above 700°. The decomposition temperature was determined in a closed system, and the decomposition temperature was taken to be the temperature at which the pressure in the system increased. The polymer of cyanic acid is also infusible. Its decomposition temperature is of the same order as that of polycyanamide. Polymers of polycyanamide and polycyanic acid dissolve in formamide and in various acids—organic and inorganic. An increase in the degree of polymerization leads to poorer solubility of the polymers.

The intrinsic viscosity of solutions of polycyanamide and polycyanic acid was determined in formamide. The results are shown in Fig. 1. The polymers obtained dissolve in acids with evolution of heat. The heat of the salt-formation reaction of the polymers with hydrochloric acid was determined in a calorimeter and compared with that for a number of other known substances (aniline, polyvinyl alcohol···).

These reactions may be represented by the following equations:

$$\text{polycyanamide} \qquad \underset{\displaystyle \big|}{\underset{\displaystyle \mathrm{NH_2}}{[-\mathrm{C}=\mathrm{N}-]_n}} + n\,\mathrm{HCl} \rightarrow \underset{\displaystyle \big|}{\underset{\displaystyle \mathrm{NH_2}\cdot\mathrm{HCl}}{[-\mathrm{C}=\mathrm{N}-]_n}} + n\,9.9\ \text{kcal}$$

$$\text{polycyanic acid} \qquad \underset{\displaystyle \big|}{\underset{\displaystyle \mathrm{OH}}{[-\mathrm{C}=\mathrm{N}-]}} + n\,\mathrm{HCl} \rightarrow \underset{\displaystyle \big|}{\underset{\displaystyle \mathrm{OH}}{[-\mathrm{C}=\mathrm{N}-]_n}} \cdot n\,\mathrm{HCl} + n\,6.7\ \text{kcal}$$

In the IR absorption spectrum of polycyanamide, the band at 1600 cm^{-1} corresponds to a system of conjugated bonds $-\mathrm{C}=\mathrm{N}-$; the band at 1372 cm^{-1} may be assigned to the vibration $\nu\mathrm{NH_2} - \mathrm{C}$. The $\delta\mathrm{NH_2}$ vibrations are characterized by a band at 789 cm^{-1}. The band in the region of 873 cm^{-1} is characteristic of the $\mathrm{C}-\mathrm{N}$ bond.

Fig. 2. IR spectra of polycyanamide (A) and polycyanic acid (B)

Figure 2: Fig. 2. IR spectra of polycyanamide (A) and polycyanic acid (B)

The absorption spectrum of the polymer that we call polycyanic acid is analogous to the first: the band at 1600 cm^{-1} corresponds to conjugated bonds $-C=N-$, but it plays a secondary role, while the band at 1497 cm^{-1} predominates,

Fig. 2. IR spectra of polycyanamide (**A**) and polycyanic acid (**B**)

belonging to secondary amino or amide groups. The hydroxyl group is clearly observed in the region of 1042 cm^{-1}; the band at 878 cm^{-1} corresponds to the $-C-N-$ bond.

The polymers obtained exhibit EPR spectra characteristic of polyconjugated systems with a number of electrons with unpaired spins of 10^{17}-10^{18} per 1 g.

Thus, new polymers with conjugated bonds have been synthesized for the first time: polycyanamide, having the structure of polyiminoamine, and polycyanic acid—polyoxyimine—in which amide units have been spectrally detected. A new synthesis of these polymers from inorganic salts—ammonium chloride, sodium carbonate, and sodium oxalate—has been developed.

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References

1. V. A. Kargin, V. A. Kabanov et al., DAN, **139**, No. 3 (1961).

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