722. *The Polymerization of Olefins with Friedel–Crafts Catalysts.*

By R. L. Meier.

Polymerization of 3 : 3-dimethylbut-1-ene by boron trifluoride causes rearrangement of at least half of the *neo*pentyl groups. *cis-trans*-Isomerization of but-2-ene does not occur at 20°. Thus the mechanisms involving catalyst and co-catalyst proposed for the polymerization of *iso*butene cannot apply to all olefins.

All the polymers obtained from gaseous propylene, but-1-ene, *cis*- and *trans*-but-2-ene, and *iso*butene with gaseous boron trifluoride at 0—60° show evidence for rearrangement, and for extensive disproportionation except in the case of *iso*butene. Detailed analysis of the liquid-phase polymerization of but-2-ene with aluminium chloride and bromide showed that (1) all products had at least eight carbon atoms, (2) C_9 and C_{10} hydrocarbons were as common as the C_8 structures, (3) most C_8 hydrocarbons were saturated while many diolefins occurred in the C_{20} group, and (4) most of the spent catalyst is found in a tarry residue combined with a conjugated polyolefinic hydrocarbon. The copolymerization constants between but-1- and -2-ene were determined.

This information suggests that RCH:CH$_2$ and RCH:CHR at 0—20° start polymerizing by a process involving two catalyst molecules, two monomers, and possibly a co-catalyst. Chain growth occurs by means of a carbonium-ion intermediate. Chain transfer is the most common form of termination. Chain cessation can be brought about by hydrogen or alkyl transfer.

Most studies of the mechanism of olefin polymerization by Friedel–Crafts catalysts have used monomers which polymerize rapidly at very low temperatures to yield high polymers. These include *iso*butene, styrene, α-methylstyrene, the vinyl ethers, and some analogues. Most olefins polymerize more easily around 0° and yield low polymers. Industrial investigations have indicated that the latter process is more complex. Olefins behaving in the more usual way and yielding products amenable to analysis were selected for this study.

A neo*Pentyl System.*—Whitmore (*Ind. Eng. Chem.*, 1934, **26**, 94) proposed that acid-catalyzed polymerization involved the formation of an intermediate containing an electron-deficient carbon atom, usually referred to as a "carbonium ion." Mechanisms proposed since then see reviews by Heiligmann (*J. Polymer. Sci.*, 1949, **4**, 183), Plesch (*Research*, 1949, **2**, 267), and Thomas (*Ind. Eng. Chem.*, 1949, **41**, 2564)] have centered around the special reactivity of the carbonium ion.

Independently, and based upon altogether different evidence, a large body of experience has accumulated concerning Wagner-type rearrangements of the *neo*pentyl group which also involve a short-lived carbonium ion. From a detailed kinetic study of *neo*pentyl and related systems Dostrovsky, Hughes, and Ingold (*J.*, 1946, 157, 173) concluded that rearrangement to *tert.*-amyl always takes place when the *neo*pentyl group is converted into a short-lived cation, but never when this group is converted into a short-lived anion. The compound chosen for this study was 3 : 3-dimethylbut-1-ene, since it should distinguish simply between carbonium ion and carbanion intermediates.

Ecke, Cook, and Whitmore (*J. Amer. Chem. Soc.*, 1950, **72**, 1511) proved that free radicals involving the *neo*pentyl system do not rearrange and also that reactions hitherto believed to involve a carbonium ion, *e.g.*, addition of hydrogen chloride to an olefinic bond, may lead under certain conditions to partial retention of the *neo*pentyl structure, and they offered a tentative explanation for this behaviour.

If these concepts of chemical behaviour are applicable to 3 : 3-dimethylbut-1-ene the following reactions will be expected (where A represents a catalyst–co-catalyst complex):

$$\underset{\text{(I.)}}{\mathrm{Me_3C{\cdot}CH{:}CH_2}} + \mathrm{A} \longrightarrow \underset{\text{(II.)}}{\mathrm{Me_3{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}\overset{-}{A}}} \longrightarrow \underset{\text{(III.)}}{\mathrm{Me_2\overset{+}{C}{\cdot}CHMe{\cdot}CH_2\overset{-}{A}}}$$

Ordinarily (III) would be expected to attack another olefin molecule, yielding eventually a polymer stemming from this structure. On the other hand, anionic or free-radical type polymerization would be expected to lead to polymer derived from intermediates which had not rearranged. The rearrangements in the *neo*pentyl structure are very easily detected by the changes in infra-red absorption. A very intense absorption caused by the C–C vibrations in the $Me_3C{\cdot}CH_2$ group at 8·03 μ. should disappear if rearrangement occurred.

Polymerization in the gaseous phase was selected for this test, both because of the simplicity of the technique and because of the limited quantity of monomer available. The process employed was very similar to that used by Evans and Weinberger (*Nature*, 1947, **159**, 437) for gaseous polymerization of di*iso*butene except that scrupulous precautions to maintain absolutely anhydrous conditions were not taken because the objective of this step was to assure a high yield of polymer.

If present theories of polymerization apply to this monomer (Norrish and Russell, *Nature*, 1947, **160**, 543; Plesch, *Research*, 1949, **2**, 267), two forms of trimer are to be expected :

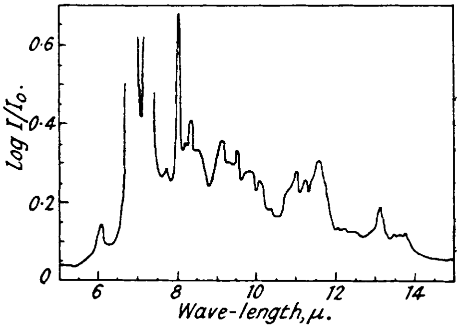
Without rearrangement : $Me_3C{\cdot}CHMe{\cdot}CH_2{\cdot}CH(CMe_3){\cdot}CH{:}CH{\cdot}CMe_3$ (IV.)

With complete rearrangement : $Me_2CH{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe{:}CMe_2$ (V.)

A few isomers with the olefinic bond moved to some neighbouring location are to be expected but the skeletal structures should remain the same.

The most striking feature of the infra-red spectrum (Fig. 1) is the peak at 8·03 μ. which suggested, on the basis of comparison with such analogues as 2 : 2 : 4-trimethylpentane, that a large proportion of the *neo*pentyl groups has entered the polymer without rearrangement. This may be as much as 50%, possibly even more. By itself this information would be an excellent confirmation of Norrish and Russell's theory, which holds that simultaneous cationic and anionic polymerization may occur, but other features of the spectrum make such an interpretation doubtful. The absorption bands associated with the olefinic bond do not show a straightforward relationship with the expected structures. The presence of the band at 6·05 μ. indicates that double bonds are present. The $R_2C{:}CR_2$ type of olefinic bond, expected in (V), has no other absorption band, but $RCH{:}CHR$, expected from (IV), should yield a peak at 10·40 μ. which definitely does not exist.

FIG. 1.



Infra-red spectrum of product of boron-trifluoride-catalysed polymerization of 3 : 3-*dimethylbut*-1-*ene*.

Simple intramolecular proton transfer in (IV) and (V) is to be expected; it would yield either $R_2C{:}CH_2$ or $R_2C{:}CHR$ olefins. The former should show up at 11·25 μ., where there is a small indication, and the latter at 12·24 μ., where no important absorption exists. Indeed the most probable olefinic group present, on the basis of the spectrum, is the mono-substituted ethylene $R{\cdot}CH{:}CH_2$. It has twin absorption peaks at 10·1 and 11·0 μ. Its existence would suggest that rather remarkable rearrangements had taken place.

There are other significant bands which cannot be identified. The absorptions at 11·6 and 13·1 μ. are also found in *iso*butene polymers. They may indicate either special vibrations set up in the neighbourhood of *tert.*-butyl groups of traces or catalyst and co-catalyst fragments (Flett and Plesch, *Proc. Roy. Dublin Soc.*, in the press).

It can be concluded from this experiment that only some of the *neo*pentyl groups have rearranged. There is some evidence that rearrangements are not only of the simple Wagner type found previously with *neo*pentyl systems. If the carbonium intermediate is assumed, intermolecular reaction must proceed about as rapidly as intramolecular rearrangement in order to account for the retention of about half of the $Me_3C{\cdot}CH_2$ structure. Thus polymerizations and co-polymerizations with 3 : 3-dimethylbut-1-ene provide no clear-cut evidence on the mechanism of Friedel–Crafts polymerizations.

A cis-trans-*Isomerization System.*—An alternative approach for studying the initiation of acid-catalyzed polymerization is to follow the isomerization of *cis*- or *trans*-forms of an olefin to an equilibrium mixture.

