

[CONTRIBUTION FROM THE ESSO LABORATORIES OF THE STANDARD OIL DEVELOPMENT COMPANY, CHEMICAL DIVISION, AND THE I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT]

## Preparation and Structure of High Molecular Weight Polybutenes

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The polymerization of isobutene at low temperatures<sup>1,2</sup> with catalysts of acidic nature<sup>3,4,5,6</sup> takes place with almost explosive violence, and is among the most rapidly completed of organic reactions. Under suitable conditions, it is possible to obtain an almost quantitative yield of rubber-like solid from liquid isobutene within a fraction of a second. This transformation is of particular interest in that it is characterized by the absence of any apparent decrease in rate of reaction with lowering of temperature, and also by the fact that polymers of the highest molecular weight as determined by the Staudinger viscosity method<sup>7</sup> are obtainable at the lowest temperatures.

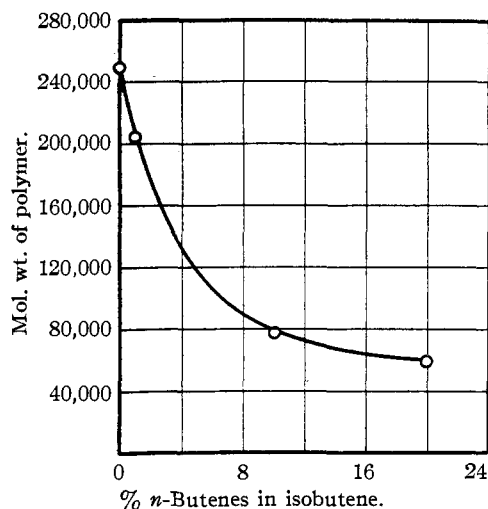


Fig. 1.—Effect of *n*-butenes on the molecular weight of polyisobutenes produced at  $-95^{\circ}$  using  $\text{BF}_3$  catalyst.

For example, a sample of isobutene maintained at its boiling point and treated with a slow stream of  $\text{BF}_3$  will show a considerable induction

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(1) M. Otto and M. Mueller-Cunradi, U. S. Patent 2,084,501 (1937).

(2) F. A. Howard, U. S. Patent 2,049,062 (1936).

(3) P. K. Frolich, U. S. Patent 2,109,772 (1938).

(4) Schering, German Patent 278,486 (1914).

(5) J. C. Zimmer and E. W. Carlson, U. S. Patent 2,074,093 (1937).

(6) H. G. Schneider, U. S. Patent 2,131,196 (1938).

(7) Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag Julius Springer, Berlin, 1932.

period followed by a vigorous reaction to produce an oil, whereas a similar sample precooled to  $-80^{\circ}$  will react immediately on introduction of the  $\text{BF}_3$  gas to produce a polymer of much higher molecular weight.

This marked difference in reaction behavior and in the character of the products is indicative of a difference in mechanism between low temperature polymerization and the more common reactions which characterize tertiary olefins. Other important factors in the polymerization of isobutene at low temperature are discussed below.

**Purity of Raw Materials.**—Under particular test conditions that have been used by the writers, certain compounds have been observed to act as poisons for the reaction. These materials in isobutene reaction mixtures result in a decided lowering of the molecular weight of the polymer product,<sup>8,9</sup> or, in extreme cases, interfere even more seriously with the course of the reaction.

It is of particular interest to note the behavior of pure isobutene intentionally contaminated with other hydrocarbon olefins. Lower olefins such as ethylene and propylene are apparently inert. Normal butenes are more reactive but they differ greatly from isobutene as regards their polymerization characteristics.<sup>10,11</sup> However, they are capable of reacting with isobutene under the low temperature conditions of reaction. This results in a lowering of the molecular weight of the polymer product as shown in Fig. 1.

Similarly, higher olefins may exhibit a depressing effect on the molecular weight of the polymer. For example, very small quantities of diisobutene will greatly decrease both the yield and molecular weight of the polyisobutene. This observation is of special interest since it shows that, although the polymerization must pass through successive stages of chain formation, the possible intermediate stage represented by molecular dimer as obtained by conventional polymerization

(8) E. L. Baldeschwieler, U. S. Patent 2,131,342 (1938).

(9) R. T. Haslam, U. S. Patent 2,145,350 (1939).

(10) British Patent 467,932 (1936).

(11) L. W. Lebedev and E. P. Filanenko, *Ber.*, **58**, 163-168 (1925)

methods cannot be present in appreciable quantity during or preceding the polymerization step in the preparation of high polymers. Triisobutene has a similar effect.

