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A NEW METHOD FOR THE SYNTHESIS OF NITROGEN-CONTAINING POLYMERS WITH CONJUGATED BONDS AND THEIR ELECTROPHYSICAL PROPERTIES

(Presented by Academician V. A. Kargin, March 18, 1965)

V. A. Kargin, V. A. Kabanov, and others (^1) showed the possibility of obtaining a new class of polymeric substances with conjugated –C=N–bonds in the main chain by polymerization of nitriles.

In the present work a new method is proposed for the synthesis of polymers with an alternating system of –C=N–bonds in the main chain, starting from amides and ammonium salts of monobasic and dibasic organic acids. It was assumed that, upon heating a mixture of an amide or ammonium salt with a dehydrating agent ($ZnCl_2$), the corresponding nitriles would form and polymerize under the reaction conditions via the cyano group. The general reaction scheme is:

$$RCOONH_4 \xrightarrow[-2H_2O]{\text{catalyst}^*} R{-}C{\equiv}N \rightarrow \begin{matrix} R \\ | \\ -C{=}N- \end{matrix}$$

Similar methods for the synthesis of polyconjugated systems without isolation of intermediate products have already been described in a number of works ([2-5]).

By the proposed method the following nitrogen-containing polymer systems were obtained (Table 1). The synthesis of the polymers was carried out in a metal autoclave.

Table 2 gives the optimum conditions for carrying out the synthesis reaction and also shows the effect of the monomer-catalyst ratio on the yield of the polycondensation products.

By the method developed, polymers with a system of conjugated –C=N–bonds can be obtained from ammonium salts of acids, without resorting to such hardly accessible substances as, for example, hydrocyanic acid, instead of which the ammonium salt of formic acid is used, etc.

The polymers obtained are colored powders (from dark brown to black), infusible, insoluble in common solvents, and distinguished by high thermostability. The weight losses of these polymers at a temperature of 800° amount to 7-12%. The IR spectra of polymers obtained by polycondensation of amides and ammonium salts of acids are identical to the IR spectra of polymers obtained by polymerization of the corresponding nitriles (the comparison was made with the IR spectra of polyacetonitrile, polybenzonitrile, polyhydrocyanic acid, and paracyanogen). Figure 1 presents IR spectra (pellets with KBr were pressed) of polyacetonitrile synthesized by various methods. The absorption band in the region of 1600 cm^{-1} characterizes the presence of –C=N–bonds in the polymer; the band in the region of 1450 cm^{-1} corresponds to deformation vibrations of the CH_3 group; vibrations of the C–N bond are represented by a band in the region of 1370 cm^{-1}.

* Zinc chloride was used as the catalyst and dehydrating agent; its use for similar purposes has already been mentioned more than once.

Table 1

Structures and electrophysical properties of polymers

No.	Starting substances	Polymer structure	Electrical conductivity σ_{50}, ohm · cm^{-1}	E_a, eV	EPR spectrum: number of mobile electrons per 1 g of polymer	ΔH, oersted	Thermo-e.m.f. α, $\mu V/°C$
1	CH_3CONH_2	CH_3 | – C=N – C=N –	$2 \cdot 10^{-5}$	0.25	$1 \cdot 10^{19}$	2.5	–19
2	CH_3COONH_4	CH_3 | – C=N – C=N –	$5.6 \cdot 10^{-5}$	0.3	$7.5 \cdot 10^{18}$	6.3	–5.0

No.	Starting substances	Polymer structure	Electrical conductivity σ_{50}, ohm · cm^{-1}	E_a, eV	EPR spectrum: number of mobile electrons per 1 g of polymer	ΔH, oersted	Thermo-e.m.f. α, μV/°C
3	$HCONH_2$	– C=N – C=N – C=NH*	$9.2 \cdot 10^{-6}$	0.256	$4.9 \cdot 10^{18}$	4.5	−126
4	$HCOONH_4$	Polymeric structure with conjugated C=N bonds and NH_2 substituents	$6 \cdot 10^{-6}$	0.16	$4.6 \cdot 10^{18}$	4.25	–
5	$C_6H_5COONH_4$	C=N – C=N – | | C_6H_5 C_6H_5	$1.2 \cdot 10^{-5}$	0.23	$1.3 \cdot 10^{19}$	4.25	–

No.	Starting substances	Polymer structure	Electrical conductivity σ_{50}, ohm · cm^{-1}	E_a, eV	EPR spectrum: number of mobile electrons per 1 g of polymer	ΔH, oersted	Thermo-e.m.f. α, μV/°C
6	$CONH_2$|CH_2|$CONH_2$	C=N – C=N – **| |CH_2 CH_2| – C=N – C=N –	$4.2 \cdot 10^{-6}$	0.1	$3.0 \cdot 10^{18}$	4.25	–
7	$COONH_4$|CH_2|CH_2|$COONH_4$	C=N – C=N – **| |CH_2 CH_2| – C=N – C=N –	$4.6 \cdot 10^{-6}$	0.1	$1.0 \cdot 10^{18}$	4.25	–
8	$COONH_4$|$COONH_4$	C=N – C=N – ***| | – C=N – C=N –	$1.67 \cdot 10^{-5}$	0.03	$1.7 \cdot 10^{18}$	5.95	−2.6

No.	Starting substances	Polymer structure	Electrical conductivity σ_{50}, ohm · cm^{-1}	E_a, eV	EPR spectrum: number of mobile electrons per 1 g of polymer	ΔH, oersted	Thermo-e.m.f. α, $\mu V/°C$
9	$CONH_2$|CH CH|$CONH_2$	C C=N — C=N — **| |CH CH CH CH| | — C=N — C=N —	$1\cdot10^{-4}$	0.012	$3.5\cdot10^{19}$	4.25	−5.0

* A similar polymer was obtained from hydrocyanic acid ([10]).
** Obtained for the first time.
*** A similar structure was obtained by Bircumshaw ([2]) from oxamide.

