PREPARATION AND REACTIONS OF POLYMERS AND
COPOLYMERS OF 2-METHYLBUT-1-EN-3-ONE, AND

RELATED STUDIES

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ABSTRACT

Poly(2-methylbut-1-en-3-one) was prepared by bulk polymerisation with azobisisobutyronitrile as initiator. Six copolymers of 2-methylbut-1-en-3-one and styrene in various ratios were prepared similarly.

The homopolymer on treatment in solution with hydrogen chloride gave a product in which water had been condensed from neighbouring acetyl side-chains to give a polymer containing series of conjugated double bonds.

The homopolymer was oxidised with aqueous alkaline potassium permanganate to give a copolymer of methacrylic acid and 3-methylbut-3-en-2-oxo-1-oic acid.

The homopolymer was reduced with lithium aluminium hydride in tetrahydrofuran to give a product containing 70% of secondary alcohol groups.

The homopolymer was treated with hydroxylamine hydrochloride in pyridine to give a product containing oxime groups, oxime anhydride groups and unreacted ketone groups.

The 1:2-copolymer was brominated to give a product in which all the methyl ketone side-chains had been converted to bromomethyl ketone side-chains.

The brominated 1:2-copolymer was reacted with thiourea to give a copolymer in which all the bromine had been replaced by
isothiourea groups.

Where possible low molecular weight analogues of the polymers were prepared, based on 2,2-dimethylbutan-3-one. The infra-red spectra of the polymers and polymeric derivatives were compared with those of the low molecular weight analogues.

The reactivities of the above polymeric compounds are discussed in relation to the characteristics of the corresponding molecular models.
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INTRODUCTION
(i) HISTORICAL INTRODUCTION

Macromolecular compounds such as proteins, polysaccharides and rubber have been known by chemists for a long time and have been the source of great interest and study. Early workers, although recognising the high molecular weights, believed the compounds to consist of units held together by some type of bond which differed from those found in common non-macromolecular organic compounds. As early as 1871 Hlasiwetz and Habermann attempted to point out the nature of these compounds in terms similar to those now accepted, but it was not until about 1930 that the picture was clarified.

In 1920 Staudinger published a paper proposing a chain structure for polystyrene and polyoxymethylene, the units being joined by normal covalent bonds. He did not attempt to explain the nature of the end-groups, but stated that the molecules were not likely to be cyclic. Staudinger supported his views with further evidence in subsequent papers.

In 1929 Carothers published a comprehensive paper clarifying the whole concept of polymer chemistry, in which he proposed certain definitions, including the classification of condensation and addition polymers. His views were accepted and now provide the basis of theoretical polymer chemistry.

Since those early dates the chemistry of polymers has developed a great deal, more and more research being undertaken as the potential
of macromolecular compounds became apparent.

(ii) GENERAL INTRODUCTION

(a) Molecular weight of polymers

As the most important and obvious difference between macromolecular compounds and low molecular weight compounds is the much larger molecular weight of the former, it is clear that the determination of this characteristic is of importance. Since any one sample of a polymer contains molecules of different chain lengths, the numerical value assigned to the molecular weight will depend on the method employed to average the heterogeneity. If the total mass of the polymer is divided by the number of molecules present, the number-average molecular weight, $\bar{M}_n$, is obtained:

$$\bar{M}_n = M_1 \frac{N_1}{\sum_i N_i} + M_2 \frac{N_2}{\sum_i N_i} + \cdots + M_i \frac{N_i}{\sum_i N_i}$$

$$\bar{M}_n = \frac{\sum_i M_i N_i}{\sum_i N_i}$$

where $N_1, N_2, N_i$ are the number of molecules having molecular weights $M_1, M_2, M_i$. If however the molecular weight of each species is measured by its weight fraction, the weight-average molecular weight, $\bar{M}_w$, is obtained:
Only when the polymer chains in a sample are the same length will $\bar{M}_w = \bar{M}_n$, otherwise $\bar{M}_w > \bar{M}_n$.

Of the methods available for determining the molecular weight of polymers, those which depend on the colligative properties of polymeric solutions, (i.e. ebulliometry, cryoscopy and osmometry,) will give the number-average molecular weight, as the phenomena utilised in these methods depend on the number of particles in solution. Similarly, end group analyses will give the number-average molecular weight. The weight-average molecular weight is determined by a light scattering technique.

Staudinger suggested in 1930 that the molecular weights of polymers could be related to the viscosities of polymer solutions. The empirical equation

$$[\eta] = K \bar{M}^\alpha$$

has been derived to relate the limiting viscosity number, $[\eta]$, to the molecular weight, $\bar{M}$, by use of the constants $K$, (in the range $0.5 - 5 \times 10^{-4}$) and $\alpha$, (usually in the range $0.6 - 0.8$.) This method gives the viscosity-average molecular weight, $\bar{M}_v$, which is
defined by the equation

\[ \bar{M}_v = \left[ \frac{\sum N_i M_i (1 + \alpha)}{\sum N_i M_i} \right] \frac{1}{\alpha} \]

It may be pointed out that as \( \alpha \to 1 \), \( \bar{M}_v \to \bar{M}_w \). The limiting viscosity number is defined by

\[ [\eta] = \lim_{C \to 0} \left[ \frac{1}{C} \ln \left( \frac{\eta}{\eta_0} \right) \right] \]

where \( C \) is the concentration of the polymer solution in g./100 ml., and \( \eta/\eta_0 \) is the viscosity ratio of solution to solvent.

When the concentration \( C \) is kept low (1% or less,) the difference in density of the solution and solvent becomes negligible, and, where \( t/t_0 \) is the ratio of flow times of equal volumes of solution and solvent in a viscometer, \( \eta/\eta_0 \approx t/t_0 \). The logarithmic viscosity number is then given by

\[ [\eta]_c = \frac{1}{C} \ln \left( \frac{t}{t_0} \right) \]

(b) Reactions of polymer side-chains

When studying the reactions and reactivity of polymer side-chains, the difference in environment of the groups comprising the side-chains and that of the same group contained in an analogous low molecular weight compound is of considerable importance. If a dilute solution of a polymeric compound is compared with a dilute solution of the low molecular weight analogue, it can be appreciated
that the reactive groups of the latter compound are separated by several molecules of solvent, while the reactive groups comprising the side-chains are only a few angstrom units apart. These may cause the following effects:

(i) If the reaction involves ionic species, a charge may develop on the polymer which will affect the rate or degree of reaction. For example, during the alkaline hydrolysis of poly(methylmethacrylate) the carboxylate groups formed during the reaction will tend to repel the hydroxyl ion reagent, and so the reaction will not go to completion.\(^{(7)}\)

(ii) Intramolecular reaction may take place. For example, if poly(vinyl chloride) is used as the halide component in a Friedel-Crafts reaction with benzene and aluminium chloride, the product is not polystyrene or a styrene-vinyl chloride copolymer, but a 1,3-indene derivative:\(^{(8)}\)

\[
\begin{align*}
\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} & \overset{n}{\longrightarrow} \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 - \text{CH} - \text{CH} & \overset{n}{\longrightarrow} \text{CH}_2 - \text{CH} - \text{CH} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

(iii) It is generally accepted that the side-chain on a polymer will experience more steric hindrance than the relevant low molecular-weight analogue.\(^{(9)}\) This may be due to the coiling of the polymer chain or to the crowding caused by neighbouring side-chains.
Another peculiarity of polymer modification arises when considering the reaction of neighbouring side-chains. Consider the polymer below in which neighbouring side-chains react to give a cyclic system:

\[
\begin{align*}
\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2
\end{align*}
\]

The side chains on carbon atoms 1 and 2 react together as do those on carbon atoms 4 and 5. This leaves the group on carbon atom 3 with no unreacted neighbour, so without cross-linking it must remain unreacted. Flory has analysed this system statistically and calculated that in such a reaction, 13.5% of the side chains remain unreacted.\(^{(10)}\) This has been confirmed experimentally, for example, metals may react with poly(vinyl chloride) to remove chlorine and yield cyclopropane structures. About 14% of the chlorine atoms remain after reaction.\(^{(11)}\)

The solubility of polymers is another important factor in polymer modification. In general, polymers tend to be less soluble
than smaller organic molecules. Highly crystalline, cross-linked or heavily branched polymers tend to be insoluble in normal solvents at moderate temperatures.

A polymer consisting of a fairly wide range of molecular weights may be partially soluble in a solvent or mixture of solvents, the lower molecular weight fractions dissolving while the higher fractions remain undissolved. This property gives a method of separating a polymer into fractions of a fairly narrow molecular weight range. In the present work no attempt was made to do this, solvents being chosen in which the polymers were completely soluble.

At the start of a reaction, a polymer may be completely soluble, but as reaction proceeds, the product may become insoluble and precipitate; this may give rise to incomplete reaction.

It is obvious that in a reaction on a polymer where there is not a 100% conversion, it is impossible to "purify" the product as both reacted and unreacted groups are contained on the same polymer chain.
REACTIONS OF I, POLY(2-METHYLBUT-1-EN-3-ONE),
AND II, POLY(BUT-1-EN-3-ONE).

The results of a literature survey are recorded here; the views of the various authors are given, although in some instances they appear based on insufficient evidence.

Reaction of I was reported in 1934 by Staudinger and Ritzenhalter, who reduced the polymer with hydrogen iodide and arsenic at 160° to give a compound \((C_5H_8)_x\), to which the authors gave the structure shown in fig.(a)

![Structure](image)

The reaction was carried out to show that I does not polymerise through the ketonic oxygen to give ether linkages in the chain. Such a polymer would not give a macromolecular product on reduction as above. The same authors note that 2-methylbut-1-en-3-one, (III) gave a black smeary product with stannic chloride, and that I was unreactive to normal ketone reagents containing nitrogen.\(^{(12)}\)

Marvel and his co-workers studied the pyrolysis of I.\(^{(13)}\) The reaction was carried out at 270-300° and at 360°. Water was distilled off together with some monomer, dimer and high boiling organic compounds. A dark brown residue remained which was soluble in acetone. This
polymer was reduced at high temperature and pressure with hydrogen and Raney nickel in dioxan. A considerable amount of oxygen was removed, and analysis indicated the structure shown in fig.(b). Ring closure had occurred to an extent of 86.5%. Chloroacetylation and acetylation gave results which confirmed the structure.

The carbonyl content of a copolymer of III and styrene was estimated by Rutovskii and Goncharov, who used a method involving the formation of the oxime. The reaction of I with aminoguanidine bicarbonate in dioxan/glacial acetic acid gave a compound in which 12% of the groups were converted to the guanohydrazone. See fig.(c) below.

When II was used in the above reaction, 69% of the ketone
groups were converted.\textsuperscript{(15)}

An aminated product was formed when ammonia was passed through a dimethylformamide solution of the copolymer of III and acrylonitrile at 30°.\textsuperscript{(16)}

Intramolecular aldol condensations occurred when I and II were treated with alkali; II reacted readily, while I required more powerful alkalis or a higher temperature.\textsuperscript{(17)} The resultant compounds were shown to be of the structures represented in figs. (d) and (e) by use of infra-red spectroscopy. It was observed that the compounds absorbed water tenaciously.

The reactions of poly(but-l-en-3-one), which has been more extensively investigated, form the remainder of this section.

The first reaction of II was reported in a German patent; a resinous product was formed by the reaction of II with formaldehyde and concentrated hydrochloric acid.\textsuperscript{(18)}

Marvel and his co-workers have studied II in some detail.\textsuperscript{(19,20,21)} They reported that a solution of II in pyridine or dioxan showed
little change when treated with zinc chloride at 50-60°, but that phosphorus pentoxide gave a highly coloured product which was insoluble and infusible, indicating cross-linking, but does not dehydrate.\(^{(19)}\) II was oxidised with selenium dioxide in dioxan, but oxygen was added to the molecule indicating that some of the acetyl groups may have been converted to hydrated glyoxal groups.\(^{(19)}\) Pyrolysis of II at 270°/3mm. under nitrogen caused loss of 20-22% water, (i.e. 1 molecule per unit of II.) Cracking of the residue gave five fractions one of which was indentified as 3-methylcyclohex-2-enone. The other fractions gave positive tests for the carbonyl group and on heating with selenium gave phenolic-smelling compounds. The red residue was soluble in acetone, showing that no cross-linking had occurred.\(^{(19)}\)

The formation of the oxime of II and its subsequent cyclising has been studied,\(^{(19-23)}\) the ease of formation being dependent on the \(pK_b\) of the amine and the molecular volume of II.\(^{(23)}\) The oxime was readily formed.\(^{(19,23)}\) When the oxime was treated with concentrated hydrochloric acid in absolute alcohol, the compound shown in fig.\((f)\) was formed.\(^{(21)}\)
Calculated:

C, 78.74; H, 7.76; N, 9.93%.

Found:

C, 79.05; H, 8.01; N, 9.87%.

