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Abstract

Full Text

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SYNTHESIS AND SOME PROPERTIES OF POLYTETRACYANOETHYLENE

(Presented by Academician N. N. Semenov, March 16, 1961)

It is well known that tetrasubstituted derivatives of ethylene, as a rule, are not capable of polymerization because of great steric hindrance. For the same reason, tetracyanoethylene is not prone to radical-chain polymerization.

There are no indications in the literature of the possibility of obtaining polymers or copolymers of tetracyanoethylene. However, on the basis of data from organic chemistry on the ability of nitriles to form cyclic compounds, one may suppose that, in the case of tetracyanoethylene, macromolecular compounds may be formed through opening of the C N bond, as a result of which it is possible to obtain heterocyclic structures of the type of linked azoporphyrin rings or condensed pyridine nuclei. In this connection, it seemed expedient to test, as initiators of the polymerization of tetracyanoethylene, organic compounds capable of opening the C N bond and converting it into $> C = NH$, which can subsequently conduct the polymerization chain.

Fig. 1. Dependence of the polymer yield on the amount of added aniline

Table 1

Dependence of the yield of polytetracyanoethylene on the catalyst*

No.	Tetracyanoethylene, g	Tetracyanoethylene, mol	Catalyst, name	Catalyst, g	Catalyst, mol. %	Yield, g	Yield, %
1	1.2809	0.01	Alcohol	0.006	1.4	0.5568	43.5
2	1.2793	0.01	Aniline	0.0158	1.7	0.3458	27.0
3	1.0001	0.0075	Phenol	0.0113	1.5	0.2533	25.3
4	1.002	0.0075	Urea	0.0075	1.6	0.1755	17.5
5	0.9985	0.0175	Triethylamine	0.0075	2.0	0.1306	13.0
6	1.0010	0.0075	Pyridine	0.0075	2.0	0.0877	8.77
7	0.64	0.005	$(NH_4)HCO_3$	0.0079	1.0	0.0061	1.0

Fig. 2. Decomposition curves of polytetracyanoethylene as a function of the temperature and duration of heating

Figure 2: Fig. 2. Decomposition curves of polytetracyanoethylene as a function of the temperature and duration of heating

No.	Tetracyanoethylene, g	Tetracyanoethylene, mol	Catalyst, name	Catalyst, g	Catalyst, mol. %	Yield, g	Yield, %
8	0.64	0.005	–	–	–	0.012	2.0

* Polymerization was carried out at 200° for 10 h.

The experiments carried out showed that tetracyanoethylene in the presence of alcohols, phenol, amines, and amides at 200° polymerizes with the formation of black, infusible, insoluble products (Table 1). As is evident from

Table 1, ethyl alcohol shows the greatest activity (polymer yield is 43.5%), followed in decreasing order by aniline (27%), phenol (25.3%), urea (17.5%), triethylamine (13%), pyridine (8.7%), and ammonium bicarbonate (1.0%). Without introducing an initiator, tetracyanoethylene polymerizes under the same conditions with a very low yield (~2%). Formation of the polymer in this case is probably associated with the presence of traces of water or of some other impurities.

Fig. 2. Decomposition curves of polytetracyanoethylene as a function of the temperature and duration of heating

Using the polymerization of tetracyanoethylene in the presence of aniline as an example, the influence of the amount of catalyst and of the reaction time on the polymer yield was studied. As a result of the experiments carried out, it was established that with an increase in the amount of added aniline the polymer yield increases. Thus, with the addition of 0.5 mol.% aniline the yield is 2%, while the introduction of 4.4 mol.% increases the yield to 36% (Fig. 1).

The polymerization of TCNE proceeds within a short time. Already after 0.5 h (the first sample) the polymer yield is 12–15%, and a further increase in the duration of the reaction does not lead to an increase in its yield.

The absence of a dependence of the polymer yield on the reaction time is probably connected with cessation of the growth of the macromolecule as a result of the formation of inactive molecular complexes of tetracyanoethylene and the growing polymeric heterocyclic compound.

Table 2

Electrical properties of polytetracyanoethylene

Fig. 3. Dependence of the electrical conductivity of polytetracyanoethylene on temperature

Figure 3: Fig. 3. Dependence of the electrical conductivity of polytetracyanoethylene on temperature

	E, kcal/mol	σ_0, ohm$^{-1}\cdot$cm^{-1}	σ_{300°, ohm$^{-1}\cdot$ cm^{-1}
Polytetracyanoethylene (without catalyst)	13.3	10	10^{-9}
Polytetracyanoethylene (catalyst aniline)	8.2	10^{-3}	10^{-9}
Polytetracyanoethylene (catalyst alcohol)	6.8	10^{-2}	10^{-7}
Polytetracyanoethylene (catalyst phenol)	9.2	10^{-1}	10^{-9}

Investigation of the thermal stability of polytetracyanoethylene obtained in the presence of aniline shows that a polymer heated in vacuum of 1-2 mm at 200° for 20 h does not change during 4-hour heating at 300°. When the temperature is raised to 350°, a weight loss of 9.6% is observed in the first 15 min, after which no change in the polymer occurs at this temperature. A further increase in temperature causes appreciable destruction of the polymer: thus, at 400° the weight loss is 38.5%, at 450°—62.6%, and at 500° the polymer is completely destroyed (Fig. 2a, b).

The electrophysical properties of polytetracyanoethylenes are analogous to those of polymeric chelates of tetracyanoethylene (1). The polymers possess an increased conductivity of 10^{-7}-10^{-9} ohm$^{-1}\cdot$cm^{-1}. The activation energy of conductivity is 7-13 kcal/mol (see Table 2).

The dependence of the logarithm of conductivity on reciprocal temperature is given in Fig. 3.

The polymers obtained show a narrow electron paramagnetic resonance signal of high intensity, with the distance between the maximu-

moments of 4-6 oersteds, with a g-factor of 2 and without hyperfine structure. The concentration of paramagnetic particles is 10^{20}—10^{21} per 1 g. The broad lines have an asymmetric character, and for some polymers the wings of the lines extend for several thousand oersteds.

Fig. 3. Dependence of the electrical conductivity of polytetracyanoethylene on temperature

At present there are still insufficient data to draw final conclusions concerning the structure of the tetracyanoethylene polymers. However, on the basis of the tendency of aromatic di- and tetranitriles to undergo cyclization (^{2}), and also of the polymerization of hydrocyanic acid and the cyclization of polyacrylonitrile ($^{3-6}$), it may be assumed that the formation of macromolecules occurs owing to the appearance of energetically favorable azoporphyrin rings linked with one another, analogous to what takes place in the synthesis of phthalocyanines (^{2}).

Structure I Structure II

Thus, for the polymer obtained in the presence of pyridine, the following was found (in percent): C 57.0, N 42.12, H 0.85; and the following was calculated (in percent) for $C_{158}N_{100}H_{20}$ (i.e., for a polymer consisting of 25 tetracyanoethylene residues with replacement of two CN groups by a pyridine residue): C 57.17, N 42.2, H 0.63 (for structure I); C 57.2, N 42.18, H 0.60 (for structure II).

For polytetracyanoethylene obtained in the presence of alcohol, the following was found (in percent): C 55.8, N 40.4, H 1.5; and the following was calculated (in percent) for $C_{62}N_{38}H_{17}O_2$ (i.e., for a polymer containing 10 tetracyanoethylene residues with replacement of two nitrile groups by an alcohol residue): C 56.0; N 40.2; H 1.3; O 2.4.

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