Boron trifluoride is an active catalyst for polymerization in the gaseous phase. It had been ascertained previously that boron trifluoride, when passed through liquid but-2-ene, did not cause polymerization. It was expected, therefore, that in the gaseous phase one would obtain a measurable rate of acid-catalyzed isomerization of the pure *cis*- or *trans*-form, much as was observed by Price and Meister (*J. Amer. Chem. Soc.*, 1939, **61**, 1595) for stilbene, but no further reaction. However, a very rapid polymerization occurred immediately on mixing of boron trifluoride with slightly moist but-2-ene. A dense fog formed in the vessel which condensed into droplets of liquid polymer on the lower walls. After a partial polymerization conducted with only a small amount of trifluoride admixed with pure *trans*-but-2-ene, infra-red analysis of the remaining gaseous olefin showed that no isomerization had occurred. Thus, at 20—60°, boron trifluoride either initiates polymerization or leaves the olefins unchanged. If a carbonium-ion intermediate is formed it cannot dissociate to yield but-2-ene, because in such a process the equilibrium mixture of isomers would be produced, but it must proceed directly to polymer. There was no significant difference between the *cis*- and the *trans*-form, either in the rate of polymerization or in the infra-red spectra obtained from the polymers. The spectra (Figs. 2 and 3) indicated that some remarkable rearrangements must have occurred. The absence of isomerization suggests that the simple interaction of boron trifluoride with olefins may resemble that of the Ag^+ and Cu^+ ions in solution or the donor–acceptor arrangement described by Laubengayer and Bauer (*J. Amer. Chem. Soc.*, 1943, **65**, 889). The amount of bimolecular association however must be very small because no shrinkage in volume could be detected on mixing of boron trifluoride and ethylene (observed also by A. G. Evans and Meadows, *J. Polymer Sci.*, 1949, **4**, 359).

Large-scale Polymerization of But-2-ene with Boron Trifluoride.—The foregoing experiments were confined to small quantities of very pure materials. The results suggested that study of the composition of the polymer would yield many clues to the unexpected rearrangements. A larger quantity of mixed but-2-ene isomers was polymerized with the concentration of water vapour present (0·1—0·2 mole %) which appears to yield maximum rates of polymerization. On the average, one boron trifluoride molecule was responsible for the polymerization of 40—60 monomer molecules. There was no product which distilled below 110°, and, with the exception of a small plateau around 115°, there was no evidence of any significant amount of any pure component. The C_8 fraction (b. p. 110—117°), amounting to 1% of the whole polymer, was isolated and analyzed by infra-red methods. It contained at least 70% of 2 : 3 : 4-trimethylpentane, and about 20% of olefin $R_2C{:}CH_2$ and $RCH{:}CHR$. These components accounted for all the major peaks in the infra-red spectrum.

The most remarkable findings here were (1) that C_9 and C_{10} hydrocarbons were more abundant than C_8 compounds, and (2) that a large proportion of the components of lower molecular weight were saturated, rather than mono-olefins. Similar polymerization of *iso*butene yielded a polymer with sharply defined fractions, all of them olefins. The yields, as determined by precision distillation, were dimer 2%, trimer (low-boiling) 32%, trimer (high-boiling) 15%, tetramer 29%, pentamer—heptamer 21%, and residue 1%. Thus the polymerization process for but-2-ene involves alkyl transfer and hydrogenation–dehydrogenation reactions not found with *iso*butene, styrene, or similar molecules. Also supporting this conclusion is the infra-red spectrum of the but-2-ene polymer where there is found a spectacular absorption at 8·02 μ., which is specific for the *neo*pentyl grouping. There is no simple rearrangement by which the *neo*pentyl grouping can be formed from but-2-ene.

Polymerization of Other Gaseous Hydrocarbons with Boron Trifluoride.—Propylene polymerized quite slowly in the 10—60° range. The rate was not sensitive to changes in temperature, the presence of water vapour, increased concentrations of catalyst, or pressure up to two atmospheres. The rates of polymer formation were highly variable and even the shape of the rate curves was not reproducible at will. Such behaviour indicates either that trace constituents are important to the polymerization process and that the traces vary in effectiveness in a random and uncontrolled manner, or that catalysis is heterogeneous, or both.

The infra-red spectrum of the propylene polymer is more complex and indeterminate than most (Fig. 4). Four of the major absorption bands have not been identified. The maximum at 13·5 μ. is ascribed to the presence of trimethylene groups, in at least a fair proportion of the molecules. The double-bond structures $R_2C{:}CH_2$ and $RCH{:}CHR$ seem to predominate; other olefinic structures do not appear.

But-1-ene polymerizes even more slowly than propylene and resembles it very closely in most aspects. The spectrum is, in general, less varied (Fig. 5). Again both $R_2C{:}CH_2$ and $RCH{:}CHR$ are present, with no other olefins in evidence. The maxima at 13·5 and 13·76 μ. are attributed to trimethylene and tetramethylene groups respectively; their intensities suggest that these groupings account for 10—20% of the polymer.

The polymerization of *iso*butene was investigated in greater detail by other workers (Dainton and Sutherland, *J. Polym. Sci.*, 1949, **4**, 37; Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246), but the infra-red spectrum of the polymer was determined (Fig. 6), and the product fractionated, in order to gain a direct comparison with the other olefins. Its polymerization is many times more rapid than that of any other simple olefin.

Figs. 2—6.

Infra-red spectra of products of boron-trifluoride-catalysed polymerizations.

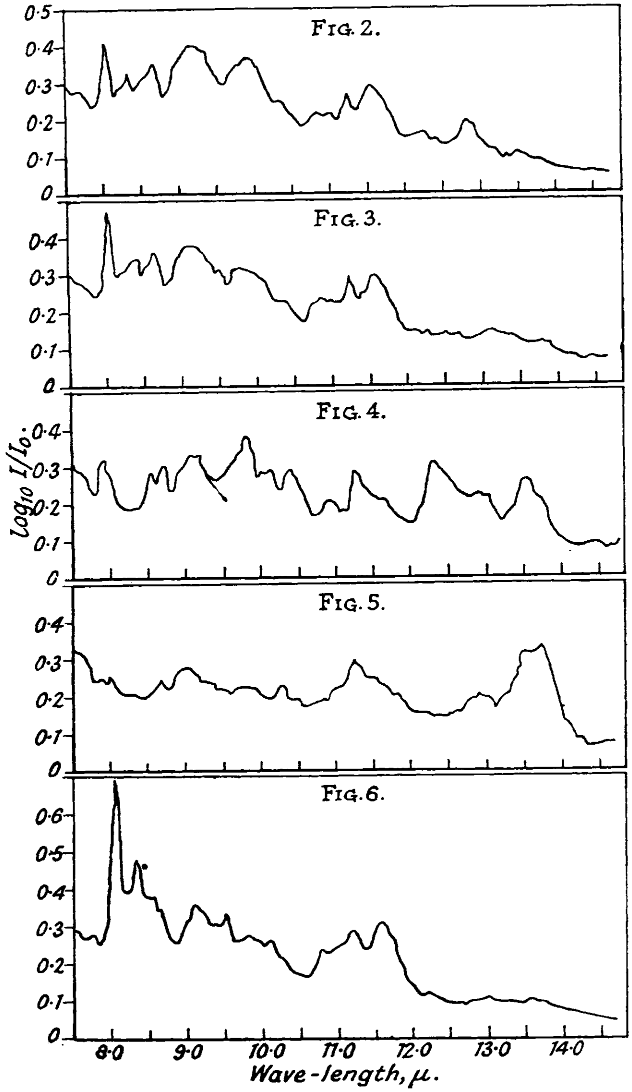


Fig. 2.—cis-*But*-2-*ene*. Fig. 3.—trans-*But*-2-*ene*. Fig. 4.—*Propylene*. Fig. 5.—*But*-1-*ene*. Fig. 6.—iso*Butene*.

Polymerization of But-2-ene in the Liquid Phase.—At low pressure, boron trifluoride does not catalyse the polymerization of liquid but-2-ene. However, aluminium chloride and bromide do catalyze this reaction, and a great many similarities could be demonstrated between their action in the liquid phase with an inert hydrocarbon solvent and the action of boron trifluoride in the gaseous phase (where the actual polymerization must occur either on the surface or in the interior of tiny droplets of liquid polymer). The significant features of the liquid-phase polymerization may be summarized briefly in the following statements.

(1) Polymerization does not begin immediately after the addition of a small amount of catalyst solution. Indeed there seems to be a fairly constant quantity of catalyst which is required in order to initiate noticeable polymerization. At 0°, with 50—70% of *n*-butane as a refrigerant-solvent, the presence of at least 0·1—0·2 mole % of aluminium halide is needed. The corresponding threshold for but-1-ene is much less, while for *iso*butene it is infinitesimal or non-existent.

