Discussion on "Some Aspects of the Chemistry of Macromolecules."

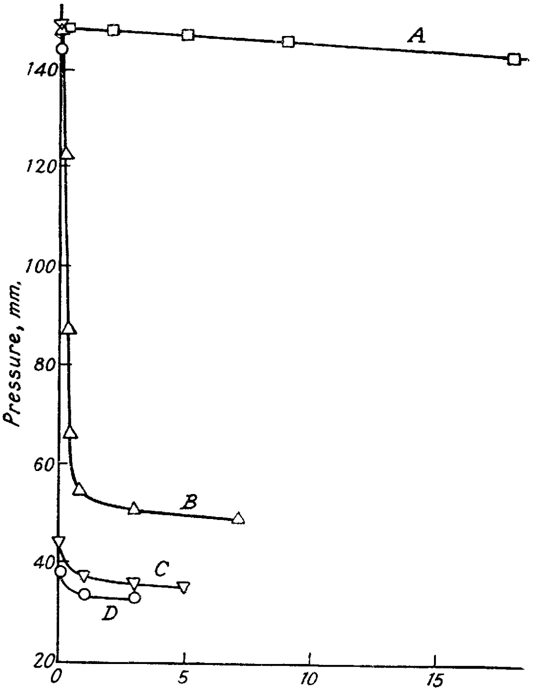
HELD AT THE INSTITUTION OF MECHANICAL ENGINEERS, LONDON, ON APRIL 4TH, 1946.

1. *Polymerisation of* iso*Butene by Friedel–Crafts Catalysts.*

By ALWYN G. EVANS and M. POLANYI.

AN investigation of the polymerisation of *iso*butene by boron trifluoride, and the study of related reactions, pursued over a number of years, have brought evidence that the presence of a trace of some third component is essential in order that the process may take place at an appreciable rate (A. G. Evans, Holden, Plesch, Polanyi, Skinner, and Weinberger, *Nature*, 1946, **157**, 102). In the case of titanic chloride acting on *iso*butene this " activator " has been now identified as water.*

FIG. 1.



Polymerisation of iso*butene catalysed by boron trifluoride.*
(The reaction is followed by the fall in the iso*butene pressure.)*

Curve A : 100 *Mm. of distilled* iso*butene* + 50 *mm. of* BF_3.
Curve B : 100 *Mm. of undistilled* iso*butene* + 47 *mm. of* BF_3.
Curve C : 90 *Mm. of distilled* iso*butene* + 11·5 *mm. of residue vapour* + 47 *mm. of* BF_3.
Curve D : 105 *Mm. of distilled* iso*butene* + 5 *mm. of* tert.*-butyl alcohol* + 33 *mm. of* BF_3.

We can now report another instance of this kind from experiments carried out in collaboration with G. W. Meadows. The normal experience, which we have confirmed by numerous experiments, is that *iso*butene, whether as pure liquid or in solution, reacts instantaneously (in the absence of inhibitors) on the passage of boron trifluoride through it at low temperatures. We find that *iso*butene in the gas phase can be mixed with the trifluoride without showing any fast reaction.† *iso*Butene, distilled in a vacuum from — 80° to liquid air, was mixed at pressures of 50—100 mm. with boron trifluoride at pressures of about 50 mm., and only a slow fall in pressure was observed. An example is shown in curve *A* of Fig. 1.

Similar mixtures reacted instantaneously when certain impurities were present. This was

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* See subsequent paper.

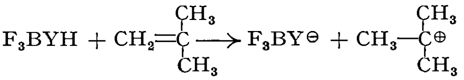
† Such mixtures always reacted on condensation in liquid air.

the case (1) for undistilled *iso*butene technically prepared from *tert.*-butanol (reported 99% pure) (Curve *B*), (2) for *iso*butene distilled as before to which the vapour from the residue of distillation was added in a fraction of 1—10% (Curve *C*), (3) for *iso*butene distilled as before to which 5% of *tert.*-butanol was added (Curve *D*). We observed that in the cases (2) and (3) the trifluoride was consumed in quantities approximately equivalent to the mols. of activator added.

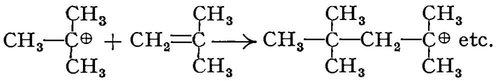
We conclude that (*a*) the trifluoride does not form a stable complex with *iso*butene; (*b*) no rapid reaction takes place in the gas phase (either at ordinary or at reduced temperatures down to about — 60°) unless a third substance is present; (*c*) in the presence of *tert.*-butanol vapour instantaneous reaction occurs, which (by the formation of a mist) can be seen to proceed in the gas phase—it is still uncertain whether this is responsible for the reaction of the undistilled *iso*butene as described above.*

In view of these points it seems necessary to conclude (in deviation from our previous assumption, *Nature*, 1943, **152**, 738) that the following carbonium mechanism plays some part in these polymerisations.

$$BF_3 + YH \longrightarrow F_3BYH \qquad (1)$$



$$F_3BYH + CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} \longrightarrow F_3BY^{\ominus} + CH_3{-}\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} \qquad (2)$$

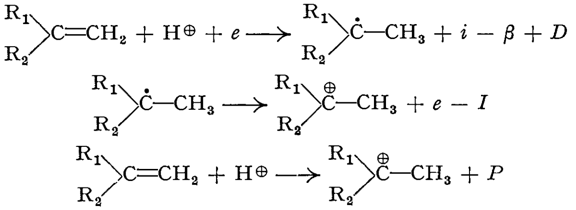


$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} \longrightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} \text{ etc.} \qquad (3)$$

Steps similar to (2) and (3) have been discussed by Whitmore (*Ind. Eng. Chem.*, 1934, **26**, 94), Hunter and Yohe (*J. Amer. Chem. Soc.*, 1933, **55**, 1248), Brunner and Farmer (*J.*, 1937, 1039), and Price (*Ann. N.Y. Acad. Sci.*, 1943, **44**, 368). It is therefore important to estimate the basicities of various olefins, in terms of "proton affinities" and "carbonium-ion affinities" as defined in the following equations:

$$H^{\oplus} + M \longrightarrow HM^{\oplus} + P \quad \text{(proton affinity)}$$
$$M_n^{\oplus} + M \longrightarrow M_{n+1}^{\oplus} + C \quad \text{(carbonium-ion affinity)}$$

The proton affinities of olefins may be determined by the following steps, the proton in this example being added to carbon 1.



$$\overset{R_1}{\underset{R_2}{>}}C{=}CH_2 + H^{\oplus} + e \longrightarrow \overset{R_1}{\underset{R_2}{>}}\dot{C}{-}CH_3 + i - \beta + D$$
$$\overset{R_1}{\underset{R_2}{>}}\dot{C}{-}CH_3 \longrightarrow \overset{R_1}{\underset{R_2}{>}}\overset{\oplus}{C}{-}CH_3 + e - I$$
$$\overset{R_1}{\underset{R_2}{>}}C{=}CH_2 + H^{\oplus} \longrightarrow \overset{R_1}{\underset{R_2}{>}}\overset{\oplus}{C}{-}CH_3 + P$$

Proton affinity: $P = i - \beta + D - I$, where i = ionisation potential of hydrogen (taken as 312 kcals.), β = energy of second half of double bond, D = carbon–hydrogen bond strength, I = ionisation potential of radical formed by addition of hydrogen atom to olefin.

For any non-symmetrical olefin the proton affinity for addition to carbon 1 will be different from that for addition to carbon 2. In Table I we give the calculated proton affinities for ethylene, propylene, and *iso*butene.

TABLE I.

Proton affinities and atom affinities of olefins.

Olefin.	β.	D_1.	D_2.	I_1.	I_2.	P_1.	P_2.	A_1.	A_2.
$CH_2{:}CH_2$	57·5	97·5	97·5	200	200	152	152	40	40
$CH_2{:}CHMe$	52·5	95	89	179	180	175·5	168·5	42·5	36·5
$CH_2{:}CMe_2$	52·0	94	86	165	178	189	168	42	34

The values of β and D (D_1 and D_2 for additions to carbon atoms 1 and 2, respectively) are taken from the revised table of bond energies of Baughan and Polanyi quoted by Butler and Polanyi (*Trans. Faraday Soc.*, 1943, **39**, 19); I_1 and I_2 are the ionisation potentials of the radicals

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* *Note Added in Proof.*—This point has since been cleared up; traces of water have been found to be responsible for this reaction (A. G. Evans, Meadows, and Polanyi, *Nature*, 1946, **158**, 94).

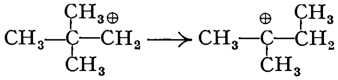
which are formed by the addition of a hydrogen atom to the olefin at carbon 1 and carbon 2, respectively. The value of I for the ethyl radical has been determined by electron-impact experiments (Hipple and Stevenson, *Physical Rev.*, 1943, **63**, 121). We have estimated the other values of I from the results of electron-impact experiments (*idem, J. Amer. Chem. Soc.*, 1942, **64**, 1590, 2766, 2769), and these values have been critically discussed elsewhere (A. G. Evans, *Trans. Faraday Soc.*, in the press).

The carbonium ion affinities (C_1 and C_2 corresponding to P_1 and P_2) will follow the same sequence as the proton affinities. The results of more detailed calculations are given later.

It is seen that P_1 (and therefore C_1) increases markedly from ethylene to *iso*butene. This would account for the increase in the ease of polymerisation as the olefin changes from ethylene, which is unaffected by these catalysts, to *iso*butene, which is so highly reactive.

It is also seen from Table I that for *iso*butene P_1 is much greater than P_2. This means that a proton will add to the *iso*butene double bond more readily at the CH_2 than at the CMe_2 end. Thus, if the addition of HX to a double bond involves an initial proton attack, then the H will add on to the carbon with the greater number of hydrogen atoms on it. We may thus interpret Markownifkoff's rule in terms of bond strengths and ionisation potentials.

The difference between C_1 and C_2 may also be expressed as follows. A carbonium ion will tend to rearrange itself so that the carbonium carbon will carry the greatest number of alkyl groups. This effect is found to operate for the *neo*pentyl derivatives in which all reactions of the carbonium-ion type yield exclusively products rearranged as follows in accordance with this prediction (Whitmore and Fleming, *J.*, 1934, 1269; Whitmore and Rothrock, *J. Amer. Chem. Soc.*, 1932, **54**, 3431) :



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2 \longrightarrow CH_3-\underset{CH_3}{\overset{\oplus\ CH_3}{C}}-CH_2$$

From the above discussion, therefore, we should expect the carbonium ion produced in the initiation reaction (2) to be the tertiary ion $CH_3\cdot\overset{\oplus}{C}Me_2$.

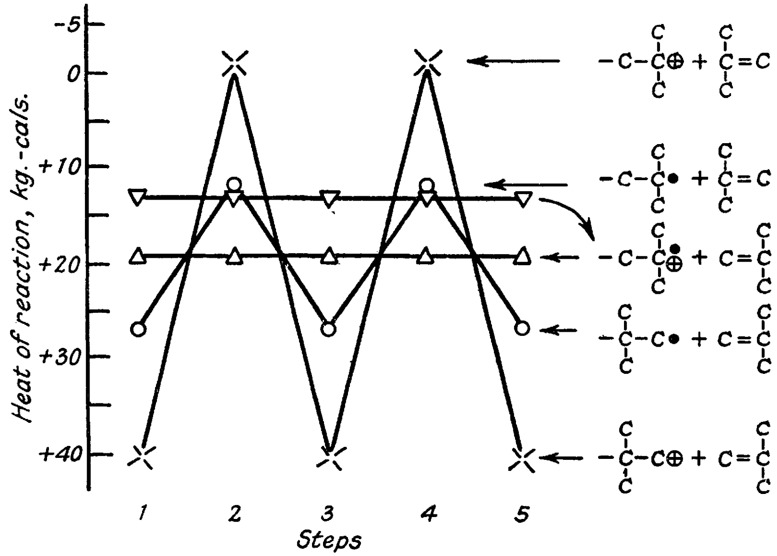
In the propagation reaction (3) the olefin monomer will be attacked by the carbonium carbon of the growing polymer chain. By analogy with the initiation reaction we might expect that at each step in the propagation the attack of the carbonium ion on the monomer is at its tail end, so that at the end of the growing polymer chain there is always a head $\cdot CH_2\cdot\overset{\oplus}{C}Me_2$ and not a *tail* $\cdot\overset{\oplus}{C}Me_2\cdot CH_2$. This would result in a head-to-tail propagation process, and would exclude the tail-to-head, and the head-to-head, tail-to-tail types of propagation.

We can give a more detailed calculation of the propagation process as follows. For the head-to-tail addition we have previously calculated the heat of reaction as 21·4 kcals. (*loc. cit.*). Using the more recent heats of formation obtained by Prosen and Rossini (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 263), we have recalculated this value for the head-to-tail step as 19·5 kcals. From the data given by Baughan and Polanyi (*loc. cit.*) and by Prosen and Rossini (*loc. cit.*), together with the ionisation potentials of the *tert.*- and *iso*-butyl radicals given in Table I, we have calculated the tail-to-tail addition step as about 40 kcals. exothermic, and the head-to-head step as slightly endothermic. Thus, of the three possible steps for the carbonium-ion mechanism, the tail-to-tail addition is most probable, the head-to-tail addition is still quite probable, but the head-to-head addition is very improbable. Since the tail-to-tail addition can only occur in chain propagation if the head-to-head addition is also involved, this discussion indicates that for a carbonium-ion mechanism, however the chain starts, it will always proceed with the head as the positive end $\cdot CH_2\cdot\overset{\oplus}{C}Me_2$, and this will lead to the head-to-tail type of addition with a constant heat of reaction of 19·5 kcals. at each step. This is shown in Fig. 2. In this figure we have also included the heats of reaction for the consecutive steps of the head-to-head, tail-to-tail mechanism, which alternate between slight endothermicity and compensating strong exothermicity.

It is found that poly*iso*butene has a head-to-tail structure (Thomas, Sparks, Frolich, Otto, and Mueller-Conradi, *J. Amer. Chem. Soc.*, 1940, **62**, 276; Fuller, Frosch, and Pape, *ibid.*, p. 1905) in accordance with what our previous considerations have led us to expect. This is the more remarkable since in the head-to-tail structure of a 1 : 1-disubstituted ethylene like *iso*butene there is a steric hindrance between the substituent groups of successive monomer units, which would be absent, or very much less, in the head-to-head, tail-to-tail structure

(A. G. Evans and Polanyi, *loc. cit.*; A. G. Evans, *Trans. Faraday Soc.*, **1945**, **41**, 273). A measure of this steric effect is given by the difference between the experimental value for the heat of polymerisation of *iso*butene, 12·8 kcals. (A. G. Evans and Polanyi, *loc. cit.*), and the value of 19·5 kcals. calculated above for the unstrained molecule. Yet the head-to-tail mechanism remains the only one possible, since the formation of the unstrained head-to-head, tail-to-tail structure is prevented by the endothermicity of the head-to-head step.

FIG. 2.



Heats of reaction for the steps involved in different types of propagation mechanisms.

△ *Head-to-tail radical or carbonium mechanism, when no steric hindrance is present.*
▽ *Head-to-tail radical or carbonium mechanism when steric hindrance is present.*
○ *Head-to-head, tail-to-tail radical mechanism.*
× *Head-to-head, tail-to-tail carbonium mechanism.*

Radical Mechanism.—In order to consider the radical mechanism of polymerisation, the "atom affinities" of the olefins are needed. These may be determined by the following step. (In the example given, the hydrogen atom is added to carbon 1.)

$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>\!C{=}CH_2 + \dot{H} \longrightarrow \begin{matrix}R_1\\R_2\end{matrix}\!\!>\!\dot{C}{-}CH_3 - \beta + D.$$

$$\text{Atom affinity}: A = D - \beta.$$

The atom affinities calculated in this way are given in Table I: A_1 and A_2 are the heats of addition of a hydrogen atom to carbon 1 and carbon 2, respectively. It is seen that, in contrast to the proton affinity of the olefin P_1, there is no marked increase in A_1 with change from ethylene to *iso*butene. Further, although for *iso*butene A_1 is greater than A_2, the difference is not so marked as the corresponding difference between P_1 and P_2. The alkyl radical affinities of the olefins vary in the same direction. We should thus expect that, for the radical mechanism, the heats of reaction of the head-to-head step and of the tail-to-tail step will not be as widely divergent from the heat of reaction of the head-to-tail step as is the case for the carbonium-ion mechanism.

We have made more detailed calculations of the heats of reaction of these steps for the radical mechanism, using the data of Baughan and Polanyi and of Prosen and Rossini (*locc. cit.*). We find that the tail-to-tail step will be exothermic by about 27 kcals., and the head-to-head step will be exothermic by about 12 kcals. The head-to-tail step, of course, would be exothermic by 19·5 kcals., but because of steric hindrance it is actually 12·8 kcals. exothermic. Thus, although in the absence of steric hindrance the radical mechanism would result in the head-to-tail type of addition, the presence of steric hindrance in this addition reduces its exothermicity and brings it close to that of the head-to-head step. This makes the head-to-head, tail-to-tail type of addition possible as well as the head-to-tail type (see Fig. 2). In this case we should expect the chain to consist of a more or less random arrangement of linkages, and to result, therefore, in a non-crystalline polymer. It is interesting in this connection, that methyl methacrylate, sharing with *iso*butene the steric properties of a 1 : 1-disubstituted ethylene but polymerising by a radical mechanism, gives a non-crystalline polymer, whereas poly*iso*butene, on the other hand, is crystalline.

Activation Energies.—The above considerations have dealt with the heats of reaction of the various steps, whereas the critical factors involved will be their energies of activation. But there is no activation energy in the carbonium-ion propagation mechanism, for the energy of approach of a carbonium ion to a system of closed shells will vary monotonously, and so this reaction involves no energy barrier. All exothermic reactions of this kind will be instantaneous at all temperatures.

The heats of reaction will also govern the course of reaction in the case of the radical mechanism, for we may expect a decrease in activation energy whenever there is an increase in the exothermicity of a reaction step.

We can see also that the carbonium mechanism offers a possibility for the occurrence of polymerisation at the lowest temperatures, whereas a free-radical process would be inevitably slowed down by extreme cold.

Some suggestions about the termination mechanism are contained in the next paper.

The authors wish to acknowledge the stimulus and help which they have enjoyed from the Research Laboratories, I.C.I., Billingham, throughout their work.

Discussion.

MR. H. S. LILLEY (communicated) : In collaboration with Mr. G. L. Foster, I have recently been studying the polymerisation of styrene in the presence of phenols, using the electrophilic borofluoroacetic acid complex as catalyst. We have observed variable induction periods and reaction rates in successive duplicate runs, such as appear to have been noted by Professor Polanyi in the dimerisation of 2 : 2 : 4-trimethylpentene with boron trifluoride. We have, in general, attributed the effects we have noted to variable traces of water, these being difficult to control, and we have formed various (unproved) views as to the mode of action of water in this case. We are very interested therefore in Polanyi's work on the $TiCl_4$–H_2O–*iso*butene system, where water shows a pronounced catalytic effect, attributed by Polanyi to a hydrate of titanic chloride and its ions. It seems, however, possible that the halide might be hydrolysed by water with formation of hydrogen chloride. Although Polanyi shows that this acid is of null effect in his case, it is known that in the not dissimilar system styrene–stannic chloride, hydrogen chloride has a marked effect, as was shown by Williams (*J.*, 1938, 1046; 1940, 775, etc.). In this case hydrogen chloride acts as a temporary inhibitor of polymerisation and markedly reduces average molecular weight, besides introducing a side reaction of hydrochlorination. It is not *prima facie* easy to reconcile the data of Polanyi and of Williams. Many explanations can, of course, be mooted, such as difference in experimental conditions of temperature and phase, relative stability against hydrolysis of the covalent halides concerned, the degree of dryness achieved by Williams, etc.

MR. L. B. MORGAN (communicated) : The boron trifluoride-catalysed polymerisation of *iso*butene at low temperatures shows some unusual features which have hitherto been difficult to explain. Attention has already been directed to some of these in the similar reaction, the dimerisation of di*iso*butene by boron trifluoride by Polanyi *et al.* (*Nature*, .1946, **57**, 102). The polymerisation does not commence unless the concentration of trifluoride is above a certain threshold value; under some conditions the polymerisation does not occur if the BF_3 is added to the system slowly, and often the polymerisation does not proceed to completion although monomer and BF_3 are present together. It would appear from this that BF_3 is not, itself, the initiating catalyst, and the simplest kinetic scheme that will explain the phenomena is one involving a two-stage reaction of BF_3 with an impurity, the first reaction forming the true initiating entity and the second reaction destroying it, *i.e.*, a similar reaction form to that of reduction activation with ferrous ion and hydrogen peroxide or persulphate and thiosulphate. The likely impurities are water and butanol. If the operating impurity is water, the two consecutive reactions might be the formation, first, of the monohydrate followed by an ionisation with the second molecule of water forming oxonium ion, the active catalyst being the intermediate monohydrate or possibly a proton arising from its dissociation. If it is assumed that these reactions occur immediately the BF_3 is added to the system and before the polymerisation, the threshold concentrations and the effect of rate of addition are readily explicable. With a carbonium-ion propagation mechanism and a termination involving reaction with anion, as proposed by Professor Polanyi, it is necessary to postulate an initiation independent of monomer concentration to explain the approximate unimolecular dependence of the polymerisation on monomer concentration and the fact that polymerisation ceases before all the monomer has been polymerised, and this suggests that the monohydrate ionises unimolecularly to give a proton which immediately initiates a polymerisation chain. This suggested initiating mechanism will not be general for all Friedel–Crafts initiated polymerisations. In the case of styrene, which is more readily initiated, the polymerisation is termolecular with respect to the monomer concentration, and Price (*Ann. N.Y. Acad. Sci.*, **1943**, **44**, 368) has suggested that the initiation here can be achieved more simply by a bimolecular reaction between monomer and monomer–catalyst complex, the association of the catalyst and the monomer being sufficient in this instance to form an incipient carbonium ion.

*iso*Butene will not polymerise under those polymerisation conditions which are believed to result in free-radical propagation, such as reduction activation, and the inference is that the chemical driving force in the free-radical propagation step is lower than in the carbonium-ion propagation step and is insufficient to overcome the strain energy required to pack the two methyl groups into the polymer chain. Although *iso*butene cannot be induced to polymerise by itself by free-radical initiators, it will interpolymerise with other vinyl monomers such as acrylonitrile and the possibility is that under these conditions the strain energy involved in the packing of the pendant groups into the interpolymer chains is much lower. An interesting case is the interpolymerisation of *iso*butene with fumaric or maleic esters under the influence of free-radical initiators: neither will polymerise alone, but in admixture the interpolymer is readily formed. There are several examples of interpolymerisation where it would appear that the interpolymerisation propagation step is faster than the propagation step of either component alone, and no stisfactory explanation has yet been advanced to explain this. One possibility is that there is association between pairs of the monomers and the interpolymerisation propagation step consists of additions of these associations as such to the growing polymer chain. Another possibility which is worth considering is that the strain energies of packing the pendant groupings into the polymer chain are less for the interpolymerisation than for the polymerisations of the individual monomers alone.

DR. A. G. EVANS, PROF. POLANYI, AND DR. SKINNER (communicated): In reply to H. S. Lilley and L. B. Morgan, we feel that the mechanism of Friedel–Crafts polymerisation has proved to be so complex that the present state of observations does not enable us to generalise much further. We would prefer therefore not to pursue the matter before we get more experiments done.

2. *The Low-temperature Polymerisation of* iso*Butene by Friedel–Crafts Catalysts.*

By P. H. PLESCH, M. POLANYI, and H. A. SKINNER.

A COMPARATIVE study of the catalytic efficiency of several halides of the Friedel–Crafts type in promoting the polymerisation of *iso*butene at low temperatures was undertaken in these laboratories by Fairbrother and Seymour * in 1941—1942 (Seymour, Thesis, Manchester, 1943), who found that the power of catalytic activity decreases over a very wide range down the series BF_3, $AlBr_3$, $TiCl_4$, $TiBr_4$, BCl_3, BBr_3 and $SnCl_4$. Under comparable experimental conditions, the polymerisation of *iso*butene is completed within a period of seconds with BF_3, and hardly extends to a few minutes with $AlBr_3$, whereas reaction times of hours are found when we apply $TiCl_4$, and periods of days are required with the weakest of these catalysts ($SnCl_4$). The marked gradations in the activity of various catalysts, assessed in terms of reaction time and percentage yield of polymer formed, are summarised in Table I. Attention should be called to the fall in the polymer molecular weight with falling activity of the catalyst (clearly shown in the final column of Table I), which is discussed later in this paper.

An important feature of all these reactions, whether catalysed by BF_3, $AlBr_3$, or $TiCl_4$ and other catalysts of this series is the lack of reproducibility in the detailed course of the reaction. Even though in our own experiments we have tried to make the experimental conditions much more rigorous than those used by Fairbrother and Seymour, this characteristic of the reaction remained.

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* The authors are indebted to Dr. F. Fairbrother and Mrs. E. L. Seymour for permission to quote results from their work.

TABLE I.

Catalytic activity of Friedel–Crafts catalysts (from Fairbrother and Seymour).

Starting temp. −78°.

Catalyst, and %.	*iso*Butene, %.	Reaction time.	Yield of polymer, %.	Mol. wt. × 10^{-3}.
BF_3, 0·05	10	Seconds	100	120—150
$AlBr_3$, 0·05	20	1—5 Mins.	70—90	120—150
$TiCl_4$, 0·12—0·25	30	20—70 Mins.	35—50	100—130
$TiBr_4$, 1·0—1·5	30—50	12—18 Hrs.	30—50	70—90
BCl_3, 0·9—1·5	40—50	,,	0·5—1·5	30—50
BBr_3, 0·6—1·0	50	,,	0·5—1·5	20—30
$SnCl_4$, 1·5—2·5	50	17—50 Hrs.	10—18	12—25

The gradation is illustrated once more in Table II, which gives the threshold concentrations of the catalyst and monomer, below which polymerisation could not be observed.

TABLE II.

Threshold concentrations for polymerisation (from Fairbrother and Seymour).

Catalyst.		$AlBr_3$.	$TiCl_4$.	$TiBr_4$.	BCl_3.	$SnCl_4$.
Composition of reaction mixture	*iso*Butene, %	1·0	7·0	20	20	10
	Catalyst, %	0·01	0·12	0·50	0·8	1·0

Our investigations have so far been confined to the polymerisation by titanic chloride as catalyst, for this reaction proceeds at an easily measurable rate which can be conveniently followed by observing the rate of increase in temperature of the reaction mixture contained in a Dewar vessel. Fairbrother and Seymour conducted their experiments on titanic chloride in a similar manner, but used as reaction vessel a large test-tube cooled externally by immersion in a suitable cooling bath. They found that for reactions started in the temperature range − 60° to − 80°, no observable rise in temperature followed the addition of the chloride to the reaction mixture for a period of 10 minutes or more. A different behaviour was observed at lower starting temperatures (− 80° to − 120°). In this lower range the reactions started instantly on the mixing of the reagents. This increased activity at temperatures below − 80° was stated to be general for the reactions catalysed by the weaker catalysts listed in Table I.

Polymerisation by Titanic Chloride.—Preliminary experiments. In our preliminary experiments, the mixture of hexane and *iso*butene (80 : 20 by vol.) contained in a large test-tube was precooled to the required starting temperature (normally *ca.* − 80°) by immersion in a low-temperature bath, and then poured rapidly into the Dewar reaction vessel. Sufficient catalyst solution to give 0·5% of $TiCl_4$ in the mixture was added from a burette to start the reaction, the progress of which was followed by measurement of the temperature of the reacting mixture with a pentane thermometer at minute intervals.

