POLYMERS AND COPOLYMERS OF (+)-1,3-DIMETHYLBUTYL METHACRYLATE.

THE STERIC STRUCTURE OF THE POLYMERIC MAIN CHAINS.

Being a Thesis submitted to the
University of London
for the Degree of
Doctor of Philosophy

by

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JULY 1959
(+)-1:3-Dimethylbutyl methacrylate has been prepared, by the reaction of methacrylyl chloride with optically pure (+)-1:3-dimethylbutanol in the presence of pyridine, and polymerised by means of benzoyl peroxide to a hard clear glass. (+)-1:3-Dimethylbutyl pivalate was similarly prepared by the reaction of pivalyl chloride with (+)-1:3-dimethylbutanol. The molecular rotations of the poly-((+)-1:3-dimethylbutyl methacrylate) and the (+)-1:3-dimethylbutyl pivalate, in solution in sym-tetrachloroethane, were determined for five wavelengths at 25°.

The effect on the rotatory power of the polymer of change in concentration of its solutions, in molecular size, and from benzoyl peroxide to α:α'-azo-isobutyronitrile as initiator has been investigated and has been shown to have little effect on the optical rotation.

Comparison of the molecular rotation of the pivalate with that of the poly-((+)-1:3-dimethylbutyl methacrylate) has been used in applying the method of molecular rotation differences to an analysis of the rotatory power of the polymer in terms of various aspects of its structure. It is concluded that dissymmetric coiling of the main chain in this polymer contributes to its rotatory power.

Copolymers of (+)-1:3-dimethylbutyl methacrylate with methyl methacrylate, acrylonitrile, styrene, and diethyl fumarate have been prepared, and the rotatory powers of solutions of these copolymers in sym-tetrachloroethane determined for five wavelengths. The structure and dissymmetry of the copolymers are discussed, and the molecular rotations
of the optically pure (+)-polymer and of the (+)-pivalate are applied in molecular rotation difference calculations. The contributions to the rotatory power made by chain-coiling of units derived from the optically inactive monomers are estimated.
ACKNOWLEDGMENT

The work described in this Thesis has been carried out in the Organic Chemistry Research Laboratories of the Battersea College of Technology, London S.W.11, under the supervision of Dr. C.L. Arcus, to whom sincere thanks are due for his invaluable guidance and help.

Thanks are also due to the Department of Scientific and Industrial Research for a Maintenance Grant, and to Mr. Godby, Chief Laboratory Technician, and his assistants for their kindness.
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INTRODUCTION
HISTORICAL INTRODUCTION

Although the phenomenon of polymerisation was first noted in 1839 when Simon (Ann., 1839, 31, 265) reported the conversion of liquid styrene to a gelatinous mass, the study of polymeric products was generally avoided, and only isolated workers made any attempt to understand them during the latter half of the 19th Century. However, at the beginning of the present Century the industrial importance of these products was recognised and in the last 30 - 40 years extensive investigations have been carried out to determine the mechanism of polymer reactions and the structure of the products.

Lebedev (J. Russ. Phys. Chem. Soc., 1913, 45, 1249) was the first person to recognise that the products were of high molecular weight, but it was Ostomysslenky (J. Russ. Phys. Chem. Soc., 1912, 44, 204; 1915, 47, 1937, 1941; 1916, 48, 1071, 1132) who first suggested that the reaction involved successive additions of the monomer to the growing polymer molecule. He studied the polymerisation of vinyl bromide and isoprene and came to the conclusion that the stepwise addition of small molecules involved the transfer of a hydrogen atom thus,

\[
\begin{array}{c}
\text{CH}_2=\text{CH} + \text{CH}_2=\text{CH} \\
\text{Ph} & \text{Ph}
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_2=\text{CPh} \\
\text{Ph}
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3-\text{CH}-\text{CH}=\text{CH} \\
\text{Ph} & \text{Ph} & \text{Ph}
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}=\text{CH} \\
\text{Ph} & \text{Ph} & \text{Ph}
\end{array}
\rightarrow
\text{etc.}
\]
and that the final products were large ring compounds. In 1920 Staudinger (Ber., 1920, 53, 1073) studying poly-(styrene) and poly-(oxymethylene) stated that he considered the polymers to be long chain compounds of formulae \[ R-\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}-\begin{array}{c} \text{CH}_2-\text{CH-CH}_2-\text{CH}-R, \\ \end{array} \text{and} \ R-\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}-\begin{array}{c} \text{CH}_2-\text{O-CH}_2-\text{O-CH}_2-R. \\ \end{array} \]

formed from a diradical, such as \[ \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}-, \]

by successive addition of the monomer molecules until an equilibrium was attained due to the reverse reaction set up because of the instability of the large molecules. He assumed that free-radicals existed at the ends of the chain but that they were rendered unreactive by the large size of the chain. He later modified this view (Ber., 1929, 62, 241) and suggested that the free-radicals at the chain ends were satisfied by cyclisation; but he still held to the view that an equilibrium was set up.

Staudinger's chain concept was not widely accepted until in 1926 Sponsler & Dove (J. Gen. Physiol, 1926, 9, 677) showed by X-Ray diffraction that cellulose fibres had a chain structure composed of an indefinitely large number of units. This method was extended to other linear polymers giving characteristic X-ray fibre patterns, and thus the idea that polymers had a chain structure was accepted.

About this time the kinetics of gas phase reactions were elucidated and these results had a great influence on the understanding of the kinetics of the polymerisation reaction. Taylor and Vernon (J.A.C.S., 1931, 53, 2527) were among the first workers to study quantitatively the course of a polymerisation reaction. They studied
the effect of oxygen and inhibiting agents, and also variations in the temperature and concentration, on the photopolymerisation of styrene and vinyl acetate, and came to the conclusion that the polymerisation proceeded by a chain reaction in a kinetic as well as a structural sense. They considered that a light quantum activated a molecule which then added to a non-active molecule in an exothermic reaction, regenerating the activation energy at the end of the molecule. This process then continued until the activation energy was lost by reaction with an inhibiting agent or by collision with the wall of the vessel.

Then in 1934 Chalmers (J. A. C. S., 1934, 56, 912) collected together the data available in the literature and from a study of this he expounded the first theory of addition polymerisation. He had studied the suggested stepwise synthesis of polymers and came to the conclusion that this did not represent the mechanism of the polymerisation of vinyl monomers, since a stepwise synthesis would give predominantly dimeric and trimeric products. He proposed that the polymerisation took place by a chain reaction consisting of a slow initiation step, leading to an active intermediate, which was followed by an extremely rapid propagation step during which a large number of successive additions to the original activated monomer molecule occurred.

The investigation of the kinetics of the reaction was then carried out by a large number of workers, including Mark, Flory, Schulz, Marvel, and Dostal, and the chain nature of the reaction finally proved. Many of the important principles of the mechanism were clarified by Schulz (Z. Physical Chem., 1936, 330, 379, and subsequent papers) from
a study of the thermal and catalysed polymerisation of styrene. He found that during the polymerisation the average molecular weight of the polymer formed was constant and also that the rate of polymerisation was proportional to, and the average molecular weight inversely proportional to, the square root of the catalyst concentration.
STRUCTURE AND FORMATION

Addition polymers are compounds in which a large number of identical units of a comparitively low molecular weight are joined by primary valency (homopolar) linkages, without the elimination of any atoms or groups, to form new independent large molecules. They differ from simple organic compounds in that they are composed of molecules having different numbers of monomeric units in the chain and thus having different chain-lengths and molecular weights. Since the individual chains possess different molecular weights, any molecular weight determination carried out on the whole sample will yield only an average value. In addition to the variation in length of polymer chains, non-linear chains may be formed by branching of the chain or by cross links formed between the chains.

The unsaturated monomeric types which undergo addition polymerisation are the olefins and their derivatives (the vinyl monomers) the dienes, the aldehydes, and certain strained cyclic monomers, and of these the vinyl group of compounds are technically the most important and have received the greatest amount of study. With the exception of
tetrafluoroethylene, monomers which do not contain the \( \text{CH}_2=\text{C} \) group (e.g., 1:2 disubstituted ethylenes) do not readily undergo addition polymerisation. The polymerisation of a monomer is greatly facilitated if electron-attracting groups are attached to the olefinic linkage, the presence of such groups increasing the stabilisation of the radical formed compared with that of the parent monomer. In addition a second substituent on the \( \alpha \)-carbon atom of a monomer of the type \( \text{CH}_2=\text{CHX} \) generally increases the reactivity of the monomer, although this is not so in the case of styrene. Marvel and his co-workers (J.A.C.S., 1946, 68, 736, and subsequent papers) have also investigated the effect of substituting the ring of styrene and they found that whilst chlorine or a nitrile group increased the polymerisation tendency, the presence of a nitro group considerably reduced the reactivity of the monomer.

The long chain compounds are formed by a kinetic chain reaction consisting of three distinct steps. Once monomer (M) has been activated (INITIATION), monomer molecules add to it in a single rapid reaction sequence (PROPAGATION) until the chain is terminated (TERMINATION). The full size of the polymer molecules is produced from the earliest stages of the reaction and therefore at any instant during the polymerisation process the reaction mixture consists almost entirely of unchanged monomer and high polymer. The polymer so formed does not usually increase in size, except so far as branching and cross-linking occur, and the time of the reaction merely determines the extent of conversion of monomer to polymer.

**Initiation:** Although a number of pure monomers will polymerise
spontaneously, most polymerisations require a catalyst (initiator) to start them, and the nature of the polymerisation reaction depends on the type of initiator used. The initiators are either free-radical or ionic in character, but only free-radical initiated polymerisations will be considered here. The monomer can be activated by the direct introduction of free-radicals into the system or by the introduction of small quantities of compounds which are known to decompose under the influence of light or heat to give free-radicals. There are a number of compounds of this class, of which the most widely used are the organic peroxides, e.g. benzoyl peroxide, and the azo compounds, e.g. \( \text{a:a'-azo-isobutyronitrile} \), although these are surpassed in activity by systems in which both oxidizing and reducing agents are present, e.g. hydrogen peroxide and ferrous ions in aqueous solution. The catalysts generally decompose giving two radicals, benzoyl peroxide \([\text{Ph.CO.O}]_2\) gives two \(\text{Ph.CO.O}\) radicals (Hey & Waters, Chem. Revs., 1937, 21, 179) and \(\text{a:a'-azo-isobutyronitrile} \ \text{CH}_3\text{C(\text{CH}_2)}_3\text{N=NN=C(\text{CH}_3)}_2\text{-CH}_3\) gives two \(\text{CN}\) radicals and nitrogen. \(\text{a:a'-Azo-isobutyronitrile} \) is a particularly good initiator for kinetic studies since it decomposes by a first order reaction, which is independent of solvent and catalyst concentration, and because it is not an oxidising agent, (Arnett, J.A.C.S., 1952, 74, 2027; Burke, U.S. Patent 2500023). A third method of introducing free-radicals into the system is the production of radicals by the photo-decomposition of the monomer itself, as was demonstrated by Jones and Melville (Proc. Roy. Soc., 1946, 187, 19) for
the photopolymerisation of methyl vinyl ketone.

\[
\text{CH}_3\text{-CO-CH=CH}_2 \quad \rightarrow \quad \text{CH}_2=\text{CH-} \cdot \text{C=O} + \cdot \text{CH}_3
\]

\[
\text{CH}_2=\text{CH-} \cdot + \cdot \text{COCH}_3
\]

The free-radicals initiate polymerisation by reacting with the double bond on the monomer. The odd electron of the free-radical interacts with the \( \pi \)-electron of the double bond which has a spin opposite to its own, eventually forming a normal electron pair bond with it; simultaneously the electron with the same spin is disengaged from the \( \pi \)-bond thus reconstituting a new free-radical which is capable of further growth. The activation can occur to give two different structures;

1/ \( R. + \text{CH}_2=\text{CHX} \rightarrow R-\text{CH}_2-\text{CHX} \quad \text{(A)} \)

2/ \( R. + \text{CHX=CH}_2 \rightarrow R-\text{CHX-CH}_2 \quad \text{(B)} \)

and the relative rates of the alternative processes should depend on the relative stabilities of the product radicals (A) and (B). In the radical (A) the substituent occurs on the carbon atom bearing the unpaired electron, and in this position it is able to provide resonance structures in which the odd electron appears on the substituent. This has the effect of stabilising the radical, the extent of such stabilisation depending on the capacity of the substituent for resonance. In radical (B) such stabilisation cannot occur and consequently radical (A) is ordinarily the most stable and its formation is more probable.

Either of these processes implies the incorporation of
fragments of the catalyst in the final polymer and this has been confirmed experimentally by the use of catalysts containing atoms that can be detected qualitatively and estimated quantitatively. Examples of this are the use of chloroacetyl peroxide (Price, J.A.C.S., 1942, 64, 1103), N-nitro-p-bromoacetanilide (Blomquist, ibid, 1943, 65, 2446), and α:α'-azo-isobutyronitrile labelled with carbon 14 (Arnett, ibid, 1952, 74, 2029).

Propagation: Considering only linear structures, i.e. neglecting for the moment branching and cross-linking, successive addition of monomer molecules, one after the other, can occur in either a regular or a random fashion. If they combine in an essentially regular manner then the polymer formed from a monomer CH$_2$=CHX would have one of the following structures

1) head-to-tail

\[
R-\text{CH}_2-\text{CH-CH}_2-\text{CH-CH}_2-\text{CH-}
\]

\[
\text{}\quad \text{X} \quad \text{X} \quad \text{X}
\]

2) head-to-head \tail-to-tail

\[
R-\text{CH}_2-\text{CH-CH-CH}_2-\text{CH}_2-\text{CH-}
\]

\[
\text{X} \quad \text{X} \quad \text{X} \quad \text{X}
\]

whilst a random addition would give

\[
R-\text{CH}_2-\text{CH-CH-CH}_2-\text{CH}_2-\text{CH-CH}_2-\text{CH-CH-CH}_2
\]

\[
\text{X} \quad \text{X} \quad \text{X} \quad \text{X} \quad \text{X} \quad \text{X}
\]

In the case of head-to-tail addition, the radical formed at the chain end has the same resonance energy as that of the initiating radical, and thus no energy changes are involved. This, however, is not the case if head-to-head growth occurs, since the resonance energy of the radical formed is less than that of the radical initiating the
reaction, whilst tail-to-tail growth produces a radical of resonance energy greater than that of the attacking radical. Since, however, head-to-head growth must always be followed by tail-to-tail or head-to-tail growth, it will be seen that head-to-tail propagation is the more favoured since it preserves the most stable radical ending.

The prevalence of the head-to-tail structure in vinyl polymers has been confirmed, both by chemical and physical means. Staudinger and Steinhofer (Ann., 1935, 517, 35) pyrolysed styrene at a temperature of 300° and obtained among the products

\[
\begin{align*}
\text{Ph} _2\text{CH}=\text{CH} _2, & \quad \text{Ph} _2\text{CH}=\text{CH}-\text{CH} _2\text{CH}=\text{CH} _2 \\
\text{Ph} _2\text{CH}=\text{CH} _2, & \quad \text{Ph} _2\text{CH}=\text{CH}-\text{CH} _2\text{CH}=\text{CH} _2 \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

but no products containing phenyl groups on adjacent carbon atoms. Marvel, Sample and Roy (J.A.C.S., 1939, 61, 3241) concluded that cyclopropane rings were formed by removal of halogen atoms from the chain when a dilute solution of poly-(vinyl chloride) in dioxane was treated with zinc.

Statistical calculations by Flory (J.A.C.S., 1939, 61, 1518) and Wall (J.A.C.S., 1940, 62, 803; 1941, 63, 821) indicate that a head-to-tail structure would result in 86.47% of the chlorine atoms being removed in this manner, whereas a random arrangement of the units would result in 81.6% of the chlorine atoms being so removed. Marvel and his co-workers found that they could remove between 84% and 87% of the chlorine and concluded that poly-(vinyl chloride) had a head-to-tail
structure. In the case of poly-(vinyl acetate) Marvel and Denoon (J.A.C.S., 1938, 60, 1045) hydrolysed the polymer to poly-(vinyl alcohol) and found that, within experimental error, the product consumed no periodic acid (which splits head-to-head linkages), indicating the absence of any but small numbers of such linkages.

\[ \text{HIO}_4 \]
\[ -\text{CH}_2-\text{CH} \longleftrightarrow \text{CH} \longleftrightarrow \text{CH}_2 \]
\[ \text{OH} \longleftrightarrow \text{OH} \]

Their results on these two polymers have been confirmed from X-ray diffraction patterns of these polymers in the crystalline state. Marvel and his co-workers also applied similar methods to poly-(methyl vinyl ketone) and a number of other polymers and have shown them to have a head-to-tail structure. This structure has not been proved for poly-(methyl methacrylate) and pyrolysis experiments give no indication as to the structure, since pyrolysis of poly-(methyl methacrylate) yields essentially pure monomer. Recently, however, Marvel, Weil, Wakefield and Fairbanks (J.A.C.S., 1953, 75, 2356) have shown that poly-(methyl α-bromoacrylate) and poly-(methyl α-chloroacrylate) both have a head-to-tail structure

\[ \text{COOCH}_3 \longleftrightarrow \text{COOCH}_3 \longleftrightarrow \text{COOCH}_3 \]

Marvel and his co-workers had earlier interpreted their results in terms of a head-to-head structure, but revised this view on reconsidering their evidence and new evidence available. One of the results which led to this earlier anomalous conclusion was the fact that all the halogen could be removed by refluxing with zinc dust,
whereas statistical calculations showed that for a head-to-tail structure only 86.4% of the halogen should be removed by formation of cyclopropane rings. The statistical calculations were based on the assumption that no other halogen-removing reactions occurred, but this is inapplicable to the present case since the infra-red spectrum of the product shows the presence of lactone carbonyl groups which are formed by a halogen-removing reaction. The polymer undergoes partial lactonization under similar conditions to that used for poly-(a-chloroacrylic acid) (Minsk and Kenyon, J.A.C.S., 1950, 72, 2650) and comparison of the infra-red spectrum of the lactonized polymer with that of the model compound (I) suggests that the polymer has a head-to-tail structure, although the closeness of the values for the lactone carbonyl bands for (I) and (II) prevent a definite conclusion based on this evidence.

Conclusive evidence for a head-to-tail structure is obtained from oxidative degradation of the lactonized polymer. The polylactone was saponified and boiled with hydrogen peroxide in strong alkaline solution. The products, acetone, acetic acid, carbon dioxide, formic acid and a mixture of solid acids, mostly aconitic acid together with traces of citric and citraconic or itaconic acids, can only be explained on the basis of a primarily head-to-tail structure of poly-(methyl-a-bromoacrylate) and its saponification product,
since a head-head structure would be expected to yield some succinic acid none of which was obtained.

When the stabilising influence of the substituent (X) is not very large, the rate of head-to-tail growth may not be very much greater than that of the other processes and in such cases a small amount of head-to-head, tail-to-tail structures may be found in the polymer.

Proof of this fact comes from the work of Flory and Leutner (J. Polym. Sci., 1948, 2, 880; 1950, 5, 267) on poly-(vinyl alcohol), which they treated with periodic acid to split any 1:2 glycol groups present, reacetylated, and determined the change in molecular weight. From their results they calculated that 1-2% of head-to-head, tail-to-tail structures were present.

Termination: The growing polymer chain may be terminated in a number of different ways the principal processes being the following

a) Reaction of the free-radical end of one chain with a similar grouping in another chain.

b) Addition of initiator radical to the active chain end.

c) Termination by reaction with impurities such as oxygen, inhibiting agents, etc.

Extensive kinetic studies have shown that the most general types of termination involve bimolecular reaction, and are as follows:-
(1) The union of the radicals by a combination reaction

\[ 2 \text{R}-\text{CH}_2-\text{CHX} \rightarrow \text{R}-\text{CH}_2-\text{CHX-CHX-CH}_2-\text{R} \]

(2) A disproportionation reaction involving transfer of a hydrogen atom, giving one saturated molecule and one having an unsaturated terminal group.

\[ 2 \text{R}-\text{CH}_2-\text{CHX} \rightarrow \text{R}-\text{CH}=\text{CHX} + \text{R}-\text{CH}_2-\text{CH}_2\text{X} \]

There has been considerable controversy as to whether the disproportionation or the combination reaction preferentially occurs and evidence in support of both reactions has been obtained. In general both reactions occur but one predominates, as was shown to be the case for the polymerisation of methyl methacrylate (Bevington, Melville, and Taylor, J. Polym. Sci., 1954, 12, 449; Bamford and Jenkins, Nature 1955, 176, 78). This will be discussed in greater detail later.

**Chain Transfer**

In addition to the normal chain growth process the propagation step may be complicated by one or more possible chain transfer reactions. Interaction of a growing polymer radical with a monomer or solvent molecule usually occurs in such a way that the free-radical character of the growing chain is destroyed whilst the molecule attacked gives rise to a new free-radical, which is capable of initiating a new polymer chain. In all cases the reaction involves migration of an atom (usually hydrogen in the case of monomer transfer) between the molecule and the attacking radical. If the molecule attacked is saturated, then such a migration can only occur from the molecule to the growing radical.
but with an unsaturated molecule such as the monomer, transfer of the hydrogen may take place in either direction.

\[
\begin{align*}
R-CH_2-CHX + CH_2=CHX &\rightarrow R-CH_2-CH_2X + CHX=CH \\
or R-CH_2-CHX + CH_2=CHX &\rightarrow R-CH=CHX + CH_3-CHX
\end{align*}
\]

If the new chain is derived from the monomer it would contain no catalyst fragments, but if it is initiated by the solvent transfer process then it would contain fragments of the solvent molecule. This has been confirmed experimentally by solution polymerisations carried out in halogenated solvents (Breitenbach and Maschin, Z. Physikal Chem., 1940, A, 187, 175) and in nitrobenzene and nitrothiophene (Price and Kell, J.A.C.S., 1942, 64, 1103; 1943, 65, 757; 2380). Breitenbach and Maschin have shown that, in the polymerisation of styrene in carbon tetrachloride, transfer with the solvent occurs readily, and that each polymer molecule contains four chlorine atoms.

\[
\begin{align*}
\dot{R}_n + CCl_4 &\rightarrow P_n Cl + \cdot CCl_3 \\
CCl_3 + M &\rightarrow RCCl_3 \rightarrow R_n \cdot CCl_3 \\
R_n CCl_3 + CCl_4 &\rightarrow ClP_n CCl_3 + \cdot CCl_3
\end{align*}
\]

where \( R \), \( M \), and \( P \), represent the growing radical, the monomer and the polymer respectively.

The phenomenon of chain transfer in the free-radical polymerisation of vinyl monomers was first suggested by Flory (J.A.C.S., 1937, 59, 241) from a study of the thermal and photopolymerisation of
methyl methacrylate. Later Mayo (J.A.C.S., 1943, 65, 2324) and others (Tobolsky et al, Ann. New York Acad. Sci., 1943, 44, 371; Medvedev et al, J. Russ. Phys. Chem. Soc., 1943, 17, 391) established the principle of the chain transfer activity of solvents and elucidated the kinetics of the process. The occurrence of chain transfer does not greatly affect the overall rate of polymerisation, since the active centre is maintained, but in general the average molecular weight or degree of polymerisation is considerably reduced.

In the polymerisation of esters of methacrylic acid, results show that the transfer reaction is generally of little importance, despite the fact that transfer with the α-methyl substituent would give rise to a resonance stabilized structure.

\[
\begin{align*}
\text{R-CH}_2\text{CH} = \text{C}X + \text{CH}_2 = \text{C}X & \rightarrow \text{R-CH} \text{CH}_2 \text{CH} \text{X} + \text{CH}_2 = \text{C}X \\
\text{CH}_2\text{C}X & \Downarrow \text{CH}_2
\end{align*}
\]

Branching, Crosslinking and Depolymerisation.