The infra-red spectra of the compound shown in fig.(f) and the oxime were studied, and the relevant absorption band frequencies given.\(^{(21)}\)

The Beckmann rearrangement of the oxime failed.\(^{(24)}\)

Ammonia, amines, amides and various related compounds have been reacted with II.\(^{(23,25-33)}\) The reaction product with ammonia was reported in 1937; this compound when reduced gave a product "suitable for coating".\(^{(25)}\) The reaction of ammonia, methylamine and ethanolamine with an aqueous suspension of II, and of phenylhydrazine, aniline and aniline hydrochloride with II in glacial acetic acid was reported in 1938.\(^{(26)}\) The reaction-product of II with ammonia has more recently been allotted the same structure, containing a pyridine ring, as is obtained by the action of concentrated hydrochloric acid
on the oxime of II.\(^{(23)}\) Reaction rates are low except for ammonia, hydroxylamine and hydrazine.\(^{(23)}\)

\(\beta\)-cyanoethyl groups were introduced on to the carbon atom adjacent to the carbonyl group by treating a 7\% solution of II in dioxan with a mixture of acrylonitrile and trimethylbenzylammonium hydroxide. 1.25 \(\beta\)-cyanoethyl groups were introduced per carbonyl group.\(^{(32)}\)

A copolymer of but-1-ene-3-one (IV) and a cross-linking monomer such as divinylbenzene (2-30\%) was treated with ammonium formate, formamide, or a mixture of formic acid and an amine, and the product hydrolysed to give a polymer with at least 15\% of the carbonyl groups converted to amine groups. The final product was used as an anion-exchange resin.\(^{(27)}\) A copolymer of IV and 5-7\% of divinylbenzene was aminomethylated by treating the copolymer in dioxan with formaldehyde and dimethylamine hydrochloride at 91-95\(^{\circ}\) for 26 hours. This formed an anion-exchange resin with a capacity for chloride and sulphate ions of 5.66 m.eq./g.\(^{(29)}\)

Reaction of II with semicarbazide in ethanol gave the semicarbazone.\(^{(33)}\) The N,N-dimethylhydrazine of II was prepared from II and N,N-dimethylhydrazine with a little glacial acetic acid. This compound, (85\% converted from II,) was reduced with lithium aluminium hydride to the amine, (60\% conversion,\(^{(31)}\)) A sample of the oxime of II (95\% converted from II,) was reduced with lithium aluminium hydride
to the amine, (65% conversion,) and a copolymer of IV with styrene, 50% ketoximated, was 100% reduced with lithium aluminium hydride to the amine.\(^{(31,22)}\)

II and copolymers of IV with styrene were reduced with lithium aluminium hydride and sodium borohydride to the corresponding secondary alcohols.\(^{(31,33-35)}\) II was 90% reduced with lithium aluminium hydride, 50% reduced with sodium borohydride. A 1:1 copolymer of IV with styrene was 100% reduced with lithium aluminium hydride, and 75% reduced with sodium borohydride.\(^{(31)}\) Linear II, linear copolymer of IV with styrene, and cross-linked copolymer of IV with styrene, were all unreactive in the Meerwein-Ponndorf reduction with aluminium alkoxides, but all were reduced with lithium aluminium hydride. The alcohols were unreactive to aluminium alkoxide and methylethylketone.\(^{(35)}\)

II was oxidised with sodium hypochlorite in dioxan to give poly(acrylic acid).

Calculated for \((C_3H_4O_2)_n\):

\[
\begin{align*}
\text{C, } & 50.0; \\
\text{H, } & 5.55%.
\end{align*}
\]

Found:

\[
\begin{align*}
\text{C, } & 53.19; \\
\text{H, } & 5.92%.
\end{align*}
\]

i.e. 90% conversion.\(^{(20)}\)

A copolymer of IV with divinyl benzene was treated with phosphorus trichloride to give α-hydroxy phosphonic acid groups on the polymer.\(^{(36)}\)
Poly(vinylacetonyl ketone) was prepared by ionic polymerisation of IV and simultaneous condensation with acetic anhydride. The product chelated metals, e.g. CuII, UO₂II, and showed a preference for NdII over PrII.\(^{(37)}\)

II in acetone mixed with IV or furfural and a small trace of alkali, condensed to give net-like compounds.\(^{(38)}\)
The preparation of 2-methylbut-1-en-3-one

The preparation of this monomer was reported by F. Bayer and Co. in 1910. Formaldehyde and methyl ethyl ketone were condensed by an alkaline catalyst to give a keto-alcohol, which was dehydrated with e.g. zinc chloride or sulphuric acid to give 2-methylbut-1-en-3-one:

\[
\text{CH}_3 - \text{CO} - \text{CH}_2 - \text{CH}_3 + \text{HCHO} \xrightarrow{\text{alk.}} \text{CH}_3 - \text{CO} - \text{CH} = \text{CH}_3
\]

\[
\text{CH}_3 - \text{CO} - \text{CH} = \text{CH}_3 \xrightarrow{\text{ZnCl}_2} \text{CH}_3 - \text{CO} - \text{C} - \text{CH}_3
\]

A more recent report of the preparation is given by White in an essentially similar method. Methyl ethyl ketone and paraformaldehyde were condensed together under the influence of sodium hydroxide to give 2-methylbutan-1-ol-3-one. The latter compound was then dehydrated with concentrated sulphuric acid to give the required monomer, b.p. 97.5-98.0°C.
Reactions of ketones have been studied extensively and are recorded in detail in the literature. In the present work, some reactions of methyl-ketonic groups present as side-chains on a polymer were studied, the ketone being poly(2-methylbut-1-en-3-one):

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \\
\text{CO} \quad \text{CO} \quad \text{CO} \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{array}
\]

Fig. (I)

The monomer polymerises in a head-to-tail manner as shown by Marvel and his co-workers, while Staudinger and Ritzenthaler showed that it polymerises solely via the isopropenyl double bond to give an all carbon back-bone, and not via the carbonyl group to give an ether linkage in the back-bone as in fig. II. (See page 9).

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_2 - \text{C} = \text{C} - \text{O} \quad \text{CH}_2 - \text{C} = \text{C} - \text{O} \quad \text{CH}_2 - \text{C} = \text{C} - \text{O} \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{array}
\]

Fig. (II)

Poly(2-methylbut-1-en-3-one) was chosen for study rather than the simpler analogue poly(but-1-en-3-one),

\[
\begin{array}{c}
\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \\
\text{CO} \quad \text{CO} \quad \text{CO} \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{array}
\]

Fig. (III)
because it was intended to brominate the polymer to give bromomethylketone units. It can be seen from comparison of the two polymers (figs. I and III,) that in poly(2-methylbut-1-en-3-one) there is only one type of hydrogen atom in the α-position to the carbonyl group, viz: those of the "ketonic" methyl group, and so on bromination there is only one site where bromine is likely to replace hydrogen, whereas in poly(but-1-en-3-one) there are two such sites.

The reactions of poly(2-methylbut-1-en-3-one) and poly(but-1-en-3-one) as recorded in the literature are summarised at the end of the Introduction, (page 9.)

The homopolymer

The preparation of poly(2-methylbut-1-en-3-one) is described in the experimental section, page 57. After consideration of the methods available for polymerising the monomer, it was decided to use the method of bulk polymerisation for reasons of simplicity, speed of preparation and ease of isolation of the polymer.

Azobisisobutyronitrile was used as initiator; this on warming decomposes to give isobutyronitrile radicals and nitrogen:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 \quad - \quad \text{C} \quad - \quad \text{N} \quad = \quad \text{N} \quad - \quad \text{C} \quad - \quad \text{CH}_3 & \quad \rightarrow \quad 2\text{CH}_3 \quad - \quad \text{C} \quad + \quad \text{N}_2 \\
\text{CN} & \quad \text{CN} \quad \text{CN} \\
\end{align*}
\]

\[ (= R. \quad \text{Fig.(IV)} \]
These radicals attack the isopropenyl double bond and so initiate the polymerisation:

\[ R^\bullet + CH_2 = C \rightarrow R - CH_2 - C\cdot \]

\[ CH_3 \quad CH_3 \quad \overset{CH_3}{\overset{CH_3}{\overset{n}{\overset{CH_3}{\overset{CH_3}{C-H_8O}}}}}} \quad \overset{CH_3}{\overset{CH_3}{\overset{CH_3}{\overset{CH_3}{\overset{CH_3}{C-H_8O}}}}} \]

Fig. (V)

The initiating radical may clearly add to the double bond in either of two ways:

\[ R^\bullet + CH_2 = C \rightarrow R - CH_2 - C\cdot \]

(i) \[ \overset{CH_3}{\overset{CH_3}{\overset{CH_3}{\overset{CH_3}{\overset{CH_3}{C-H_8O}}}}} \]

(ii) \[ \overset{CH_3}{\overset{CH_3}{\overset{CH_3}{\overset{CH_3}{\overset{CH_3}{C-H_8O}}}}} \]

Fig. (VI)

It is probable that the addition is of the type shown in Fig. (VI)(i), as in this form, the resulting monomer radical may be stabilised by resonance with the acetyl group.

Termination of the polymerisation may occur by:

(i) the joining of two growing chains,
(ii) combination with initiator radicals, or

(iii) disproportionation:

\[
\begin{align*}
(i) & \quad R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CH}_2 \rightarrow \text{CXY}^* + R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CH}_2 \rightarrow \text{CXY}^* \\
& \quad \rightarrow R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CXY}^* \overset{m+n}{\rightarrow} R
\end{align*}
\]

(ii) \[ R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CH}_2 \rightarrow \text{CXY}^* \overset{m}{\rightarrow} R \]

(iii) \[ R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CH}_2 \rightarrow \text{CXY}^* + R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CH}_2 \rightarrow \text{CXY}^* \\
\rightarrow R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CH} = \text{CXY} + R \overset{\text{CH}_2 - \text{CXY}}{\leftarrow} \text{CH}_2 \rightarrow \text{CXYH}. \]

Fig. (VII)

Of these three methods of termination, method (ii) is usually considered unimportant. Various workers have shown that both methods (i) and (iii) occur in the polymerisation of methyl methacrylate, but that at 90°, method (iii) occurs about ten times as frequently as method (i).\(^{(41)}\) Although in the polymerisation of 2-methylbut-1-en-3-one the prevalent type of termination is not known, by analogy with the polymerisation of methyl methacrylate, method (iii) is thought to prevail.

Theoretically the homopolymer can take up several configurations and conformations, most of which were studied by making up various molecular structures using Courtauld atomic models. It may polymerise
in the isotactic form (VIII), the syndiotactic form (IX) or in an atactic form. In each of the two first mentioned forms, the acetyl side-chain may be oriented so that the carbonyl groups point (i) away from, (ii) towards the chain methyl groups, (iii) alternate in these positions, or be arranged in a random manner. Once these various structures have been made up, it is impossible to orientate the acetyl group about the carbon-carbon bond joining it to the back-bone. The whole molecule is inflexible, especially when compared with a model of the homologous poly(but-1-en-3-one). If each successive acetyl group along the chain is displaced away from its predecessor in the same direction normal to the back-bone, a helical molecule is obtained (iv). If the acetyl groups are similarly displaced alternately up and down, a zig-zag structure is obtained (v).

See next page.
In Figs. VIII and IX above, the atoms and groups comprising the structure lie in the same plane, this plane being normal to the axis of the main carbon chain.

- O = carbon;
- ◦ = methyl;
- ○ = carbonyl oxygen.
Photographs 1 and 2 show the model of the polymer made up as in Fig. IX (i); photographs 3 and 4 show the model of the polymer made up as in Fig. IX (ii). It is noticeable that the acetyl methyl groups tend to stick out from the main bulk of the polymer, whereas the chain methyl groups are more "buried".

By comparing the degrees of alkaline hydrolysis of various types of poly(methyl methacrylate), Glavis has shown that the polymer prepared by conventional free radical initiation is largely syndiotactic. (The degrees of hydrolysis, under stated conditions, of free radical initiated, syndiotactic and isotactic poly(methyl methacrylate) were 11; 13; and 49% respectively.) It is suggested that by analogy with the example above, poly(2-methylbut-1-en-3-one) is also largely syndiotactic as the two monomer molecules are similar in constitution:

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2 = \text{C} \\
\text{CO} \\
\text{CH}_3
\end{align*}
\quad
\begin{align*}
\text{CH}_3 \\
\text{CH}_2 = \text{C} \\
\text{CO} \\
\text{O} \text{CH}_3
\end{align*}
\]

although this configuration was not proved.

It was noted that in all conformations of the two configurations, the carbon atom of the carbonyl group was well buried in the molecule. (See photographs.) This would render attack of the positively polarised carbon atom by a nucleophilic reagent very difficult, as
the nucleophilic species probably approaches the carbonyl group from the side, leading to a tetrahedral product:

\[
X^- + C = O \xrightarrow{\text{[tetrahedral]}} C - O^- X
\]

This explains why such normal ketone reactions as the cyano-hydrin and bisulphite formations did not take place. It is known that sterically hindered carbonyl compounds such as 2,2-dimethylbutan-3-one will not form bisulphite compounds in very high yields; similarly, the cyanohydrin derivative does not form with many ketones, although 2,2-dimethylbutan-3-one will form a cyanohydrin.

The logarithmic viscosity numbers of the various preparations of the homopolymer (and of the copolymers) were determined as a means of characterisation. In the absence of knowledge of \( K \) and \( \alpha \) in the equation connecting limiting intrinsic viscosities and molecular weights, \([\eta] = K\bar{M}^\alpha\), the latter could not be derived.

The infra-red spectrum of the homopolymer was determined and compared with that of 2,2-dimethylbutan-3-one, which, as can be seen from fig.(XI) is a close analogue of the repeating units of the polymer:

![Chemical structure](image)
The frequencies of various absorption bands in the spectrum of the homopolymer are given below, with the corresponding band in the spectrum of the model compound given in parentheses:

- **C = C stretch:** 1710, (1710)
- **C - H bend:** 1480, (1480); 1430, (1430); 1390, (1390); 1360, (1365 - 1355 doublet)
- **C-C or C-O stretch:** 1250, (1275); 1130, (1135)
- **C - H stretch:** 2995, (2980); 2950, (2920) cm$^{-1}$

From the close similarity of the spectra above, it is clear that the model compound was a good analogue of the homopolymer for spectroscopic study. This is of importance as it was intended to use infra-red spectroscopy as a means of identifying and characterising reaction products.

