436. *The Structure and Mechanism of Formation of the Polymer obtained from* cyclo*Propane by Mercury Photosensitisation.*

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The low polymer formed as the main product of the mercury-photo-sensitised reaction of *cyclo*propane has been examined by infrared absorption spectrometry and other methods. The polymer contains one methyl group for every 3—5 carbon atoms and probably not more than 1·25 methylene groups for every methyl group. Between 30% and 50% of the polymer molecules made at room temperature are unsaturated, the greater part of the unsaturation being due to vinyl groups. The remaining molecules appear to contain a ring structure of five carbon atoms. Neither *cyclo*propane nor propene was polymerised by alkyl radicals at room temperature.

The spectrum of the polymer partially resembles that made by the mercury-photosensitised polymerisation of propene but does not closely resemble that of polymers made from propene by other methods. Mass-spectrometric evidence was obtained for the setting-up of a low steady-state concentration of diallyl. The proposed mechanism involves the initial formation of diallyl and other olefins, followed by addition of excited *cyclo*-propane molecules or trimethylene diradicals at the olefinic linkages. Three competing addition processes are postulated, resulting in the formation of a higher olefin, a ring structure, or a *n*-propyl group respectively.

THE formation of an involatile oil by the action of mercury resonance radiation (2537 Å) on a mixture of *cyclo*propane and mercury vapour was first noted by Harris, Ashdown, and Armstrong.[1]   The kinetics of this mercury-photosensitised reaction and the nature of the product were further investigated by Gunning and Steacie,[2] and by Scott and Gunning.[3] However, the mechanism proposed by these workers involves the opening of successive *cyclo*propane rings by the attack of a propagating alkyl radical.   In view of the known immunity of the three-membered carbon ring to attack by hydrogen atoms,[2] chlorine atoms,[4] and radicals,[5] this mechanism cannot be accepted.

Scott and Gunning [3] showed that the molecules of polymer prepared at 30° had molecular weights distributed about a most probable value of 222.   From this it is evident that the

[1] Harris, Ashdown, and Armstrong, *J. Amer. Chem. Soc.*, 1936, **58**, 852.
[2] Gunning and Steacie, *J. Chem. Phys.*, 1949, **17**, 351.
[3] Scott and Gunning, *J. Phys. Chem.*, 1952, **56**, 156.
[4] Roberts and Dirstine, *J. Amer. Chem. Soc.*, 1945, **67**, 1281.
[5] Hammond and Todd, *ibid.*, 1954, **76**, 4081; and present work.

reaction must proceed *via* intermediates more reactive than *cyclo*propane itself, but we have seen above that these are unlikely to be radicals.

The purpose of the present work has been to make a closer examination of the polymer, particularly of its infrared absorption, with a view to obtaining further evidence on which to base a more convincing theory of the mechanism.

<div align="center">RESULTS</div>

Attempted Polymerisation of cyclo*Propane by the Action of Alkyl Radicals at Room Temperature.*—Although it appeared unlikely that the polymerisation could proceed by a radical-chain mechanism, it was thought desirable to check this by generating alkyl radicals in the presence of *cyclo*propane.

The following compounds were used as sources of alkyl radicals : acetone, dimethylmercury, diethyl ketone, diethylmercury, and di*iso*propyl ketone. Up to 50 mm. of the vapour of one of these compounds was mixed with 200—300 mm. of *cyclo*propane in a 10 cm. quartz cell at room temperature, normal vacuum-technique being used, and alkyl radicals were then generated by the action of ultraviolet light from a hot mercury arc. In no case did the pressure–time curves indicate the occurrence of polymerisation even though in most cases the radical source had largely decomposed. Similar results were obtained when the *cyclo*propane was replaced by propene. Thus neither the mercury-photosensitised polymerisation of *cyclo*propane nor that of propene can be regarded as radical-chain reactions at room temperature. It was also found by infrared analysis that the C_3 hydrocarbons produced in the photolysis of di*iso*propyl ketone contained at least 50% of propene, a result which would not have been obtained had much of the propene undergone secondary polymerisation.

The addition of methyl radicals to propene has been shown to occur at temperatures well above room temperature,[7] but the reaction has an energy of activation of about 6 kcal./mole and evidently does not occur readily at room temperature.

Evidence for the Presence of Radicals during the Mercury-photosensitised Reactions.—It is well established that molybdenum oxide becomes blue in the presence of hydrogen atoms and alkyl radicals.[8] This test was applied to the mercury-photosensitised polymerisation of *cyclo*propane and propene severally at 100 mm. and room temperature. The molybdenum oxide became blue at about the same rate in the two cases, namely, about one-fifth of that observed when the cell was filled with hydrogen at 100 mm. and irradiated. Thus, although radicals are produced in a fairly efficient manner, they do not propagate a polymerisation chain and must disappear by some other means.

The Infrared Absorption of the Polymer : *General Description.*—The spectrum of the polymer made at room temperature is shown in Fig. 1. Slight changes occur in the 1125 cm.$^{-1}$ region when the polymer is stored or subjected to a vacuum. Most of this change is due to the removal of small amounts of volatile constituents. On one or two occasions a substantial peak appeared at 675 cm.$^{-1}$, apparently due to some secondary product. The volatile polymer formed only a few per cent of the total, but sufficient was separated to obtain the spectrum of a thin film; this is shown in Fig. 1. There is quite a close resemblance to the spectrum of a thin film of the involatile polymer.

The infrared spectrum of the involatile polymer was independent of the pressure of *cyclo*propane (200—400 mm.), the incident intensity (factor of 2), and the period of irradiation (factor of 3). This was to be expected from the known constancy of the quantum yield (0·136) under these conditions.[2] When the surface of the reaction vessel adjacent to the lamp was horizontal and above the lamp, the polymer formed after prolonged irradiation (several days) showed an additional peak at 1710 cm.$^{-1}$: this appears to be caused by secondary photochemical reactions of the oil deposited on the horizontal surface and will not be considered further.