Not only can a growing chain transfer its activity to a monomer or solvent molecule, but it can also transfer its activity to a "dead" polymer molecule, i.e. a polymer molecule that is already terminated, as first suggested by Tobolsky and Taylor (J.A.C.S., 1945, 67, 2063). The active centre can be transferred to any position along the chain as well as to the chain ends. If this occurs the new radical in the chain can give rise to branching and crosslinking of the chain, as follows:-
Branching:

\[ \text{R-CH}_2\text{-CHX-R}^* + \text{R}^-\text{-CH}_2\text{-CHX} \rightarrow \text{R}^4\text{CH}_2\text{-CH}_2\text{-X} + \text{R-CH}_2\text{-CX-R}^* \]

Crosslinking:

In view of the steric requirements of the crosslinking process, the probability of the two radicals coming together in this way is very small and in general crosslinking is an infrequent process under normal polymerisation conditions. It is, however, more likely to occur if the polymer is heated at a high temperature for a time, since in this case transfer with the "dead" polymer will occur more readily. It also occurs more readily in the case of the polymerisation of the dienes, which polymerise leaving \( \equiv \text{double bonds in the chain} \), i.e.

\[ \text{R-[CH}_2\text{-CH}=\text{CH-CH}_2\text{-]}\] \( \text{-R}^* \quad \text{or} \quad \text{R-CH}_2\text{-CH-CH}_2\text{-CH-R}^* \]

The presence of free-radicals along the chain may also lead to depolymerisation by analogy with the disproportionation reaction.
This splitting may be followed by a continuous cleavage of the radical fragments formed, and thus the depolymerisation to monomer units is a chain process.

Experimental evidence that transfer can occur with "dead" polymer was obtained by Bevington and Melville (Nature, 1952, 170, 1026) using radioactive tracers in the thermal polymerisation of styrene in the presence of its own polymer. They showed that the branched polymer formed was produced as a result of transfer to the added polymer.

**OXYGEN IN POLYMERISATION.**

The effect of oxygen on the polymerisation of vinyl monomers gives rise to several conflicting results. Small traces of oxygen frequently accelerate the polymerisation in the absence of other initiators (Staudinger and Urich, Helv. Chim. Acta., 1929, 12, 1107), whilst it has also been shown that the presence of excess oxygen results in the retardation or inhibition of the polymer reaction, (Price, J.A.C.S., 1945, 67, 1674; Kolthoff, ibid, 1945, 67, 1672; 1947, 69, 441; Staudinger, Schwalbach and Kohlschuetter, Ann. 1931, 488, 8; Ber., 1931, 64, 2091). Barnes (J.A.C.S., 1945, 67, 217) studied the reaction between oxygen and a large number of vinyl monomers and found that in all cases oxygen was absorbed and that peroxides were formed. He also found (J.A.C.S., 1950, 72, 210) that a low molecular weight polymeric peroxide
with probable structure \[
\left[ \begin{array}{c}
\text{CH}_3 \\
\text{COOCH}_3
\end{array} \right]_n
\]
was formed from methyl methacrylate. Oxygen may function in one of two ways, it may deactivate the chain by formation of stable peroxides, or the peroxides formed may generate new free-radicals as a result of their thermal instability and thus initiate polymerisation. Which process occurs depends on the concentration of oxygen and the conditions of the polymerisation.

THE GEL EFFECT IN VINYL POLYMERISATION

In 1937 Norrish and Brookman (Proc. Roy. Soc., 1937, A, 171, 1947) observed that, in the free-radical bulk polymerisation of methyl methacrylate, the rate of polymerisation underwent a marked acceleration at about 10-20 percent. conversion of monomer to polymer, but returned to normal at approximately 90 percent. conversion. A similar acceleration is observed during the course of the homogeneous polymerisation of many other vinyl monomers, styrene being a notable exception, but its occurrence in methyl methacrylate has received the most attention.

It was found that not only was the maximum rate approximately ten times the initial rate, but also that the average molecular weight of the product was markedly increased. This effect was thought, at first, to be due to local overheating but in 1942 Norrish and Smith (Nature, 1942, 150, 336) showed that the acceleration was still present when the monomer was polymerised using conditions where overheating could not occur. They also carried out the polymerisation in various
solvents and found that although the rate acceleration was present when
the polymerisation was carried out in poor solvents, in good solvents
practically no increase of rate occurred. Trommsdorff, Kohle and Lagally
(Makromol Chem., 1948, 1, 169) found that the initial rate of bulk
polymerisation could be substantially increased and the "Gel effect"
prematurely induced by the addition of preformed polymer or cellulose
tripropionate to the reaction mixture and proposed the following explana-
tion. They suggested that the increase in viscosity of the medium, due
to the long chains produced, could eventually result in the rate of
diffusion of the radicals becoming the controlling factor in the rate of
reaction. The rate of the propagation reaction, which is the rate
determining stage, will be much less affected than the rate of the
termination reaction, since the former involves only the migration of
the comparatively small monomer molecule to the radical ending of the
large polymer chain, whilst the latter involves the migration together
of two large polymer chains. Thus the polymerisation rate increases,
since the propagation process continues for much longer than is normally
the case, using up much more monomer. At approximately 90 percent
conversion; when the medium is extremely viscous, the movement of the
monomer molecules is much slower and thus also is the rate of the
propagation reaction, with the result that the overall rate of poly-
merisation also decreases.

This explanation is consistent with the experimental evidence
available particularly that of polymerisation in various solvents. In
poor solvents the growing chains are clumped or coiled and whilst the
monomer can still diffuse into the coil and attack the radical chain ending, the radical is protected from termination. In good solvents the rate of diffusion of radicals can never become the controlling factor in the rate of the reaction and thus the rate increase is absent. Addition of chain transfer reagents to the reaction mixture usually prevents the occurrence of the "Gel effect". This is due to the fact that the chain transfer agents reduce the primary chain length of the polymer and thus the medium of the reaction does not become highly viscous. No quantitative interpretation of this effect is yet available, because of the absence of an adequate theory for diffusion-controlled reactions of large molecules.

**Effect of Structure on the Polymerisation of Methacrylates.**

The effect on the rate of polymerisation of increasing the alcohol chain length has been investigated in the case of esters of methacrylic acid. It was found that the rate of the propagation reaction remain practically constant but that the rate of the termination reaction decreased, as the alcohol chain lengthened. Burnett, Evans and Melville (Trans. Farad. Soc., 1953, 49, 1105) have explained this on the basis of steric hindrance. They state that "examination of a model of the n-butyl methacrylate molecule shows that the alkyl group screens the double bond only very slightly, but with the corresponding radical there is considerable obstruction". Therefore, in the inter-radical reaction involved in termination where the α-carbon atom is the reaction point for both reactants, the steric effect would be expected to be more marked.
than in the radical-molecule reaction involved in propagation where the β-carbon atom is the point of the reaction in the monomer molecule.

\[
\begin{align*}
R_n\text{CH}_2\text{C}^* + \text{CH}_2=\text{C}^* & \xrightarrow{\text{propagation}} R_n\text{CH}_2\text{C}-\text{CH}_2\text{C}^* \\
R_n\text{CH}_2\text{C}^* + \text{C}-\text{CH}_2\text{R}_m & \rightarrow \text{termination}
\end{align*}
\]
THE KINETICS OF VINYL POLYMERISATION BY A FREE-RADICAL MECHANISM

In the derivation of the kinetics of free-radical vinyl polymerisation several simplifying assumptions must be made. The first is that the rate of the propagation and termination reactions are independent of the length of the growing polymer chains, and the second is that the average chain length is great. The use of this second assumption in calculations amounts to putting the rate of monomer consumption equal to the rate of propagation, and the justification for this and the first assumption is that they lead to equations which are in accord with experimental results. The third assumption is the use of the 'stationary state' method, first introduced by Bodenstein (Z. Physikal Chem., 1913, 85, 1929). In the stationary state the reaction is proceeding at a constant rate and any radical intermediates present are formed at the same rate as they are destroyed. This means that the concentration of radicals present is independent of time, and if \([R']\) is used to denote the concentration of the radicals, then \(d[R']/dt = 0\). This concentration cannot always be experimentally measured but it is usually possible to determine the rate of formation and destruction of radicals in terms of the initial reactant concentrations.

For a polymerisation initiated by a typical peroxide radical-initiator, the reaction is represented by the following scheme, neglecting any transfer reactions and assuming unimolecular initiation:
\[
\begin{align*}
\text{Cat} & \xrightarrow{k_1} 2R_c^* & \text{INITIATION} \\
R_c^* + M & \xrightarrow{k_2} R_1^* \\
R_1^* + M & \xrightarrow{k_2} R_2^* \\
R_m^* + M & \xrightarrow{k_2} R_{m+1}^* \\
R_n^* + R_m^* & \xrightarrow{k_{3c}} P_{m+n} \\
R_n^* + R_m^* & \xrightarrow{k_{3d}} P_n + P_m \\
\end{align*}
\]

\[
\begin{align*}
\{ \text{PROPAGATION} \} \\
\{ \text{TERMINATION} \} \\
\end{align*}
\]

where Cat. = initiator, \( R_c^* \) = radical produced from initiator, \( R_m^* \) = radical of \((m)\) monomeric units, \( M \) = monomer molecule, and \( P \) = terminated polymer.

For kinetic purposes the two termination processes are equivalent and it is usually convenient to combine them as

\[
R_m + R_n \xrightarrow{k_{3c} + k_{3d}} P_{m+n} + P_n + P_m = k_3
\]

Let \([R']\) be the total concentration of free-radicals of all types.

Then

\[
[R'] = \sum_n [R_n^*]
\]

At the stationary state the rate of formation of radicals is equal to their rate of disappearance.

Therefore

\[
k_1 [\text{Cat}] = [R']^2 k_3 \quad (1)
\]

and therefore

\[
[R'] = \left( \frac{k_1}{k_3} \right)^{1/2} [\text{Cat}]^{1/2} \quad (2)
\]

Also the rate of the reaction (i.e. conversion of monomer to polymer)
is given by

\[-\frac{d[M]}{dt} = k_2 [R^*] [M]\]

and substituting for [R*] from equation (2)

\[-\frac{d[M]}{dt} = k_2 \left(\frac{k_1}{k_3}\right)^{\frac{1}{2}} [Cat]^{\frac{1}{2}} [M]\]

Introducing the kinetic chain length \(\bar{v}\), which is the average number of monomer molecules consumed per polymer chain started, we have

\[\bar{v} = \frac{-d[M]}{dt} \times \frac{1}{k_1 [Cat]}\]

therefore

\[\bar{v} = k_2 \frac{[M] [R^*]}{k_1 [Cat]}\]

substituting for \(k_1 [Cat]\) from (1) we have

\[\bar{v} = k_2 \frac{[M] [R^*]}{k_3 [R^*]^2}\]

again substituting for \([R^*]\) from (2) gives

\[\bar{v} = k_2 \frac{[M]}{\left(k_1 k_3\right)^{\frac{1}{2}} [Cat]^{\frac{1}{2}}}\]

The relation between \(\bar{v}\) and the average degree of polymerisation \(\bar{P}\) depends upon the relative importance of chain termination by dis-
proportionation and combination, the former giving $\bar{P} = \bar{v}$ and the latter $\bar{P} = 2\bar{v}$.

Equations (3) and (4) show that for a catalysed polymerisation the rate of polymerisation is PROPORTIONAL to, and the average degree of polymerisation INVERSELY PROPORTIONAL to, the square root of the catalyst concentration.
HISTORICAL INTRODUCTION AND KINETICS

When two different polymerisable monomers are mixed together in the presence of an initiator, the resulting macromolecules in general contain both types of monomer, since the growing chain free-radical can attack either type of monomer. Such a reaction is called a copolymerisation and the resulting product is a copolymer.

Although the first deliberate copolymerisation reactions were carried out about 1910-1912, when the research on the polymerisation of the diolefins intensified, it was not until 1937 that the inclusion of both monomers in the final chain was actually demonstrated (Norrish and Brookman, Proc. Roy. Soc., 1937, A163, 205). A number of early workers studied the copolymerisation of a series of vinyl derivatives and dienes, but the industrial application of the products was not recognised until 1917, when Baeyer (Brit. Patent 27361) patented a method for the copolymerisation of isoprene and butadiene. The workers in this field soon found that copolymerisation gave rise to modifications in the properties of the original polymers, and that in this way copolymers having many desirable properties could be obtained.

Among the many surprising things discovered about the copolymerisation reaction during these early years was the fact that 1:2-disubstituted ethylenes, which showed no tendency to homopolymerise, would often copolymerise readily with other vinyl monomers. A notable example of this is the copolymerisation of maleic anhydride and styrene,
first reported by Voss and Dickhauser (German Patent, 540101), to give a copolymer with an alternating structure. Even more surprising was the discovery that a copolymer could often be prepared from two 1:2-disubstituted olefins neither of which would undergo homopolymerisation, as for example in the copolymerisation of maleic anhydride and trans-stilbene, (Wagner-Jauregg, Ber., 1930, 63, 3213).

During these years the emphasis of the research on copolymers was on the preparation and development of the products and no systematic attempt was made to elucidate the mechanism of the reaction until about 1936. Previous to this, however, during the course of numerous copolymerisation experiments, certain peculiarities about the reaction were observed. One notable fact was that a particular monomer had different copolymerisation tendencies with different monomers, i.e. it copolymerised more easily with some monomers than with others. A second feature of the reaction was the fact that the individual components of the monomer mixture were being used at different rates and that copolymer samples removed at different degrees of conversion contained the two components in different ratios. Further evidence of this fact was obtained in 1937, when Staudinger and Schneider (Ann., 1939, 541, 151) reported the fractionation of a vinyl chloride-vinyl acetate copolymer produced from a 1:1 mixture of the monomers. The composition of the fractions varied between 3:1 and 1:2 with none of them having the monomers present in the 1:1 ratio of the initial mixture. This indicated that one of the monomers was more reactive than the other and thus the copolymer initially formed contained more of this monomer. However, as
the reaction proceeded the proportion of the more reactive monomer in the mixture decreased and, therefore, the copolymer formed towards the end of the reaction became richer in the less reactive monomer.

The first attempt at an explanation of these facts was by Dostal (Monatsh, 1936, 69, 424), who regarded the behaviour of the free-radical chain-ending as depending entirely upon the terminal group (i.e., the monomer unit last added to the chain) and to be independent of the length or overall composition of the chain. If these assumptions were true only two types of free-radical chain endings would exist in the copolymerisation of any monomers, and for long polymer chains the formation of the copolymer would be determined by competition between the four propagation reactions represented as follows, where \( M_1 \) and \( M_2 \) are the monomers and \( M_1^* \) and \( M_2^* \) are the radicals derived from \( M_1 \) and \( M_2 \) respectively.

\[
\begin{align*}
(i) \quad & M_1^* + M_1 \xrightleftharpoons[k_{11}]{k_{12}} M_1^1M_1^1 \\
(ii) \quad & M_1^* + M_2 \xrightleftharpoons[k_{12}]{k_{12}} M_1^1M_2^* \\
(iii) \quad & M_2^* + M_2 \xrightleftharpoons[k_{22}]{k_{22}} M_2^2M_2^* \\
(iv) \quad & M_2^* + M_1 \xrightleftharpoons[k_{21}]{k_{21}} M_2^1M_1^* 
\end{align*}
\]

Rate equals

\[
\begin{align*}
(i) \quad & k_{11}[M_1][M_1^*] \\
(ii) \quad & k_{12}[M_2][M_1^*] \\
(iii) \quad & k_{22}[M_2][M_2^*] \\
(iv) \quad & k_{21}[M_1][M_2^*] 
\end{align*}
\]

Although Norrish and Brookman (Proc. Roy. Soc., 1939, 117, 147) produced experimental evidence, on the copolymerisation of styrene and methyl methacrylate, which supported Dostal's theory, in applying their results they made the further assumption, later shown to be an
over-simplification, that the overall steady state radical concentration in a copolymer mixture would depend only on the concentration of the catalyst and would not depend on the composition of the mixture itself. Thus their results did not lead to a final clarification of the mechanism of the reaction and further work was necessary before the mechanism was finally elucidated. The next important step came in 1941 when Wall (J.A.C.S., 1941, 63, 1862) attacked the problem of the copolymer composition as a function of the monomer ratio. He considered that there were only two distinct propagation steps in the copolymerisation of two monomers, namely the attack on each of the two monomers by the growing chain free-radical. He thus made no distinction between the two types of growing free-radical present. If $M_1$ reacts with the growing free-radical with a rate constant $k_1$, and $M_2$ with rate constant $k_2$, then Wall expressed the ratio of the disappearance of the two monomers as

$$\frac{d[M_2]}{d[M_1]} = \frac{\alpha [M_2]}{[M_1]}$$

where $[M_1]$ and $[M_2]$ represent the molar concentrations of the monomers and $\alpha = k_2/k_1$ and is constant.

At first experimental evidence by Marvel and his co-workers (J.A.C.S., 1942, 64, 2356; 1943, 65, 2054; 1944, 66, 2135) seemed to confirm the conclusions drawn from this simple relation, but later studies showed that $\alpha$ was not constant but varied with the initial monomer mixture.

In 1944 the mechanism of the copolymerisation reaction was
finally solved by three independent groups of workers who developed the 'Copolymer Composition Equation', (Mayo and Lewis, J.A.C.S., 1944, 66, 1594; Wall, ibid, 2050; Goldfinger and Alfrey, J. Chem. Phys., 1944, 12, 205). This equation was also subsequently derived by Goldfinger and Kane, (J. Polym. Sci., 1948, 2, 462) from a purely statistical approach. These workers reverted to the four propagation steps (i), (ii), (iii), and (iv) which had been suggested by Dostal and Norrish and Brookman.

For the rate of disappearance of monomer \( M_1 \), we have, neglecting any loss in the initiation process,

\[
\frac{-d[M_1]}{dt} = k_{11}[M_1][M_1'] + k_{21}[M_1][M_2']
\]

and for \( M_2 \)

\[
\frac{-d[M_2]}{dt} = k_{22}[M_2][M_2'] + k_{12}[M_2][M_1']
\]

In a steady state of copolymerisation (as in polymerisation) each type of free-radical is maintained at a certain level of concentration; that is, the rate of formation of \( M_1' \) is equal to the rate of consumption of \( M_1' \) and likewise for \( M_2' \).

\[
\frac{-d[M_1']}{dt} = k_{12}[M_1'][M_2] - k_{21}[M_2'][M_1] = 0
\]

and

\[
[M_2'] = \frac{k_{12}}{k_{21}} \frac{[M_1'][M_2]}{[M_1]}
\]
substituting for \([M']_2\) in (4) and (5) we have

\[
\frac{-d[M_1]}{dt} (k_{11}[M_1] = k_{12}[M_2])
\]

(8)

and

\[
\frac{-d[M_2]}{dt} = [M'_1] \left( k_{12}[M_2] = \frac{k_2k_{12}[M_2]^2}{k_{21}[M]} \right)
\]

(9)

dividing (8) by (9) gives

\[
\frac{d[M_1]}{d[M_2]} \frac{k_{21}}{k_{12}} \frac{k_{11}[M_1] + k_{12}[M_2]}{k_{21}[M_1] + k_{22}[M_2]}
\]

(10)

Introducing the parameters \(r_1 = k_{11}/k_{12}\) and \(r_2 = k_{22}/k_{21}\) we have

\[
\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}
\]

(11)

The parameters \(r_1\) and \(r_2\) are called the monomer reactivity ratios and are in fact measures of the preference of a radical to attack a monomer of its own type or of a second type. Thus if \(r_1 > 1\) then radical with type \(M_1\) end group will attack monomer \(M_1\) rather than \(M_2\). Since equation (11) is derived from the propagation steps only, changing the mode of initiation (provided e.g. free-radical reaction is maintained and the propagation mechanism is unaltered) should have no effect on the results obtained, a fact which has been substantiated experimentally.

It follows from equation (11) that the ratio \(d[M_1]/d[M_2]\) is not equal to the ratio \([M_1]/[M_2]\) except when both reactivity ratios are unity, or for a special value of \([M_1]/[M_2]\). When the feed
composition and the copolymer composition are equal, equation (11) reduces to

\[
\frac{[M_1]}{[M_2]} = \frac{1-r_2}{1-r_1}
\]

value of \([M_1]/[M_2]\) is called an 'azeotropic' copolymer, by analogy with binary distillation. At all other values of \([M_1]/[M_2]\) the reaction mixture becomes relatively richer in one or other of the monomers with a corresponding drift in the composition of the copolymer formed.

Equation (11) is valid at any percentage conversion for relating the instantaneously forming copolymer with the instantaneous monomer mixture. It is often important, however, to calculate the average total copolymer composition for a known percentage conversion of the total monomer mixture and, since the composition of the copolymer and the feed are continually changing, this requires a complex calculation. It involves the use of the integrated form of equation (11), first obtained by Mayo and Lewis (J.A.C.S., 1944, 66, 1594), or more conveniently the use of the method of graphical or numerical integration developed by Skeist (J.A.C.S., 1946, 68, 1781), who expressed equation (11) in the form

\[
\frac{d[M_1]}{d([M_1]+[M_2])} = F_A = \frac{r_1f_A^2 + f_Af_B}{r_2f_A^2 + 2f_Af_B + r_1f_A^2}
\]

where \(f_A\) and \(f_B\) are the molecular fractions of the monomers \(M_1\) and \(M_2\), respectively, in the feed. The method is, however, very complicated and does not concern us here.
STRUCTURE AND REACTIVITY IN ADDITION COPOLYMERISATION.

The chemical structure of a monomer can affect the copolymerisation behaviour of that monomer in three different ways:

(1) by steric hindrance
(2) by resonance stabilisation
(3) by polar effects.

(1) Steric hindrance: The influence of steric hindrance on the copolymerisation of vinyl monomers can most readily be observed by comparing the copolymerisation behaviour of di-substituted olefins, where the substituents are in the 1:1 and the 1:2 positions respectively. In general, for a monomer of the type $\text{CH}_2=\text{CHY}$ the addition of a second substituent on the $\alpha$-carbon atom increases the reactivity of the monomer but the addition of a substituent on the $\beta$-carbon atom markedly decreases this factor. The magnitude of the variation in reactivity can most probably be explained on the basis of the steric hindrance produced by the substituent in the 2 position. From a consideration of the two general reactions

$$\text{R-CH}_2\cdot\text{CHY} + \text{CHX} = \text{CHX} \rightarrow \text{R-CH}_2\cdot\text{CHY-CHX-CHX}$$

and

$$\text{R-CH}_2\cdot\text{CHY} + \text{CH}_2 = \text{CX}_2 \rightarrow \text{R-CH}_2\cdot\text{CHY-CH}_2\cdot\text{CX}_2$$

it can be seen that the steric hindrance which would occur between the $X$ and $Y$ groups would be expected to be much less in the second reaction that in the first.

An interesting aspect of the copolymerisation of
disubstituted olefins is the different reactivities exhibited by cis- and trans-isomers of the same monomer. Marvel and Schertz (J.A.C.S., 1943, 65, 2054; 1944, 66, 2135) noted that diethyl fumarate entered into copolymerisation more easily than the maleic ester, although the cis-isomer, being the least stable, would in general be expected to be more reactive. A similar result is obtained with cis- and trans-stilbene and Mayo and Lewis (J.A.C.S., 1948, 70, 1533) have ascribed this result to the steric inhibition of resonance in the radical adduct formed with the cis-isomer. They point out that when the radical $R^\cdot$ adds to the fumarate the following resonance configurations are possible.