In this connection it is also of interest to point out that while dimers or trimers of isobutene are capable of slow polymerization at room temperature to give oily products, when using the low temperature technique discussed here, high polymers have not been obtained.

Other poisons are sulfur compounds such as hydrogen sulfide or mercaptans, and hydrogen halides such as anhydrous hydrogen fluoride or hydrogen chloride. The latter have a marked depressing effect on the molecular weight of the polymer in spite of their well-known promoter action in certain metallic halide catalyzed alkylation<sup>12</sup> or dimerization reactions. At elevated temperatures, the use of hydro-halogen acids has been found beneficial for the polymerization of olefins with boron fluoride.<sup>13</sup>

This difference in behavior of halogen acids in polymerization and in alkylation reactions appears to support the view that the formation of high polymers and the well-known dimerization reactions result from different types of activation. The poisoning effect of hydrogen chloride may therefore result from the formation of diisobutene which is known to be a polymerization depressor in the formation of polyisobutene at low temperatures. The negative action of halogen acids observed here has also been found in the case of the polymerization of styrene by stannic chloride.<sup>14</sup>

**Catalysts.**—A variety of catalysts for the polymerization of isobutene has been reported.<sup>15</sup> The effectiveness of these depends upon the conditions employed for carrying out the reaction, but good results are generally obtained with such materials as titanium tetrachloride,<sup>16</sup> boron fluoride, and aluminum chloride.

In general, the suitability of a catalyst for the low temperature polymerization of isobutene cannot be predicted. Double compounds of the Friedel-Crafts type catalysts with various polar solvents have been found effective in polymerizing olefins at temperatures in the neighborhood of

0°,<sup>17</sup> but appear to be inactive at considerably lower temperatures.

**Temperature.**—Temperature control is of great importance in the polymerization process since the reaction is rapid and exothermic. Experimentally, the heat of reaction is somewhat difficult to measure accurately, but it has been established to be in the neighborhood of 10,000 calories per mole at about -78°. Higher values would be expected on the basis of theoretical calculations.

The general effect of temperature upon the molecular weight of isobutene polymers produced under otherwise constant conditions is shown in Fig. 2 for one type of catalyst.<sup>18</sup>

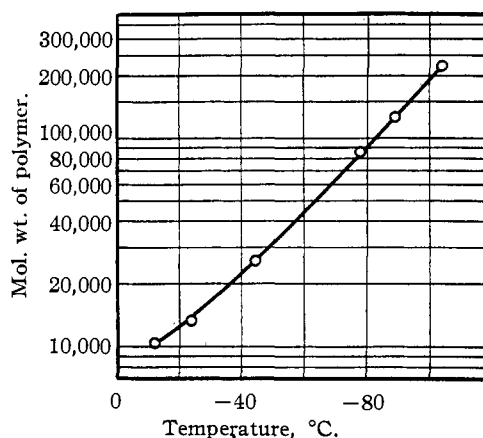


Fig. 2.—General effect of reaction temperature on the molecular weight of polymers produced from isobutene.

**Diluents.**—Diluents are employed in the polymerization to moderate the violence of the reaction and thereby make for better temperature control, so that products of uniformly high molecular weight can be obtained.<sup>19</sup>

The important role played by diluents in the preparation of polyisobutene is clearly indicated by the data presented in Fig. 3, where, under a given set of experimental conditions, the molecular weights of products obtained are plotted against corresponding amounts of an inert diluent in the reaction mixture. It will be noted from these results that the molecular weight of the product increases according to an exponential func-

(17) British Patent 358,068 (1931).

(18) It may be mentioned here that the molecular weights cited throughout this paper, while comparable insofar as the one variable under consideration is concerned, are not necessarily the maximum values obtainable. By proper manipulation of the different reaction variables, it is possible to extend considerably the molecular weight range of the polymers in a number of cases.

(19) P. J. Wiezevich, U. S. Patent 2,138,895 (1938).

(12) V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).

(13) F. Hofman, M. Otto and W. Stegemann, German Patent 504.-730.

(14) G. Williams, *J. Chem. Soc.*, 1046 (1938).

(15) British Patent 483,563 (1936).

(16) R. P. Russell, U. S. Patent 2,139,038 (1938).