The spectrum of the polymer (and of all other spectra unless otherwise stated,) was determined from a 1% solid suspension of the compound in a potassium bromide disc. The spectrum of 2,2-dimethylbutan-3-one was determined from a liquid film between sodium chloride plates.

**Copolymers of 2-methylbut-1-en-3-one and styrene**

The preparation of these copolymers is described in the experimental section, page 57; polymerisation was again effected in bulk using the same initiator. There arise various possibilities
when considering the building of the copolymer chain during propagation. The unit at the growing end of the chain may be either a styrene radical ($M_{S}^\cdot$) or a ketone unit radical ($M_{K}^\cdot$), and this may add to either of the two monomers, ($M_{S}$ and $M_{K}$):

\[
M_{S}^\cdot + M_{S} \rightarrow M_{S}^\cdot \quad (k_{SS})
\]

\[
M_{S}^\cdot + M_{K} \rightarrow M_{K}^\cdot \quad (k_{SK})
\]

\[
M_{K}^\cdot + M_{S} \rightarrow M_{S}^\cdot \quad (k_{KS})
\]

\[
M_{K}^\cdot + M_{K} \rightarrow M_{K}^\cdot \quad (k_{KK})
\]

Assume that the steady state applies to each radical separately. Thus the rate of conversion of $M_{S}^\cdot$ to $M_{S}^\cdot$ must equal the rate of conversion of $M_{K}^\cdot$ to $M_{K}^\cdot$ and

\[
k_{KS} [M_{S}^\cdot] [M_{K}] = k_{SK} [M_{K}^\cdot] [M_{S}] \quad (1)
\]

The rates of disappearance of $M_{S}$ and $M_{K}$ are given by:

\[
- \frac{d[M_{S}]}{dt} = k_{SS} [M_{S}^\cdot] [M_{S}] + k_{KS} [M_{K}^\cdot] [M_{S}] \quad (2)
\]

and

\[
- \frac{d[M_{K}]}{dt} = k_{SK} [M_{S}^\cdot] [M_{K}] + k_{KK} [M_{K}^\cdot] [M_{K}] \quad (3)
\]

Dividing equation (2) by equation (3) and eliminating the terms $[M_{S}^\cdot]$ and $[M_{K}^\cdot]$ by use of equation (1) gives:

\[
\frac{d[M_{K}]}{d[M_{S}]} = \frac{[M_{K}]}{[M_{S}]} \cdot \frac{r_{K} [M_{K}] + [M_{S}]}{r_{S} [M_{S}] + [M_{K}]} \quad (4)
\]

where $r_{S} = \frac{k_{SS}}{k_{SK}}$ and $r_{K} = \frac{k_{KK}}{k_{KS}}$.
\( r_S \) and \( r_K \) are known as the monomer reactivity ratios, and it is clear from their definition that they give a measure of the probability of the monomer radical on the growing chain combining with another monomer of the same type or of the other type. If \( r_S = r_K = 0 \), each monomer radical will combine exclusively with the other type of monomer, and a regularly alternating 1:1-copolymer will be formed. If \( r_S \) and \( r_K \) are both greater than unity, the two monomers will homo-polymerise independently. If \( r_S = \frac{1}{r_K} \) (or \( r_S \cdot r_K = 1 \)), the monomer units will be arranged at random along the chain.

No precise estimation of the monomer reactivity ratios was made, but calculation of the copolymer composition from analysis figures showed that the ratio of the monomers in the copolymer was fairly close to the original ratio of liquid monomers; in all cases however the resultant copolymer was rich in styrene compared with the initial ratio of monomers. (See Table IIb, page 59).

The copolymers were carefully dried and analysed for carbon and hydrogen. The ratio of ketone to styrene units was calculated as shown below:

Consider an average specimen of the copolymer chain 100 units long. If \( a \) units are 2-methylbut-1-en-3-one, then \((100-a)\) units are styrene. The molecular weight of 2-methylbut-1-en-3-one, \((C_9H_{16}O)\), is 84.119 and that of styrene, \((C_8H_8)\), is 104.152. The percentage of carbon in the 100 unit length is given by:
\[
\begin{align*}
\%c & = \frac{5a + 8(100-a)}{84.119a + 104.152(100-a)} \times 100 \\
\therefore a & = \frac{960.880 - 104.152 \times \%c}{3603.3 - 20.033 \times \%c}
\end{align*}
\]

E.g. when \(\%c = 86.84\), \(a = 30.28\) and \((100-a) = 69.72\).

The ratio of 2-methylbut-1-en-3-one units to styrene units is therefore 1:2.303.

The results for the prepared copolymers are summarised in Table IIb, page 59.

(Although the ratios are not whole numbers, the copolymers will be referred to by the initial monomer ratios in further discussion, e.g. the 1:2.303-copolymer will be referred to as the 1:2-copolymer.)

A molecular model of the 1:2-copolymer showed that the acetyl group of the ketonic unit was very much less hindered than in the homopolymer.

The logarithmic viscosity numbers of all the copolymers were determined and are summarised in Table IIIb, page 61. Again these were determined as a means of characterising the copolymers; the constants requisite for conversion to molecular weight are not known.

The infra-red spectra of the copolymers were determined as before, and as might be expected showed a combination of the spectra of poly(2-methylbut-1-en-3-one) and polystyrene, with an increase in intensity of the absorption bands of polystyrene as the fraction of
the latter groups increased in the copolymer. These will not be
further discussed as the polystyrene bands corresponded to those cited
in the literature, and those due to the ketone units have been
discussed previously.

The condensation product

As mentioned earlier, it was intended to brominate the homo­
polymer to give poly(1-bromo-3-methylbut-3-en-2-one), upon which
replacement and cyclisation reactions were to have been carried out.
When this was attempted using liquid bromine, a black rubbery insoluble
compound was obtained. Although the product contained some bromine,
the bad discolouration and the unexpected insolubility suggested that
hydrogen bromide initially formed from the bromination had catalysed
the condensation of water from neighbouring acetyl side-chains on
the polymer. Staudinger and Ritzenthaler (12) had earlier noted that
2-methylbut-1-en-3-one on treatment with stannic chloride gave a
black smeary product. It seems likely that the stannic chloride
catalysed the polymerisation of the monomer, and then hydrogen chloride
from the easily hydrolysable stannic chloride catalysed the conden­
sation as above.

The treatment of a solution of the homopolymer with hydrogen
chloride gas gave a black insoluble compound containing no chlorine.
Two methods were used in the preparation of this product. In one,
hydrogen chloride gas was passed through a refluxing solution of the
homopolymer in benzene, and in the second, a solution of the homopolymer in benzene was added dropwise to refluxing benzene through which the gas was passed. In each method some of the product precipitated out as a deep red, almost black solid, some remaining in solution, giving it a very deep red colour. By Soxhlet extraction of the isolated product it was shown that almost all the product was soluble in benzene, although the solubility was low. The condensation product when isolated was a hard very deep red solid, which on powdering lightened in colour to a deep red-brown powder.

It is suggested that water is removed from the polymer by the mechanism shown below to give series of conjugated carbon-carbon double bonds:

\[\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - & \quad \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \\
\text{CO} & \quad \text{CO} & \quad \text{C} = \text{O} & \quad (i) & \quad \text{CO} & \quad \text{CO} & \quad +\text{C-OH} & \quad (ii) \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}\]

\[\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - & \quad \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - \\
\text{CO} & \quad \text{CO} & \quad \text{C-OH} & \quad (iii) & \quad \text{CO} & \quad \text{CO} & \quad \text{C-OH}_2 \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}\]
No discolouration or insolubility was observed when the 1:2-copolymer was similarly treated with hydrogen chloride gas, indicating that cross-linking does not occur in the homopolymer by the above condensation reaction. (This also shows that the two monomer units in the copolymer must be arranged with a fair degree of alternation, as long sequences of the ketone units would condense as above.)

The degree of condensation was calculated from elemental analysis figures by considering a typical length of the polymer chain 100 units in length from which $n$ molecules of water had been condensed. An equation was established equating the percentage of carbon found by analysis with the percentage of carbon as a function of $n$, and
solving for \( n \). In all cases however, the percentage of oxygen found in the compound, (whether by direct analysis or by difference) was greater than that inferred by the calculation as above. This discrepancy suggested that the compound might have absorbed oxygen, but experiments to test this hypothesis showed it to be invalid, as the compound neither absorbed oxygen after standing in an atmosphere of the gas for several hours, nor evolved oxygen when heated under vacuum for several hours. When the compound was prepared under anaerobic conditions, and the product kept under an atmosphere of nitrogen at all stages up to its analysis, coherent analytical data was found, showing the compound to be a simple dehydration product where 30 molecules of water had been lost per 100 chain units. This compound did not absorb oxygen on standing in an atmosphere of the gas for 3 days at room temperature and pressure.

The infra-red spectra of both types of product, (i.e. those from the anaerobic and non-anaerobic experiments) were almost identical, both showing a diminished carbonyl \( C = O \) stretch absorption band at 1700 \( \text{cm}^{-1} \), and \( C = C \) stretch absorption bands in the region 1620 - 1640 \( \text{cm}^{-1} \).

The ultra-violet and visible spectra of both condensation products from the anaerobic and non-anaerobic preparations showed a blanket absorption:
It is known that the series of diphenyl polyenes,

\[
\begin{array}{c}
\text{CH} \quad \text{CH} \\
\text{CH} \quad \text{CH} \\
\vdots \\
\text{CH} \quad \text{CH}
\end{array}
\]

absorb in the ultraviolet and visible regions, the colour of the compounds varying from colourless (when \( n = 1 \), i.e. stilbene,) through yellow to green and orange; when \( n = 8 \), the compound has a bluish coppery-red colour.\(^{(45)}\) The deep red, almost black colour of the condensation product may be explained by series of conjugated double bonds in the compound, the different degrees of conjugation in separate series absorbing at different wavelengths. The blanket absorption in the ultra-violet and visible spectrum lends further support to this theory. (The spectrum was determined from a solution of the compound
in chloroform, (ca. $10^{-4}$ M.) in a cell of 1 cm. thickness).

The condensation product in very dilute solution in concentrated sulphuric acid exhibits an intense purple-blue colour. This is a property of the carotenes and related compounds which contain a series of conjugated double bonds. The colour is thought to be due to protonation of the double bond;

\[
\text{H}^+ \quad \rightarrow \quad \text{CH}_2
\]

This property again supports the theory of the structure of the condensation product.

**The brominated copolymers**

The attempted bromination of poly(2-methylbut-1-en-3-one) led, as stated, to a condensation product containing bromine. However, a true bromomethyl ketone - containing copolymer which presented no evidence of self-condensation was prepared from the 1:2-copolymer. Here the spacing out of the ketone units is sufficient to avoid self-condensation.
Two mechanisms have been suggested for the bromination of a methyl ketone, resulting respectively from homolytic and heterolytic fission of the bromine molecule.

(i) \[ \text{Br}_2 \rightarrow 2 \text{Br}^- \]
\[ R - \text{CO-CH}_3 + \text{Br}^- \rightarrow R - \text{CO} - \text{CH}_2^- + \text{HBr} \]
\[ R - \text{CO-CH}_2^- + \text{Br}_2 \rightarrow R - \text{CO} - \text{CH}_2\text{Br} + \text{Br}^- \]

(ii) \[ \text{Br}_2 \rightarrow \text{Br}^- + \text{Br}^+ \]
\[ R - \text{C} - \text{CH}_3 \rightarrow R - \text{C} = \text{CH}_2 \rightarrow R - \text{C} - \text{CH}_2\text{Br} + \text{H}^+ \]
\[ \text{H}^+ + \text{Br}^- \rightarrow \text{HBr} \]

In either case hydrogen bromide is evolved. The present reaction was performed under illumination from a 500w. lamp. Absorption of this radiation promotes homolytic fission of the bromine molecule as in (i).

Analysis showed that the reaction had gone to completion, but that slight fractionation had occurred during the working up process; the ratio of styrene to C5-units before reaction was 69.7:30.3, and 71.5:28.5 after reaction. The ratio was calculated
by a procedure similar to that above (page 31.) It was initially assumed that only two types of unit were present, styrene and bromomethyl ketone units. From the derived ratio of 71.5:28.5, the percentages of the elements composing the copolymer were calculated and found to be in good agreement with those found by analysis.

From the analyses of the brominated 1:1- and 1:0.75- copolymers it was found impossible to calculate satisfactory styrene:bromomethyl ketone or styrene:bromomethyl ketone:ketone ratios, and this suggested that in addition to bromination, condensation had also occurred. As it was impossible fully to characterise these two polymers, only the brominated 1:2-copolymer was used in subsequent work.