![Resonance configurations](image)

This can only occur if both the carbonyl groups are coplanar, a condition that is not possible in the cis-maleic ester. A similar argument holds for the cis- and trans-stilbenes, in this case the phenyl groups being coplanar in the trans-but not in the cis-isomer.

(2) Resonance stabilisation: The amount of resonance stabilisation of the radical adduct, which is formed by reaction of the monomer and the growing chain end, is an important factor in determining the reactivity of a vinyl monomer, since the reaction producing the most stable product is in general the favoured one. Mayo and Walling (Chem. Revs., 1950, 46, 191) conclude, from a study of the monomer reactivity ratios, that for
the monomer CH₂=CHY the reactivity of the monomer is given by the following order, where Y =

\[-C_6H_5 > -CH=CH_2 > -COCH_3 > -CN > -COOR > -Cl > \text{other} > -OCOCH_3\].

Furthermore an α-methyl group generally increases the reactivity, e.g.
methyl methacrylate > methyl acrylate and methacrylonitrile > acrylonitrile.

In general a given substituent is considerably more effective in stabilising a radical than in stabilising the molecule from which the radical is formed, and, therefore, the important factor in determining the monomer reactivity ratios is not the stabilisation of the monomer or the radical but the change in resonance energy in going from one to the other. Complications may, however, arise in this general scheme when substituents are introduced into the aromatic ring. Thus a single ortho-chlorine atom substituted into styrene increases the reactivity of the monomer, whilst the introduction of a second ortho-chlorine atom markedly reduces its activity. This is attributed to the fact that the second chlorine atom prevents the side chain lying in the same plane as the ring.

(3) Polar effects: The third factor of importance in the relation between reactivity and structure is the electrical polarity of the double bond. The theory of this factor has been developed by Price (J. Polym. Sci., 1946, 1, 83 and subsequent papers) and Alfrey and Price have endeavoured to express the monomer reactivity ratios in terms of the electrostatic interaction between permanent charges, particularly to explain the alternating effect in copolymerisation. A substituent such as -C≡N would be expected to withdraw electrons from the double bond
giving it a positive character, and Price has suggested that the free-radical formed from such a monomer would also have positive character. Similarly a substituent such as -Ph, -OCH₃, or -CH₃ is able to donate electrons (the first two electromerically, the last by hyperconjugation) giving a radical with negative characteristics. Thus a free-radical with a positive character would be expected to exhibit a particular preference for a monomer with negative character and vice versa. The Alfrey-Price treatment of the polar effects has been criticised by Mayo and Walling (J. Polym. Sci., 1948, 3, 895) on the grounds that it would predict a pronounced dependence of the monomer reactivity ratios upon the dielectric constant of the medium, a fact which is not observed. Walling et al. (J.A.C.S., 1948, 70, 1537) suggest that the transition state is stabilised by contribution of the structures arising from electron transfer between radical and monomer, e.g. for the polymerisation of maleic anhydride and styrene, mesomeric structures of the type

\[
\begin{align*}
\text{Ph} & \quad \text{CH}^+ \\
\text{CH} & \quad \text{O}^0
\end{align*}
\]

may exist and contribute to the transition state.

The theory of the effect of polar groups has not been finally settled and a large amount of experimental work has still to be carried out before any of the current theories can be finally accepted.
STEREOCHEMICAL ASPECTS OF ADDITION POLYMERISATION.

Vinyl polymers having the structure \((-\text{CH}_2\text{-CX}_2\text{-Y}_n\) are subject to a further element of dissymmetry in addition to that arising from the variation of head-to-tail, tail-to-tail etc. arrangements. The substituted carbon atom is asymmetric and as such can exist in enantiomeric forms, both of which occur in a more or less random sequence along the polymer chain in a normal free-radical polymerisation where no sterically-directive influences affect the course of the polymerisation. In the fully extended polymer molecule having the chain atoms in the hypothetical planar zig-zag arrangement the substituents \(\text{Y}\) (or \(\text{X}\)) may all occur on one side of the chain or some may occur on one side and some on the other. Thus three distinct types of arrangement are possible for the units in a vinyl polymerisation.

1. Where all the substituent groups \(\text{Y}\) are on the same side of the plane of the polymer chain:

\[
\begin{align*}
\text{Y} & \quad \text{Y} & \quad \text{Y} & \quad \text{Y} & \quad \text{Y} \\
\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 \\
\text{X} & \quad \text{X} & \quad \text{X} & \quad \text{X} & \quad \text{X}
\end{align*}
\]

2. Where the \(\text{Y}\) groups are alternatively above and below the plane of the polymer chain:

\[
\begin{align*}
\text{Y} & \quad \text{X} & \quad \text{Y} & \quad \text{X} \\
\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 \\
\text{X} & \quad \text{Y} & \quad \text{X} & \quad \text{Y}
\end{align*}
\]

3. Where the \(\text{Y}\) groups are randomly arranged on both sides of the polymer chain:

\[
\begin{align*}
\text{X} & \quad \text{Y} & \quad \text{Y} & \quad \text{X} & \quad \text{X} \\
\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 & \quad \text{C}-\text{CH}_2 \\
\text{Y} & \quad \text{X} & \quad \text{X} & \quad \text{X} & \quad \text{Y}
\end{align*}
\]
These three arrangements have been designated 'isotactic', 'syndiotactic' and 'atactic' respectively by Natta (J.A.C.S., 1955, 77, 1708). The presence of stereoisomeric structures in vinyl polymers has been recognised for many years (Staudinger "Die Hochmolekularen Organische Verbindungen", Julius Springer, Berlin, 1932, p. 114; Marvel et al., J.A.C.S., 1943, 65, 1647; Huggins, ibid 1944, 66, 1991) and it is considered that the irregular structures produced under normal free-radical polymerisation conditions are primarily responsible for the largely amorphous character of most vinyl polymers, since polymer chains with asymmetric carbon atoms in irregular orientation to one another would be incapable of packing together in a perfectly crystalline array. Evidence of this fact is the recent work by Natta and his co-workers (J. Polymer Sci., 1955, 16, 143, and subsequent papers) on the polymerisation of \( \alpha \)-olefins \([\ce{CH2=CHR}]\) and aromatic vinyl monomers, e.g. styrene and substituted styrenes, by various heterogeneous catalysts produced by reaction between aluminium alkyl compounds and transition metal halides, in particular titanium trichloride. These catalysts affect the propagation stage of the polymerisation and control the mode of addition of the monomer units to a growing chain, thus ensuring the regular arrangement of the units into an 'isotactic' or 'syndiotactic' structure. In this way Natta and his co-workers have produced polymers which are highly crystalline and consequently have higher melting points and better mechanical properties than the usual amorphous materials. X-ray analysis of the products has shown that, in poly-(styrene), long sequences of units are in the 'isotactic' arrangement and that 1:3-poly-(butadiene) has the 'syndiotactic' structure.
When a fully-substituted ethylene CKI=CAB is polymerised under normal free-radical conditions the total number of possible chain configurations of the resulting polymer is quite large, although this total may be greatly reduced by steric effects and by interactions between substituent groups. There are, however, a number of chain-forms in which the configurations of the successive atoms are arranged with a regular relationship to one another and these "configurations of maximum order" have been derived by Arcus (J.C.S., 1955, 2801) both for the polymerisation of a fully-substituted ethylene and for the polymerisation of partially-substituted ethylenes. He based his calculations on the assumptions that the step-wise addition of monomer units to the growing chain end is controlled by three steric factors; (1) whether addition is cis- or trans- (2) the mode of presentation of the monomer to the chain end (3) whether initiation was D or L. In addition he also made the assumptions that only head-to-tail polymerisation occurred, and that in any individual polymerisation addition is always either all cis- or all trans- and the mode of presentation of the monomer is always the same. In the initiation process when an ion or radical reacts with an olefin \( I\begin{array}{c} C=C \end{array}\) a type of three membered ring intermediate is set up in which the radical or ion \( R \) is bonded to both carbon atoms of the original double bond \( I\begin{array}{c} C=C \end{array}\) (Roberts and Kimball, J.A.C.S., 1937, 52, 947; Bawn, Ann. Reports 1950, 47, 36; Collinson and Dainton ibid, 1953, 50, 62). This is a resonance hybrid of the forms

\[
\text{cis-} \quad I\begin{array}{c} C=C \end{array}_K \quad \text{and} \quad I\begin{array}{c} C=C \end{array}_K
\]

in which the three membered ring is
perpendicular to the plane occupied by the groups I, K, A, and B. The addition of the second monomer unit to this three membered ring can be cis or trans-to R, although the experimental evidence indicates that addition to a double bond is normally trans-(McKenzie, J.C.S., 1912, 101, 1196; Winstein & Lucas, J. A.C.S., 1939, 61, 1576, 2845). Also the monomer unit, in adding to the chain end, can be presented in one of two ways, either I\(\overset{K}{C}C=\overset{B}{A}\) or I\(\overset{I}{C}C=\overset{K}{A}\). Further, the initial attack by the radical or ion on the olefin can occur in two ways giving rise to I\(\overset{R}{C}C=\overset{A}{A}\) or I\(\overset{K}{C}C=\overset{B}{B}\) with equal probability. These two adducts give rise to two series of polymeric chains which are enantiomeric with each other and which are designated D and L respectively. Thus these three steric factors give rise to eight alternative configurations, having maximum regularity, which are represented by the Fischer projection formulae, shown in Figs. (1 - 8). On inspection of these configurations it can be seen that there are four pairs of enantiomeric chains, each pair diastereoisomeric with the others. None of these configurations can give rise to a polymer with an optically active main chain, since for isolated sections of the chains enantiomeric pairs are identical and configurations (1), (5), (4) and (8) contain many planes of symmetry.

For a normal vinyl polymerisation giving a polymer of structure (CH\(_2\)-CAB-) it can be shown, by a simplification of figs. 1 - 8 (by substituting I and K by H), that only four different configurations arise from an application of the three steric factors. These are represented in
CONFIGURATIONS OF MAXIMUM ORDER FOR THE POLYMERISATION OF CIA=CKB

A → I I → A A → I I → A I → A A → I I → A A → I
K → B B → K B → K K → B B → K K → B B → K
A → I I → A I → A I → A I → A I → A I → A
K → B K → B K → B B → K B → K B → K
A → I I → A A → I A → I A → I A → I A → I
K → B K → B K → B B → K B → K B → K
A → I I → A A → I A → I A → I A → I A → I
K → B K → B K → B B → K B → K B → K

(1) (2) (3) (4) (5) (6) (7) (8)

CONFIGURATIONS OF MAXIMUM ORDER FOR THE POLYMERISATION OF CH₂=CXY

X → Y Y → X X → Y Y → X
H → H H → H H → H H → H
X → Y X → Y Y → X Y → X
H → H H → H H → H H → H
X → Y X → Y Y → X Y → X
H → H H → H H → H H → H
X → Y X → Y Y → X Y → X
H → H H → H H → H H → H
X → Y X → Y Y → X Y → X
H → H H → H H → H H → H

(9) (10) (11) (12)
figs. 9 - 12 and it can be seen that these are the structures termed 'isotactic' and 'syndiotactic'. Again none of these configurations are capable of giving an optically active main chain and it can be shown that the only polymerisations capable of producing such a polymer are the polymerisation of symmetrical and unsymmetrical cyclic olefins. In these polymerisations configurations are possible which contain no planes of symmetry and in which enantiomeric pairs are not identical.

**Termination:** The mode of termination of the polymerisation reaction also has an effect on the stereochemistry of the resultant polymer molecules, termination by combination between two polymer molecules producing several stereoisomeric types of molecule. In contrast, all other means of termination, including disproportionation, result in the formation of simple molecules whose symmetry properties are effectively represented by the Fischer projection formulae given above. Since, in the derivation of the chain structures above, cis-or trans-addition and the mode of presentation of the monomer were regarded as constant for any particular polymerisation, termination can only occur between the two enantiomeric forms of the chain present. If two chains of length (a) and (b) combine, then the resultant molecule approximates in structure to a molecule in which two sections of length (b) are united, together with a simply terminated molecule of length (a-b). In this way four types of chain can arise:

(i) In which both (a) and (b) are D initiated thus giving two molecules DD and D;

(ii) In which (a) is D initiated and (b) is L initiated giving rise to DL and D;
(iii) In which both (a) and (b) are L initiated giving molecules \text{LL} and \text{L};

(iv) In which (a) is L initiated and (b) is D initiated giving \text{LD} and \text{L}.

It can be seen that in certain instances termination by combination, results in the formation of a meso-type chain molecule, that is a molecule which has, ignoring the small irregularity of one tail-to-tail unit at the point of combination, the same 'pattern' or arrangement throughout the chain and which also has many 'local' planes of symmetry. This type of structure can, therefore, only arise from mutual termination of enantiomeric chains which themselves possess planes of symmetry. Thus mutual termination in a system containing the two enantiomeric 'isotactic' configurations, figs. (9) and (12) above, can give rise to this type of meso-structure, but only if the chains arise from terminations (ii) and (iv), since chains derived from (i) and (iii) have no exceptional symmetry. In a system containing the 'syndiotactic' configurations, figs. (10) and (11), all four types of chain combination (i - iv) give rise to a meso-structure, two of which however, those derived from (i) and (iii), have an uncompensated unit at one end of the molecule. If enantiomeric chains of exactly the same length combine then the molecule formed is meso in the classical meaning of the word, irrespective of the presence of planes of symmetry in the individual chains. This is, however, an event of low probability and such molecules will only form a very small percentage of the total number of molecules formed.

Copolymerisation: Arcus (J.C.S., 1957, 1189) has also derived the configurations of maximum regularity for an alternating copolymerisation,
firstly for a fully substituted ethylene, and then again by simplification for partially-substituted ethylenes. Here the mode of presentation of the second monomer (II) to the first monomer (I) as well as that of

(I) to (II) must be taken into account since in an alternating copolymerisation each monomer in turn is the last unit in the growing chain. The configurations of the copolymer chains is thus governed by four factors, each presenting two alternatives and sixteen configurations of maximum order arise as follows:

<table>
<thead>
<tr>
<th>Presentation of II to I</th>
<th>Presentation of I to II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. [1]</td>
<td>[2] Addition cis or trans</td>
</tr>
<tr>
<td>B. [1']</td>
<td>[2'] Initiation D or L</td>
</tr>
<tr>
<td>C. [2]</td>
<td>[2']</td>
</tr>
<tr>
<td>D. [2']</td>
<td></td>
</tr>
</tbody>
</table>

where the modes of presentation [1], [1'], [2], [2'] are considered independent.

In deriving the configurations for the more usual vinyl-type monomer Arcus has taken into account the tendency of the groups, on the chain end and the approaching monomer, to associate or to repel in the following way. In the case of the copolymerisation of the molecules (III) and (IV) the modes of presentation are represented as [3], [3'], [4] and [4'].

 '..
CONFIGURATIONS OF MAXIMUM ORDER FOR THE COPOLYMERISATION OF

(A) \( \text{CH}_2=\text{CAB} \) with \( \text{CH}_2=\text{CXY} \)

\[
\begin{array}{cccc}
X & Y & Y & X \\
H & H & H & H \\
A & B & A & B \\
H & H & H & H \\
X & Y & X & Y \\
H & H & H & H \\
A & B & A & B \\
H & H & H & H \\
X & Y & X & Y \\
H & H & H & H \\
A & B & A & B \\
H & H & H & H \\
R & R & R & R \\
\end{array}
\]

(B) \( \text{CH}_2=\text{CAB} \) with \( \text{cis-} \) and \( \text{trans-} \) \( \text{CHX} = \text{CHX} \)   D forms only

\[
\begin{array}{cccc}
X & H & H & X \\
H & X & X & H \\
A & B & A & B \\
H & H & H & H \\
X & H & H & H \\
H & X & X & H \\
A & B & A & B \\
H & H & H & H \\
X & H & H & H \\
H & X & X & H \\
A & B & A & B \\
H & H & H & H \\
X & H & H & H \\
H & X & X & H \\
A & B & A & B \\
H & H & H & H \\
X & H & H & H \\
H & X & X & H \\
A & B & A & B \\
H & H & H & H \\
R & R & R & R \\
\end{array}
\]

CIS   TRANS
Here, if $[3]$, in which $X$ is relatively close to $A$, is appropriate for the presentation of (IV) to (III), then $[4]$ not $[4']$ is probable for the presentation of (III) to (IV); similarly, if $[3']$, in which $X$ and $A$ are relatively remote, is appropriate, then $[4']$ not $[4]$ is probable; i.e. the application of the general case is limited in that here $[1]$ is coupled with $[2]$ and $[l']$ with $[2']$. The configurations derived from $A.$ and $D.$ are, therefore, more likely than those derived from the remaining forms, and these lead to only four different configurations represented by the Fischer projection formulae (figs. 13 - 16). The configurations for the copolymerisation of $\text{CH}_2=\text{CAB}$ with cis-and trans-$\text{CHX}=$CHX have also been derived by the same means and are represented by figs. (17 - 24). It can be seen that of these copolymerisations only those derived from the copolymerisation of $\text{CH}_2=\text{CAB}$ with cis-$\text{CHX}=$CHX are capable of giving rise to an optically active polymer, since in this case enantiomers are nowhere identical, nor do they contain any planes of symmetry.

The experimental problem of producing a polymer having an optically active main chain has been attempted by a number of workers, but it is only since the recent theoretical papers of Arcus (loc. cit.) and Frisch, Szwarc and Schwerch, (J. Polym. Sci., 1953, 11, 559) that the requirements for optical activity in polymers is now clear. The first, although indirect, attempt at this problem was by Walden (Z. Physikal Chem., 1896, 20, 383) who prepared optically active di-amyl itaconate and found no appreciable change in its optical rotation after polymerisation. The next attempt, after a gap of many years, was in 1943 by Marvel and his co-workers (J.A.C.S., 1943, 65, 1647), who attempted to prepare optically active
poly-(styrene), poly-(methyl methacrylate) and poly-(acrylonitrile) by the
use of optically active acyl peroxide free-radical initiators. In fact the
resulting polymers showed no sign of optical activity and were indistinguish­able from the products prepared using benzoyl peroxide. From a purely
statistical approach Frisch, Szwarc and Schuærch (loc. cit.) have shown that
this is the result to be expected and that an excess of one configuration in
the polymer chain can only be achieved by influencing the propagation step
of the reaction, a fact that has been confirmed by Natta's recent work (loc.
cit.).

All subsequent investigations in this field have involved the use
of optically active monomers, which affect the growth of the polymer chains
in three distinct ways. If the optically active monomer is the first unit
of a growing chain then the adduct formed between the monomer and the radical
by D initiation will be the diastereoisomer of that formed by L initiation.
Diastereoisomers, unlike optical isomers, differ in their rate of formation
and thus one or the other diastereoisomer will be preferentially formed.
The second difference in using optically active monomers concerns the
symmetry of the molecule. Arcus, in the derivation of the chain configura­tions for addition polymers, considers that a monomer which possesses a
plane of symmetry through the C\(^\alpha\) bond system, presents a certain side of the
molecule to a growing D chain and, with equal facility, the other side to
a growing L chain. With an optically active monomer which does not possess
this plane of symmetry this equality is absent and the transition states
comprised of the monomers of one configuration and the polymer main chains
of D and L configuration become diastereoisomeric. Thus their rates of
reaction and hence chain growth will be different. A further element of
dissymmetry is contributed to the transition states by the incorporation in
the growing chain of optically active side groups which render the chains
themselves diastereoisomeric. These three factors, therefore, operate so
that two enantiomeric chains are not initiated or propagated at equal rates.
In addition to these three factors a monomer molecule may occasionally be
added irregularly either as regards cis- or trans-addition, or mode of
presentation of the monomer, and when such irregularities do occur the second
and third factors above will assist the propagation of one configuration
rather than the other. Thus the use of optically active monomers can
potentially give rise to a polymer, the main chain of which will be optically
active provided it does not contain any planes of symmetry.

The polymers and copolymers so far reported in the literature as
being prepared from optically active monomers have mostly been prepared from
monomers of the type CH$_2$=CHA or CH$_2$=CIA where the substituent A contains the
asymmetric carbon atom. In each case the experimental procedure has
involved polymerisation or copolymerisation of the monomer, followed by
removal of the optically active side group and measurement of the rotatory
power of the remaining polymer or copolymer. Marvel and Overberger (J.A.C.S,
1946, 68, 2106) polymerised (+)-s-butyl p-vinylbenzoate, hydrolysed the
polymer and obtained optically inactive poly-(p-vinylbenzoic acid).
Overberger and Palmer (J.A.C.S., 1956, 78, 666) polymerised (+)-o-(s-butyl
butylthiomethyl) styrene, and copolymerised it with methyl methacrylate.
They removed the sulphur, and thus the sec-butyl groups by catalytic
hydrogenation and obtained optically inactive products in each case.
Beredjick and Schuerch (ibid, 2646; 1958, 25, 1933) polymerised (-)-1-phenylethyl methacrylate, removed the phenylethyl groups by reduction with phosphonium iodide and obtained optically inactive poly-(methacrylic acid). A consideration of the possible configurations for these products shows that they contain many planes of symmetry and, therefore, should be optically inactive, as was found.

Beredjick and Schuerch (loc. cit.) also copolymerised their monomer with maleic anhydride and found that the copolymer remaining after removal of the phenylethyl groups was optically active. Arcus considers this result and points out that the hydrogen content of the reduced copolymer is 49% in excess of the calculated value and it is not impossible for some structure in the copolymer to have been reduced asymmetrically. However, he continues, assuming that this has not occurred, the configurations possible for the copolymerisation of CH$_2$=CIA with CH=CH are the same as those for the copolymerisation of CH$_2$=CIA with cis CHX=CHX, and that these configurations contain no local planes of symmetry and are thus capable of giving an optically active main chain.

The configurations so far considered are only applicable to the primary chain structure of the molecule, but to consider all the stereo-chemical factors that contribute to the optical rotatory power of a polymer molecule it is necessary to consider the various 'conformations' that the primary chain structure can assume. Bernal (Diss. Farad. Soc., 1958, 25, 1) has classified these conformations into a regular sequence, the first of which is the primary chain structure, which we have already considered.
This is the actual covalent structure of the chain as determined by chemical analysis. This primary chain can be randomly coiled, it can be coiled in the form of a regular helix, or it can be folded, and Bernal has classified these various forms as the secondary structure of the polymer. These coils, etc. arise from non-covalent links between relatively close members of the chain, such as hydrogen bonds in the polypeptides, or by steric hindrance between the side groups of the polymer, which prevents the molecules packing into their normal planar zig-zag arrangement. This occurs with 'isotactic' poly-(styrene) which is shown by X-ray analysis to exist in the form of a regular helix, imposed on the molecule by the regular orientation of the large phenyl groups. Often the previously-formed helices are themselves folded or coiled together and Bernal has designated this the tertiary structure of the polymer. Quarternary structures exist involving arrangements of the tertiary structure, but these are much less well defined and do not concern us here.

The secondary structure contributes to the optical rotatory power of the polymer by reason of the fact that the coil imposed on the primary structure may be in the sense of a right-handed or left-handed screw, producing two dissymmetric molecules which are capable of optical activity. Under normal polymerisation conditions both right-handed and left-handed helices occur with equal probability, but under conditions where the propagation step is controlled, for instance in the polymerisation of an optically active monomer, the polymer molecule may preferentially coil in one direction, giving rise to an excess of either the right-handed or left-handed coil which will, therefore, contribute to the optical rotatory power.
of the resultant polymer. The actual contribution due to the secondary structure cannot be measured directly but it can be determined by using the method of molecular rotation differences.
The method of molecular rotation differences has been of great use in the determination of the structures of many naturally occurring compounds and, in particular, it has been used with success in the field of steroids, polypeptides and carbohydrates.

