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Abstract

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POLYMERIZATION OF ACETONITRILE AND OTHER NITRILES

In a previous work (^{1}), using acetone as an example, we showed that, by employing the principle of ordering the monomer molecules in the reaction system, it is possible to carry out the polymerization of monomers which, in accordance with the laws of thermodynamics, cannot be converted into polymers directly from the liquid state. In the case of acetone this can be achieved by preliminary freezing of the monomer and its polymerization in the solid state. Freezing apparently leads to a change in the sign of the entropy of polymerization (the difference between the entropies of the final and initial states of the system) as a result of a decrease in the entropy of the initial state.

In the present work the same principle has been applied for the purpose of carrying out the polymerization of nitriles through the $C \equiv N$ bond. Polymerization of nitriles should be accompanied by the formation, in place of each $C \equiv N$ bond, of one $C = N$ bond and one C—N bond. This process, if the energy of conjugation is disregarded, would proceed with absorption of heat approximately equal to 11 kcal/mole (the bond energies $C \equiv N$, $C = N$, and C—N are respectively 149, ~ 84, and 53.5 kcal/mole (^{2})). The energy of conjugation released upon formation of the system of bonds —C = N—C = N—... would, in the best case, cover this deficit, making the thermal effect of the reaction close to 0. Since the transition liquid monomer → solid polymer is always accompanied by a decrease in entropy ($\Delta S < 0$), polymerization of nitriles under ordinary conditions through the $C \equiv N$ bond is impossible (with the change in heat content $\Delta H = -Q \simeq 0$ and $\Delta S < 0$, the change in the isobaric-isothermal potential $\Delta Z = \Delta H - T\Delta S > 0$). We succeeded in carrying out the polymerization of a number of nitriles (acetonitrile, propionitrile, tolylonitrile, benzonitrile, trifluoroacetonitrile, and others) by ordering the monomer molecules in solid complexes which they readily form with coordinatively unsaturated metal halides ($ZnCl_2$, $BeCl_2$, $TiCl_4$, $AlCl_3$, $SnCl_4$, and others). These complexes are crystalline substances of constant composition (usually $MeX_n \cdot 2R(CN)$). The formation of such complexes from the starting substances is accompanied by a considerable decrease in the entropy of the system, reaching, for example, in the case of the complex $TiCl_4 \cdot 2Py$, 49 cal/deg • mole (^{3}). There are some grounds for believing that the monomer molecules in such complexes form packings fa-

Fig. 1. IR spectrum of polyacetonitrile

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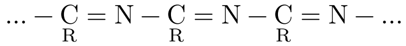
vorable for their union into molecular chains (^{4}). When complexes of nitriles and metal halides are heated at temperatures of 180–350° in hermetically sealed vessels (sealed glass ampoules or an autoclave), in the absence of moisture and atmospheric oxygen, polymerization of the ordered nitrile molecules takes place with the formation of conjugated chains built from alternating carbon and nitrogen atoms:



$$\ldots - \underset{\mathrm{R}}{\mathrm{C}} = \mathrm{N} - \underset{\mathrm{R}}{\mathrm{C}} = \mathrm{N} - \underset{\mathrm{R}}{\mathrm{C}} = \mathrm{N} - \ldots$$

The metal halide in this process actually plays the role of an agent that makes it possible to shift the chemical equilibrium in the monomer—poly-

toward polymer formation. After the reaction is complete, the inorganic salt can be washed out of the polymer with suitable solvents (water, ammonia, or acids). Heating nitriles in which only small amounts of the above-mentioned salts are dissolved, as well as attempts to polymerize nitriles at superhigh pressures (of the order of 10 thousand atm.) (5), leads only to the formation of cyclic trimers.

Fig. 1. IR spectrum of polyacetonitrile

The data of IR spectroscopy are consistent with the structural formula for polynitriles given above. Figure 1 presents the IR spectrum of polyacetonitrile obtained by polymerization of acetonitrile in a complex with $ZnCl_2$ ($2CH_3CN \cdot ZnCl_2$). Samples for investigation were prepared from polymer powder by pressing it into tablets with KBr. The broad intense band in the region of 1580 cm^{-1} corresponds to absorption by the system of conjugated $C = N$ bonds. The absorption bands in the regions of 1409 and 1352 cm^{-1} may be assigned to symmetric deformation vibrations of the CH_3 group. Absorption in the region of 1138 cm^{-1} is probably due to pendulum vibrations of the methyl group.