The infra-red spectra of the brominated 1:2-copolymer and the 1:2-copolymer were compared with each other, and with those of 2,2-dimethylbutan-3-one and 1-bromo-3,3-dimethylbutan-2-one. (The spectra of the latter two compounds were determined from liquid films between sodium chloride plates.) The spectra of the two copolymers were very similar, as were the spectra of the two model compounds. In both cases, the intensity of the carbonyl C=O stretch absorption band at 1705-1725 cms.\(^{-1}\) was less in the brominated compound. A change in intensity of the C-H bend bands in the 1350-1400 cms.\(^{-1}\) region was noted:
It can be seen that in both the polymeric compounds and the low molecular weight compounds the absorption band in the region 1355-1370 cm$^{-1}$ is relatively less intense than the band at 1380-1395 cm$^{-1}$ after bromination, although the effect is less marked in the low molecular weight compounds.

The logarithmic viscosity number of the brominated copolymer, 0.231, was less than that of the original copolymer, 0.296.

The isothiourea derivatives

It is known that α-haloketones condense with thiourea to give 2-aminothiazoles. For example, monochloroacetone condenses with thiourea to give 2-amino-4-methylthiazole:

\[
\text{NH}_2\text{C}=-\text{NH}_2 \xrightarrow{\text{Cl}} \text{NH}_2\text{C}=-\text{NH} \quad \xrightarrow{\text{CH}_3\text{COCH}_2\text{Cl}} \quad \text{CH}_3\text{CO}-\text{CH}_2\text{S}-\text{C}-\text{NH}_2
\]

+ HCl

\[
\text{CH}_3\text{CO}-\text{CH}_2\text{S}-\text{C} \xrightarrow{\text{NH}_2} \text{CH}_3\text{C}=-\text{CH}-\text{S}-\text{C}-\text{NH}_2 \xrightarrow{\text{OH}} \text{CH}_3\text{C}=-\text{N} \quad \xrightarrow{\text{NH}} \text{CH}_3\text{C}=-\text{NH}_2
\]

+ H$_2$O
This reaction was confirmed experimentally. The low molecular weight analogue of the brominated 1:2-copolymer, 1-bromo-3,3-dimethylbutan-2-one, was similarly reacted with thiourea to give 2-amino-4-t-butylthiazole:

\[
\text{(CH}_3\text{)}_3\text{C - CO - CH}_2\text{Br} + (\text{NH}_2)_2\text{CS} \rightarrow \text{(CH}_3\text{)}_3\text{C - C - N}
\]

\[
\text{CH} \quad \text{S - NH}_2
\]

\[
+ \text{H}_2\text{O} + \text{HBr}.
\]

Thioacetamide was reacted with monochloroacetone to give 2,4-dimethylthiazole, a known compound. When the thioamide was reacted with 1-bromo-3,3-dimethylbutan-2-one however, a compound resulted which, from elemental analysis, had the empirical formula C₈H₁₅NOS, and m.p. 69.5-70°. It was thought that the structure was

\[
\text{(CH}_3\text{)}_3\text{C - CO - CH}_2 - \text{S - C - NH}
\]

but the infra-red spectrum of the compound contained no C=O stretch absorption band. No further work was done to elucidate the structure. Because of the uncertainty concerning the nature of this product, the reactions of the brominated 1:2-copolymer with thioamides were confined to reaction with thiourea.

The infra-red spectra of all these low molecular weight
derivatives were determined. (See below.)

When the brominated 1:2-copolymer was reacted with thiourea in dioxan as the reaction medium, the product precipitated, the reactants both having been soluble. The isolated product was insoluble in most common organic solvents, but dissolved easily in dimethylformamide. As it appeared likely that incomplete reaction would result from the precipitation of the product, the experiment was repeated in dimethylformamide. The solution remained homogeneous throughout. The product from dioxan and that from dimethylformamide each contained nitrogen and sulphur, and very little or no bromine. The infra-red spectrum of each compound showed a carbonyl C=O stretch absorption band however, indicating that only step (i) (see above,) had occurred, with no cyclisation to the thiazole, step (ii).

Elemental analysis showed the nitrogen:sulphur:oxygen ratio to be approximately 2:1:1, confirming the suggested cessation of reaction at step (i). On the assumption that the product contained only styrene and isothiourea derivative units, the ratio of these units was calculated as before:

\[
\begin{align*}
\text{CH}_2 - \text{CH} \\
\text{CH}_2 \\
(100-a) \quad \text{CH}_3 \\
\end{align*}
\]
when it was found that again some fractionation had occurred. The ratio of styrene:isothiourea unit was found to be 75.0:25.0 and 74.2:25.8 for the dioxan and dimethylformamide solvent reactions respectively. Assuming these ratios, and calculating the percentages of each element in the products, a fairly close agreement was found with the original analytical data.

The infra-red spectra of the isothiourea derivatives were compared with those of the known thiazoles, 2-amino-4-t-butylthiazole and 2-amino-4-methylthiazole. A strong band appeared at 1520 cms.\(^{-1}\) in the spectra of the thiazoles, and at 1530-1535 cms.\(^{-1}\) in the spectra of isothiourea derivatives of the polymer. This band was absent from the spectra of the \(\alpha\)-haloketone starting materials, and the spectrum of thiourea. It seems likely that this band is associated with the structure:

\[
\begin{align*}
| & S - C = N \\
& \text{as it occurred in both the spectra of the thiazoles and the isothiourea derivatives, this being the region where C=X stretch absorption bands appear.}
\end{align*}
\]

The polymeric isothiourea compounds retained the strong carbonyl C=O stretch band at 1700 cms.\(^{-1}\). A large double band in the region 3350-3460 cms.\(^{-1}\) in the spectra of the polymeric derivatives appeared where none existed in the starting material, and corresponds to a band at 3340 cms.\(^{-1}\) in the spectrum of 2-amino-4-t-butylthiazole.
These bands are probably associated with $\equiv N-H$ and $\equiv N-H$ stretch absorption. Strong bands are present at 1610 and 1330 cm$^{-1}$ in the spectra of both 2-aminothiazoles, due to N-H bend and C=N stretch respectively. New bands appeared at 1645 and 1280 cm$^{-1}$ in the compound from reaction in dimethylformamide, and at 1650 and 1315 cm$^{-1}$ in the compound from the reaction in dioxan.

The oxidation product of poly(2-methylbut-1-en-3-one)

2,2-Dimethylbutan-3-one is oxidised in high yield by alkaline potassium permanganate to trimethylpyruvic acid. This was confirmed experimentally. Poly(but-1-en-3-one) is oxidised to poly(acrylic acid) by sodium hypochlorite. An attempt was made to prepare a polymeric $\alpha$-ketoacid by the alkaline permanganate oxidation of poly(2-methylbut-1-en-3-one):

$$\begin{align*}
\text{CH}_2 & \quad \text{C} \\
\text{CO} & \quad \text{CH}_3
\end{align*}\quad \quad \quad 3n[O]\quad \quad \quad \begin{align*}
\text{CH}_2 & \quad \text{C} \\
\text{CO} & \quad \text{CH}_3
\end{align*} + n\text{H}_2\text{O}
$$

but it was noted that the solution from the reaction contained excess carbonate. This indicated that some of the $\alpha$-ketocarboxylic acid groups had decomposed with the evolution of carbon dioxide to give aldehyde groups, the latter groups then being further oxidised to
carboxylic acid groups:

\[
\begin{array}{c}
\text{CH}_2 - C - COO_2^-
\end{array}
\quad \text{m}
\]

It is known that pyruvic acid is oxidised by potassium permanganate to acetic acid and carbon dioxide. The initial concentration of carbonate in the mixture was known, and the total amount in the final reaction mixture was measured by displacing carbon dioxide with sulphuric acid from a known volume of this solution. The volume of carbon dioxide evolved indicated that about half of the α-ketocarboxylic acid groups had decomposed as above. (See page 76.)

It was found impossible to obtain consistent results for the equivalent weight of the product by normal titrimetric techniques, (titration of the polymeric acid against standard sodium hydroxide using phenolphthalein and thymolphthalein indicators, and using a pH-meter,) so the silver salt was prepared and analysed. Assuming all the carboxylate groups to have been converted to their silver salts, and only the above two types of group to be present in the polymer, it was calculated that these groups existed in the ratio 50:50. Assuming this ratio, the percentages of elements in the polymeric silver salt were calculated; a fairly close agreement
was found with the original analytical data, although the percentage of carbon was higher than that found by analysis.

The logarithmic viscosity number of the oxidation product, (solvent water), 0.071, was lower than that of the original poly (2-methylbut-1-en-3-one), 0.310, indicating that although some chain-scission had probably occurred, the product was still macro-molecular.

The infra-red spectra of the sodium salts of the oxidation product and of poly(methacrylic acid) were compared, and found to be very similar. Both contained the absorption bands due to the carboxylate ion at 1400 and 1550 cm$^{-1}$. The latter band in the spectrum of the oxidation product was much broader than that in the spectrum of poly(sodium methacrylate) exhibiting a fairly intense shoulder at 1700 cm$^{-1}$ due to the C=O stretch absorption. This is further evidence for the structure already postulated.

The reduction product of poly(2-methylbut-1-en-3-one)

It is known that on treatment with hydrogen and Raney nickel at high temperature and pressure poly(2-methylbut-1-en-3-one) gives a product containing both secondary alcohol groups and cyclic ether groups. Poly(but-1-en-3-one) has been reduced with lithium aluminium hydride with high conversion to the secondary alcohol. The hydride reacts with four molecules of the ketone, the resultant complex then being decomposed with dilute aqueous mineral acid to
give the secondary alcohol and inorganic salts: 

\[ 4RR'CO + LiAlH_4 \rightarrow LiAl(RR'CHO)_4 \]

\[ \text{H}_2\text{O} \]

\[ LiAl(RR'CHO)_4 \rightarrow RR'\text{CHOH} + AlCl_3 + LiCl \]

Poly(2-methylbut-1-en-3-one) was reduced with lithium aluminium hydride to give a fairly high conversion to the secondary alcohol. By analysing the product for carbon and hydrogen, the ratio of reduced to non-reduced groups was calculated as 70.0:30.0. As the accuracy of this calculation depended on the relatively small increase in weight of hydrogen in the product (2.016 g. increase per 84.119 g. of the parent homopolymer for 100% reduction,) the p-nitrobenzoyl ester was prepared from p-nitrobenzoyl chloride. Assuming a complete conversion of alcohol groups to ester groups and calculating the percentages of carbon, hydrogen and nitrogen in the polymer for a ratio of 70.0:30.0:: ester:ketone, a good agreement with the analytical data was found.

The infra-red spectra of the reduced polymer and of 2,2-dimethylbutan-3-ol were compared. The frequencies of various absorption bands in the spectra are given below, those of the model compound being given in parenthesis. The spectrum of the model compound was determined from a liquid film between sodium chloride plates.
O - H stretch 3430; (3390)
C = O stretch 1690 (weak), ( - )
C - H stretch 2980, (2970); 2940, (2920); 2880, (2880)
C - H bend 1460, (1480, 1460 doublet); 1380, (1390, 1370, 1365, triplet)
C-O or C-C stretch 1085, 1065 doublet; (1100-1085 doublet.)

All frequencies given in cms. -1

The logarithmic viscosity number of the reduced polymer was 0.260, that of the parent homopolymer, 0.310.

It seems likely that poly(2-methylbut-1-en-3-one) was not reduced to such a great extent as poly(but-1-en-3-one) under similar conditions because of the inflexible nature of the former polymer chain relative to the latter. To be highly efficient in the reduction, each molecule of lithium aluminium hydride must complex with four carbonyl groups. This is more easily brought about when the carbonyl side-groups are attached to the more flexible polymer chain.

The oxime derivative of poly(2-methylbut-1-en-3-one)

The oxime of a copolymer of styrene and 2-methylbut-1-en-3-one has been prepared, as has the oxime of poly(but-1-en-3-one). In the present work an attempt was made to prepare the oxime of poly(2-methylbut-1-en-3-one) by a standard method, i.e. by warming
the polymer and hydroxylamine hydrochloride in an excess of pyridine. The isolated product was analysed for carbon, hydrogen and nitrogen, the percentage of oxygen was assumed by difference. The ratio of these elements was calculated and found to be:

\[ C_5H_8N_0.7C_0.78O_0.78 \]

It is clear that even for partial oximation the relative number of oxygen atoms should remain constant, (i.e. \( C_5O_{1.00} \) or one oxygen atom per repeating unit.) In view of the low oxygen and hydrogen figures it was thought that water had condensed from neighbouring oxime side-chains as shown below:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 - \text{C} - \text{CH}_2 - \text{C} - & \rightarrow \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\text{CH}_3 \quad \text{N} & \quad \text{N} \quad \text{CH}_3 \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

Assuming the presence of only oxime units, unreacted ketone units and units as shown above, the ratio of these units was calculated as shown below, where there are \( p \) oxime units, \( q \) "condensed" oxime units and \( (100 - p - q) \) ketone units in a 100 unit polymer chain:
The number of oxygen atoms present in the 100 unit polymer chain is 74.8 and is given by:

\[
100 - p - q + p + \frac{1}{2} q = 74.8
\]

\[
\therefore \quad q = 50.4
\]

The number of nitrogen atoms present in the 100 unit polymer chain is also 74.8 and is given by:

\[
p + q = 74.8
\]

\[
\therefore \quad p = 24.4
\]

This means that the polymer structure is as shown below:

On calculation of the percentage of elements in such a polymer,
close agreement was found with the original analytical data.

