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Academician V. A. Kargin, V. A. Kabanov, V. P. Zubov, I. M. Papicov,

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Abstract

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CHEMISTRY

Academician V. A. Kargin, V. A. Kabanov, V. P. Zubov, I. M. Papicov, and G. I. Kurochkina

POLYCONDENSATION OF ACETONE AND OTHER CARBONYL-CONTAINING COMPOUNDS

In previous works we showed that an ordered arrangement of monomer molecules in the reaction system leads to the appearance of a number of important features manifested in polymerization processes. Among such features, first of all, are the very high, often explosive rates of polymerization of solid monomers at very low temperatures ([1–5]). Rapid polymerization processes are possible under certain conditions, when the ordered arrangement of small molecules is combined with their somewhat coordinated mobility—for example, at the moment of a phase transition in a frozen monomer ([4]). Ordering of monomer molecules in the initial system also makes it possible to carry out polymerization of a number of substances for which transition to the polymeric state under ordinary conditions proves impossible for thermodynamic reasons ([6,7]). In some cases, by making use of complex formation among monomer molecules, polymer radicals, and molecules of a third substance introduced as an additive into the reaction system, it is possible to regulate the structure of polymer chains formed in the course of polymerization ([8]).

In the light of the results mentioned, it was natural to suppose that an ordered arrangement of monomer molecules in the reaction system should also have a noticeable effect on polycondensation processes. This circumstance is indicated by the recently published data of Skuratov and co-workers ([9]).

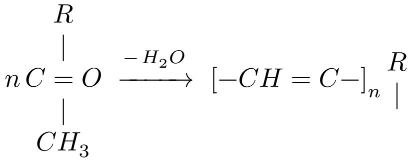
Attempts are known to synthesize polyvinylenes from carbonyl-containing monomers using methods of aldol-crotonic polycondensation ([10]), which up to now have led only to the preparation of readily oxidized low-molecular-weight products.

We succeeded in obtaining very stable high-molecular-weight polyvinylenes based on ketones and aldehydes (acetone, 1,1′,1″-trifluoroacetone, acetophenone, acetaldehyde, and others) by polycondensation of these substances in the

Fig. 1. IR spectrum of the acetone polycondensate. For comparison, the IR spectrum of polyacetonitrile is shown by the dotted line.

Figure 1: Fig. 1. IR spectrum of the acetone polycondensate. For comparison, the IR spectrum of polyacetonitrile is shown by the dotted line.

presence of comparatively large amounts of dehydration catalysts capable of forming complexes with monomer molecules ($\mathrm{ZnCl_2}, \mathrm{BeCl_2}, \mathrm{TiCl_4}$, and others). Ordering of monomer molecules in these complexes makes possible the course of deep polycondensation processes. Polycondensation was carried out by heating mixtures of the reagents in sealed glass ampoules or in an autoclave in the absence of atmospheric oxygen at temperatures of 70—250°. In general form, the polycondensation reaction may be described by the equation:



$$n\,\overset{\displaystyle R}{\underset{\displaystyle CH_3}{C}} = O \xrightarrow{-H_2O} [-CH = C-]_n \overset{R}{|}$$

In this process, acetaldehyde gives polyacetylene, acetone gives polymethylacetylene, acetophenone gives polyphenylacetylene, etc.

The polymers obtained are dark-brown or black powders, possessing the increased thermal stability characteristic of high-molecular-weight polyconjugated systems; they exhibit semiconductivity and give characteristic EPR spectra (11). At low degrees of polycondensation the polymers formed are soluble in organic solvents (acetone, benzene). At high degrees of polycondensation the solubility is completely lost. The degree of polycondensation and the yield of solid polymers increase with increasing catalyst content, temperature, and reaction time. This is illustrated by the data in Table 1.

Fig. 1. IR spectrum of the acetone polycondensate. For comparison, the IR spectrum of polyacetonitrile is shown by the dotted line.

Table 1

Monomer	Molar ratio monomer/$\mathrm{ZnCl_2}$	Polycondensation conditions	Product characteristics	Yield, % of monomer taken
Acetone	0.24	180°, 8 h	Solid powdery	3
Acetone	0.33	Same	Same	10
Acetone	0.49	» »	» »	14.5
Acetone	0.8	» »	» »	46

Monomer	Molar ratio monomer/$ZnCl_2$	Polycondensation conditions	Product characteristics	Yield, % of monomer taken
Acetaldehyde	0.05	40°, 5 h, then 70°, 15 h	» »	30.1
Acetaldehyde	0.065	Same	» »	40.5
Acetaldehyde	0.1	» »	» »	45
Acetaldehyde	0.16	» »	» »	52
Acetophenone	0.18	3 h at 170°, then 15 h at 200°	Solid resin, softening temp. 100°	40.5
Acetophenone	0.27	Same	Solid, powdery	60
Acetophenone	0.36	» »	Same	70

The proposed structure of the polyvinylenes is consistent with the data of IR spectroscopy. Figure 1 presents the IR spectrum of polymethylacetylene obtained by polycondensation of acetone in the presence of $ZnCl_2$. This spectrum has much in common with the spectrum of polyacetonitrile obtained by us···

···, in its structure close to polymethylacetylene (7):

$$\underset{\text{polymethylacetylene}}{[-CH=C(CH_3)-]_n} \qquad \underset{\text{polyacetonitrile}}{[-N=C(CH_3)-]_n}$$

The broad intense band in the region of 1593 cm^{-1} is due to absorption by a system of conjugated $C=C$ bonds. The absorption bands in the regions of 1352 and 1380 cm^{-1} may be assigned to symmetric deformation vibrations of CH_3 groups. The absorption band at 960 cm^{-1}, in all probability, is due to out-of-plane deformation vibrations of $C-H$ in the main chain. In subsequent publications the IR spectra of various polyvinylenes will be analyzed in greater detail.

Thus, the preliminary ordering of monomer molecules in their complexes with coordinatively unsaturated metal halides, which simultaneously act as dehydration catalysts, makes it possible to carry out deep polycondensation of carbonyl-containing monomers and to obtain diverse heat-resistant polyvinylenes of sufficiently high molecular weight.

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