The two most striking features of the spectrum are, first, the complete absence of absorption at the frequency (725 cm.$^{-1}$) characteristic of a polymethylene chain containing more than three methylene groups;[9] and, secondly, the intense absorption at 1370 cm.$^{-1}$ which can only be ascribed to the presence of methyl groups. Further, the fact that there is no splitting of this peak indicates that most of the methyl groups are attached to separate carbon atoms, while the absence of a peak at 1130—1115 cm.$^{-1}$ indicates that few of the methyl groups are attached to

[6] Gunning and Steacie, *J. Chem. Phys.*, 1948, **16**, 926; 1946, **14**, 57.
[7] Mandelcorn and Steacie, *Canad. J. Chem.*, 1954, **32**, 474.
[8] Melville and Robb, *Proc. Roy. Soc.*, 1949, *A*, **196**, 479.
[9] McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318.

adjacent carbon atoms. Estimates given below indicate that methyl groups may account for nearly one-third of the carbon atoms. The structure of the polymer thus appears to be more like polypropene than polymethylene.

Other important features of the spectrum are the presence of strong peaks at the frequencies characteristic of vinyl groups [3070, 1830 (overtone), 1645, 992, 910 cm.$^{-1}$] and possibly of other olefinic groups (967, 890 cm.$^{-1}$) and *n*-propyl groups (740 cm.$^{-1}$). An examination of the 3000 cm.$^{-1}$ C–H stretching band under higher disperion (lithium fluoride prism) revealed no further bands and it is concluded that cyclopropyl groups, which are normally characterised [10] by two bands at 3023 $\pm$ 12 and 3090 $\pm$ 12 cm.$^{-1}$, are absent.

Further Evidence on Unsaturation.—Scott and Gunning [3] reported that the polymer did not take up bromine, but nevertheless the infrared spectra of some of their polymer fractions seem to indicate the presence of olefins. It was therefore desirable to obtain further evidence on this point.

The total olefin content of the polymer was estimated in three ways : first, by the uptake of hydrogen; secondly, by bromination; and, thirdly, from the intensities of the infrared

Fig. 1. *Absorption spectrum of polymer made from* cyclo*propane.*
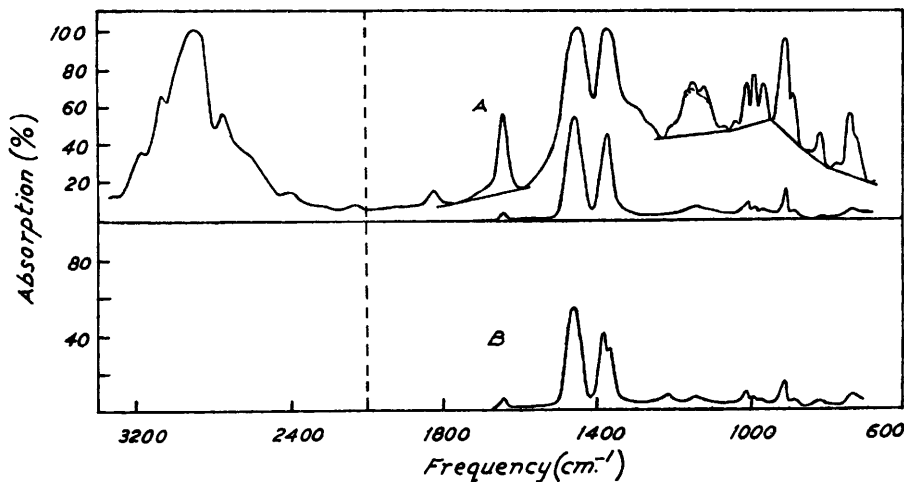
A : total polymer, 0·117 mm. and thinner layer; *B* : volatile polymer, thin layer.

absorption bands. In addition, the hydrogenated polymer was recovered and its spectrum provides further evidence.

Hydrogenation. 2·50 × 10^{-4} Mole of polymer (average mol. wt. 230 $\pm$ 4) took up 0·88 × 10^{-4} mole of hydrogen in 1·33 hr., correction being made for a slow uptake of hydrogen after the main reaction. This means that only 35% of the polymer molecules prepared at room temperature contain an unsaturated group. If no correction is made for drift and the hydrogen uptake measured after 16 hr., this figure is raised to 43%. The 1830, 992, and 910 cm.$^{-1}$ peaks were completely eliminated on hydrogenation (2 hr.). There was a small residual peak at 1645 cm.$^{-1}$ and a shoulder remaining at 3070 cm.$^{-1}$. These observations confirm the presence of vinyl groups. It was difficult to assess whether the 890 cm.$^{-1}$ peak had been affected on account of the large change in the neighbouring 910 cm.$^{-1}$ peak ; but it was little changed and it is unlikely that it is due to an olefin of type R·CMe:CH$_2$. The 967 cm.$^{-1}$ peak was diminished and broadened on hydrogenation and may be ascribed in part to an olefin of type *trans*-R'·CH:CHR. No new peaks appeared on hydrogenation and the only peak to increase in height was that at 740 cm.$^{-1}$ ascribable to *n*-propyl groups, which increased by about 13% (as measured from a line drawn across the base of the peak). This increase is of the right order of magnitude when the relative group extinction coefficients for vinyl and *n*-propyl groups are taken into consideration (see below). This suggests that the vinyl group is attached to a single methylene group as in R·CHMe·CH$_2$·CH:CH$_2$, giving rise to *n*-propyl groups on hydrogenation.

Bromination. A polymer of molecular weight 251 (prepared at room temperature) took up an amount of bromine corresponding to 49% of unsaturated molecules.

[10] Wiberley and Bunce, *Analyt. Chem.*, 1952, **24**, 623.

Infrared absorption intensities. Measurements were made on a polymer of molecular weight 244. The density of the polymer was 0·83, so that the concentration was 3·40 mole/l. The depth of the cell was $1·17 \times 10^{-2}$ cm., so that if the observed optical density is D at a frequency where the group extinction coefficient is ε ml. mole^{-1} cm.$^{-1}$, the percentage p of molecules containing the group is given by $p = D/(3·40 \times 1·17 \times 10^{-7}\varepsilon) = 251D/10^{-4}\varepsilon$. Group extinction coefficients vary from one compound to another and it is only possible to estimate probable limits for p. Values for ε have been taken from McMurry and Thornton,[9] and the results are given in Table 1. The value of p for *trans*-R'·CH:CHR can only be taken as a guide to the maximum amount of such olefins which could possibly be present. The values of p for vinyl groups are more reliable.

