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Polymerization of Tetramethylethylene at Pressures up to 27,500 Atmospheres.

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S. V. Lebedev and E. P. Filonenko studied the polymerization of ethylene derivatives in the presence of floridin /1/. They observed that under the conditions of their experiments only unsymmetrical di-substituted and tri-substituted ethylene derivatives polymerized. V. V. Korshak and K. K. Samplavskaya /2/ analyzed the data of the cited work /1/ and other studies and came to the conclusion that stereochemical factors play an important role in the polymerization of ethylene derivatives. Tetramethylethylene (2,3-dimethyl-2-but<sup>e</sup>ane) is one of those ethylene derivatives whose polymerization has not been studied up to now. Experiments on the ionic polymerization of tetramethylethylene in the presence of boron trifluoride led to the formation, predominantly, of 2,2,3,5,6-pentamethyl-3-heptene /3/. Analogous results were obtained when tetramethylethylene is polymerized in the presence of 80% sulfuric acid /4/. The structure of the polymerization products provide evidence that the polymerization reaction proceeds not with tetramethylethylene itself, but with its isomers. Actually, in the presence of acid catalysts tetramethylethylene is converted <sup>into</sup> with an equilibrium

mixture of isomers- tetramethylethylene, methylisopropylethylene and tertiary butylethylene.\* Polymerization of methylisopropylethylene (2,3-dimethyl-1-butene) in the presence of 80% sulfuric acid afforded a mixture of dimers indistinguishable from those obtained from tetramethylethylene /4/.

This paper describes the results of experiments on the thermal polymerization of tetramethylethylene under conditions of elevated and ultra-high pressures.

The tetramethylethylene\*\* which we used, was distilled through a rectification column containing 30 theoretical plates, and had the following properties:b.p. .... (literature values /6/): b.p. ....

A. Experiments at elevated pressures were conducted in a steel ampoule of 7.5 ml vol., into which was inserted a lead rod.\*\*\* The ampoule was filled to the top with tetramethylethylene after which it was heated at 300° for 50 hours. The calculated pressure in the ampoule amounted to about 200 atm (based on a graph of the dependence of the compressibility

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\* At 300° in the presence of P<sub>2</sub>O<sub>5</sub> on silica gel, the products are present at the respective concentrations of 64%, 33% and 3% /5/.

\*\*Tetramethylethylene and methylisopropylethylene were generously provided for our use by L.V. Petrov and A. P. Meshcheryakov for which we are sincerely grateful.

\*\*\*To establish conditions analogous to those applicable to experiments at ultra-high pressures.

coefficient on temp. and pressure) /7/. The clear product that was discharged was characterized by its increased refractive index ( $n_D^{20}$  1.4205). On distilling off the starting monomer (80% of the charge) through a column with 20 theoretical plates, we observed a very small quantity (a few drops<sup>s</sup>) of low-boiling products (57.0-71.5° fraction;  $n_D^{20}$  of the first drops was 1.3890). Vacuum distillation of the residue afforded the unsaturated dimer: ....., bromine number 97.7. Calculated for  $C_{12}H_{24}$ : mol. wt. 168; C 85.62%; H 14.38%; bromine number 95.3. After distillation of the dimer, there remained a thick liquid of av mol. wt. 248,  $n_D^{20}$  1.4650, bromine number 68.8; calculated bromine number 64.5.

Thus it was shown that, under the conditions of the investigation, tetramethylethylene forms an unsaturated dimer,  $C_{12}H_{24}$ , and higher mol. wt. unsaturated polymers.

Let us consider the possible pathways for the thermal dimerization of tetramethylethylene. The first of these is the reaction of two molecules of olefin to form octamethylcyclobutane. This pathway requires overcoming very great steric hindrance. The dimer we obtained was not cyclic; therefore, the reaction did not proceed in this direction. The second pathway is the saturation of the double bond of one mol. of tetramethylethylene by a methyl group from another mol. By this route the most probable product is 2,3,5,5,6-pentamethyl-2-heptene:

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This pathway appears to be very much easier from a

stereochemical viewpoint.\* However, there is, in theory, a third pathway - isomerization of tetramethylethylene, particularly to methylisopropylethylene (2,3-dimethyl-1-butene)

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with subsequent polymerization of the latter, apparently proceeding without steric hindrance (judging from the results of previous work /1/).