Fifty-five experiments, in which the starting temperatures varied between − 30° and − 120° were completed with this procedure. The main points emerging from these observations were as follows :

(1) At starting temperatures above − 90° (approx.) the addition of catalyst produced only a small immediate temperature rise, followed, after a variable and irreproducible induction period, by a reaction of autocatalytic type, *i.e.*, having an S-shaped time–temperature curve [see Fig. 1(*A*)]. This is approximately the same result as observed by Fairbrother and Seymour at these temperatures. Below − 90°, the addition of catalyst produced an immediate fast reaction which did not go to completion, but the extent of which increased with reduction in the starting temperature. After this initial activity, the reaction slowed down and remained quiescent for a period, following which a second reaction set in of the same autocatalytic type as those observed at higher starting temperatures [see Fig. 1(*B*)]. Curve *B* shows that in the interval of quiescence between the first and the second stage of the reaction, the temperature fell by a few degrees ; this fall cannot be attributed to the external cooling, and its true nature is not yet understood.

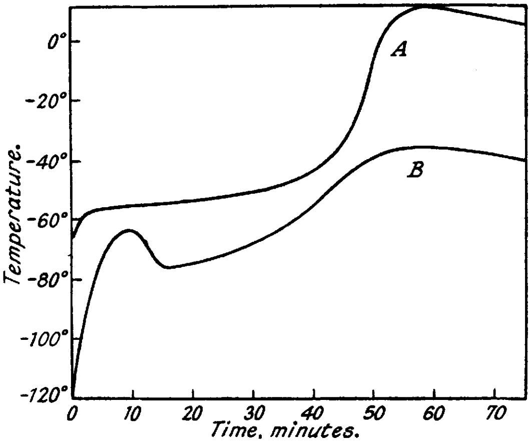
(2) The molecular weight of the polymers increased as the starting temperature of the reaction was reduced.

(3) The polymer yields in all the reactions we carried out indicated that the reactions had gone to completion or nearly so. This is at variance with some of the results of Fairbrother and

Seymour, who frequently obtained low yields, especially at low starting temperatures. This difference may be due to the more rigorous adiabatic conditions used in our experiments.

Later experiments : The effect of moist air. At this stage some alterations in the experimental technique were introduced, for apart from the cumbersome method used to precool the reactants, the earlier procedure allowed an uncontrolled access of laboratory air to the reaction mixture. The modified apparatus is shown diagrammatically in Fig. 2. The reaction vessel *R* is a double-walled " Pyrex " container, with a side arm cone-joint *C* connecting *R* to a high-vacuum pumping system; *R* is closed by a rubber stopper *S*, through which pass a mercury-sealed stirrer, pentane thermometer, and various inlet and exit tubes. Measured quantities of hexane and titanic chloride (purified by standard methods from the commercial products, and stored under dry air in sealed glass containers) were run into *R* from burettes, the transference of the liquids being effected by pressure-blowing with dry air or nitrogen. The *iso*butene (supplied by I.C.I., Billingham, and stated to be over 99% pure) was run into the reaction vessel from a graduated " Pyrex " trap. The cooling of the hexane–*iso*butene mixtures (20% *iso*butene by volume) was performed in the vessel *R*, by immersing it in the liquid-air bath *D*. When the desired low temperature had been attained in *R*, the annular space between the walls of the reaction vessel was evacuated *via* the high-vacuum system, and *R* thereby temporarily converted into a Dewar vessel. Catalyst solution sufficient to give $\frac{1}{2}$% $TiCl_4$ in the reaction mixture was then run into *R*, and the reaction carried out under adiabatic conditions and followed as previously in terms of the temperature changes. Improved thermal stability within the reaction vessel was attained by immersing the body of the Dewar flask in a liquid-air bath, and fitting a lead collar round its neck. With this arrangement there was very little leakage of heat into the reaction vessel from outside, and the mixture at — 80° could be kept at this temperature (± 1°) for long periods.

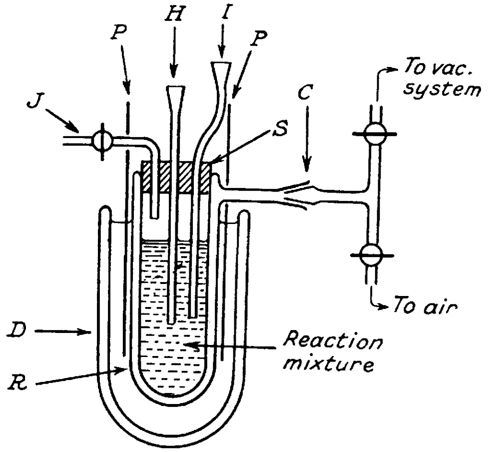
FIG. 1.



(A) *Expt.* 40.
(B) *Expt.* 23.

In both experiments 0·5% *of catalyst was added to* 20% iso*butene in hexane at time* = 0.

FIG. 2.



The reaction vessel.

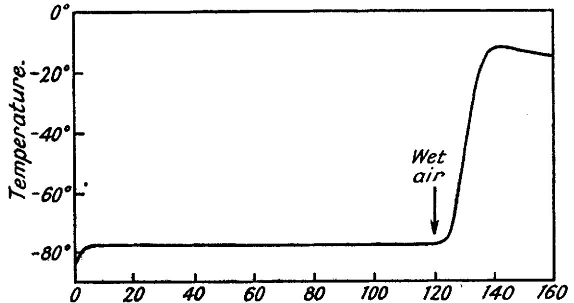
R = *Reaction vessel,* 20 *cm. long,* 5 *cm. diameter.* C = B.14 *cone joint to vacuum system.* S = *Rubber stopper carrying pentane thermometer and mercury seal stirrer* (*not shown*), *and hexane and catalyst inlet* H, iso*butene inlet* I, *and gas exit* J. P = *Lead collar.* D = *Dewar vessel.*

Using the modified apparatus, we were surprised to find that the addition of catalyst to the monomer solution at — 80° failed to induce polymerisation. This observation was confirmed several times. That this inability to enter into reaction was due in some way to the absence of laboratory air from the reaction vessel was clearly demonstrated by passing a brisk stream of laboratory air through the chemically quiescent reaction mixture, upon which polymerisation took place rapidly. A typical time–temperature curve for a reaction induced by laboratory air is given in Fig. 3.

Suspicion naturally fell on the moisture content of laboratory air as the activating agent for reaction, as it is well known that in some reactions Friedel–Crafts catalysts are active only in the presence of water (see Hickinbottom, *Nature*, 1946, **157**, 520; Heldman, *J. Amer. Chem. Soc.*, 1944, **66**, 1786; Leighton and Heldman, *ibid.*, 1943, **65**, 2276; Heldman and Thurmond, *ibid.*, 1944, **66**, 427). That water is in fact the active agent was demonstrated by several experiments, the results of which are summarised in Table III. For instance, it was found that the passage of carefully dried oxygen, nitrogen, or atmospheric air through the reaction mixture does not induce reaction; on the other hand, moist air and moist nitrogen did act as promoters.

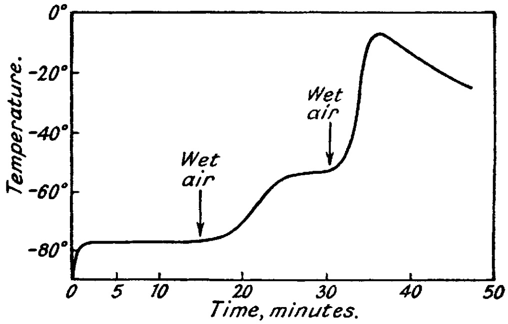
To be effective, laboratory air or moistened inert gases must be passed through for a certain time, at a sufficiently high rate. Positive effects were invariably found on passing atmospheric air for 1 minute at a rate of 3 l./min.: but the passage of the same quantity of air at the slower rate of 0·4 l./min. proved much less effective. An " effective " dose of laboratory air bubbled through at — 80° (passage for 1 min. at 2 l./min.) sometimes proved insufficient to drive the reaction to completion, but treatment with a second dose of air usually restarted the reaction and carried it to completion (see Fig. 4). It is noteworthy that the effect of the second dose was usually stronger than that of the first, probably owing to the higher temperature of the reaction mixture when the second dose was given.

FIG. 3.



Expt. 86. *Catalyst added at time = 0. At time = 120 mins., 3 l. of laboratory air were blown through the chemically quiescent reaction mixture in* 1 *min.*

FIG. 4.



Expt. 81. *Catalyst added at time = 0. At time = 15 mins. and 30 mins., 4 l. of laboratory air were passed through the reaction mixture in* 1 *min.*

The addition of small quantities of water in bulk form, as liquid, snow, or ice, to the reaction mixture did not initiate polymerisation. If the *iso*butene–hexane mixture at — 80° was treated with moist air before the addition of the catalyst, the subsequent addition of catalyst induced immediate reaction. This establishes a link with the preliminary experiments reported above.

Several experiments were carried out in an effort to find out whether or not polymerisation can be induced in the quiescent solutions by substances other than laboratory air or moistened inert gases. These experiments are quoted in Table III. As regards these substances the table shows that: (*a*) Hydrogen chloride is ineffective whether passed through the mixture at 1 atm. pressure, or at low partial pressures in admixture with dry nitrogen. (*b*) The results with carbon dioxide on the whole suggest that it is inactive, but are perhaps not quite conclusive. The slight positive effect obtained on one occasion was probably caused by incomplete removal of moisture from the gas. (*c*) The effect of ammonia is limited to combination with the catalyst: if the ammonia is added in small quantities only, subsequent addition of moist air allows reaction to proceed normally. Sulphur dioxide seems to behave in like manner. (*d*) Alcohol and ether, even when applied in small quantities, seem to prevent the initiation of polymerisation on the subsequent addition of moist air. They may be regarded as true poisons.

These results refer to reactions in which the starting temperatures were above — 90°. Experiments in which the catalyst was added to mixtures cooled to the lower range of temperature (— 90° to — 120°) gave inconclusive results. On the other hand, we have found that the quiescent state obtained on addition of catalyst to the mixture at — 60° is not disturbed by rapidly cooling this mixture down to — 120°, and that the passage of moist air then initiates polymerisation. In such cases we observed a considerable time lag (10—15 mins.) from the moment of passage of the moist air until the attainment of the maximum rate of reaction, so that the resulting time–temperature curves are markedly S-shaped (see Fig. 5). This shape is generally observable in the time–temperature curves for reactions initiated by moist air, but the

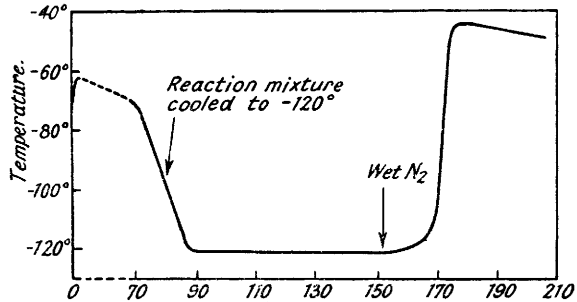
TABLE III.

Effect of substances added to the quiescent reaction mixture.

Substance (X) added.	Partial pressure of X (mm. Hg).	Rate of throughput (l./min.).	Time of throughput (mins.).	Observed effect.
O_2	760	4	1	Nil
N_2	760	4	1	Nil
Dry air	760	4	1	Nil
CO_2/N_2	10	3	1	Nil
	25	3	1	Nil
	500	3	1	Slight + ve
HCl	760	?	1	Nil
HCl/N_2	30	3	1	Nil
SO_2/N_2	15	3	1	Nil
NH_3	760	2	1	Temp. rise due to reaction with catalyst. No polymer
NH_3/N_2	40	2	1	Nil
$EtOH/N_2$	12	3	1	Poison
EtOH	0·1 c.c. (liquid)	—	—	Poison
Et_2O	0·25 c.c. (liquid)	—	—	Poison
H_2O	1 c.c. (liquid)	—	—	No effect
H_2O/N_2	17—20	2	1	+ ve
,, ...	4—5	4	1	+ ve
,, ...	17—20	0·6	1	No effect at −80°
,, ...	17—20	0·6	1	Slight + ve at −50°

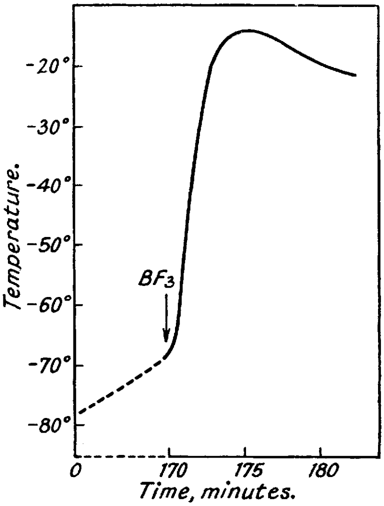
upward bend of the S is much sharper at higher starting temperatures, and there is no appreciable time lag before reaction sets in.

FIG. 5.



Expt. 104. *Catalyst added at time* = 0. *At time* = 70 *mins. air was admitted to the space between double walls of the reaction vessel. At time* = 88 *mins. the air space was re-evacuated. At time* = 150 *mins.* 3 *l. of nitrogen saturated with water vapour at room temperature were passed through the reaction mixture in* 1 *min.*

FIG. 6.



Expt. 88. *Catalyst added at time* = 0. *At time* = 170 *mins.* BF_3 *at atm. pressure was passed through the reaction mixture for* 1 *min.*

Discussion.—The discovery of the effect of moist air in the reactions catalysed by titanic chloride necessitates a re-evaluation of the earlier experimental results. The positive results obtained in our preliminary experiments were clearly due to the flow of air into the reaction vessel, and the lack of reproducibility was partly due to the fact that this inflow was uncontrolled. Similar remarks apply to Fairbrother and Seymour's experiments using titanic chloride. For the more powerful catalysts, such as boron trifluoride and aluminium bromide, definite evidence is yet lacking as to whether water is a necessary promoter of their catalytic activity. In the case of boron trifluoride we have indications that the critical water concentration is at any rate very much less than for titanic chloride. Davies (Thesis, Manchester, 1941) found that the careful exclusion of moisture from the boron trifluoride–*iso*butene system did not prevent rapid polymerisation; and we have observed that the addition of the trifluoride to a quiescent mixture of *iso*butene and titanic chloride at − 80° brought about an immediate and rapid polymerisation (see Fig. 6). It may seem, on the other hand, plausible to generalise from the example of titanic chloride to all the weaker catalysts; but this point has not yet been investigated. In any case the gradation in the catalytic activity of different halides observed by Fairbrother and Seymour seems not to require alteration, for it is unlikely that there were marked differences in water accessibility in the course of the comparative experiments of these workers.

The action of water in the titanic chloride polymerisation is paradoxical, for water at temperatures of − 60° to − 80° can be present only in the solid phase, its solubility in hexane at such temperatures being only of the order of 10^{-10} g.-mol/l. Since the addition of liquid water to the reaction vessel, giving lumps of ice in the reaction mixture, was not able to start polymerisation, it seems essential that the water be present as an extremely fine dispersion, as might be expected to result from a rapid bubbling of moist air through a liquid at a very low temperature. The ineffectiveness of too slow a stream of moist air may be due to the fact that the slow through-put rate allows the moisture to condense in the delivery tube, so that it does not reach the reaction mixture, or at least not in the required state of fine dispersion. The active dispersion may be molecular, the water molecules being brought to react with titanic chloride at the liquid surface; or else a fine colloidal dispersion of ice may be formed.

We conclude that water, in some highly disperse state, can act as a chain starter in combination with titanic chloride for the polymerisation of *iso*butene. A possible mechanism of the reaction would then be :

$$\text{(i)}\quad \mathrm{TiCl_4 + H_2O \longrightarrow TiCl_4{\cdot}OH_2{}^*}$$

$$\text{(ii)}\quad \mathrm{TiCl_4{\cdot}OH_2{}^* + M \longrightarrow M\overset{+}{H} + TiCl_4\overset{-}{O}H}$$
$$\mathrm{(M = monomer = CH_2{:}CMe_2.)}$$

extending to

$$\text{(iii)}\quad \mathrm{M\overset{+}{H} + M \longrightarrow M_2\overset{+}{H}} \qquad \text{(iv)}\quad \mathrm{M_2\overset{+}{H} + \mathit{n}M \longrightarrow M_{\mathit{n}+2}\overset{+}{H}}$$
$$\mathrm{(M_{\mathit{n}} = polymer.)}$$

and terminating by

$$\text{(v)}\quad \mathrm{M_{\mathit{n}+2}\overset{+}{H} + TiCl_4\overset{-}{O}H \longrightarrow M_{\mathit{n}+2} + TiCl_4{\cdot}OH_2}$$

or alternatively by

$$\text{(vi)}\quad \mathrm{M_{\mathit{n}+2}\overset{+}{H} + TiCl_4\overset{-}{O}H \longrightarrow M_{\mathit{n}+2}H{\cdot}OH + TiCl_4.}$$

We may add to this scheme by including the possibility of chain transfer in the sense :

$$\text{(viii)}\quad \mathrm{M_{\mathit{n}}\overset{+}{H} + M \longrightarrow M_{\mathit{n}} + M\overset{+}{H}}$$

The initiator is presumed to be the acid hydrate, $\mathrm{TiCl_4{\cdot}OH_2{}^*}$, in which the asterisk is added to indicate that the initiating complex may be in an active state by carrying the heat liberated by (i). In the case of termination by (vi), and if we exclude the possibility of the chain transfer in (vii), each water molecule would give rise to one polymer molecule. This is still the case for termination by (v), if we impose the condition that only the activated $\mathrm{TiCl_4,OH_2{}^*}$ molecules can act as initiators. Although it is too early to discuss these possibilities much further, we note that the molar quantity of water added to initiate polymerisation was of the same order as the number of molecules of polymer formed, but it seems unlikely, in the circumstances of the experiments, that each water molecule introduced could enter into reaction. Moreover, the observation that the addition of an " effective " dose of moist air sometimes resulted in an incomplete reaction (see Fig. 4) certainly suggests that a molecule of water cannot continue to produce new chain centres indefinitely. Possibly the water is removed and rendered inactive by precipitation of the $\mathrm{TiCl_4{\cdot}OH_2}$ molecules from solution or by their decomposition to give $\mathrm{TiOCl_2}$.

The efficiency of titanic chloride as catalyst in *initiating* the polymerisation is clearly dependent upon the acid strength of the $\mathrm{TiCl_4{\cdot}OH_2}$ complex. If a scheme of the type outlined for titanic chloride is applicable to the polymerisation of *iso*butene by Friedel–Crafts catalysts in general, it seems likely that the activity of these catalysts will be directly proportional to the acid strengths of their hydrates. Reliable measurements by independent methods of the acid strengths of the various catalysts in the Friedel–Crafts group are not yet available, although we understand from Dr. Fairbrother (who is at present engaged upon this problem) that without question the acid strengths of the strong catalysts such as $\mathrm{BF_3}$ and $\mathrm{AlBr_3}$ are markedly greater than those of the weaker catalysts such as $\mathrm{SnCl_4}$. The same point is made by Martin (*Chem.*

Reviews, 1944, **34**, 461) in respect of the relative acid strengths of BF_3 and BCl_3 in a review of the power of these two compounds to form complexes.

Similarly the efficiency of titanic chloride as *terminator* should be related to the base strength of the complex anion $TiCl_4\overset{-}{O}H$, and in the general case of Friedel–Crafts catalysts, the terminator efficiency should be related to the base strength of the anions $MX_n\overset{-}{O}H$. This quantity is *inversely* proportional to the acid strength of the complex $MX_n{\cdot}OH_2$, so that the more active the catalyst as initiator, the less active will it be as terminator. It follows immediately from this that the polymer molecular weight should be greater the more effective, *i.e.*, the stronger, the catalyst. We have previously drawn attention to the experimental evidence confirming this point, given in Table I.

The suggested mechanism of polymerisation would be liable to inhibition by bases, but in view of the strong acid properties of the catalyst, it might be expected that the addition of a base would merely neutralise the catalyst, and reduce to that extent its effective concentration. This seems to be the case for ammonia and sulphur dioxide.

It is curious that alcohol and ether cannot replace water in starting polymerisation, and still more remarkable that, when added in small quantities, they prevent the normal action of water. A similar poisoning effect was found by Miss Mandel (Thesis, Manchester, 1943) in the *iso*butene polymerisation with aluminium bromide, which is inhibited by the addition of acetone, and by the complex $2AlBr_3,COMe_2$. We postpone discussion of these points until more evidence is available.

The S-shaped time–temperature curves also present a difficulty to the proposed mechanism. They may signify the presence of a poison which is removed during the preliminary stage of the reaction. Or alternatively, they may be explained by postulating a "chain-branching" phenomenon, similar to that suggested by Semenov in respect of explosive gas reactions: in this case the carbonium-ion mechanism would require amplification by some kind of energy chain.

The experimental work described in this paper is still in progress, and we hope to be able to elaborate the theory and clarify some of its obscure points later when we have more experimental data.

The authors are indebted to the Research Laboratories of I.C.I., Billingham, for the original stimulus to this investigation and for supplying them with *iso*butene of the requisite quality. They were also assisted by grants from the D.S.I.R. and from the Anglo-Iranian Oil Company Ltd.

Discussion.

PROF. M. G. EVANS: (1) Professor Polanyi reports a very great difference between the catalytic effect of water and that of hydrogen chloride in the presence of metal halides of the type $AlCl_3$. If the proton is the catalytic agent in the polymerization of *iso*butene, the difference in the action of water and hydrogen chloride should be revealed in the energetics of the reactions:

$$MCl_3 + ClH \longrightarrow MCl_4^- + H^+$$
$$MCl_3 + HOH \longrightarrow MCl_3OH^- + H^+$$

The energy changes involved in these reactions are respectively

$$- D_{HCl} - I_H + E_{Cl} + S_{Cl^-}$$
$$- D_{HOH} - I_H + E_{OH} + S_{OH^-}$$

in which D is the bond strength of the molecules, I_H the ionization potential of the hydrogen atom, E the electron affinity of the chlorine atom or the OH radical, and S the solvation energy of the Cl^- or OH^- ion by the metal halide MCl_3.

The ratio of the dissociation constants K_1 and K_2 will be given by $\ln K_1/K_2 = (Q_1 - Q_2)/\boldsymbol{R}T$, and at the temperature of these experiments, *viz.*, 100° K., a value of $(Q_1 - Q_2) = - 4{\cdot}6$ kg.-cals. will lead to a value of $K_1/K_2 = 10^{-10}$. Using the following values: $D_{HCl} = 4{\cdot}45$, $D_{HOH} = 4{\cdot}77$, $E_{Cl} = 3{\cdot}78$, $E_{OH} = 2{\cdot}04$ electron volts, the value of $(Q_1 - Q_2) = - 4{\cdot}6$ kg.-cals. would necessitate a value of $(S_{OH^-} - S_{Cl^-}) = 1{\cdot}62$ e.v. This is not an unreasonable value; the difference in the heats of solvation of Cl^- and OH^- in water is $1{\cdot}87$ e.v.

The catalytic action of both water and hydrogen chloride with aluminium chloride in the isomerization reactions of hydrocarbons seems now to be well established. These reactions which are attributed to a proton attack occur, however, at relatively elevated temperatures where the value of $(Q_1 - Q_2)$ will not be so important in differentiating between the action of water and of hydrochloric acid.

(2) The influence of the stability of the active ending of a growing polymer chain upon the structure of the polymer chain is not peculiar to an ionic active ending. Thus in a radical-polymerization reaction the energy change E of a polymerization step will depend upon the resonance energies R_a and R_f of the attacking radical and the radical formed :

$$E = - D_{C=C} + D_{C-C} - R_a + R_f$$

For " head-to-tail " polymerization, when the attacking radical is identical with that formed as a result of the chain-propagation step, $R_a = R_f$ and $Q = - D_{C=C} + D_{C-C}$.

For " head-to-head " reaction followed by a " tail-to-tail " step the energy changes of the successive reactions will be

$$E_1 = - D_{C=C} + D_{C-C} - R_a + R_f$$
$$E_2 = - D_{C=C} + D_{C-C} + R_a - R_f$$

and hence the heat of reaction will alternate from step to step by an amount $2R_a - 2R_f$ and will influence in a similar way the activation energy of reaction.

FIG. 1.

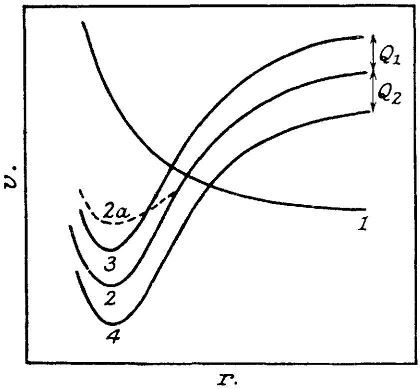
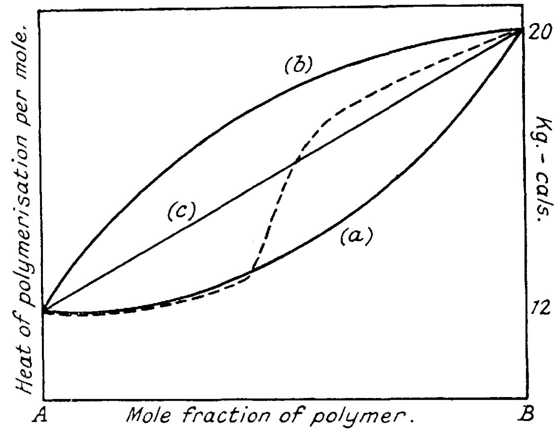


FIG. 2.



That difference in the resonance energy of radicals is sufficient to give rise to selectivity in the opening of a double bond is seen in the " Karasch effect ". In this case the increased stability of $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\overset{|}{C}\text{—}CH_2X$ as compared with $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!\overset{X}{\overset{|}{C}}\text{—}CH_2\text{–}$ gives rise to the reversal of the " Markownikov rule ".

It is surprising that *iso*butene can be polymerized by an ionic initiator and not by a free radical. Fig. 1 shows diagramatically the change in potential energy involved in a chain-propagation step.

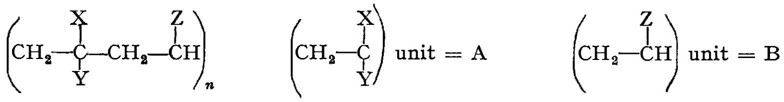
Curve 1 represents the change in potential energy with r for the bond assignment $\sim\!\sim CH_2\text{—}CH_2\overset{r}{\cdots}CH_2{=}CH_2$, and Curve 2 that of $\sim\!\sim CH_2\text{—}CH_2\overset{r}{\text{—}}CH_2\text{—}CH_2$.

Curve 2a is the corresponding curve to 2 when " steric energy " effects are present, and Curves 3 and 4 correspond to the two cases in which $R_a \neq R_f$, $Q_1 = Q_2 = (R_a - R_f)$.

The potential-energy diagram for an ionic reaction will in the main differ from the above in the magnitude of Q_1 and Q_2; $Q_1 = Q_2 = (I_a - I_f)$ (in which I refers to the ionization potentials). We would conclude, therefore, that in an ionic polymerization reaction the larger value of $(I_a - I_f)$ compared with $(R_a - R_f)$ for radical reaction would lead to greater *differences between the activation energies* of head-to-head, tail-to-tail, and head-to-tail polymerization steps.

(3) *Heats of polymerization.* Professor Polanyi and his co-workers have shown that the repulsion energy between the side groups in a polymer chain of the type $\left(\text{—}CH_2\text{—}\overset{X}{\underset{Y}{C}}\text{—}\right)_n$ leads

to a reduction in the heat of polymerization. In Leeds we have studied the influence of such side groups as $X = Y = Cl$; $X = CH_3$, $Y = CO_2R$ (in which R is $CH_3,C_6H_{13},C_{10}H_{23}$) on the heat of polymerization and found results similar to those of Polanyi. An interesting extension of this is to be found in the heat of copolymerization of a di- and a mono-substituted monomer :



$$\left(CH_2{-}\overset{X}{\underset{Y}{C}}{-}CH_2{-}\overset{Z}{CH}\right)_n \qquad \left(CH_2{-}\overset{X}{\underset{Y}{C}}\right) \text{ unit} = A \qquad \left(CH_2{-}\overset{Z}{CH}\right) \text{ unit} = B$$

There are three extreme possibilities : (*a*) that the polymer is a random distribution of A's and B's and the heat of an A–B link is equal to that of A–A ; (*b*) that the heat of an A–B link is equal to that of B–B ; and (*c*) that the co-polymer is built up of large units of A polymer and B polymer, thus $-[A - A]_n - A - B - [B - B]_m$.