(2) The medium in which the catalyst is dissolved appears to play an important part in catalyst activity. Ethyl chloride, methyl chloride, 1 : 2-dichloroethane, and lower aliphatic hydrocarbons were satisfactory in most respects, whereas carbon disulphide, sulphur dioxide, higher alkyl chlorides, ethers, and other oxygenated compounds are unsatisfactory owing either to an inhibiting action or to solvent decomposition.

(3) Once polymerization has been initiated the catalyst appears to be lost within a few minutes owing to side reactions. Thus the addition of a little catalyst solution causes an immediate burst of polymerization which after 1—10 minutes can no longer be detected. For other butenes the burst of polymerization reaches greater intensity but subsides more rapidly.

(4) Towards the beginning of polymerization each molecule of aluminium halide causes the polymerization of 300 monomer molecules, but this ratio declines rapidly as the but-2-ene is exhausted.

(5) The major product is a butane-soluble oil, while 2—10% of the monomer is converted into a heavy red tar which also contains most of the aluminium halide added.

(6) The tar contains one $AlCl_4^-$ for every olefinic bond and about three double bonds per hydrocarbon molecule, irrespective of chain length. Most of the unsaturation exists in the form of conjugated trienes.

(7) The butane-soluble product contains no products with less than eight carbon atoms, but contains more C_9 and C_{10} than C_8 hydrocarbons. About 70—90% of the polymer falls within the C_8—C_{30} hydrocarbon range and no plateaux are observed in its distillation curves.

(8) The C_8 fraction contains approximately : 2 : 3 : 4-trimethylpentane 50%, 2 : 3 : 3-trimethylpentane 40%, and about 10% of an olefin of b. p. *ca.* 115° ($CH_2\!:\!CPr^n\cdot CHMe_2$ or $CH_2\!:\!CEt\cdot CHMeEt$). The infra-red spectrum of the C_8 fraction is very similar to that of the C_9 fraction, so the skeletal structures of the C_9 hydrocarbons should resemble those of the C_8 compounds.

(9) In the C_8—C_{10} fraction of but-2-ene polymer a large proportion of saturated hydrocarbons is found. In fractions above C_{16} a mixture of mono- and di-olefins is obtained.

(10) No evidence could be obtained for the occurrence of alkylation under the conditions used for polymerization, even when *iso*butane was used as a solvent.

(11) No isomerization to but-1-ene occurs as a side reaction. Since polymeric products obtained from but-1-ene are quite different, one can conclude that there is no isomerization during the polymerization process between −40° and +10°. Polymer from but-1-ene yields no appreciable volatile fraction and has a viscosity-average molecular weight of 1000—1500.

(12) The heat of reaction, as measured by the volume of solvent evaporated, is about 16 kcals./g.-mole.

(13) Copolymerization occurs very readily with but-1-ene, but the copolymerization constants obtained ($\sigma = 0{\cdot}15$, $\mu = 3$) indicated that but-1-ene is incorporated more readily into the polymer than is but-2-ene under such conditions of competition.

(14) Copolymerization with *iso*butene was not observed at −10°.

Other minor points, useful in completing an argument concerning mechanisms, will be dealt with in the general discussion.

DISCUSSION.

It is simpler to discuss the reactions associated with polymerization in terms of a list of all known and carefully defined general transformations of hydrocarbons which are catalysed by acid-acting salts. It is possible then to establish which occur and which do not occur under the conditions used in this survey.

The following compilation summarizes the transformations of aliphatic systems in contact with aluminium halide :

1. *Polymerization.*

$$n_0\text{M} \xrightarrow[\text{(ROH)}]{\text{AlX}_3} n_2\text{M}_2 + n_3\text{M}_3 + n_4\text{M}_4 \ldots n_i\text{M}_i$$

(where M_i represents a polymer of i monomer units, and n_i the total number of the species formed).
Temperature range of reaction : −150° to +150°.
Rate of reaction : usually very fast.
Catalyst required : very little.

2. *Alkylation.*

$$\text{Olefin} + \textit{iso}\text{paraffin} \xrightarrow{\text{AlX}_4^-} \text{branched paraffin.}$$

Temperature range : 0° and above.
Rate of reaction : slow at lower temperatures.
Catalyst required : high catalyst contact.

3. *Isomerization.*

$$\text{Paraffin} \xrightarrow{\text{AlX}_4^-} \textit{iso}\text{paraffin (C atoms randomized).}$$

Temperature range : −20° and above.
Rate of reaction : in general slow, but a function of acid strength.
Catalyst required : excellent contact.

4. *Hydrogen–dehydrogenation.*

$$\text{Two olefins} \xrightarrow{\text{AlX}_4^-} \textit{iso}\text{paraffin and diolefin.}$$

Temperature range : unknown.
Rate of reaction : very fast.
Catalyst required : not known, but probably large amount.

5. *Alkyl transfer.*

$$\text{Two olefins} \xrightarrow{\text{AlX}_4^-} \left\{\begin{array}{l}\textit{iso}\text{paraffin } (+1, 2, 3, \text{ or } 4 \text{ C}).\\ \text{and diolefin } (-1, 2, 3, \text{ or } 4 \text{ C}).\end{array}\right.$$

Temperature range : unknown.
Rate of reaction : fast.
Catalyst required : not known, but probably large amount.

6. *Scission.*

$$\text{Hydrocarbon} \xrightarrow{\text{AlX}_4^-} \left\{\begin{array}{l}\text{CH}_4 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + i\text{-C}_4\text{H}_{10} \ldots \text{tar}\\ \textit{or } \text{C}_3\text{H}_8 + \textit{iso}\text{-C}_4\text{H}_{10} \ldots + \text{tar}\\ \textit{or } \text{depolymerization.}\end{array}\right.$$

Temperature range : above 100°.
Rate of reaction : slow.
Catalyst required : large amount.

7. *Ring closure.*

$$\text{Olefin} \xrightarrow{\text{AlX}_4^-} \text{naphthene.}$$

Temperature range : somewhat higher than alkylation.
Rate of reaction : slow.
Catalyst required : not known.

8. *Hydrogen exchange.*

$$\text{Hydrocarbon} \xrightarrow[\text{H}_2\text{O} + \text{HX}]{\text{AlX}_3} \text{hydrocarbon}$$

(if hydrogen is deuterium or tritium the products are " labelled ").

It is implied, not that there are eight known reactions, since there are likely to be more, but that there are now known eight distinct types of changes in molecular size and structure. At higher temperatures and catalyst concentrations all such changes occur simultaneously. The total process has been described by Ipatieff and Pines (*J. Org. Chem.*, 1937, **1**, 464) as "conjunct polymerization." However, at reduced temperatures and with very small catalyst concentrations, alkylation, isomerization, and ring closure can be eliminated. For *iso*butene at low temperatures all processes other than polymerization (and possibly hydrogen exchange) do not occur to an observable extent, but for *n*-butenes this simplification apparently cannot be achieved. Even at −40°, where it is much more difficult to supply the amount of aluminium chloride necessary for catalysis and where the liquid phase polymerization of but-2-ene is on the verge of becoming a slow reaction, several types of structural transformations, including alkyl exchange, occur as an intrinsic part of the overall reaction.

Chain Initiation.—The studies of the *n*-butenes show that the conditions necessary for initiating polymer chains are more complex than was previously imagined. Absence of *cis-trans*-isomerization in the presence of Friedel–Crafts catalysts, either in the liquid or the gaseous phase, indicates that a proton is not accepted reversibly by a but-2-ene molecule. This is contrary to what would be expected from the theories presented by Plesch (*Research*, 1949, **2**, 272) and by Evans and Meadows (*J. Polymer. Sci.*, 1949, **4**, 359) for *iso*butene.

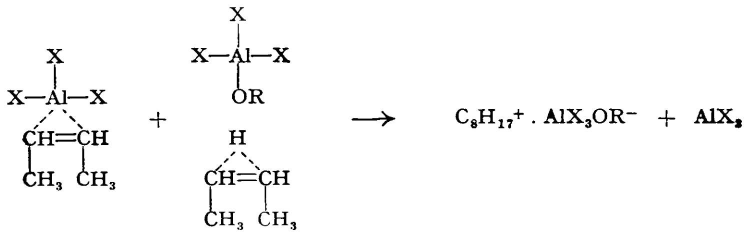
The proton-donor rôle of the co-catalyst has been emphasized by these investigators. Its importance in the cases of gaseous but-2-ene and *iso*butene is easily recognizable, but in those of but-1-ene and propylene, if water or alcohol is needed at all, the optimum must be a very small amount. The need for ROH as co-catalyst for olefins of the aliphatic monosubstituted ethylene type, $R \cdot CH\colon CH_2$, is yet to be proved. It is recognized now that very refined techniques will be needed to demonstrate the relationships.