TABLE 1. *Estimates of olefin content of the polymer.*

Group	ν (cm.$^{-1}$)	$10^{-4}\,\varepsilon$(ml. mole^{-1} cm.$^{-1}$)	D	p (%)
R·CH:CH$_2$	1830	0·50—0·67	0·072	36—27
	1645	2·8—4·4	0·310	28—18
	992	3·3—5·7	0·546	43—25
	910	10·9—15·2	1·13	26—19
trans-R'·CH:CHR	967	9·2—11·9	0·535	15—11

Summarising, we may say that of the polymer molecules prepared at room temperature, about 40%, and certainly not more than 50%, contain a double bond. Well over half of the unsaturated molecules contain a vinyl group attached to a single methylene group; small amounts of *trans*-R'·CH:CHR olefins may also be present.

End-groups and Repeating Groups.—The average composition of each polymer molecule is given by (CH$_2$)$_n$. Each molecule must therefore contain, on average, either a double bond or a carbon ring. Thus it appears that more than half of the molecules of polymer made at room temperature contain a ring system, which, we have seen, must contain more than three carbon atoms. The molecules containing a double bond may be regarded as linear, with an unsaturated group at one end and a saturated group at the other. If therefore the average molecular weight of the polymer is varied, or if a given polymer is separated into fractions of different average molecular weight, it should be possible from the spectra to distinguish peaks due to end-groups from those due to repeating groups.

Variation of average molecular weight : effect on peak heights. Temperature was the only variable which had an effect on the molecular weight of the polymer (above 50 mm. pressure). Increasing the temperature increased the molecular weight, as shown in Table 2. This increase

TABLE 2. *Peak heights for 0·117 mm., measured as described in text.*

Approx. prep. temp.	Average mol. wt.	Peak heights for the frequencies (cm.$^{-1}$) stated										
		ν: 1645	992	910	967	740	820	890	1015	1045	1152	1170
22°	244 ± 3	42·2	30·2	49·3	24·3	32·6	15·7	23·4	26·0	6·7	25·4	22·7
60	274 ± 5	28·3	17·5	40·4	19·8	36·2	14·8	23·4	25·5	6·1	25·7	23·0
100	383 ± 16	13·2	3·2	13·2	9·0	38·0	7·7	20·0	14·6	3·2	23·4	21·5

was also manifested in an increased viscosity of the polymer. The peak heights in the absorption spectra of 0·117 mm. thickness of polymer, measured from base lines as drawn in Fig. 1, are shown in Table 2. The change in the spectrum is more severe in going from 60° to 100° than from 22° to 60°, and for the examination of the effect of molecular weight on peak heights the 100° results should be ignored.

The first three peaks, due to vinyl groups, decline with increasing molecular weight as would be expected of end-groups. However the magnitude of the decrease is several times greater than would be expected if the sole effect of temperature were an effect on the average chain length of a linear polymer. The difference is accounted for if the fraction of polymer molecules containing a ring increases with increase of preparation temperature. The 967 cm.$^{-1}$ peak also declines with increasing preparation temperature, probably indicating a ·CH:CHR end-group attached in the *trans*-position. All other peaks remain approximately constant, with the exception of that at 740 cm.$^{-1}$ which *increases* with increasing molecular weight. It thus appears that any variation in the height of a peak due to a saturated end-group is masked by an opposing effect of temperature on the concentration of identical side-groups.

Separation into fractions : variation of peak heights. 2·71 g. of polymer prepared at room temperature were separated by microdistillation into 20 fractions and a residue. The weight percentage of polymer distilled at the mid-point of each fraction was computed from the

measured weights of the fractions.   The results are shown in Fig. 2 where the refractive index is plotted against fraction number and weight % distilled.   The figures given to the right of the curve indicate the approximate degree of polymerisation as estimated from Scott and Gunning's data [3] relating refractive index to degree of polymerisation, obtained by measurements on

FIG. 2.   *Refractive index of the polymer fractions.*

(Numbers to the right of the curve indicate approximate degree of polymerisation as estimated from Scott and Gunning's data.[3])
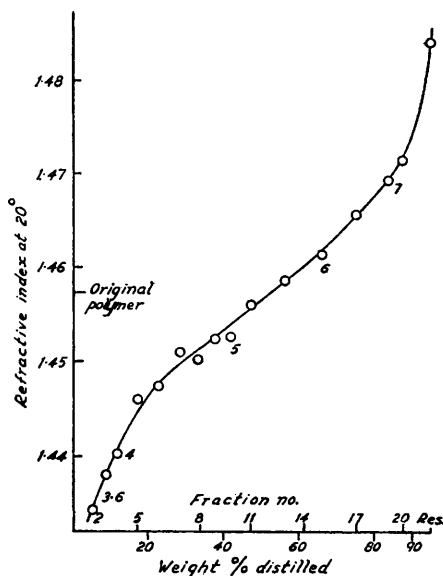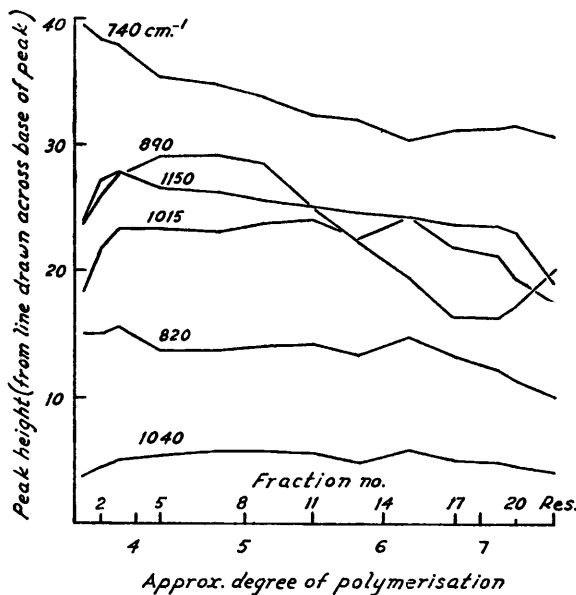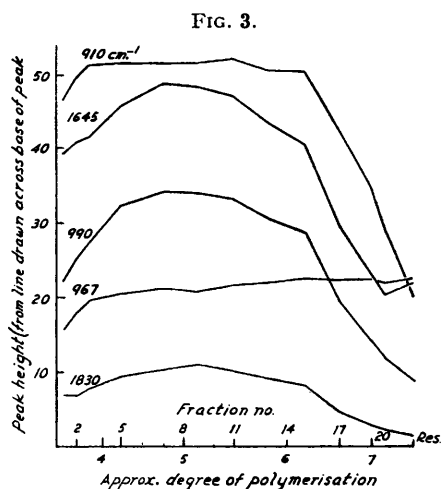
FIG. 4.