We carried out experiments to clarify whether, during thermal polymerization there is any increase in the isomer content of the starting tetramethylethylene. Considering the large difference in the refractive indices of the isomers (.....) one should expect that in the first stages of heating tetramethylethylene the index of refraction should decline somewhat, as a consequence of methylisopropylethylene formation. This hypothesis was not confirmed.

Experiments on the polymerization of methylisopropylethylene under these conditions showed that this substance polymerizes significantly faster than tetramethylethylene. After three hours we obtained more than 20% of polymer, from which, however, the dimer was virtually absent. Tetramethylethylene was not observed among the reaction products.

The results of these experiments constitute evidence opposing the hypotheses that the polymerization of tetramethylethylene proceeds by preliminary isomerization into methylisopropylethylene.

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\*Evidently, the reaction according to equation (1) proceeds by a radical mechanism. In principle this dimer is capable of subsequent cyclization (see below).

It should be noted that the dimer we obtained boils at a somewhat higher temp. than does the 2,2,3,5,6-pentamethyl-3-heptene obtained by ionic polymerization (b.p. 54.9-56.5° at 12 mm) /6/. No other physical constants for this hydrocarbon have appeared in the literature.

Thus, thermal polymerization of tetramethylethylene at 300° and at pressures of about 200 atm, apparently results in the formation of products different from those of ionic polymerization.

B. Experiments at ultra-high pressures were conducted in a two-stage intensifier with internal electrical heating, using the arrangement for temp. and pressure measurement described previously /8/. A 0.3-0.4 g charge was placed in a lead ampoule, which was then sealed. The "hot" junction of a differential thermocouple was inserted into its thickened upper portion. The intensifier channel was filled with a mixture of n-pentane and isopentane. Pressure was measured by means of a manganin manometer inserted in the cool zone of the intensifier channel.

Expt. No. 1. Pressure 23,000 atm; temp. 280 ± 5°; duration three hours. The product was a thick colorless liquid; mol. wt. 297; bromine no. 30.5 which corresponds to 57% of unsaturated hydrocarbons present in the polymer. No starting monomer was observed in the products.

Expt. No. 2. Pressure 27,000-27,500 atm; temp. 300 ± 5°; duration 6.5 hours. Mol. wt. of the viscous product was about 400;  $n_D^{20}$  1.4742; bromine no. 13.3, corresponding to 33% of unsaturated hydrocarbons present in the polymer.

Expt. No. 3. Pressure 24,300-25,700 atm; temp.  $300 \pm 5^{\circ}$ ; duration 11.5 hours. Mol. wt. of the product was 343;  $n_D^{20}$  1.4730; bromine no. 17.7, corresponding to 38% of unsaturated hydrocarbons present in the polymer.

Examination of these exptl. results leads to the following conclusions on the effect of ultra-high pressure on the polymerization of tetramethylethylene.

1. Rate of polymerization is increased. At 200 atm pressure only about 20% of tetramethylethylene was polymerized after 50 hours; at 23,000 atm all the monomer was polymerized within three hours.

2. The degree of polymerization is increased. At 200 atm, 75% of the polymer was only the dimer, while the remaining 25% had an av mol. wt. of 248, corresponding to the trimer. At 27,000-27,500 atm the av mol. wt. of all products was about 400, despite the fact that the expt. lasted only one-eighth as long as did the expt. at 200 atm.

3. The polymers obtained at ultra-high pressures are characterized by low bromine nos., corresponding to a 33-38% content of unsaturated hydrocarbons. Polymers obtained at 200 atm pressure have bromine nos. corresponding to 100% content of unsaturated compounds (which is true even of the fraction of highest mol. wt.).

This circumstance leads to the conclusion that, at ultra-high pressures the formation of polymers with cyclic structure occurs to some extent. Such cyclic polymers might be formed by overcoming the steric hindrance (see above) of

either the dimers, or of higher polymers formed according to equation (1).\*

Thus, ultra-high pressure not only accelerates the polymerization of unsaturated hydrocarbons and shifts the polymerization ~~сбалансированного~~ equilibrium in the direction of formation of higher mol. wt. polymers, but it can lead to a substantial alteration in the chemical structure of the polymers.

It should be noted that the combination of ultra-high pressure (23,000-27,500 atm), a temp. of 280-300° and exptl. duration up to 11.5 hours, which we achieved in our work, are herein described in the literature for the first time.

M. D. Pushkinskii and V. A. Kuznetsov assisted in this work.

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\*Analogous to the cyclization of isobutylene dimer to form 1,1,3-trimethylcyclopentane /9/.