The data on elemental composition attest to the identity of the polymers and polynitriles obtained by us, which, together with the IR spectra, apparently may serve as confirmation of the proposed reaction mechanism and polymer structure.

X-ray structural studies established the high crystallinity of the polymers obtained. For these polymers the dependence was studied—

Table 2

Polycondensation of amides and ammonium salts of organic acids

Fig. 1. IR spectra of polymers obtained from acetonitrile (soluble part) (a), from acetonitrile (insoluble part) ( ), from acetamide (soluble part) ( ), from ammonium acetate (insoluble part) ( )

Figure 1: Fig. 1. IR spectra of polymers obtained from acetonitrile (soluble part) (a), from acetonitrile (insoluble part) ( ), from acetamide (soluble part) ( ), from ammonium acetate (insoluble part) ( )

No.	Starting substances	Taken for experiment, g	Experimental conditions: ratio* of starting substance : catalyst (mol.)	Experimental conditions: temp., °C	Experimental conditions: duration, h	Polymer yield, g	Polymer yield, % of theory
1	CH_3CONH_2	15	1 : 2	400	5	2.9	29
2	CH_3COONH_4	15	1 : 4	400	5	1.9	24
3	$HCONH_2$	15	1 : 2	400	5	0.8	9
4	$HCOONH_4$	15	1 : 4	400	5	0.4	7
5	$C_6H_5COONH_4$	15	1 : 4	400	5	2.5	21
6	$CONH_2\|CONH_2$	15	1 : 4	400	5	2.6	30
7	$COONH_4\|COONH_4$	15	1 : 8	400	5	0.7	14
8	$CONH_2\|CH_2\|CONH_2$	15	1 : 4	400	5	2.7	29
9	$COONH_4\|CH_2\|CH_2\|COONH_4$	15	1 : 8	400	5	3.7	48
10	$CONH_2\|CH\|CH\|CONH_2$	15	1 : 4	400	5	2.8	37

* Optimal ratios are given.

···the dependence of electrical conductivity on temperature; and, for some specimens, the sign of the charge carriers was determined by the thermo-emf method. Measurements were carried out in vacuum of 10^{-5}–10^{-6} mm Hg in the range 20–300°. Before measurement, specimens in the form of pressed tablets were heated in vacuum (∼ 20–30 h); well-reproducible data were obtained, and the forward and reverse runs of the curves $\sigma = \sigma(T)$ and of the differential thermo-emf coincided.

Fig. 1. IR spectra of polymers obtained from acetonitrile (soluble part) (a), from acetonitrile (insoluble part) (b), from acetamide (soluble part) (c), and from ammonium acetate (insoluble part) (d).

Table 1 presents some data on the electrophysical properties of the polymers studied after prolonged heating in vacuum. Attention is drawn to the presence

of a correlation between the magnitude of the thermal activation energy, measured under conditions excluding the influence of surface adsorption ([6]), and the features of the chemical structure of the polymer chain. Whereas for polymers with an acyclic conjugation system (polymers 1-7) in the temperature range studied $E_a \simeq 0.1$-0.2 eV, for polymers with a cyclic system of conjugated bonds (polymers 8, 9) $E_a \simeq kT$. The fact that electrical conductivity over a wide interval does not depend on temperature was established earlier for polymers that also have a cyclic structure ([7–9]).

As was shown in ([8]), this phenomenon is not associated with a change in the chemical structure of the polymers during heating in vacuum. Our data also indicate that it is characteristic both of crystalline (polymers 8, 9) and amorphous substances (heat-treated polyacrylonitrile, polynitrileacetylene, poly-1,1-diacetylferrocene). Therefore, the peculiarities of electrical conductivity observed by us in these polymers should apparently be associated primarily with the features of their chemical structure. If one proceeds from the assumption that a macromolecule with a system of conjugated bonds is an analogue of a one-dimensional crystal with a narrow forbidden band, the width of which is determined by the length of the chain of continuous conjugation ([6,7]), then the experimentally found activation energy should be interpreted as the energy required to excite current carriers from the ground levels to excited levels in individual macromolecules or in sections of continuous conjugation.

Within the framework of such a concept, the reason for the correlation between the found value of the activation energy and the chemical structure of the polymers studied becomes clear.

If it is assumed, for example, that the probability of disruption of continuous conjugation for polymers with an acyclic chain (polymers 1-7) is of the order of 10^{-2} (one disruption per unit length of macromolecule corresponding to 100 units), then the probability of disruption of conjugation for polymers with a cyclic system of conjugated bonds (polymers 8, 9, heat-treated polyacrylonitrile, polynitrileacetylene, poly-1,1-diacetylferrocene), all other conditions being equal, will be $\sim 10^{-4}$.

This is probably the main reason for the correlation between the chemical structure and the found magnitude of the activation energy. These data are consistent with the concept of an activationless mechanism of motion of current carriers from one macromolecule to another or within sections of continuous conjugation.

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