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Abstract

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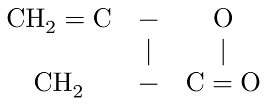
THE INFLUENCE OF THE PHASE STATE OF DIKETENE ON THE CHEMICAL STRUCTURE OF MACROMOLECULES FORMED DURING ITS POLYMERIZATION

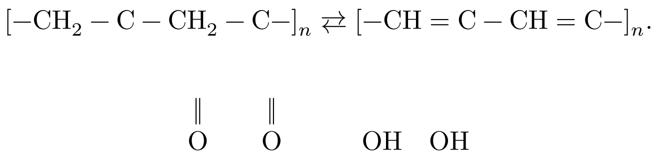
In studies on polymerization in the solid state, questions of the influence of the phase state of solid monomers on the reaction rate ([1,2]) and on the orientation of macromolecules of the polymers obtained ([3,4,5]) have usually been considered. Along with this, the study of the influence of the phase state of the monomer on the chemical structure of the polymer chains formed is of great interest. The aim of the present work is to investigate this influence using the polymerization of diketene as an example.

It is known that diketene, being the β-lactone of 3-hydroxybutenoic acid,



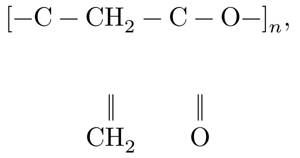
$$\begin{array}{ccc} CH_2=C & - & O \\ & | & | \\ CH_2 & - & C=O \end{array}$$

is capable of polymerizing in the liquid phase with opening of the lactone ring under the action of BF_3 etherate. In this case an amorphous polymer is formed, having the structure of poly-β-diketone (PDK) ([6]).



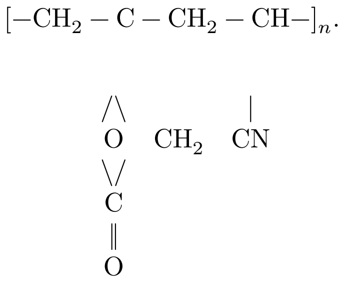
$$[-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-]_n \rightleftarrows [-CH=\underset{OH}{C}-CH=\underset{OH}{C}-]_n.$$

During polymerization in the liquid phase under the action of $HgCl_2$, a crystalline polymer is formed, having the structure of a complex unsaturated polyester (PE) ([7])



$$[-\underset{\underset{CH_2}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-O-]_n,$$

Radical copolymerization of diketene via the vinyl bond has also been described, in which the four-membered ring remains unaffected ([8]):



$$[-CH_2-\underset{\substack{/\backslash \\ O\quad CH_2 \\ \backslash/ \\ C \\ \| \\ O}}{C}-CH_2-\underset{\underset{CN}{|}}{CH}-]_n.$$

Thus, depending on the polymerization conditions, diketene can form units of at least three types.

In the solid phase, diketene polymerizes under the action of ionizing radiation with formation of PE ([9]). However, the question of whether the formation of the polyester structure is due to the influence of the crystal lattice of the monomer or to the nature of the active centers arising during radiation initiation remains open, since liquid diketene does not polymerize under irradiation. There is only an indication that the geometrical parameters of the crystal lattice of diketene and the parameters of the polyester macromolecule are in a certain correspondence ([3]).

To carry out the polymerization of frozen diketene, we used a method developed earlier by us for the co-condensation of monomer vapors—

monomer and catalyst onto a cooled surface (10). This method is very convenient for studying solid-phase polymerization, since it makes it possible easily to regulate the temperature and phase state of the frozen mixture of monomer and catalyst, and also to vary the catalyst.

The experiments were carried out in an apparatus analogous to that described in (10). The monomer was purified by freezing out diketene at −10° and subsequent double distillation in vacuum. The physical constants of the monomer thus purified agreed well with the literature data (11): n_D^{20} 1.4379, m.p. −6.5°. Metallic magnesium was used as the polymerization initiator. Diketene and magnesium vapors were simultaneously condensed in a high vacuum (10^{-4} mm Hg) on the surface of a glass sphere cooled with liquid nitrogen (−196°). Upon slow thawing of the condensate layer, polymeric products were found; their

Fig. 1. IR spectra of diketene polymers

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yield, calculated on the evaporated diketene, was about 20%. In the reaction a certain amount of water-soluble low-molecular-weight products is also formed; their yield was not determined by us.

The structure of the polymerization products was investigated by comparing their IR spectra with reference spectra of diketene polymers of various structure, synthesized by us according to known methods. The IR spectra of diketene polymers with PE and PDK structures are shown in Fig. 1 (curves *a*, *b*). In the spectrum of the reaction product under study (curve *v*, Fig. 1) there are absorption bands present in the spectra of the reference PE and PDK, for example the intense bands at 1740 and 1600 cm^{-1}, corresponding to vibrations of carbonyl groups in the polyester and poly-β-diketone, respectively (marked by arrows in Fig. 1). Such a spectrum may correspond both to a copolymer containing polyester and poly-β-diketone units, and to a mixture of homopolymers of both types.