The polymerization process, in all probability, proceeds by a stepwise mechanism. The molecular weight of the polymer increases with time during polymerization. At first, yellow low-molecular-weight water-soluble products are formed; with increasing polymerization time the color of the polymer gradually changes from yellow to dark brown and black. Thus, polyacetonitrile obtained by heating the acetonitrile complex with $ZnCl_2$ at 250° for 5 h is a dark-brown powder soluble in dimethylformamide. With increasing duration of heating, polymers are formed that are soluble only in concentrated acids (formic, phosphoric, sulfuric). Increasing the polymerization time at 250° to 10 h and more leads to the formation of black insoluble polymers.

Fig. 2. Dependence of the reduced viscosity of polyacetonitrile samples obtained

Fig. 2. Dependence of the reduced viscosity of polyacetonitrile samples obtained under various conditions on the concentration of solutions

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under various conditions on the concentration of solutions. Polymerization temperature 250°; polymerization duration: 1—4 h, 2—5 h, 3—6 h, 4—7 h.

Figure 2 presents the results of measuring the viscosity of solutions of polyacetonitrile samples in sulfuric acid, obtained at different polymerization times. With increasing polymerization time, the intrinsic viscosity increases up to the point where the polymers pass into an insoluble state. Similar dependences may be observed with increasing reaction temperature. Thus, at 300° a black insoluble polymer is formed already 5 h after the start of polymerization. If it is assumed that each polymer chain in the complex grows by a stepwise mechanism independently of the others from a preformed molecular precursor, then the change

the degree of polymerization (P) with time (t) can be described by the equation

$$\frac{dP}{dt} = k \quad \text{or} \quad P = kt,$$

where k, to a first approximation, may be taken as a constant depending on the temperature and structure of the complex. The intrinsic viscosity is related to the degree of polymerization by the known relation $[\eta] = KP^{\alpha}$. For very rigid polymers, such as polynitriles, α is probably close to 2. Therefore

$$[\eta] \simeq k^2 K t^2 = K t^2.$$

It can be seen from Fig. 3 that the experimental dependence of $[\eta]$ on t^2 can indeed be described by a straight line extrapolated to the origin.

Polynitriles possess high thermal stability, semiconductor properties, and exhibit EPR spectra characteristic of polyconjugated systems. The electrical conductivity of polymer powders varies reproducibly over wide limits when the polymerization temperature is changed. The results of measuring the electrical conductivity of samples of polyacetonitrile obtained under various conditions show that it increases with increasing polymerization time and temperature. When the polymerization temperature is changed from 250 to 350° and the polymerization time from 5 to 8 h, the electrical conductivity at room temperature increases by 6 orders of magnitude. The temperature dependence of the electrical conductivity in the temperature interval 20–200°C for all samples strictly obeys the equation $\sigma = \sigma_0 e^{-E/kT}$.

Fig. 3. Dependence of the intrinsic viscosity of polyacetonitrile on the square of the polymerization time. Polymerization temperature 250°.

Table 1

Polymerization regime	$\sigma_{20^\circ C}$, ohm^{-1} · cm^{-1}	σ_0, ohm^{-1} · cm^{-1}	E, eV
250°, 5 h	$1.7 \cdot 10^{-11}$	$3.0 \cdot 10^{-5}$	0.35
250°, 6 h	$1.9 \cdot 10^{-9}$	$7.3 \cdot 10^{-4}$	0.30
250°, 8 h	$3.2 \cdot 10^{-8}$	$2.4 \cdot 10^{-3}$	0.28
300°, 8 h	$1.9 \cdot 10^{-6}$	$7.7 \cdot 10^{-2}$	0.25
350°, 8 h	$1.0 \cdot 10^{-5}$	$6.8 \cdot 10^{-2}$	0.21

The activation energies of electrical conductivity have been determined; they decrease with increasing polymerization temperature and duration, varying for the samples studied within the range from 0.35 to 0.2 eV (Table 1). The decrease in activation energy is accompanied by an increase in the preexponential factor, which indicates the absence of a "compensation effect."

Thus, in the present work it has been shown that, by using the principle of preliminary ordering of monomer molecules, it is possible to include, among the polymerizing bonds, one more multiple bond, the $C \equiv N$ bond. This opens the possibility of obtaining a new class of polymeric substances with conjugated bonds in the main chain on the basis of various nitriles.

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