Fig. 2 shows the heat of polymerization per mole as a function of the composition of the polymer for these three cases. Preliminary results obtained for the co-polymer of methyl methacrylate and acrylonitrile lie approximately on the dotted line of Fig. 2.

From these results it would appear that a $CH_2{-}\overset{X}{\underset{Y}{C}}$ unit flanked by $CH_2{-}\overset{Z}{CH}$ units is under less constraint than when flanked by $CH_2{-}\overset{X}{\underset{Y}{C}}$, and hence the heat of the A–B link approaches that of B–B, whereas a $CH_2{-}\overset{Z}{CH}$ unit when flanked by $CH_2{-}\overset{X}{\underset{Y}{C}}$ units is under constraint from the neighbouring side groups and hence the heat of A–B approaches that of the A–A.

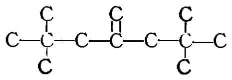
T. A. KLETZ and W. C. PRICE : *The infra-red spectra of butene trimer and tetramer.* We have had the opportunity of examining the infra-red spectra of the butene trimer and tetramer referred to by Professor Polanyi in his opening paper. This provides an interesting application of the principles discussed by Dr. H. W. Thompson in his paper on the infra-red spectra of macromolecules.

The original materials were believed to be mono-olefins. After their infra-red spectra had been recorded, they were hydrogenated and the spectra of the hydrogenated material also obtained. The spectra of the unsaturated trimer and tetramer in the region 5—15 μ show the following points of interest. First, the spectra of both trimer and tetramer are rather similar, indicating that the basic sub-groupings in both molecules are the same. Both trimer and tetramer have strong bands in the neighbourhood of 1200 and 1237 wave-numbers which indicate the presence of terminal *tert.*-butyl groups. The intensity of these bands compared with the corresponding bands in the spectrum of 2 : 2 : 4-trimethylpentane suggests at least two *tert.*-butyl groups per molecule. The absence of bands in the region 1163—1176 wave-numbers shows that there is no terminal *iso*propyl group, while the absence of a band at 1136 wave-numbers shows there are no adjacent tertiary carbon atoms. The presence of non-adjacent internal tertiary carbon atoms is not excluded.

Both samples show the frequency of the C=C bond at 1650 wave-numbers. The trimer has a well-defined band at 893 and the tetramer at 897 wave-numbers, indicating that the double bond is of the type $CR_1R_2{:}CH_2$. The tetramer has an additional strong band at 859 wave-numbers, but it has not yet been possible to correlate this with any special structural feature.

The infra-red spectra of the hydrogenated trimer was found to be identical with that of a sample isolated from the high-boiling residue from an *iso*octane plant. This specimen had been identified by its physical data (b. p. 178·3, $n_D^{20°} = 1{\cdot}4200$) with 2 : 2 : 4 : 6 : 6-pentamethylheptane (b. p. 174—175°, $n_D^{20°} = 1{\cdot}4199$) and its infra-red spectrum—first obtained by Sutherland and Willis—strongly supports this identification.

This information, taken together with that on the unsaturated compound, points to the structure :

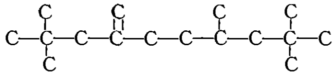


$$C{-}\overset{C}{\underset{C}{C}}{-}C{-}\overset{C}{\overset{\|}{C}}{-}C{-}\overset{C}{\underset{C}{C}}{-}C$$

for the trimer. This formula is consistent with the inability of the molecule to polymerise further, as the *tert.*-butyl groups protect the double bond.

The spectrum of the saturated tetramer is almost identical with that of the saturated trimer, showing that it must contain very similar groupings.

A formula for the unsaturated tetramer which is consistent with all the evidence is :



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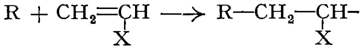
3. *Polymerisation of Monomers in Aqueous Solution.*

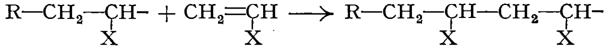
By M. G. Evans.

It has now been well established that free radicals or reactions yielding free radicals are able to initiate the polymerisation of unsaturated monomers both in the gas phase and in the liquid monomer phase; such initiating reactions can be written :



$$\mathrm{R + CH_2{=}\underset{X}{C}H \longrightarrow R{-}CH_2{-}\underset{X}{C}H{-}}$$

and the free radical thus formed can undergo a similar reaction with another monomer molecule :



$$\mathrm{R{-}CH_2{-}\underset{X}{C}H{-} + CH_2{=}\underset{X}{C}H \longrightarrow R{-}CH_2{-}\underset{X}{C}H{-}CH_2{-}\underset{X}{C}H{-}}$$

There are a number of reactions in aqueous solution in which free radicals or free radical ions are probably produced as intermediates in a reaction sequence. These reactions are usually electron-transfer reactions; *e.g.*,

(1) $\mathrm{Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + HO^- + OH}$; $\mathrm{Fe^{++} + OH \longrightarrow Fe^{+++} + OH^-}$

(2) Quinone + $e \longrightarrow$ Semiquinone; Semiquinone + $e \longrightarrow$ Quinone ion

The free radicals or radical ions are formed in the above cases because electron-transfer reactions, involving a change of two or more electrons, occur as a sequence of one-electron transfer steps. A preliminary investigation showed that such reactions were very effective in initiating polymerisation reactions with monomers such as methyl methacrylate, methacrylic acid, methyl acrylate, acrylonitrile, styrene, vinylidine chloride, etc., in aqueous solution. The system ferrous ions–hydrogen peroxide was much more effective, *i.e.*, it led to a much more rapid formation of polymer, than was hydrogen peroxide alone.

In the absence of a polymerisable monomer, ferrous ions in excess of hydrogen peroxide catalyse the decomposition of hydrogen peroxide leading to the evolution of oxygen. Haber and Weiss (*Proc. Roy. Soc.*, **1939**, *A*, **147**, 332) put forward the following reaction sequence to account for this overall reaction :

$$\mathrm{H_2O_2 + Fe^{++} \longrightarrow HO^- + OH + Fe^{+++}}$$
$$\mathrm{HO + Fe^{++} \longrightarrow HO^- + Fe^{+++}}$$
$$\mathrm{HO + H_2O_2 \longrightarrow H_2O + HO_2}$$
$$\mathrm{HO_2 + H_2O_2 \longrightarrow HO + H_2O + O_2}$$

In the presence of a polymerisable monomer we found that the evolution of oxygen could be very considerably reduced or even stopped.

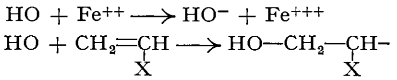
This observation means that the monomer molecules are reacting with the chain carriers and that this reaction leads, not only to a breaking of the chain of events leading to oxygen evolution, but also to the polymerisation of the monomer.

The Stoicheiometry of the Reaction between Ferrous Ions and Hydrogen Peroxide in the Absence and in the Presence of Monomers.—The preliminary observations referred to above can be explained on the basis of the Haber–Weiss mechanism for the reaction between ferrous ions and hydrogen peroxide, if we postulate that the hydroxyl radical attacks the double bond of the monomer thus :

(I) $\mathrm{H_2O_2 + Fe^{++} \longrightarrow HO + OH^- + Fe^{+++}}$

(II) $\mathrm{HO + Fe^{++} \longrightarrow HO^- + Fe^{+++}}$

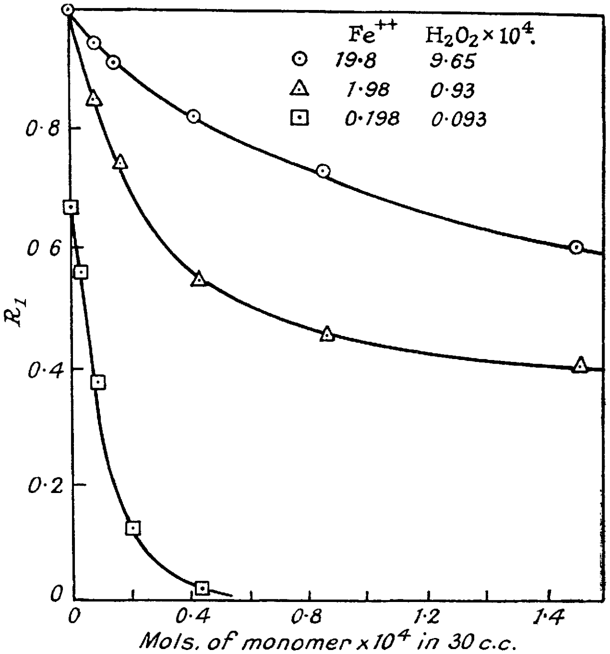
(III)



$$\mathrm{HO + CH_2{=}\underset{X}{C}H \longrightarrow HO{-}CH_2{-}\underset{X}{C}H{-}}$$

This idea has been tested by a study of the stoicheiometry of the reaction in the absence and in the presence of monomers. When the molality of ferrrous ions is equal to or in excess of that of the hydrogen peroxide, the reaction in the absence of monomer is limited to reactions (I) and (II) and the stoicheiometry of the reaction corresponds to 1 mole of $H_2O_2 \equiv 2$ moles of ferrous ions. If, however, reaction (III) occurs, then since reactions (II) and (III) are in competition for the OH radicals produced in step (I), the presence of monomer should lead to a deviation in stoicheiometry from 1 mole $H_2O_2 \equiv 2$ mole Fe^{++} towards that of 1 mole $H_2O_2 \equiv 1$ mole Fe^{++}. Fig. 1 shows the effect of monomer concentrations on the stoicheiometry, and the changes are consistent with the above scheme. Increasing the concentration of ferrous ions necessitates a higher concentration of monomer to bring about a given change. Fig. 2 shows that different monomers react with OH radicals at different rates and hence compete to different extents with reaction (II). All the reactions so far reported in this section were carried out in an atmosphere of nitrogen. It was found that the presence of oxygen gave rise to long induction periods in the polymerisation, and with sufficiently low concentrations of reactants suppressed it altogether; further, that in a system in which reactions (I), (II), and (III) were taking place oxygen was absorbed and the amount absorbed was measured.

FIG. 1.



Effect of initial Fe^{++} *concentration on the value of* R_1 *in the presence of methyl acrylate, where* $R_1 = \frac{[Fe^{+++}]_t - [H_2O_2]}{[H_2O_2]_0}$.

Wieland and Franke (*Annalen*, 1927, **457**, 1; 1929, **459**, 1; see also Fenton *et al.*, *J.*, 1894, **65**, 899; 1900, **77**, 69) showed that hydrogen peroxide, together with catalytic amounts of ferrous ions, forms an effective oxidising system for organic substrates such as lactic and glycollic acids, alcohols, etc. Systems were therefore studied in which both a polymerisable monomer and an oxidisable substrate were present, and the results showed that polymerisation and oxidation were competing reactions and that the presence of a large amount of monomer reduced very considerably the oxidation of the glycollic or lactic acid by the hydrogen peroxide–ferrous ion system. It would appear probable, therefore, that the same entity is responsible for the opening of the double bond of the monomer and for initiating the oxidation chain of the glycollic acid :

$$HO + CH_2{=}\underset{X}{C}H \longrightarrow HO{-}CH_2{-}\underset{X}{C}H{-} \longrightarrow \text{polymerization}$$

$$HO + HR \longrightarrow HO_2 + R \longrightarrow \text{oxidation}$$

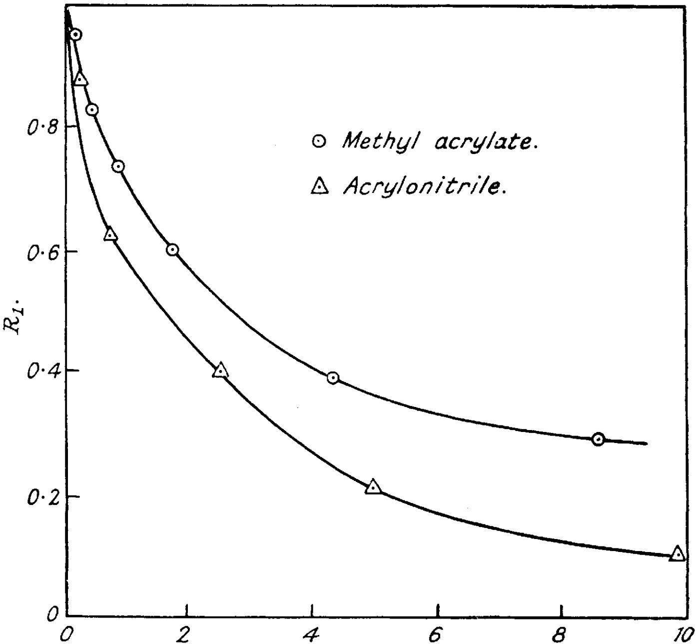
The Kinetics of the Hydrogen Peroxide–Ferrous Ion Reaction.—The rates of formation of ferric ions in the absence and in the presence of monomers have been measured, colorimetric methods being used for determining the concentration of ferrous and ferric ions. The kinetics in the absence of monomers arise from reaction (I) and (II), whereas in the presence of a large excess of monomer reaction (II) is suppressed completely. Table I gives a comparison of the values of the velocity constant for reaction (I) obtained from the different kinetic expressions which arise in the absence and in the presence of monomers. The close correspondence of the two sets of results is additional evidence in favour of the proposed mechanism.

TABLE I.

Absence of monomer (k_1 25°)	61	59	59	67	67	56
Presence of monomer (k_1 25°)	58	55	49	72		
Concn. of monomer, moles/l.	0·070	0·070	0·065	0·25		

The value of k_1 for step (I) is $k_1 = 1{\cdot}78 \times 10^9 \exp.\{-10{,}000/\boldsymbol{R}T\}$ (moles/l.)$^{-1}$ sec.$^{-1}$.

FIG. 2.*



* For definition of R_1, see Fig. 1.

The Kinetics of Polymerisation.—The whole reaction scheme proposed for the polymerisation of aqueous solutions of monomers is :

$$\begin{array}{rll}
\mathrm{Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + HO^- + OH} & \quad . \quad . \quad . & k_1 \\
\mathrm{HO + M \longrightarrow HO{-}M{-}} & \quad . \quad . \quad . \quad . \quad . \quad . \quad . & k_i \\
\left.\begin{array}{r}\mathrm{HOM{-} + M \longrightarrow HO{-}M{-}M{-}} \\ \cdots\cdots \\ \mathrm{HO(M)_n{-} + M \longrightarrow HO(M)_{n+1}} \\ \cdots\cdots\end{array}\right\} & \quad . \quad . \quad . \quad . \quad . \quad . & k_p \\
\mathrm{HO(M)_n{-} + {-}(M)_mOH \longrightarrow HO(M)_{n+m}OH} & \quad . \quad . \quad . \quad . \quad . & k_t \\
\mathrm{HO(M)_n + OH \longrightarrow HO(M)\ OH} & \quad . \quad . \quad . \quad . \quad . \quad . & k'_t
\end{array}$$

Two possible chain-termination steps are given, one resulting from the mutual interaction of growing polymer chains, and the other from the reaction between a growing polymer chain and an hydroxyl radical.

Assuming that k_p and k_t are independent of chain length and employing stationary-state conditions, we have the relation between monomer concentrations and time t:

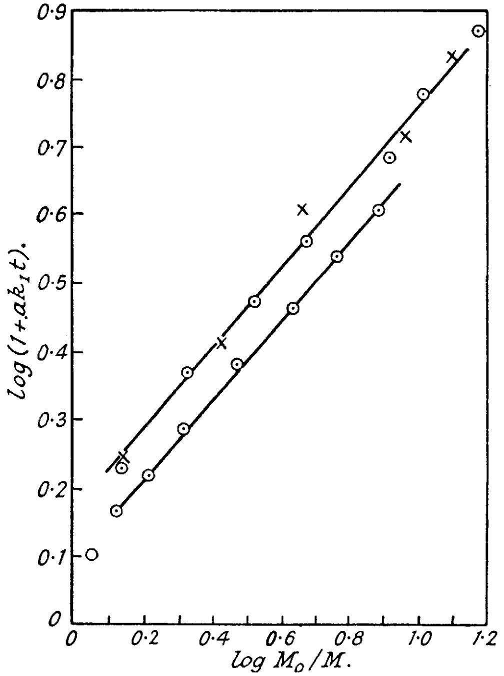
$$\log \frac{M}{M_0} = \frac{k_p}{\sqrt{k_1 k_t}} \log (1 + a k_1 t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for mutual termination, in which a is the molality of both ferrous ions and hydrogen peroxide and M_0 is the initial concentration of monomer. For hydroxyl-radical termination the expression is

$$\frac{1}{M} - \frac{1}{M_0} = \frac{k_1 k_p}{k_t} \cdot t$$

Fig. 3 shows that equation (1) fits the experimental results for methyl methacrylate, and that the slope $k_p/\sqrt{k_1 k_t}$ is independent of both M_0 and initiator concentration a.

Fig. 3.



Although the monomers are in aqueous solution, the polymer produced is insoluble, so it was not surprising to find that added emulsifying agents had a profound effect upon the rate of polymerisation. Fig. 4 shows the effect of trimethylcetylammonium bromide on the rate of polymerisation. The emulsifying agent does not change the mechanism of reaction; at all concentrations of emulsifying agent the kinetics obey equation (1), but the value of $k_p/\sqrt{k_1 k_t}$ increases with increasing concentration of emulsifying agent.

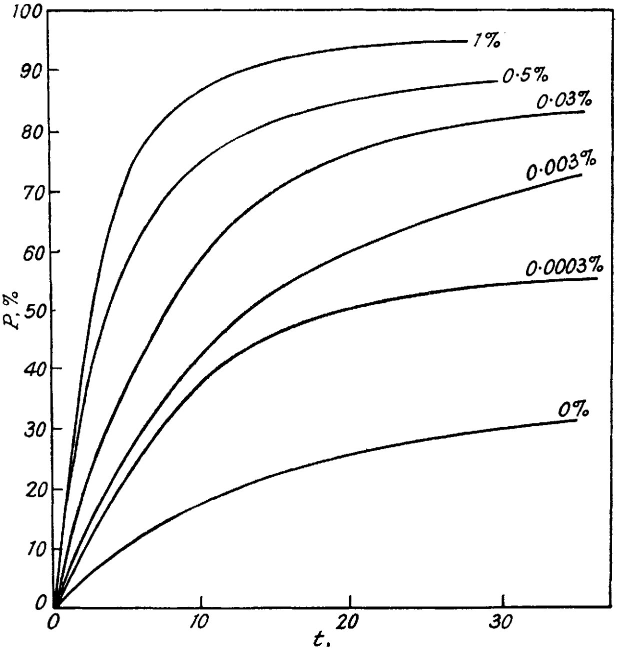
This is not an effect upon k_1 which is found to be independent of emulsifying agent concentration. Measurements at different temperatures lead to a value of $(E_p - \frac{1}{2}E_t)$, in which E_p is the activation energy of the propagation step and E_t that for the mutual termination reaction: $E_p - \frac{1}{2}E_t = 5000$ cals./mole, and this value is practically independent of emulsifying agent concentration.

Molecular Weights and their Distribution.—The reaction scheme outlined above leads to a very simple connection between the reaction conditions and the mean number molecular weight. The number of moles of polymer formed in a reaction is equal to one-half the number of moles of hydrogen peroxide used, since each polymer molecule contains two OH groups each of which originated from one hydrogen peroxide molecule. Thus if a is the amount of hydrogen peroxide used in the reaction and ΔM is the amount of monomer polymerised

$$\bar{N} = 2\Delta M/a$$

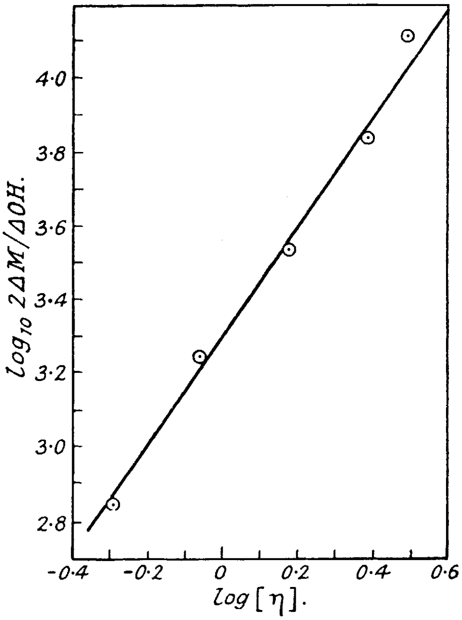
In Fig. 5 the value of log $(2\Delta M/a)$ is plotted against log $[\eta]$ (where $[\eta]$ is the intrinsic viscosity of the polymer) for a series of different reaction conditions, methyl methacrylate being used as the monomer, and it is seen that the mean number molecular weight and the intrinsic viscosity are related by

FIG. 4.



Effect of varying emulsifying agent concentration.

FIG. 5.



$$\log (2\Delta M/a) = \log K + a \log [\eta]$$

In order to obtain a much better test of the above reaction scheme, the distribution of molecular weights has been calculated on the basis of the kinetics, and the results compared with those obtained by fractionation and osmotic measurements.

Using the methods outlined by Gee and Melville (*Trans. Faraday Soc.*, 1935, **32**, 54) and by Herrington and Robertson (*ibid.*, 1942, **38**, 490; Herrington, *ibid.*, 1944, **40**, 236), one can calculate the distribution of molecular weights from the kinetics. This is possible because the kinetics of the reactions leading to initiation of polymerisation are known. This leads to an expression

$$\frac{\mathrm{d}P_N}{\mathrm{d}M} = \tfrac{1}{2}\frac{a^3\beta^3}{M^3}\left(\frac{M_0}{M}\right)^{-3\beta}(N-2)\left\{1+\frac{a\beta}{M}\left(\frac{M_0}{M}\right)^{-\beta}\right\}^N \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which P_N is the amount of polymer of chain length N, $\beta = \sqrt{k_1k_t}/k_p$, M_0 the initial monomer concentration, and a the initiator concentration. Figs. 6 and 7 show the integrated form of equation (3) for different values of a and at different stages in the reaction. Fig. 8 shows a comparison of the theoretical distribution curve with the experimental curves obtained by a single and a double fractionation. The molecular weights were determined from osmotic pressures. The agreement is good when one takes into consideration the difficulties of fractionation and molecular-weight determination.

FIG. 6.

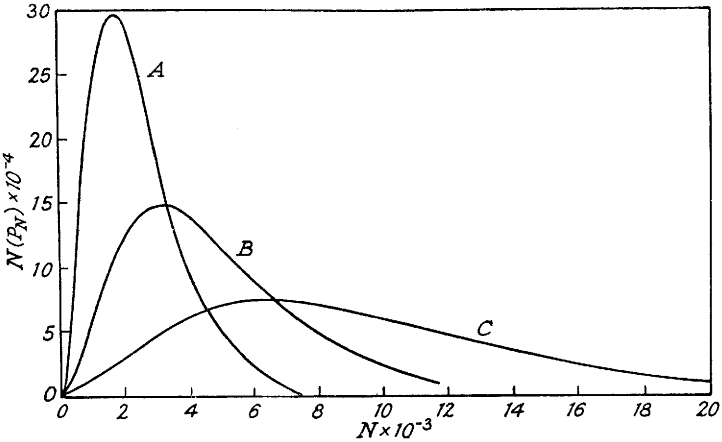
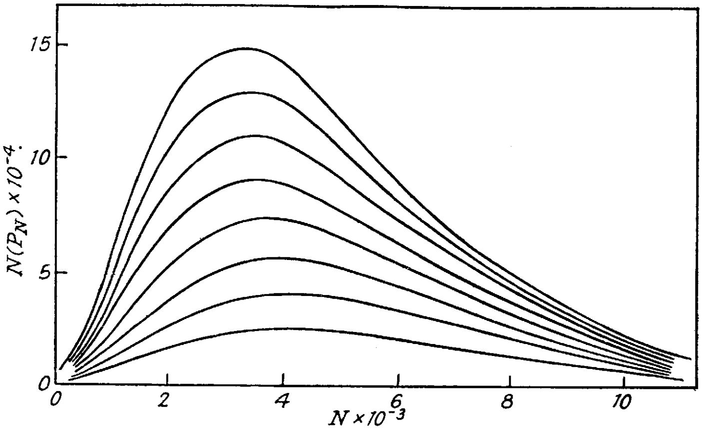


FIG. 7.



A more striking comparison is afforded by the theoretical and experimental values of the viscosity chain length. This property is related to the distribution curve by

$$\overline{N}_v = \left[\frac{\Sigma w_i N_i^{1/a}}{\Sigma w}\right]^a$$

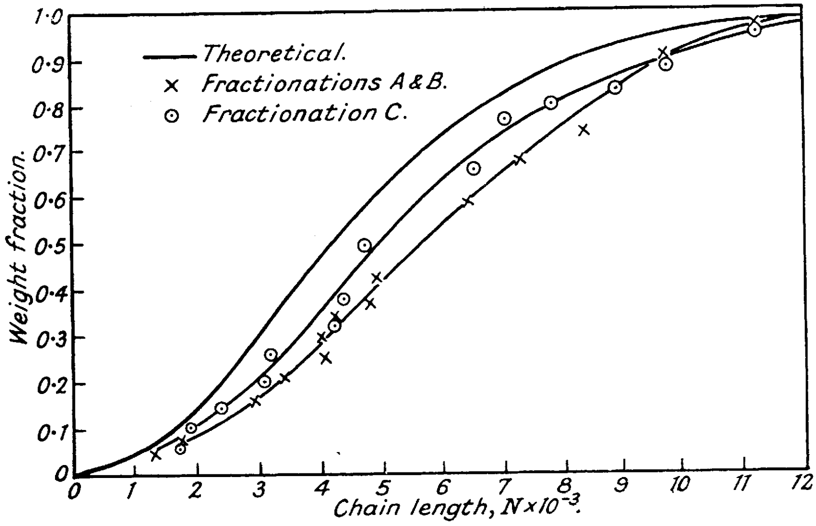
in which α is the exponent in relation between number molecular weight and intrinsic viscosity of sharp fractions, N_i the chain length, and w_i the weight of the ith species can be obtained from the theoretical distribution curve.

Table II compares the theoretical values of the viscosity average molecular weight with those determined experimentally for methyl methacrylate polymer samples produced under different conditions. Not only do the values change with initiator concentration in the way which one would expect, but the actual values compare very well with the theoretical values.

TABLE II.

Concn. of initiator, moles/l.	2×10^{-4}	1×10^{-4}	$0{\cdot}5 \times 10^{-5}$
Viscosity mol. wt. Calc.	24,300	45,400	91,400
Viscosity mol. wt. Found	23,200	48,500	92,900

FIG. 8.



Integral weight distributions.

Fig. 7, which shows the theoretical change in the distribution curve during the course of a reaction, indicates that we should expect only a slight decrease in mean molecular weight with percentage polymerisation. Table III shows that this is so, although the decrease is less than would be predicted from the theory.

TABLE III.

Time, secs.	235	360	600	782
$[\eta]$	1·51	1·51	1·50	1·50
P, %	62	72	82	90

End-group Determinations.—The above reaction scheme leads to the conclusion that each polymer molecule contains two terminal hydroxyl groups. A determination of these groups in the polymer should therefore lead to values of the number molecular weight which should be comparable with those obtained from the kinetics and from osmotic-pressure measurements. The method we have used for the determination of hydroxyl groups is similar to that used by Bolland (*I.R.I. Trans.*, **1941**, **16**, 267), based on the reaction between methylmagnesium chloride and a hydroxy-compound. We are very conscious of the fact that incomplete drying of these polymer samples formed in aqueous systems would completely vitiate the results, and extreme care has therefore been taken. The following are put forward only as preliminary results.

The polymer used for this comparison was polystyrene, and the results of end-group determination are compared with the value of the molecular weight M for unfractionated samples and with the molecular weight from osmotic-pressure measurements for fractionated samples. The results (Table IV) show a fair agreement between the values of molecular weight obtained by the two methods.

TABLE IV.

