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Abstract

Full Text

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ON PRODUCTS WITH AN ODD NUMBER OF MONOMER UNITS FORMED DURING THE THERMAL POLYMERIZATION OF CYCLOHEXADIENE-1,3

Of the products formed during the thermal polymerization of cyclohexadiene-1,3, the dimer has so far been studied; its structure corresponds to 1,4-etheno-1,4,5,6,9,10-hexahydronaphthalene ([1],[2]). From the products of thermal polymerization we also isolated higher solid polymers, whose molecular weight ranged from 396 to 1088 ([3]). In order to establish the mechanism of polymerization of cyclohexadiene-1,3 to higher polymers, it seemed of interest to isolate and study other low-molecular products that might be formed, besides the dimer. For this purpose we carried out a spectrophotometric study of the monomeric products, always present in some amount in the crude product after polymerization, and performed experiments to determine the content of trimeric product in the liquid portion of the polymer. In the mixture of monomeric products remaining at the end of the polymerization experiments, we found benzene, identified by peaks on the absorption curve at 249, 255, and 261 mμ. From the magnitude of the absorption at these peaks, the amount of benzene was determined. The absorption due to the presence of cyclohexadiene-1,3, which strongly absorbs light in this region of the spectrum, was calculated from the absorption at $\lambda \geq 270$ mμ, i.e., in the region where benzene does not absorb, and was then subtracted from the absorption found experimentally at the above-mentioned wavelengths.

Thus it was found that the benzene content in the monomeric products after polymerization at 180° was $16.1 \pm 3.9\%$ in an experiment lasting 8 hr and $21.8 \pm 5.1\%$ in an experiment lasting 10 hr. In experiments at 200°, benzene was found to be 47.1, 40.4, and 23.5% in the monomeric products for polymerization times of 2, 10, and 40 hr, respectively. In experiments at 140, 150, and 160°, benzene was not found, possibly because of its small amount, on the one hand, and the difficulty of spectrophotometric determination of benzene in the presence of the strongly absorbing cyclohexadiene-1,3, on the other. To calculate the amount of trimer, the molecular weight of the liquid portion of the polymer precipitated with methyl alcohol was determined cryoscopically. Numerous determinations always gave a molecular weight between 160 and 240, from which it follows that the liquid portion of the polymer isolated from the methanol-precipitated product contains only dimer and trimer.

The amount of trimer was calculated by the formula

$$\alpha = \frac{300}{\text{M. w.}}(\text{M. w.} - 160),$$

where M. w. is the molecular weight determined experimentally, and α is the percentage of trimer in the mixture. As can be seen from Table 1, the trimer content in the liquid portion was up to 10%.

The data obtained indicate that, in the process of thermal polymerization of cyclohexadiene-1,3, active intermediate monomer particles are formed which are capable either of adding to the dimer with formation of trimer or of disproportionating to benzene. On the basis of the results obtained, the first stages of polymerization

Table 1

Amount of cyclohexadiene-1,3 trimer obtained in the thermal polymerization of cyclohexadiene-1,3

Polymerization temp., °C	140°	140°	140°	140°	150°	150°	150°	150°	150°	160°	160°
Polymerization duration, h	10	30	50	70	5	10	20	30	42	5	10
Degree of polymerization, %	23.6	48.7	64.3	68.8	27.4	41.1	49.0	56.2	66.7	38.5	44.7
Amount of trimer, %	0.6	1.3	4.2	3.8	1.0	1.7	3.5	3.6	4.8	2.0	1.4

Polymerization temp., °C	160°	160°	160°	180°	180°	180°	200°	200°	200°	200°	200°	200°
Polymerization duration, h	20	30	70	2.5	5.0	10	1.0	2.5	5	10	20	30
Degree of polymerization, %	63.2	68.7	78.3	49.5	60.9	68.0	57.6	70.6	76.5	83.0	87.2	88.6
Amount of trimer, %	8.4	10.0	11.1	4.7	4.6	7.9	5.3	5.6	6.2	8.5	10	9.8

Note. The degree of polymerization is less than the degree of overall conversion, since, along with polymers, the products contain a certain amount of monomeric products other than cyclohexadiene (benzene, etc.).

can be formulated as follows:

$$C_6H_8 + C_6H_8 \rightarrow C_6H_7^{\cdot} + C_6H_9^{\cdot}. \quad (1)$$

$$C_6H_7^{\cdot} \text{ (or } C_6H_9^{\cdot}) + C_6H_8 \rightarrow C_6H_7 \cdot C_6H_8^{\cdot} \text{ (or } C_6H_9 \cdot C_6H_8^{\cdot}) \quad (2)$$

and so on. Simultaneously with reaction (2), disproportionation may proceed:

$$C_6H_7^{\cdot} + C_6H_8 \rightarrow C_6H_6 + C_6H_9^{\cdot} \quad (3)$$

$$C_6H_7^{\cdot} + C_6H_9^{\cdot} \rightarrow C_6H_6 + C_6H_{10}. \quad (4)$$

(The dots mark unpaired electrons present in the free radicals.) At the same time, the possibility remains of a polymerization mechanism involving the initial formation of dimeric biradicals, whose subsequent recombination gives the polymer (4).

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