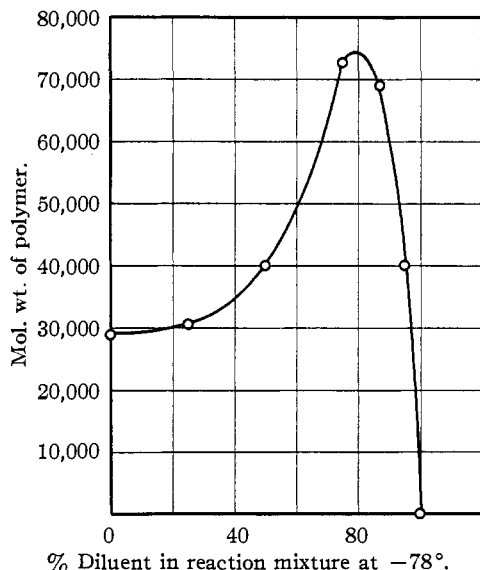


Fig. 3.—General effect of diluent concentration on the molecular weight of polymers produced from isobutene.

tion with increasing proportions of diluent until a limiting concentration of approximately 80% by volume is reached, at which point there occurs a precipitous drop in the molecular weight. Closely similar curves are obtained using different diluents. In some instances, the actual values for molecular weight may be somewhat shifted by as much as 10,000 due to the difficulty in controlling other variables. In all cases, however, the general shape of the curve remains the same.

**Catalyst Concentration.**—With regard to the concentrations in which catalysts are employed, several interesting effects have been observed. In one specific case, it has been demonstrated that a critical concentration of catalyst (approximately 0.03%) has to be exceeded for the production of polymer. Some idea of the actual quantity of polymer which may be obtained from a given amount of an aluminum chloride catalyst is shown in Figs. 4 and 5, the latter being constructed from the limiting slopes of Fig. 4. The catalyst efficiency is noted to be highest at the greatest dilutions, presumably because of a lower loss due to mechanical occlusion of unreacted catalyst in the polymer. Figure 5 is of interest in giving an extrapolated ratio of about three moles of polymer per mole of aluminum chloride at an infinitely low concentration. However, this should not be taken as definite proof that one molecule of aluminum chloride produces three molecules of polymer, for the data may be subject

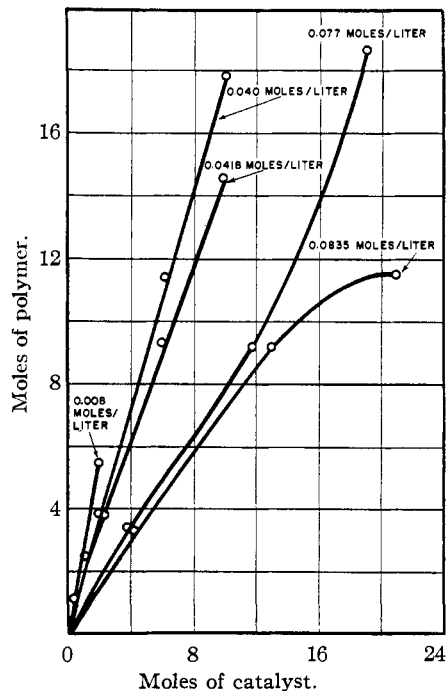


Fig. 4.—Moles of isobutene polymer produced vs. moles of  $\text{AlCl}_3$  catalyst added for different catalyst concentrations.

to some question because of possible uncertainties involved in the determination of exact molecular weights by viscosity methods.

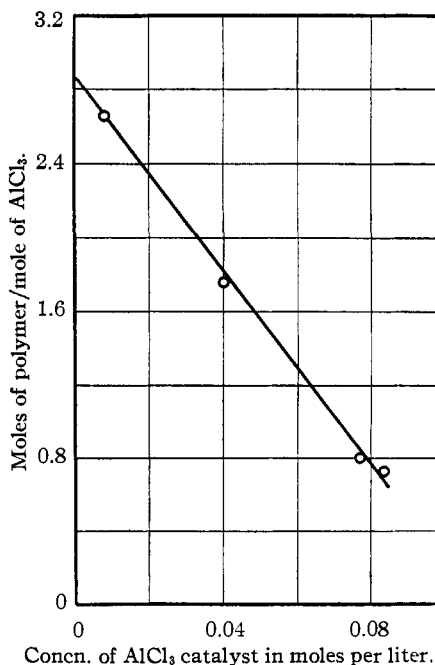


Fig. 5.—Efficiency of catalyst in polymerizing isobutene at  $-78^\circ$  as a function of catalyst concentration.

**Yield.**—The polymerization of isobutene to high molecular weight products can be carried out with yields of 90% or better. Within reasonable limits, the yield to which the reaction is carried has not been found to influence the average molecular weight of the products.

**Structure of Polybutene.**—A discussion of the low temperature polymerization of isobutene quite naturally raises the question of the structure of the polymers produced by that technique.