FIGS. 3 & 4.   *Variation of peak heights with fraction number.*

fractions of a polymer made under similar conditions to those used here.   There is an approximately two-fold increase in molecular weight in going from fraction 2 to fraction 20.

There was a fairly smooth variation in the height of a given peak in the infrared spectrum from one fraction to the next.   There were no discontinuities such as might have been found had one fraction contained markedly different structural groupings from the next.   The observed variations are shown in Fig. 3 for the olefin peaks and in Fig. 4 for the other peaks.

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All the peaks due to vinyl groups are a maximum for one of the middle fractions. Taking into account the variation in molecular weight of the fractions it may be concluded that the fraction of molecules containing a vinyl group is a little higher for fractions 8—15 (approx.) than in the original polymer, and lower for other fractions. The variation of the 967 cm.$^{-1}$ peak, ascribed above to a *trans*-olefin, and that of the 890 cm.$^{-1}$ peak, are difficult to explain in relation to the results on the effect of temperature. The 740 cm.$^{-1}$ peak decreases to some extent with increasing molecular weight, suggesting that it may be due in part to an end *n*-propyl group, and in part to side *n*-propyl groups. If so, then it appears from the results shown in Table 2 that on increase of temperature the increase in concentration of side-groups outweighs the decrease in the concentration of end-groups. The other peaks remain approximately constant and are attributable mainly to repeating structures.

Estimation of CH$_3$, CH$_2$, *and* n-C$_3$H$_7$ *Groups.*—CH$_3$ *groups.* The extinction coefficient at 1380 cm.$^{-1}$ for isolated methyl groups [9] is $(1.8 \pm 0.3) \times 10^4$ ml. mole^{-1} cm.$^{-1}$. The optical density of a thin film (*ca.* 0.015 mm.) of polymer was measured, the thickness then being estimated by comparing the spectrum with that of 0.117 mm. at a suitable frequency. Polymers made at all temperatures, and all fractions of a given polymer were found to contain between
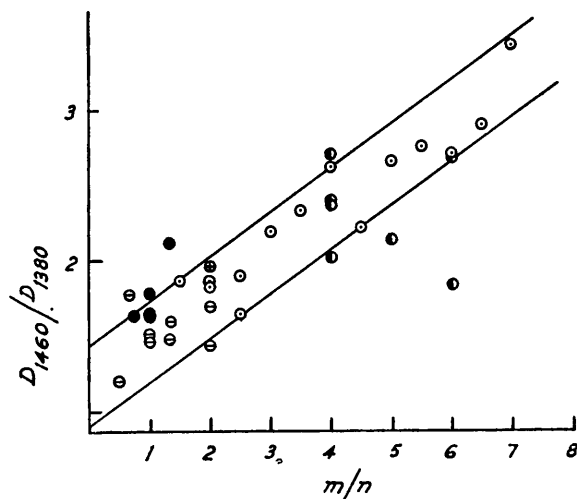

Fig. 5. *Optical density ratio at 1460 and 1380 cm.$^{-1}$ plotted against the ratio of the number of* CH$_2$ *groups* m *to the number of* CH$_3$ *groups* n.

$\oplus$ Direct observation on *n*-hexane; all other points derived from the A.P.I. tables [11] for hydrocarbons in the liquid state, not containing (CH$_3$)$_3$C groups : $\odot$ straight chain paraffins; $\ominus$ methyl-substituted *n*-paraffins; $\bullet$ other paraffins; $\mathbb{C}$ cyclic hydrocarbon derivatives.

20 and 32 methyl groups per 100 carbon atoms. The fractions all gave the same value as the original polymer, while an increase of preparation temperature tended to increase the proportion of methyl groups.

CH$_2$ *groups.* The ratio of the number of CH$_2$ groups *m* to the number of CH$_3$ groups *n* may be estimated from the ratio of optical densities at 1460 and 1380 cm.$^{-1}$. In Fig. 5 these two ratios are plotted against each other for various liquid hydrocarbons, none of which contains more than one methyl group attached to a given carbon atom. Most of the points lie between two parallel lines. In an unknown compound the ratio *m*/*n* may be estimated with an error which is unlikely to be greater than ± 0.9. The observed optical-density ratio D_{1460}/D_{1380} was 1.27 ± 0.03 under all preparation conditions. From Fig. 5 it may be concluded that the ratio *m*/*n* lies between zero and 1.25; in other words, for every methyl group there are not more than 1.25 methylene groups. Measurements on the polymer fractions showed that D_{1460}/D_{1380} decreased steadily from 1.40 for fraction 1 to 1.20 for fraction 15 and remained constant for the higher fractions and residue. It is not possible to be sure that this reflects a real variation in *m*/*n*.

n-C$_3$H$_7$ *groups.* The extinction coefficient at 740 cm.$^{-1}$ for compounds containing *n*-propyl groups is somewhat variable. A value of $(0.7 \pm 0.35) \times 10^4$ ml. mole^{-1} cm.$^{-1}$ was computed from the spectra of 11 compounds given in tables.[11] From this it was calculated that each molecule of polymer prepared at room temperature contained 1.6 ± 0.8 *n*-propyl groups.

The position may be summarised by considering an average polymer molecule containing 6 monomer units. Let us assume for the moment that the molecule contains no quaternary

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[11] American Petroleum Institute Research Project 44, Catalog of Infrared Spectral Data.

carbon atoms. The molecule contains 18 carbon atoms of which 4—6 are accountable as CH_3 groups. The molecular formula is $C_{18}H_{36}$. We must therefore have present 4—6 CH groups and 10—6 CH_2 groups. But we have seen that m/n is unlikely to exceed 1·25 so that the number of CH_2 groups is unlikely to exceed 8. The argument is not materially affected if CH groups are neglected in favour of quaternary carbon atoms.

The close approximation to the requirements of a polypropene structure led, first, to an examination of the gaseous products for propene and, secondly, to a comparison with the spectra of polymers made from propene.