Sterols:

The investigation of the correlation between the optical rotatory power of steroids and their structure was initiated by Callow and Young (Proc. Roy. Soc., 1936, A157, 194) who noticed that the inversion of the C3 hydroxyl group from cis to trans, with respect to the C10 methyl group, increased the dextro rotation of many natural sterols.

They also investigated the effect of olefinic linkages on the optical rotatory power and discovered that a 4,5- double bond increased dextro-rotation but that a 5,6- double bond augments laevorotation. This investigation was extended by Wallis and his co-workers (J. Org. Chem., 1941, 6, 319; 1942, 7, 103) and later by Barton (J. Chem. Soc., 1945,
813) who greatly improved the use of molecular rotation differences in structural determinations.

The success of this method with complex organic molecules containing many centres of asymmetry depends on the 'rule of optical superposition' (van't Hoff, "The Arrangement of Atoms in Space", London, 1898, p.160; Guye and Gautier, Compt. rend., 1894, 119, 740, 953) and on the 'rule of shift' (Freudenberg, Ber., 1933, 66, 177). The 'rule of optical superposition' states that in a compound containing two or more asymmetric carbon atoms the optical activities of the individual atoms can be added algebraically, whilst the 'rule of shift' states that if two similar asymmetric molecules B and A are altered in the same way, then the change in the molecular rotation of each compound will be of the same sign.

Wallis and his co-workers, by gathering together data available in the literature, were able to show that this 'rule of shift' was applicable to two similar steroid molecules provided that the molecules only differed from one another in a portion of the molecule far removed from the reacting centre. They were also able to show that the change in molecular rotation of the molecule was not only of the same sign but also of approximately the same magnitude. Thus their work indicated that the optical rotatory power of many compounds could be calculated provided that the relationship to a series of basic sterol skeletons was known.

Barton later showed that certain functional groups contributed to the optical rotatory power of the molecule and that the contribution
of each group (called $\Delta$ values) was dependent not only on the position of the group but also on the characteristics of the ring into which the group is substituted. Thus for substituents in or near the rings A and B the $\Delta$ values are dependent on the configuration at $C_5$ but for substituents in rings C and D the $\Delta$ values are approximately independent of the configuration at $C_5$ but are affected by the configuration at $C_{14}$ and $C_{17}$. Barton also showed that these $\Delta$ values were constant for a certain group in a certain position but only if they were unaffected by other functional groups present, i.e. they are only constant if highly unsaturated groups (e.g. $\alpha\beta$ unsaturated keto groups) are absent and if they are separated from other functional groups by a certain number of carbon atoms. Experience has shown that hydroxyl and keto groups and olefinic double bonds do not affect each other's $\Delta$ value if they are separated by three carbon atoms. On the other hand a separation of five carbon atoms is required to prevent this "vicinal action" between acetoxy and benzoxy groups and between these groups and olefinic double bonds, hydroxyl or keto groups.

Thus the $\Delta$ values form important evidence of molecular type and it is often possible, by comparison of the rotation of a steroid of unknown structure with that of a known compound, to obtain useful evidence about the position of its functional groups. These $\Delta$ values have been used in this way in deducing the structures of sterols of the ergosterol and cholesterol series and of the rarer natural sterols.

Barton has shown that the method of molecular rotation differences is applicable to the field of triterpenoids (J. Chem. Soc.,
1944, 659) and Klyne has recently extended this method to the di- and sesqui-terpenes by using a modification of the "Hudson sugar lactone rule". This rule (Hudson, J.A.C.S., 1909, 31, 66) states that in the ordinary $\delta$ or $\delta$ lactones of the sugar acids the sign of the rotation of the lactone

\[
\begin{align*}
\text{O=}&\text{C} \\
\text{H}_2\text{CH}_n\text{O} \\
\text{H-C*} &\text{C} \\
\end{align*}
\]

is determined by the spatial configuration of the asymmetric carbon atom C* where lactonisation took place. If C* is (+) with the hydroxyl group to the right in the Fischer projection formula then the lactone is dextro-rotatory, but it is laevo-rotatory if C* is (-). Hudson later modified this rule to state that the rotation difference between the lactone and the sugar acid from which it was derived was positive if C* was (+). This rule proved of great help in determining a number of sugar formulae and is another example of the use of molecular rotation differences. Klyne applied this rule to the rotations of compounds of general type (I) in which the lactone rings were fused to other rings, and in all the cases examined by him the rotation contribution of the lactone ring was of the sign deduced by applying the modified lactone rule. He was thus able to show the applicability of this rule to the determination of structures in the field of terpene
chemistry, and he has also extended the use of the rule to include bridged ring lactones (II) and condensed ring systems (III).

**Polypeptides and Proteins:**

Polypeptides consist of long chains of amino acids joined together by peptide bonds -CO-NH- and they exist in the solid state in two different molecular conformations (Pauling and Corey, *Proc. Natl. Acad. Sci. Wash.*, 1951, *37*, 205). One of these is the α-helical form, in which the long chain molecule is wound in the form of a right-handed or left-handed helix with a regular number of residues per turn. The best fit to the data obtained by X-ray analysis of this form is provided by a helix of 3.7 residues per turn (Pauling and Corey, loc. cit.) but Huggins (*J.A.C.S.*, 1952, *74*, 3963) suggests that a helix of 11 residues per turn would also fit the X-ray data. The molecules are held in the shape of the helix by intra-molecular hydrogen bonds between relatively close amino acid residues in each turn of the helix. The other conformation of the solid polypeptide is the β-extended form, and here the molecules are bonded together by inter-molecular hydrogen bonds to form an extended layer or sheet of molecules. The individual chains have a zig-zag formation giving the extended sheet a 'pleated' or 'corrugated' appearance. Doty, Holtzer, Bradbury and Blout (*J.A.C.S.*, 1954, *76*, 4493) have shown that both these forms also exist in solution, together with a third confirmation in which the individual molecules are in the form of a solvated random coil. They also discovered that high molecular weight polypeptides exist in highly polar solvents, mainly as the random coiled form, but that in non-polar solvents the α-helix is the favoured form.
Polypeptides are optically active, since they contain many asymmetric centres and also because the helices form dissymmetric molecules, although the contribution to the optical rotatory power due to this fact was not fully realised until 1955. Previous to this, however, it was discovered by Robinson and Bott (Nature, 1951, 168, 325) that a copolymer of \( \beta \)-methyl-L-glutamate and DL-phenylalanine had a positive rotation in \( m \)-cresol, which increased with the molecular weight of the copolymer, but that the same copolymer had a nearly constant negative rotation in formic acid. They also found that films cast from the formic acid solution contained the peptide in the \( \beta \)-extended form and that films cast from the \( m \)-cresol solution contained the peptide partly as the \( \beta \)-extended form and partly as the \( \alpha \)-helical form, and that the amount of this form present increased with the molecular weight until all the peptide molecules present assumed this formation. It was, however, Cohen (Nature, 1955, 175, 129) who first made the suggestion that the helix of the peptide made a direct contribution to its rotation, and the main use of molecular rotation differences in this field has been to determine this contribution and to use it to estimate the number of polypeptide residues in this form in a normal protein.

Support for this suggestion by Cohen came from a study of the infra-red spectra of a number of polypeptides (Elliot, Proc. Roy. Soc., 1956, A221, 104) and from the work of Doty and Yang (J.A.C.S., 1956, 78, 498) on the optical rotatory power of polypeptides. They measured the rotation of poly-(\( \gamma \)-benzyl-L-glutamate) in ethylene dichloride (in which the peptide exists as the \( \alpha \)-helix), in dichloroacetic acid (in
which the peptide exists as the random coil), and in a mixture of the two solvents. They found that addition of ethylene dichloride to a solution of the peptide in dichloroacetic acid produced a transition from the randomly coiled form to the helical form which was paralleled by a change in the specific rotation of the solution from a negative value to a small positive value. They also discovered that the optical rotatory dispersion of the randomly coiled form was normal but that of the helical form was anomalous. From these results they concluded that the increase in rotation was not due to an environmental change but due to the helical conformation supplementing the rotation of the asymmetric centres, and that one screw-sense of the helix was predominantly present. They pointed out, however, that the rotation due to the helix could not be determined by subtracting the rotation of the random coiled form from that of the helical form because the environmental effects on the peptide bonds in the two forms are sufficiently different to alter the intrinsic residue rotations on transformation.

This problem has been solved by Doty and Yang (J.A.C.S., 1957, 79, 749) and by Elliott and his co-workers (Proc. Roy. Soc., 1957, A242, 325) who measured the optical rotatory power of various copolymers of D- and L-polypeptides, starting with the L-polypeptide and gradually incorporating an increasing number of D-residues in the chain. Doty and Yang used solutions of poly-(γ-benzyl D- and L-glutamate) in chloroform (in which the α-helix is stable) and Elliot and his co-workers used the same polypeptide in a number of different non-polar solvents and also solutions of D- and L-poly-(leucines) in benzene. They found
that as the number of D-residues was increased the positive rotation of the L-polypeptide increased linearly to a maximum and then fell sharply to zero for a copolymer composed of equal numbers of D- and L-residues. They plotted a graph of their results (fig. 25) and extrapolated the linear portion of the curve to obtain a rotational value, which would be the optical rotation of a polypeptide composed of equal numbers of D- and L-residues, but possessing a helical form of a single screw-sense, if the linear relationship held over the whole range.

This derivation is based on their conclusion that the linearity of the right-hand portion of the graph meant that over this range only one screw-sense of the helix is present, due to the fact that the small amount of D-residues present continue in the conformation of the L-polypeptide. As the amount of the D-residues increases the contribution of the L-residues is cancelled out to an increasing extent and the conformation of the L-polypeptide becomes increasingly unstable. Thus when the fraction L/D+L is less than 0.7 the helices are no longer all like-handed and it must be supposed that whole chains, or parts of chains, have their helices wound in the opposite screw-sense to that of the L-polypeptide.
They obtained a value which was in fair agreement with the value, theoretically calculated by Fitts and Kirkwood (J.A.C.S., 1956, 78, 2650), for the rotation of a right-handed helix containing no asymmetric carbon atoms. Moffitt (J. Chem. Phys., 1956, 25, 467; Proc. Natl. Acad. Sci. Wash., 1956, 42, 736) has, however, criticised the model on which these calculations are based and has himself calculated the contribution of a right-handed helix and has obtained a result which is in closer agreement with the experimental value. Moffitt and Yang (Proc. Natl. Acad. Sci. Wash., 1956, 42, 596) on the basis of the same calculations have also shown that the anomalous dispersion observed by Doty and his co-workers for the helical form of the peptide is of the type to be expected.

Doty and Lundberg (ibid., 1957, 43, 213) have experimentally obtained a value for this rotation contribution, which is in agreement with Moffitt's calculated value, by initiating the polymerisation of racemic $\beta$-benzyl-glutamate with preformed L-polymer. At first they thought that the optical activity of the resultant polymer was due to the screw-sense of the initiator being preserved but on subtracting the rotation of the initiating polymer from that of the product they obtained a value for the contribution of the helix which disagreed with Moffitt's calculated value. Further experimental work showed that the screw-sense of the initiating polymer would only be continued if the number of D-residues in the original material was such that quartets or longer sequences of D-residues did not occur. They, therefore, repeated the experiment, reducing the number of D-residues relative to the L- and
again obtained an optically active polymer. By subtracting the rotation of the excess L-units from the observed rotation of the polymer they could thus determine the rotation due to the helix.

Thus both from experimental and theoretical work it appears that the α-helical form of L-polypeptides exist in the sense of a right-handed screw, and this contributes about 50° to the specific rotation of the peptide.

Doty and Yang (J.A.C.S., 1957, 79, 761) have also extended their dispersion measurements to include a number of proteins in aqueous solution, and from the results obtained have suggested structures for a number of polypeptides and proteins, on the surmise that the rotatory dispersion of native and denatured proteins is effectively represented by the sum of the contributions from the helical and non-helical regions and that the dispersion characteristics of these two forms closely resemble those observed in synthetic polypeptides. They suggest that this simple hypothesis seems adequate for the interpretation of the data thus far available and leads to the estimate that in aqueous solution typical globular proteins have only 20-40% of their amino acid residues in the helical conformation. They have also suggested that the results so far obtained strengthen the general guide proposed for relating optical rotations and protein structures; that is "each degree change in the specific rotation of a protein corresponds to a change of one percent in the number of residues in the α-helical conformation".
EXPERIMENTAL
Pyridine was dried over stick potassium hydroxide for four hours and then distilled from potassium hydroxide. When a portion of the pyridine was dissolved in acetic anhydride and powdered sodium iodide added, an intense orange-yellow colouration developed which indicated the presence of peroxides, (Nozaki, Ind.Eng.Chem.Anal.Ed., 1946, 18, 583). The bulk of the peroxides present in the pyridine were removed by passing the pyridine down a column of activated alumina.

Benzenesulphonyl chloride was distilled and the fraction boiling at 167°/66mm. collected.

Methacrylic acid, stabilised by pyrogallol, was distilled at 100°/70mm. to remove the stabiliser.

1:3-Dimethylbutanol was dried over potassium carbonate and distilled through a small Vigreux column; it had b.p. 128-130°.

Symmetrical tetrachloroethane (400ml.) was stirred and heated on a steam bath for thirty minutes with concentrated sulphuric acid (50ml.). The acid layer became a dark straw colour and was removed. This was repeated until the acid layer no longer became coloured. The sym.-tetrachloroethane was finally steam-distilled, the steam-distillate dried (CaCl₂) and distilled. It had b.p. 144-146°, \( \frac{d^{25}}{25} = 1.587 \).

Methyl methacrylate was distilled at 40-41°/100mm. to remove the stabiliser.
PREPARATION OF OPTICALLY INACTIVE COMPOUNDS

Methacrylyl Chloride

(Heyboer and Staverman, Rec. Trav. Chim., 1950, 69, 787)

Pyridine (39.5g., 0.5mol.) was mixed with methacrylic acid (43g., 0.5mol.), and the mixture added to benzenesulphonyl chloride (106g., 0.6mol.) in a 250ml. flask, with continuous shaking and cooling. Methacrylyl chloride was distilled immediately from the reaction mixture at a pressure of 140mm., by means of an oil bath. The receiver was cooled by an ice-salt bath and the apparatus protected against direct radiation to reduce polymerisation. The temperature of the oil bath was kept below 195° to prevent excessive foaming of the contents of the flask. The crude acid chloride, which contained a white solid, was purified by distillation at atmospheric pressure through a small Vigreux column. It yielded methacrylyl chloride b.p. 96-98° (44.4g., 85%). The clear colourless liquid polymerised under the influence of light and was preserved in the refrigerator in the dark. The preparation was carried out in a fume cupboard because the material is volatile and strongly lachrymatory.

Pivalic Acid (Trimethyl Acetic Acid)

(Organic Synthesis, Vol.1, p.524)

Magnesium turnings (30.5g., 1.25atoms) were placed in a three-necked flask fitted with a reflux condenser, a dropping funnel, and a mercury sealed stirrer. The magnesium was covered with sodium-dried ether (100ml.), and pure tertiary-butyl chloride (2.5ml.) together with
a crystal of iodine was added to start the reaction. Stirring was commenced and tertiary-butyl chloride (113.5g., 1.25mol.) in sodium-dried ether (550ml.) was added over a period of seven hours. The stirring was continued for a further fifteen minutes after all the halide had been added.

After the mixture had been cooled to 0° in an ice-salt bath, the dropping funnel was replaced by a bung carrying a gas outlet tube and a thermometer. The outer end of the tube was connected to a mercury bubbler, to prevent moist air coming into contact with the reaction mixture, and the thermometer was adjusted so that the bulb was immersed in the mixture. The condenser was replaced by a gas inlet tube, 10mm. internal diameter, which was adjusted so that the end was ca. 50mm. above the surface of the liquid. Carbon dioxide, generated from a flask containing solid carbon dioxide and led through two drying bottles containing concentrated sulphuric acid, was added through this tube as rapidly as it combined. The temperature was controlled by the rate of stirring and by a freezing mixture applied to the flask, and was not allowed to rise above 8°. After 90 minutes the temperature had fallen to 0° but the carbon dioxide was added until the temperature dropped to -5°.

The reaction mixture was then poured into a mixture of ice and 25% sulphuric acid in a large separating funnel and the organic acid, which separated, was removed. The aqueous layer was extracted with ether (4x50ml.) and the combined ether layers washed with 25% sodium hydroxide solution to remove any pivalic acid from the ether. The alkaline extracts were heated to 100° to remove ether and other volatile impurities before
being cooled with ice and acidified with 25% sulphuric acid. The organic acid again separated and was removed as before.

The aqueous layer was distilled, the distillate saturated with salt, and the organic acid which separated again removed. This water layer, together with the low boiling fraction from the distillation of the crude pivalic acid, was distilled and the distillate saturated with salt as before. The combined acid layers were distilled from a Claisen flask connected, via an air condenser, to a receiver cooled by running water. The fraction of b.p. 163-165° gave on redistillation pivalic acid b.p. 165°, (62.2g., 45%).

Pivalyl Chloride
(Brown, J.A.C.S., 1938, 60, 1325-8)

Pivalic acid (20.6g., 0.2mol.) and benzoyl chloride (56.2g., 0.375mol.) were mixed together and the mixture heated strongly. Pivalyl chloride distilled from the reaction mixture through a 25cm. rod and disc column. The temperature at the top of the column was not allowed to rise above the boiling point of the pivalyl chloride (105-6°). Redistillation through a small fractionating column yielded pivalyl chloride having b.p. 105-6°, (20.6g., 85%).

1:3-Dimethylbutyl Pivalate

Ice-cold pivalyl chloride (12.0g., 0.1mol.) was added in small portions to a stirred ice-cold mixture of pyridine (15.8g.,
0.2 mol.), 1:3-dimethylbutanol (10.2 g., 0.1 mol.) and a little copper powder. The mixture was then heated to reflux for two hours. After cooling, the solution was poured into dilute hydrochloric acid (concentrated acid (12.5 ml.) in water (200 ml.)) and extracted thrice with light petroleum (b.p. 40-60°, 30 ml.). After drying (CaCl₂), the reaction product was distilled at reduced pressure. The product b.p. 114-8°/97 mm., was twice redistilled and then had b.p. 97-98°/52 mm., n²⁵⁹₅₈₉₃ 1.4061. This was then kept over one-tenth of its weight of ignited sodium sulphate and redistilled; it yielded (†)-1:3-dimethylbutyl pivalate b.p. 97°/52 mm., n²⁵⁹₅₈₉₃ 1.4067, (15.3 g., 83%). Found; C; 70.28, H; 11.78, C₁₁H₂₂O₂ requires C; 70.92, H; 11.90%.

1:3-Dimethylbutyl Methacrylate by the Acid Chloride Method

Ice-cold methacrylyl chloride (11.5 g., 0.11 mol.) was added gradually to a stirred ice-cold mixture of pyridine (9.9 g., 0.125 mol.) and 1:3-dimethylbutanol (10.2 g., 0.1 mol.). The mixture was heated to 85° in five minutes and kept at that temperature for five minutes. The mixture, which contained a white sludge, was kept overnight at 25° and then poured into dilute hydrochloric acid (concentrated acid (2.5 ml.) in water (100 ml.)). The solution was thrice extracted with 10 ml. portions of light petroleum (b.p. 40-60°) and the extracts washed with saturated sodium bicarbonate solution. After drying (Na₂SO₄), quinol (0.17 g.) was added and the mixture distilled. 9.41 g. of the ester of b.p. 75°/19 mm. were obtained. Quinol (0.17 g.) was again added and the mixture on redistillation gave (†)-1:3-dimethylbutyl methacrylate b.p. 76°/19 mm. (8.5 g., 50%).
This was the best preparation of a series carried out under varying conditions, as follows:

(A) Methacrylyl chloride (10.45g., 0.1mol.), pyridine (15.8g., 0.2mol.), 1:3-dimethylbutanol (10.2g., 0.1mol.) and some copper powder were mixed as above but the mixture was kept at 100° for one hour. The mixture, on cooling, was poured into water (200ml.) containing concentrated hydrochloric acid (12.5ml.). This solution was then extracted with light petroleum, the extracts were washed with water, dried (CaCl₂) and distilled yielding 6.19g., (36%) of the ester of b.p. 73°/16mm.

(B) Methacrylyl chloride (0.1mol.) and 1:3-dimethylbutanol (0.1mol.) were used as before but only 0.1mol., 7.9g. of pyridine was used and no copper powder. This mixture was not heated but was kept at 25° for 23 hours before being poured into concentrated hydrochloric acid (2.5ml.) in water (150ml.). The acid solution was extracted, and the extracts were washed, dried and distilled as before, yielding 8.5g., (50%) of the ester, boiling range 85-90°/33mm.

(C) The quantity of 1:3-dimethylbutanol was kept the same but the methacrylyl chloride was increased to 11.5g., 0.11mol., and the pyridine to 9.9g., 0.125mol. The procedure followed was as before with the exception that the extracts were washed with saturated sodium bicarbonate solution instead of water. This preparation yielded 7.5g., (44%) of the ester having b.p. 76-79°/20mm.

(D) The quantities used were as in the last run, but the mixture was heated at 60° before being left overnight at 25°. The procedure was
then the same as used in preparation (C) except that sodium sulphate was used for drying instead of calcium chloride. On distillation, approximately one half of the material had distilled at 74°/19 mm. when the remainder polymerised in the distillation flask.

With the object of eliminating unwanted polymerisation, a further series of preparations was carried out; the best preparation, which henceforth became the standard procedure, was as follows:

Ice-cold methacrylyl chloride (11.5g., 0.11mol.) was added gradually to an ice-cold stirred mixture of 1:3-dimethylbutanol (10.2g., 0.1mol.), peroxide-free pyridine (9.9g., 0.125mol.) and tertiary-butyl catechol (0.2g.). A white sludge formed slowly during the reaction. The mixture was kept at 85° for five minutes before being left overnight at 25°. It was then poured into concentrated hydrochloric acid (2.5ml.) in water (100ml.) and the acid solution extracted with three 10ml. portions of light petroleum (b.p. 40-60°). The extracts were thrice washed with 10ml. portions of sodium hydroxide solution (N/2) and once with water (10ml.) before being dried (MgSO₄). The solution was a light green at this stage. The light petroleum was removed, and the ester distilled, after the addition of quinol (0.2g.), it, 9.4g. (55%), had b.p. 63-5°/11mm. Quinol (0.2g.) was again added and the product redistilled, yielding 1:3-dimethylbutyl methacrylate b.p. 70-71°/14mm., (8.5g., 50%).
1:3-Dimethylbutyl Methacrylate by the Fischer-Speier Esterification

The best preparation of a series was as follows:

1:3-Dimethylbutanol (71g.), quinol (2.0g.), sulphuric acid (98%, 2.6g.), methacrylic acid (55.9g.) and trichloroethylene (81.3g.) were mixed in the above order and the mixture heated to reflux for twelve hours. An azeotrope (40ml.) of 1:3-dimethylbutanol, water and trichloroethylene distilled at 76° and was collected in a modified Dean and Stark separator. The reaction mixture was then left overnight before being washed once with water, thrice with 2N sodium hydroxide solution and then twice more with water. Quinol (1g.) was added and the mixture distilled through a small rod and disc column. Three fractions were obtained:

1. b.p. 21-22°/20mm.
2. b.p. 52-69°/18mm.
3. b.p. 71-72°/18mm.

This third fraction was redistilled after the addition of quinol (1g.) and yielded 1:3-dimethylbutyl methacrylate b.p. 71-72°/18mm., n\textsubscript{25}^25 \text{d} 1.4234, (63.7g., 57%).