M by end-group method.	*M*.	Method.	*M* by end-group method.	*M*.	Method.	*M* by end-group method.	*M*.	Method.
33,600	34,200	2*M*/*a*	86,300	97,000	Osmotic pressure	71,600	80,600	Osmotic pressure
40,600	34,200	2*M*/*a*	88,700	97,000		72,800	80,600	

The Values of k_p *and* k_t *and their Dependence upon Chain Lengths.*—In the kinetic treatment above it has been assumed that k_p and k_t are both independent of chain length, and the agreement between theory and experiment suggests that this is a valid assumption. Melville and Burnett (*Nature*, **1945**, **156**, 661) have recently reported that in the case of bulk polymerisation of vinyl acetate both k_p and k_t are independent of chain length.

The transition states of both chain-propagation and chain-termination reactions are associated states, and it has been shown that for such cases the entropy change accompanying the formation of the transition state can be set equal to that of the formation of a final state of the same configuration. An investigation of the entropy changes of such reactions as

$$\mathrm{P}_x + \mathrm{M} \longrightarrow \mathrm{P}_{x+1} \qquad \mathrm{P}_{x_1} + \mathrm{P}_{x_2} \longrightarrow \mathrm{P}_{x_1+x_2}$$

will, therefore, help in understanding the temperature-independent factors of propagation and termination reactions, since we can equate the entropy changes of the above reactions to the entropy changes accompanying the formation of the corresponding transition states.

Many expressions have been developed for the partition functions of long-chain molecules in solution; *e.g.*,

$$\mathrm{F} = \mathrm{f}_0^{\,n_0}\,\mathrm{f}_1^{\,N}\,\frac{1}{\sigma N}\,\frac{(n_0 + N)\,!}{n_0\,!\,\Pi\, n_x\,!}\left(\frac{\gamma}{n_0 + N}\right)^{\Sigma(x-1)n_x}$$

in which n_0 is the number of solvent molecules, $N = \Sigma x n_x$ where n_x is the number of molecules of chain length x, σ is the symmetry number of units of solute molecules, f_0 and f_1 are the partition functions for the motions of solvent and solute molecules, and γ is the co-ordination number of the space lattice. This equation makes no distinction between the behaviour of a free monomer unit and a monomer unit incorporated in a polymer chain. If we consider that the monomer unit in a free state will be able to rotate and oscillate more freely than a unit in a polymer chain, then the equation must be modified to

$$\mathrm{F} = \mathrm{f}_0^{\,n_0}\,\mathrm{f}_m^{\,N-\Sigma' x n_x}\,\mathrm{f}_p^{\,\Sigma' x n_x}\,\frac{1}{\sigma N}\,\frac{(n_0 + N)\,!}{n_0\,!\,\Pi n_x\,!}\left(\frac{\gamma}{n_0 + N}\right)^{\Sigma(x-1)n_x}$$

in which f_m is the partition function of the free monomer unit and f_p that of monomer units in the polymer chains, and the summation Σ' is taken over all values of x except $x = 1$. From this expression the standard entropy changes accompanying chain propagation and termination are respectively

$$\frac{\Delta S^\circ_p}{RT} = 1 - \log\gamma - \log \mathrm{f}_m/\mathrm{f}_p \quad \text{and} \quad \frac{\Delta S^\circ_t}{RT} = 1 - \log\gamma$$

when concentrations of monomers and polymers are expressed as moles per total number of moles of monomer units, *i.e.*,

$$C_x = \frac{n_x}{\Sigma x n_x} \quad \text{and} \quad C_m = \frac{n_m}{\Sigma x n_x}$$

Identifying these entropy changes with those between the corresponding initial and transition states, we see that both k_p and k_t are independent of chain length. Moreover, the temperature-independent factors for propagation and termination are related by

$$A_p/A_t = \mathrm{f}_p/\mathrm{f}_m$$

The value of $A_p/A_t = 10^{-3}$ found by Melville is understandable on the model that the monomer units in the liquid phase are free to rotate whereas in the polymer chain their motion is greatly restricted to a libration or vibration.

These ideas developed here are not, however, applicable to reactions in which the polymer chains are insoluble in the reaction medium, which is the case in polymerisation of aqueous solutions of monomers. Under such conditions, when the heat of solution of the polymer chains is a large negative quantity, the polymer chains will behave like lyophobic colloids. Termination of polymerisation will occur by the coagulation of the active polymer chain with other active chains, and hence equations for the kinetics of colloidal coagulation might be applicable.

The velocity constant for coagulation of spheres of radii r_1 and r_2 is

$$k = \frac{8\boldsymbol{R}T}{3000\,\eta}\left\{\frac{2 + r_1/r_2 + r_2/r_1}{4}\right\} \text{ (moles/l.)}^{-1}\text{ secs.}^{-1}$$

and if the polymer chains of length x are coiled up into spheres then in terms of chain length

$$k_t = \frac{8\boldsymbol{R}T}{3000\,\eta}\left\{\frac{2 + (x_1/x_2)^{\frac{1}{3}} + (x_2/x_1)^{\frac{1}{3}}}{4}\right\} \text{ (moles/l.)}^{-1}\text{ secs.}^{-1}$$

The velocity constant is therefore only very slightly dependent upon chain length, being independent of chain length when $x_1 = x_2$, and is only increased by 4% when $x_1 = 10x_2$. It would appear justifiable therefore to consider k_t virtually independent of chain length.

The effect of added emulsifying agent upon the value of $\frac{k_p}{\sqrt{k_1 k_t}}$ can now be understood as an effect upon the coagulation constant k_t. An emulsifying agent such as trimethylcetylammonium bromide will be adsorbed on the polymer colloidal particle, setting up a Helmholtz double layer which will stabilise the colloidal system.

The work reported in this survey was carried out in collaboration with Mr. J. H. Baxendale, Mr. G. S. Park, Mr. J. H. Kilham, and Mr. S. Bywater.

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4. *Polymerisation of Vinyl Compounds in the Gas and in the Liquid Phase.*

By H. W. MELVILLE.

THIS section of the discussion is confined to a review of the present position regarding the mechanism of polymerisation of ethylene derivatives in the liquid and in the gas phase at temperatures from 0° to 200°. A great deal of pioneering work has now established the following general points. The reactions are all of the chain type, though the possibility of non-chain processes is not excluded. The growth reaction always involves a bimolecular interaction of some kind of polymer molecule which is specially reactive, for example, a free radical, and a monomer. The size to which the polymer molecule grows is determined by the relative probabilities of the growth reaction and another reaction which removes the activity of the polymer. Kinetic analysis along conventional lines has indicated so far only two types of collision whereby the activity is destroyed. The first, and by far the most common, involves the participation of two active polymer molecules, a reaction which is readily explicable if the activity is a free valency. The second is apparently a special type of collision with the monomer but of a different nature from that occurring during propagation. This is a comparatively rare type of process and so far has only been observed in the gas-phase polymerisation of acetylene and of butadiene, the chain lengths in both reactions being comparatively small. A third type of growth-stopping process has been suggested, namely, the spontaneous loss of activity by the active polymer. No experimental evidence has yet appeared which supports such a mechanism. The only case where something of the kind occurs is in the photopolymerisation of vinyl acetate vapour. In this reaction the photo-excited monomer can, in fact, lose its energy spontaneously before the molecules of monomer add on. The loss of activity does not occur once the chain has started growing (Tuckett and Melville, unpublished). The activity can also be removed by intentionally added inhibitors. Occasionally it is difficult to remove very small traces of inhibitors, and in this case it is difficult to discriminate between monomer and inhibitor termination since the concentration of the inhibitor would be proportional to the monomer concentration. Then, with regard to the generation of activity, a great variety of methods exist such as the addition of free radicals, radiation, and substances such as peroxides and diazo-compounds which are now firmly believed to give rise to free radicals on thermal decomposition. There are therefore many systems still to be explored from this point of view, for the number of possible monomers is very large and the variety of catalysts very great. This general type of exploration must go on since it is only by the discovery of suitable ideal systems from the kinetic point of view that further analysis can be attempted.

The next stage in this kind of work is to seek for some further fundamental measurements, since the primary aim of the experiments is to establish a relationship between the structure of the monomer and its ability to polymerise, this ability being expressed numerically as a bimolecular velocity coefficient. Before this can even be contemplated, the following matters have to be settled. (1) The velocity coefficients for the bimolecular growth reaction have to be determined as a function of size and of temperature, so that the energy of activation and the steric factors may be computed. (2) It has to be established whether or not the activity can be transferred to molecules of monomer thereby initiating the growth of another molecule of polymer, the original molecule of polymer losing its activity. (3) The magnitude of the velocity coefficient for the cessation of growth must likewise be determined as a function of molecular size and of temperature. It is also necessary to gain some idea of the nature of the products in this reaction. (4) The exact rate of the initiation process must be determined. (5) The precise nature of the active polymer or polymers, for there may be more than one variety, must be determined. (6) The distribution of molecular weights about the mean value must be known. These factors are enumerated on the assumptions that a reliable method exists for the determination of the number average molecular weight of the polymer, that the molecules are linear, and that means of efficient fractionation of the heterodisperse samples exist.

Exploratory investigations have revealed a system in which precise numerical answers to the above-enumerated questions may be obtained. This is the photopolymerisation of liquid vinyl acetate, which readily occurs with radiation at about 2500 A., with the production of linear polymers (for preliminary results, see Burnett and Melville, *Nature*, 1945, **156**, 661). No matter whether the polymerisation takes place in the gas phase, in the pure monomer, or in a solution of the polymer in an inert solvent, there is a very simple mathematical relationship defining the average rate of polymerisation, *viz.*,

$$\text{Rate} = k_p[\text{M}]I^{\frac{1}{2}}/k_t^{\frac{1}{2}}$$

where k_p is the average value of the bimolecular velocity coefficient for the interaction of active polymer with monomer, [M] is the monomer concentration, I the rate at which activity is induced in the monomer, and k_t the bimolecular coefficient for the reaction of the active polymer molecules leading to their destruction. There is also another simple expression, *viz.*,

$$\text{Rate} = k_p[\text{P}][\text{M}] = k_p I\tau[\text{M}]$$

where [P] is the total concentration of active polymer, which is numerically equal to its rate of production multiplied by its mean life τ to a close approximation.

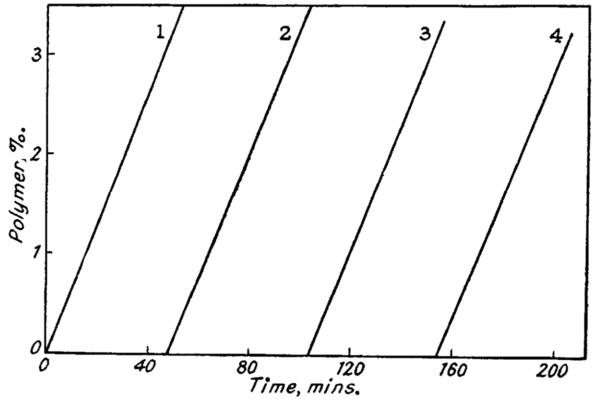
The determination of I is not easy for the following reasons. Suppose polymerisation is initiated by the decomposition of a peroxide; then it is possible to measure the rate of decomposition of the peroxide in the monomer, and from this rate we might infer that two radicals each capable of initiating growth would be produced, *e.g.*,

$$(C_6H_5{\cdot}CO{\cdot}O)_2 = C_6H_5 + C_6H_5{\cdot}CO{\cdot}O + CO_2$$

The difficulty here is to determine whether each radical so produced will, in fact, start a chain. To overcome this difficulty, some experimenters have introduced bromine atoms into the benzene ring of benzoyl peroxide and in that way have established qualitatively that the peroxide fragments enter the polymer molecule, thus enabling one to obtain the number average molecular weight of the polymer if no transfer occurs. In the gas phase, methyl radicals from photochemically decomposed acetone may likewise be employed. Acetone primarily decomposes into CH_3 and $CH_3{\cdot}CO$ and there is evidence that the $CH_3{\cdot}CO$ radical may be incorporated in the resultant polymer. At present, it would be true to say that all known catalytic substances react chemically with the monomer and thus become incorporated in the resulting polymer. There is no well-authenticated case where the catalyst induces physical activation of the double bond in the initial step in polymerisation. (It may be in some polymerisation reactions, for example, the thermal polymerisation of styrene, that primary activation in a bimolecular reaction between two monomers results in the production of an active polymer.) Therefore, in principle, by extension of these techniques, there is no barrier to our obtaining precise values of the rate of initiation.

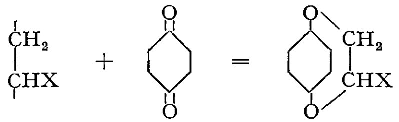
When using radiation, which is particularly convenient in other respects, matters become much more complicated. There are three possibilities : (*a*) the electrons of the double bond are raised to a higher energy level, thus giving rise to an activated monomer molecule; (*b*) a diradical is formed by the opening of the double bond, though this may be an extreme case of (*a*); (*c*) the molecule may be dissociated into fragments which themselves may be free radicals. We cannot, unfortunately, assume that each quantum of radiation activates a molecule in one or other of these modes. However, it may be noted that mechanisms (*b*) and (*c*) give rise to a free-radical growth, while (*a*) is of a completely different type, and a discrimination may be possible. Once more we must devise some specifically chemical method of detecting the number of molecules activated. This can be done by the judicious use of inhibitors. Fig. 1 shows the kind of inhibition obtained in the photopolymerisation of liquid vinyl acetate, which behaves ideally in the kinetic sense of the term. With pure vinyl acetate the plot of percentage polymerisation as a function of time is accurately linear over a considerable range. This reaction is of zero order. If a small amount of benzoquinone is added, a well-defined induction period appears, but thereafter the rate is precisely identical with that of the uninhibited reaction. Simultaneously, the faint colour of the quinone is destroyed. The induction period is accurately proportional to the amount of quinone added, and consequently we infer that each molecule of vinyl acetate photochemically activated reacts chemically with one molecule of quinone. The rate of removal of quinone therefore measures the rate at which vinyl acetate molecules are activated. The precise chemistry of this reaction is not known, but it is easy to assume that a cyclic molecule might be formed in the following way:

FIG. 1.



1. *No quinone.* 2. 0·0023 *G.*
3. 0·0050 *G.* 4. 0·0075 *G.*

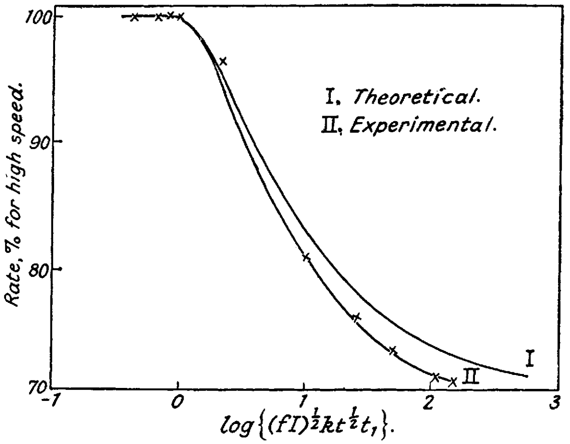
Inhibition of photopolymerisation of vinyl acetate by benzoquinone.



a scheme which would presuppose the formation of a diradical. The only assumption then made is that every molecule of acetate so activated can actually react with another ordinary molecule of acetate. This is so reasonable an assumption that it is unlikely to be wrong. In this particular case, it turns out that each quantum of radiation is effective in removing exactly one molecule of benzoquinone and therefore in activating one molecule of vinyl acetate. It is also noteworthy that one molecule of polymer is produced for each quantum absorbed. There is no question of the quinone becoming photoexcited and removing a molecule of vinyl acetate, for the extinction coefficient of the acetate is much greater than that of the quinone.

The next important problem is to determine the lifetime of the active polymer. This can only be done by utilising photochemical excitation, and therefore it renders photochemical methods particularly useful in dealing with this problem. Photochemical polymerisations are almost unique in that in a few cases, *e.g.*, methyl methacrylate and chloroprene, reaction may continue in the dark for minutes, hours, or even days after the light is switched off. In other cases, reaction is finished in a few milliseconds. The former type is extraordinarily difficult to investigate though it is of paramount interest, but unfortunately not much progress has been made towards elucidating the nature of this long-continued activity. This behaviour is not exhibited by vinyl acetate. The second class is more amenable to analysis. Here we have to measure the lifetime, *i.e.*, the time required for the polymer to grow to a specified size. This can be done in two ways : If intermittent radiation is used to irradiate the system, it is found experimentally that the rate of polymerisation depends on the frequency of flashing. Fig. 2 shows the kind of behaviour observed. An accurate mathematical analysis of the shape of the rate–frequency curve enables one to compute the mean life of the active polymer when there is steady illumination. To show the sort of agreement obtained, it is predicted theoretically that the ratio of extreme rates should be 0·707 : 1, which is what is found. The theoretically calculated curve will be seen to lie very close to the experimental curve. Values of the lifetime to within a few % may readily be obtained by this method. The flashing technique may be applied to liquid and gas-phase reactions. Another method is applicable in the gas phase. If two parallel beams of light are projected into a reaction vessel, and if means are provided for varying the distance between the beams, then the velocity of polymerisation is a function of the distance because the chain started in one beam interferes with the chain started by the other beam (Jones and Melville, *Proc. Roy. Soc.*, 1940, *A*, **175**, 392). An estimate of the time of diffusion of such molecules may be made, and consequently the mean life may be computed. Owing to optical difficulties, such a method is not nearly so accurate as the flashing technique.

FIG. 2.



Rate of polymerisation–frequency of flashing curve.

The determination of the *I* and the τ together with the rate of polymerisation under defined conditions, thus enables the all-important quantity k_p to be calculated. The first question therefore is : how does k_p vary with molecular size ? As the molecule grows, does the monomer find it more and more difficult to locate and to add on to the active end of the growing polymer ? If it does, what is due to an increase in activation energy and what is due to a change in the temperature-independent factor of the bimolecular coefficient ? So far, exact measurements have only been made for vinyl acetate polymers and the following typical results obtained :

Chain length	174	339
k_p, l. mols.$^{-1}$ sec.$^{-1}$	$7{\cdot}7 \times 10^2$	$6{\cdot}7 \times 10^2$

It will be seen that k_p only decreases very slightly when the molecular weight is doubled. Measurements have not yet been extended to low chain lengths owing to technical difficulties, but it is quite possible that there may be a greater variation during the early stages of growth. The temperature coefficient of k_p shows that the energy of activation for growth is 4·4 kcals. Values of this order have often been mentioned, but this is the first exact and unambiguous value for any reaction. This low value naturally accounts for the rapidity of polymer growth. The temperature-independent factor, 10^{-5}, is much lower than the normal value, thus implying that in every collision where energy of activation is present reaction does not necessarily occur This is not surprising in view of the fact that a small molecule has to react with a relatively small spot in a large molecule, and it is not certain in what shape the polymer molecule exists in solution. The determination of k_p, in turn, enables the magnitude of the k_t to be calculated. All the data are available and we need only quote the following results :

Chain length	174	340
k_t, l. mols.$^{-1}$ sec.$^{-1}$	$3{\cdot}1 \times 10^9$	$2{\cdot}5 \times 10^9$

The remarkable result is that k_t only decreases very slightly with increased molecular weight. Further, k_t is unaffected by temperature; therefore no activation energy is necessary for the interaction of the active polymers. Curiously enough, the steric factor is quite large, about 10^{-2}, so it would appear that the active ends of the polymer have no special difficulty in colliding and in interacting.

Though the evidence is not yet absolutely conclusive quantitatively, there are very strong grounds for believing that the active polymer in this case is a very large diradical. It is most unlikely that polymerisation would cease by interaction of the two ends of such a radical to produce a large cyclic molecule. On the other hand, it is equally unlikely that termination of growth would occur by the combination of the end of these radicals with each other, for then extremely long molecules would be produced and such a process would not result in complete destruction of activity. On the other hand, a disproportionation reaction between the ends of the active polymer, if it did occur, would mean that each diradical initially produced would ultimately form an inactive polymer, thus:

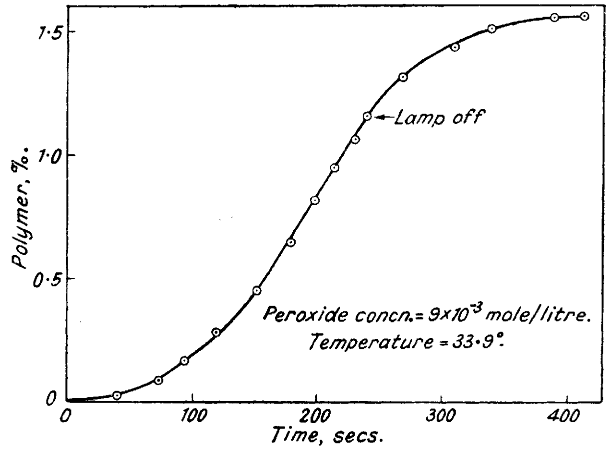
$$\begin{array}{ll} R\text{—}CH_2\text{—}CHX\text{—} & \text{—}CHX\text{—}CH_2\text{—}R \\ R\text{—}CH_2\text{—}CH_2X & HCX{=}CH\text{—}R \end{array}$$

This matter may, however, be complicated by the transfer reaction of the following type:

$$R + CH_2{=}CHX \longrightarrow R\text{—}H + \text{—}CH{=}CHX$$

In this particular event, it is evident that many polymer molecules will be produced for each monomer initially activated. With vinyl acetate this does not occur, for each quantum absorbed produces only one polymer molecule and not several such molecules. Further, each molecule of polymer corresponds exactly to one molecule of monomer initially photoactivated, and hence there is no question that the diradicals undergo disproportionation. Therefore, by a combination of the measurements of number average molecular weights and the number of monomers initially activated, it is immediately possible to detect the existence of transfer, and of other types of reaction peculiar to polymer kinetics.

FIG. 3.



Polymerisation of vinyl acetate photosensitised by benzoyl peroxide.

As has already been mentioned, it is now believed that many vinyl polymerisations proceed by the free-radical mechanism, but because there appear to exist other mechanisms whose nature is not yet established, it is absolutely essential to prove that, in a given reaction, free radicals are actually involved. Again, considering vinyl acetate, the matter can be settled in this way. With methyl methacrylate and styrene it can be shown that free radicals of the triphenylmethyl type initiate polymerisation, giving rates and molecular weights which are comparable with those obtained by the use of peroxides. A considerable amount of quite independent evidence shows that peroxides decompose thermally to free radicals; therefore it seems an inescapable conclusion that peroxide-induced polymerisation occurs by the free-radical mechanism. Similarly, it has recently been found that peroxides may be decomposed photochemically, and that photodecomposition in the presence of vinyl monomers gives rise to polymerisation having similar characteristics to the direct photochemical reaction on the one hand and to the thermal benzoyl peroxide-catalysed reaction on the other. The study of the benzoyl peroxide-photosensitised reaction is of particular interest in another connexion in addition to providing the connecting link in support of the free-radical mechanism. Fig. 3 shows the relationship between amount of polymer formed and time. There is a well-marked induction period, and when the light is switched off the reaction continues in the dark. No such behaviour is obtained in the direct photoreaction. The dark-rate curve is, however, precisely the reverse of the induction-period curve. But the induction period is not due to the presence of inhibitors, and the dark rate is not due to polymer molecules where activity persists in the dark. The whole phenomenon is due to the fact that the radicals, phenyl and benzoate, from the benzoyl peroxide do not immediately react with vinyl acetate, and that it takes quite a time to build up a stationary concentration of such radicals. Similarly, when the light is switched off the concentration of the radicals decreases slowly, fewer and fewer vinyl acetate chains being started. By an analysis of the induction-period and dark-rate curves it is possible to measure the magnitude of the bimolecular coefficient for the reaction of a free radical from benzoyl peroxide with vinyl acetate. This may be done at different temperatures, and hence the energy of activation and steric factor evaluated. These are 8·5 kcals. and 10^{-8}, respectively. It is surprising that vinyl acetate molecules can add on to a free radical of polyvinyl acetate much more readily than a phenyl or benzoate radical. Therefore, the general conclusion must be that, when such an initial process is involved in a polymerisation, it may be necessary to correct for the relative inactivity of radicals even in the presence of fairly reactive monomers. These observations thus provide a connecting link between the photo- and the peroxide-catalysed reactions and show them to be identical in mechanism. We therefore conclude that, when radiation activates vinyl acetate, a diradical is in fact produced. This is not a general conclusion, for it may be mentioned that in the vapour phase, with, *e.g.*, methyl vinyl ketone (Jones and Melville, *Proc. Roy. Soc.*, in the press), the behaviour is quite different, since this molecule is decomposed into free radicals and only the methyl radical initiates polymerisation.

The final matter relates to the distribution of molecular weights. Since all kinetic coefficients relating to the reaction are known and since no transfer occurs, it is theoretically possible to set down equations describing the rate of production of inactive polymers. If there is no simple mathematical relationship between the velocity coefficient and molecular size, it is difficult to solve these equations which define the shape of the distribution curve. To a very close approximation, however, it is possible to state that the ratio of propagation to termination coefficients is practically independent of molecular size, and hence the precise shape of the weight-distribution curve can be computed, and previous calculations confirmed. The real difficulty here is to fractionate the polymer sufficiently well to see whether the observed distribution agrees with the theoretical curve. It is easy by the usual fractional procedure to show that the general shape is all right but its precise shape cannot so easily be determined. There is in fact an urgent need for a fractionation method of some automatic kind to give really good fractionation, for this method would be invaluable in producing additional evidence in support of conclusions arrived at by kinetic methods alone.

These notes may have shown how much further kinetic analysis may be pushed when ideal enough systems can be found. There is by no means finality in this phase, for many fundamental problems have still to be tackled. Structurally, there are many stereoisomers in even simple vinyl polymers. At present there is no knowledge how reaction conditions affect structural detail. There is very little evidence to show whether environment affects velocity coefficient. Many polymers may be branched or even cross-linked, thus complicating kinetic experiments. There is no reliable information regarding the nature of the processes that give rise to chain branching. There are mechanisms leading to the formation of polymers that do not involve radicals at all, and their nature has not yet been determined nor have the kinetics been investigated in detail.

Discussion.

DR. G. B. B. M. SUTHERLAND : I should like to ask Professor Melville whether he has considered the possibility of applying spectroscopic methods to the detection and estimation of the free radicals assumed present in polymerisation of vinyl compounds ? It may be that the concentrations present or the life times are impossibly small, but it would be interesting to have the precise figures.

MR. W. COOPER : The rates of reaction of oxidation–reduction polymerisations are very fast, and the molecular weights of the products very high (B.PP. 573,366, 573,369). This leads to the suggestion that the principal influence of the reducing agent is on the mechanism of the termination reactions. Molecular oxygen, because of its unpaired electrons, can terminate growing chains (in the same way as mesomeric free radicals and inhibitors which can form semi-quinonoid free radicals; Waters, *Trans. Faraday Soc.*, 1941, **37**, 774). The ferrous reducing agent, by removing any free oxygen present and suppressing its formation from the oxidising catalyst, together with the free hydroxyl radicals of high activity formed, would produce a rapid reaction rate with formation of high polymers.

MR. J. H. BAXENDALE : From the observation that each quantum absorbed in the initiating reaction leads to one polymer molecule, Melville concludes that the terminating reaction in vinyl acetate polymerisation is a disproportionation, *viz.*,

$$—CH_2— + —CH_2—CHX— \longrightarrow —CH_3 + CH_2{=}CX—$$

However, the observed values of the velocity constant for this reaction show that it has no activation energy. It would seem unlikely that a reaction involving an atom transfer will go without activation energy, and for a reaction such as

$$H + CH_4 \longrightarrow CH_3— + H_2$$

it is found to be about 10 kcals. (Steacie, *Chem. Reviews*, 1938, **22**, 333). We should expect a value of this order (probably somewhat smaller because of the greater exothermicity) for the disproportionation. It would appear more probable that termination occurs by mutual combination of two growing polymer chains, which is apparently the case for aqueous solution polymerisation, and which requires little or no activation energy. However, such a mechanism would mean that each polymer molecule originates from two initiating radicals produced by the radiation, compared with one in the case of disproportionation. Since each quantum yields one polymer molecule, a mutual termination mechanism would imply that the photochemical initiation reaction produces two separate atoms or free radicals per quantum, instead of the proposed diradical.