Search for Propene; Evidence for Diallyl.—The possibility of intermediate formation of propene is permitted by the low quantum yield of the cyclopropane reaction [2] (0·136 at 30°) and the known ability of propene to undergo mercury-photosensitised polymerisation.[6]

Gunning and Steacie [2] sought but failed to detect propene in the products of polymerisation at 50—400 mm. Their limit of detection was about 1%. It was found possible to lower this limit to 0·1% by using a pressure of 400 mm. in a 10 cm. infrared absorption cell and looking for the olefin peak at 1655 cm.$^{-1}$. The reference cell was filled with cyclopropane to the same total pressure as in the sample cell. Propene could still not be detected in the products of polymerisation at 55—550 mm. If it was formed, the steady-state concentration must be less than 0·05 mm. at the lower pressure.

Gunning and Steacie [2] found that addition of propene to the cyclopropane caused a limited reduction in the rate of polymerisation. When a small amount of propene was added this was rapidly removed on irradiation and the rate regained its normal value.[2] We have found that after this no propene can be detected by the above method. If propene is an intermediate in the mercury-photosensitised polymerisation of cyclopropane, then initial addition of the steady-state amount will not reduce the rate. Gunning and Steacie's results [2] show that at 50 mm. pressure the steady-state concentration of propene would have to be less than 0·02 mm.

The ease with which added propene is removed, and the presence of olefins in the polymer, suggest a possible method of growth of polymer through the formation of intermediate reactive olefins. The volatile portion of the polymer was therefore examined for the presence of olefins. Sufficient was obtained after 118 hours' irradiation to run the spectrum of a thin layer; this is shown in Fig. 1. Definite olefin peaks occur at 1645 and 910 cm.$^{-1}$. Comparison of the spectrum with that of a thin layer of the involatile polymer shows, first, that the fraction of volatile polymer molecules containing a double bond must be much less than for the involatile polymer (since the peak heights for a given thickness are comparable but the molecular weights are rather different); and, secondly, that there is a definite splitting of the 1380 cm.$^{-1}$ band, indicating the presence of a certain number of *iso*propyl groups in the volatile polymer.

The volatile polymer was also examined mass spectrometrically. The advantage of this lay in the smaller amount of material required and hence the shorter irradiation period which could be used. Unchanged cyclopropane was first removed from the products by evacuation at −80°. The products volatile at room temperature were then distilled to a small tube and transferred to the mass spectrometer. The following peak heights were observed for the products isolated after 25 minutes' reaction :

	C_6 fragments				C_5 fragments						C_4 fragments						
Mass no.	85	84	82	81		71	70	69	68	67	65		58	57	56	55	54	53	51
Peak height (cm.)	2·4	3·0	0·45	3·6		4·8	3·6	6·0	1·4	30·5	1·4		2·3	10·2	14·6	10·8	18·0	4·5	1·8
A.P.I. spectrum no. 243 : diallyl	—	—	0·5	2·6		—	—	—	1·7	30·5	1·0		—	—	—	2·1	19·9	3·7	2·1

All observed peaks greater than 1 cm. have been given. Traces of peaks due to C_9 hydrocarbons were found. Many of the peaks given above may be ascribed to C_8 and C_9 paraffins and mono-olefins; but the largest peak at mass 67 and the smaller peaks at masses 54 and 81 must be due to a compound C_6H_{10}. This is readily seen when the peak heights are compared with those for known compounds. The spectra of three compounds of formula C_6H_{10} (cyclohexene, 2 : 3-dimethylbutadiene, and diallyl) are published in tables : [12] the first two may be eliminated on account of the low observed 82 peak. Diallyl is therefore the only compound of known spectrum which fits the facts. The A.P.I. spectrum no. 243 for diallyl is given above for comparison, the peak heights being referred to 30·5 cm. for mass 67.

If the theory of reactive olefin intermediates is correct the concentration of the diolefin responsible for masses 67, 54, and 81 should build up to a steady-state value. The following

[12] American Petroleum Institute Research Project 44, Catalog of Mass Spectral Data.

were the observed peak heights in the mass spectrum of the volatile polymer formed after various periods of irradiation of 220 mm. of *cyclo*propane :

Time (min.)	Pressure fall (mm.)	67 peak (cm.)	54 peak (cm.)	81 peak (cm.)
5	2·1	8·5	5·2	1·1
25	14·2	30·5	18·0	3·6
170	77·8	48·3	28·2	6·2

There is in fact a tendency for these peaks to rise to a steady value. A similar tendency was noted for masses 84, 69, 56, and 55, all of which may be due to fragments from C_6 mono-olefins.

Assuming the 67 peak to be due to diallyl it was calculated that after 170 minutes' irradiation of 220 mm. of *cyclo*propane the reaction vessel contained 0·3 mm. of diallyl, and that this formed approx. 50% of the polymer volatile at room temperature.

The infrared spectrum of the volatile polymer formed after 118 hours' irradiation is rather different from that of diallyl. It is therefore concluded that either (1) the compound responsible for masses 67, 54, and 81 is not diallyl but an isomer, perhaps 2-methylpentadiene, or (2) the amount of other volatile products increases relatively to diallyl as the irradiation time increases.

The mass spectrum of the volatile polymer formed in the early stages of the mercury-photo-sensitised reaction of propene was also examined. Although there were appreciable peaks at masses 67 and 54, diallyl was a relatively minor product. This conclusion may also be drawn from the work of Gunning and Steacie.[6]

Comparison with Other Polymers.—The infrared spectrum of the polymer made from *cyclo*propane by mercury photosensitisation was compared with the spectra of polymers made from propene by the following methods : (1) mercury-photosensitised polymerisation at room temperature and 60 mm.; (2) polymerisation at −40° and −80° with a 5% solution of aluminium bromide in hexane as catalyst; and (3) polymerisation by the method of Natta and his co-workers.[13]

The polymers made by method (3) are thought to be mainly linear in structure. Polymer made by method (2) is thought to be considerably branched,[14] the extent of branching decreasing as the preparation temperature is lowered. The structure of the polymer made by method (1) is not known.