Plesch has shown that, in a closed system, polymerization of *iso*butene in hexane with titanium tetrachloride tends to exhaust the co-catalyst (*Nature*, 1947, **160**, 868; *J.*, 1950, 543). The reaction ceases altogether until a small amount of additional co-catalyst is added, whereupon there is a resurgence of polymerization. Since polymerizations of the *n*-butenes and propylene with aluminium or boron halides tend to cease with both catalyst and monomer present, an analogous experiment was undertaken. Plesch's co-catalyst, trichloroacetic acid, was added at various stages of the polymerization of but-2-ene but no variation in behaviour resulted. Nor did the addition of moist butane have any effect. If a co-catalyst were operative in these polymerizations, it would undoubtedly be traces of water; therefore these observations strongly suggest that lack of co-catalysts is not the cause of the subsidence of polymerization after the addition of a limited amount of catalyst.

If the initiation were a three-centred process, involving catalyst, co-catalyst, and *n*-butene, as hitherto proposed, then the catalyst added at the beginning of the polymerization should yield more polymer than subsequent additions. The catalyst efficiency should be a maximum at the beginning and decline as the monomer disappears (always assuming that sufficient co-catalyst is supplied). This is what happens in the polymerization of *iso*butene in butane or propane by aluminium chloride. It does not occur with *n*-olefins, which show a definite maximum catalyst efficiency after about 25—30% polymerization. The first additions cause no measurable polymerization. Later, when initiation did occur with added quantities of catalyst, the efficiency of initiation was still poor. As catalyst concentration built up, owing to continued addition of catalyst solution, the efficiency improved for a while, reached the maximum, and then declined. The dependence on the accumulation of catalyst was quite consistent—there was no evidence that an inhibitor was involved. Thus two molecules of catalyst may be needed, for the *n*-butenes and propylene at least, to initiate polymerization in the liquid phase.

It may also be argued that two monomers are necessary. This depends on the finding that no product is obtained from but-2-ene in the region between C_4 and C_8 hydrocarbons although a fair proportion (*ca.* 6—8%) is always obtained between C_8 and C_{12} hydrocarbons. Without going into the mechanism of this disproportionation we suggest that the carbonium ion is first formed with a C_8 rather than a C_4 moiety. The ionic C_8 component can thereupon add methyl, ethyl, and *iso*propyl fragments, whereas the results indicate that these alkyl groups are not added to a butyl carbonium ion. The alkyl transfer process will be considered later.

In assessing all these points the simplest possible mechanism becomes rather cumbersome. It requires the bringing together of two molecules of catalyst, two of monomer, and probably one of co-catalyst. This need not be too difficult however, because a catalyst molecule, such as aluminium halide, would tend to associate with the olefins rather than with the paraffinic solvent owing to their greater polarizability. There may even be a loose, easily dissociated molecular compound formed with olefins in the liquid phase. Then the initiation step can be represented as the reaction of two molecular compounds which results in a rearrangement and the formation of a carbonium ion :



The structures of the carbonium ion would undoubtedly be various; they cannot be deduced directly because of the number of rearrangements that are possible. It should be emphasized that polymerisation of *iso*butene or α-methylstyrene does not depend on similar molecular compound formation. This proposal applies only to aliphatic olefins of the type R·CH:CH$_2$ and RCH:CHR.

Chain Growth.—If one assumes that chain growth occurs whenever a relatively free carbonium ion is available, then the proton affinities of the various olefinic bonds calculated by Evans and Polanyi (*J.*, 1947, 252) become highly significant. Their data make it possible to estimate the energetics of reactions both in initiation and in chain growth. They show that the difference in heat content between unhindered secondary and tertiary carbonium ions is 13·5 kcals./g.-mol. (column P_1 in the table, p. 253). Thus an important distinction can be drawn between Δ^1- and Δ^2-olefins in the chain-growth process :

$$\overset{+}{\mathrm{R}} + \mathrm{CH_2{:}CHEt} \underset{\Delta H \sim -20\ \text{kcals.}}{\longrightarrow} \mathrm{R{\cdot}CH_2{\cdot}\overset{+}{C}HEt} \underset{\Delta H \sim 0}{\rightleftharpoons} \mathrm{\overset{+}{R}{\cdot}CHPr}\ \text{or}\ \mathrm{R{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{C}HMe}$$

$$\overset{+}{\mathrm{R}}' + \mathrm{CHMe{:}CHMe} \underset{\Delta H \sim -4\ \text{kcals.}}{\longrightarrow} \mathrm{R'{\cdot}CHMe{\cdot}\overset{+}{C}HMe} \underset{\Delta H \sim -13\ \text{kcals.}}{\longrightarrow} \mathrm{R'{\cdot}\overset{+}{C}MeEt}$$

The primary reaction product from but-1-ene must be a secondary carbonium ion whose simple rearrangements still leave a secondary carbonium ion. However, with but-2-ene a rapid rearrangement to a more stable tertiary form appears highly probable (only the migration of a proton is involved, as against that of a methyl group for but-1-ene). The $\overset{+}{\mathrm{R}}'$ in but-2-ene polymerization is therefore taken to be the tertiary form. The small amount of energy evolved in the addition step may explain why competing reactions, such as transfer and final termination, are more probable for but-2-ene than for similar C_3 and C_4 olefins.

The relationships are seen more clearly in experiments on copolymerization. It was shown that *iso*butene does not copolymerize to any significant extent with but-2-ene, but that either of these will copolymerize with but-1-ene. If the growing end of the polymer chain can be assumed to contain a carbonium ion formed at a tertiary position the following comparison can be made for the addition reaction :

$$\overset{+}{\mathrm{R}} + \textit{trans}\text{-but-2-ene} \longrightarrow \mathrm{R{\cdot}CHMe{\cdot}\overset{+}{C}HMe} \quad \Delta H\ -4\ \text{kcals.}$$

$$\overset{+}{\mathrm{R}} + \text{but-1-ene} \longrightarrow \mathrm{R{\cdot}CH_2{\cdot}\overset{+}{C}HEt} \quad \Delta H\ -7\ \text{kcals.}$$

$$\overset{+}{\mathrm{R}} + \textit{iso}\text{butene} \longrightarrow \mathrm{R{\cdot}CH_2{\cdot}\overset{+}{C}Me_2} \quad \Delta H\ -11\ \text{kcals.}$$

(It is assumed in these figures that the heat of polymerization of but-1-ene is very close to 20 kcals./g.-mol. The value for *trans*-but-2-ene would be almost 3 kcals. less than this, owing to the loss of " hyperconjugation " energy in the monomer. From both of these is subtracted the 13 kcals. difference between tertiary and secondary carbonium ions. Evans and Polanyi obtained 12·8 kcals. for *iso*butene polymerization, but this was at very low temperatures; at around 0° the value was experimentally observed to be close to 11 kcals., owing probably to increased steric hindrance.)

Since activation energies for this sort of reaction are very small and appear to be dominated by thermal effects (see Evans and Polanyi, *loc. cit.*) these small energy differences can be expected to control the course of copolymerization. A growing chain with *iso*butene as the terminal addendum would prefer *iso*butene, and might add but-1-ene, but would reject but-2-ene in favour of either. In similar circumstances but-2-ene (when rearranged to a tertiary carbonium ion) would also prefer *iso*butene or but-1-ene. However, when copolymerization of but-2-ene and *iso*butene is attempted the first portion of catalyst added initiates only *iso*butene polymerisation, and, since this addendum adds preferentially to *iso*butene, practically all the *iso*butene disappears before the catalyst concentration suffices to initiate polymerization of but-2-ene. Thus a mixture of the separate polymers is formed, rather than a true copolymer.

The amount of heat evolved changes greatly when growth occurs from a but-1-ene addendum which presumably retains a secondary carbonium ion. Actual values cannot be calculated, because unknown amounts of steric hindrance are involved, but experimental evidence indicates that the secondary carbonium ion becomes preferentially attached to *iso*butene and that no preference exists in regard to the *n*-butenes.

The copolymer of but-2-ene and but-1-ene shows properties intermediate between those of the pure but-2-ene and the pure but-1-ene polymer. Increasing the proportion of but-1-ene decreases the proportion of low polymers and increases the average molecular weight. The characteristics of the copolymerization are only slightly affected by changes in temperature or in aluminium halide catalyst between −40° and +10°.

FIG. 7.