1:3-Dimethylbutyl Methacrylate by Transesterification with Methyl Methacrylate

Tetra n-butyl titanate (Ti(OBu)\textsubscript{4}), the catalyst for the transesterification, was distilled and had b.p. 159°/1.2mm.

1:3-Dimethylbutanol (22.4g., 0.2mol.), benzene (70ml.), methyl
methacrylate (24g., 0.24mol.) and quinol (0.34g.) were heated together, in a stream of oxygen, until any water present had been removed as an azeotrope with the benzene. Tetra n-butyl titanate (2.2g.) was added quickly to the refluxing mixture which became a deep orange. The mixture was kept at reflux for two hours and then a further 2.2g. of the tetra n-butyl titanate was added. The mixture was heated at reflux for a further two hours before being left overnight. During the refluxing period an azeotrope of benzene and methyl alcohol was formed and was removed by means of a modified Dean and Stark separator.

The mixture was shaken for thirty minutes with water (375ml.) and the organic layer which separated removed. The aqueous layer was extracted once with ether, and the ethereal extract combined with the organic layer, which was then dried (MgSO₄). Quinol (0.34g.) was added to the dried ethereal solution which was then distilled through a rod and disc column. Two fractions were obtained

1. b.p. 75⁰/95mm.
2. b.p. 83-86⁰/95mm.

This second fraction was redistilled through a small Vigreux column after the addition of quinol (0.2g.) and gave 1:3-dimethylbutyl methacrylate b.p. 64⁰/13mm., n²⁵ 1.4221, (18.38g., 53%).
PREPARATION OF OPTICALLY ACTIVE COMPOUNDS

All the rotations were measured at 25° in a one decimetre tube unless otherwise stated.

Resolution of (†)-1:3-Dimethylbutanol

(Kenyon and Strauss, J.C.S., 1949, 2153)

(†)-1:3-Dimethylbutyl hydrogen phthalate: A mixture of (†)-1:3-dimethyl-
butanol (112g.), phthalic anhydride (163g.) and pyridine (88g.) was
heated on a steam bath until it became homogeneous. Next day the
resultant oil was dissolved in acetone (300ml.) and mixed with dilute
hydrochloric acid (concentrated acid (140ml.), ice and water (140ml.))
the whole being well stirred. The mixture was finally diluted with ice
and water (3-4L.) before being set aside for four days with occasional
stirring. During this period the aqueous layer was twice decanted and
replaced by water to which concentrated hydrochloric acid (10ml.) had
been added. The ester had still not solidified so the oil was dissolved
in aqueous sodium carbonate, the solution extracted with ether to remove
any unesterified alcohol, and then acidified with hydrochloric acid to
liberate the acid ester. This was extracted with ether and the extracts
washed twelve times with dilute hydrochloric acid to ensure the complete
removal of pyridine. The ethereal solution was finally washed with water,
dried (CaCl₂) and evaporated to yield (†)-1:3-dimethylbutyl hydrogen
phthalate (250g., 92%). The oil which resulted was inoculated with a
seed, which was obtained by placing a little of the oil in a vacuum
desiccator in a refrigerator overnight; it then crystallised and had m.p. 43-44°.

(+) -1:3-Dimethylbutyl hydrogen phthalate: Brucine (394g., anhydrous) was added quickly to a hot solution of the (±)-ester (250g.) in acetone (3.1L). On cooling, a crop (A) of the crystalline brucine salt readily separated. This, after one recrystallisation, yielded crop (B) (185g.) of the optically pure brucine salt of (+)-1:3-dimethylbutyl hydrogen phthalate m.p. 166-8°. By concentration of the mother liquor from crop (B) and recrystallisation of the salt that separated, a further 34.8g. of the optically pure brucine salt were obtained.

The brucine salt (191.1g.) was decomposed by adding it to a mechanically stirred mixture of acetone (300ml.), water (172ml.) and concentrated hydrochloric acid (47ml.). The resultant product was diluted with water (2750ml.), whereupon the brucine hydrochloride dissolved and the acid ester separated as an oil. This (82.6g.) was removed by means of ether, the extract washed with water, dried (CaCl₂) and the ether removed. The (+)-1:3-dimethylbutyl hydrogen phthalate was obtained as an oil and had [a]₂³^0 +52.3° (c= 5.00 in CHCl₃; 1=2).

(-)-1:3-Dimethylbutyl hydrogen phthalate: The filtrate left after removal of crop (A) of the brucine salt was concentrated to approximately 700ml. and mixed with dilute hydrochloric acid (concentrated acid (80ml.) ice and water (160ml.)); the product after dilution with water (3L.) was extracted with ether. The resultant hydrogen phthalate crystallised when
seeded with a small crystal of the \((\dagger)\)-ester, yielding \((128\text{g.})\)

\((\dagger)\)-1:3-Dimethylbutanol: \((\dagger)\)-1:3-Dimethylbutyl hydrogen phthalate was dissolved in a warm solution of potassium hydroxide \((46\text{g.})\) in water \((200\text{ml.})\) and steam distilled. The distillate was saturated with salt and the alcohol removed. The aqueous layer was thrice extracted with ether and the alcohol combined with the ethereal extracts. After drying \((\text{K}_2\text{CO}_3)\) and distillation of the product, \((\dagger)\)-1:3-dimethylbutanol b.p. \(61-3^\circ/35\text{mm.}, \alpha_{5893} +16.76^\circ, (26.4\text{g.})\) was obtained.

\((-\dagger)\)-1:3-Dimethylbutanol: \((-\dagger)\)-1:3-Dimethylbutyl hydrogen phthalate \((127\text{g.})\) was hydrolysed with potassium hydroxide \((69\text{g.})\) in water \((300\text{ml.})\) as described above and yielded partially resolved \((-\dagger)\)-1:3-dimethylbutanol b.p. \(64^\circ/42\text{mm.}, \alpha_{5893} -10.33^\circ\)

The resolution was thrice repeated:

(1) yielding \((\dagger)\)-1:3-dimethylbutanol b.p. \(61-2^\circ/36\text{mm.}, (24.15\text{g.})\), \(\alpha_{5893} +16.58^\circ\); \((-\dagger)\)-1:3-dimethylbutanol b.p. \(45-6^\circ/14\text{mm.}, (44.5\text{g.})\), \(\alpha_{5893} -10.05^\circ\).

(2) yielding \((\dagger)\)-1:3-dimethylbutanol b.p. \(71-3^\circ/52\text{mm.}, (20.1\text{g.})\), \(\alpha_{5893} +16.80^\circ\).

(3) yielding \((\dagger)\)-1:3-dimethylbutanol b.p. \(64-6^\circ/41\text{mm.}, (11.2\text{g.})\), \(\alpha_{5893} +16.84^\circ\).
Preparation of (+)-1,3-Dimethylbutyl Pivalate

Pivalyl chloride (9.6g., 0.165mol.) was added to an ice-cold mixture of pyridine (12.46g., 0.165mol.), (+)-1,3-dimethylbutanol (8.16g. 0.081mol.) and a small amount of copper powder. The mixture was heated to reflux and so kept for seventy-five minutes. After cooling, the mixture was poured into concentrated hydrochloric acid (10ml.) in water (160ml.) and the solution extracted with three 25ml. portions of light petroleum (b.p. 40-60°). After drying (Na₂SO₄) the ester was distilled; it had b.p. 65°/13mm., (12.61g., 78%). The ester was redistilled and yielded (+)-1,3-dimethylbutyl pivalate b.p. 77-8°/22mm., n°25 1.4010, d°5893 1.959°, (11.8g., 73%).

Found: C; 70.82, H; 11.63, C₁₁H₂₂O₂ requires C; 70.92, H; 11.90%

Preparation of (+)-1,3-Dimethylbutyl Methacrylate

Methacrylyl chloride (17.3g.) was added to an ice-cold mechanically stirred mixture of (+)-1,3-dimethylbutanol (16.32g.) and pyridine (15.8g.). The mixture was heated to 85° and kept at that temperature for five minutes. The mixture was left over-night at 25°, and then poured into concentrated hydrochloric acid (4ml.) in water (160ml). A further 0.5ml. of concentrated hydrochloric acid was required to render the solution acid to Congo Red. The mixture was thrice extracted with 20ml. portions of light petroleum (b.p. 40-60°), washed with saturated sodium bicarbonate solution and dried over sodium sulphate. The light
petroleum was removed, quinol (0.28g.) added, and the ester distilled: it had b.p. 73-6°/19mm., (15.05g., 55%). Quinol (0.28g.) was again added and on redistillation there was obtained (+)-1:3-dimethylbutyl methacrylate b.p. 75-8°/19mm., $c_{5893}^{23}$ +33.66°, (11.06g., 40%).

Found: C; 70.15, H; 10.77, $C_{10}H_{18}O_2$ requires C; 70.57, H; 10.67%

This preparation was thrice repeated using optically active alcohol produced in the second, third, and fourth resolutions, with the modification that tertiary-butyl catechol was initially added to the pyridine and the extracts were washed thrice with 10ml. portions of sodium hydroxide solution (N/2), and once with water before being dried over magnesium sulphate.

(1) yielded (+)-1:3-dimethylbutyl methacrylate b.p. 65-8°/11mm., $c_{5893}^{25}$ +34.95°, (18.45g., 54.3%)
(2) yielded (+)-1:3-dimethylbutyl methacrylate b.p. 74-7°/20mm., $n_{5893}^{25}$ 1.4224, $c_{5893}^{25}$ +34.59°, (17.91g., 52%).
(3) yielded (+)-1:3-dimethylbutyl methacrylate b.p. 83-4°/27mm., $n_{5893}^{25}$ 1.4224, $c_{5893}^{25}$ +35.22°, (7.06g., 38%).

This method was also used to prepare the (-)-1:3-dimethylbutyl methacrylate from the partially active (-) alcohol obtained from the first resolution: it gave (-)-1:3-dimethylbutyl methacrylate b.p. 70-1°/14mm., $c_{5893}^{25}$ -21.69°, (17.1g., 50%).
Methyl alcohol was redistilled for use as a precipitation solvent. The tubes used in the bulk polymerisation were chilled in solid carbon dioxide, after the heating period, causing the polymer to contract away from the walls, so that on breaking the tubes the polymer could be easily recovered.

SUSPENSION POLYMERISATIONS

Of Methyl Methacrylate using Sodium Poly-(methacrylate) as a Dispersing Agent

a. Preparation of sodium poly-(methacrylate): (Modified from U.S. patent 2326078). Potassium persulphate (0.0125g.) was dissolved in sodium chloride solution (22%, 20g.). The mixture was heated and stirred to 75° on a steam bath and methacrylic acid (5g.) added slowly over a period of 90 min. At first a white precipitate formed and this was swept into a large spherical ball by the stirrer. Further addition of acid gave more white precipitate, until the acid remained as globules in the liquid. When all the acid had been added the solution was heated to 95° and so kept for five minutes, during which time the large ball of material turned yellowish-brown. It, and more flaky white precipitate settled out and were removed, washed with dilute hydrochloric acid (5%) and dried, yielding poly-(methacrylic acid) (5.5g.).

This material was dissolved in sodium hydroxide (2.54g.) in
water (750ml.) giving an approximately 1% solution of sodium poly-(methacrylate).

b. Preparation of the buffer solution: Disodium phosphate (1.7g.) and monosodium phosphate (0.1032g.) were dissolved in water (10ml.).

c. The polymerisation: A solution of benzoyl peroxide (0.1g.) in methyl methacrylate was added to a mixture of sodium poly-(methacrylate) (30ml., 1% solution) and the buffer solution (1ml.). This mixture was stirred and heated in a two-necked flask fitted with a thermometer, stirrer, and condenser. The stirrer was operated at a speed such that the monomer was suspended in the form of fine droplets. The mixture was heated at 80-85° for forty minutes during which time it became milky. On cooling a mixture of clear granules and hard white solid was obtained: it was filtered off, washed with water and dried.

This was repeated using the improved stirrer shown. This stirrer by its rotating motion draws the material up through the central orifice and throws it out through the horizontal arms. The monomer is thus being continually broken up into fine droplets. In this experiment nearly all the monomer was obtained as clear granules, soluble in toluene. This stirrer was used in all future suspension polymerisations.

Of 1:3-Dimethylbutyl Methacrylate using Sodium Poly-(methacrylate)

(A) A mixture of 1:3-dimethylbutyl methacrylate (5g.), benzoyl
peroxide (0.05g.), sodium poly-(methacrylate) (30ml., 1% solution) and
the buffer solution (1ml.) was stirred and heated at 85° for fifty minutes.
The temperature was then increased to 95° for sixty-three minutes. The
monomer had still not polymerised; the globules floated to the surface
and coalesced.

The heating was discontinued and tertiary-butyl hydroperoxide
(0.0468g.) was added. The mixture was then heated on a boiling water
bath for two hours. Heating and stirring were then ended and it was
seen that the monomer had still not polymerised properly. The globules
were sticky whilst hot and coagulated to form larger globules which in
turn formed large groups. These were soluble in toluene.

(B) 1:3-Dimethylbutyl methacrylate (10g.) containing α:α'-azo-iso-
butyronitrile (0.2036g.) was mixed with sodium poly-(methacrylate)
solution (1%, 30ml.) and the buffer solution (1ml.). The mixture was
stirred and heated at 82-85°. After thirty minutes the monomer globules
began to coagulate and finally formed a large mass of milky white solid
spinning with the stirrer. After forty-five minutes the stirring and
heating were stopped and the polymer was obtained as a hard brittle white
mass, which dissolved in toluene.

(C) This was repeated but the water bath was only heated to 61° to
ascertain if the lower temperature would prevent the globules coagulating.
After three and a half hours at this temperature, during which time
polymerisation had not appreciably occurred, the temperature was increased
to 76-78°. After one hour at this temperature two large globules of
incompletely polymerised material were obtained.

**Of Methyl Methacrylate using Talc as a Dispersing Agent**

Talc (0.375g., 2.5% on monomer) was stirred with water (45ml.) for seventy-five minutes to obtain a suspension. Methyl methacrylate (15g.) containing α:α'-azo-isobutyronitrile (0.15g.) was added to the stirred suspension which was then heated to 80° and so kept for fifty minutes. The polymer was obtained as a solid white mass which only swelled in toluene.

**Of 1:3-Dimethylbutyl Methacrylate using a Mixture of Talc and Sodium Poly-(methacrylate)**

Talc (0.125g.) was stirred with sodium poly-(methacrylate) (30ml., 1% solution) for one hour in the presence of the buffer solution (1ml.) to obtain an adequate suspension. 1:3-Dimethylbutyl methacrylate (5g.) containing α:α'-azo-isobutyronitrile (0.1g.) was added to the stirred suspension which was then heated at 82-85° for ninety minutes. The hot solution was filtered and the polymer obtained as separate globules which were washed and dried. The globules were heated with a number of solvents. They only became swollen in toluene, chloroform, chlorobenzene, anisole, xylene, phenol, and dimethylformamide. They were, however, soluble in sym-tetrachloroethane.
Of Methyl Methacrylate using Magnesium Trisilicate as a Dispersing Agent
(Modified from U.S. patent 2440808)

Magnesium trisilicate \([2\text{MgO}.3\text{SiO}_2.X\text{H}_2\text{O}] (0.025\text{g.})\) was stirred in water (40ml.) for ninety minutes. Methyl methacrylate (10g.) containing benzoyl peroxide (0.1g.) was added to the suspension and the mixture stirred and heated at 82-85°. Small globules were formed at first but these coalesced after approximately thirty minutes to form a large mass. After forty-five minutes the stirring and heating were stopped and the polymer was obtained as a hard white mass.

ii) This was repeated using magnesium trisilicate (0.1g., 1% on monomer) and benzoyl peroxide (0.05g.). Heating was ended after fifty minutes, when incompletely polymerised beads were obtained.

iii) This last procedure was repeated but heating was continued for ninety minutes. The aqueous milky dispersion then cleared and the monomer was seen to be dispersed in the liquid as small milky globules. The temperature rose to 87° at the same time. The solution was filtered and the polymer obtained as hard milky beads which were washed with water and dried. In toluene the beads swelled only.

Of 1:3-Dimethylbutyl Methacrylate using Magnesium Trisilicate

Magnesium trisilicate (0.5g.) was stirred in water (20ml.) for one hour to form a suspension. 1:3-Dimethylbutyl methacrylate (5g.) containing \(\alpha:\alpha'-\text{azo-isobutyreronitrile} (0.1g.)\) was added and the mixture heated and stirred at 82-85° for twenty minutes. Heating was then
discontinued and the mixture poured into cold water (100ml.). The monomer had polymerised in the form of small globules, the majority of which had clustered together to form large groups which were easily broken up. The polymer beads were shaken in a small conical flask, in an attempt to remove the magnesium trisilicate, but only a small amount could be so removed. The beads only swelled in toluene and chloroform but dissolved in sym-tetrachloroethane.

SOLUTION POLYMERISATIONS

Of Methyl Methacrylate in Toluene

Toluene (12g.) was stirred and heated to reflux in a two-necked flask, and a solution of benzoyl peroxide (0.12g.) in methyl methacrylate (14g.) was added over a period of seventeen minutes. The temperature was allowed to fall to 98±2° and heating continued for three hours. On cooling a colourless viscous solution resulted.

A portion of this solution (5g.) was diluted with toluene (25ml.) and the resulting solution poured into methyl alcohol (50ml.). The polymer precipitated as a white solid, which was filtered, washed with methyl alcohol and dried at 60°. It was soluble in toluene.

A further portion of the viscous solution (5g.) was diluted with toluene (25ml.) and was poured into methylene chloride (50ml.). No polymer precipitated.
Of Methyl Methacrylate in Ethyl Acetate

Methyl methacrylate (15.3 g.) containing benzoyl peroxide (0.015 g.) was added slowly to refluxing ethyl acetate (14.7 g.) and the mixture stirred and heated for five hours during which time some of the monomer polymerised in the form of a clear solid crust on the sides of the reaction vessel. On cooling, apart from the portion of the polymer in the clear crust, the polymer was obtained as a clear viscous solution in the ethyl acetate.

A portion of the polymer solution was diluted with ethyl acetate (100 ml.) and 7 ml. of this solution were poured into methyl alcohol (50 ml.) giving a white precipitate. This was filtered, washed four times with methyl alcohol and dried at 60°. It was insoluble in toluene. A further 7 ml. of the above solution was poured into methylene chloride (50 ml.) but no polymer precipitated.

Of 1:3-Dimethylbutyl Methacrylate in Toluene

A solution of 1:3-dimethylbutyl methacrylate (10 g.) in toluene (30 ml.) was placed in a flask fitted with a stirrer, a reflux condenser, and a dropping funnel. The solution was stirred and heated at 105 ±2° and a solution of benzoyl peroxide (0.2 g.) in toluene (8 ml.) added over a period of three hours. The mixture was heated for a further thirty minutes and then allowed to cool.

Of this solution 5 ml. was poured into methyl alcohol (50 ml.) when the polymer precipitated as an oil.
b. To toluene (10g.) and 1:3-dimethylbutyl methacrylate (10g.) was added benzoyl peroxide (0.075g.) and the resultant mixture stirred and heated as above. A solution of benzoyl peroxide (0.075g.) in toluene (2ml.) was added to the hot solution in \( \frac{1}{2} \)ml. portions every forty-five minutes. Finally the mixture was heated and stirred for a further hour. On cooling a soft sticky polymeric mass was obtained which swelled only in toluene.

c. Toluene (10g.), benzoyl peroxide (0.075g.) and 1:3-dimethylbutyl methacrylate (10g.) were heated and stirred at 90° for forty-five minutes. The temperature was then increased to 105° and after about fifteen minutes the mixture became viscous and on cooling a gel resulted. A portion (1g.) was added to toluene (5ml.) and the solution poured into methyl alcohol (50ml.). The polymer precipitated as a white oil.

BULK POLYMERISATIONS OF 1:3-DIMETHYLBUTYL METHACRYLATE

1. A solution of benzoyl peroxide (0.0045g.) in 1:3-dimethylbutyl methacrylate (3.43g.) in a tube was heated at 70° for two hours, during which time the contents became almost solid. The temperature was then reduced to 45° for sixty hours and finally increased to 110° for one hour, during which time bubbles appeared in the polymer. The polymer was finally obtained as a hard clear brittle block, soluble in toluene.

2. The monomer (9.78g.) containing benzoyl peroxide (0.01271g.) was heated in a conical flask for one hour at 80°, eighty-seven hours at
45° and five hours at 110°. The polymer was a hard clear block soluble in toluene.

3. The monomer (1g.) containing benzoyl peroxide (0.01g.) was heated in a tube, from which the air had been displaced, with nitrogen, before stoppering. After sixty-two hours at 82° the monomer polymerised to a hard clear block containing bubbles. It only swelled in toluene.

4. This last experiment was twice repeated using, firstly α:α'-azo-isobutyronitrile (0.01g.) and then tertiary-butylhydroperoxide (0.01g.) in place of the benzoyl peroxide. Neither specimen of the polymer was soluble in toluene.

5. Two tubes, one containing the monomer (1g.) and benzoyl peroxide (0.01g.) and one containing the monomer (1g.) and α:α'-azo-isobutyronitrile (0.01g.), were heated for two hours and thirty minutes at 90°. Both polymerised to give hard blocks, which were toluene-soluble.

6. α:α'-Azo-isobutyronitrile (0.01g.), dissolved in 1:3-dimethylbutyl methacrylate (1g.) contained in a corked tube, was heated at 85° for two hours. The polymer obtained was soluble in toluene.

7. This last experiment was repeated but the mixture was heated at 85° for three hours. The polymer so obtained was insoluble in toluene.

8. The polymer obtained by heating 1:3-dimethylbutyl methacrylate (1g.) with benzoyl peroxide (0.01g.) in a tube at 85° for two hours was only swollen by toluene.

9. This last experiment was repeated but the air was displaced
with nitrogen and the mixture heated for two hours at 80°. The polymer was again insoluble in toluene.

10. 1:3-Dimethylbutyl methacrylate (1.0076g.) containing α:α'-azo-isobutyronitrile (0.0149g.) was heated in a tube, from which the air had been displaced by nitrogen, for two hours at 90°. The polymer, again in the form of a hard clear block containing bubbles, was insoluble in chloroform and in toluene.

11. This last experiment was repeated but the stopper of the tube was replaced by a cork carrying a small capillary tube to allow the nitrogen produced by the decomposition of the initiator to escape. The polymer was again insoluble in both toluene and chloroform.

12. Six tubes, each containing the monomer (1g.) and α:α'-azo-isobutyronitrile (0.01g.) were heated at 80° for varying lengths of time:

<table>
<thead>
<tr>
<th>Tube No.</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30min.</td>
</tr>
<tr>
<td>2</td>
<td>80min.</td>
</tr>
<tr>
<td>3</td>
<td>105min.</td>
</tr>
<tr>
<td>4</td>
<td>2 hours</td>
</tr>
<tr>
<td>5</td>
<td>2½ hours</td>
</tr>
<tr>
<td>6</td>
<td>3 hours</td>
</tr>
</tbody>
</table>

Nitrogen was again used to displace the air in the tubes which were then corked as in the last experiment. Specimen No.2 was insoluble in toluene and chloroform but specimens No.1 and No.6 were soluble in sym-tetra-chloroethane.

13. The monomer (1g.) containing benzoyl peroxide (0.001g.) was heated for ninety minutes at 70-80° and then twenty four hours at 45°. The monomer polymerised to a hard clear block, the surface of which, however, was still soft. The polymer only swelled in toluene.
POLYMERISATION OF THE OPTICALLY ACTIVE MATERIALS

(+)1:3-Dimethylbutyl Methacrylate

(Modified from Crawford, J. Soc. Chem. Ind., 1949, 201)

**First specimen:** The monomer (first preparation, 9.23g.) was added to a small conical flask containing benzoyl peroxide (0.0102g.). The air was displaced from the flask by nitrogen and the flask stoppered, before being heated at 82° for thirty minutes. It was then kept at 45° for eighty hours and finally at 110° for five hours. The polymer was obtained as a hard colourless block containing bubbles.