The spectra are shown in Fig. 6. There is a striking resemblance between the spectra of the polymers made by the mercury-photosensitised reactions of propene and *cyclo*propane, particularly in the region 2—12 μ. When allowance has been made for the absence of appreciable absorption by vinyl end-groups in the polymers made by methods (2) and (3), it may be seen that the polymer made from *cyclo*propane bears a closer resemblance to the branched polymers than to the linear polymers of propene, though the resemblance is not striking. The following were the values of D_{1460}/D_{1380} for the various polymers :

Method of preparation		D_{1460}/D_{1380}
*cyclo*Propane + Hg*	volatile polymer	1·45
	involatile polymer	1·24
Propene + Hg*	volatile polymer	1·37
	involatile polymer	1·22
Propene + AlBr₃ at −40° ...	—	1·30

The similarity of the values suggests that the ratio of CH_3 to CH_2 groups is similar for all three polymers.

Raman Spectrum : Evidence for C_5 Rings.—The Raman spectrum of a 20% solution of the polymer (prepared at room temperature) in CCl_4 showed the frequency shifts expected for the major groups inferred from the infrared spectrum. In addition, a line was observed at 880 cm.$^{-1}$ together with a weaker line at 1015 cm.$^{-1}$. The former may be assigned with fair confidence to the skeletal vibration of the *cyclo*pentyl ring. Its intensity was about the same as that for the double bond (1650 cm.$^{-1}$). The Raman spectrum of a 20% solution of a 1 : 1 mixture of methyl-*cyclo*pentane and hex-1-ene also gave approximately equally intense lines at 880 and 1650 cm.$^{-1}$; it may be concluded that the polymer contains roughly equal numbers of double bonds and C_5 rings. Since we have already seen that nearly half the polymer molecules (prepared at room temperature) contain a double bond, it is possible that *all* the remaining molecules contain a C_5 ring.

[13] Natta, Pino,.Corradini, Danusso, Mantica, Mazzanti, and Moraglio, *J. Amer. Chem. Soc.*, 1955, **77**, 1708.
[14] Fontana *et al.*, *ibid.*, 1948, **70**, 3745; *Ind. Eng. Chem.*, 1952, **44**, 1688, 2955.

The 890 cm.$^{-1}$ peak in the infrared spectrum can now be assigned to the C_5 ring. We have seen that it does not appear to be affected by hydrogenation of the polymer and is not likely to be due to an olefinic grouping. The variation of the peak height with fraction number (Fig. 4) follows a similar pattern to that for the vinyl peaks (Fig. 3), as would be expected if the peak were

Fig. 6. *Comparison of absorption spectrum of polymer made by cyclopropane + Hg* (curve A) with the spectra of polymers made from propene by the following methods: Hg*, curves B and C, involatile and volatile product respectively; AlBr$_3$, curves D and E, made at —40° and —80° respectively; Natta's method,[13] F, G, and H, amorphous, molten, and crystalline material respectively.*
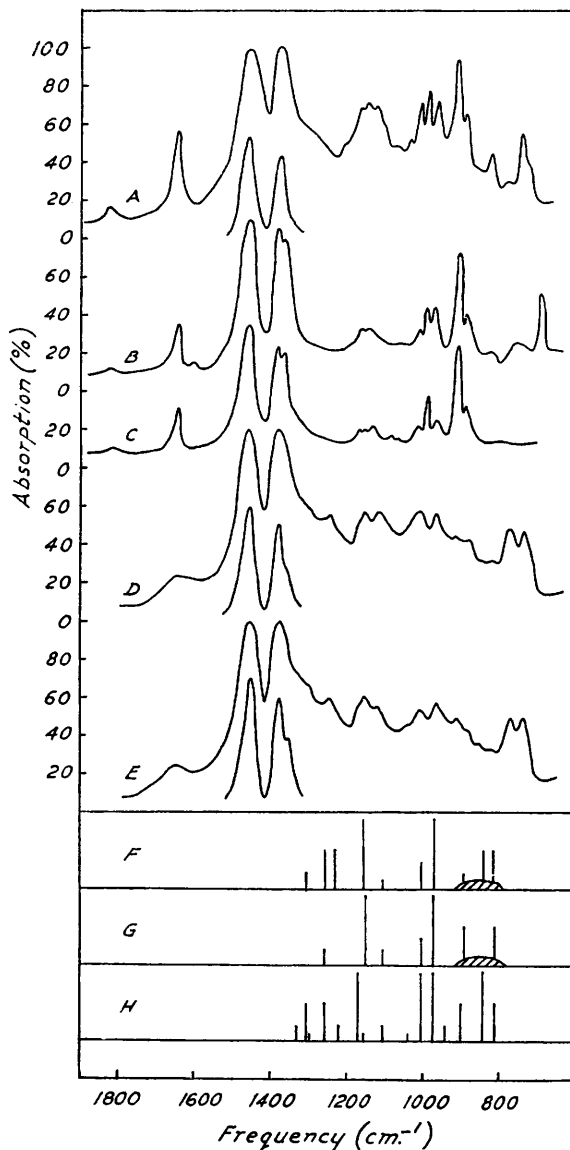
due to a C_5 ring. The relative constancy of the peak height with changing preparation temperature can be explained by the opposing effects of temperature on the average molecular weight and on the ratio of ring to double-bond structures.
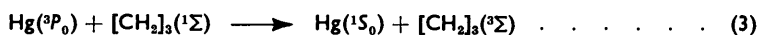
DISCUSSION

The two main problems to be considered are (i) whether propene is an intermediate and (ii) the nature of the growth reaction and the means whereby this leads to the observed structural groups.

Let us first examine the quenching reaction and see how this may lead to the formation of propene. There are two possible quenching processes :
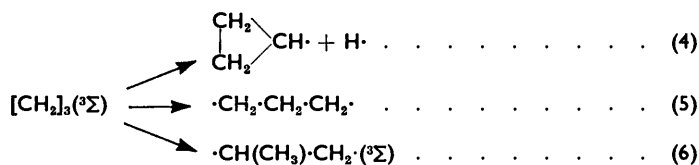
$$Hg(^3P_1) + [CH_2]_3(^1\Sigma) \quad \longrightarrow \quad Hg(^1S_0) + [CH_2]_3(^3\Sigma) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (I)$$
$$\longrightarrow \quad Hg(^3P_0) + [CH_2]_3(^1\Sigma) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$
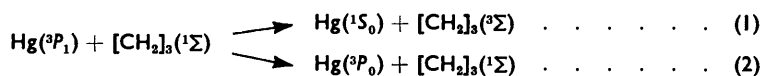
which, if the spin conservation rules are obeyed, result in the formation of a triplet state and a vibrationally excited singlet state of *cyclo*propane respectively. The second process involves the transfer of only 0·22 ev and does not seem very probable as *cyclo*propane does not have a fundamental frequency approximately equivalent to this amount of energy. The thermal isomerisation [15] of *cyclo*propane to propene has an activation energy of 65·0 kcal./mole, so that the energy available in the second quenching process (5 kcal./mole) is insufficient to cause subsequent isomerisation of the *cyclo*propane. The second quenching process may, however, eventually be followed by :

$$Hg(^3P_0) + [CH_2]_3(^1\Sigma) \quad \longrightarrow \quad Hg(^1S_0) + [CH_2]_3(^3\Sigma) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