Catalyst efficiency in n*-butene polymerization.*

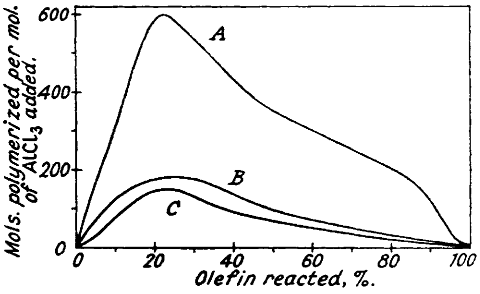
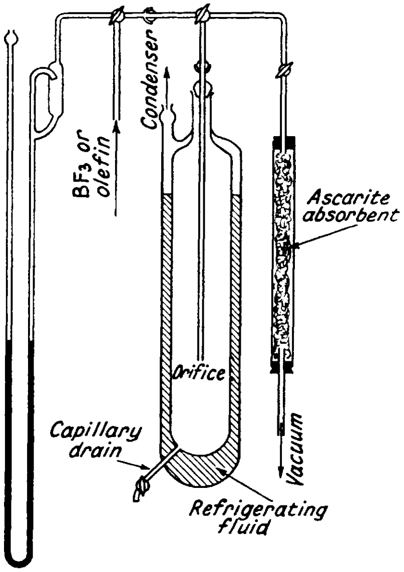


FIG. 8.

Apparatus for polymerization of gases.



Chain Transfer.—The most common mode of termination is proton transfer. It is at the same time the most common process of chain initiation. In optimum circumstances a molecule of catalyst may be responsible for the formation of hundreds of polymer chains before some other mode of termination becomes effective (Fig. 7). The efficiency of the co-catalyst, however, is many times greater (Evans and Meadows, *loc. cit.*).

Chain-transfer differences between the various olefins are best illustrated by the rate relationship which determines polymer sizes:

	But-2-ene.	But-1-ene.	Propylene.	*iso*Butene.
$k_p/(k_t + k_s)$	4	20	40	20—10,000

$k_t \gg k_s$, except for *iso*butene at low temperatures.

(k_p, k_t, and k_s are rate constants for growth, transfer, and cessation, respectively; the values are the average degrees of polymerization.)

One might assume, with Plesch (*Research*, 1949, **2**, 272), that chain transfer is reduced with decrease in temperature. It might be claimed, in other words, that the loss of a proton has a small activation energy. This would explain very elegantly why polymers of *iso*butene, styrene, and α-methylstyrene achieve high molecular weights and greater polymerization velocities at very low temperatures. However, propylene and the *n*-butenes do not have this property over the −40° to 10° range and yet they exhibit a large amount of chain transfer. Chain transfer for these two classes of olefin differs in some essential characteristic. It is possibly significant that the above ratio involving the chain-transfer rate constant decreases with monomer concentration in the instance of *iso*butene but does not vary noticeably for *n*-butenes over the same ranges (0·5—5·0 g.-mols./l.).

It may be concluded then that chain transfer for those olefins that differ from *iso*butene is relatively independent of temperature, olefin concentration, and catalyst concentration. These properties suggest that each time the growing end of a chain comes into contact with a monomer molecule there exists a relatively constant probability that transfer will occur rather than addition. Activation energies appear to be virtually the same for the alternative processes; however, at low temperatures this equivalence is obscured by the effects on the solubility of the catalyst and a consequent change in initiation rate, whereas at higher temperatures (*ca.* 20°) a series of side reactions such as chain scission come into play. The work on the polymerization of the gaseous olefins did not reveal any useful additional information on chain transfer other than that it was very prevalent.

Chain Termination.—The principal mechanism of final chain termination appears to be different for various sets of olefins. Plesch (*J.*, 1950, 543) proposed that at termination the ion pair at the growing end of the polymer rearranged either by forming an oxygenated compound, such as an ester, ether, or alcohol, or by leaving the polymer with a terminal double bond. The latter possibility has two alternatives : either the catalyst–co-catalyst complex is re-formed as a separate molecular compound, or it may add to the terminal olefin bond of a dead polymer molecule (adding to a monomer unit constitutes chain transfer, a process already discussed), neither of which appears very probable. Evidence was presented to show that esters were formed when a trichloroacetic acid co-catalyst was used in *iso*butene polymerization with titanium tetrachloride. Once an ester is formed it will remove one or two molecules of Friedel–Crafts catalyst from the reaction since tightly-bound molecular compounds will be formed (see Thomas, " Anhydrous Aluminium Chloride," Reinhold, 1941). This explanation of chain termination is satisfactory as long as roughly the same quantities of co-catalyst are consumed as of catalyst—which is certainly not the case for most olefins.

Other termination processes may involve the formation of a red tarry residue evident in all polymerizations in paraffinic solvents. It contained relatively constant proportions of aluminium halide and unsaturated hydrocarbon. Little tar was formed from *iso*butene or α-methylstyrene, but notable amounts were obtained from propylene and but-1-ene. It was soluble in chlorinated and aromatic solvents, but insoluble in aliphatic and naphthenic hydrocarbons.

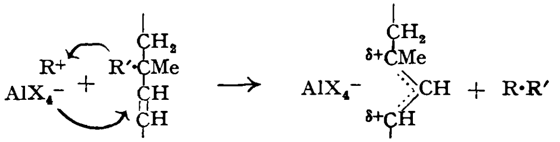
The tar resembled that obtained in other acid-catalyzed reactions. Oblad and Gorin (*Ind. Eng. Chem.*, 1946, **38**, 822) noted such a product after isomerization with aluminium bromide and a promoter. Burk, Lankelma, *et al.* (*J. Amer. Chem. Soc.*, 1945, **67**, 910, 914) obtained a red tar while cracking hexanes and heptanes at 20—100° with aluminium bromide; they found that the hydrocarbon portions were highly unsaturated and that there were 3·5 halogen atoms for every aluminium ion present.

In the liquid-phase polymerizations of but-2-ene (the only experiments which yielded sufficient tar for analysis), the residue consisted mainly of hydrocarbon molecules to which are attached AlX_4^- fragments. On hydrolysis the metal–halogen–carbon bonds are broken and an unsaturated oil, with an average of at least three double bonds per molecule, is released. Altogether about 60% of the aluminium and 80% of the halogen introduced as an ethyl chloride solution of AlX_3 finds its way into the insoluble tar. A small additional quantity exists in suspended form when polymerization is complete.

The tars had approximately twice the molecular weight of the butane-soluble polymer, and their unsaturation was largely conjugated, according to the ultra-violet spectrum. They have undoubtedly lost hydrogen and, almost certainly, alkyl groups to the butane-soluble polymer of lower molecular weight. This conclusion is strengthened by the observation that the polymerization of but-2-ene at lower temperatures (−40°) showed no significant change in alkyl transfer, hydrogenation–dehydrogenation, or the formation of tar. Careful drying of reagents over alumina similarly had no effect.

Some observations suggest that tar formation is oxygen-promoted. Oblad and Gorin (*loc. cit.*) found that oxygen is the best promoter for isomerization with aluminium halides. A. G. Evans and Meadows (private communication) found that on addition of air to an *iso*butene–BF_3–H_2O system which had already polymerized but had remained colourless for months, visible quantities of tar formed within a few weeks. Hydroperoxides and free-radical reactions therefore may contribute to tar formation, but they appeai not to be essential for this and related reactions. Hydroperoxide formation, for instance, has a high energy of activation in comparison with any process involved here. The elegant experiments of Beeck and his co-workers (*J. Chem. Physics*, 1949, **17**, 418; 1948, **16**, 255, 745) with isotopes also do not admit the possibility of extensive free-radical reaction in acid-catalysed isomerization processes.

The facts available fit a mechanism which utilizes the resonance energy of an allylic carboniun ion as the driving force of the reaction. It employs a three-centred push–pull process acting on positions adjacent to an olefinic bond. A similar mechanism has been proposed by Caviet, van Steenis, and Waterman (*Rec. Trav. chim.*, 1949, **68**, 553) for the formation of alkylation tar, except that they suggested that a chain scission occurred simultaneously. However, if scission was at all prevalent in polymerization, then C_5, C_6, and C_7 fractions would be found in the product. Therefore we are forced to conclude that a somewhat simpler process operates :



where R′ presumably is H, Me, Et, or Pr.

Hydrolysis of the complex produced yields conjugated diolefins, such as become common in $C_{>20}$ fractions. Molecules containing one, or even two, stabilized $R^+AlX_4^-$ ion pairs remain dispersed in paraffinic solvents. The insoluble tar would have had to undergo several such steps before the high degree of unsaturation could be produced. The presence of one such ion pair seems to make the attachment of others to the same molecule more probable, so that instead of obtaining a normal distribution of spent catalyst throughout the medium a large fraction is found condensed in the tar phase.