Found: C; 71.12, H; 10.81, C_{10}H_{18}O_2 requires C; 70.57, H; 10.67%.

**Second specimen:** The monomer (third preparation, 3.99g.) containing benzoyl peroxide (0.004lg.) was placed in a small conical flask, which was then flushed with nitrogen and stoppered. The flask was heated for one hour at 85° and then twenty-four hours at 79°. The polymer was obtained as a hard colourless disc, but the centre of the disc had 'crazed' into a white soft opaque mass and there were small patches of this 'crazing' dotted around the rest of the disc. No crystal facets could be seen in this white material under a low power microscope; the material was not crystalline, X-ray crystallographic analysis (for which I thank Dr. C.W. Bunn of I.C.I. Ltd., Plastics Division) showing only amorphous polymer to be present. This white material was also subjected to elementary analysis.
Found: C; 70.42, H; 10.88, \( \text{C}_{10}\text{H}_{18}\text{O}_2 \) requires C; 70.57, H; 10.67%
The polymer was crushed and lost no weight after one day at room
temperature/0.5mm.

\((-\)\text{-1:3-Dimethylbutyl Methacrylate}\)

The monomer (3.4g.) was placed in a tube containing benzoyl
peroxide (0.0068g.), which was then flushed with nitrogen, stoppered,
and heated for five hours at 79\(^\circ\). The polymer was again obtained as a
very hard colourless glass, which was crushed and heated at 70-80\(^\circ\)/0.5mm.
for two days and then left for four days at room temperature /0.5mm.

The polymerisation was repeated with this monomer (3.4g.) and
an equimolar amount of \( \alpha:\alpha' \)-azo-isobutyronitrile (0.0059g.), in place of
the benzoyl peroxide. The polymer, again a hard clear glass, was crushed
and heated to constant weight at 70-80\(^\circ\)/0.5mm.

\text{Copolymerisation of } (+)-\text{1:3-Dimethylbutyl Methacrylate with Methyl}
\text{Methacrylate}

The second preparation of (+)-1:3-dimethylbutyl methacrylate
was used for these two copolymerisations.

A. Molar ratio of methyl methacrylate to (+)-1:3-dimethylbutyl meth-
acrylate approximately 2:1.

Methyl methacrylate (4.096g.), (+)-1:3-dimethylbutyl meth-
acrylate (3.406g.) and \( \alpha:\alpha' \)-azo-isobutyronitrile (0.0747g.) were mixed
together in a boiling tube. The initiator was dissolved, by warming and stirring the mixture, before flushing the tube with nitrogen and stoppering it with a cork carrying a capillary tube. The mixture was heated in an oven at 76° for one hundred minutes, when the copolymer was obtained as a clear brittle glass containing bubbles. The copolymer was then crushed and heated to constant weight at 70°/0.3 mm.

Found: C; 64.29, H; 9.27, \([C_5H_8O_2]_{2.33n} : [C_{10}H_{18}O_2]_n \) requires C; 64.45 H; 9.16%

B. Molar ratio of methyl methacrylate to (+)-1:3-dimethylbutyl methacrylate approximately 3:1.

Methyl methacrylate (5.995 g.), (+)-1:3-dimethylbutyl methacrylate (3.428 g.) and α:α'-azo-isobutyronitrile (0.0934 g.) were caused to react as before. The copolymer, a hard clear brittle glass, was heated to constant weight after being crushed, as before.

Found: C; 63.79, H; 8.86, \([C_5H_8O_2]_{3.20n} : [C_{10}H_{18}O_2]_n \) requires C; 63.67, H; 8.96%

Copolymerisation of (+)-1:3-Dimethylbutyl Methacrylate and Acrylonitrile

Acrylonitrile was distilled and had b.p. 76-77°. Dimethylformamide distilled at 70°/45 mm.

A mixture of acrylonitrile (1.65 g.) and (+)-1:3-dimethylbutyl methacrylate (5.17 g.) was added to a tube containing benzoyl peroxide (0.0252 g.). The mixture was degassed twice by cooling the tube in solid
carbon dioxide and then connecting it to a high vacuum pump. The tube was sealed under vacuum, then heated for twenty-two hours at 79°. After this period the bulk of the monomers had polymerised to a transparent yellow solid but the surface of the mixture was still a thick viscous liquid. The copolymer was dissolved in dimethylformamide (50ml.) and the solution poured into water (1500ml.) from which the copolymer precipitated as a white solid. This was redissolved in dimethylformamide (50ml.) and the solution again poured into water (1500ml.). Only about one-third of the material precipitated this time and so the water/dimethylformamide solution was concentrated, by distillation under reduced pressure, to approximately 50ml. and then poured into water (300ml.). The bulk of the copolymer precipitated and was filtered off. This was washed twice with methyl alcohol, and, after being crushed to a coarse powder, was heated to constant weight at 40°/1mm. This required approximately sixty hours.

Found: (i) N, 5.10; (ii) N, 5.13%.

\[ C_{10}H_{18}O_2 \cdot 1.30n : [C_{3}H_{5}N]_n \text{ requires N, 5.12%.} \]

Copolymerisation of (+)-1:3-Dimethylbutyl Methacrylate with Styrene

Styrene was washed thrice with 2N sodium hydroxide solution, to remove the inhibiting agent, and then thrice with water before being dried (Na₂SO₄). It distilled at 64°/19mm. in an atmosphere of nitrogen.

A mixture of styrene (3.097g.), (+)-1:3-dimethylbutyl methacrylate (5.033g.) and benzoyl peroxide (0.0086g.) was heated in a sealed
glass tube at 79° for twenty-three hours, the (+)-1:3-dimethylbutyl methacrylate being from the same batch as that used for the acrylonitrile copolymer, i.e. the third preparation of the (+)-monomer. The copolymer was obtained as a hard transparent glass, insoluble in chloroform and benzene. It was dissolved in sym-tetrachloroethane (approximately 100ml.) and poured into methyl alcohol (1000ml.) from which it precipitated as a white solid. This was crushed and heated to constant weight in thirty days at 50-60°/1mm.

Found: (i) C, 78.44; H, 9.13; (ii) C, 78.35; H, 9.37%.

$$[C_{10}H_{18}O_2]_{1.17n} : [C_8H_8]_n$$ requires C, 78.01; H, 9.65%.

**Copolymerisation of (+)-1:3-Dimethylbutyl Methacrylate with Diethyl Fumarate**

Diethyl fumarate distilled at 97°/11mm.

Diethyl fumarate (3.0g.) together with (+)-1:3-dimethylbutyl methacrylate (6.0g., fourth preparation of (+)-monomer) and benzoyl peroxide (0.1g.) was sealed in a glass tube under nitrogen. The mixture was then heated at 79° for seven and a quarter hours when the mixture copolymerised to a slightly milky block. This dissolved in sym-tetrachloroethane (100ml.) giving a dark brown solution. The solution was filtered and poured into methyl alcohol, (approx. 1L.). The copolymer precipitated as a white solid which was redissolved in sym-tetrachloroethane and reprecipitated by methyl alcohol. It was heated to constant weight in ten days at 80°/1.5mm. Found: (i) C, 70.12; H, 10.34 (ii) C, 70.36; H, 10.35%.

$$[C_{10}H_{18}O_2]_{30.1n} : [C_8H_{12}O_4]_n$$ requires C, 70.07; H, 10.61%.
Preparation of the Polymer and Copolymer Solutions

First method; diagram (A)

The polymer (lg.) was weighed into tube A. Sym-tetrachloroethane (20ml.) was then added and the mixture heated and stirred in an oil bath until the polymer had dissolved.

Second method; diagram (B)

The polymer (lg.) was again weighed into the tube A. and the sym-tetrachloroethane (20ml.) added. The tube B. contained n-butanol (b.p. 116°C) which was heated to reflux. In this way the mixture could be heated without the tube A. coming into contact with the heating medium. The condenser C. was a sliding fit on the tube D. through which passed the glass stirrer. The weight of the solution could thus be determined after the polymer had dissolved by weighing together, tube A, the stirrer, and tube D.

Preparation of the Solutions of the Pivalate

The pivalate (lg.) was weighed into a 20ml. graduated flask which was then filled to the mark with sym-tetrachloroethane, and the whole weighed. Thus, when the density of the solution had been measured the concentration in grams of pivalate in 100ml. of the solution could easily be calculated, as for the polymer solutions.
Determination of the Densities of the Solutions

The density of a solution was determined by filling a pyknometer with the solution, immersing it in a thermostat at $25^\circ$ for thirty minutes, adjusting the level of the liquid in the pyknometer to the mark and weighing the pyknometer full of the liquid. This was repeated with distilled water and the density calculated from the datum that at $25^\circ$, one gram of water occupies 1.00294 cc.

Determination of the Concentration of the Polymer Solutions

A. For the polymers prepared by the first method above.

A portion of the solution was poured into a weighed evaporating dish and the whole weighed. The dish and contents were then heated at 90-100$^\circ$ on a bath of copper turnings and to facilitate the removal of the solvent, a funnel, connected to a filter pump, was supported over the evaporating dish. After the bulk of the solvent had been removed in this manner, the dish was heated to constant weight in an oven at 80$^\circ$.

Thus the weight of polymer in a known weight of solution is determined and if the density of the latter is also known then the concentration in grams of polymer in 100 ml. of the solution can be calculated.

B. For the polymers prepared by the second method above.

The weight of polymer in a known weight of solution can be measured directly and thus the concentration can be calculated when the
density of the solution has been determined

Comparison of the Two Methods of Concentration-Determination

The polymer (0.5157g., specimen 5. of the bulk polymerisations) was heated and stirred with sym-tetrachloroethane (approximately 20ml.) in the apparatus shown in diagram (B), until it had dissolved. The tube D., the stirrer, and the tube A. containing the solution were then weighed together and knowing the dry weight of the tubes A and D. and the stirrer, it was found that the solution weighed 15.7273g. Thus 0.5157g. of the polymer was dissolved in 15.7273g. of solution. The density of this solution was then determined as before and then a portion of the solution (15.1781g.) was evaporated to constant weight as described above. The polymer residue remaining after evaporation of the solution weighed 0.4818g. Thus by the method of evaporation 0.4818g. of the polymer were dissolved in 15.1781g. of the solution and the concentration of the solution is therefore

\[
\frac{0.4818 \times 1.563 \times 100}{15.1781} = 4.961 \text{ grams per 100ml. of solution}
\]

where 1.563 is the density of the solution.

But originally 0.5157g. of the polymer were dissolved in 15.7273g. of solution giving a concentration of

\[
\frac{0.5157 \times 1.563 \times 100}{15.7273} = 5.029 \text{g. per 100ml. of solution.}
\]

Thus the two methods give comparable results.
Determination of the Viscosities of the Polymer Solutions

5g. of the polymer solution of known concentration was diluted in a 20ml. graduated flask with sym-tetrachloroethane, and the flow-time of this solution determined in a No.1 Ostwald viscometer, taking an average of four or five measurements. This was repeated for the pure solvent and for each fresh batch of solvent. From the results obtained the intrinsic viscosity of the polymer could be calculated from the following relationships.

\[
\frac{\text{flow-time of solution}}{\text{flow-time of solvent}} = \frac{\eta_r}{\text{concentration}}
\]

\[
\ln(\eta_r) = \text{the intrinsic viscosity } [\eta]_c
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration of solution</th>
<th>Flow-time solution</th>
<th>Flow-time solvent</th>
<th>(\eta_r)</th>
<th>([\eta]_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully active polymer (1)</td>
<td>0.657 g./100ml. soln.</td>
<td>611.2secs</td>
<td>318.4secs</td>
<td>1.919</td>
<td>0.99</td>
</tr>
<tr>
<td>Fully active polymer (2)</td>
<td>0.345</td>
<td>686.5</td>
<td>320.5</td>
<td>2.144</td>
<td>2.21</td>
</tr>
<tr>
<td>Part active poly. Bz.2O initiated</td>
<td>0.621</td>
<td>587.0</td>
<td>320.5</td>
<td>1.831</td>
<td>0.95</td>
</tr>
<tr>
<td>Part active poly. A.I.B.N init.</td>
<td>0.614</td>
<td>437.7</td>
<td>320.5</td>
<td>1.367</td>
<td>0.51</td>
</tr>
<tr>
<td>Copolymer with styrene</td>
<td>0.959</td>
<td>710.8</td>
<td>259.7</td>
<td>2.737</td>
<td>1.05</td>
</tr>
<tr>
<td>Copolymer with acrylonitrile</td>
<td>0.696</td>
<td>369.1</td>
<td>259.7</td>
<td>1.421</td>
<td>0.51</td>
</tr>
<tr>
<td>Copolymer with diethyl fumarate</td>
<td>0.787</td>
<td>431.3</td>
<td>263.1</td>
<td>1.639</td>
<td>0.63</td>
</tr>
<tr>
<td>Copolymer with Me. Meac. 2,33:1</td>
<td>0.674</td>
<td>385.6</td>
<td>316.9</td>
<td>1.217</td>
<td>0.29</td>
</tr>
<tr>
<td>Copolymer with Me. Meac. 5,20:1</td>
<td>0.682</td>
<td>377.3</td>
<td>316.9</td>
<td>1.191</td>
<td>0.26</td>
</tr>
</tbody>
</table>

TABLE 1.
Measurement of the Rotatory Dispersion of the Solutions

The rotations of the solutions were measured at 25° at the five wavelengths; 6438A°; 5893A°; 5461A°; 5086A°; 4358A°; The rotations were generally measured in a two decimetre polarimeter tube but the rotations of the solutions (iii) and (iv) of the first specimen of the fully active polymer, both solutions of the diethyl fumarate copolymer and the second solution of the acrylonitrile copolymer were all measured in a one decimetre tube.

The results obtained with these solutions are recorded in Table 2., and it should be noted that in this table and in all others relating to these solutions,

\[
\begin{align*}
\text{Bz}_2\text{O}_2 &= \text{benzoyl peroxide} \\
\text{A.I.B.N.} &= \alpha: \alpha'-\text{azo-isobutyronitrile} \\
\text{Me. Meac.} &= \text{methyl methacrylate}
\end{align*}
\]

Duplicate solutions were prepared of each specimen of polymer and copolymer, in sym-tetrachloroethane, at a concentration of approximately five grams of polymer in 100ml. of solution. In addition two solutions of the first specimen of the fully active homopolymer were prepared at a concentration of seven percent weight/volume.
### TABLE 2.

Density, Concentration, and Rotations of the Solutions of the Polymers and Copolymers of (+)-1:3-Dimethylbutyl Methacrylate, of (+)-1:3-Dimethylbutyl Pivalate, and of (+)-1:3-Dimethylbutyl Methacrylate Monomer.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution No.</th>
<th>Concentration g./100g. of solution</th>
<th>Density</th>
<th>Measured Rotation λA°</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6438</td>
</tr>
<tr>
<td>Pivalate</td>
<td>(i)</td>
<td>3.04</td>
<td>1.552</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>3.07</td>
<td>1.546</td>
<td>1.91</td>
</tr>
<tr>
<td>Monomer</td>
<td>(i)</td>
<td>-</td>
<td>--</td>
<td>3.19</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>-</td>
<td>--</td>
<td>3.20</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fully active</td>
<td>(i)</td>
<td>3.07</td>
<td>1.563</td>
<td>1.36</td>
</tr>
<tr>
<td>(1)</td>
<td>(ii)</td>
<td>3.22</td>
<td>1.560</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>(iii)</td>
<td>4.28</td>
<td>1.549</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>(iv)</td>
<td>4.65</td>
<td>1.546</td>
<td>1.08</td>
</tr>
<tr>
<td>Fully active</td>
<td>(2)</td>
<td>3.18</td>
<td>1.563</td>
<td>1.44</td>
</tr>
<tr>
<td>Part. active</td>
<td>(i)</td>
<td>3.16</td>
<td>1.563</td>
<td>0.95</td>
</tr>
<tr>
<td>BzO2 init.</td>
<td>(ii)</td>
<td>3.11</td>
<td>1.563</td>
<td>0.91</td>
</tr>
<tr>
<td>Part. active</td>
<td>(i)</td>
<td>3.12</td>
<td>1.562</td>
<td>0.88</td>
</tr>
<tr>
<td>A.I.B.N.init.</td>
<td>(ii)</td>
<td>3.08</td>
<td>1.563</td>
<td>0.88</td>
</tr>
<tr>
<td>Copolymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>with Me.Meac</td>
<td>(i)</td>
<td>3.37</td>
<td>1.567</td>
<td>0.66</td>
</tr>
<tr>
<td>1:2.33</td>
<td>(ii)</td>
<td>3.30</td>
<td>1.568</td>
<td>0.72</td>
</tr>
<tr>
<td>with Me.Meac</td>
<td>(i)</td>
<td>3.40</td>
<td>1.568</td>
<td>0.53</td>
</tr>
<tr>
<td>1:3.20</td>
<td>(ii)</td>
<td>3.28</td>
<td>1.570</td>
<td>0.62</td>
</tr>
<tr>
<td>with acrylo-</td>
<td>(i)</td>
<td>3.19</td>
<td>1.559</td>
<td>1.38</td>
</tr>
<tr>
<td>nitrile</td>
<td>(ii)</td>
<td>3.22</td>
<td>1.561</td>
<td>0.70</td>
</tr>
<tr>
<td>with styrene</td>
<td>(i)</td>
<td>3.22</td>
<td>1.565</td>
<td>0.33</td>
</tr>
<tr>
<td>(ii)</td>
<td></td>
<td>1.567</td>
<td>0.31</td>
<td>0.43</td>
</tr>
<tr>
<td>with diethyl</td>
<td>(i)</td>
<td>3.16</td>
<td>1.564</td>
<td>0.64</td>
</tr>
<tr>
<td>fumarate</td>
<td>(ii)</td>
<td>3.17</td>
<td>1.562</td>
<td>0.73</td>
</tr>
</tbody>
</table>
The Variation of Rotation with Temperature

Poly-((+)-1:3-dimethylbutyl methacrylate) (0.5012g. second specimen) was heated and stirred in sym-tetrachloroethane (approximately 10ml.) in the apparatus shown in diagram (B). The apparatus was weighed when the polymer had dissolved and it was found that 0.5012g. of the polymer were dissolved in 15.4645g. of sym-tetrachloroethane. This solution was placed in a jacketed one decimetre polarimeter tube and water pumped through the jacket from a thermostat at a constant temperature. The rotation of the solution was then measured at $\lambda_{5893}^\circ$ over the temperature range 25-95$^\circ$, and then at 25$^\circ$ again when the solution had cooled. This was repeated for a solution of (+)-1:3-dimethylbutyl pivalate, prepared by dissolving 0.5371g. of the ester in sym-tetrachloroethane (14.8691g.).

The densities of both solutions were determined at 25$^\circ$, 55$^\circ$, and at 85$^\circ$ and the densities at the intermediate temperatures read from a graph of density against temperature. The temperature of the contents of the tube and of the water in the thermostat were recorded over the range used, the former, which are slightly lower, being those at which the rotations were determined. The results obtained are shown in Table 3.

Graphs were then plotted of [M] against temperature for the polymer and the pivalate, and the molecular rotation differences, taken at 10$^\circ$ intervals over the temperature range, also plotted. (Graph 1.)
TABLE 3.
Variation of Rotation with Temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Density</th>
<th>Concentration g./100ml. soln</th>
<th>Rotation</th>
<th>[M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-(+)1:3-dimethylbutyl methacrylate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°</td>
<td>1.564</td>
<td>5.00</td>
<td>0.88</td>
<td>30.0</td>
</tr>
<tr>
<td>34.4</td>
<td>1.549</td>
<td>4.95</td>
<td>0.84</td>
<td>28.9</td>
</tr>
<tr>
<td>44.1</td>
<td>1.534</td>
<td>4.90</td>
<td>0.80</td>
<td>27.8</td>
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<tr>
<td>53.7</td>
<td>1.520</td>
<td>4.86</td>
<td>0.77</td>
<td>27.0</td>
</tr>
<tr>
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<td>1.505</td>
<td>4.81</td>
<td>0.71</td>
<td>25.1</td>
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<tr>
<td>73.0</td>
<td>1.490</td>
<td>4.76</td>
<td>0.66</td>
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<tr>
<td>82.6</td>
<td>1.476</td>
<td>4.72</td>
<td>0.62</td>
<td>22.4</td>
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<tr>
<td>91.4</td>
<td>1.462</td>
<td>4.67</td>
<td>0.57</td>
<td>20.8</td>
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<tr>
<td>25</td>
<td></td>
<td></td>
<td>0.89</td>
<td></td>
</tr>
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<td>(+)-1:3-Dimethylbutyl pivalate</td>
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<td></td>
</tr>
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<td>24.8</td>
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<td>1.24</td>
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<td>39.0</td>
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<tr>
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<td>1.06</td>
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<tr>
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<td>5.09</td>
<td>1.02</td>
<td>37.3</td>
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<tr>
<td>84.5</td>
<td>1.445</td>
<td>5.04</td>
<td>0.96</td>
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<tr>
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<td></td>
<td></td>
<td>1.27</td>
<td>44.1</td>
</tr>
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</table>
DISCUSSION
SECTION (1)

GENERAL DISCUSSION

Selection of a Suitable Polymer

The object of the present investigation has been to attempt the assessment of the contribution of the main chain (as distinct from the asymmetric side groups) to the optical rotatory power of a disymmetric polymer by the method of molecular rotation differences. In choosing a polymer for this investigation it is important to remember that to apply the method of molecular rotation differences it is necessary to be able to compare the rotation of the polymer with a standard substance of similar structure. On consideration of this point it was decided that the similarity of structure between the poly-(methacrylates) and the corresponding pivalates (trimethyl acetates), at least as regards the immediate environment of the asymmetric side group, would provide a feasible basis on which to proceed with the investigation.

Three methacrylic acid esters of secondary alcohols were prepared and each was polymerised by means of benzoyl peroxide. From a preliminary survey of the results obtained, poly-(1:3-dimethylbutyl methacrylate) was chosen as the dissymmetric polymer to be investigated. This particular polymer was chosen for the following reasons:

(1) The optical rotatory dispersion of 1:3-dimethylbutanol is simple in the visible region, i.e. a plot of the reciprocal of the specific rotation against the wavelength squared is a straight line, showing that
a single term Drude equation \[ [\alpha] = \frac{K}{(\lambda^2 - \lambda_0^2)} \], only, is necessary. This is a desirable characteristic in the alcohol; rotation measurements on the polymer and the pivalate were determined for five wavelengths in the visible region, in order to provide a check on the possible incidence of anomalous dispersion in the rotatory powers investigated. Obviously if the rotatory dispersion of the alcohol is itself anomalous it would not be possible to check this factor.

(2) The monomer is of comparatively low molecular weight and the (\dagger)-monomer had already been prepared and polymerised to a hard clear colourless block by Crawford (J. Soc. Chem. Ind., 1949, 201).

(3) The resolution of the alcohol is comparatively simple, only two crystallisations of the brucine salt of the hydrogen phthalate being required to give the optically pure (+)-alcohol.

