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Abstract

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INVESTIGATION OF THE POLYMERIZATION OF 2,3-DIMETHYLBUTENE-2; 2,3-DIMETHYLBUTENE-1 AND 3,3-DIMETHYLBUTENE-1 AT PRESSURES UP TO 4000 atm

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In a previous work ([1]) it was shown that high pressure very significantly increases the rate of polymerization of 2,3-dimethylbutene-2. Thus, at 300° and a pressure of 200 atm, only 20% of this olefin polymerized in 50 hr, whereas at 23000 atm the entire monomer was polymerized in 3 hr.

In the present work our aim was to study the kinetics of the polymerization of 2,3-dimethylbutene-2 under high pressure, as well as the properties and composition of the polymers obtained. We also studied the polymers of 2,3-dimethylbutene-1 and 3,3-dimethylbutene-1 obtained under analogous conditions.

The olefins used were distilled immediately before the experiment on a rectification column with an efficiency of 30 theoretical plates and were characterized by the following constants: 2,3-dimethylbutene-2, b.p. 72.8—73.1° (760), d_4^{20} 0.7084, n_D^{20} 1.4122; 2,3-dimethylbutene-1, b.p. 55.2—55.3° (760), d_4^{20} 0.6775, n_D^{20} 1.3900; 3,3-dimethylbutene-1, b.p. 41.0—41.2° (760), d_4^{20} 0.6530, n_D^{20} 1.3760. The indicated constants are close to the literature data ([2]).

The experiments were carried out in lead ampoules of 14–15 ml capacity, placed in a reactor made of 40Kh steel. The pressure was created by oil and measured with a spring manometer up to 10000 kg/cm^2. The temperature in all experiments was $290 \pm 2°$ and was measured with a thermocouple introduced into the reactor to its middle in a long steel sheath. The duration of the experiments was counted from the moment the specified temperature was reached until the electric heating of the reactor was switched off. After the ampoules were opened, the monomeric fraction of the reaction product was distilled off on a rectification column, and the dimeric and higher fractions were distilled off in vacuum from a Claisen flask. The polymeric fractions were transparent liquids.

Fig. 1. Polymerization of 2,3-dimethylbutene-2 at 290° and 3660–3870 atm: **1** –total polymer yield; **2**–yield of dimeric fraction

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Figure 1 shows the results of experiments on the polymerization of 2,3-dimethylbutene-2 at 3660–3870 atm and τ from 2 to 32 hr. From consideration of Fig. 1 it is seen that the yield of the dimeric fraction passes through a maximum at τ about

16 h, which indicates that polymerization proceeds, at least in part, stepwise—through the intermediate formation of a dimer. Special experiments showed that the dimer fraction is indeed capable of further polymerization. Under the conditions studied, the average degree of polymerization n is small (polymerization of 2,3-dimethylbutene-2 at 290°, $\tau = 6$ h):

P, atm	Polymer yield, % of charge*	n
1900	9.1	2.3
2700	11.7	2.3
3820	17.7	2.5

In the head portion of the monomer fraction distilled off from the polymerization products of 2,3-dimethylbutene-2, the presence of 2,3-dimethylbutene-1 was established (by examination of the combination light-scattering spectra); no structural isomers of 2,3-dimethylbutene-2 were found. See below for the composition of the dimer fractions.

Under the same temperature and pressure conditions, 2,3-dimethylbutene-1 and 3,3-dimethylbutene-1 polymerize considerably faster than 2,3-dimethylbutene-2

Table 1

Polymerization of 2,3-dimethylbutene-2, 2,3-dimethylbutene-1, and 3,3-dimethylbutene-1 at 290°

Starting olefin	τ, h	P, atm	Unreacted starting olefin in % of charged product	Content of product with average degree of polymerization $n > 3$ as % of total polymer
2,3-dimethylbutene-2	5	3700–3780	11.6	–
Same	32	3740–3860	79.4	26.8
2,3-dimethylbutene-1	4	3410–3590	75.0	45.5
3,3-dimethylbutene-1	3	3500–3640	61.0	34.1

and form polymers of higher molecular weight (Table 1). The properties of several fractions (close in molecular weight) of the polymerizates of the three hexenes studied are given in Table 2. From examination of the data in Table 2 it follows that the polymerizates of the three hexenes studied, although close in molecular weight, differ substantially from one another in their properties, and also from the products of ionic polymerization.

In view of the fact that 2,3-dimethylbutene-1 was found in the monomer fraction of the polymerization product of 2,3-dimethylbutene-2, we carried out experiments on the polymerization of a mixture of these two hexenes. It turned out that small additions of 2,3-dimethylbutene-1 (about 4%) do not substantially affect the rate of polymerization of 2,3-dimethylbutene-2. In the polymerization under pressure of a mixture of both isomers in a 1:1 ratio, 2,3-dimethylbutene-2 enters into the reaction considerably faster, while 2,3-dimethylbutene-1 reacts somewhat more slowly than in the separate polymerization of these olefins under the same conditions. This fact indicates that a copolymerization reaction occurs. The values of the refractive index and specific gravity of the dimer fraction of the polymerizate of the mixture of 2,3-dimethylbutene-2 and 2,3-dimethylbutene-1 also indicate that this fraction is not a simple mixture of the corresponding fractions of the polymerizates of the pure olefins (see Table 2). The difference between the properties of the dimer fraction of the polymerizate of 2,3-dimethylbutene-2 and the properties of the dimer fractions of the polymerizate of 2,3-dimethylbutene-1 and of the copolymerizate of these two olefins confirms the conclusion made earlier (1)

* The difference between the weights of the charged and discharged material in all experiments did not exceed 0.2 g (2%).

conclusion that polymerization of 2,3-dimethylbutene-2 does not proceed through a stage of preliminary isomerization of it into 2,3-dimethylbutene-1.