The catalyst efficiency curves for polymerizations of pure but-1-ene and but-2-ene (Figs. 7 and 11) show that the chain termination reactions are a minimum around 15—25% of complete polymerization when the catalyst added is less than 10% of the ultimate total. Later, as olefin concentration diminishes and both catalyst and polymer concentrations increase, the final chain termination is more common. This is in good accord with the proposals. There is lacking, however, any good indication of what happens to the AlX_2^+ fragment of the catalyst. Is an aluminium–carbon bond formed analogous to a Grignard reagent in its activities? In these experiments the $AlCl_2^+$ fragment was adsorbed on clay, along with dispersed tar and other acid constituents. There was no means of detecting it.

EXPERIMENTAL.

Polymerization of 3 : 3-*Dimethylbut*-1-*ene*.—The 3 : 3-dimethylbut-1-ene was a National Bureau of Standards Standard Sample, No. 287—5S, which was claimed to be 99·91 ± 0·06% pure. Only 5 ml. were available. Boron trifluoride was obtained from the General Chemicals Corp. (U.S.).

The olefin was introduced into a 1-l. glass bulb. The temperature was raised to about 45° in order to ensure that all was in the gas phase when the boron trifluoride was introduced. A dense fog formed immediately on contact of the two gases and later condensed to a clear liquid. Very little tar was formed. The total volume of clear liquid was 3·0 ml.

3 : 3-*Dimethylbut*-1-*ene Polymer*.—The product, diluted with *n*-pentane (20 ml.) was dropped slowly through a column of cold floridin clay (8 ml., of 30—50 mesh, in a 10-ml. burette), to remove spent catalyst. The *n*-pentane was distilled off through a packed column, so that no components boiling above 60—70° should have been lost. The product had η *ca.* 5 centistokes at room temperature and *d ca.* 0·82. The bromine number was 57, after correction for substitution. Thus the mean polymer size was approx. that of a trimer. The amount of volatile constituents was very low, only 3·5% being lost from a thin film at 110° during an hour. The infra-red spectrum was measured with a National Technical Laboratories' instrument in the 5—15-μ. range.

The possibility of rearrangement of the *neo*pentyl group after polymerization was investigated by carrying out a similar polymerization of *iso*butene. In one case catalyst was removed within a few minutes, and in the other the next day. Analytical distillations gave the same values for the respective constituehts, including *neo*pentyl groups in each instance. Thus, if independent rearrangement does occur it must be simultaneous with the polymerization.

Polymerization of trans-*But*-2-*ene*.—0·75 Atm. of *trans*-but-2-ene was introduced into a bulb, and then an additional 0·25 atm. of boron trifluoride. The pressure dropped immediately, reaching 0·40 atm. in a few minutes. The uncondensed gas was passed through sodium hydrated asbestos (Ascarite) to remove the boron trifluoride, and then analyzed by infra-red methods. The remaining olefin was pure *trans*-but-2-ene within the accuracy of the method (1—2%).

But-1-ene polymerized in a 2-l. bulb at room temperature with 10—30% of boron trifluoride. The rate was slow, about 5—10 g. of polymer being formed per day. The product contained very little volatile hydrocarbon. It was dissolved in *iso*pentane and passed through a floridin column sufficient to adsorb the tar and the residual boron trifluoride. The *iso*pentane was evaporated off in a partial vacuum before analyses were made.

Propylene was polymerized in like manner. The rate of polymer formation was variable, but usually less than that of but-1-ene. The amount of volatile material disappearing with the *iso*pentane was less than 3%.

cis-But-2-ene was polymerized in the presence of boron trifluoride (20—30% by volume) so rapidly that 40—50 ml. of polymer were obtained per hour. *trans*-But-2-ene under the same conditions polymerized one-third to one-half as fast. However, the appearance of the products was the same. The polymers were purified by floridin, as above.

*iso*Butene polymerised exceedingly rapidly. With sufficient moisture present it was possible to drain off 150—200 ml. of polymer per hour, using equipment shown in Fig. 8. In subsequent processing it was evident that a larger fraction of this polymer was lost through evaporation.

The physical properties and infra-red spectra of the polymers are given in Table I and Figs. 2—6. The olefins used were in most cases 99% pure, with the expected contaminant saturated or acetylenic rather than olefinic.

TABLE I.

Properties of olefin polymers formed in the presence of gaseous BF_3 *at room temperature.*

	η, cstks.					
Monomer.	38°.	99°.	n^{20}.	d^{20}.	Br no.	*M*.
Propylene	3·3	—	1·4481	0·7720	26	300
But-1-ene	19·5	3·6	1·4610	0·8227	36, 37	317
cis-But-2-ene	5·3	1·7	1·4524	0·8032	61, 62	228
trans-But-2-ene	4·3	1·45	1·4510	0·8006	65, 66	223
*iso*Butene	4·8	1·6	1·4518	0·7999	50, 61	255
3 : 3-Dimethylbut-1-ene ...	5·0 (25°)	—	—	0·82	57	250

Effect of Other Variables on Gas-phase Polymerization.—Pure but-2-ene (at least 99%; about 90% of *cis*- and 10% of *trans*-) did not polymerize in absence of moisture. Glass surfaces on which acetone was adsorbed caused a slow polymerization. The rates of polymerization obtained were erratic but there was no evidence for effects of temperature between 10° and 77°, or of pressure between 400 and 1500 mm. Propylene, dried over activated alumina and passed into a dry vessel containing boron trifluoride, polymerized more rapidly than when the monomer contained 0·5—0·6% of boron trifluoride and 0·1—0·2% of water vapour. Neither the rate nor the form of the rate curves was reproducible in the exploratory experiments with propylene.

Distillation of But-2-ene Polymer.—A series of consecutive polymerizations of but-2-ene containing 0·1—0·2% of water with boron trifluoride was undertaken, the product being combined and a precision distillation carried out. The highest-boiling fractions were distilled with ethylene glycol as carrier. The results were as follows:

% distilling	1	5	10	30	50	75	95
Characterization	117°	125°	144°	210°	C_{16}	C_{20}	C_{30}

Liquid-phase Polymerization of But-2-ene.—Into a 5-l. stainless-steel flask were introduced 1500 ml. of but-2-ene (at least 99% pure) and technical-grade *iso*butane. An attached condenser containing solid carbon dioxide–acetone permitted rapid polymerization at atmospheric pressure under essentially isothermal conditions.

The catalyst solution of anhydrous aluminium chloride in commercial ethyl chloride, analyzed by Snyder's method (*Ind. Eng. Chem., Anal.*, 1945, **17**, 37), contained 1·28 equivs. of Cl^- and 1·36 equivs. of Al^{+++} per l. Its addition to the but-2-ene solution caused rather violent ebullition. In order to prevent loss of hydrocarbon a deflated rubber balloon was attached to the condenser outlet. Reaction was apparently complete after 550 ml. of catalyst solution had been added. The *iso*butane solution of polymer was decanted from the tar and diluted with *iso*pentane (which caused the precipitation of more tar), and the cold solution (0°) was dropped through a 1-m. floridin column. The clear polymer solution was distilled so as to remove butanes and pentanes. As the low-boiling distillates contained only traces of olefins (permanganate; bromine in carbon tetrachloride), nearly all the but-2-ene had reacted. No products boiling between 30° and 100° were found. The tar originally obtained had a volume of 52 ml. After 1 hour at 35° butane and pentane, and a small amount of hydrogen chloride, were evolved, the volume being reduced to 49 ml. The tar then had a d_4^{20} *ca.* 1·05. This material was hydrolyzed at 0° with ice and water, *iso*pentane added, and the hydrocarbon fraction separated from the water-soluble fraction. Evaporation of the *iso*pentane gave a heavy red oil [17·7 g., 35%; Br no. (corrected for substitution), 135]. The layer contained 0·444 g.-equivs. of Al^{+++} and 0·557 g.-equiv. of Cl^-, showing that most of the aluminium is present as $AlCl_4^-$, which makes up 38% by wt. of the tar obtained. The remaining 27% were volatile constituents, mainly *iso*pentane, *iso*butane, and ethyl chloride.

Aluminium chloride tars from similar polymerizations carried out in *n*-butane at slightly higher temperatures (0°) were similarly hydrolyzed and analyzed. The unsaturated oil had d_4^{20} 0·8651, η^{99} 5·95 cstks., $\eta^{37·8}$ 68·5 cstks., n_D^{20} 1·4867, *M* 440, and Br no. 126. The oil in this case comprised 45% of the original tar and resinified slowly in the presence of air at 110—120°. A sample, distilled with ethylene glycol as carrier, gave the following approximate fractions: trimer–tetramer range, 6% (Br no., 182), pentamer range 15% (Br no., 176), hexamer range 19%, heptamer range >15%, and octamer plus <55%. Thus all fractions have multiple unsaturation. On the average, three double bonds per molecule absorb bromine.