PROF. H. W. MELVILLE : In reply to Dr. Sutherland's question I would say that very unfortunately the method is unlikely to be sufficiently sensitive since the concentration of the free radicals is only 10^{-8} mole/litre whereas the concentration of monomer is 10 moles/litre. Unless the radicals possessed a very high extinction coefficient indeed it would be difficult to detect their presence. Even magnetic measurements are not sensitive enough for this purpose.

Mr. Cooper's suggestion that the reducing agent in oxidation–reduction polymerisation affects the course of termination reaction is not supported by what kinetic evidence is available. Even in aqueous systems interaction of two radicals is usually the determining factor. The reason for the high velocities and high molecular weights at low temperatures is most probably the so-called "gel" effect in which the value of the termination velocity coefficient is diminished because the active free-radical ends of the polymer cannot easily meet owing to the fact that the polymer is precipitated out of the system in the act of growing.

Mr. Baxendale's suggestion that monoradicals rather than diradicals take part in the polymerisation is of course a possibility provided the two free radicals combine in the termination reaction. The facts are that one polymer molecule is produced for each quantum absorbed, and there is no evidence that the molecule of vinyl acetate is dissociated. In fact experiments with the vapour have shown clearly that the vinyl acetate molecule is activated electronically and can lose its energy by collision with helium and argon atoms. The best evidence, however, comes from the action of inhibitors. Although benzoquinone gives rise to a well-marked induction period in the direct photo-reaction, yet, when the reaction is initiated by the decomposition of benzoyl peroxide, benzoquinone acts only as a retarder. This differentiation is common also to the polymerisation of styrene and of methyl methacrylate and seems to provide a general method for discriminating between diradicals and monoradicals.

5. *Equilibrium Properties of High Polymer Solutions and Gels.*

By GEOFFREY GEE.

THE equilibrium between a polymer and liquid is of fundamental importance in a number of problems of considerable practical as well as theoretical interest. As examples may be mentioned : (1) the choice of a solvent or plasticiser for a given polymer, (2) choice of a suitable polymer for use, *e.g.*, as a gasket in contact with specified liquids, (3) the combined solvent or swelling action of mixture of liquids, (4) the effect of mechanical deformation, *e.g.*, compression, on the solvent resistance of a polymer, (5) the separation of a polymer into fractions by the use of solvent-precipitant mixtures. It must be emphasised at the outset that in some of them other factors are involved; these will not be considered in the present paper. The basic assumption is made here that, given time, a system comprising polymer and liquid will reach a steady state, and that if two condensed phases are then present, they must be in true thermodynamic equilibrium. The disturbing influence of such time-dependent processes as degradation and plastic flow may in certain practical cases prevent the attainment of a steady state, but these possibilities require separate discussion. Within the limited space available, all that can be attempted is a brief outline of the general methods which have been used, illustrated by applying them to the first two of the above problems.

Thermodynamic Formulation of the Problem.—The function which will be used in discussing polymer–liquid equilibria is the Gibbs free energy of dilution of a polymer–liquid mixture by the pure liquid. It is denoted by ΔG_0 and defined as the increase in the Gibbs free energy G when 1 mole of liquid is transferred from a reservoir of pure liquid to an infinitely large bulk of a polymer–liquid mixture. Formally, if n_0 and n_r are the numbers of moles of liquid and of polymer in the mixture, at temperature T,

$$\Delta G_0 = \left(\frac{\partial G}{\partial n_0}\right)_{n_r,\,T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Experimental measurements of ΔG_0 are based on observations of the vapour pressure p_0^m or other related properties of the mixture. If p_0^0 is the vapour pressure of the pure liquid, it may be shown (Gee and Treloar, *Trans. Faraday Soc.*, 1942, **38**, 147) that

$$\Delta G_0 = \boldsymbol{R}T \ln (p_0^m/p_0^0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The temperature dependence of ΔG_0 may be employed to calculate the heat ΔH_0 and entropy ΔS_0 of dilution; these are respectively the increases in heat content H and entropy S accompanying the transfer of liquid as defined above. Their relations to ΔG_0 are :

$$\Delta S_0 = (\partial \Delta G_0/\partial T)_{n_0,\,n_r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\Delta H_0 = \Delta G_0 + T\Delta S_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The condition for a polymer–liquid mixture to be in equilibrium with excess of liquid is simply $\Delta G_0 = 0$. If a swollen polymer is placed in contact with excess of liquid, further absorption of liquid will occur so long as the Gibbs free energy of the system is thereby decreased (ΔG_0 negative). If this is true at all concentrations of the mixture, the polymer and liquid in question will be miscible in all proportions. It is clear, therefore, that if some general expression could be found, giving ΔG_0 as a function of the composition of a polymer–liquid mixture, then equating this function to zero would give at once the composition of the mixture which would be in equilibrium with excess liquid. The next section describes some of the attempts which have been made to deduce such an expression.

The discussion so far has neglected the dispersion and solution of polymers in the liquid. This is only strictly justified in the case of polymers which are completely cross linked into a network. Linear polymers have, in principle, a finite solubility in any liquid, and in order to define an equilibrium between polymer and liquid it is necessary to specify the relative volumes of the two phases and the amount of polymer present in each. There are then two equilibrium conditions to be observed; namely, that the Gibbs free energy of the system shall be unaffected by transfer of small amounts of either liquid or polymer from one phase to the other. In practice it is found that in almost all cases in which the polymer and liquid are not miscible in all proportions, the amount of polymer present in the liquid phase is so small that the liquid is virtually indistinguishable from pure liquid. The conditions under which two phases in equilibrium may both contain appreciable concentrations of polymer are so critical that they are encountered only when a range of molecular weights is present.

The extension of this formulation to systems containing more than one type of liquid is straightforward (Gee, *ibid.*, 1944, **40**, 463, 468), and will not be discussed in detail. The two important problems are (*a*) the swelling of an insoluble polymer in mixtures, and (*b*) the fractionation of soluble polymers. In the former, differential absorption of the two liquids generally occurs, and two equations are required to define the complete composition of the swollen polymers at equilibrium. These are obtained from the conditions that the Gibbs free energy of the system must be unaffected by small transfers of either liquid from one phase to the other. The problem of fractionation is very complicated; even if the distribution of molecular weights is represented by a mixture of two only, there are four components distributed between the two phases, and therefore four conditions to be satisfied for equilibrium. These are readily written down but are too complex to be of any practical value in their complete form.

The Statistical Approach to the Problem.—It has been shown above by thermodynamic reasoning that the problem of the equilibrium between a polymer and a liquid would be solved if an expression could be found for the dependence of the free energy of dilution on composition and temperature. The deduction of such an expression in terms of molecular properties of the polymer and liquid is a problem in statistical mechanics, and several attempts have been made to solve it (Flory, *J. Chem. Physics*, 1941, **9**, 660; 1942, **10**, 51; Huggins, *ibid.*, 1941, **9**, 440; *Ann. N.Y. Acad. Sci.*, 1942, **43**, 1; *J. Physical Chem.*, 1942, **46**, 1; *Ind. Eng. Chem.*, 1943, **35**, 216; Miller, *Proc. Camb. Phil. Soc.*, 1942, **38**, 109; 1943, **39**, 54, 131; Guggenheim, *Proc. Roy. Soc.*, 1944, *A*, **183**, 203, 213; *Trans. Faraday Soc.*, 1945, **41**, 107; Orr, *ibid.*, 1944, **40**, 306, 320). The detailed description of these attempts is outside the scope of the present paper, and reference will be made only to the basic assumptions and the final results. To a first approximation the calculation of ΔG_0 may be reduced to the two independent problems of finding expressions for ΔS_0 and ΔH_0. This approximation is valid if the mixing of polymer and liquid occurs in a completely random way.

Statistical derivations of ΔS_0 depend on Boltzmann's equation relating the entropy S of a state to its thermodynamic probability W

$$S = \boldsymbol{k} \ln W \qquad . . . . (5)$$

where $\boldsymbol{k}$ is Boltzmann's constant. Considering an assembly of polymer molecules and liquid molecules, if W_1, W_2, and W_3 are the respective probabilities of the polymer molecules alone, the liquid molecules alone, and a random mixture, then by equation (5) the increase of entropy ΔS^m consequent upon mixing the components is given by

$$\Delta S^m = \boldsymbol{k} \ln \left(\frac{W_3}{W_1 W_2}\right) \qquad . . . . (6)$$

By analogy with equation (1), ΔS_0 is then defined as $(\partial \Delta S^m/\partial n_0)_{n_r, T}$. In order to compute the probabilities it is necessary to have a definite molecular model of the assembly; the one which has been used divides the space occupied by the assembly into a series of sites arranged in a regular lattice formation, defined by a fixed co-ordination number Z (*i.e.*, the number of nearest neighbours of any selected site). Each site is assumed to be capable of holding a single molecule of the liquid, and the spacing of the sites fixed by the known density of the liquid, " holes " being neglected. It is then imagined that the polymer can be divided into sections, each having the same volume as a molecule of liquid, and therefore capable of occupying a single site. The flexibility of the polymer is taken into account by supposing that a molecule of polymer can be arranged on any set of sites subject only to the restriction that adjacent sections of the polymer chain must occupy adjacent sites. The thermodynamic probability of the assembly is then obtained by computing the number of ways of arranging it on the lattice. In this way an expression will be obtained for ΔS_0 in terms of the composition of the mixture, the number of sites (x) occupied by a single molecule of polymer, and the co-ordination number Z. It is clear from the description of the model that x is equal to the ratio between the molecular volumes of the polymer and liquid, and that the natural unit of composition is the volume fraction v_r of polymer, *i.e.*, the fraction of the total volume occupied by polymer.

The enumeration of the configurations of a polymer presents difficulties, arising from the necessity to exclude impossible arrangements in which two sections of a chain occupy the same site. Considering the process of adding a polymer molecule, section by section, to a partly filled lattice, the difficulty arises in estimating the probable number of sites available for the i'th section. The $(i - 1)$'th section is supposed to be in place; of its Z neighbouring sites one must be occupied by the $(i - 2)$'th section, but the probable number of the remaining $(Z - 1)$ which are vacant will clearly depend both on i and on the fraction of the total space which has already been filled. Flory (*loc. cit.*) neglected the dependence on i, and obtained the final result in a remarkably simple form :

$$\Delta S_0 = - \boldsymbol{R}\{\ln (1 - v_r) + v_r (1 - 1/x)\} \qquad . . . . (7)$$

ΔS_0 is seen to be independent of Z, while the dependence on x is only important when v_r is small enough to be comparable with $1/x$. Huggins (*loc. cit.*) attempted a partial correction for the dependence on i, and obtained finally

$$\Delta S_0 = - \boldsymbol{R}\left\{\ln (1 - v_r) - \tfrac{1}{2}Z' (1 - 1/x) \ln \left(1 - \frac{2v_r}{Z'}\right)\right\} \qquad . . . . . (8)$$

where Z' is nearly identical with Z. Miller (*loc. cit.*), by a different method of computation which will not be described here, obtained the very similar result

$$\Delta S_0 = -\boldsymbol{R}\left[\ln(1 - v_r) - \tfrac{1}{2}Z\ln\left\{1 - \frac{2v_r}{Z}(1 - 1/x)\right\}\right] \quad . \ . \ . \ . \ . \quad (9)$$

It will be seen that Flory's result is identical with the asymptotic limit of (8) or (9) for large values of Z.

The heat of dilution has its origin in the exchange of partners between polymer and liquid during mixing. The transfer of a molecule of liquid from liquid to polymer may be imagined to take place in three steps, involving (1) evaporation of a molecule of liquid, (2) separation of the polymer chains so as to form a hole into which (3) the molecule of liquid is condensed. The first two steps require an absorption of energy in overcoming the cohesive forces of the liquid and the polymer; in the third, energy is recovered, and the heat of dilution is the algebraic sum of the three. A complete theory should predict the form of dependence of ΔH_0 on composition, and relate its magnitude to those of the intermolecular forces. The problem is very similar to that of calculating the heat of dilution ΔH_1 of a mixture of two liquids (1 and 2) by liquid 1; this has been discussed by van Laar (*Z. physikal. Chem.*, 1928, *A*, **137**, 421), Hildebrand (" Solubility," Reinhold, N.Y., 1936), Scatchard (*Chem. Reviews*, 1931, **1**, 321), and others. For random mixing of liquids it is easily shown that ΔH_1 should be proportional to the square of the concentration of species 2, but it is not at once clear in what units the concentration should be expressed. If the number of contacts is taken to be the important factor, then concentrations should be in mole fractions; if the effective surface of contact is the determining factor, volume fractions will be more appropriate. Experimental evidence (Hildebrand, *op. cit.*) is strongly in favour of the latter, and in most treatments of polymer solutions, it has been assumed that the same relation would apply, *i.e.*,

$$\Delta H_0 = \alpha v_r^2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (10)$$

where α is a constant. Although this type of expression will be used below, it must be pointed out that it is not strictly consistent with the model used in calculating ΔS_0. This would relate the heat of dilution to the number of polymer–liquid contacts, and (10) should be replaced by

$$\Delta H_0 = \alpha'\left\{\frac{qv_r}{1 + (q - 1)v_r}\right\}^2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (11)$$

where

$$q = 1 - \frac{2}{Z} - \frac{2}{xZ} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (12)$$

Equations (10) and (11) are only identical in form in the physically meaningless case of $Z = \infty$.

In order to complete the calculation of ΔH_0 it is necessary to find an expression for α (or α'), and the only suggestion which has been made (Gee, *Trans. Faraday Soc.*, 1942, **38**, 418) is to use the method applied by Hildebrand to liquid mixtures. The energy required to separate all the molecules in 1 c.c. of the liquid is the cohesive energy density of the liquid (E_{00}) given by

$$E_{00} = (L_0 - \boldsymbol{R}T)/V_0 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (13)$$

where L_0 is the molar latent heat of evaporation and V_0 the molar volume. Although equation (13) cannot be applied to the polymer, it is perfectly logical to speak of its cohesive energy E_{rr}, to be estimated as described below. It is still necessary to know how the energy of a polymer–liquid contact is related to those of liquid–liquid and polymer–polymer contacts. The assumption of a geometric mean is likely to be valid when the forces involved are purely dispersion forces, and leads to the result

$$\alpha = V_0(\sqrt{E_{00}} - \sqrt{E_{rr}})^2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (14)$$

Experimental evidence as to the usefulness of this relationship will be given in a later section.

The simplest equation which can be obtained for the free energy of dilution results from combining equations (4), (7), and (10), to give

$$\Delta G_0 = \boldsymbol{R}T\left\{\ln(1 - v_r) + v_r(1 - 1/x) + \frac{\alpha}{\boldsymbol{R}T}v_r^2\right\} \quad . \ . \ . \ . \ . \ . \quad (15)$$

If equation (8) or (9) were used in place of (7) the final result would be almost identical, except that $\alpha/\boldsymbol{R}T$ would be replaced by

$$\mu = \mu_0 + \alpha/\boldsymbol{R}T \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (16)$$

where μ_0 is a function of Z but is nearly independent of v_r. This is the general form of the free-energy equation as deduced by the approximate method outlined. For convenience it may be written in two approximate forms

(*a*) for dilute solution,

$$-\Delta G_0 = \boldsymbol{R}T\left\{\frac{v_r}{x} + (\tfrac{1}{2} - \mu)\, v_r^{2}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

(*b*) at higher concentrations ($v_r > 0{\cdot}1$)

$$\Delta G_0 = \boldsymbol{R}T\{\ln\,(1 - v_r) + v_r + \mu v_r^{2}\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

So far it has been assumed that the mixture is completely random, but it is clear that, unless the heat of dilution is zero, some configurations will be energetically favoured, and should accordingly be weighted in computing the configurations of the system. This has been done in different ways by Orr and by Guggenheim (*locc. cit.*), but the detailed results will not be quoted. The general conclusion is that a positive heat of dilution ($\Delta H_0 > 0$) results in non-random mixing which increases ΔS_0 at low v_r and decreases it at high v_r. The effect, however, is very small, even when the heat of dilution is large, and seems unlikely to be important compared with the assumptions and approximations inherent in the method.

All methods of calculation used hitherto break down seriously for solutions sufficiently dilute for the polymer molecules to be individually dispersed, with relatively little overlap. In this region it is evident that, although the fraction of sites occupied by polymer is small, there will be a relatively high probability of finding an occupied site adjacent to any selected site known to be occupied. In other words, the assembly may more properly be thought of as a dispersion of regions of fairly high concentration in a medium which elsewhere is pure liquid. This conclusion may be put in another way by saying that in an infinitely dilute solution there will still be a fairly large number of points at which sections of a polymer chain occupy adjacent sites. According to the method of calculation described above, in an infinitely dilute solution there would be no polymer–polymer contacts. The present theory of dilute solutions is therefore definitely wrong, and two attempts to provide a new treatment may be mentioned. (*a*) Orr (*Trans. Faraday Soc.*, in the press) has considered the arrangement of a single chain on a lattice, and has made tentative estimates of the number of polymer–polymer contacts to be expected, as a function of the heat of mixing. (*b*) Flory (*J. Chem. Physics*, 1945, **13**, 453) has used the experimentally observed viscosity to make a rough estimate of the number of sites enclosed within the " envelope " of a single polymer molecule which, in the examples he quotes, is of the order of $50x$. On this basis he has estimated that the quadratic term in the expansion for ΔS_0 may be several times smaller than that given by equation (17). There is no doubt of the reality of this discrepancy, but its quantitative treatment by purely statistical methods has not yet been accomplished.

One other factor which must be mentioned is the effect of cross linking of the polymer. So far the polymer has been assumed linear, and it is clear that the introduction of cross links between different polymer chains will reduce the number of configurations of the system, and therefore diminish ΔS_0. It is not proposed to describe here how this effect on ΔS_0 has been calculated; the result obtained (Flory and Rehner, *ibid.*, 1943, **11**, 521) is

$$\Delta S_0 = -\frac{\boldsymbol{R}\rho_r V_0}{M_c}\, v_r^{-\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

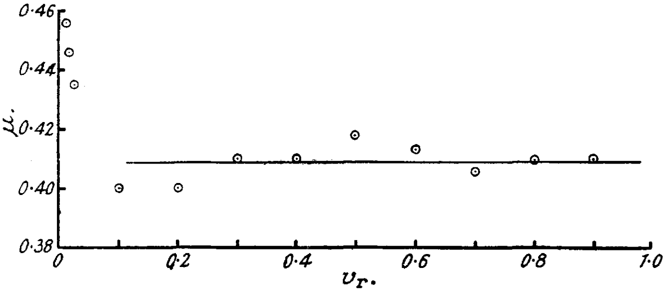
where ρ_r is the density of the polymer, and M_c the " molecular weight " of the portion of the polymer between adjacent junction points. The free energy of dilution of a cross-linked polymer is therefore given by

$$\Delta G_0 = \boldsymbol{R}T\left\{\ln\,(1 - v_r) + v_r + \mu v_r^{2} + \frac{\rho_r V_0}{M_c}\, v_r^{-\frac{1}{3}}\right\} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The last term is always positive and tends to infinity as $v_r \longrightarrow 0$; it therefore gives a formal representation of the fact that the amount of any liquid which can be imbibed by a cross-linked polymer is finite.

Experimental Determination of the Free Energy of Dilution.—The theory outlined in the previous section leads to the conclusion that the driving force responsible for the imbibition of liquids by polymers is the large increase of entropy thereby produced; this increase has been estimated quantitatively. The controlling factor in determining the free energy of dilution in various systems is, on this view, the heat of dilution, and the form and approximate magnitude of this have also been estimated. There is at present a great lack of precise data by which these conclusions may be tested. Rough vapour-pressure data for a number of polymer–liquid systems give reasonably accurate values of ΔG_0 [by equation (2)] but in very few cases is even the sign of the heat of dilution known with certainty. There is, however, abundant evidence that aqueous systems in general are not covered by the theory as developed, since for these ΔH_0 and ΔS_0 are both usually negative (Katz, *Ergeb. exakt. Naturwiss.*, 1924, **3**, 316; Urquhart and Williams, *J. Text. Inst.*, 1924, **15**, 559; Fricke and Lüke, *Z. Elektrochem.*, 1930, **36**, 309). This discrepancy undoubtedly arises from the attachment of the water molecules to the polymer by hydrogen bonds, thus giving the swollen polymer a relatively high degree of order. It is clear that effects of this nature become increasingly probable as the system considered becomes more polar, and that the theory which has been developed can only be expected to hold for relatively non-polar materials. In the following discussion, aqueous systems will therefore be ignored. It must also be pointed out that volume changes accompanying swelling have been implicitly neglected. Where these occur they will make quite large contributions to both the heat and the entropy of dilution, but always in the same direction, leaving the free energy approximately that to be expected if the volume had remained constant. Thus, *e.g.*, the

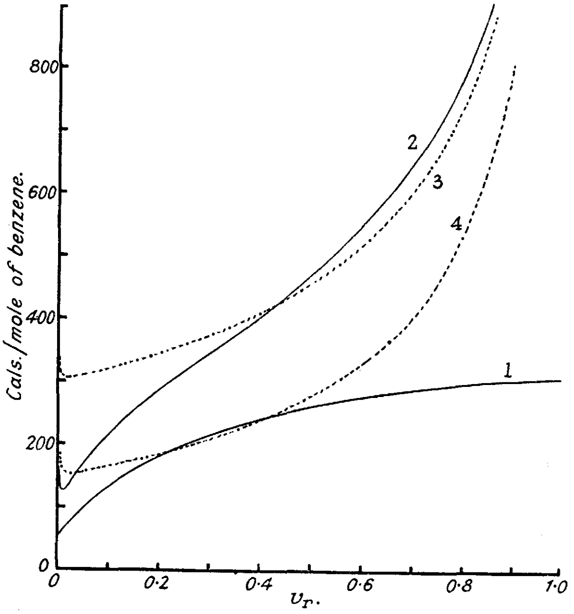
FIG. 1.



Free energy of dilution : natural rubber + benzene.

$$\mu = \frac{1}{v_r^2}\left\{\frac{\Delta G_0}{RT} - \ln(1 - v_r) - v_r\left(1 - \frac{1}{x}\right)\right\}.$$

FIG. 2.



Thermodynamic data for natural rubber and benzene.

Curve 1 : $\Delta H_0/v_r^2$. *Curve* 3 : $T\Delta S_0/v_r^2$, *theoretical* ($z = \infty$

Curve 2 : $T\Delta S_0/v_r^2$. *Curve* 4 : $T\Delta S_0/v_r^2$, *theoretical* ($z = 4$).

swelling of natural rubber in *n*-pentane is accompanied by a considerable contraction, and in consequence both ΔH_0 and ΔS_0 must be much lower than would otherwise have been the case (Gee, unpublished).

By far the most complete data available are those for natural rubber and benzene, which cover practically the whole range of composition at different temperatures (Gee and Treloar, *loc. cit.*; Gee and Orr, *Trans. Faraday Soc.*, 1946, **42**, 507). The free energy of dilution is therefore known accurately from $v_r = 0{\cdot}005$ to $0{\cdot}999$, and the heat and entropy of dilution approximately. The results are summarised in Figs. 1 and 2; the former shows how accurately equations (17) and (18) describe the data, with a single value of μ. Despite this striking success, Fig. 2 reveals that $\Delta H_0/v_r^2$ is far from being constant, while $T\Delta S_0/v_r^2$ shows corresponding deviations from the predicted form. The data for the heat of dilution cannot be represented by equation (11), the dependence of $\Delta H_0/v_r^2$ on v_r being different in form from that to be expected from this equation. Furthermore, the heat of dilution of squalene, which contains 6 isoprene units, by benzene (Ferry, Gee, and Treloar, *ibid.*, 1945, **41**, 340) is in good accord with equation (10). These deviations are therefore believed to arise from the failure of the theory to allow correctly for intramolecular polymer–polymer contacts. This defect in the theory of dilute solutions has already been discussed; the experimental data suggest that the effect extends to quite high concentrations. It is found that the data can be understood by supposing that in an infinitely dilute solution of natural rubber in benzene some 23% of the contacts made by sections of the rubber chain are intramolecular. The constancy of μ means that the low heat of dilution is balanced by a correspondingly low entropy of dilution, leaving ΔG_0 almost equal to the theoretical value.

Data for other polymer–liquid systems are for the most part confined to a single temperature, or of insufficient accuracy to justify the calculation of ΔS_0 from equation (3). Huggins (*loc. cit.*) has shown that the bulk of such data can be satisfactorily represented by equations (17) and (18) with constant μ. The results for non-solvents which are very poor swelling agents show small deviations. For instance, for natural rubber + acetone at 35° Lens's data (*Rec. Trav. chim.*, 1932, **51**, 971) require a variation of μ from $1{\cdot}5$ at $v_r = 1$ to $1{\cdot}3$ at $v_r = 0{\cdot}75$ (the limit of imbibition). Similarly (Ferry, Gee, and Treloar, *loc. cit.*), for natural rubber + methyl alcohol at 30° μ diminishes from 4·7 to 3·6 during the absorption of 2·5% of alcohol, while $\Delta H_0/v_r^2$ falls by a factor of at least 10.

Perhaps the most striking success of the theory lies in giving so accurately the absolute magnitude of the entropy of dilution. Although Fig. 2 reveals errors in the form of the ΔS_0–v_r curve, it shows that ΔS_0 has been calculated correctly within a factor of 2. When it is recalled that the theories current before the modern statistical treatment gave values of ΔS_0 too small by a factor of 1000, it is evident that a very great advance has been made.

These limited tests of the validity of the fundamental statistical results are sufficiently successful to warrant the use of the theory in discussing equilibrium properties of polymer solutions and gels; two examples are given in the next section.

(a) *Oil-resisting Rubbers.* (b) *Solvents and Plasticisers for Polymers.*—The greater resistance of certain synthetic rubbers to hydrocarbons such as petrol, as compared with natural rubber, has led to their being termed "oil-resisting". This description is a complete misnomer, since these rubbers differ from natural rubber only in being resistant to a different class of liquid. The general problem is to find a polymer which is relatively unaffected by a specified liquid or liquids. The problem of selecting a solvent or plasticiser for a given polymer is the exact converse and the two can be discussed together. It will be assumed that a plasticiser is simply a liquid of low vapour pressure which is readily compatible with the polymer.

It has been shown that the behaviour of a polymer–liquid system can be characterised by a single constant μ. Now the thermodynamic condition for a polymer to be resistant to a liquid is that ΔG_0 shall be zero at a fairly large value of v_r. Inspection of equation (18) shows that this will be the case when μ is large; the controlling effect of μ is illustrated by Fig. 3 in which $\Delta G_0/Tv_r^2$ is plotted against the degree of swelling Q ($= 1/v_r - 1$) for various values of μ. If μ is small, the liquid is a solvent or a good swelling agent; as μ increases, the maximum swelling decreases rapidly. It is clear, therefore, that in order to be able to choose a plasticiser for a given polymer, or a polymer to be used in contact with a specified liquid, it is necessary to find what physical properties of the polymer and liquid determine the magnitude of μ. Equations (14) and (16) give the basis of the answer to this problem; combining them, we have

$$\mu = \mu_0 + \frac{V_0}{RT}(\sqrt{E_{00}} - \sqrt{E_{rr}})^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

μ_0 will in general be small ($< 0{\cdot}5$), so that the magnitude of μ will be determined essentially by the difference between the cohesive energy densities of the liquid and the polymer. Equation

FIG. 3.