112·2 kcal./mole are transferred in process (1) and 107·1 kcal./mole in process (3), so that in both cases the triplet-state *cyclo*propane may have sufficient energy for spontaneous rupture of either a C–H or a C–C bond. In the mercury-photosensitised reactions of the paraffins [16] and of *cyclo*butane, *cyclo*pentane, and *cyclo*hexane,[17] there is good evidence that only the C–H bond is broken, though it is stronger than the C–C bond. With *cyclo*-propane the position may be modified by the fact that the C–H bond is slightly stronger and the C–C bond probably somewhat weaker than in the paraffins and other *cyclo*paraffins. By using Stevenson's value [18] of $D(CH_3 \cdot CH_2 \cdot CH_2 \text{–} H) = 99·0 \pm 0·9$ kcal./mole and assuming $D(H \text{–} CH_2 \cdot CH_2 \cdot CH_2 \cdot)$ to be the same, it may readily be calculated [19] that the formation of the trimethylene diradical from *cyclo*propane, $[CH_2]_3 \longrightarrow \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot$ is endothermic by 57 kcal./mole. The reverse reaction is likely to have an appreciable activation energy since it probably involves the deformation of the angle between the three carbon atoms and involves a change in the state of hybridisation of the orbitals.[20] Thus the amount of energy required to break a C–C bond in *cyclo*propane is probably somewhat greater than 57 kcal./mole though less than for a paraffinic C–C bond.

Three possible fates for the triplet-state *cyclo*propane molecule must therefore be considered, namely, C–H rupture, C–C rupture, and isomerisation to propene :

$$[CH_2]_3(^3\Sigma) \quad \longrightarrow \quad \begin{matrix} CH_2 \\ | \quad \rangle CH \cdot + H \cdot \\ CH_2 \end{matrix} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$
$$\longrightarrow \quad \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$
$$\longrightarrow \quad \cdot CH(CH_3) \cdot CH_2 \cdot (^3\Sigma) \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

The occurrence of one or more of these processes is indicated by the molybdenum oxide experiments. The fact that the photochlorination of *cyclo*propane results in the formation of *cyclo*propyl chloride [4] shows that the *cyclo*propyl radical formed in process (4) is unlikely to isomerise to the more stable allyl radical. However, it is possible that there is an additional disruptive process which results directly in the formation of an allyl radical and a hydrogen atom. The combination of two such allyl radicals, or possibly of two *cyclo*propyl radicals, could then result in the formation of diallyl. There is evidence that any trimethylene diradicals produced by process (5) will spontaneously isomerise to propene at room temperature.[21] The triplet-state propene produced in process (6) will descend to

[15] Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563.
[16] Steacie, " Atomic and Free Radical Reactions," Reinhold, New York, 1954.
[17] Gunning *et al.*, *J. Chem. Phys.*, 1954, **22**, 672, 678; 1953, **21**, 1797.
[18] Stevenson, *Trans. Faraday Soc.*, 1953, **49**, 867.
[19] Seubold, *J. Chem. Phys.*, 1954, **22**, 944.
[20] Coulson and Moffitt, *ibid.*, 1947, **15**, 151.
[21] Kistiakowsky and Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 88.

the ground state after a favourable collision. Thus, whatever the immediate fate of the triplet-state *cyclo*propane, the formation of propene is probable.

The intermediate formation of propene was suggested, first, by the number and disposition of the methyl groups in the polymer and, secondly, by the resemblance of the spectrum to that of the polymer formed in the mercury-photosensitised reaction of propene. Three facts, however, weigh against secondary polymerisation of propene, even though it may be formed in the *cyclo*propane reaction. In the first place the proportion of volatile polymer is much higher in the mercury-photosensitised polymerisation of propene than in the corresponding reaction of *cyclo*propane. Secondly, propene cannot be polymerised by the action of monoradicals in the gaseous phase at room temperature. Any subsequent reaction is therefore more likely to be with a diradical or an excited molecule. Such a reaction will lead to a stable molecule, rather than a higher diradical which can attack a further molecule of propene. The third and most telling point is that the quantum yield of the mercury-photosensitised polymerisation of propene [6] at pressures below 1 mm. appears to be much less than that of the *cyclo*propane reaction.

The quenching cross-section of *cyclo*propane [22] is $1 \cdot 1 \times 10^{-16}$ cm.^{2}, while that of propene [23] is probably about 50×10^{-16} cm.^{2}. We have seen that, if formed, propene builds up to a concentration less than 0·1% of the *cyclo*propane concentration. Under such conditions the *cyclo*propane will still do the major part of the quenching, so that, as suggested above, any propene formed is likely to disappear by a reaction $CH_3 \cdot CH \colon CH_2 + [CH_2]_3^* \longrightarrow C_6H_{12}$ where $[CH_2]_3^*$ represents the triplet state of *cyclo*propane, or, more probably, the trimethylene diradical. Diallyl may undergo a similar reaction. The main experimental results are qualitatively accounted for if it is postulated that this addition can occur in three ways, which may be called olefin addition, ring addition, and propyl addition, according to the nature of the product, *viz.* :
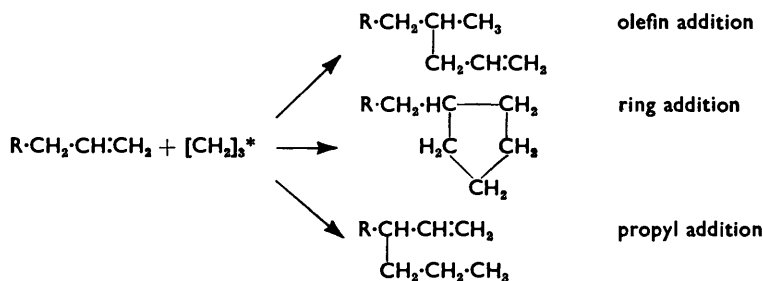
Olefin and propyl addition involve the transfer of a hydrogen atom. Successive olefin additions, occurring in the manner indicated, will lead to a polypropene structure :
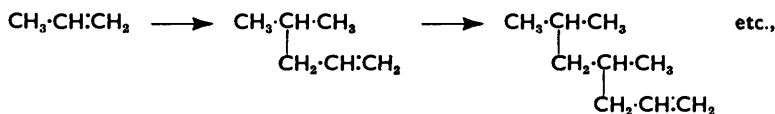
and this is postulated as the main addition process. The absence of *iso*propyl groups in the polymer favours the initial formation of diallyl rather than propene.