The infra-red spectra of the polymeric derivative and of methyl t-butyl ketoxime were compared. No striking resemblances were found except that each had a large band in the O-H and N-H stretch region at 3300-3400 cms.\(^{-1}\), and a large band at 930-940 cms.\(^{-1}\). The spectrum of the polymeric compound contained a fairly strong band at 1635 cms.\(^{-1}\) due to C=N stretch and a shoulder at 1695 cms.\(^{-1}\) due to the C=O stretch of unreacted carbonyl groups. The spectrum of the low molecular weight compound contained a small band at 1665 cms.\(^{-1}\) due to the C=N stretch, and no trace of a carbonyl C=O stretch band in the region of 1700 cms.\(^{-1}\)
SUMMARY

Poly(2-methylbut-1-en-3-one) was prepared by bulk polymerisation of the monomer under carbon dioxide in sealed glass tubes at 70° for 20 hours; 1% of azobisisobutyronitrile was used as initiator. The homopolymer was characterised by determination of the logarithmic viscosity numbers of 1% solutions in dioxan at 25.00 ± 0.01°; the main preparations each had the value 0.310. The infra-red spectrum of the homopolymer was compared with that of 2,2-dimethylbutan-3-one and found to be remarkably similar.

A solution of the homopolymer in benzene was treated with hydrogen chloride to give a deep red product which, from spectroscopic, analytical and chemical examination is concluded to contain series of conjugated double bonds formed by the condensing of water from neighbouring acetyl side chains on the polymer. (See page 32.)

An aqueous suspension of the homopolymer was oxidised with alkaline potassium permanganate. The product was separated from the low molecular weight impurities by use of "Sephadex", (see appendix.) A proportion of the expected α-ketocarboxylic acid side-chains underwent decarboxylation and further oxidation to carboxylic acid groups. The sodium salt of the final product was examined by infra-red spectroscopy and compared with the spectrum of poly(sodium methacrylate). The silver salt of the product was prepared and analysed. The evidence obtained suggests that the
product is a 50:50 copolymer of methacrylic acid and 3-methylbut-3-en-2-oxo-l-oic acid. The logarithmic viscosity number of this compound was determined from a 1% aqueous solution and found to be 0.071.

The homopolymer was reduced in tetrahydrofuran with lithium aluminium hydride to give a 70:30 copolymer of 2-methylbut-1-en-3-ol and 2-methylbut-1-en-3-one. The infra-red spectrum of this reduced product was compared with that of 2,2-dimethylbutan-3-ol, when a close similarity was again noted. The p-nitrobenzoyl ester was prepared using p-nitrobenzoyl chloride in pyridine, and elemental analysis confirmed the 70:30 ratio for reduced to unreduced units in the reduced polymer. The logarithmic viscosity number of the reduction product was 0.260.

The oxime derivative, prepared from a solution of the homopolymer and hydroxylamine hydrochloride in excess pyridine, was found on analysis to contain oxime units, oxime anhydride units and unreacted ketone units in almost exactly equal numbers.

Six copolymers of 2-methylbut-1-en-3-one and styrene were prepared in the same way as the homopolymer. The molar ratios of ketone:styrene monomers were 1:0.25, 1:0.5, 1:0.75, 1:1, 1:1.5, 1:2 in the initial monomer mixture, but the resultant copolymers were all styrene-rich, (see page 59.) The logarithmic viscosity numbers were determined from 1% solutions of the copolymers in toluene at
25.00 ± 0.01°, these being in the range 0.2 to 0.3, (see page 61.) The infra-red spectra were recorded.

An attempt to brominate the homopolymer led to a compound similar to the condensation product, but when the 1:2-copolymer was brominated, the ketone units were sufficiently spaced out to prevent the condensation, and a copolymer containing bromomethyl ketone units was prepared with no evidence of self-condensation. The copolymer was fully monobrominated in the α-position to the carbonyl group. The infra-red spectrum of the brominated 1:2-copolymer was compared with those of the 1:2-copolymer and 1-bromo-3,3-dimethylbutan-2-one. The logarithmic viscosity number of the brominated 1:2-copolymer was 0.231.

An attempt was made to prepare a 2-aminothiazole from the brominated 1:2-copolymer and thiourea. Bromine was completely replaced by isothiourea groups, but cyclisation did not occur. The structure was confirmed by elemental analysis and infra-red spectroscopy.

Molecular models of many of these polymers and copolymers have been prepared, and the course of the reactions is discussed in relation to characteristics of the models.
EXPERIMENTAL
Purification of 2-methylbut-1-en-3-one

The monomer, 2-methylbut-1-en-3-one, as received from Distillers Company Limited, contained water. It was dried over calcium chloride in a refrigerator for several days. t-Butylcatechol (0.5%) was added to the filtered liquid to prevent polymerisation, and the liquid distilled at atmospheric pressure, a 6 inch column packed with glass beads being used. The fraction boiling at 95-8° was collected and redistilled, the fraction boiling at 96-97° being collected. It had $\frac{n}{D}^{25} 1.4212$. (Lit; b.p. 97-98°; $\frac{n}{D}^{25} 1.4214$).

Purification of Styrene

The monomer styrene, as received, contained t-butylcatechol as inhibitor. This was removed by washing with 2N sodium hydroxide until the washings were colourless, and then with water until the washings were no longer alkaline. The liquid was dried over anhydrous sodium sulphate for several days in a refrigerator. The filtered liquid was distilled under vacuum under nitrogen. B.p. 65°/47 mm., $\frac{n}{D}^{25} 1.5450$; (lit; B.p. 64°/50 mm; $\frac{n}{D}^{25} 1.5439$).

Azobisisobutyronitrile

This compound was used as the initiator in the polymerisations. After the third recrystallisation from aqueous acetone, the melting point was constant at 103-4°. (Lit: m.p. 105°)
Preparation of poly(2-methylbut-1-en-3-one) and the copolymers with styrene

A preliminary experiment was performed to determine the optimum amount of initiator to be used. 4g. portions of 2-methylbut-1-en-3-one were bulk polymerised in sealed soft-glass test-tubes, as below, with 1.0%, 0.67% and 0.33% by weight of azobisisobutyronitrile as initiator. All but the specimen containing 0.33% initiator had become hard glass-like solids after 20 hours at 70°. The exceptional sample was still soft after 43.5 hours. After solution in acetone (25 ml.) the polymers were precipitated by dropwise addition of the acetone solutions to six times their volume of vigorously stirred cyclohexane. The polymers tended to be tacky, but were filtered off, washed with cyclohexane and dried in a vacuum desiccator over calcium chloride and paraffin-wax shavings. The yields for the 1.0%, 0.67% and 0.33% initiated polymerisations were 88%, 73% and 53% respectively.

The monomer or mixture of monomers were bulk polymerised with azobisisobutyronitrile as initiator. The polymerisations were carried out in sealed glass tubes which were made from thin-walled soda-glass tubing of internal diameter 1.7 cms. Approximately 40 ml. of the monomer or mixture of monomers was contained in each tube, making them approximately half-full. 1.0% by weight of initiator was dissolved in the monomer or mixture of monomers prior to filling the tubes, which were then evacuated to 100 m.m. and flushed with carbon dioxide. This process was repeated three times and the
tubes, already "necked", were sealed quickly and placed in an oven at 70° for 40-50 hours. After cooling the tubes in solid carbon dioxide to detach the polymer from the walls, they were carefully opened, and the polymers removed as clear, glass-like hard rods. These were broken up and dissolved in refluxing acetone to give a 10% solution in the case of the homopolymer, and 20% solutions in the case of the copolymers. The solutions so formed were cooled, filtered and added at a fast drop-rate to an eight-fold excess of vigorously stirred precipitating liquid, which was water in the case of the homopolymer, 1:1 aqueous methanol in the case of the two copolymers of lower styrene content, and methanol for the remaining copolymers. The precipitated white fibrous polymers were filtered, washed in more of the precipitating liquid and dried in a rotating cylindrical vessel at 50°/10-20 m.m. The yields were approximately 80% based on the original weight of the monomers. See Table I below.

### TABLE I

<table>
<thead>
<tr>
<th>Molar Ratio of Monomers A : B</th>
<th>Weight Ratio of Monomers (Grams.)</th>
<th>Volume Ratio of Monomers (Ml.)</th>
<th>% Initiator</th>
<th>Temp°C/Timehrs.</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 0</td>
<td>191 : 0</td>
<td>225 : 0</td>
<td>1.00</td>
<td>73-8/20</td>
<td>78</td>
</tr>
<tr>
<td>1 : 0.25</td>
<td>76.3:23.7</td>
<td>89.8:26.0</td>
<td>1.00</td>
<td>70/45.5</td>
<td>75</td>
</tr>
<tr>
<td>1 : 0.50</td>
<td>61.8:38.2</td>
<td>72.6:42.0</td>
<td>1.00</td>
<td>70/45.5</td>
<td>77</td>
</tr>
<tr>
<td>1 : 0.75</td>
<td>51.9:48.1</td>
<td>61.0:53.0</td>
<td>1.00</td>
<td>70/41</td>
<td>85</td>
</tr>
<tr>
<td>1 : 1.00</td>
<td>44.7:55.3</td>
<td>52.5:60.8</td>
<td>1.00</td>
<td>70/41</td>
<td>84</td>
</tr>
<tr>
<td>1 : 1.50</td>
<td>35.0:65.0</td>
<td>41.2:71.5</td>
<td>1.00</td>
<td>70/470</td>
<td>89</td>
</tr>
<tr>
<td>1 : 2.00</td>
<td>28.8:71.2</td>
<td>33.8:78.3</td>
<td>1.00</td>
<td>70/470</td>
<td>83</td>
</tr>
</tbody>
</table>

A = 2-methylbut-1-en-3-one;  B = styrene.
Ø Tubes remained unopened at room-temperature for a further 24 hours.
It was found on analysis that the fraction of styrene in the copolymers was greater than in the original mixture of monomers. The ratios of 2-methylbut-1-en-3-one units to styrene units as calculated from analysis are given in Table II below. Three large batches of the homopolymer were prepared during the work. Analysis details are given for all three.

TABLE II

(a) Poly(2-methylbut-1-en-3-one)

Calculated for \((\text{C}_5\text{H}_8\text{O})_n\) : C, 71.39; H, 9.59%.

Found:

1 C, 69.95, 69.98; H, 9.20, 9.04%.

2 C, 71.74, 71.63; H, 9.59, 9.42%.

3 C, 71.37, 71.35; H, 9.46, 9.56%.

(b) Copolymers

<table>
<thead>
<tr>
<th>Initial Monomer Ratio (Moles)</th>
<th>Previous Column Requires %C ; %H</th>
<th>Found %C ; %H</th>
<th>Monomer Ratio in Copolymer A : B</th>
<th>Previous Column Requires %C ; %H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 0.25</td>
<td>76.32; 9.15</td>
<td>77.28; 77.40; 8.86; 8.93</td>
<td>1 : 0.322; 77.34; 9.06</td>
<td></td>
</tr>
<tr>
<td>1 : 0.50</td>
<td>79.37; 8.88</td>
<td>80.70; 80.66; 8.36; 8.35</td>
<td>1 : 0.648; 80.68; 8.77</td>
<td></td>
</tr>
<tr>
<td>1 : 0.75</td>
<td>81.44; 8.70</td>
<td>82.33; 82.33; 8.74; 8.68</td>
<td>1 : 0.890; 82.33; 8.62</td>
<td></td>
</tr>
<tr>
<td>1 : 1.00</td>
<td>82.94; 8.57</td>
<td>83.55; 83.53; 8.39; 8.41</td>
<td>1 : 1.125; 83.54; 8.51</td>
<td></td>
</tr>
<tr>
<td>1 : 1.50</td>
<td>84.96; 8.39</td>
<td>85.71; 85.78; 8.35; 8.42</td>
<td>1 : 1.782; 85.74; 8.32</td>
<td></td>
</tr>
<tr>
<td>1 : 2.00</td>
<td>86.26; 8.27</td>
<td>86.92; 86.75; 8.27; 8.11</td>
<td>1 : 2.303; 86.84; 8.22</td>
<td></td>
</tr>
</tbody>
</table>

A = 2-methylbut-1-en-3-one; B = styrene
The infra-red spectra of the homopolymer and the copolymers were determined, the compounds being thoroughly ground with potassium bromide to give approximately 1% of the polymer by weight in potassium bromide, the mixture being pressed into thin discs of approximate weight 0.2 g.

The logarithmic viscosity numbers of the three preparations of the homopolymer and the copolymers were determined by use of an Ostwald viscometer. For the homopolymers dioxan was used as solvent, for the copolymers, toluene. The viscometer and the solutions used in the determinations were kept at a temperature of 25.00 ± 0.01° in a thermostated water-bath. All viscosities were determined in duplicate, approximately 1% solutions being used. The equation used to calculate the logarithmic viscosity number \([\eta]\) is given by:

\[
[\eta] = \frac{2.303}{C} \log_{10} \frac{t_1}{t_2},
\]

where \(C\) = the concentration of the solution in grams/100 ml.,

\(t_1\) = the flow time of the solution in seconds,

\(t_2\) = the flow time of the solvent in seconds.