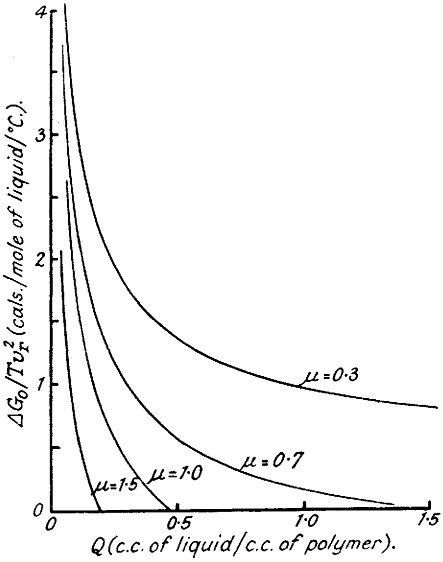
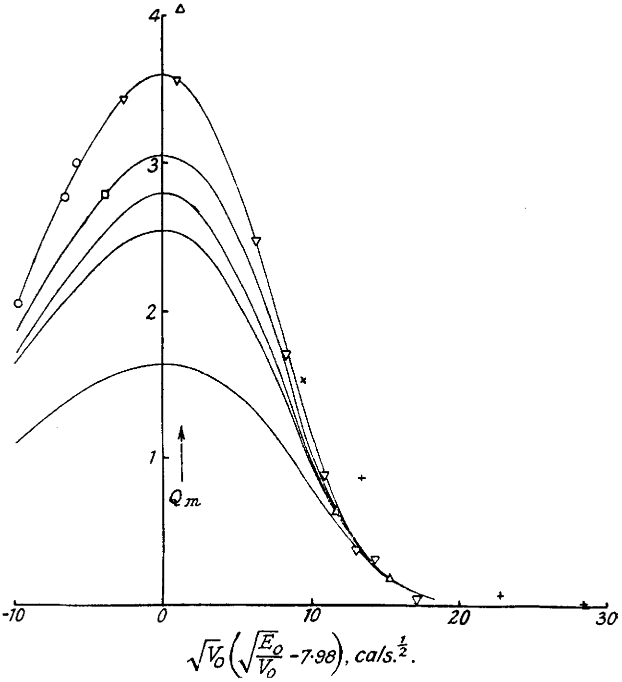


FIG. 4.

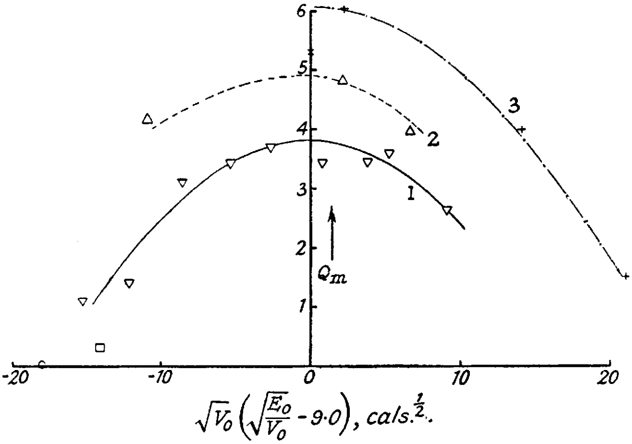


Swelling of five natural rubber vulcanisates in a range of aliphatic liquids.
Points (*top curve only*) : ○ *Hydrocarbons,* □ *Ethers,* ▽ *Esters,* △ *Ketones,* × *Aldehydes,* + *Nitriles.*

(21) is not found to be quantitatively valid; values of μ calculated by its aid are generally too small, but it has been used with considerable success in the following qualitative manner. Consider the swelling or solution of a given polymer in a range of liquids, arranged in order of

increasing cohesive energy density. Equation (21) requires that μ should be large for the liquids of lowest E_{00}, pass through a minimum for the liquids having $E_{00} \sim E_{rr}$, and then increase again. Corresponding with these changes of μ, the liquids having greatest solvent or swelling power should be found at that point of the range where $E_{00} \sim E_{rr}$. In general, E_{rr} is not known, although it can be estimated approximately from the chemical nature of the polymer. A quantitative estimate may be made by using a cross-linked polymer, finding the liquid having the greatest swelling power, and then assuming its cohesive energy density to be equal to that of the polymer.* Given E_{rr}, a plot of the maximum swelling Q_m in this range of liquids against $(\sqrt{v_0})(\sqrt{E_{00}} - \sqrt{E_{rr}})$ should, according to equation (21), give a smooth curve, on which liquids of different chemical type should all fall. This in general is not quite true, but it holds surprisingly well for the swelling of natural rubber vulcanisates in a wide range of aliphatic liquids (Gee, *Trans. Inst. Rubber Ind.*, 1943, **18**, 266), as is shown in Fig. 4. The five curves are for very different compounds, and it is clear that there is no essential difference between their swelling behaviour. Aromatic liquids have in general a greater swelling power than aliphatic, for a given value of the abscissa (Gee, *loc. cit.*, 1942). With some of the more polar synthetic rubbers, different groups of aliphatic liquids do not fall on the same curve, although as illustrated in Fig. 5 the positions of the maxima usually agree. In order to fit the data quantitatively it is therefore necessary to generalise equation (21) empirically to the form

FIG. 5.



Swelling of a thiokol RD *vulcanisate in a range of aliphatic liquids.*
Curve 1 : *Esters.* *Curve* 2 : *Ketones.* *Curve* 3 : *Nitriles.*

$$\mu = \mu_0 + \beta \frac{V_0}{RT} (\sqrt{E_{00}} - \sqrt{E_{rr}})^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where μ_0 and β may be somewhat dependent on the chemical natures of the liquid and the polymer. This limitation is not sufficient seriously to diminish the usefulness of this method of approach to the converse problems of selecting (*a*) polymers having solvent resistance and (*b*) solvents and plasticisers.

Conclusions.—In this brief survey, an attempt has been made to outline the statistical thermodynamic approach to the equilibrium properties of polymer solutions. It is clear that current theories, although crude, do give a surprisingly accurate quantitative account of the free energy of dilution. The separate calculations of the heat and entropy of dilution are less satisfactory, particularly in the region of dilute solutions, where a new statistical approach appears to be required. A more adequate statistical treatment of polymer–liquid systems, in which the heat of dilution is large or in which considerable volume changes occur, will almost certainly have to await advances in the understanding of the liquid state. Notwithstanding these limitations, the theory in its present form is capable of giving a semi-quantitative answer to a number of practical problems. One of these has been discussed above; a similar order of agreement between theory and experiment can be obtained in the other problems listed in the introduction.

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* This process can be refined by using a graphical method of finding the maximum of the swelling–E_{00} curve (Gee, *loc. cit.*, 1943).

6. *The Study of Macromolecules by Infra-red Spectroscopy.*

By H. W. Thompson.

I can do no more today than mention some of the principles underlying the application of infra-red spectroscopy to the study of macromolecules, and give a few examples to illustrate them. In recent years a survey has been made of the spectra of many classes of substance in order to discover the kind of information which they may give (*J.*, 1944, 1833; Torkington and Thompson, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3, 21; *Trans. Faraday Soc.*, 1945, **41**, 246). We have now reached a stage when more detailed work on particular aspects may be more profitable.

There is now no sharp boundary between the infra-red region and that of ultra-short radio, or micro-waves, and I ought to mention that very significant information about the properties of rubbers and plastics is now being obtained from work in the latter region. We are, however, mainly concerned today with the region of wave-length 1—25 μ, which is most easily explored experimentally. In this range the absorbed energy excites molecular vibrations, which may range in value from 50 to 3600 cm.$^{-1}$. However, the changes of molecular dipole moment associated with the different vibrations will vary considerably, and in consequence some vibrations are strongly excited in the infra-red, others more weakly, and some so feebly as to escape detection. Also, with complex molecules built up from recurring groups, there is often a grouping of some of the frequencies around particular values. These factors lead to a simplification of the spectrum as a whole, and while the spectra of many macromolecules remain complex and not fully interpretable in terms of a vibrational assignment, others are even simpler in general appearance than the spectra of those containing only half a dozen atoms.

Recent progress with complicated molecules has been due to two causes. First, recording spectrometers are now available with which a wide spectral range can be measured rapidly (Sutherland and Thompson, *ibid.*, p. 174; Wright, *Ind. Eng. Chem. Anal.*, 1941, **13**, 1; Barnes, Williams, and Liddel, *ibid.*, 1943, **15**, 83, 659; Barnes, McDonald, Williams, and Kinnaird, *J. Appl. Physics*, 1945, **16**, 77; Roess and Dacus, *Rev. Sci. Instr.*, 1945, **16**, 164; Whiffen and Thompson, *J.*, 1945, 268), and the technique of handling solid films and insoluble powders has been much improved. Secondly, much more is now known on the theoretical side about the correlation of vibration bands with particular types of vibration of the different nuclear skeletons. Ideally, greater progress would be made with these correlations if it were possible to treat the vibrations of complex molecules mathematically as mechanical models or lattices subject to harmonic oscillations. Although some attempts have been made in this direction, little has yet been achieved, as might be expected in view of the complicated inter- and intra-molecular interactions. We must therefore proceed at present by an essentially empirical method, in which the correlation of frequencies with structure is based upon comparisons of the spectra of related series of molecules (see, *e.g.*, *Proc. Roy. Soc.*, 1945, *A*, **184**, 3; *J.*, 1944, 303, 597; 1945, 640).

The use of the infra-red spectra is essentially analytical, and is governed by two main considerations. Since the molecular vibration frequencies are determined in magnitude by the nuclear masses and the interatomic forces, any molecule will have a characteristic set of frequencies, differing in principle at least from the set for any other molecule except an optical enantiomorph. In practice, of course, with two molecules of great complexity and close similarity, the difference in the vibrational spectra may be slight, and require more elaborate methods—higher resolving power—for detection. The second consideration is that, although a molecule vibrates as a whole, a favourable conjunction of circumstances may lead to the result that in some of the vibrations certain linkages or groupings effectively control the oscillation, so that the frequencies characteristic of a group may appear almost unchanged in all molecules containing it. For example, linkages involving hydrogen such as C–H, O–H, N–H, S–H or Si–H each have an almost constant frequency; the same is true of double bonds such as C:C, C:O, or C:N, while groups such as the acetyl or *tert.*-butyl radical or the ether linkage C–O–C also give rise to almost constant sets of frequencies. The greater precision of recent measurements has made it possible, moreover, to infer from the small variations in the frequency of certain groups the exact nature of the other groups attached to them.

The applications of these principles can be classified roughly as follows: (i) the measurement of the rate and mechanism of polymerisation reactions, (ii) the elucidation of the structure of molecules of a polymer or other macromolecule, (iii) the derivation of facts likely to bear upon the order or arrangement of the macromolecules in a given state of aggregation, (iv) the study of changes brought about by special treatment of a macromolecule affecting its physical or chemical behaviour, (v) the general analysis of mixtures of macromolecules, or other analytical problems which are less easily tackled by other methods. This analysis can be either empirical, or based upon a theoretical background of one sort or another.

The rate of polymerisation of an unsaturated molecule such as styrene, *iso*butylene, methyl acrylate, or the condensation of butadiene with a vinyl derivative can be followed either by measuring the rate of disappearance of the vibration band due to the unsaturated C:C bond, or of the appearance of some band due to the polymer (Barnes, Williams, and Liddel, *loc. cit.*, p. 659). The unsaturated link gives rise to a band in the region of 1650 cm.$^{-1}$, but if a band of the product is to be used it must of course be chosen, after measuring the spectra of starting materials and product, so as to be as distinct as possible. In the past, the procedure has been to remove samples of the reacting mixture at stages of the reaction, and then measure their spectrum over the required spectral range, using standard experimental conditions. Two other methods of analysis now promise to revolutionise the whole method. In one, an infra-red analyser is used, comprising a system of differential filters by means of which some fairly narrow selected spectral range of radiation is passed through the material and the transmitted energy is recorded continuously (Luft, *Z. techn. Physik*, 1943, **5**, 97).* This obviates the use of a spectrometer, and provides a robust, subtle instrument of wide applicability, particularly in gas analysis. It seems possible that fairly soon the use of such apparatus will make the automatic control of flow lines possible. The other development is the use of extremely rapid infra-red detectors with a spectrometer in which the prism is rotated rapidly, and a trace of the spectrum obtained on the screen of a cathode-ray tube. By this means the spectrum is scanned very rapidly, and part of it can be watched continuously. Such an instrument was first developed by Baker and Robb (*Rev. Sci. Instr.*, 1943, **14**, 362), and an improved model has now been described by Daly and Sutherland (*Nature*, 1946, **157**, 547). We are building another instrument of this kind in my laboratory (*ibid.*, 1946, **158**, 196).

The spectrum of the reaction mixture or product may also indicate the mechanism of the reaction. In the condensation of butadiene, for example, either 1 : 4- or 1 : 2-addition can occur, leading respectively to a skeleton of the type R_1·CH:CH·R_2, and to pendent vinyl groups (–CH:CH_2). Criteria are now available for differentiating the various kinds of olefinic linkage (*Proc. Roy. Soc.*, 1945, *A*, **184**, 3), so that the relative proportions of the two types can be estimated. This method can be applied in the same way to condensation of butadiene with styrene or acrylonitrile, or the polymerisation of other dienes such as isoprene. It has served very well to indicate the different proportions of 1 : 2- and 1 : 4-addition in the polymerisation of butadiene by different methods, for example, with sodium, potassium, or by emulsion polymerisation; and in many cases seems a quicker and more reliable guide than chemical methods such as ozonolysis. There are still some outstanding difficulties in making it more accurate, such as the problem of obtaining films of known and uniform thickness, and the more fundamental question of whether the extinction coefficients of the key bands for the different types of nuclear skeleton remain sufficiently constant in different molecules. A similar instance in which the spectrum reveals the course of polymerisation is the detection of polystyrene in some samples of a copolymer of butadiene with styrene.

The presence in a macromolecule of unexpected groups can also be revealed by the spectrum. For example, methyl groups in polythene are shown by characteristic bands near 3·4 μ and 7·2 μ, and their number can be estimated from the intensities of the key bands. Similarly, C:O and C:C linkages can be found when present in small amount. Fig. 1 shows diagrammatically the spectra of four hydrocarbon waxes made in different ways, and almost indistinguisable chemically though differing in physical properties. All the samples show the main features of a long-chain paraffinic hydrocarbon with some side chains. In addition, however, *B* shows bands in the region 850—1000 cm.$^{-1}$ due to the deformational vibrations of different types of olefinic skeleton, *D* has well-marked bands at about 1165 and 1720 cm.$^{-1}$, indicating carbonyl (probably CH_3·CO) groups, and *A* shows many bands suggesting both ketonic and aromatic groupings. The variation of intensity of the bands at about 1640 and 1720 cm.$^{-1}$, which indicate C:C and C:O groups respectively, is important. It becomes clear that small differences in the methods of preparation can thus be revealed, which may have an important bearing not only upon the value of the products but also on an understanding of the reactions involved. For example, it seems possible to correlate the dielectric loss factor of such materials with the content of the particular polar groups. It may also be noted that a quantitative determination of groups such as C:O and C:C can be made

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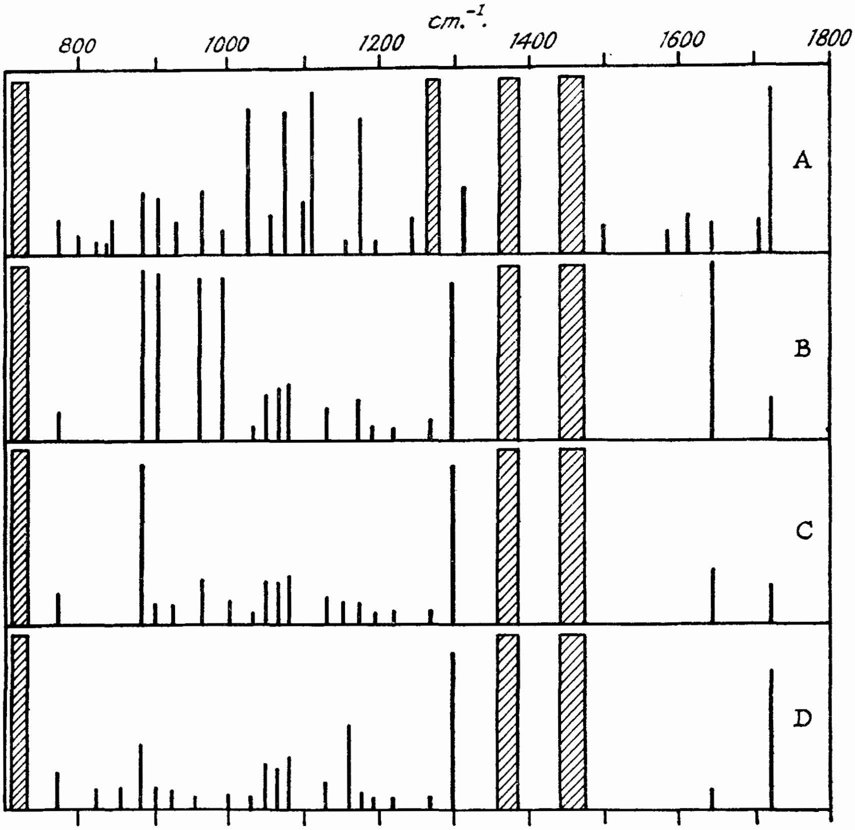
* British and American instruments of this kind will be described shortly.

from the measured intensities, down to very small concentrations. Oxygen of a carbonyl group embedded in a hydrocarbon such as polythene can be determined down to 0·01% or less, but naturally such high sensitivity will only apply in the most favourable cases where the intrinsic extinction coefficient of the important band far exceeds those of the other vibration bands of the molecule, or when the particular band being examined lies in a region where overlap by other bands is very small and thicker layers of material can be used without obscuring the issue.

A natural question is whether the spectrum affords any direct clue to the molecular weight of a polymer. As regards the arrangement—positional frequencies—of the bands, it does not. Thus, while some small changes occur in the position of bands of lower normal paraffinic hydrocarbons as the chain length increases, with more than about ten carbon atoms the spectrum is hardly affected. The same has been found with poly*iso*butenes of molecular weight between 1000 and 100,000, and with other polymers built up from a recurring skeleton. On the other hand, a careful examination of the intensities of bands, as opposed to the frequencies, and the determination of end groups, may lead to estimates of the chain length in some cases. We thus encounter again the new aspect of infra-red work, namely, the accurate measurements of intensities. Some exploratory work which Mr. Mann and I have been doing suggests that in normal paraffins the intensity of the band at about 725 cm.$^{-1}$ is determined by the length of the hydrocarbon chain. Such relationships may be very useful.

FIG. 1.

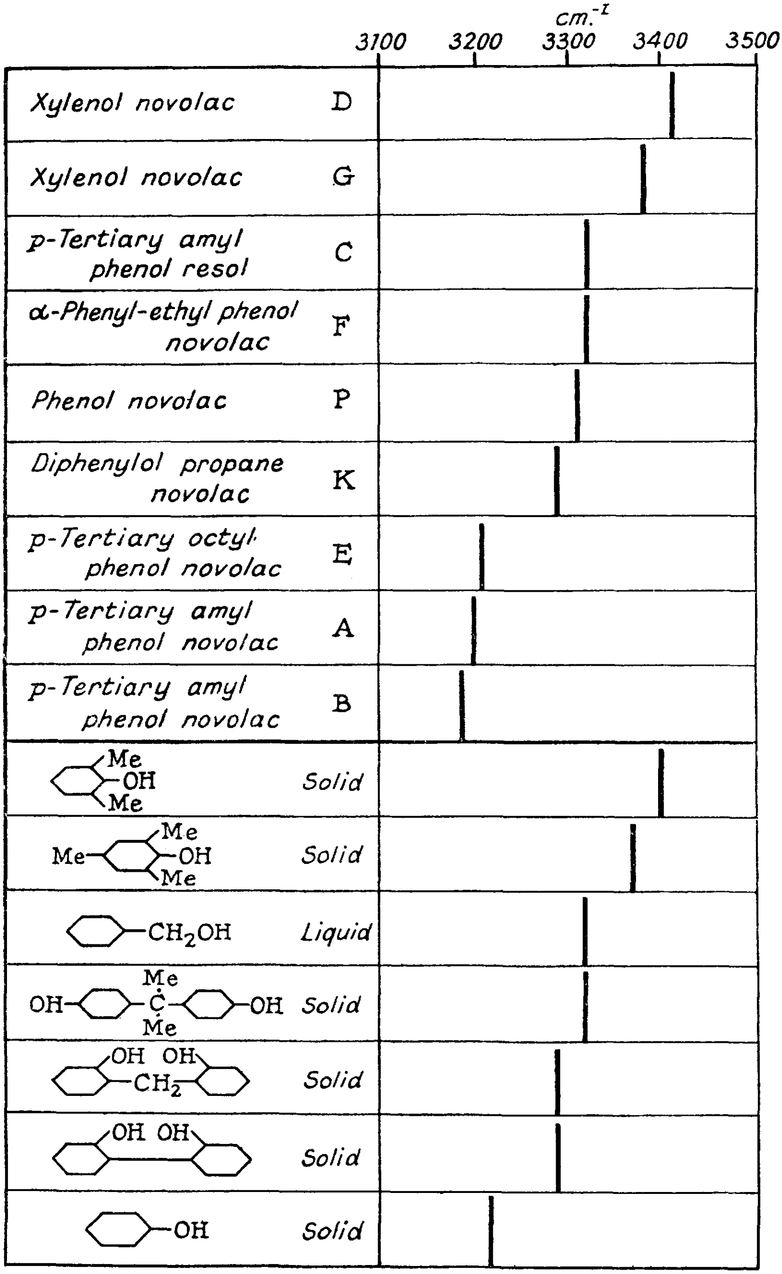


Hydrocarbon waxes.

Another similar problem is the determination of the disposition of particular side-chain groups in a long molecular chain. It has been found, for example, that the spectra of polyvinyl chloride and polyvinylidene chloride differ from those of halothene (chlorinated polythene) having the same percentage of chlorine, and this must be interpreted as being due to a different arrangement of the chlorine atoms along the carbon skeleton in the different cases (*Trans.*

Faraday Soc., 1945, **41**, 255). The spectra of simple chloro-paraffins suggest that it may be possible to obtain correlations for the detection of $-CHCl-$ or $-CCl_2-$ groupings, and the frequencies of C–H bonds are also affected by the proximity of halogen atoms. Also, the presence in a skeleton of a chain of four or more carbon atoms may be revealed by the band at about 725 cm.$^{-1}$. By such diagnostic methods, as well as by measurements of the intensities of bands, it is worth tackling the problem just indicated. The same applies to the determination of the number and position of hydroxyl groups in an interpolymer of ethylene with vinyl alcohol.

FIG. 2.



OH *Association band.*

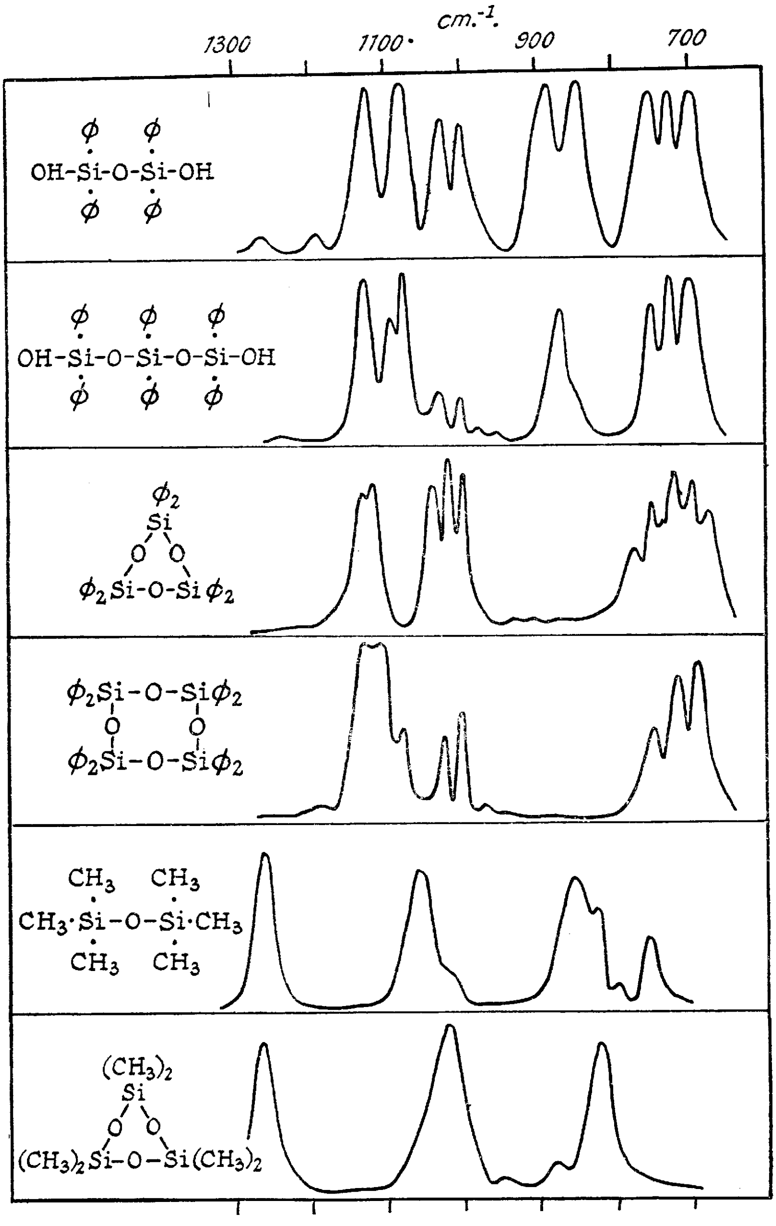
I will refer briefly to some other points which arise with other kinds of macromolecules. A number of condensates of phenols with aldehydes have been examined. There are noticeable differences between the spectra of novolacs made from formaldehyde and differently substituted phenols, which are in part due to the different substituents on the aromatic nuclei but may also arise from differences in the method of condensation. The spectra of a resin on the one hand, or resol on the other, made from a given phenol and formaldehyde, show differences which can to some extent be correlated with differences in structure, and another rough correlation rule has been found for finding the positions through which the aromatic nuclei are linked together (*ibid.*, p. 258). Some small changes have also been found between the spectra of one- and two-stage resins, and between the " fusible " and " infusible " varieties. Although some of the differences can be interpreted in terms of structure, many must at present be used empirically. One unexpected feature promises to be specially important. It is well known that the " normal " hydroxyl group gives rise to a band at about 3600 cm.$^{-1}$ which is displaced towards lower frequencies and broadened if this group enters into a hydrogen bond. In the latter case the centre of the association band lies at 3100—3400 cm.$^{-1}$ and its exact position depends on the strength of the hydrogen bonds. It appears that in novolac resins made from a given aldehyde but from different phenols the position of the hydroxyl association band varies over a wide range. Some examples are shown in Fig. 2. In the substituted phenols themselves there is a similar variation in the position of this association band. Details are given in a forthcoming paper with R. E. Richards in this *Journal*. An interesting feature is that there seems to be no direct connexion between the positions found with a given phenol and its corresponding novolac. The results with the simple phenols suggest that screening and steric influences of groups may minimise or weaken the hydrogen bonding, and presumably a similar interpretation may apply to the resins. There may well be some correlation between the degree of hydrogen bonding in such resins and some of their physical characteristics and behaviour.

A start has also been made in the construction of correlation rules for compounds of silicon, with the object of examining silicones and related compounds (R. E. Richards, to be published shortly). Straight-chain compounds of the type $R_3Si{-}[OSiR_2]_n{-}SiR_3$, in which R is an alkyl or aryl group, ring polymers of the type $[{-}R_2SiO{-}]_n$, alkoxysilanes, silicols and other related molecules have been examined. Fig. 3 shows some of the spectra over a small range. It seems possible to distinguish, empirically at least, between the open-chain compounds on the one hand and the corresponding ring polymers on the other; and if high resolving power is used, and the relative band intensities are carefully measured, to differentiate polymers of a given type with different values of *n*. The hydrogen-bonding relationships in the silicols are also interesting. Correlations of the frequencies with specifically localised vibrations are still somewhat tentative, although the Si–H bond gives a band at about 2240 cm.$^{-1}$, and the vibrations of alkyl or alkoxy-groups can in some cases be assigned. It is worth noting that the deformational frequency of the methyl group found with hydrocarbons at about 1375 cm.$^{-1}$ appears to be displaced to another roughly constant value when this group is attached to silicon, and the differences between about 10 and 12 μ between the open-chain compounds having the group $-Si(CH_3)_3$ and the ring compounds may suggest vibration frequencies for the group $-Si(CH_3)_3$ analogous to those found for the *tert.*-butyl group $-C(CH_3)_3$ in hydrocarbons at about 8 μ. Preliminary results suggest that much useful information about the silicon derivatives will be obtained from the spectra between 12 and 30 μ.