Crawford prepared his material by Fischer-Speier esterification and polymerised it by heating the monomer containing 1% benzoyl peroxide in a cell composed of two glass plates held 3mm. apart by gummed paper. He heated the mixture at 70\(^\circ\) until it was viscous and then poured the viscous mixture into the cell which was then heated at 45\(^\circ\) until the polymer was converted to a solid resin, and then at 110\(^\circ\) to ensure that the reaction was complete. He finally obtained the block of polymer by cutting the paper away from the glass and chilling the cell with solid carbon dioxide. Cooling in this fashion caused separation of the resin from the glass.
Preparation of the Monomer and of the Pivalate

Although Crawford had used the Fischer-Speier method for the preparation of his material, he had only prepared the inactive monomer and it was thought that, since this method involves refluxing the alcohol with concentrated sulphuric acid, to use it as a means of preparing the optically active (+)-1,3-dimethylbutyl methacrylate would risk racemisation of the alcohol. As a result it was decided to prepare the optically active monomer by reacting the alcohol with methacrylyl chloride.

The preparation of the methacrylyl chloride was carried out by the method of Heyboer and Staverman (Rec. Trav. Chim., 1950, 69, 787). Earlier preparations of this acid chloride had involved, either the reaction of methacrylic acid with phosphorus trichloride, or the reaction between potassium methacrylate and phosphorus oxychloride, both methods, however, giving products from which it is difficult to remove the phosphorus compounds. Ullmann and Nadai (Ber., 1908, 41, 1870) discovered that the reaction between toluenesulphonyl chloride and picric, benzoic, and cinnamic acid, in the presence of pyridine gave the corresponding acid chloride in good yield, and Heyboer and Staverman found this method to be very good for the preparation of methacrylyl chloride, equimolar amounts of pyridine and methacrylic acid, together with benzene-sulphonyl chloride in twenty percent excess, giving pure methacrylyl chloride in over eighty percent yield.

Heyboer and Staverman had also prepared tertiary-butyl meth-
acrylate by reaction of the acid chloride and the alcohol, and their procedure was followed for the initial preparation of the inactive 1:3-dimethylbutyl methacrylate. Unfortunately the maximum yield achieved by this means was only thirty-eight percent of the theoretical and before proceeding to the preparation of the optically active monomer a series of preparations was carried out in an attempt to improve the yield of the required ester. However the maximum yield obtained from this series of preparations was only fifty percent and we thus had to accept the loss of nearly one half of the optically active material in any preparation carried out by this method. The optically active (+)-1:3-dimethylbutyl methacrylate was subsequently prepared as stated in the experimental section. This monomer was then polymerised, following Crawford's procedure, by heating the material, containing benzoyl peroxide, at 70° until it was viscous, then at 45° for eighty hours, and then at 110°.

As stated above it was hoped to compare the molecular rotation of the poly-(methacrylate) with that of the corresponding pivalate and it was thus necessary to prepare a specimen of (+)-1:3-dimethylbutyl pivalate. This entailed preparation of pivalic acid by the reaction of carbon dioxide with tertiary-butylmagnesium chloride, and then of pivalyl chloride. An attempt to prepare this acid chloride in a similar manner to that used for the methacrylyl chloride was unsuccessful, and the pivalyl chloride was finally prepared by heating the pivalic acid with benzoyl chloride.

A large amount of inactive monomer was required for the series of polymerisation experiments and so the scale of the preparation using
methacrylyl chloride was increased. It was discovered, however, that this reaction could not be carried out on a scale greater than 0.2 molar owing to the occurrence of polymerisation. In view of this and also since the reaction gave only a fifty percent yield it was decided to try Fischer-Speier esterification as a means of preparing the inactive monomer. After a series of preparations using various procedures it was found that the optimum conditions gave a maximum yield that was only slightly better than that obtained by the acid chloride preparation. The method, however, had the advantage that it could be carried out on a molar scale giving a large amount of inactive material for the polymerisation experiments.

A private communication from Dr. Crawford of I.C.I. Ltd., Plastics Division, suggested that methacrylates could be prepared in high yield by a transesterification reaction with methyl methacrylate using tetra-butyl titanate \([\text{Ti(OBu)}_4]\) as the exchange catalyst. If this method gave a good yield with the present secondary alcohol it would probably be the best method of preparing the optically active material and so a series of preparations was carried out to determine the best conditions for the reaction. It was noticed, however, that in each preparation of the series the reaction mixture turned a deep orange on the addition of the catalyst, and that as the reaction proceeded a red solid was precipitated from the mixture. Titanium alkyl compounds are extremely sensitive to moisture and it seemed possible that the secondary alcohol could have been dehydrated causing production of butyl alcohol and titanium hydroxide which would account for the solid precipitated.
from the reaction mixture. The butyl alcohol could react to give butyl methacrylate which would then contaminate the required ester. This, combined with the fact that the maximum yield obtainable was again only just over fifty percent, seemed to indicate that the reaction using methacrylyl chloride was after all the best way of producing the optically active monomer, despite the fact that it could only be performed on an 0.1 molar scale.

However, when preparations on this scale were resumed, polymerisation again occurred during the reaction and it became necessary to carry out a further series of preparations, in order to evolve more suitable conditions, before proceeding to the preparation of a second batch of optically active monomer. The main alterations which it proved necessary to make were, the introduction of a stabilising agent into the pyridine at the start of the reaction (tertiary-butyl catechol proving to be better than quinol for this purpose), and the removal of peroxides from the reagents by using freshly distilled materials, and by passing the pyridine through a column of alumina. The yield, however, remained at fifty percent and in an attempt to recover the remaining optically active material the following steps were taken.

When the methacrylyl chloride had reacted with the alcohol the reaction mixture was poured into dilute hydrochloric acid to remove excess pyridine. This acid layer was then extracted with light petroleum to remove the monomeric ester, and it was obvious that the "lost fifty percent" of the optically active material was remaining in the acid layer. No liberation resulted from saturating this acid layer with salt
or from making it alkaline with caustic soda, but the addition of concentrated ammonium hydroxide until the mixture was strongly alkaline produced an orange solution from which separated a deep red organic layer. This layer was removed with light petroleum and was washed with dilute hydrochloric acid and then with water, since it smelt strongly of pyridine. The extracts were dried (MgSO$_4$), the light petroleum removed, and the solution distilled after the addition of quinol. A product was obtained which had the same boiling point, refractive index, and optical rotation as the pure ester and was obviously identical with it. However, since an explanation of this behaviour is not available it was decided to keep this material separate from the main yield of the ester.

Polymerisation of the Inactive Monomer

In order to compare the molecular-rotation of the poly-(meth-acrylate) with that of the pivalate, it was decided to prepare solutions of both in toluene or chloroform, normally good solvents for poly-(meth-acrylates), and to carry out the rotation measurements on these. The optically active block, initially prepared, was therefore crushed to a coarse powder and portions were stirred and heated, under reflux, in the solvent for prolonged periods. Unfortunately the polymer specimen proved to be insoluble in both solvents, swelling to a large extent, only. This was surprising, particularly as Crawford's specimen of poly-(1:3-dimethylbutyl methacrylate) had dissolved easily in chloroform, and the only explanation possible was that in the polymerisation of the monomer, either the polymer molecules formed were of high molecular
weight, or a certain amount of crosslinking had occurred, both of which would tend to make the polymer insoluble.

Two courses of action were then adopted. It was decided to study the polymerisation of the monomer under a variety of conditions, in an attempt to prepare a sample of the polymer which was soluble in these solvents, and if this proved impossible, to carry out a search for effective solvents for the polymer.

There are four methods of polymerising a vinyl-type monomer: (a) bulk polymerisation, (b) suspension or granular polymerisation, (c) solution polymerisation, (d) emulsion polymerisation. In the bulk polymerisation of a vinyl monomer, a small quantity of initiator is added to the homogeneous monomer which is then heated to start the polymerisation. The polymerisation continues until all the monomer has reacted, and the kinetics of this process are as given in the introductory section. Suspension or granular polymerisation is essentially the same as bulk polymerisation, as far as the kinetics are concerned, but the monomer containing the initiator is suspended in the form of small droplets in a medium, usually water, in which it is insoluble. Thus each separate droplet of monomer may be considered as undergoing bulk polymerisation. Rapid stirring is necessary to maintain the monomer in the form of a fine suspension and in addition dispersing agents (usually insoluble inorganic salts) are added to the mixture to prevent the droplets coagulating when the polymerisation passes through the "sticky" stage. The polymers produced by this means are generally of low molecular weight and it is for this reason that this method of polymerisation was
investigated.

In solution polymerisation a portion of the monomer is dissolved in a suitable solvent, which is then heated to reflux. A solution of the monomer containing the initiator is added to the refluxing solvent in which both the monomer and initiator are soluble. The kinetics of this method of polymerisation are complicated by the fact that chain transfer reactions can occur with the solvent and as a result the polymers produced are generally of low molecular weight. The polymers are generally isolated by pouring the solution into a solvent which is miscible with the original solvent used in the polymerisation but in which the polymer itself is insoluble. The polymer thus precipitates and is removed and dried. A further method of polymerisation is by the emulsion technique in which the monomer is generally emulsified with an organic soap. Since these organic soaps are difficult to remove from the final product, and since this method, in general, gives very high molecular weight products, it was not used.

In the series of suspension and solution polymerisations each different technique was initially carried out with methyl methacrylate since it was thought that the behaviour of this monomer would be sufficiently similar to that of the 1:3-dimethylbutyl methacrylate to give an indication of the results to be expected. Unfortunately this was not so, and no satisfactory technique of polymerising the monomer by the solution method could be found, the polymer precipitating as an oil in each instance. Again, although the methyl methacrylate could easily be polymerised in the form of hard granules, the only successful
method with 1:3-dimethylbutyl methacrylate necessitated the use of magnesium trisilicate as a dispersion agent and it proved difficult to remove this from the product. It was thus decided to revert to bulk polymerisation in an attempt to prepare a soluble sample of the polymer. Although a variety of conditions for the bulk polymerisation was investigated, no repeatable method was found for preparing a block of the polymer which was soluble in toluene or chloroform. In view of this it was decided to investigate the solubility of the polymer in solvents other than toluene and chloroform.

From this last investigation it was discovered that most of the specimens produced, including the initial specimen of poly-(+)-1:3-dimethylbutyl methacrylate), were soluble in sym-tetrachloroethane. It was thus possible to proceed with the comparison of the optical rotatory powers of the polymer and the pivalate.

Preparation of the Solutions

Two solutions were prepared of the first specimen of poly-((+)-1:3-dimethylbutyl methacrylate) at \( c = 5 \) (where \( c \) = the concentration of the solution in grams of solute in 100ml. of the solution), and the rotatory dispersion of these solutions was measured for the five wavelengths stated in the experimental section. This was repeated for the (+)-1:3-dimethylbutyl pivalate, and the rotatory dispersions of the four solutions compared. (Duplicate solutions were prepared throughout the investigation to check possible experimental errors). It can be seen from the results given in Table 4 that the rotations of the polymer...
solutions differ from those of the pivalate solutions by a substantial amount; the difference is discussed below.

The preparation of polymer solutions of known, and relatively high, concentrations presented some difficulty, owing to the time required for dissolution and to the high viscosity of the solutions, these factors making it difficult to maintain a given volume of solvent against evaporation and difficult to wash the final solution quantitatively into a standard flask. For this reason the concentration of the solutions was initially determined by evaporation of a known amount of the solution to constant weight, and the concentration of the solutions, both of the first specimen of poly-((4)-1:3-dimethylbutyl methacrylate) and of the copolymers with methyl methacrylate, were determined in this way. Later, however, the apparatus was so modified that it proved feasible to determine, directly, the weight of solution containing a known weight of polymer, which data, together with the density of the solution, gave as described in the experimental part. The concentration of all the other polymer and copolymer solutions was determined in this manner. In order to check the validity of comparing the results obtained from solutions whose concentrations were determined by different methods, a comparison of the concentration of a solution obtained by the two different methods was carried out: the first method gave \( c = 4.96 \), and the second gave \( c = 5.03 \).
Relationship of Rotatory Power to Concentration, Initiator, and Molecular size

When it had thus been found practicable to prepare, and measure the rotation of, solutions of the polymer it was decided to investigate the effect of change of concentration, initiator, and molecular weight on the rotatory power, since little is known of the optical rotatory power of solutions of polymers bearing optically active side groups. In order to vary the concentration of the solutions an attempt was made to prepare a solution of the first specimen of poly-(+)-1:3-dimethylbutyl methacrylate at $c = 10$. However, this appeared to be outside the limit of solubility of the polymer in sym-tetrachloroethane, and the highest concentration at which solutions of the polymer could be prepared was approximately seven percent weight/volume. These solutions were duly prepared and their rotatory dispersions measured. It can be seen, (Table 4), by comparison of the data with those of the five percent solutions, that this change in concentration produced no significant change in the specific rotation of the polymer.

For investigation of the variation of the initiator, it was decided to use the partially active (-)-1:3-dimethylbutyl methacrylate, which had been prepared from the partially active (-)-1:3-dimethylbutanol by the method used for the fully active monomer. Two portions of the partially active monomer were polymerised under the same conditions with the exception that one was initiated with benzoyl peroxide and the other with an equimolar amount of $\alpha:\alpha'$-azo-isobutyronitrile. Duplicate solutions were prepared of each specimen at $c = 5$ in sym-tetrachloro-
ethane and the rotatory dispersion of each solution measured. The rotatory powers of the two polymer specimens are seen to be substantially the same, indicating that the steric course of the polymerisation is unaffected by the nature of the radicals initiating the reaction. This is in agreement with the theoretical results of Frisch, Schuerch, and Szwarc (J. Polym. Sci., 1953, 11, 559) mentioned in the introductory section.

Since the results for the poly-((+)-1:3-dimethylbutyl methacrylate) are of such importance in interpreting the results obtained with the copolymers, a second block of fully active polymer was prepared from monomer derived from a second batch of fully active alcohol. The rotatory dispersion of duplicate solutions \((c = 5)\) was again measured, and on comparison of the results with those for the first specimen (Table 4), it is seen that there is fair agreement.

A characteristic property of solutions of long chain molecules is their high viscosity which for dilute solutions is related to the length of the polymer molecules, and thus to their molecular weight, and to the concentration of the solution. This relationship is expressed by the following equation;

\[
[\eta]_c = KM^\alpha
\]

where \([\eta]_c\) is the intrinsic viscosity of the polymer solution at concentration \((c)\), \(K\) is a constant dependent on the type of polymer, solvent and temperature, and \(\alpha\) is a variable index, dependent on the shape of the molecules, but which averages 0.66 for a variety of polymers.
To measure the viscosity of a polymer it is necessary to prepare a fairly dilute solution of the polymer and to compare the flow-time of the solution with that of the solvent in the same viscometer. The ratio of the flow-times of the solution and the solvent are related to the intrinsic viscosity of the polymer by the following:

\[ \frac{1}{\text{concentration}} \left[ \ln \left( \frac{\text{flow-time solution}}{\text{flow-time solvent}} \right) \right] = [\eta]_c \]

Rigorously, this relationship is only true at infinite dilution and values of \([\eta]_c\) as \(c \to 0\) should be employed, but for the simple characterisation of polymer specimens values, at the value of \(c = 0.6\) approximately, have been used.

Since the intrinsic viscosity of a polymer is related to its molecular weight, it is possible to compare the molecular weights of different specimens by measuring the viscosity for each. The intrinsic viscosity of all the polymers and copolymers prepared was determined in this way, an Ostwald viscometer being used at 25°C, and the results obtained are recorded in Table 1. On comparing these results with those given in Table 4, it can be seen that a change in the molecular weight of poly-(1:3-dimethylbutyl methacrylate), both fully active and partially active specimens, corresponding to a doubling in the intrinsic viscosity, does not significantly alter the specific rotations.

The Preparation and Rotatory Powers of the Copolymers

In addition to the variation in concentration, initiator, and
molecular weight, the effect on the rotatory power of introducing into the polymer chain units other than 1:3-dimethylbutyl methacrylate, was also investigated. For this purpose copolymers were prepared of (+)-1:3-dimethylbutyl methacrylate with methyl methacrylate, with acrylonitrile, with styrene, and with diethyl fumarate, the ratio of each component present being calculated from an elementary analysis of the copolymer. In the case of methyl methacrylate two copolymers were prepared having molar ratios of (+)-1:3-dimethylbutyl methacrylate to methyl methacrylate of 1:2.33 and 1:3.20. Each of the copolymers mentioned above was initially prepared from inactive 1:3-dimethylbutyl methacrylate and the monomer in question. It was then heated to constant weight at high vacuum, and analysed; the analysis in each case having been found to correlate with substantial entry of the second monomer into the copolymer, a specimen of the latter was then prepared with the fully active monomer. It was necessary to heat the copolymer in a high vacuum to remove any unpolymerised monomers, and in the case of the copolymers with acrylonitrile, styrene and diethyl fumarate, which had been purified by the precipitation technique, to remove entrapped solvent. For the styrene copolymer purification by this means necessitated dissolving the copolymer in sym-tetrachloroethane, which proved extremely difficult to remove, and it was necessary to heat the precipitated copolymer for thirty days to remove the last traces of the solvent.

Purification by precipitation generally involves a certain amount of fractionation of the copolymer with consequent loss of material, since the lower-molecular weight fractions of the polymer are often
soluble in the precipitating solvent. This was particularly noticeable with the acrylonitrile copolymer where nearly half the material was initially lost in this way.

An attempt was also made to prepare copolymers of 1:3-dimethylbutyl methacrylate with trans-stilbene, dimethyl fumarate, and maleic anhydride. Unfortunately all these monomers are solids which are insoluble in the 1:3-dimethylbutyl methacrylate and although these mixtures did indeed copolymerise it proved impossible to remove the unreacted monomers.
SECTION 2.

Evaluation of the Contributions to the Rotatory Powers

In order to discuss the results obtained it is necessary to use the distinction that has been made by Bernal (Diss. Farad. Soc., 1958, 25, 1) between the primary and secondary chain structure of a macromolecule. The following treatment provides a provisional analysis of the rotatory power of the polymers, and copolymers, in terms of various aspects of their structure. There are potentially three contributions to the rotatory power of the polymer;

(a) that due to the (+)-1:3-dimethylbutyl methacrylate groups, together with the groups to which they are immediately bonded in the polymer

(b) that due to possible dissymmetry in the primary chain structure of the polymer

(c) that due to possible dissymmetry in the secondary chain structure

Fully Active Polymers

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{C} & \quad \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} & \quad \text{CH}_3 \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{C}_6\text{H}_{13} & \quad \text{C}_6\text{H}_{13} & \quad \text{C}_6\text{H}_{13}
\end{align*}
\]

(I)

\[
\begin{align*}
\text{H} & \quad \text{CH}_2 - \text{C} - \text{CH}_2 - \text{H} \\
\text{CO} & \quad \text{CO} & \quad \text{CO} \\
\text{C}_6\text{H}_{13} & \quad \text{C}_6\text{H}_{13} & \quad \text{C}_6\text{H}_{13}
\end{align*}
\]

(II)
It is considered that the contributions of the asymmetric side
groups, (+)-1:3-dimethylbutyl, together with their immediate environment
in the molecule, is substantially equal to the molecular rotation of
(+)-1:3-dimethylbutyl pivalate, since the structures within the square
brackets of (I) and (II) are identical. A further factor in favour of
this view is that the effect of a particular group on the optical
rotation of an asymmetric centre becomes smaller the further away the
group is from the asymmetric centre. Thus the individual (+)-1:3-di-
 methylbutyl groups in the polymer should have little or no effect on
each other's rotatory power since the asymmetric centres in each side
group are separated by at least five carbon atoms and two oxygen atoms.

It can be seen, on comparing the molecular rotations of the
fully active poly-((+)-1:3-dimethylbutyl methacrylate)[whose molecular
weight in this connection is taken as that of the monomeric unit] with
that of the pivalate, that the algebraic difference between the molecular
rotations is a series of negative values of about one-third the magnitude
of those of the pivalate. This rotatory power (designated \([M]_s\) in Table
4) must therefore be ascribed to structural features other than those of
the individual ester units. The present polymers all contain the poly-
(methacrylate) main chain, the 'isotactic' and 'syndiotactic' structures of
which are represented by the Fischer projection formulae (III) and (IV).

\[
\begin{align*}
\text{(III)} & \quad X = \text{COOCH(Me)CH}_2\text{CH(Me)}_2 \\
\text{(IV)}
\end{align*}
\]
As discussed earlier in relation to the literature, each of these structures has numerous 'local' planes of symmetry, the first at every carbon atom, the second at every methylated carbon atom, whence it is inferred that neither configuration, nor random sequences of short sections of (III) and (IV) alternatively, can give rise to optical activity. This conclusion is supported by the experimental evidence discussed in the introductory section.

As also discussed earlier, the mode of termination of the polymerisation reaction could have an effect on the stereochemistry of the polymer molecules, but only if termination is by combination. In fact Bevington, Melville and Taylor (J. Polym. Sci., 1954, 12, 449) have shown that at 60° methyl methacrylate terminates predominantly by disproportionation. They initiated the polymerisation with α:α'-azo-iso-butyronitrile labelled with carbon 14 and found that the product contained 1,2 fragments of 'C(CH₂)₂-CH₂ per polymer molecule. More recently

Bamford and Jenkins (Nature, 1955, 176, 78) found that poly-(methyl methacrylate ) terminated entirely by disproportionation in benzene at 90°. They initiated the polymerisation with δ:δ'-azo-(δ-cyano-n-valeric acid) under conditions such that chain transfer reactions were negligible. This initiator decomposes thermally, giving radicals of the structure

'C(CH₂)₂-CH₂-COOH. Termination by a combination reaction would produce a polymer molecule containing two such fragments, one at each end of the chain, whilst disproportionation yields polymer molecules having this functional group at only one chain end. Bamford and Jenkins
then converted the carboxyl group to the acyl chloride and reacted the chloride grouping with either 1:6-hexane diol or 1:10-decane diol, thus coupling two polymer molecules together. If the polymer chains each contained only one of these chloride groups then only two polymer chains could be so coupled and the number-average degree of polymerisation (as indicated by the intrinsic viscosity of the polymer) could increase, at the most, to twice its original value (neglecting the weight of the ligand). If, however, termination occurred by combination, theoretically all the polymer molecules could be joined together and under suitable conditions the degree of polymerisation would be expected to increase to much more than twice its original value. These workers found that the intrinsic viscosity of the poly-(methyl methacrylate) increased from 0.145 to 0.201 indicating a coupling ratio (i.e. ratio of initial and final number-average degree of polymerisation) of 1.6. As stated this shows that no significant amount of combination occurs.

Since disproportionation is the mode of termination of poly-(methyl methacrylate) it is probable that the present poly-(methacrylate) terminates in a like manner, since the size of the ester grouping in poly-(1:3-dimethylbutyl methacrylate) would be an additional factor preventing two polymer chains coupling. If this is indeed the case then the polymer chains possess the symmetry properties associated with simple terminations, that is, they would have essentially the same symmetry properties as non-terminal sections of the chains, together with relatively small terminating groups. It is thus concluded that the primary chain structure exhibits an overall symmetry, and therefore does
not contribute to the rotatory power of the polymer.

Since, as mentioned in the introductory section, a regular right-handed or left-handed helix is dissymmetric, the secondary structure can, in principle contribute to the rotatory power, and the rotations \([M]_s\) are ascribed to this source. As stated, these rotations are a series of negative values for the poly-\((+)-1,3\)-dimethylbutyl methacrylate) and it is interesting to compare this with the \(\text{L}\)-poly-peptides where the rotations due to the secondary structure (a right-handed helix) are a series of positive values. Dissymmetric coiling of the main chain, conforming more to a right-handed than a left-handed helix (or \textit{vice-versa}) may have arisen during the polymerisation, or alternatively it may be the most stable conformation of the chain molecule in solution.