We have carried out an investigation of the composition of the combinational light-scattering spectra of the dimeric fractions of the three hexenes studied. The method of obtaining the spectra and of measurement has been described previously ([4]). In view of the absence in the literature of data on the spectra of most olefins $C_{12}H_{24}$, in studying the dimeric fractions we used empirical criteria found by Goubau ([5]), primarily the lines in the region 1640–1680 cm^{-1}. In the spectrum of each olefin in the indicated region there is one line, the position of which, according to Goubau, depends on the nature of substitution in the ethylene group. Our spectral apparatus made it possible to observe in mixtures of olefins three lines in this region: 1640–1645, 1650–1660, and 1665–1680 cm^{-1}. The first of these belongs to monosubstituted ethylene, the second to cis- and unsymmetrical disubstituted ethylene, the third to trans-disubstituted, tri- and tetrasubstituted ethylene. Further refinement of the structure of the olefins from other lines proved not always possible.

The results of the investigation of the composition of the dimeric fractions, which in each case represent a mixture of not fewer than two olefins, are given in Table 3.

Table 2

Properties of polymeric fractions obtained from 2,3-dimethylbutene-2, 2,3-dimethylbutene-1, and 3,3-dimethylbutene-1

Polymer	b.p., °C (mm)	Mol. wt.	n_D^{20}	d_4^{20}	Bromine number	% unsaturated
Dimeric fraction of 2,3-dimethylbutene-2	68–70 (9)	162	1.4496	0.7963	102	103
Dimeric fraction of 2,3-dimethylbutene-1	51–125 (6)	164	1.4441	0.7906	70.5	72.3
Same	68.8–70.5 (10)	164	1.4417	–	69.5	71.3

Polymer	b.p., °C (mm)	Mol. wt.	n_D^{20}	d_4^{20}	Bromine number	% unsaturated
1st dimeric fraction of 3,3-dimethylbutene-1	69–73 (20)	153	1.4229	0.7443	79.6	76.0
2nd dimeric fraction of 3,3-dimethylbutene-1	75–140 (20)	177	1.4316	0.7620	–	–
Polymeric fraction of 2,3-dimethylbutene-2	120–147 (5)	242	1.4652	0.8303	62.0	93.0
Polymeric fraction of 2,3-dimethylbutene-1	125–159 (6)	234	1.4590	0.8232	60.4	88.5
Polymeric fraction of 3,3-dimethylbutene-1	200–232 (20)	348	1.4578	0.8231	50.0	109
Polymeric fraction of 2,3-dimethylbutene-2	147–191 (5)	285	1.4729	0.8476	55.5	99.0

Polymer	b.p., °C (mm)	Mol. wt.	n_D^{20}	d_4^{20}	Bromine number	% unsaturated
Polymeric fraction of 2,3-dimethylbutene-1	residue above 149 (5)	345	1.4706	0.8470	49.5	107
Dimeric fraction of polymerizate of a mixture of 2,3-dimethylbutene-2 and 2,3-dimethylbutene-1 (1 : 1)	58–125 (6)	–	1.4441	0.7997	87.3	–
Dimeric fraction in ionic polymerization of 2,3-dimethylbutene-2 ([3])	70–110 (100)	–	1.4280–1.4351	–	–	–
Dimeric fraction in ionic polymerization of 2,3-dimethylbutene-1 ([3])	70–111 (100)	–	1.4257–1.4353	–	–	–

Consideration of the data of Table 3 leads to the conclusion that in the process of polymerization of the three hexenes studied structural isomerization occurs. Indeed, if no structural isomerization occurred, then from 2,3-dimethylbutene-2 during polymerization one could not expect formation of cis-dialkylethylenes; however, in actuality, in

in the dimer fraction, cis-dialkylethylenes are present in predominant amount. Likewise, it is impossible to account, without assuming structural isomerization, for the formation of monoalkylethylenes from 2,3-dimethylbutene-1 during its dimerization. It might be supposed that the initial monomer first isomerizes and that the structural isomer thus formed then polymerizes itself and enters into a copolymerization reaction with the original olefin. However, in the monomer fraction of the polymerizate of 2,3-dimethylbutene-2, no structural isomers of it were found. This fact permits the supposition that, in the polymerization of this olefin, structural isomerization is undergone not by monomer molecules or radicals, but by dimer molecules or radicals, $C_{12}H_{23}$.

Table 3

Composition of the dimer fractions of 2,3-dimethylbutene-2, 2,3-dimethylbutene-1, and 3,3-dimethylbutene-1

Structural groups in the dimer fraction	2,3-Dimethylbutene-2	2,3-Dimethylbutene-1	3,3-Dimethylbutene-1
$H_2C{=}CH{-}R$	−	+	−
$H_2C{=}C(R){-}R$	−	?	?
$RHC{=}CHR$(cis)	+(predominates)	?	+
$RHC{=}CHR$(trans)	?	?	?
$RHC{=}C(R){-}R$	+	+	?
$R{-}C(R){=}C(R){-}R$	+	+	+

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References Cited

1. M. G. Gonikberg, V. P. Butuzov, V. M. Zhulin, DAN, **97**, 1023 (1954).

2. R. D. Obolentsev, *Physical Constants of Hydrocarbons of Liquid Fuels and Oils*, 1953.

3. F. C. Whitmore, P. L. Meunier, *J. Am. Chem. Soc.*, **63**, 2197 (1941).

4. V. T. Aleksanyan, Kh. E. Sterin et al., *Izv. AN SSSR, ser. fiz.*, **19**, No. 2, 225 (1955).

5. J. Goubeau, *Die Raman-Spektren von Olefinen*, Beih. Zs. angew. Chem., No. 56 (1948).

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