Fig. 1. IR spectra of diketene polymers: *a*—polymerization with $HgCl_2$; dashed line—radiation polymerization in the solid state; *b*—polymerization with $BF_3(Et)_2O$; *v*—polymerization in a molecular mixture with magnesium; *g*—fraction extracted with benzene; *d*—fraction extracted with methanol.

To resolve the question of the composition and structure of the polymerization product, it was fractionated with solvents. Upon prolonged extraction with boiling benzene, a polymer passes into solution, the IR spectrum of which (curve *g*, Fig. 1) practically coincides with the spectrum of the polyester (curve *a*, Fig. 1). The X-ray diffraction pattern of the polymer indicates its high crystallinity and coincides with the X-ray diffraction patterns of polyester samples synthesized by known methods.

···(Fig. 2, see insert, p. 346). An amorphous polymer remains in the precipitate, the IR spectrum of which (curve *d*, Fig. 1) corresponds to PDK.

Another method of separating the reaction products consists in treating them with methanol. In this case PDK passes into solution, while PE remains in the precipitate. Thus, the polymerization product is a physical mixture of two polymers—PDK and PE, whose characteristic viscosities, measured in *m*-cresol at 30°, are respectively 0.04 and 0.10.

The ratio of polyester to poly-β-diketone in the mixture varies somewhat from experiment to experiment. Usually the poly-β-diketone predominates. Thus, the sample of the reaction product whose IR spectrum is shown in Fig. 1 (curve *a*) contains 80% PDK and 20% PE (estimated from the results of fractionation and quantitative analysis of the IR spectra of the products, which were compared with the spectra of standard mixtures of PDK and PE).

The formation of a mixture of two polymers during the polymerization of frozen diketene with one and the same initiator (magnesium) can be explained by assuming that the formation of polymer chains of the one and the other type occurs in different phases. To clarify this question, a series of experiments was carried out in which the temperature of the condenser surface during the condensation of monomer and magnesium, and the duration of holding the resulting condensate layer at various temperatures, were varied.

When vapors of diketene and magnesium are condensed on a surface cooled to −196°, a glassy layer is formed, in which, after a critical thickness has been reached, a rapid exothermic reaction occurs. It turned out, however, that if, without preliminary heating, the condensate in which the rapid reaction had occurred is treated with water, polymer is practically not detected. This means that in the present case, in contrast to the polymerization previously studied by us under analogous conditions for a number of vinyl monomers ([12]) at temperatures close to that of liquid nitrogen, growth of macromolecules does not occur. It is possible that the rapid low-temperature exothermic reaction is associated with the formation, or transformation, of low-molecular-weight organomagnesium compounds, which initiate polymerization at higher temperatures.

If vapors of diketene and magnesium are condensed on a surface cooled to −70°, the monomer crystallizes at the moment of condensation. At the moment of condensation, partial polymerization of the diketene occurs, leading to the formation of PDK in a yield of about 6%. Further holding of the crystalline mixture at this temperature does not lead to any noticeable increase in yield.

Significantly higher polymer yields (20%) are achieved if the frozen molecular mixture, obtained by condensation on a surface cooled to −196° or to −70°, is rapidly heated above the melting point of diketene (−6.5°). Upon melting, rapid polymerization of diketene occurs. The principal product of the polymerization is PDK.

If, however, the frozen condensate layer is rapidly heated to a temperature of −8° and held for a long time (up to 4 hours) at this temperature, then PE proves to be the principal product of polymerization of the crystalline diketene.

Thus, polymerization of diketene at the moment of melting and its polymerization in the crystalline state at 1.5-2° below the melting point, which in both cases are initiated by products of the interaction of the monomer with magnesium, lead to the formation of polymers of entirely different chemical structure.

If the frozen condensate layer is slowly passed through the entire temperature interval from −196° to the melting point of the monomer, then, naturally, a mixture of PE and PDK is formed.

An explanation of the results obtained may be as follows. In the work of Natta et al. [13] it was mentioned that, upon polymerization of ketene in solution on catalysts containing Al, Be, and Zn, a polymer with the PDK structure is formed. Catalysts containing magnesium are similar to them in nature. It should be expected that polymerization of diketene on organomagnesium catalysts in the liquid phase should also lead to formation of a polymer with the PDK structure. Indeed, in our experiments, upon polymerization of diketene in the melt, chains of precisely this structure are formed.

Near the melting point of crystalline diketene, at −8°, sufficiently rapid chain growth in the monomer crystals apparently becomes possible. The fact that, under these conditions, a polymer having the PE structure is formed indicates that, in this case, the crystal lattice of the monomer influences the formation of a polymer chain of a definite structure. This agrees with the earlier conclusion [3] that the formation of PE chains in crystalline diketene does not cause significant stresses in the monomer lattice. In contrast, the formation of PDK chains should lead to destruction of the crystal lattice and therefore proves to be less energetically favorable.

The formation of small amounts of PDK upon condensation of diketene and magnesium onto a surface cooled to −70° is apparently explained by the fact that polymerization occurs in a pseudo-liquid layer during the process of crystal growth. Growth of chains in already formed crystals at this temperature is extremely slow. Therefore, prolonged holding of crystalline monomer containing active centers at −70° does not lead to an increase in polymer yield. The question of the nature of the particles initiating polymerization requires further investigation.

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7 II 1964

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