\(t_1\) and \(t_2\) were determined from at least four time readings for each solvent or solution. The viscosities are given in Table III.
### TABLE III

(a) Poly(2-methylbut-1-en-3-one)

<table>
<thead>
<tr>
<th>Solvent or Solution</th>
<th>( C ) (g./100ml.)</th>
<th>( t_1 ) Mins:Secs</th>
<th>( t_2 ) Mins:Secs</th>
<th>( [\eta]_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxan I</td>
<td>-</td>
<td>-</td>
<td>4 : 22.3</td>
<td>-</td>
</tr>
<tr>
<td>Dioxan II</td>
<td>-</td>
<td>-</td>
<td>4 : 21.4</td>
<td>-</td>
</tr>
<tr>
<td>Homopolymer 1 in I</td>
<td>0.9940</td>
<td>5 : 14.6</td>
<td>4 : 22.3</td>
<td>0.183</td>
</tr>
<tr>
<td>(ii) 0.9568</td>
<td>5 : 14.0</td>
<td>4 : 22.3</td>
<td>0.188</td>
<td></td>
</tr>
<tr>
<td>Homopolymer 2 in II</td>
<td>0.9808</td>
<td>5 : 53.7</td>
<td>4 : 21.4</td>
<td>0.309</td>
</tr>
<tr>
<td>(ii) 1.0464</td>
<td>6 : 01.4</td>
<td>4 : 21.4</td>
<td>0.310</td>
<td></td>
</tr>
<tr>
<td>Homopolymer 3 in II</td>
<td>1.0044</td>
<td>5 : 56.3</td>
<td>4 : 21.4</td>
<td>0.309</td>
</tr>
<tr>
<td>(ii) 0.9980</td>
<td>5 : 55.7</td>
<td>4 : 21.4</td>
<td>0.309</td>
<td></td>
</tr>
</tbody>
</table>

(b) Copolymers

<table>
<thead>
<tr>
<th>Solvent or Solution</th>
<th>( C ) (g./100ml.)</th>
<th>( t_1 ) Mins:Secs</th>
<th>( t_2 ) Mins:Secs</th>
<th>( [\eta]_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>-</td>
<td>-</td>
<td>2 : 27.0</td>
<td>-</td>
</tr>
<tr>
<td>1:0.322 Copolymer</td>
<td>0.9892</td>
<td>3 : 02.9</td>
<td>2 : 27.0</td>
<td>0.221</td>
</tr>
<tr>
<td>(ii) 1.0232</td>
<td>3 : 03.6</td>
<td>2 : 27.0</td>
<td>0.218</td>
<td></td>
</tr>
<tr>
<td>1:0.648 Copolymer</td>
<td>1.0032</td>
<td>3 : 08.5</td>
<td>2 : 27.0</td>
<td>0.248</td>
</tr>
<tr>
<td>(ii) 0.9932</td>
<td>3 : 07.7</td>
<td>2 : 27.0</td>
<td>0.244</td>
<td></td>
</tr>
<tr>
<td>1:0.890 Copolymer</td>
<td>1.0032</td>
<td>3 : 17.5</td>
<td>2 : 27.0</td>
<td>0.295</td>
</tr>
<tr>
<td>(ii) 1.0072</td>
<td>3 : 17.6</td>
<td>2 : 27.0</td>
<td>0.294</td>
<td></td>
</tr>
<tr>
<td>1:1.125 Copolymer</td>
<td>1.0056</td>
<td>3 : 13.5</td>
<td>2 : 27.0</td>
<td>0.273</td>
</tr>
<tr>
<td>(ii) 1.0160</td>
<td>3 : 14.8</td>
<td>2 : 27.0</td>
<td>0.277</td>
<td></td>
</tr>
<tr>
<td>1:1.782 Copolymer</td>
<td>1.0116</td>
<td>3 : 28.4</td>
<td>2 : 27.0</td>
<td>0.345</td>
</tr>
<tr>
<td>(ii) 1.0112</td>
<td>3 : 29.5</td>
<td>2 : 27.0</td>
<td>0.351</td>
<td></td>
</tr>
<tr>
<td>1:2.303 Copolymer</td>
<td>1.0000</td>
<td>3 : 17.7</td>
<td>2 : 27.0</td>
<td>0.296</td>
</tr>
<tr>
<td>(ii) 1.0396</td>
<td>3 : 20.0</td>
<td>2 : 27.0</td>
<td>0.296</td>
<td></td>
</tr>
</tbody>
</table>
Brominations

(i) **Bromination of poly(2-methylbut-1-en-3-one)**

The homopolymer (2.49 g.) was dissolved in chloroform (25 ml.) and placed in a 250 ml. round-bottomed 3-necked flask fitted with a dropping funnel, a water condenser and a mercury-sealed stirrer. The solution was stirred and warmed to refluxing temperature on an oil-bath. Bromine (2.6 g.) in chloroform (4 ml.) was then added to the polymer solution from the dropping-funnel, while the reaction was illuminated with a 40 w. light bulb. A brown tarry deposit formed and hydrogen bromide was evolved. The rubbery black solid which remained on evaporation of the chloroform was only slightly soluble in acetone, chloroform and methylene chloride. Bromine was found in the product.

On pyrolysis the compound gave off yellow fumes and moisture. On pyrolysis with zinc dust, a thick yellow oil distilled over, which had an aromatic smell and which was soluble in benzene.

In a similar experiment the homopolymer (0.998 g.) in chloroform (25 ml.) was brominated with bromine (2.005 g.) in chloroform (7.5 ml.), the reaction being illuminated throughout with a 500 w. light bulb. The bromine was added over 30 mins., and the solution refluxed for a further 90 mins. As refluxing continued, the solution became dark-brown, and the black crust which had formed initially tended to dissolve. The cooled solution was added to vigorously stirred
methanol (300 ml.), when the polymer came down as a dark brown powder. It was filtered off, washed with methanol and dried. Yield 1.059 g. A Lassaigne sodium fusion test showed bromine to be present.

(ii) Bromination of the copolymers

Test brominations were carried out on 1 g. samples of the copolymers in chloroform (25 ml.). Bromine, (107.5% based on the methyl ketone units in the copolymers,) in chloroform (7 - 10 ml.), was added dropwise to the stirred refluxing copolymer solutions over 30-60 mins., the resultant dark coloured solutions being refluxed for a further 1-2 hours. The reaction was heated on a steam-bath, and illuminated by a 500 w. light bulb throughout. The products were precipitated by addition to vigorously stirred methanol or aqueous methanol (300 ml.), to which 1% of sodium bromide had been added to aid coagulation, and collected on a filter. The products, washed and dried, were yellow to yellow-brown, the colour deepening to brown as the styrene content in the copolymer decreased. Yields were 60-70%, and all the products contained bromine by the Lassaigne sodium fusion test.

The 1:0.890, 1:1.125 and 1:2.303 copolymers were brominated on a larger scale by the method used above. The bromine solution was added dropwise to a stirred refluxing copolymer solution, placed in a 500 ml., 3-necked round-bottomed flask fitted with a dropping-funnel, a water-condenser and a mercury-sealed stirrer. The flask was warmed
on a steam bath, and the reaction was illuminated throughout by a 500 w. light-bulb. The whole apparatus was placed in a fume-cupboard as copious fumes of hydrogen bromide were evolved in the course of the reaction.

(a) The 1:0.890 copolymer

The copolymer (26.60 g.) was dissolved in chloroform (200 ml.), and bromine (27.18 g.) in chloroform (50 ml.) was added dropwise over 2 hours. Refluxing was continued for a further 3 hours, and the cooled solution was then added dropwise to vigorously stirred methanol (2 l.). The final yield of the dried product, a yellow powder, was 31.5 g. The logarithmic viscosity number determined in toluene at 25.0°, was: \( \left[ \eta \right]_c 0.142, 0.145. \)

Found: C, 63.49, 63.80; H, 6.20, 6.38; Br, 26.99; O, 4.65%.

(b) The 1:1.125 copolymer

The copolymer (23.78 g.) was dissolved in chloroform (200 ml.), and bromine (21.76 g.) in chloroform (50 ml.) was added dropwise over 90 mins. Refluxing was continued for a further 2 hours and the solution stood overnight at room temperature. The solution was then added dropwise to vigorously stirred methanol (2 l.,) the final yield of the dried product, a yellow powder, being 26.5 g. The logarithmic viscosity number determined in toluene at 25.0° was: \( \left[ \eta \right]_c 0.164, 0.160. \)

Found: C, 63.86, 63.60; H, 6.00, 6.11; Br, 26.50; O, 4.56%.
(c) The 1:2.303 copolymer

The copolymer (9.812 g.) was dissolved in chloroform (100 ml.), and bromine (5.241 g.) in chloroform (5 ml.) was added dropwise over 20 mins. Refluxing was continued for a further 3 hours, and the cooled solution was then added dropwise to vigorously stirred methanol (800 ml.). The final yield of the dried product, a pale yellow powder, was 10.01 g. The logarithmic viscosity number determined in toluene at 25.0°C, was: \([\eta]\) \(0.232, 0.230\).

Found: C, 70.95; H, 6.54; Br, 18.75, 18.94; O, 3.62, 3.69%.

\((C_6H_8)_{71.5} (C_5H_7BrO)_{28.5}\) requires: C, 71.16; H, 6.43;
Br, 18.83; O, 3.77%.

The self-condensation product of poly(2-methylbut-1-en-3-one)

Two methods were used to prepare the self-condensation product of poly(2-methylbut-1-en-3-one). In one, hydrogen chloride gas was passed through a stirred, refluxing solution of the polymer, and in the other a solution of the polymer was added dropwise to stirred refluxing solvent through which hydrogen chloride gas was passed. The hydrogen chloride gas was obtained from a cylinder, and passed through an empty trap, a concentrated sulphuric acid bubbler, a calcium chloride U-tube, another empty trap, and finally into the reaction vessel via a narrow-bore tube passing below the surface of the reaction solvent. The reaction vessel consisted of a 3-necked, round-bottomed
flask fitted with an inlet tube for the gas, a mercury-sealed stirrer, and either a water condenser (used in the former method above,) or a Y-shaped adaptor fitted with a dropping-funnel and water condenser, (used in the latter method above,) . The flask was heated on a heating mantle, and the whole apparatus was placed in a fume-cupboard.

(i) Dry hydrogen chloride gas from a cylinder was passed for 15 mins. through a stirred refluxing solution of the homopolymer (3.00 g.) in benzene (30 ml.). The black tarry product which quickly formed was isolated by evaporating the reaction mixture to dryness on a steam-bath and drying the resulting black solid in a vacuum desiccator over calcium chloride, potassium hydroxide pellets and paraffin-wax shavings. The product was tested for chlorine by the following method.

The reaction product was dried at 65°/0.1 mm. over phosphorus pentoxide. A portion of the dried material (0.1904 g.) was placed in a clean nickel crucible, and solid sodium hydroxide (2.0 g.) was added. The contents of the crucible were covered with a layer of sodium carbonate, and the crucible was heated strongly in a Bunsen flame for 15 mins. The cooled crucible and flux was placed in a beaker containing chloride-free water (175 ml.) and digested for 90 mins. at boiling temperature. The crucible was removed from the cooled solution and rinsed into the beaker, the final solution being acidified with dilute nitric acid. A solution of silver nitrate was added (10.00 ml. of 0.0504 N.,) and this solution titrated against a solution of potassium
thiocyanate (0.0487 N.) using ferric alum indicator, 10.25 ml. of thiocyanate being consumed, equivalent to 0.1% by weight of chlorine in the sample.

Found: C, 80.55, 80.52; H, 9.17, 9.00%.

(ii) The experiment as described above was repeated with a solution of the homopolymer (10 g.) in benzene (100 ml.). The hydrogen chloride gas was passed for 15 mins, and the black product isolated as before, yield 9.68 g. A portion of the dried product (4.53 g.) was placed in the thimble of a Soxhlet extraction apparatus and extracted with benzene for several days. The benzene was distilled from the resulting solution and the residual black solid was dried as above. Yield 3.65 g. (80%).

Found: C, 77.38, 78.01; H, 8.96, 9.17%.

A portion of the non-fractionated material from above (0.45 g.) was pyrolysed. A dark red-brown oil distilled over together with a clear non-miscible liquid, all at a fairly moderate temperature. The oil had a strong pine-like smell.

(iii) The homopolymer (3.00 g.) dissolved in benzene (40 ml.) was added dropwise over 8 minutes to stirred refluxing benzene (10 ml.) through which hydrogen chloride gas was passed. The solution became green initially, changing through brown to very deep red, almost black, with the precipitation of a black solid. Refluxing with the passage of the gas was continued for a further 1 hour. The cooled
reaction mixture was carefully poured into a Soxhlet thimble placed in
the extraction apparatus, and the contents extracted with benzene until
the syphoning liquid was colourless. The benzene was distilled from
the extract which contained some precipitated material. The residue,
a black solid (2.25 g.) was found to contain no chlorine by the method
described above in Section (i).

Found: C, 82.23, 82.03; H, 9.17, 9.06%.

A sample of the condensation product (8.628 g.) freshly prepared
exactly as above was pyrolysed in the apparatus described below.

A test-tube with a ground-glass socket was joined to an air-
condenser by a piece of glass-tubing of wide bore bent at 120° and
having a ground-glass cone fitted at each end. A small round-bottomed
flask was loosely fitted to the end of the condenser as a receiver,
being supported by packed ice in a small bath.