Inspection of a C.R.L.-catalin model of the polymer in the 'syndiotactic' configuration, with all the side groups in the same configuration, shows that the main chain conforms to a planar zig-zag only if the chain methyl groups and the carbonyl groups of the ester \((\text{\#}\text{\#}\text{\#})\) are closely packed. As can be seen from the photographs of this conformation, the methyl groups form two long lines and it is possible to fit the side groups on so that the molecule as a whole is flat with empty space above and below the chain. However, Coumoulos (Proc. Roy. Soc., 1944, \textit{A}182, 166) from electron diffraction patterns of multilayers of the polymers has deduced for a series of five poly-(alkyl methacrylates) that the best structural fit to the experimental data is provided by a zig-zag carbon atom main chain, which has a head-to-tail
LEGEND

All the models are in the 'syndiotactic' configuration

(I) Six complete units of the poly-(1:3-dimethylbutyl methacrylate) chain.

(II) The poly-(methacrylate) main chain without the alkyl groups.

(III) Poly-(1:3-dimethylbutyl methacrylate). The chain end-on.
Poly-(1:3-dimethylbutyl methacrylate)
The Chain End-On.
structure with the 'syndiotactic' configuration, and with the side chains on planes perpendicular to the axis of the main chain. He further states that these side groups are subject to lateral cohesive forces which group them in clusters and that in these clusters the side chains tend to arrange themselves parallel to each other at the distance of closest approach. Coumoulos also notes that the methacrylate main chain, in the 'syndiotactic' configuration, can coil in a spiral of approximately 65Å diameter, the 'height' of the polymer determining the distance apart of the successive loops of the spiral. Since this is a feature of the methacrylate main chain and since in the optically active poly-((+)-1:3-dimethylbutyl methacrylate) the side groups are asymmetric and all of one configuration, a preference is to be expected for either a right-handed or a left-handed helix.

An inspection of a C.R.L.-catalin model of the 'isotactic' configuration, with the side groups in the same configuration as before, indicates that, with these C.R.L.-catalin models, the main chain is forced into a helical form by reason of the methyl groups themselves.

From the stability of the rotatory power of the polymer to change in molecular size, and in end groups, and to the alteration of the larger-scale coiling, i.e. that due to solvation of the molecule, associated with the change in concentration of its solutions, it is inferred that the secondary coiling, for a given temperature and solvent, is a stable, and if averaged over more than a minimum number of units, a constant feature of the polymer chain.
Partially Active Polymers

Experimentally the partially active polymers were prepared from partially active (-)-monomer. However, to facilitate comparison and discussion with the fully active polymer etc., the signs of rotation of the partially active polymer have been reversed throughout, this being permissible since every component in the (-)-polymer would find equal expression, though of opposite sign, in the corresponding (+)-polymer. The data thus become strictly comparable, in sign as well as magnitude, with those for the other polymers, and the pivalate.

These polymers can be considered as copolymers of the optically pure (+)-methacrylate with the (•)-methacrylate, and, with respect to these polymers, and the copolymers of the (+)-1:3-dimethylbutyl methacrylate with methyl methacrylate, acrylonitrile, styrene, and diethyl fumarate, it is of use to calculate the molecular secondary rotation due to units of the chain other than those of the optically pure monomer. That is, to calculate the contribution to the rotatory power of that part of the secondary structure derived from the optically inactive monomer. Evaluation of this quantity, \([M]_\text{sn}^\prime\), requires subtraction of a molecular rotation component equivalent to the proportion of the optically pure monomer present.

In any copolymer where \(x\) is the weight fraction of the optically pure monomer present, \(\alpha\) is the observed rotation of the copolymer solution, \(\alpha^\prime\) that part of it due to the optically pure units and \(\alpha_\text{sn}\) that due to the second monomer, then:  
\[
\alpha_\text{sn} = \alpha - \alpha' 
\]
Also \( [a]_{sn} = \frac{100 a_{sn}}{1 c(1-x)} \); \( [a] = \frac{100 a}{1 c} \); and \( [a'] = \frac{100 a'}{1 c x} \) \\

where \( [a]_{sn} \) is the specific rotation of the second-monomer units in the copolymer, (this rotation being entirely due to the secondary structure contributed by these units), \( [a] \) is the specific rotation of the copolymer, and \( [a'] \) is the specific rotation due to the optically pure monomer units including contributions from both the primary and secondary structure: i.e. it equals the specific rotation of the optically pure homopolymer.

therefore

\[
[a]_{sn} \frac{1 c(1-x)}{100} = \frac{[a] 1 c - [a'] 1 c x}{100}
\]

\[
[a]_{sn} (1-x) = [a] - [a'] x
\]

thus

\[
[a]_{sn} = \frac{1}{(1-x)} \left( [a] - [a'] x \right)
\]

and

\[
[M]_{sn} = \frac{m}{(1-x)100} \left( [a] - [a'] x \right)
\]

where \( m \) is the molecular weight of the second monomer.

The assumption made is that, at least for the partially active polymers and for the copolymers with methyl methacrylate, the \((+)-monomer unit, in its situation in the copolymer, contributes the same rotatory power as in the fully active \((+)-polymer: that is, not only the component \((a), above, but also that due to the secondary coiling \((c) above). In the partially active polymers, the contribution \([M]_{sn} \) from the \((\pm)-units is found to be a series of small quantities of variable sign. From
this it is inferred that these units are essentially optically inert, \(d\)-contributions of whatever kind, i.e. both primary and secondary, being cancelled by the corresponding \(l\)-contributions.

Copolymers with Methyl Methacrylate

With respect to these copolymers, the rotations deduced for the secondary structure of the methyl methacrylate units, given in Table 4, are quantities of positive value, opposite to that found for the secondary structure of the 1:3-dimethylbutyl methacrylate units. A further interesting point is that the copolymer richer in the \((+)-1:3\)-dimethylbutyl methacrylate, i.e. the copolymer with the two monomeric units in the ratio of 1:2.33, has the larger \([M]_{sn}\) values. It is not possible to give an exact explanation of these results and in particular it is difficult to furnish a reason for the sign difference. However, with respect to the difference in magnitude it is possible that a left-handed rather than a right-handed helical form (or vice-versa) of the methyl methacrylate sequences conforms better to adjacent \((+)-1:3\)-dimethylbutyl methacrylate units, whence a greater proportion of the latter will increase the dissymmetry in coiling of the methyl methacrylate sequences, giving rise to a larger value of \([M]_{sn}\).

Copolymers with Acrylonitrile, Styrene, and Diethyl Fumarate

The acrylonitrile copolymer was prepared by heating together a mixture of acrylonitrile, \((+)-1:3\)-dimethylbutyl methacrylate and benzoyl peroxide in a sealed tube, the monomers being approximately in
the ratio of 1:1. The mixture was degassed and the tube evacuated before being sealed. This is necessary since the polymerisation of acrylonitrile is inhibited by oxygen, so much so that acrylonitrile can be easily distilled in the absence of any other inhibiting agent. The copolymer, after purification by precipitation from dimethylformamide by water, was analysed in duplicate for its nitrogen content from which the ratio of the two monomeric units present was calculated, and found to be 1.30 units of (+)-1:3-dimethylbutyl methacrylate to every acrylonitrile unit. This ratio was then used to calculate the weight-fraction of the optically pure units present and this value, together with the measured rotations of duplicate solutions of the copolymer in sym-tetrachloroethane, to calculate the value \[ [M]_{sn} \] given in Table 4.

The copolymer with styrene was prepared in a similar manner except that it was not necessary to degas the mixture or evacuate the tube before sealing since oxygen has much less effect on the polymerisation of styrene than on the polymerisation of acrylonitrile. The copolymer was again purified by precipitation, this time from sym-tetrachloroethane by methyl alcohol, and analysed. The duplicate analysis figures were averaged and the indicated oxygen content used in the calculation of the ratio of the monomeric units present. This ratio, one molecule of styrene to 1.17 molecules of (+)-1:3-dimethylbutyl methacrylate was again used, via the calculated monomer weight-fractions, and together with the measured rotations of the solutions of the copolymer in sym-tetrachloroethane, to calculate the values of \[ [M]_{sn} \] for the copolymer.
The diethyl fumarate copolymer was prepared and purified in an exactly similar manner to that used for the styrene copolymer. The duplicate analysis figures were averaged to give the oxygen content of the copolymer, which again was used to calculate the monomeric-unit ratio, 30.1 units of the optically pure monomer to every diethyl fumarate unit, and hence \([M]_{Sn}\).

With these three copolymers it is interesting to calculate, in addition to the values \([M]_{Sn}\), the average total molecular secondary rotation of the monomer, i.e. that contributed by units derived from both the optically active and optically inactive monomers.

If \((c)\) is the concentration of the copolymer solution then the concentration of the optically active units present is given by

\[
c_u = cx\quad \text{where} \quad x \quad \text{is the weight-fraction of the optically pure units}
\]

Therefore

\[
[a]_p = \frac{100 \alpha_p}{1cX}
\]

where \(\alpha_p\) is the rotation due to the primary chain structure of the copolymer and \([a]_p\) is the corresponding specific rotation.

Thus

\[
\alpha_p = \frac{[a]_p,1cX}{100}
\]

Now the total secondary rotation, \(\alpha_s = \alpha - \alpha_p\) where \(\alpha\) is the rotation of the solution therefore

\[
[a]_s = \frac{100}{1c} \left( \frac{\alpha - [a]_p,1cX}{100} \right)
\]
and \[ [\alpha]_s = [\alpha] - x [\alpha]_p \] \hspace{1cm} (1)

We can calculate the average molecular secondary rotation on the basis of the average molecular weight of the two-carbon chain unit. Thus if there are \(a\) units of (+)-1:3-dimethylbutyl methacrylate of molecular weight \(Y\) in every one hundred units, then there are \((100-a)\) of the second monomer of molecular weight \(m\). Therefore the average molecular weight of the two-carbon chain unit is

\[
\frac{aY + m(100-a)}{100}
\]

and therefore the total molecular secondary rotation \([M]_s\) is

\[
\left(\frac{aY + m(100-a)}{10000}\right) [\alpha]_s \hspace{1cm} (2)
\]

The value of \([\alpha]_p\) can be calculated from the specific rotation of the (+)-1:3-dimethylbutyl pivalate as follows:

For a pivalate solution having \(\alpha_{piv} \), \(l\), \(c_{piv}\); the concentration of the corresponding solution of (+)-1:3-dimethylbutyl methacrylate units is given by

\[
c_u = c_{piv} \left(\frac{\text{molecular weight of monomer } (Y)}{\text{molecular weight of pivalate } (Z)}\right)
\]

whence

\[
[\alpha]_p = \frac{100 \alpha_p}{l \cdot c_{piv} \left(\frac{Y}{Z}\right)} = [\alpha]_{piv} \left(\frac{Y}{Z}\right) \hspace{1cm} (3)
\]

Finally bringing together (1), (2), and (3) we have

\[
[M]_s = \left(\frac{aY + m(100-a)}{10000}\right) \left(\frac{[\alpha] - x [\alpha]_{piv} \left(\frac{Y}{Z}\right)}{10000}\right)
\]
We thus have two derived quantities \([M]_{sn}\) and \([M]_{s}\). \([M]_{sn}\) provides a series of quantities which express the rotatory power due to the units derived from the symmetrical monomer on the assumption that the (+)-1:3-dimethylbutyl methacrylate units exert both primary and a secondary rotation equal to that which they exert in the homopolymer. \([M]_{s}\) provides a measure of the average rotatory power of the two-carbon chain-unit, whether derived from the methacrylate or from the second monomer, it here being assumed that the (+)-1:3-dimethylbutyl methacrylate units continue to exert only the primary rotatory power which they exert in the homopolymer.

Before comment is made on the validity of these assumptions, the values of \([M]_{s}\) and \([M]_{sn}\) are compared with those of the homopolymer. For the acrylonitrile copolymer, it is seen that the values of \([M]_{s}\) are, like those of the homopolymer, a series of negative rotations, but numerically smaller than those of the homopolymer. I.e., the relatively large (-)-component ascribed to the secondary structure of the (+)-1:3-dimethylbutyl methacrylate units is not shown by the acrylonitrile units. This finds expression in the \([M]_{sn}\) for these units, which form a series of positive rotations.

For the styrene copolymer, the \([M]_{s}\) values are negative and numerically larger than those of the homopolymer, whence the styrene units contribute a rotation of the same sign, but higher than, that of the methacrylate units. This is re-expressed in the \([M]_{sn}\) values, which are seen to be of this description.
With respect to the diethyl fumarate copolymer, the \([M]_s\) values are negative and a little larger than those of the homopolymer, whence the diethyl fumarate units exert a larger negative rotation than the methacrylate units. Further, these units are present only in a small amount, whence the rotatory power calculated for them \([M]_{sn}\) is relatively large, particularly for the shorter wavelengths.

It is extremely difficult to explain all these results for the acrylonitrile, styrene, and diethyl fumarate copolymers at the present stage, and it is only possible to point out the following facts concerning the stereochemical structures of these copolymers.

The monomer reactivity ratios for the copolymerisation of styrene \((M_1)\) with methyl methacrylate \((M_2)\) are \(r_1=0.52\) and \(r_2=0.46\), showing a tendency to alternation. For the present copolymer of styrene \((M_1)\) with (+)-1:3-dimethylbutyl methacrylate \((M_2)\), the monomer reactivity ratio \(r_2\) for the 1:3-dimethylbutyl methacrylate would be expected to be much less than the corresponding value for methyl methacrylate, since the large size of the side group on both the methacrylate radical-end and the methacrylate monomer would sterically inhibit their reaction. Further this bulk-factor would act so as to reduce the tendency of a styrene radical-end to react with the methacrylate, thus tending to increase the value of \(r_1\). The total effect on the copolymerisation would probably be that a 1:3-dimethylbutyl methacrylate unit would almost always be followed by a styrene unit, although the converse would not necessarily be true.
A similar situation arises for the copolymer with acrylonitrile. The monomer reactivity ratios for the copolymerisation of acrylonitrile \((M_1)\) with methyl methacrylate \((M_2)\) are \(r_1 = 0.18\) and \(r_2 = 1.35\); the value of \(r_2\) would again be expected to be reduced for the 1:3-dimethylbutyl methacrylate, the small value of \(r_1\) being raised somewhat; in total, the tendency to alternation would probably be greater in the present copolymer than in the copolymer of acrylonitrile with methyl methacrylate. Thus in trying to explain the results obtained it must be pointed out that the assumptions made in deducing the \([M]_s\) and \([M]_{sn}\) values are not necessarily correct, since the presence of these second monomer units prevent strict comparison of the structure of the copolymer with that of the pivalate, particularly in view of the tendency to alternation probably present in these copolymers.

Three further interesting points concern the possible contributions to the molecular rotations of the styrene and acrylonitrile copolymers; first, since the copolymers are not strictly alternating the stereochemical properties deduced by Arcus (J.C.S., 1957, 1189, discussed in the introductory section), for the alternating copolymerisation of \(\text{CH}_2=\text{CHA}\) with \(\text{CH}_2=\text{CXY}\), need not strictly apply to these copolymers. There is, therefore, the possibility of dissymmetry in the primary chain to be borne in mind as a contributor to the molecular rotation.

A second feature of these two copolymers concerns their mode of termination: Bamford and Jenkins (Nature, 1955, 176, 78; Trans. Farad. Soc., 1959, 179) using the method of coupling preformed polymer with
reactive end groups, as for the polymerisation of methyl methacrylate, have shown that both styrene and acrylonitrile in homopolymerisation terminate by a combination reaction. They found that the intrinsic viscosity of the styrene increased from 0.143 to 0.818, indicating a coupling ratio of 11.5, and for the acrylonitrile from 0.265 to 1.13, indicating a coupling ratio of 11.2. Thus, as discussed in the introduction, meso, or other, stereoisomeric structures could arise in these copolymers and would have to be considered in assigning the molecular rotations to any particular structural features.

In addition the different sizes of the substituents on the second monomer may also affect the rotations of the copolymers. Both styrene and acrylonitrile are monomers of the type CH$_2$=CHX, that is they do not carry the $\alpha$-methyl group characteristic of the methacrylates. Cooumoulos (loc. cit.) carried out electron diffraction studies on a number of poly-(acrylates), which again do not bear the $\alpha$-methyl group, and found that these polymer chains were much more flexible than the corresponding poly-(methacrylates). Thus the introduction of monomers of the type CH$_2$=CHX into the main chain of the 1:3-dimethylbutyl methacrylate should increase the flexibility of the chain. However, the phenyl group of styrene is a large group and for styrene to fit into the chain in a regular fashion requires that the chain be twisted into a helical form (Natta's 'isotactic' poly-(styrene)). Thus the copolymer with styrene would be expected to have a stiffer chain than the acrylonitrile copolymer where the comparatively small -CN group should be able to fit easily between the 1:3-dimethylbutyl methacrylate groups and
should markedly increase the flexibility of the chain, since, due to the alternation tendency, the effect of the acrylonitrile units is to space out the 1:3-dimethylbutyl methacrylate units and so reduce steric effects between them.

The effect of change in flexibility of the chain on the $[M]_{sn}$ values for the two copolymers cannot be estimated at present and attention can only be drawn to the numerical difference in $[M]_s$ (large negative $[M]_{sn}$) for the styrene copolymer, having the tighter coiling, and the numerical decrease in $[M]_s$ (positive $[M]_{sn}$) for the acrylonitrile copolymer, having the looser coiling, in comparison with the values for the homopolymer.

As has been stated, with the diethyl fumarate copolymer the negative $[M]_s$ values are greater than the expected values by an amount that is large in comparison with the small amount of diethyl fumarate units present, with the result that the molecular rotations due to these units are large negative values. It thus appears that there is some effect present which does not appear in the acrylonitrile or styrene copolymers. The small amount of diethyl fumarate present in the copolymer would not have been expected to have much effect on the symmetry properties of the chain or on the degree of helical coiling of the polymer. In addition, since the (+)-1:3-dimethylbutyl methacrylate units are in such large excess, it seems likely that termination is again mainly by disproportionation and the steric effects due to termination by combination probably need not be considered.

The presence of diethyl fumarate, however gives rise to new
optical centres in the chain, these centres being asymmetric carbon atoms of classical type (stared in I).

\[ \text{CH}_2\text{C}^\text{CH}^\text{CH}_2\text{C}^\text{CH}_3 \]

Further it is possible that all the diethyl fumarate units assume the same configuration in order to fit into the chain, since the 1:3-dimethyl-butyl methacrylate units are all of one configuration. This could account for the high rotation due to these units.

The Temperature Coefficient of Rotation

The rotation of solutions of the fully active polymer and of the pivalate were measured at \(\lambda_{5893}\) over the temperature range 25-95\(^\circ\) and the results plotted. It can be seen that the plot of the molecular rotation against temperature is not notably different for the polymer and the pivalate.

On the postulate that the change shown is substantially due to the temperature coefficient of rotation of

\[ \text{CH}_2\text{C}^\text{CH}^\text{CH}_2\text{C}^\text{CH}_3 \]

then the temperature coefficient of rotation due to the secondary coiling is small. We have, however, to consider two components:

(a) The amount of coiling versus temperature;
(b) The variation of the molecular rotation, due to a given amount of coiling, with temperature;

Their product is small (difference curve of graph), but we cannot be certain whether both $a$ and $b$ are insensitive to temperature, or whether they move in compensating directions.
TABLE 4.

Rotatory Powers of Polymers and Copolymers of (+)-1:3-Dimethylbutyl
Methacrylate, of (+)-1:3-Dimethylbutyl Pivalate, and of (+)-1:3-
Dimethylbutyl Methacrylate Monomer in sym-Tetrachloroethane at 25°.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution No.</th>
<th>Concentration g./100ml. of solution</th>
<th>Nature of Rotation</th>
<th>Rotation $\lambda^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6438</td>
</tr>
<tr>
<td>Pivalate</td>
<td>(i)</td>
<td>4.71</td>
<td>[a]</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>4.74</td>
<td>[a]</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M]</td>
<td>37.9</td>
</tr>
<tr>
<td>Monomer</td>
<td>(i)</td>
<td>5.06</td>
<td>[a]</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>5.01</td>
<td>[a]</td>
<td>31.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M]</td>
<td>54.1</td>
</tr>
<tr>
<td>Polymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fully active specimen (1)</td>
<td>(i)</td>
<td>4.79</td>
<td>[a]</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>5.01</td>
<td>[a]</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>(iii)</td>
<td>6.63</td>
<td>[a]</td>
<td>13.9</td>
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<tr>
<td></td>
<td>(iv)</td>
<td>7.19</td>
<td>[a]</td>
<td>15.0</td>
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<td></td>
<td></td>
<td></td>
<td>[M]</td>
<td>24.3</td>
</tr>
<tr>
<td>Fully active specimen (2)</td>
<td>(i)</td>
<td>4.96</td>
<td>[a]</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>4.88</td>
<td>[a]</td>
<td>14.8</td>
</tr>
<tr>
<td></td>
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<td>[M]</td>
<td>24.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M]$_s$</td>
<td>-13.0</td>
</tr>
<tr>
<td>Part. active B$_2$O$_3$-initiated</td>
<td>(i)</td>
<td>4.93</td>
<td>[a]</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>4.85</td>
<td>[a]</td>
<td>9.4</td>
</tr>
<tr>
<td>Part. active A.I.B.N.init.</td>
<td>(i)</td>
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<td>[a]</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>4.81</td>
<td>[a]</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[M]$_{sn}$</td>
<td>1.3</td>
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</table>
### Copolymers

<table>
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<tr>
<th>Compound</th>
<th>Solution No.</th>
<th>Concentration g./100ml. of solution</th>
<th>Nature of Rotation</th>
<th>Rotation $\lambda A^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>with Me.Meac. 1:2.33</td>
<td>(i)</td>
<td>5.27</td>
<td>[a]</td>
<td>6.3  8.8  10.1  11.9  16.6</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>5.17</td>
<td>[a]</td>
<td>7.0  8.7  10.3  11.7  15.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[M]_{sn}$</td>
<td>1.1  2.2  3.0  2.8  3.5</td>
</tr>
<tr>
<td>with Me.Meac. 1:3.20</td>
<td>(i)</td>
<td>5.33</td>
<td>[a]</td>
<td>5.0  6.8  8.3  9.6  12.5</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>5.14</td>
<td>[a]</td>
<td>6.0  7.0  8.1  9.3  12.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[M]_{sn}$</td>
<td>0.8  1.0  1.7  1.8  1.1</td>
</tr>
<tr>
<td>with acrylonitrile</td>
<td>(i)</td>
<td>4.82</td>
<td>[a]</td>
<td>14.3 17.0 19.7 23.1   --</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>4.87</td>
<td>[a]</td>
<td>14.4 16.9 19.5 23.0   --</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[M]_{s}$</td>
<td>-5.5 -5.6 -6.0 -6.5   --</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[M]_{sn}$</td>
<td>16.7 8.4 7.6 6.2   --</td>
</tr>
<tr>
<td>with styrene</td>
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<td>4.88</td>
<td>[a]</td>
<td>3.4  4.7  4.9  5.6  6.5</td>
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<tr>
<td></td>
<td>(ii)</td>
<td>4.87</td>
<td>[a]</td>
<td>3.3  4.4  4.7  6.2  6.7</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$[M]_{s}$</td>
<td>-15.9 -17.1 -20.2 -23.1 -35.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[M]_{sn}$</td>
<td>-19.2 -22.3 -27.1 -31.5 -36.5</td>
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<tr>
<td>with diethyl fumarate</td>
<td>(i)</td>
<td>4.94</td>
<td>[a]</td>
<td>13.0 16.2 18.4 21.9  30.0</td>
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<tr>
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<td>(ii)</td>
<td>4.95</td>
<td>[a]</td>
<td>14.7 16.0 19.0 21.8  27.9</td>
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<td>$[M]_{s}$</td>
<td>-13.1 -14.9 -16.4 -17.3 -30.4</td>
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<td>$[M]_{sn}$</td>
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