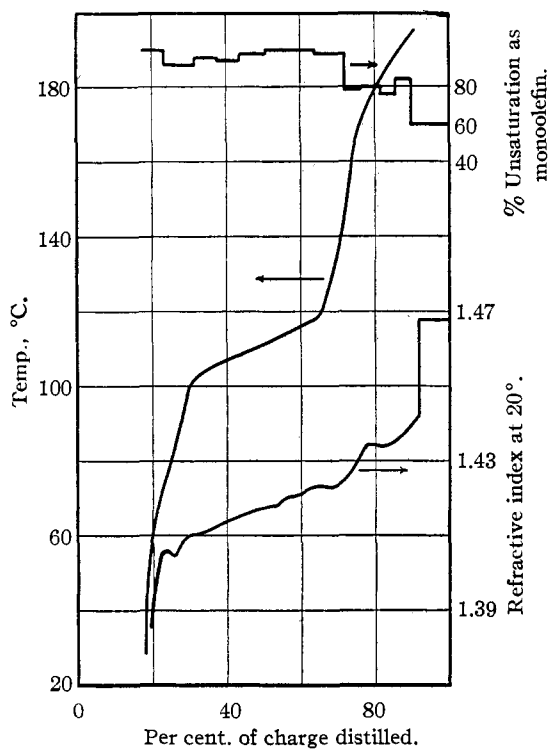
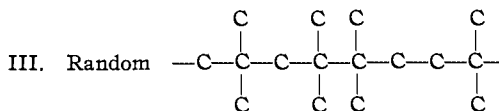
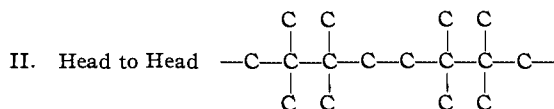
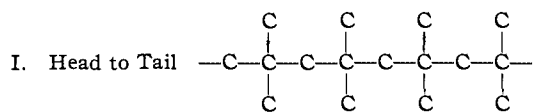


Fig. 6.—Analytical distillation of C<sub>4</sub> to C<sub>12</sub> hydrocarbons from the thermal decomposition of polyisobutene in an iron still at 350°.

On the basis of numerous observations which would lead too far to be included in a condensed report, it is the writers' belief that the polymers are linear, and that therefore there are only four structural possibilities to consider, namely



IV. Mixture of Type I, II or III molecules.

It is assumed that all of these structures include one residual terminal double bond, which seems to be borne out by determination of unsaturation of the product as related to average molecular weight.

Of these various structures, type I is most probable for the polyisobutene molecule. Its decomposition would be expected to give the ordinary diisobutenes, 2,4,4-trimethyl-1-pentene and its -2-isomer. It is a fact that an isobutene polymer of about 20,000 molecular weight on decomposition at 350° gave degradation products, an analytical distillation of which is shown in Fig. 6. The polymer gave about 50% of monomer and about 20% hydrocarbons boiling in the octene range. Figure 7 shows the result of a refractionation of the dimer cut. A portion of fraction 1 reacted with phenol to give a 65% yield of the characteristic tetramethylbutylphenol, m. p. and mixed m. p. 84°.

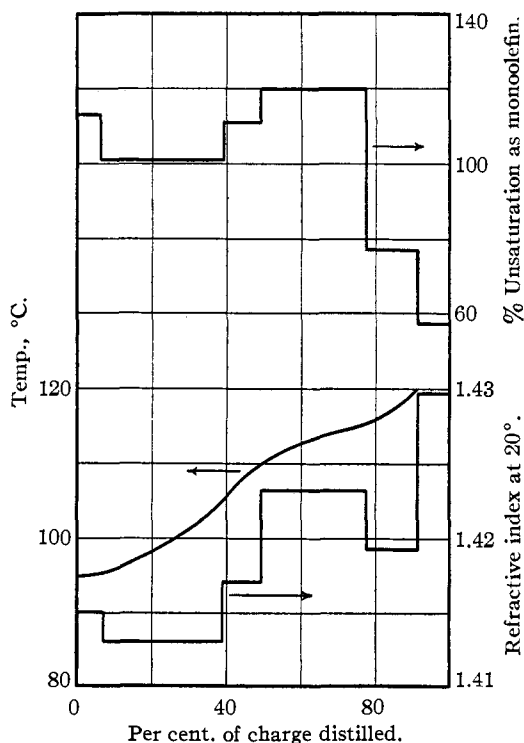


Fig. 7.—Analytical distillation of C<sub>8</sub> fraction from the thermal decomposition of polyisobutene in a glass still at a controlled temperature of 350°.