The sample was placed in the test-tube and heated in a Bunsen
flame. A heavy oily liquid condensed in the cooled receiver, a
residue of 1.534 g. remaining in the pyrolysis tube. The distillate
was dissolved in diethyl ether and dried over anhydrous sodium
sulphate. Ether was removed from the filtered solution by evaporation,
and the liquid heated at 100° at atmospheric pressure, after which it
was distilled at 17 mm. from an oil bath, and finally an air-bath.
No precise fractions could be obtained, but distillation was continuous
from 102° to 204°.
(iv) The homopolymer (100 g.) in benzene (1 l.) was converted to the self-condensation product as in Section (iii), the solution being added dropwise over 2.5 hours. Refluxing was continued for a further 30 mins., the solution stood at room temperature overnight, then refluxed with the passage of hydrogen chloride gas for 2 hours. Air was bubbled through the reaction mixture for 30 mins. to remove most of the dissolved hydrogen chloride, and benzene, water and some low-boiling organic liquids were removed by distillation from a steam-bath at 10-20 mm. The residual black solid was extracted in a Soxhlet apparatus with benzene, and the benzene removed from the extract solution by distillation. The black product was dried in a vacuum desiccator over calcium chloride, potassium hydroxide pellets and paraffin-wax shavings. The compound contained no chlorine by the test as described in Section (i) above.

Found: C, 75.96, 75.98; H, 8.63, 8.74; O, 12.36, 12.08%, and subsequently: C, 75.18, 75.18; H, 8.55, 8.61; O, 12.63, 12.82%.

(v) The preparation of the condensation product under anaerobic conditions

The apparatus used in this experiment was the same as that described previously for the preparation of the condensation product by the "inverse addition" method, with the following modification. A glass tube through which nitrogen could be passed was introduced into the dropping-funnel, reaching almost to the bottom. The neck
of the funnel was loosely stoppered with cotton-wool.  

The homopolymer (5.00 g.) in benzene (500 ml.) was placed in the dropping-funnel. Benzene (250 ml.) was placed in the three-necked flask and brought to a gentle reflux. Nitrogen was then bubbled through the polymer solution, and dry hydrogen chloride gas was passed through the stirred refluxing benzene for 30 mins. The polymer solution was then added dropwise to the stirred refluxing benzene over 1.75 hours, the nitrogen and hydrogen chloride gases both being passed throughout the addition of the polymer solution. Stirring, refluxing and the passage of the hydrogen chloride gas were continued for a further 1.5 hours. Nitrogen was then passed through the warm reaction mixture (a deep red solution,) and the benzene distilled off under nitrogen. The reaction flask containing a deep-red solid was then attached to a flask containing phosphorus pentoxide by means of an inverted U-tube, and one of the remaining necks stoppered. The flask was flushed with nitrogen and then evacuated to 10 mm. via the remaining neck, sealed, and stood overnight. The vacuum was released by introduction of nitrogen into the flask, and the hard, deep-red product detached from the flask with a spatula, nitrogen being passed at a fast rate through the flask to exclude air. The product was placed in clean, dry, soft-glass test-tubes, which were flushed with nitrogen and quickly sealed.
The product contained no chlorine by the test as given in Section (i).

A sample of the product (0.340 g.) was placed in a flask connected to a gas burette which was filled with liquid paraffin. Oxygen was introduced and readings of the volume, atmospheric pressure and temperature were taken. The readings were taken again after 3 days, but after correction to normal temperature and pressure, the volume of oxygen in the apparatus remained unchanged.

Found: C, 76.07, 76.21; H, 9.30, 9.35; O, 14.60, 14.61%.

Absorption of oxygen by the condensation product

The condensation product from Section (iv) (0.4793 g.) was placed in a weighed porcelain boat which was then placed in the apparatus described below.

A pyrex tube of internal diameter 5 cms. and 50 cms. in length was fitted at one end with a B40 cone. This was closed by a B40 socket attached to a one-way tap through which dry oxygen could be admitted to the vessel. At the other end was attached a two-way tap one arm of which led to a liquid paraffin bubbler, the other arm being attached to a vacuum-pump. A section of the cylindrical vessel was heated by an electrically powered heating jacket. A thermometer was placed inside the vessel. The oxygen was dried by passage through a calcium chloride tower.
The sample contained in the boat was submitted to the following sequence of operations. (When the boat and sample were weighed, they were contained in a weighing bottle closed with a ground-glass stopper.)

<table>
<thead>
<tr>
<th>Operation</th>
<th>Weight of Sample</th>
<th>Gain or loss of wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Dried at 16.5°/0.1mm. for 4,0 hrs.</td>
<td>0.4761</td>
<td>- 0.0032 g.</td>
</tr>
<tr>
<td>(ii) Dried at 100°/0.05mm. for 1.0 hrs.</td>
<td>0.4599</td>
<td>- 0.0162</td>
</tr>
<tr>
<td>(iii) Oxygen passed for 4.0 hrs. at 20°</td>
<td>0.4609</td>
<td>+ 0.0010</td>
</tr>
<tr>
<td>(iv) 20°/0.05mm. for 4.0 hrs.</td>
<td>0.4629</td>
<td>+ 0.0020</td>
</tr>
<tr>
<td>(v) 100°/0.10mm. for 1.0 hrs.</td>
<td>0.4566</td>
<td>- 0.0063</td>
</tr>
<tr>
<td>(vi) Oxygen passed for 2 hours, sample stood under oxygen overnight, oxygen passed for 2 hours</td>
<td>0.4599</td>
<td>+ 0.0033</td>
</tr>
<tr>
<td>(vii) 20°/0.05mm. for 4.0 hrs.</td>
<td>0.4593</td>
<td>- 0.0006</td>
</tr>
<tr>
<td>(viii) 100°/0.1 mm. for 1.0 hrs.</td>
<td>0.4536</td>
<td>- 0.0057</td>
</tr>
</tbody>
</table>

General properties of the condensation product

All the condensation products were only sparingly soluble in organic solvents such as benzene, chloroform, acetone, carbon tetrachloride and methylene chloride, giving very deep red solutions. The intensity of colour of the solutions was very strong, a solution of approximately $10^{-4}$ M being deep ruby red.

When dissolved in concentrated sulphuric acid the condensation product gave a very intense deep purple colour even in very dilute
solution. This colour was not observed with concentrated nitric or hydrochloric acids.

The reaction of thiourea with the brominated 1:2-copolymer

(i) Thiourea (0.238 g., 125% based on available bromomethyl ketone groups,) in dioxan (5 ml.) and ethanol (5 ml.) was added drop-wise over 10 mins. to a stirred refluxing solution of the bromo-copolymer (1.00 g.) in dioxan (20 ml.). A yellow-brown precipitate formed. The mixture was stirred at refluxing temperature for a further 2 hours, when the polymer had coagulated to a sticky lump. The mixture was cooled and poured into stirred dilute ammonium hydroxide solution (250 ml.). The resultant brown solid was filtered off, and the filtrate tested for bromide ions by acidifying the solution and adding silver nitrate. A white precipitate indicated that bromide ions were present. The solid from the reaction was dissolved in dimethylformamide (30 ml.) and the solution so formed was added drop-wise to vigorously stirred ammonium hydroxide solution (300 ml., pH 9-10). The light-brown precipitate was filtered off, washed with dilute ammonium hydroxide and finally with water. It was dried in a vacuum desiccator over calcium chloride. A fusion with zinc and sodium carbonate showed the presence of nitrogen, sulphur and a very small trace of bromine in the product.

Found: C, 77.61; H, 7.07; N, 5.62; O, 3.32; S, 6.53%.

\((\text{C}_6\text{H}_5)_75.0 \ (\text{C}_6\text{H}_{10}\text{N}_2\text{Os})_{25.0}\) requires: C, 76.5; H, 7.28; N, 5.95; O, 3.40; S, 6.80%.
(ii) Thiourea (0.46 g., 125% based on available bromomethyl ketone groups) in dimethylformamide (5 ml.) was added dropwise over 5 mins. to a stirred refluxing solution of the bromo-copolymer (1.946 g.) in dimethylformamide (20 ml.). No precipitation occurred. The solution was stirred at refluxing temperature for a further 2 hours. The solution was cooled and added dropwise to a vigorously stirred ammonium hydroxide solution (250 ml., pH 10). The buff-coloured precipitate was filtered off, washed with dilute ammonium hydroxide solution and water. The product was dried in a vacuum desiccator over calcium chloride. Yield 1.77 g. A fusion with zinc and sodium carbonate showed the presence of nitrogen and sulphur, and the absence of bromine in the product.

Found: C, 76.09, 76.15; H, 7.09, 7.13; N, 5.42, 5.45; O, 3.54, 3.55; S, 7.02, 7.12%.

\((C_8H_6)_74.2 (C_6H_{10}N_2O_8)_{25.8}\) requires: C, 76.12; H, 7.27; N, 6.12; O, 3.49; S, 7.00%.

The oxidation product of poly(2-methylbut-1-en-3-one)

The polymer (25.7 g.) was suspended in water (700 ml.) in a 5 l., three-necked, round-bottomed flask fitted with a water condenser, a dropping funnel and a stirrer. Sodium carbonate (14.02 g.) was added to the suspension and the flask warmed on an oil-bath at 110-120°. A solution of potassium permanganate in water was added dropwise to
the stirred suspension until a faint permanent pink colour remained for 30 mins. The polymer gradually dissolved, and manganese dioxide was precipitated; 163.8 g. (1.7 equivalents) of potassium permanganate was consumed. The manganese dioxide was filtered off, and the pale yellow filtrate of approximately 5 l. was reduced in bulk to 912 ml. by gentle warming under reduced pressure. A portion of this solution was retained, (see below,) and the main bulk adjusted to pH 9.5 by addition of dilute hydrochloric acid. A vigorous evolution of carbon dioxide was observed. The solution was evaporated to dryness under reduced pressure in a rotary film evaporator to give a pale cream coloured solid.

Purification was effected by use of "Sephadex", (cross-linked dextran,) which has the property of separating macromolecules from smaller molecules, (see appendix.) A column of this material (28 x 2 cms.) was made up from the suspension in 1% sodium chloride solution, the sodium chloride being finally eluted with distilled water. Portions of the crude reaction product (5 g.) were dissolved in water (15 ml.) and passed down the column. The polymeric material was the first to appear in the eluate, detected by the precipitate which formed on addition of a few drops of the eluate to dilute nitric acid. The carbonate was similarly detected by the evolution of carbon dioxide, and the chloride by addition to acidic silver nitrate when silver chloride was precipitated. The pH of the eluate was
followed by use of universal indicator paper. During elution of the polymeric material, the pH remained at 8 - 8.5, jumping to pH 9.5 with the appearance of the carbonate, and then slowly rising to about pH 11.

A clean separation of the polymeric material was effected. The fractions containing the polymer were combined and evaporated to dryness using a rotary film evaporator under reduced pressure; yield of a clean, off-white solid 7.86 g. The product was soluble in water, was precipitated on the addition of dilute mineral acid, and was re-dissolved on basification. The logarithmic viscosity number was determined in water at 25.0°C, and was found to be 0.071, a mean of two determinations.

The amount of carbonate in the solution from the reaction was determined by adding excess 2 N sulphuric acid to 5.00 ml. portions of the solution and collecting the evolved carbon dioxide in a gas burette over saturated sodium chloride solution. 39.5 ml. of carbon dioxide was collected at 295.2°C and 758.9 mm. pressure, showing the original solution of 912 ml. to have contained the equivalent of 6.66 l. of carbon dioxide at standard temperature and pressure. The original sodium carbonate in the reaction mixture (14.02 g.) was equivalent to 2.96 l. of carbon dioxide, which shows that 3.70 l. of the gas was evolved from the decomposition of the polymeric keto-acid.

Complete decomposition, which involves oxidation of "acetyl" methyl groups followed by decarboxylation and oxidation of aldehyde to
carboxyl groups, yielding poly(methacrylic acid) would evolve 6.85 l. of carbon dioxide from the original polymer; thus approximately half of the acetyl side-groups had been degraded by this route.

The silver salt of the polymeric acid was prepared by neutralising it with dilute sodium hydroxide to pH 10, and adding this warmed solution to a 30% excess of silver nitrate in warm water. The resultant white precipitate was kept in its liquor overnight in a dark cupboard, and then centrifuged. The supernatant liquid was decanted from the pad, the pad broken up under distilled water and the suspension recentrifuged. This process was repeated until the washings were free from silver ions. The final wet pad was dried in a vacuum desiccator over calcium chloride, the desiccator being placed in a dark cupboard. The resultant off-white solid was finally dried at 65°/0.1 mm. and analysed. It was necessary to exclude light as much as possible from the product during the working-up process, as it appeared to be light-sensitive, and decomposed on exposure, turning black.

Found: C, 23.10, 23.11; H, 2.58, 2.51; Ag, 51.87, 51.62%.

1:1: : C$_5$H$_5$O$_2$Ag: C$_4$H$_5$O$_2$Ag requires: C, 26.15; H, 2.44; Ag 52.1%.

The reduction product of poly(2-methylbut-1-en-3-one)

Two methods were used:

(i) Using hydrogen and Raney nickel;

(ii) Using lithium aluminium hydride.
(i) The polymer (5.78 g.) in tetrahydrofuran (50 ml.) and B.D.H. Raney nickel (0.5 g.) were placed in an autoclave which was filled with hydrogen at 17°/135 atmos. The apparatus was left for 30 mins. during which time no drop in pressure was observed, indicating a sealed apparatus. The temperature was raised to approximately 200° and maintained at this temperature for about 7.5 hours. The maximum temperature and pressure observed was 202°/213 atmos. The heaters were switched off and the apparatus allowed to cool overnight, the temperature and pressure then reading 17°/132 atmos. The autoclave was vented, the solution pipetted out and filtered. The filtrate was added dropwise to vigorously stirred light petroleum (b.p. 40-60°, 300 ml.). The fine white precipitate which resulted was filtered off, washed with light petroleum and dried first in air and then in a vacuum desiccator. Yield 5.73 g.