Another group of compounds worth attention comprises those containing the peptide link, such as nylon, polyamides, polyester-amides, and proteins. There are two main aspects in the examination of the spectra of this class : first, the regions of 3 μ and 5—7 μ where vibrations of the –CO–NH– groups will usually occur, and secondly, the rest of the spectral range where bands due to the main body of the chain or to side groups will occur. Differences in the character of the carbonyl group as a result of hydrogen bonding or electronic influences are revealed in small displacements of the carbonyl frequency. The latter is found at about 1720 cm.$^{-1}$ in ketones, but falls to about 1640 cm.$^{-1}$ in simple solid amides. The shifts in this carbonyl frequency can also be correlated with changes in the region of 3 μ, where the " normal " or " bonded " N–H vibration frequency will occur (*J.*, 1944, 301). We have also found differences between the spectra of fibroin before and after denaturation, although a complete interpretation of them cannot yet be made. This is a field in which progress must at present be empirical, and before any real contribution is made towards the chemistry of proteins, more must be understood about the spectra of amides and amino-acids and the nature of the peptide linkage in such simpler systems (Richards and Thompson, *J.*, in the press).

We have carried out similar measurements with cellulose, esters of cellulose, and their degradation products (I. F. Trotter, to be published shortly). Again, as a possible background of reference, the spectra have been measured of a large number of simple sugars and their derivatives. Over the range 5—15 μ these substances have very complex spectra, an analysis of which is at present impossible, although they provide numerous examples of two very closely related molecules having marked spectral differences. Some correlations are possible, and it may be possible to differentiate between primary and secondary alcoholic groups, a useful point in connexion with the work on cellulose esters. Some promising results have been

FIG. 3.



Derivatives of silicon.

obtained in the detection of particular groups in the degradation products of the celluloses, but there is no doubt that the interpretation of the spectra of this type of compound can only be limited. As in the case of some of the other classes already mentioned, however, there appear to be some peculiar variations in the bands due to hydroxyl groups in the different molecules, and in this spectral range around 3 μ work with higher resolving power should be profitable. In this region it seems likely that the rôle of hydrogen bonding in the swellng of cellulose esters by special reagents can be examined.

Among the processes involving special treatment of macromolecules I should mention vulcanisation and oxidation of rubber, plasticisation, and the effect of ultra-violet radiation or of heat. All these topics have been explored in special cases. When crepe rubber is vulcanised by sulphur chloride new bands appear in the spectrum, and others disappear (Torkington and Thompson, *Trans. Faraday Soc.*, 1945, **41**, 276). The problem is to correlate these bands with the formation or destruction of linkages such as C–S, S–S or C=C. For this purpose reference spectra of thiols, sulphides and disulphides have been measured, and key bands have been deduced for the C–S bonds (Trotter and Thompson, *J.*, 1946, 481). The vulcanisation of rubber by sulphur and other reagents has also been followed in the infra-red spectrum (Sheppard and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 262), and it is interesting to compare the results with those obtained for the alternative process. In the oxidation of rubber, OH, C=O, and possibly other groups are formed. The spectrum shows new bands near 3 μ, 6 μ, and 9 μ and in other regions. There is still some doubt about the interpretation of the fresh absorption near 9 μ, since several groupings, including the ether linkage, lead to bands at about this wave-length. However, in some cases such as that of polythene mentioned above, the carbonyl and hydroxyl groups can be determined even when present in only small amount. Further work is required by this method on the oxidation of rubber itself. Some experimental difficulties still remain in this connexion, such as the preparation of suitable films in which the interference from fillers such as carbon black is avoided or minimised.

An alteration in the mode of packing of fibrous molecules in the solid or the liquid state might in principle be expected to affect the vibrational spectrum, since there should be a change in the force field or potential-energy function, as well as in the symmetry of the assemblage. We should expect that effect to be relatively more marked with molecules containing polar groups. In the case of rubber it might lead to alteration in the spectrum upon stretching, and there is some evidence in support of this (Williams and Dale, *J. Appl. Physics*, 1944, **15**, 585). On the other hand, no differences have yet been found between the spectra of the sol and the gel form of rubber. With molecules capable of molecular orientation in the solid state, for example, nylon, polythene, and polyvinylidene chloride, there should be a change in the relative intensities of bands if the sample is examined in plane-polarised radiation with the direction of orientation of the chains successively parallel and perpendicular to the plane of polarisation (*Proc. Roy. Soc.*, 1945, **184**, *A*, 3). This effect has been examined with oriented polythene and nylon, and small changes in the relative intensities of bands have been found. Further measurements on the phenomenon are desirable.

From the examples which I have cited it is clear that valuable information on a number of points can be obtained. It is equally evident that the infra-red method cannot provide other data such as are obtained from *X*-ray measurements, and the two methods should be regarded as complementary to each other and to other physicochemical lines of work. If the infra-red diagnosis is to be really successful it is necessary that much other knowledge be first obtained about the structure, so that the spectroscopic evidence can be used to decide between two or three possible alternative formulations.

I should refer finally to the general problem of analysis by infra-red methods (Sutherland and Thompson, *loc. cit.*, p. 197; Wright, *loc. cit.*; Brattain and Beeck, *J. Appl. Physics*, 1942, **13**, 699; Barnes *et al.*, *ibid.*, 1945, **16**, 77; *Ind. Eng. Chem. Anal.*, 1943, **15**, 659; Nielsen and Smith, *ibid.*, p. 609; Thompson, *J.*, 1944, 183; *Analyst*, 1945, **70**, 443). It is now possible, for example, to use key groups for the cyano-group (about 2230 cm.$^{-1}$) or phenyl radical (about 750 cm.$^{-1}$) to estimate the amount of acrylonitrile or styrene taken up in copolymerisation with butadiene, although for accurate quantitative work there still remains the difficulty of obtaining films of known and uniform thickness. It is possible also to estimate acetyl, propionyl, or butyryl groups in a cellulose ester or mixed ester. In cellulose acetate there are bands in the region of 3 μ due to stretching vibrations of the methyl groups and of the un-acetylated hydroxyl groups, and by empirical calibration of the change in relative intensities of these bands as the acetylation proceeds, a fairly precise estimate can be made of the percentage of acetyl groups when the latter is in the range 50—60%. By using key bands for the separate isomers, mixtures of natural and synthetic rubbers can be analysed (Barnes, Williams, Davis, and Giesecke, *Ind. Eng. Chem. Anal.*, 1944, **16**, 9).

Future work in this field may proceed along four main lines. First, more correlation rules are required for structural diagnosis, and a more thorough study should be made of hydrogen bonding where it is relevant. Secondly, the whole question of the intensities of bands must now be examined, in order to supplement structural diagnosis based upon the independent method of correlation by frequencies. Thirdly, measurements with grating spectrometers giving higher resolving power should lead to a more exact knowledge in some cases. Finally, use should be made of the newer types of infra-red recorder, either the analysers based upon special filters for following reaction rates, or the oscilloscope method of observing an infra-red spectrum continuously, so that changes can be observed as they actually take place.

Discussion.

Dr. G. B. B. M. Sutherland : It might be useful for people to have a few more details of the performance of the " instantaneous " infra-red spectrometer (referred to by Dr. Thompson in his paper) which has been developed at Cambridge by Mr. E. F. Daly and myself, as it may have direct applications to polymerisation problems. Our purpose was to get a continuous picture of an infra-red spectrum, so that when the spectrum altered because of chemical reactions or other causes, the changes in the spectrum would be literally visible. For instance, this would enable one to follow chemical reactions going too fast to be studied by the usual sampling method. By using a very fast bolometer as the radiation detector, we are able to scan in 14 seconds a range of about 2 mμ in any region of the spectrum between the visible region and 15 mμ. The spectrum is displayed on a cathode-ray screen of such long persistence that, when the spectrum begins to be retraced (after 14 seconds), the afterglow from the preceding trace is still strong enough to be easily visible. Although the applicability of this instrument is at present limited to reactions completed in a few minutes, it should be possible to increase the speed of scanning considerably in the future, particularly if one is prepared to restrict the region scanned. The slide now shown illustrates the picture obtained of the spectrum of 2 : 2 : 4-trimethylpentane between 7 and 9 mμ. The five absorption bands at 7·3, 7·8, 8·0, 8·3 and 8·6 mμ are seen to be well resolved.

There are, of course, many points which one would like to discuss at length in Dr. Thompson's paper, but in view of the late hour I shall confine myself to two questions. First, in the spectra of certain silicone polymers, differences were remarked which appeared to be reliable in classifying these into straight chain or cyclic compounds. Has Dr. Thompson any interpretation of this spectroscopic difference and how it might be related to the structural difference? Secondly, what interpretation would Dr. Thompson give to the difference between the spectra of the raw and denatured silk fibroin ?

Is not part of the answer to the question whether more accurate determination of band positions would enable us to detect still finer changes in structure that we are not seriously limited by resolving power of the spectrometers now used. It is the natural widths of the bands in the liquid state which generally prevent more accurate determination of differences.

Dr. J. L. Stoves : I am very interested in Dr. Thompson's reference to the importance of hydrogen bonds in macromolecular systems. In this connexion I should be pleased to learn if there is any hope of applying infra-red spectroscopy to a study of the rôle of hydrogen bonding in certain gross-structural changes occurring in fibrous proteins, I refer to the hydrothermal shrinkage of collagen and to the supercontraction of keratin fibres. Recently, Gustavson (*J. Amer. Leather Chem. Assoc.*, 1946, **41**, 47) has brought forward evidence which suggests that the shrinkage of collagen in water at temperatures above *ca.* 60° is due to fission of hydrogen bonds between intermolecularly co-ordinated peptides, rather than to rupture of side-chain linkages. In the case of keratin, supercontraction is usually associated with fission of cystine disulphide and salt linkages; rupture of hydrogen bonds, however, may be of considerable importance. Can infra-red spectroscopy help in elucidating the mechanisms of these phenomena ?

Mr. W. Cooper : Zinke and his co-workers (*Ber.*, 1942, **75**, 151) have shown that phenolic ethers of the type ·Ar·O·CH_2· are formed during the resinification of condensates from phenols and formaldehyde, and these break down at high temperatures to give numerous other products. Much other evidence including that from infra-red spectroscopy (Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 258) has been adduced to show the presence of methylene linkages between the aromatic nuclei. Suggestions have been made (Redfarn, *Brit. Plastics*, 1942, 481) that in the cross-linking of phenolic resins, where the normal reactive positions in the nucleus are occupied, reaction occurs involving the phenolic hydroxyl to give ether linkages.

It would be interesting to know whether these ether groupings have been detected at any stage and, if so, to what extent they are present.

MR. FRANK BROWN : Could Dr. Thompson give any information on the use of infra-red spectroscopy in distinguishing between true copolymerisation (*e.g.*, between two monomers, A and B) as opposed to simultaneous individual polymerisation ?

DR. THOMPSON : Apart from the instance quoted in the lecture, *e.g.*, the copolymerisation of vinyl and vinylidene chloride where small amounts of separate polyvinylidene chloride were detected, I am not aware of any other instances. It will probably be possible, however, to apply infra-red spectroscopy for the above purpose in certain cases.

As regards the assignment of bands with the silicon polymers, it is too early yet to be very definite. Although we have now measured a fairly comprehensive set of compounds the obvious correlations are few, except for those already mentioned. We hope to report in detail on these results soon.

Similarly, more work has yet to be done before the spectral changes in denaturation can be fully explained. There are marked alterations near 3 μ and between 6 and 10 μ which can be tentatively correlated with changes in hydrogen bonding and also of side-chain groups.

There are also not yet sufficient data to answer some of the other interesting questions raised. In some cases too it is not possible to predict whether the infra-red method is going to give a clear answer without actually measuring the spectra involved, since we cannot yet predict exactly enough the positions and intensities of bands with some of the more complex molecules.

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7. *The Study of High-polymer Structure by X-Ray-diffraction Methods.*

By C. W. BUNN.

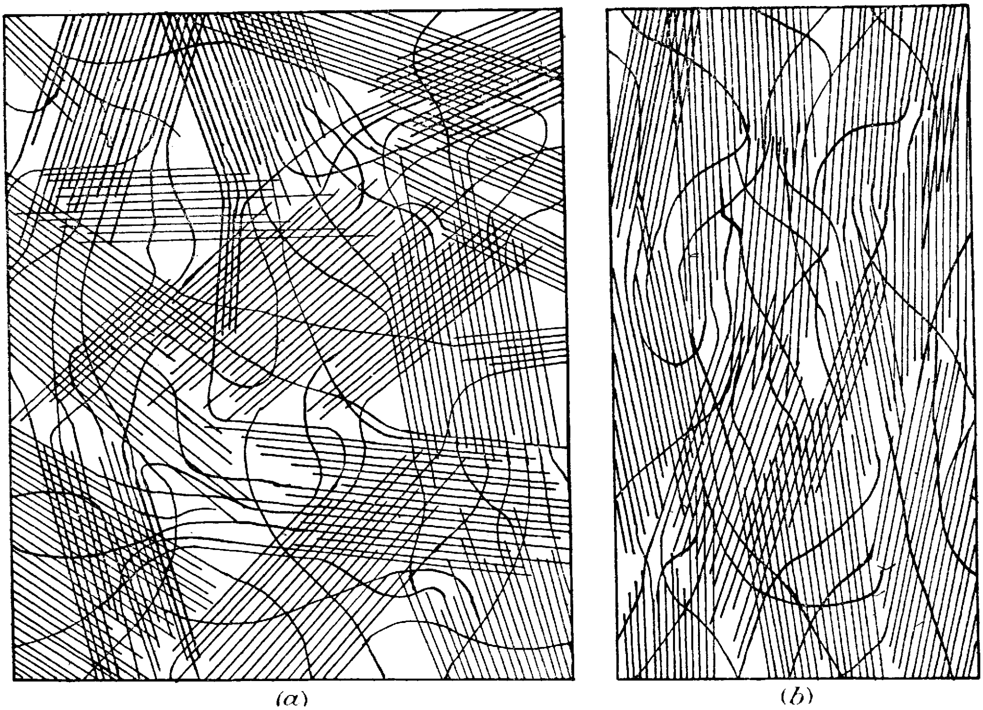
THE information obtainable by a study of high polymers by *X*-ray diffraction methods is geometrical in character. In favourable circumstances it is possible to determine with fair precision the configuration of the molecules (or rather, of sections of molecules) and the way in which they are arranged. Usually the detailed interpretation of *X*-ray diffraction patterns in terms of molecular configuration and arrangement is only attempted for polymers of known chemical structure : interpretation might possibly be achieved for polymers of doubtful chemical constitution, in which case the chemical constitution would be settled by the *X*-ray method; but the difficulties are severe, and this has not been done so far. The contributions of *X*-ray methods, being mainly stereochemical, are thus complementary to those of infra-red methods which are concerned largely with questions of chemical constitution.

A knowledge of the stereochemistry of high-polymer molecules is important, not only for its own sake, but also in the attempt to correlate molecular structure with the physical properties which give to high polymers their great practical usefulness. A knowledge of the arrangement of the molecules may throw light on the part played by intermolecular forces in determining the physical and mechanical properties of particular polymers. It is also possible to obtain from *X*-ray diffraction photographs other types of information which relate to the texture of specimens prepared in particular ways : information about the size and orientation of those ordered regions we call crystalline—information which is of great practical value in understanding the variations of the properties of high polymer specimens treated in specific ways—but I shall not deal here with questions of texture; I shall confine what I have to say to questions of stereochemistry and molecular arrangement.

Detailed interpretation of *X*-ray diffraction patterns in terms of molecular configuration and arrangement is not always possible, even when there is no doubt about the chemical structure of the molecules. If an *X*-ray beam is sent through a small specimen of a glass-like polymer, such as polystyrene or polymethyl methacrylate, a pattern of very diffuse rings is obtained : this is evidence of lack of any ordered molecular structure, and it is obviously not possible, from two or three diffuse rings, to deduce anything very certain or precise. On the other hand, other polymers, such as polythene, the polyesters and polyamides, give patterns showing a number of fairly sharp diffracted beams; for these polymers there is a possibility of detailed interpretation, though this has only been achieved so far for polymers of comparatively simple chemical structure. The fairly sharp diffraction patterns given by these polymers are evidence that the molecules are precisely arranged, and such polymers we call crystalline. They are not completely crystalline : there is usually, in addition to the pattern of fairly sharp reflections, a diffuse ring showing the presence of a certain proportion of disarranged molecules.

How is it that molecules of high polymers are able to arrange themselves in a precise manner to form a largely crystalline mass? This is best approached by forming a mental picture of a melted polymer : very long-chain molecules of irregular configuration are tangled together, and are continually wriggling and changing their configurations by rotation round single bonds. When the specimen is cooled, those sections of chains which happen to be approximately straight can pack parallel to each other to form small crystalline regions which then grow by accretion of parts of other molecules. As a result of this process, any one molecule, in the course of its length, may pass through a number of different crystalline regions; where it wanders from one crystalline region to another, there is no regular arrangement, and such pieces of molecules constitute the amorphous regions (see Fig. 1, *a*).

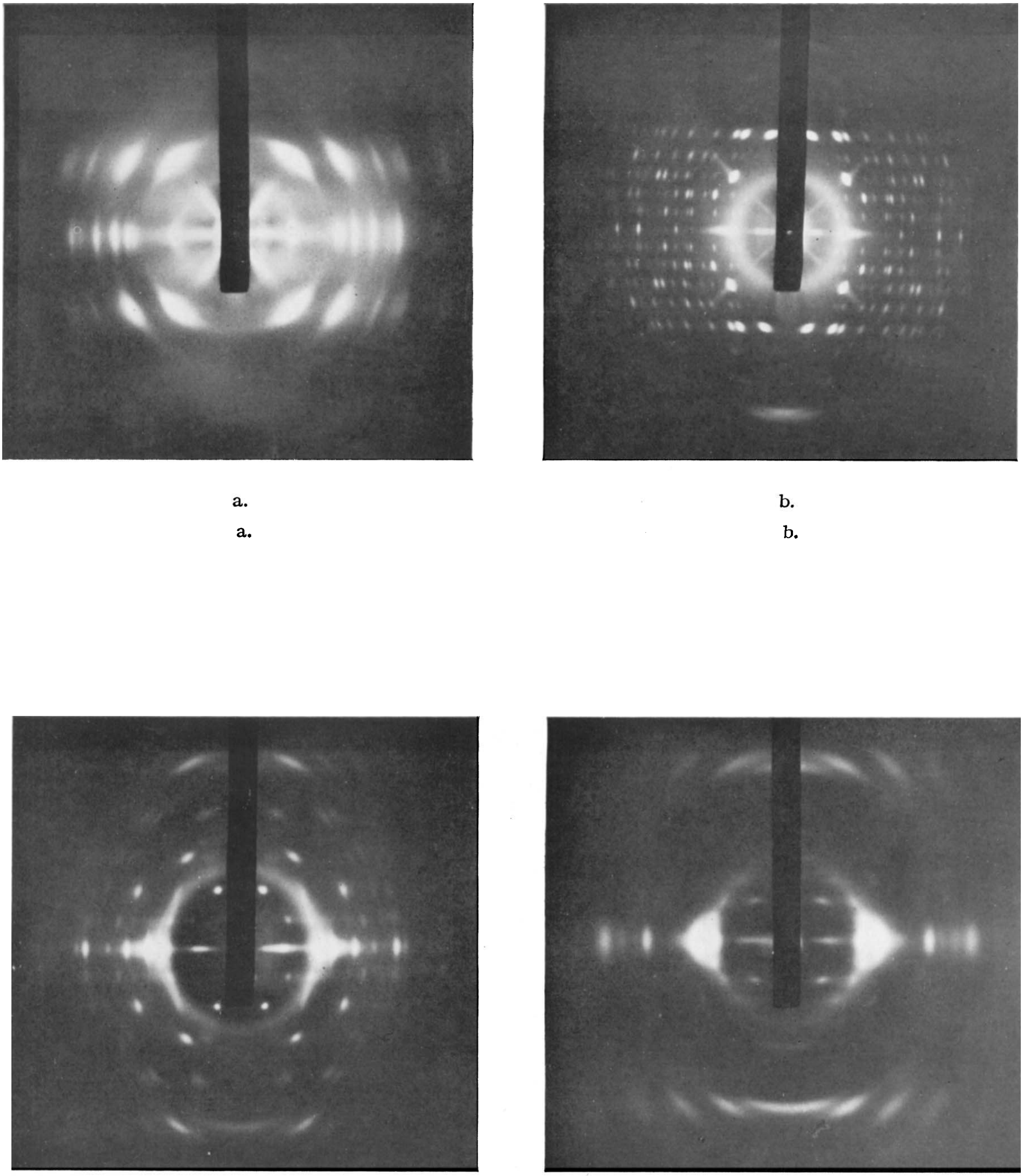
FIG. 1.



(a) *Two-dimensional representation of structure of crystalline polymer.*
(b) *Structure of drawn fibre (direction of drawing vertical).*

Such a specimen of a crystalline polymer, produced by cooling, gives an X-ray diffraction pattern consisting of a number of complete rings; each ring may be regarded as the reflection of X-rays by a particular type of crystal plane (the ring being complete because crystals of all orientations with respect to the beam are present in the specimen); but unless we can gain some knowledge about the relative orientations of the different crystal planes, interpretation of the pattern is much too difficult and uncertain. To gain such knowledge of the mutual orientation of reflecting planes, we must get the crystals into something like order. This is usually done by drawing threads : the molecules are drawn into roughly parallel alignment (Fig. 1, *b*), and thus the crystalline regions which are formed by the regular side-by-side packing of sections of molecules all have one axis roughly parallel to the direction of drawing (the " fibre axis "). Rubber-like polymers, which are not crystalline at room temperature (being above their melting points), may sometimes be crystallised by stretching; but to preserve the crystallinity it is necessary to clamp the specimen in the stretched condition.

When an X-ray beam is sent through such a specimen at right angles to the fibre axis, the diffraction pattern produced (see Plate) shows spots or short arcs arranged in parallel lines



a. b.

a. b.

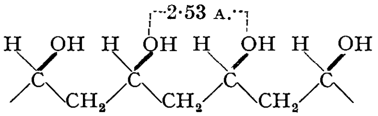
c. d.

X-*Ray diffraction photographs of fibres.*

a. *Polyvinylidene chloride.*
b. *Poly*iso*butene.*
c. *Polyethylene adipate.*
d. *Polyhexamethyleneadipamide* (*nylon* 66).

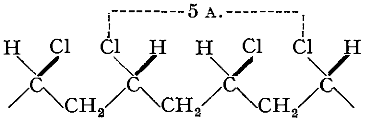
(" layer lines "). This is the type of photograph from which most of our information on the crystal structure of high polymers has been deduced. An additional type of orientation may sometimes be imposed by pressing or rolling fibres; particular crystal planes tend to set themselves in the plane of the sheet-like specimen thus produced; and such specimens, in their behaviour to *X*-rays, simulate single crystals or twinned crystals, and may be studied by the methods developed for single crystals.

For the simplest types of polymers it is sometimes possible to obtain valuable information in a very simple way. The repeat distance along the fibre axis is readily and directly determined from the spacing of the layer lines on the diffraction photograph; and since the crystal axis in this direction is also the molecular axis, the repeat distance is a distance *within* the molecule. Consequently, it is possible in the simpler cases to deduce with considerable confidence the complete stereochemistry of the molecule from the fibre repeat distance. Thus, in polythene the repeat distance is 2·53 A. (Bunn, *Trans. Faraday Soc.*, 1939, **35**, 482); this is just the repeat distance of a fully-extended carbon chain having a plane zigzag configuration (the interatomic distances and bond angles having the normal values C–C 1·54 A., C< about 110°), and therefore it appears that the chains in polythene have this configuration. The repeat distance in polyvinyl alcohol (Halle and Hofmann, *Naturwiss.*, 1935, **23**, 770; Mooney, *J. Amer. Chem. Soc.*, 1941, **63**, 2828) is the same as that of polythene, and therefore the configuration of the chains is similar; and further, it appears that in this substance the OH groups are all in corresponding stereo-positions, *i.e.*, all above or all below the plane of the zigzag, which is the plane of the paper in the following representation :

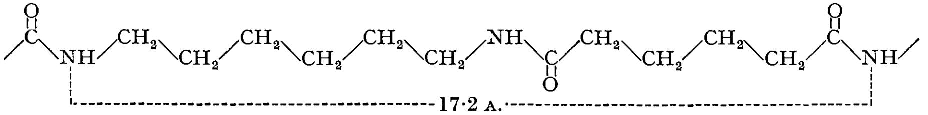


[For if they were, for instance, alternately on each side of the plane of the zig-zag (alternately above and below the paper), the repeat distance would be 2 × 2·53 A.] Thus, in this particular case, the complete stereochemistry of the molecule appears to be settled by one simple measurement on an *X*-ray diffraction pattern.

Polyvinyl chloride does not crystallise well: fibre diagrams can be obtained, but they are very diffuse, showing that the crystalline regions are very small or very imperfectly formed; however, the repeat distance can be determined approximately. It is 5·0—5·1 A. (Fuller, *Chem. Reviews*, 1940, **26**, 143), *i.e.*, double that of polyvinyl alcohol; it is therefore likely that the chain is a plane zigzag and that the chlorine atoms are alternately on each side of the plane of the carbon chain :



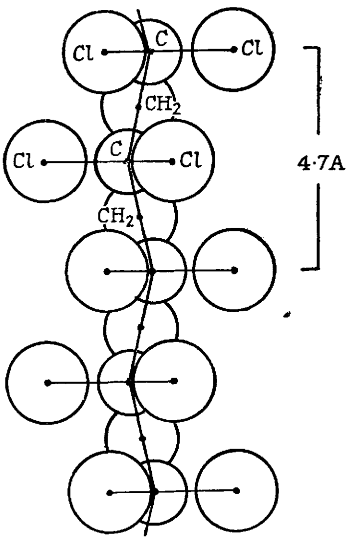
Whenever the fibre repeat distance for a particular polymer is the maximum to be expected in view of our knowledge of the chemical structure and the known bond lengths and angles, we can be reasonably certain of the configuration of the molecules. This is true for polymers with long repeat distances, no less than for the short-period polymers discussed so far. For instance, the repeat distances of the polyamides (Fuller, Baker, and Pape, *J. Amer. Chem. Soc.*, 1940, **62**, 3275) indicate that the chains are planar or very nearly so. Nylon 66, for instance (polyhexamethyleneadipamide), has a repeat distance of 17·2 A., and this is about right for a planar molecule of 7 zigzags comprising one chemical unit :



It is, of course, just possible that there might be a meandering or helical configuration of two or more chemical units in each geometrical repeat (much reduced in length by being curled up); but it would be a surprising accident if the repeat distance of such a chain happened to correspond with that of a fully-extended one-unit repeat. (In actual fact, a detailed interpretation of the *X*-ray pattern has shown that the chain is indeed a simple zigzag with a one-unit repeat; see below.)

If, however, the measured fibre repeat distance of a polymer is appreciably less than that expected for a fully-extended chain, it is usually not possible to deduce the configuration, except in very simple cases. For, when there are many atoms in the repeating unit, there are many different ways of shortening the chain by rotation round single bonds; the question arises, " Round which bonds must rotation occur to give the required shortening? Or is there perhaps a small rotation round each bond? " And the greater the number of atoms in the repeat, the greater the number of possible ways of accounting for the observed shortening. The point is an important one and needs emphasis. Much of the discussion of the configuration of molecules of high polymers is based on fibre repeat distances and very little else. We have seen that this is sound if the repeat distance is the maximum, but is unsafe if it is appreciably less than the maximum; and it is increasingly hazardous with increase in the number of atoms in the repeat. For repeat distances of 10—20 A. (at least 8—16 atoms), where the shortening is an appreciable fraction of the length of the fully-extended chain, suggestions of configurations based on repeat distances alone must be regarded as preliminary speculations.