The occurrence of the higher boiling octenes

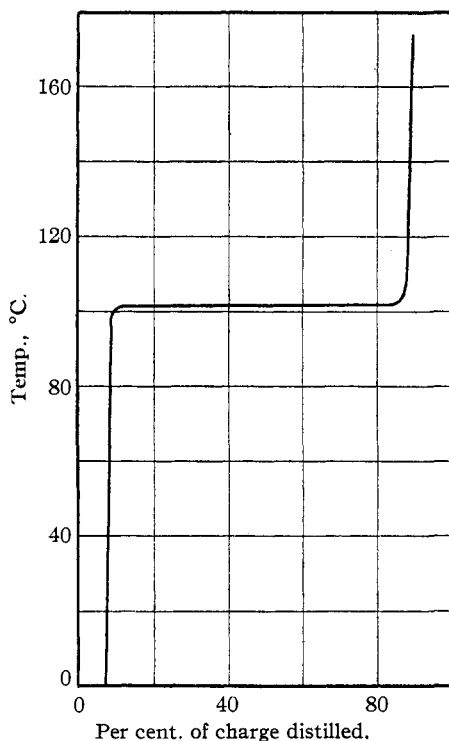


Fig. 8.—Fractionation of 2,4,4-trimethylpentene-1 subjected to a temperature of 350° for one hour.

may be due either to isomerization during the pyrolysis or to the possibility of some random structure (III) in the polymer. The material boiling at 110–115° on ozonization or chromic acid oxidation gave acetone, acetic acid and an odor of fatty acids. This may indicate the presence of 2,5-dimethyl-2-hexene.

The possibility of isomerization of the octenes after their liberation from the polymer was tested by heating diisobutene (b. p. 101.5–101.9°) at 350° for an hour. As shown in Fig. 8, cracking and polymerization took place but there was no noticeable degree of isomerization.

**Acknowledgment.**—The writers wish to acknowledge the active participation of many of their associates in obtaining the large amount of information from which this paper is abstracted.

#### Summary

The catalytic polymerization of isobutene at low temperatures to form a homologous series of polymers ranging to very high molecular weights is discussed in detail.

The structure of the polymers is partially established.

ELIZABETH, NEW JERSEY

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[CONTRIBUTION FROM THE UNIVERSITY OF MISSOURI]

## The Action of Aluminum Chloride on Aromatic Hydrocarbons. II. The 1,3-Dimethyl-4-propylbenzenes

BY DOROTHY NIGHTINGALE AND BENOIST CARTON, JR.<sup>1</sup>

When the 1,3-dimethyl-4-butylbenzenes are warmed with aluminum chloride, the butyl group migrates to the 5 position.<sup>2</sup> During the rearrangement, the *n*- and *s*-butyl radicals are isomerized to *s*- and *t*-butyl radicals, respectively.

We have now completed a similar study of the 1,3-dimethyl-4-propylbenzenes. The results, showing that both the 4-*n*-propyl and the 4-isopropyl hydrocarbon rearrange to yield 1,3-dimethyl-5-isopropylbenzene, should be compared with those of Baddeley and Kenner,<sup>3</sup> who reported that 1,3,4-tri-*n*-propylbenzene when heated to 100° with aluminum chloride yielded 1,3,5-tri-*n*-propylbenzene. These authors, how-

ever, gave no evidence to support their statement that the migrating propyl group did not isomerize to an isopropyl group and, in view of our results, their conclusion is questionable. Similarly, Heise and Tohl's<sup>4</sup> conclusions that *n*-propylbenzene and aluminum chloride yielded *m*- and *p*-di-*n*-propylbenzene are also doubtful.

The present investigation has shown that the *n*-propyl radical in 1,3-dimethyl-4-*n*-propylbenzene does not readily shift to the 5 position but that its migration is accompanied by isomerization. At 55° the rearrangement is far from complete; at 85 and 100° the product appeared to consist largely of 1,3-dimethyl-5-isopropylbenzene along with some of the starting material.

Rearrangement of 1,3-dimethyl-4-isopropyl-

(1) Abstract of a dissertation to be presented by Benoist Carton, Jr., in partial fulfillment of the requirement for the degree of Master of Arts at the University of Missouri.

(2) Nightingale and Smith, *THIS JOURNAL*, **61**, 101 (1939).

(3) Baddeley and Kenner, *J. Chem. Soc.*, 303 (1935).

(4) Heise and Tohl, *Ann.*, **270**, 155 (1892).