Found: C, 71.87; H, 9.93%.

(ii) A suspension of lithium aluminium hydride (3.28 g.) in sodium dried tetrahydrofuran (120 ml.) was placed in a 500 ml., three-necked round-bottomed flask, fitted with a dropping-funnel, a double-surface water-condenser and a mercury sealed stirrer. The condenser and dropping-funnel were closed with calcium chloride tubes. The polymer (14.51 g.) in sodium-dried tetrahydrofuran (200 ml.) was placed in the dropping-funnel and added dropwise to the stirred
refluxing suspension in the flask over 30 mins. A white curdy precipitate formed which was stirred at refluxing temperature for 3 hours. The mixture was cooled and water (150 ml.) was added with extreme caution to decompose the excess lithium aluminium hydride. The curdy precipitate disappeared and was replaced by a heavy white suspension. Hydrochloric acid (150 ml., 3 N) was added to dissolve the aluminium hydroxide, and two layers formed. The top, organic layer was separated from the bottom aqueous layer, and washed with saturated sodium chloride solution until the washings were neutral. The solution was dried over anhydrous sodium sulphate and precipitated in vigorously stirred light petroleum (b.p. 40-60°, 2.5 l). The fine white precipitate was filtered off, washed with petroleum ether, air-dried and finally dried over calcium chloride in a vacuum desiccator. Yield 12.7 g.

Found: C, 70.66, 70.79; H, 11.05, 11.11%.

\((C_2H_8O)_{30.0} (C_5H_{10}O)_{70.0}\)
requires: C, 70.21; H, 11.08%.

The p-nitrobenzoyl ester of the reduction product of poly(2-methylbut-1-en-3-one).

The reduction product (0.335 g.) and p-nitrobenzoyl chloride (1.133 g.) were dissolved in pyridine (10 ml.) and warmed in a water-bath at 80-85° for 2.5 hours. The cooled solution was added to stirred dilute hydrochloric acid (1 N., 150 ml.) and the pale yellow-brown precipitate was filtered from the liquid. The
precipitate was washed with dilute hydrochloric acid until the pyridine smell was no longer evident, then with dilute ammonium hydroxide until free of chloride ions, and finally with water. The dried polymer was dissolved in a dioxan/acetone mixture (35 ml.) and reprecipitated by dropwise addition of the solution to 10% ammonium hydroxide solution (175 ml.). The resultant pale yellow precipitate was filtered from the liquid and washed with distilled water until the washings were pH 7. The polymer was dried in a vacuum desiccator over calcium chloride. A fusion with zinc and sodium carbonate showed the presence of nitrogen and absence of halogen in the polymer.

Found: C, 64.96, 64.92; H, 6.86, 6.73; N, 5.07, 5.02%.

(C$_{15}$H$_{8}$O)$_{30.0}$ (C$_{12}$H$_{13}$NO$_{4}$)$_{70.0}$ requires: C, 62.61; H, 6.10; N, 5.16%.
PREPARATION OF MODEL COMPOUNDS

(i) 2,2-Dimethylbutan-3-one

This compound was prepared from pinacol hydrate and concentrated sulphuric acid. It had b.p. 103-107°, n_D^25 1.3950. A small portion was distilled through a 10 in. column packed with glass rings, for spectroscopic examination and had b.p. 105.5°, n_D^25 1.3949. (Lit: 106.3°, n_D^25 1.3944.) 55% yield.

(ii) 1-Bromo-3,3-dimethylbutan-2-one

A three-necked, round-bottomed flask of capacity 500 ml. was fitted with a dropping-funnel, a mercury-sealed stirrer and a reflux condenser. In the flask was placed a solution of 2,2-dimethylbutan-3-one (40 g.) in carbon tetrachloride (100 ml.) and the solution was stirred and refluxed. Bromine (68.8 g., 107.5%) was added dropwise over 40 mins. from the dropping-funnel. The bromine colour was discharged immediately, and copious fumes of hydrogen bromide were evolved. After addition of the bromine, the solution was stirred and refluxed for a further 30 mins. The carbon tetrachloride was distilled off, and the residual 1-bromo-3,3-dimethylbutan-2-one was distilled; it had b.p. 68-72°/11 mm. and on redistillation b.p. 69-71°/11 mm. (Lit: 71.5-72°/10 mm.) Yield of a clear, very lachrymatory liquid, 20 ml.
(iii) 2-Amino-4-t-butylthiazole

This compound was prepared from thiourea (1.855 g.) and 1-bromo-3,3-dimethylbutan-2-one (4.39 g.) in ether (75 ml.), the mixture being stirred at room-temperature for 3 hours.\(^\text{52}\) The precipitated hydrobromide of the 2-amino-4-t-butylthiazole was filtered from the ether, dissolved in water and reprecipitated by the addition of powdered sodium hydroxide. The white solid was filtered from the alkaline liquor, and washed with a little cold water. The dried solid was distilled under reduced pressure; it had b.p. 122°/12 mm., m.p. of solidified distillate 99.5°. (Lit: 100-101°.) \(\text{Yield 2.13.}\)

(iv) The condensation of thioacetamide with 1-bromo-3,3-dimethylbutan-2-one

1-Bromo-3,3-dimethylbutan-2-one (6.60 g.) was added dropwise over 10 mins. to a stirred suspension of thioacetamide (2.76 g.) in ether (100 ml.), and stirring continued for 3 hours at room-temperature. The hydrobromide was filtered off, dissolved in water (25 ml.) and powdered sodium hydroxide (2.0 g.) was added slowly with stirring. The white precipitated solid was filtered, washed with water and dried. It had m.p. 67-8°, and was purified by sublimation at 2.5-3.5 mm., heating being by an oil bath at 70-75°. The melting-point was constant at 69.5°-70° after two sublimations. \(\text{Yield 2.7 g.}\)

Found: C, 56.03, 56.14; H, 8.47, 8.47; N, 7.95, 7.94; S, 18.02, 18.03%.
(v) 2,4-Dimethylthiazole

This compound was prepared from chloroacetone (7 ml.) and thioacetamide (6.17 g.) in benzene (13.5 ml.)(47) The product was distilled from an oil-bath and had b.p. 142-144°. (Lit: 144-145°.)

(vi) 2-Amino-4-methylthiazole

This compound was prepared from chloroacetone (9.4 g.) and thiourea (7.6 g.) in water (20 ml.).(46) The product was distilled from an oil-bath under reduced pressure. It had b.p. 130-133°/18mm. The yellow distillate solidified and was recrystallised from aqueous acetone; it had m.p. 44°. (Lit: 42°.)

(vii) Trimethylpyruvic acid

Trimethylpyruvic acid was prepared by the oxidation of 2,2-dimethylbutan-3-one with alkaline potassium permanganate.(48) 2,2-Dimethylbutan-3-one (4 g.) sodium carbonate (2 g.) and potassium permanganate (15 g.) in water (300 ml.) were refluxed for 3 hours. Manganese dioxide was precipitated and the permanganate colour lessened slightly in intensity during the course of the reaction. The solution was cooled, the manganese dioxide was filtered off, and the filtrate acidified with dilute sulphuric acid. The aqueous solution was extracted with ether (3 x 50 ml.) and the ethereal extracts dried over calcium chloride overnight. The solution was then filtered, the ether removed on a steam-bath, and the residue distilled under reduced pressure; it had b.p. 70-71°/10 mm. (Lit: 80°/15 mm.)
The equivalent weight of the product was determined by titration against standard sodium hydroxide solution, with phenolphthalein as indicator.

Equivalent found: 129.2, 129.4. Calculated for:

\[(\text{CH}_3)_3\text{C.CO.COOH}: \text{130.2.}\]

(viii) 2,2-Dimethylbutan-3-one

2,2-Dimethylbutan-3-one (16 g.) in tetrahydrofuran (50 ml.) was hydrogenated in an autoclave with Raney nickel, (0.5 g. B.D.H.), as catalyst. The maximum temperature and pressure were 204°/13 atm. The reaction-mixture was under pressure at an elevated temperature for 8 hours. It was filtered, and tetrahydrofuran was removed from the filtrate by distillation. The residual liquid was distilled from an oil-bath through a 3 in. column; a small residue remained, after the following fractions had been collected:

- b.p. 66-110° (3 ml.)
- b.p. 110-118° (3 ml.)
- b.p. 119-120° (15 ml.)

The last fraction on redistillation had b.p. 119-120°,

\[n_D^{25} 1.4130. \text{ (Lit: b.p. 120°, } n_D^{25} 1.4132.)\]

(ix) Poly(methacrylic acid)

Methacrylic acid monomer was distilled under reduced pressure in an atmosphere of nitrogen, and had b.p. 65.5°/15 mm. The monomer was polymerised in a sealed soft glass tube under nitrogen at 70°.
for 2 hours, 1% by weight of azobisisobutyronitrile being used as initiator. The monomer solidified after 30 mins. The hard porous polymer was removed from the tube and ground to a fine powder using a percussion mortar, finally being dried in a rotating cylindrical vessel at 57°/0.05 mm. for 4 hours. 87% yield.

The equivalent weight was determined by potentiometric titration against standard sodium hydroxide using glass and calomel electrodes.

Equivalent found: 88.0, calculated for \( \text{C}_4\text{H}_6\text{O}_2 \)_n 86.1.

The silver salt of the acid was prepared as follows. Poly (methacrylic acid), (0.300 g.) was dissolved in water and neutralised to pH 10 with sodium hydroxide solution. The solution was warmed and added dropwise to a warm stirred solution of silver nitrate which was in 30% excess. The precipitated white solid was kept in the mother liquor in a dark cupboard overnight, centrifuged, and the supernatant liquid decanted from the pad. The pad was broken up under distilled water and the suspension recentrifuged. This process was repeated until the washings were free of silver ion. The final wet pad was placed in a vacuum desiccator over calcium chloride in a dark cupboard overnight, and the resulting slightly brown product dried at 65°/0.05 mm. It was necessary to exclude light from the product as much as possible during the working-up process, as it was light-sensitive and turned black on exposure. 0.617 g yield.
Found: C, 25.12, 25.08; H, 3.25, 3.29; Ag, 49.79, 49.84%.

\((\text{C}_4\text{H}_9\text{O}_2\text{Ag})_n\) requires: C, 24.90; H, 2.61; Ag, 55.94%.

The oxime of 2,2-dimethylbutan-3-one

2,2-Dimethylbutan-3-one (2 g.) and hydroxylamine hydrochloride (2.25 g.) were dissolved in pyridine (20 ml.) and methanol (10 ml.). Sodium hydroxide (5 ml. of 2 N) was added and the solution was heated on a steam-bath for 2 hours. The crystals which separated from the cooled solution were filtered off and after recrystallisation from aqueous methanol, had m.p. 76°. (Lit: 75.5-76°.) 2g yield.
(1) **Infra-red spectra**

All infra-red spectra were recorded by means of a Grubb-Parsons G.S.2A. Spectrometer.

(2) **Ultra-violet spectra**

The ultra-violet spectra were recorded by means of Unicam S.P.800 and Optica CF4 spectrometers.

(3) **Sephadex**

Sephadex consists of small grains of a hydrophilic insoluble substance made by cross-linking the polysaccharide dextran. When placed in water the grains swell forming a gel. A column of this gel may be prepared giving two water phases, one contained in the gel lattice, the other as a "free" phase. Only relatively small molecules may penetrate the gel lattice, entering the water phase therein, while larger molecules are excluded and remain in the "free" phase.

If the volume of water held in the gel lattice is $V_i$, that in the "free" phase $V_o$, and the volume of solid material comprising the gel $V_g$, then the total volume of the column $V_t$ is given by:

$$V_t = V_i + V_o + V_g.$$

The distribution coefficient of a solute between the two aqueous phases is $K_D$; when $K_D = 0$, the solute remains exclusively in the "free" phase, while when $K_D$ lies between 0 and 1, the solute may enter the aqueous phase contained in the gel lattice.
If a solution containing two solutes of distribution coefficients $K_D = 0$ and $K_D = 1$ is added to the column, the former will appear in the effluent after a volume $V_0$ has passed. After an additional volume $V_i$ has passed, the latter solute will appear in the effluent. When complete separation is required, two solutes with distribution coefficients $K_D$ and $K_D^{1}$ must be introduced in a volume of solvent $V$, where

$$V < \left( K_D - K_D^{1} \right) V_i$$

Molecules of a very high molecular weight such as proteins generally have $K_D = 0$, while solutes of lower molecular weight such as glucose or sodium chloride have $K_D$ values between 0.7 and 1.

The column of the gel was prepared as follows. The dry powdered Sephadex was stirred in a beaker with a 1% solution of sodium chloride in water; the electrolyte was added to hinder aggregation of the gel particles. After sedimentation the solution was decanted to remove the finest gel particles. The column was filled with a similar saline solution and the gel suspension added via a funnel. The solution in the column was gently stirred to ensure an even sedimentation of the gel. When a small layer of the gel had formed, the tap at the base of the column was opened to allow a slow flow of the solution. When addition was complete, the surface of the column was covered with a disc of filter paper to prevent disturbance of the surface. The sodium chloride was removed by
washing with distilled water, and the column was then ready for use.

The sample was introduced by draining the column just to the level of the surface and pipetting the sample on to the surface of the bed. As soon as the sample had entered the column, the top surface was washed with a small quantity of the solvent, and followed by a larger quantity of solvent to start the elution. Small fractions of the effluent were collected in clean dry test-tubes.

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