The butane-soluble polymer was fractionally distilled so that all portions boiling below 250° were taken overhead, amounting to 27% by volume of the total. This more volatile portion was refractionated in a column of 80—100-plates efficiency. The distillation curve is given in Fig. 9. Analytical data on some representative fractions are given in Table II:

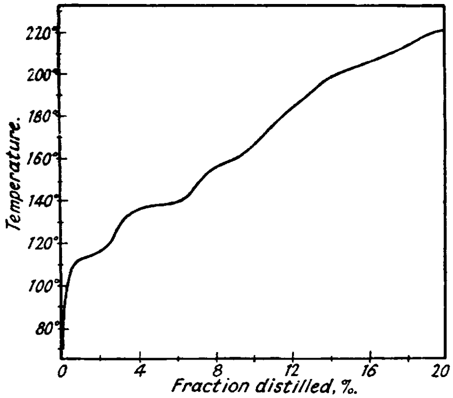
TABLE II.

Total polymer distilled, %.	B. p.	Br equiv.*	*M.*	Olefin, %.	C, %.	H, %.	% Unsatd. by C/H.
0·7	110·5°	1100	111	10			
1·4	113·2	1215	112	9	84·2 84·05	15·83 15·48	4—19
2·0	115·0	1130	113	10			
3·3	126·7	530	120	23			
5·1	137·8	334	127	38	84·6 84·7	15·30 15·25	27—30
8·2	154·4	285	138	48			
9·6	160·0	257	140	54	84·55	14·85	
10·5	165·0	303	143	47			
12·5	187·2	254	155	60			
13·2	199·4	218	168	78			
15·3	219·9	183	185	101			

* In terms of g. of oil per mol. of Br_2 absorbed.

FIG. 9.

Distillation curve for lower-boiling portion of but-2-ene polymer.



Infra-red spectra were obtained on the middle portions of the C_8 and C_9 hydrocarbon plateaux. The C_8 spectrum appeared to be relatively simple and could be interpreted unambiguously with the aid of existing spectra (A.P.I. Project 44). The approximate composition assigned was 2:3:4- 50% and 2:3:3-trimethylpentane 40%, and 10% of olefins $R_2C{:}CH_2$ (of which only 2-*iso*propylpent-1-ene and 3-methyl-2-ethylpent-1-ene fall within this boiling range). The spectrum for the C_9 compounds is remarkably similar to that of the C_8 compounds, so it is expected that most of the basic skeletal structures is the same in both fractions. The polymer contained C_8 hydrocarbons *ca.* 2·5%, C_9 hydrocarbons 4·2%, C_{10} hydrocarbons 3·3%, and C_{11}–C_{12} fractions *ca.* 6%. According to infra-red spectra the higher fractions are composed of mixed olefins of the types $RCH{:}CHR$ and $R_2C{:}CH_2$. There was no evidence of $RCH{:}CH_2$ being present, and the $R_2C{:}CR_2$ cannot be detected by infra-red absorption.

Br nos. for C_{16} fractions indicated about theoretical absorption for mono-olefins, but in C_{20} hydrocarbons at least 10—15% of diolefin was present.

Molecular-weight distribution was investigated by means of preliminary distillation through an 18-in. column with small hold-up. The volatile product boiling up to 215° (C_{13}) was taken off directly. Then ethylene glycol was added and distillation continued until the glycol: hydrocarbon ratio reached approx. 50 : 1. The residual polymer contained virtually no hydrocarbons of mol. wt. less than 400. Typical data from five comparable runs are presented in Fig. 10. Other runs showed that molecular-weight distributions were not materially different when the concentration of but-2-ene monomer in *n*-butane solvent was 10, 20, or 50%.

For comparison with aluminium chloride as a catalyst for but-2-ene polymerization, aluminium bromide (Westvaco) was dissolved in ethyl chloride. Both chloride and bromide solutions were added to butene (>99% pure; 30%) and *iso*butane (96% pure; 70%) (both dried over activated alumina) until no further polymerization resulted. The aluminium bromide appeared to cause less reaction. The very similar results of two comparable runs are shown in Table III.

The relatively poor yield recorded in Table III suggested investigation of the presence of butane or pentane. Calkins and Stewart (*J. Amer. Chem. Soc.*, 1949, **71**, 4144) showed that but-2-ene was converted into *iso*butane by 96% sulphuric acid at these temperatures. Such compounds would have escaped notice with the experimental techniques thus far described.

A 40% solution of but-2-ene in *n*-butane was polymerized almost to completion with a solution of aluminium chloride in ethyl chloride (65 ml. containing 0·028 mol. of aluminium chloride for 500 ml. of butane–butene). The spent catalyst was adsorbed on dry floridin and the refined reaction mixture distilled in a 60—80-plate low-temperature column. The butane–butene fraction, b. p. −6·0° to −0·5°, was shown by mass-spectrography to consist mainly of an azeotrope containing about 10% of ethyl

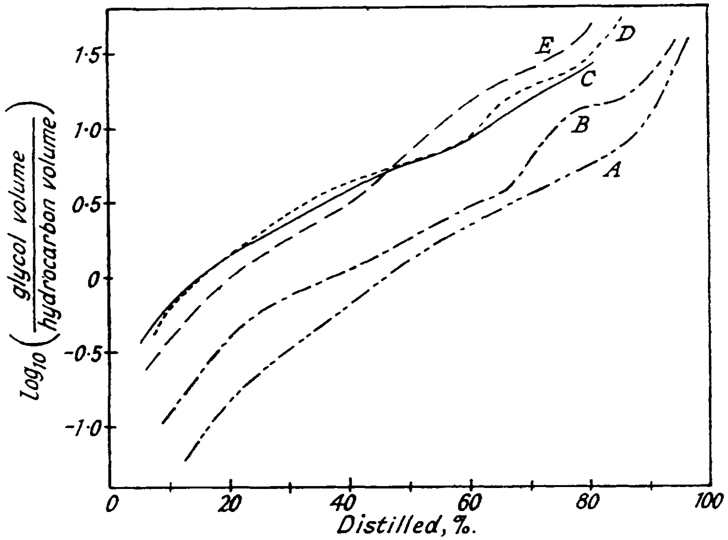
TABLE III.

Polymerization of a 30% *solution of but-*2-*ene in* iso*butane; initial volume,* 500 *ml.*

	$AlCl_3$.	$AlBr_3$.
Catalyst added, mole	0·41	0·021
Net reflux returned, ml.	491	440
Product (butane-soluble, refined), ml.	86	79
Yield (net), %	73	66
Residual tar obtained, ml.	2—3	*ca.* 5
Catalyst required for initiation, mols.	0·0029	0·0022
Probable fraction polymerized	90%	80—85%
Monomer units converted/mol. of catalyst	45	70
,, at 33·3% conversion	114	133
,, at 66·7% conversion	87	102
Net yield, C_8—C_{12} range (ml.)	12·5	20
Vol. Br no. (g. per 100 ml.). C_8—C_{12} range	36	65
Net yield, C_{13}—C_{18} range (ml.)	16	21
Vol. Br no. (g. per 100 ml.). C_{13}—C_{18} range	51	62
Net yield, C_{19}—C_{23} range (ml.)	24	17
Vol. Br no. (g. per 100 ml.). C_{19}—C_{23} range	51	59
Proportion olefin, C_{19}—C_{23} range	*ca.* 1·2	*ca.* 1·3
Net yield, residual polymer, C_{23} and greater, ml.	22	9

FIG. 10.

*Molecular-weight distribution of but-*2-*ene polymers.*



A, Partial polymerization with $AlCl_3$. *B, Partial polymerization with* $AlBr_3$. *C, Complete polymerization with* $AlCl_3$, *but-*2-*ene* 30%. *D, Complete polymerization with* $AlBr_3$, *but-*2-*ene* 30%. *E, Complete polymerization with* $AlCl_3$, *but-*2-*ene* 50%.

Polymer ranges: trimer ~ —0·9; *tetramer* ~ —0·4; *pentamer* ~0·1; *hexamer* ~0·6; *heptamer* ~1·1.

chloride. A set of results expected from the experimental data were compiled on the assumption that no reaction other than polymerization affected but-2-ene:

	*iso*Butane.	*n*-Butane.	But-2-ene.	EtCl.	C_5.	C_6–C_7.	Residue.
Found, %	0·5	59·5	2·6	11·1	0·1	0	26·5
Expected, %	0·5	58	7·5	11·5	—	—	22·5

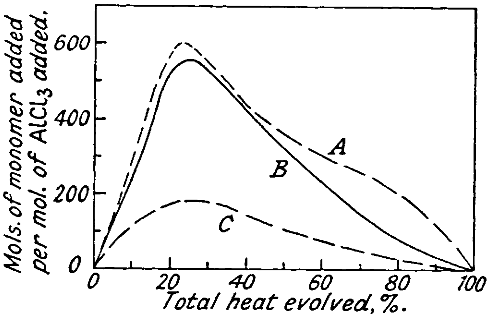
Apparently polymerization had proceeded somewhat further than expected on the basis of the measured heat evolved, but no *iso*butane or pentane was formed. It had already been ascertained that hexanes and heptanes were absent. The slight possibility remained that some but-2-ene was being transformed into *n*-butane. A parallel reaction, carried out with *iso*butane as a solvent, proved that if but-2-ene is being reduced to *n*-butane the rate must be less than 1% of the polymerization reaction.