The propyl addition may occur at any carbon atom but is likely to be easiest when a tertiary or secondary carbon atom is attacked; in this way side-chain propyl groups will be formed. End propyl groups can arise through secondary hydrogenation caused by the hydrogen atoms formed in process (4), or through propyl addition at the CH_2 end of a vinyl group. The latter process will also account for the formation of *trans*-R·CH:CHR′ olefins which appear to be present in small amounts. The propyl addition may be compared with other diradical reactions such as $RH + O_2 \longrightarrow RO_2H$, commonly postulated as the initial

[22] Darwent and Phibbs, *J. Chem. Phys.*, 1954, **22**, 110.
[23] Steacie, *Canad. J. Res.*, 1948, B, **26**, 613.

step in oxidation reactions, $RH + CH_2 \longrightarrow R \cdot CH_3$ [24] and $RH + SO_2{}^* \longrightarrow R \cdot SO_2H$.[25] It is to be noted that the propyl frequency (740 cm.$^{-1}$) does not appear in the spectrum of the polymer obtained from propene by mercury photosensitisation.

Ring addition to form a monosubstituted *cyclo*pentane seems a likely process since it can occur without the transfer of any atoms. We have seen that there is good evidence for the presence of a considerable proportion of a ring structure and that these rings may always consist of five carbon atoms. The 890 cm.$^{-1}$ infrared frequency which has been ascribed to a C_5 ring in the polymer from *cyclo*propane, also appears in the spectrum of the polymer formed from propene by mercury photosensitisation. But it is clear that C_5 rings cannot be formed in the latter reaction by a process analogous to that postulated for the *cyclo*-propane reaction. Nevertheless small amounts of *cyclo*pentanes have been reported in the polymer from propene.[6] These may contribute towards the 890 cm.$^{-1}$ peak, as also may olefins of the type $R \cdot CMe \vdots CH_2$ which may be present in the complex mixture of products.

It is recognised that the proposed mechanism, consisting as it does of a number of consecutive reactions, should give rise to a period of increasing rate while the steady-state concentrations of intermediate olefins are being built up. The experimental evidence indicates that the stationary concentrations of intermediates will be very low, so that the period of increasing rate will be quite short. Gunning and Steacie [2] did in fact observe that the pressure fall reached a constant rate only after 5 minutes' irradiation. In one of their experiments, when the light was switched off there was a further pressure fall of 0·11 mm. (incorrectly given in the text as 0·21 mm.), whereas the linear portion of the graph of change of pressure against time when extrapolated back to zero time gave an intercept of $-0 \cdot 18$ mm. This shows that at least part of the increase in the rate of pressure fall with time was due to a genuine increase in rate of reaction, though part was due to a temperature rise. Actually we have seen that the total diallyl in the system, as measured by the 67 mass-spectrometer peak, increases further after the rate of pressure fall has become steady; but it must be remembered that some of the diallyl will dissolve in the condensed polymer so that the total diallyl in the system will not be a true measure of its pressure in the gas phase.

Finally it is suggested that the main factor which limits the molecular weight of the polymer is its removal from the gas phase by condensation, or solution in polymer already formed. In agreement with this suggestion, the average molecular weight increases with the preparation temperature.

EXPERIMENTAL

Materials.—The *cyclo*propane was " anæsthetic " grade and contained no detectable propene. It was distilled twice from $-80°$ to $-190°$ *in vacuo*. Propene was obtained as Philips Research Grade material from the Chemical Research Laboratory, Teddington. The alkyl compounds used as radical sources were distilled *in vacuo*.

Apparatus for Mercury-photosensitised Polymerisation.—A little mercury was placed in a 100 ml. cylindrical quartz reaction vessel which was then pumped out, isolated, and connected to a manometer and 5-l. reservoir containing the *cyclo*propane (or propene). The vessel was then irradiated with mercury resonance radiation from a Hanovia spiral " Detectolite " lamp. For the preparation of polymer above room temperature the vessel was heated electrically. The temperature inside the vessel for a given heater current was determined from the observed pressure change when the current was switched off.

Molecular-weight Determinations.—The depression of the freezing point of benzene was used to estimate the molecular weights. The errors quoted are based on the reproducibility of the freezing points.

Infrared Absorption Spectra.—The spectra were obtained under identical operating conditions by means of a Grubb-Parsons S4 double-beam spectrometer with a rock-salt prism. The sample was normally contained in a cell of 0·117 mm. depth, and reflection losses were balanced by placing a single rock-salt plate in the reference beam.

Hydrogenation of the Polymer.—Hydrogenation was carried out in alcoholic solution with a palladium–charcoal catalyst. The reaction flask and compensating flask (containing alcohol

[24] Rosenblum, *J. Amer. Chem. Soc.*, 1941, **63**, 3322.
[25] Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 374.

only) were immersed in a beaker of water. The product was recovered by extraction with hexane.

Bromination of the Polymer.—The method of Uhrig and Levin [26] was used. 0·1 g. of polymer was dissolved in 1 ml. of chloroform and titrated with a standardised 0·2M-solution of bromine in acetic acid. Best results were obtained if a slight excess of bromine was added and the excess estimated colorimetrically. With hexadec-1-ene this method gave results consistently 1·5% high.

Fractionation of the Polymer.—The microstill was similar to that described by Craig,[27] the jacket being electrically heated.

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[26] Uhrig and Levin, *Ind. Eng. Chem. Anal.*, 1941, **13**, 90.
[27] Craig, *ibid.*, 1937, **9**, 441.