FIG. 2.



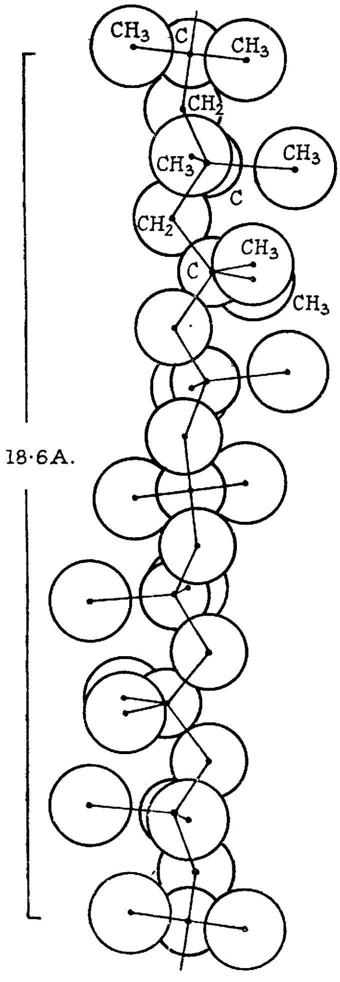
Configuration suggested for polyvinylidene chloride (Fuller).

To determine the configurations of shortened chains, it is necessary to attempt a much more detailed interpretation of the *X*-ray diffraction patterns. And I think it is usually necessary to determine the complete atomic structure of the crystalline regions, by finding first of all the dimensions of the unit cell from the positions of the reflections, and then the co-ordinates of the atoms by a consideration of the relative intensities of all the reflections. It is not sufficient to consider a few outstanding reflections or a particular set of reflections: very plausible reasons for the strength or weakness of particular reflections can often be devised, which fail to account for the intensities of other reflections when these are brought into consideration. The aim should be to account for the entire diffraction pattern.

Let us look at two examples in this light: the two chemically similar polymers, polyvinylidene chloride and poly*iso*butene, which, if polymerisation is consistently head-to-tail in both cases, are $[-CCl_2-CH_2-]_n$ and $[-C(CH_3)_2-CH_2-]_n$. For polyvinylidene chloride the repeat distance is 4·7 A. (Fuller, *loc. cit.*)—very appreciably less than the length of two zigzags in a fully-extended chain (5·06 A.). For a four-atom repeat the number of ways of achieving the observed shortening is not large; and it being assumed that the polymer is head-to-tail so that the chlorines are on alternate carbon atoms, the probable origin of such shortening is to be seen in the overcrowding of the chlorine atoms. Fuller finds that if rotation round chain bonds is made to the extent necessary to ease the packing of the chlorine atoms, the rotation being in opposite directions for alternate chemical units (see Fig. 2), the correct repeat distance is achieved. This seems significant, and it is not easy in this simple case to think of other ways of obtaining the required shortening. It is not, however, certain that the substance is a head-to-tail polymer; the *X*-ray evidence, as far as it has been interpreted, does not establish this. Complete structure determination is desirable to settle the question.

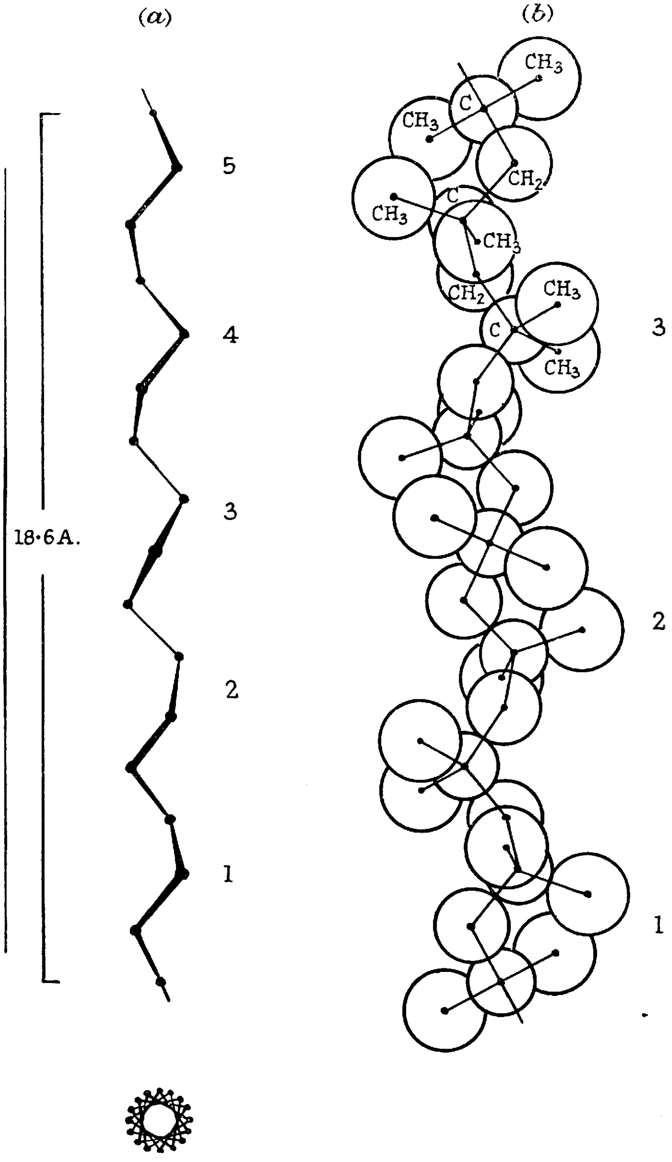
For a stretched thread of the rubber-like substance poly*iso*butene, the repeat distance (Brill and Halle, *Naturwiss.*, 1938, **26**, 12; Fuller, Frosch, and Pape, *J. Amer. Chem. Soc.*, 1940, **62**, 1905) is very much longer—18·7 A.—and is also of such a magnitude that shortening of the chain is indicated: 18·7 A. is more than 7 and less than 8 times the length of one zigzag in a fully-extended chain. There are evidently at least 8 chemical units in the geometrical repeating unit; and the occurrence of strong reflections on the eighth layer line suggests a sub-period of one-eighth of the whole repeat and is thus consistent with the idea that the number of chemical units is eight and not more. The number of ways of shortening a sixteen-atom chain unit from 20·2 A. (the fully-extended length) to 18·7 A. is large; and in looking for clues to the correct configuration it is natural to consider the effects of overcrowding of the methyl groups, which is even more severe than in the case of polyvinylidene chloride because methyl groups are larger than chlorine atoms. Fuller, Frosch, and Pape (*loc. cit.*) found that if a rotation of the same type as that suggested for polyvinylidene chloride is made, but in this case consistently in the same direction, a helix is formed (Fig. 3) which has a sixteen-atom repeat distance of 18·7 A. The correspondence with the measured repeat distance seems significant; but I do not think this configuration is likely to be correct, for the following reason. The methyl side groups on such a helix stand well out from the chain, and in a side view the carbon atoms of the methyl groups form a pronounced S curve (with of course only one S in the complete period); this feature would give some strong reflections on the first layer line, yet actually all the first-layer-line reflections in the diffraction pattern of poly*iso*butene are

FIG. 3.



Helical configuration suggested for polyisobutene by Fuller, Frosch, and Pape.

FIG. 4.



Configuration now suggested for polyisobutene.
(a) *Chain alone (below—end view of chain).*
(b) *Chain with methyl groups.*

weak. Moreover, there are other outstanding features of the diffraction pattern which the simple helix does not account for : just as the group of strong reflections on the eighth layer line suggests a sub-period of $c/8$, so a group of strong reflections on the fifth layer line suggest a sub-period of $c/5$. The simple helix does not account for this ; nor does another configuration suggested by Fuller, Frosch, and Pape, obtained by four rotations in one direction followed by four in the opposite direction. The combination of $c/8$ and $c/5$ seems in fact a very odd combination of sub-periods, difficult to account for by any straightforward scheme of shortening. Just before the war, I spent some time trying to solve the problem in detail. All the data for a detailed solution are present in the diffraction pattern, which is probably the sharpest and most perfect given by any chain polymer; and interpretation as far as the deduction of unit cell dimensions and the indexing of the reflections has been achieved by Fuller, Frosch, and Pape (I can confirm their conclusions from my own work) ; but the determination of atomic co-ordinates in the unit cell is a problem of great complexity, because the repeat distance is so long and there are so many possible chain configurations. After examining many possibilities, I did come across a type of helix which can account for the odd combination of sub-periods ($c/5$ and $c/8$), as well as for the intensities of many of the reflections. Although the interpretation is not complete and it is still not certain that this is the correct configuration, it is worth mentioning as by far the most promising of the many configurations which have been considered. It is illustrated in Fig. 4. To make a model, starting from the plane zigzag, it is necessary to rotate each unit much further than in Fuller, Frosch, and Pape's helix, all the units being rotated in the same direction. The chain itself then forms a helix which can be represented, using the nomenclature I have suggested (*Proc. Roy. Soc.*, 1942, *A*, **180**, 67), as a distorted form of B_{16} or the enantiomorphous C_{16} (Fuller, Frosch, and Pape's helix being a distorted form of A_{16}). In a side view the chain (Fig. 4*a*) exhibits five " crinkles ", and this feature accounts for the strong reflections on the fifth layer line; the methyl groups are so disposed that there are three groups along each side of the chain (Fig. 4*b*), and this feature accounts for the great strength of one reflection on the third layer line (113 + 203) ; these statements have been confirmed by calculations, and in fact the intensities of most of the low-order reflections are satisfactorily accounted for. The bond angles of the chain carbon atoms must be opened a little to give the correct repeat distance; this increase of bond angles seems not improbable, in view of the gross overcrowding of the methyl groups. I hope to be able to resume this work, for the configuration of this molecule is of great interest. Poly*iso*butene is a rubber-like substance with very high extensibility and remarkably perfect crystallisation on stretching; both these properties would seem to suggest very great (not to say unique) molecular flexibility, which is remarkable for a molecule in which there is extreme overcrowding of the side groups.

This discussion has brought out the necessity of detailed interpretation of *X*-ray diffraction patterns for the determination of the configuration of those polymer molecules which are not fully extended; the aim should be to account for the entire diffraction pattern. It has also included some mention of one of the possible causes of chain-shortening, namely, the mutual repulsion of substituent atoms or groups of atoms. This factor may also be partly responsible for the non-planar configurations of molecules of the polyisoprene group, which have been determined (Bunn, *ibid.*, p. 40) by detailed interpretation of the *X*-ray diffraction patterns. In rubber and gutta-percha, which are *cis*- and *trans*-isomers of polyisoprene $[-CH_2-C(CH_3){=}CH-CH_2-]_n$, the repulsion between the methyl group and the adjacent CH_2 group of the chain would be expected to favour a non-planar chain configuration. The same is true for polychloroprene, in which a chlorine atom takes the place of the methyl substituent. It is not certain, however, that this is the only factor concerned. It has been pointed out (Bunn, *ibid.*, p. 67) that in saturated molecules the most stable configurations (those found in crystals) are those in which the bonds of linked carbon atoms are staggered, the planar zigzag configuration of polythene (*idem, loc. cit.*, 1939) and other chains being one of the possible staggered configurations, and the meandering configuration in rubber hydrochloride (Bunn and Garner, *J.*, 1942, 654) being another; and there are suggestions (Bunn, *Proc. Roy. Soc.*, 1942, *A*, **180**, 67) that the reason why the staggered configuration is favoured is not to be found simply in the repulsions between the atoms held by the bonds, but that there is some bond-orientation effect. The " principle of staggered bonds ", applied to a polymer molecule having a double bond in the chain, gives a non-planar configuration like that actually found in these substances (if account is taken only of the single bonds, or if the double bond is regarded as two distorted single bonds) (*idem, ibid.*). The relative importance of these two factors—the repulsion between substituents, or between substituents and chain atoms, on the one hand, and possible bond-orientation effects on the other—in determining the chain configuration is not known. The question is of great interest, not only from the point of view of understanding the configurations of chain-polymer molecules in crystals, but also from the point of view of correlating molecular structure with physical properties. These two problems are closely bound up with each other. The melting points and the mechanical properties of chain polymers depend, at any rate partly, on the flexibilities of the molecules themselves; molecular flexibility depends on the energy associated with changes of configuration, and this energy is determined by the two factors mentioned—the forces between atoms on the one hand, and any bond-orientation effect on the other. The melting points of the polymers of the polyisoprene group have been discussed (*idem, ibid.*, p. 82) in relation to these stereochemical conceptions; and likewise, in the case of poly*iso*butene, it has been suggested (*idem, ibid.*) that its low melting point may be due to an opposition between the two factors, as a result of which the energy associated with a change of configuration is very small.

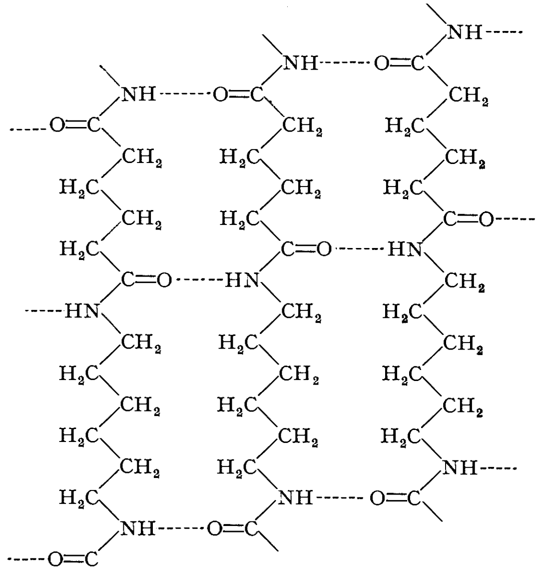
Problems of the relations between physical properties, molecular flexibilities and stereochemical factors are also presented by another interesting group of substances—the polyesters. Most of the *X*-ray diffraction information on these substances we owe to Fuller and his collaborators (*Chem. Reviews*, 1940, **26**, 143; *J. Amer. Chem. Soc.*, 1937, **59**, 344; 1939, **61**, 2575; *J. Physical Chem.*, 1939, **43**, 323). Detailed interpretations of the diffraction patterns have not yet been published, but the fibre repeat distances for many different polyesters are known, and show that varying degrees of shortening occur. In the decamethylene glycol series the chains are only slightly shortened (by about 0·2 A. per chemical unit), and therefore have an almost fully-extended plane zigzag configuration.

In the ethylene glycol series of polyesters there is a small, almost constant shortening of 0·3—0·4 A. per chemical unit, suggesting that in the region of the glycol group there is a uniform departure from the plane zigzag chain form. The configuration of the ester group in these substances will not be known until detailed interpretation of the *X*-ray patterns is achieved, and at present can only be a matter for speculation. Likewise, the question to what extent this departure from the planar chain form is bound up with the molecular flexibility suggested by the low melting points (Carothers and Arvin, *J. Amer. Chem. Soc.*, 1929, **51**, 2560; Fuller, Frosch, and Pape, *ibid.*, 1942, **64**, 154) of these substances is also a matter for speculation. Flexibility at the ester group is also suggested by the very interesting behaviour of some of the polyesters of the trimethylene glycol series, drawn fibres of which show a change of diffraction pattern on stretching (*idem, ibid.*); the change of diffraction pattern, since it involves a lengthening of the fibre repeat distance, indicates that the chains, which are at first considerably shortened (much more so than in the majority of polyesters), are straightened out by stretching. This behaviour recalls that of the fibrous protein, keratin (Astbury and Woods, *Phil. Trans.*, 1934, *A*, **232**, 333); these polyesters are the first synthetic polymers of comparatively simple chemical structure which exhibit this phenomenon, and it is to be hoped that detailed studies of the molecular configuration before and after stretching will be undertaken.

The manner of arrangement of polymer molecules in the crystalline regions is, from the point of view of physical properties, probably of no great significance in the case of hydrocarbon polymers or others in which there are no strongly polar groups; the type of packing probably depends chiefly on the effective shape of the molecules. It is of greater importance for molecules containing polar groups; a knowledge of the manner of arrangement may throw light on the part played by intermolecular forces in determining the physical properties. Detailed interpretation of *X*-ray diffraction patterns is necessary to obtain this knowledge. A discovery of the unit cell dimensions may give a partial knowledge of the relative positions and orientations of the molecules, but the suggestions arising from unit cell dimensions need testing by the determination of atomic positions from the relative intensities of the reflections.

In the case of the majority of the polyesters, the lateral unit cell dimensions obtained from the side spacings (the equatorial reflections on a fibre photograph) are very similar to those of polythene and therefore suggest that the molecules are packed side by side in much the same way as in polythene; and the shape of the complete unit cell suggests the relative positions of ester groups in neighbouring molecules (Fuller, *loc. cit.*, 1940); but confirmation by complete structure determination is desirable.

In the polyamides it has long been supposed that the molecules are linked side by side by hydrogen bonds, and that these are responsible, not only for the high melting points of these polymers, but also perhaps for the high tensile strength of the fibres. Mrs. Garner and I, in an investigation finished in 1941 and soon to be published, have worked out detailed interpretations of the *X*-ray diffraction patterns of two polyamides (polyhexamethylene-adipamide and -sebacamide) and have found good evidence for the existence of hydrogen bonds. We find, not only that the oxygen atom of one molecule is on the same level as the nitrogen of the next, but also that the distance between these two atoms is that characteristic of hydrogen bonds in other crystals (2·8 A.). The hydrogen bonds do not link the molecules together three-dimensionally, but only in sheets thus :



The links between sheets (which are packed in such a way as to give triclinic symmetry) are evidently much weaker. This type of arrangement influences the orientation taken up in the cold-drawing of fibres : Fankuchen and Mark (*J. Appl. Physics*, 1944, **15**, 364) found that in the early stages of drawing, a sheet orientation occurs, and we find that it is the hydrogen-bonded sheets that become parallel to the direction of drawing; only in the later stages is the well-known chain orientation (with the chain molecules parallel to the direction of drawing) obtained. The sheet structure of the crystalline regions is also responsible for the fact that it is possible, by pressing or rolling specimens, to impose a remarkably good plane orientation in addition to the usual longitudinal (fibre) orientation; the hydrogen-bonded sheets become roughly parallel to the plane of the pressed or rolled specimen.

The detailed study of the configuration and arrangement of molecules of the comparatively simple synthetic polymers is interesting, not only in connection with the properties of these substances themselves, but also because it may throw light on the much more complex problems presented by natural polymers such as proteins. This is well illustrated by the work on nylon just mentioned, for there are some striking correspondences between the crystallography of nylon and that of β-keratin. The double orientation in pressed nylon specimens is entirely in line with that found by Astbury and Sisson (*Proc. Roy. Soc.*, 1935, *A*, **150**, 533) in β-keratin pressed in steam, and the crystal planes involved appear to correspond; the weakness or absence of reflections for certain zones in the β-keratin photograph (Astbury and Street, *Phil. Trans.*, 1931, *A*, **230**, 75) is also paralleled in nylon; and the photographs of both substances often show streaks on the layer lines, indicative of partial disorder in some of the crystalline regions.

The contributions of *X*-ray diffraction studies to our knowledge of the structure of high polymers are mostly confined to crystalline polymers. In the attempt to understand the physical properties of polymers in terms of their molecular structure, the policy of the *X*-ray worker must be to learn as much as possible about the crystalline polymers, and it may then be possible to apply the fruits of that knowledge to the non-crystalline, glass-like polymers. But it is worth remarking that even the negative evidence of non-crystallisation (of polystyrene, polymethyl methacrylate, and polyvinyl acetate, for example) is instructive. It is noteworthy that those polymers which do not crystallise or crystallise poorly, like polyvinyl chloride, are those in which there is the possibility of the occurrence of left- and right-handed groups indiscriminately along the chain; in polystyrene, for instance, the benzene ring may be attached indiscriminately to either of the two available bonds of the chain carbon atom. Molecules which are geometrically irregular in this way would not be able to form crystalline arrangements. On the other hand, this type of irregularity cannot occur in the case of molecules bearing two identical atoms on the same chain carbon atom, and it is significant that such polymers (*e.g.*, polythene itself, polyvinylidene chloride, poly*iso*butene, the unsubstituted polyesters and polyamides) crystallise well. The point is of practical importance : anyone setting out to make new glass-like polymers would be ill-advised to use symmetrical monomers.

Discussion.

DR. D. J. CRISP : The idea put forward by Mr. Bunn, that randomly arranged optical antipodes might account for the lack of crystallinity in certain vinyl polymers such as polyvinyl acetate, was suggested by Staudinger ("Die hochmolekularen organischen Verbindungen," Berlin, 1932, p. 114), and criticised by Meyer (" Natural and Synthetic High Polymers," New York, 1942, p. 106). The difficulty lies in the fact that polyvinyl alcohol, derived by simple hydrolysis of the acetate, presumably without intramolecular rearrangement, is crystalline. Hence structural regularity about the main valency chain does not appear to be the only factor.

MR. C. W. BUNN : The apparent geometrical regularity of polyvinyl alcohol (the evidence for which is the crystalline X-ray diagram) does not prove that polyvinyl acetate is geometrically regular. If, in the hydrolysis, the acetate groups come off whole (*i.e.*, the break is between the oxygen and the chain carbon atom), then momentarily the chain carbon atom has a free bond, the hydrogen atom on this carbon atom might change over from one stereo-position to the other. In this case there is the possibility that geometrically regular polyvinyl alcohol might be produced from irregular polyvinyl acetate. Thus it is not certain that polyvinyl acetate has a regular structure.

PROF. MELVILLE : If polyvinyl alcohol is reconverted into polyvinyl acetate, the latter is found to be again non-crystalline.

MR. C. W. BUNN : That seems a more serious objection : from regular polyvinyl alcohol one would expect to get regular polyvinyl acetate, but even this is not certain; a change of configuration may take place when there are free bonds on the chain carbon atoms, if the break occurs between the oxygen and the chain carbon atom. But whatever is the truth about this particular case, the statement I made is generally true—that those polymers whose molecules may be geometrically irregular through the occurrence of left- and right-handed groups indiscriminately along the chain are either non-crystalline (polystyrene, polymethyl methacrylate) or poorly crystalline (polyvinyl chloride, polyacrylonitrile), whilst those polymers in which such irregularity cannot occur (polythene, polyvinylidene chloride, poly*iso*butene) crystallise well. I do not think polyvinyl acetate has a regular structure and even if the explanation I have suggested of the polyvinyl alcohol–acetate case is not correct, then I think some other explanation will be found which is consistent with geometrical irregularity in the acetate.

DR. IAN MACARTHUR : Structural discussion today has centred on the chain type of macromolecule. The characterising features of all types are the relative strength and stability of the constituent (as against the inter-) links. The nature of these, and particularly their directional bias, determine the conditions under which the metrical techniques are most serviceable. Where the polar groups are not too numerous, bulky, or reactive, and the physical state allows mobility, statistical and thermodynamic methods, as Dr. Gee has stressed, give a close approximation to experiment; entropies, not energies, are the dominant factor in long chains as such : chemical nature is subsidiary. The infra-red technique is more specific. With the speed and accuracy of the newer instruments, the present stage of collection, correlation, and semi-empirical diagnosis is still more profitable than approximate synthetic calculation.

I agree with most of Mr. Bunn's remarks, and appreciate that he deliberately restricted to crystallographic aspects. The view (Fankuchen, *Ann. Rev. Biochem.*, 1945, **14**, 210) that a complete crystallographic cell parameter determination is the sole or sometimes even the highest aim of an X-ray investigation in the macromolecular field, is unduly narrow. Macromolecules are usually protean systems with configuration a function of state of aggregation In polythene, the confirmation, in the crystalline chain parts, of Müller's earlier structure for n-$C_{29}H_{60}$, is not more fundamental than the anomalies found in the determination, the composite crystalline–amorphous nature of the material, and the whereabouts of the small percentage of methyl groups; while structural progress in proteins has derived more real impetus and secured broader findings from the combined experimental fibrous protein and virus researches, synthetic model building, and co-operation with practical fibre industries, than from the purely

X-ray crystallographic approach. Precise atomic placings are excellent, but as a stage in indicating bond types, the genesis of aggregation, and the equilibria resulting from potential fields. Such features are often best investigated by selection and systematic treatment of the macromolecule, and by the co-operative use of all the relevant physicochemical methods. Among these the wave range of X-rays is specially serviceable to the physical chemist; but it is a tool to employ, not a subject for votaries; it gives evidence, not verdicts.

Quite apart from the fact that the full impact of X-rays on real matter is only now beginning to receive comprehensive notice, and that much of the information so yielded—questions of texture and secondary structure, deformation, thermal and elastic vibration systems, particle (as opposed to crystallite) size and orientation, degree of crystallinity, nature and degree of disorders—is frequently of more relevance than intracrystallite atomic arrangements, a too rigorous parameter analysis in macromolecules keeps length as a difficulty rather than as an opportunity. The advantages of small polar molecules to the X-ray analyst are that in packing neatly, they crystallise easily, have few parameters, and the answer is usually more or less known. The disadvantages are that bond lengths deduced are specially subject to local perturbation whose precise evaluation by quantum-mechanical calculation is in its earlier stages. When atomic parameters becone too numerous for rigorous treatment, simply put in more! The asymptotic approach so made gives a more standard environment, proportionately diminishes end-group effects, and reduces many problems to two-dimensional ones, for the natural tendency of chains in aggregating to a minumum potential is to form a rod-like shape and pack in pseudo-hexagonal parallel array. Such packings are a function of molecular shape, polarity, and internal rigidity. To a first approximation they yield cells of standard cross-section and length corresponding to the unit involved. To a second approximation these dimensions do vary, and " straight " crystal analysis, on one individual only, fails to reveal them.

Long n-aliphatic chains form the simplest illustration. Long-chain n-paraffins usually build crystal cells with a standard cross-section and a length (C) given by $C/2 = k(n - 1) + p$, where n = carbon-atom content in chain, and k and p are constants. As n or temperature varies, polymorphic transitions appear, pseudo-rhombic giving place to pseudo-hexagonal or pseudo-monoclinic forms, but zigzag chain shape and packings are essentially the same. With the insertion of small polar groups rigidly attached to the chain axis (*e.g.*, in n-ketones) polymorphism disappears, the addition of dipole layer to van der Waals chain forces having a stabilising effect, especially with respect to temperature variation. The position of the $C{=}O$ substituent along the chain causes systematic variation. The degree of stability increases with the dipole moment of the group inserted. In all cases, temperature increase causes a nearer approach to a radial symmetry which may (certain paraffins and alcohols) or may not (acids) be reached before melting. The phenomenon argues an increased rotational or torsional vibration about the chain axis, probably of a co-operative type. The nature of this is helpfully investigated through thermal energies (Garner), intensity analysis along the chain (MacArthur), or by temperature–polarisation studies on *cis-* or *trans*-diketones (Müller). Transitional energies can be subdivided into chain and end-group elements. In general, strain in bond lengths and angles may be indicated by abnormal heats of combustion (poly*iso*butylene; Polanyi), or its absence reduces isomeric possibilities for test (benzene hexachlorides). Localised molecular weighting is valuable. Swelling or isotopic replacements may indicate particular (*e.g.*, hydrogen-bond) links. Force field theory is useful in simple cases. Although the plate (graphite, clays) and skeleton (protein) types are a natural extension from chains, they lie outside present discussion; but, particularly here, the new technique of the electron microscope with its resolving power of 25 A. has, in conjunction with X-rays, been of valuable and potentially enormous service.

It may well be, therefore, that the fundamental structural developments in macromolecules will be achieved, not through routine precision crystal analysis, but, as instanced in the pioneer long-chain work of the Royal Institution and the Bristol school, and in the fibre methods at Leeds, in co-ordination with ancillary techniques. Scientifically, this demands an extensive physicochemical background; technically, greater concentration on X-ray power, sensitivity and speed of recording, and flexibility in conditioning specimens while undergoing X-radiation.