Various catalyst solvents can be used for the polymerization of butenes. Methyl chloride was satisfactory but the concentration of aluminium chloride was low (<1%). About 1½% dissolved in ethylene dichloride, but the solution was not stable, even at —20°. Such a solution would initiate polymerization. *n*- and *iso*-Propyl, *n*-, *sec.*-, and *tert.*-butyl chloride were unstable in presence of aluminium chloride, hydrogen chloride being copiously evolved. With sulphur dioxide, ethers, and other oxygen compounds aluminium chloride does not catalyze polymerization, probably because of strong molecular-compound formation. At 40—70° butane and *n*-pentane dissolve appreciable quantities of aluminium chloride and these solutions are generally satisfactory.

Low-temperature polymerizations of but-2-ene were carried out, with propane as the self-refrigerating solvent. To a mixture of propane (300 ml.) and but-2-ene (>99% pure; 200 ml.) a solution (45 g./l.) of aluminium chloride in ethyl chloride was added slowly, the temperature being kept at $-40°$. The polymerization rate was noticeably slower than at 0°, and the polymerization could not possibly get out of control when an excess of catalyst was added, yet it could be completed in less than half an hour. The catalyst efficiency was a maximum at about 30% polymerization, 70 mols. of but-2-ene having reacted per mol. of aluminium chloride added (compare with Figs. 7 and 11). Overall catalyst efficiency was half that obtained in *n*-butane at 0°. The molecular-weight distribution was identical up to C_{13}, and the amount of alkyl transfer was the same, within experimental error. The C_8 fraction had a Br no. corresponding to 13% of unsaturation, and its infra-red spectrum indicated somewhat increased quantities of 2 : 3 : 4-trimethylpentane and olefin.

FIG. 11.

*Catalyst efficiency in the copolymerization of equal quantities of but-*1*-ene and but-*2*-ene in* iso*butane.*
*A, But-*1*-ene. B, Copolymer. C, But-*2*-ene.*



The interpolymerization of but-2-ene and *iso*butene was investigated. To *iso*butane (400 ml.) *iso*butene (100 ml.), and but-2-ene (10 ml.) a 0·13M-solution of aluminium chloride in ethyl chloride was added slowly and the amount of heat evolved by polymerization was measured by determining the volume of condensed solvent before returning it to the reactor. The violent reaction had completely subsided before 11·0 ml. of catalyst solution had been added. The amount of reflux returned (254 ml. net) indicated that little or none of the but-2-ene had been polymerized up to that point. The polymeric product had properties expected of poly*iso*butene formed at this temperature and dilution (η^{99} 757 cstks; $[\eta]$ 0·08; n_D^{20} 1·49498).

A similar experiment was carried out with but-2-ene as the major constituent : *iso*butane 300 ml., but-2-ene 160 ml., *iso*butene 40 ml., and 0·52M-aluminium chloride in ethyl chloride. By using earlier data for heat evolution caused by polymerization catalyst efficiencies were calculated in terms of mols. polymerized per mol. of aluminium chloride added. The catalyst efficiency remained high, around 230—260, until the reaction was more than half complete; then it began to decline to levels expected of pure but-2-ene. The molecular weight distribution was that of ordinary but-2-ene polymer. If copolymerization occurs it must involve only a very small proportion of but-2-ene. The two olefins seem to polymerize separately and successively.

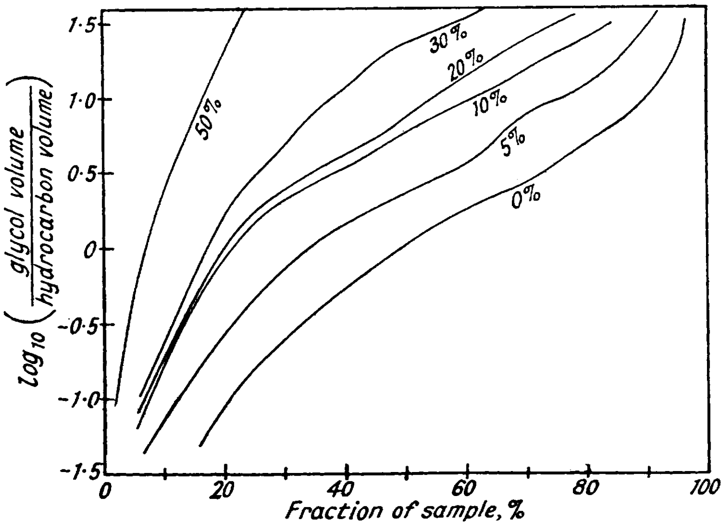
Copolymerization was definite however in the but-1-ene–but-2-ene system. The but-1-ene was first polymerized as was the but-2-ene. But-1-ene (200 ml.; 95·5% pure) in *iso*butane (200 ml.) was polymerized at reflux by the addition of 0·45M-aluminium chloride solution in ethyl chloride. The catalyst needed to initiate the first observable polymerization was 2—3 ml. As further catalyst was added the rate of polymerization increased, so that when half the monomer was exhausted 400—500 mols. of but-1-ene were being polymerized for every additional mol. of catalyst added. Thereafter the catalyst efficiency declined very rapidly toward zero (Fig. 11). Very little tar formed. Spent catalyst was removed in a floridin adsorption column, and all solvent evaporated at 80° in a simple still. A 99% yield of very pale yellow oil was obtained, having η^{99} 59 cstks, n_D^{20} 1·4738, $[\eta]$ 0·034. The approximate viscosity average molecular weight was 1200, and less than 5% had a molecular weight less than 400.

A series of runs similar to this established that the polymerization of but-1-ene, and the properties of the polymer obtained, are virtually unaffected by the presence of added moisture, the initial concentration of olefin, the chemical structure of the hydrocarbon solvent, and the temperature of polymerization between $-40°$ and 0°.

Copolymerization was effected by treating but-1-ene (100 ml.; 95·5% pure), but-2-ene (>99% pure; 100 ml.), and *iso*butane (300 ml.) with the above 0·47M-catalyst solution, and completed while measuring the catalyst added and the heat evolved. Catalyst efficiency curves are shown in Fig. 11. Spent catalyst and solvent were removed. The product had η^{99} 9·07 cstks., $\eta^{37\cdot8}$ 98·5 cstks., and n_D^{20} 1·4660. Molecular-weight distribution of the polymer was determined as described before for but-2-ene polymer. Comparisons are shown in Fig. 12 with a series of copolymers prepared in the same manner but containing 5, 10, 20, and 30% of the butene portion as but-1-ene. In each of these last cases 0·026 mol. of aluminium chloride was added as catalyst, and 75—90% yields were obtained.

FIG. 12.

Molecular-weight distribution of n-*butene copolymers.*



*Percentages adjacent to the curves indicate the proportion of but-*1*-ene originally present. All runs were polymerized to* 75—90% *completion. Polymer ranges are as in Fig.* 10.

Copolymerization constants for the but-1-ene–but-2-ene system were obtained by a series of partial polymerizations in the absence of hydrocarbon solvent. As before, the spent catalyst was adsorbed on floridin clay. An analytical distillation then revealed the extent of polymerization and the composition of the residual olefins remaining. The results obtained from three separate runs are as follows (B_1 = but-1-ene, B_2 = but-2-ene) :

Temp.	Initial composition.	Polymerised, %.	Final composition.
−3° to −5°	50% B_1, 50% B_2	46—47	30·5% B_1, 69·5% B_2
−4° to −6°	75% B_1, 25% B_2	46	63% B_1, 37% B_2
− 20° [a]	40% B_1, 20% B_2	33 ± 2	21·0% B_1, 15·7% B_2

$\sigma = 0{\cdot}15 + 0{\cdot}05;\ \mu = 3{\cdot}1 \pm 0{\cdot}7.$[b]

[a] In MeCl. [b] For other values see Simha and Wall (*J. Res. Nat. Bur. Stand.*, 1948, **41**, 521) and Walling, Briggs, Cumming, and Mayo (*J. Amer. Chem. Soc.*, 1950, **92**, 48).

In all cases the but-2-ene fraction contained 90% of *cis*-form, indicating again that little, if any, isomerization of the *cis-trans*-forms of but-2-ene occurs in liquid-phase polymerization.

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