803. *The Kinetics of Ionic Polymerisations. Part III.* The Side-chain Effect in the Vinyl Ethers.*

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This paper presents rate of polymerisation and molecular-weight data for the system alkyl vinyl ether–iodine, in diethyl ether solvent at 25°.

The side groups examined are: *cyclo*hexyl, *iso*butyl, 2-ethylhexyl, *n*-butyl, ethyl, and 2-chloroethyl. The initial velocities at low values of [M] fit the expression $v = k[I_2]^2[M]$, where [M] denotes monomer concentration, but reach a maximum value at a certain value of [M], *viz.*, $[M]_t$. It is postulated that a part of the iodine is bound as a complex with the monomer (Type II complex), which is inactive in initiating polymerisation. The percentage of inactive complex increases with monomer concentration, and the $[M]_t$ value may be explained in terms of the formation equilibrium constant for the inactive complex, K_c; k, and to a less extent K_c, increase as one passes to side groups with a greater electron-repulsive effect, but the degree of polymerisation of the product shows no systematic variation. These results fit in with the expectations for the individual kinetic steps concerned in the chain reaction.

THE catalytic action of iodine in polymerising ethyl vinyl ether was discovered by Wislicenus (*Annalen*, 1878, **192**, 106) and further investigated by Chalmers (*Canadian J. Res.*, 1932, *B*, **7**, 464). Eley and Richards (*Trans. Faraday Soc.*, 1949, **45**, 425) established the kinetics for the polymerisation of 2-ethylhexyl vinyl ether in three solvents and postulated that the polymerisation involved carbonium ions and was initiated by I^+. In this paper, we examine quantitatively the effect of the nature of the side chain R, in $RO{\cdot}CH{:}CH_2$, on the rate of polymerisation and the molecular weight of the product. In the discussion we show that the results obtained may be fitted into the kinetic scheme advanced by Eley and Richards, with one addition.

EXPERIMENTAL

The rate of polymerisation was followed in an evacuated, sealed, dilatometer at 25°. Densities of monomer and polymer were determined, so that the initial rate of volume change could be converted into a reaction velocity in moles $l.^{-1}$ $min.^{-1}$.

The polymer densities were determined separately for every specimen, usually with a micropyknometer but in the case of solids by a flotation method. Average values are listed in Table 1. The monomer densities agree with such values as are given in the literature (Schildknecht, Zoss, and McKinley, *Ind. Eng. Chem.*, 1947, **39**, 180).

TABLE 1. *Polymerisation of vinyl ethers.*

No.	Side chain	ρ_m	ρ_p	$[I_2]$	k	$[M]_t$	v_t
1	*cyclo*Hexyl	0·878	1·019	4·37	22,000	0·8	0·32
2	*iso*Butyl	0·764	0·902	4·37	1,900	0·8	0·025
3	2-Ethylhexyl	0·812	0·866	4·37	1,000	1·5	0·027
4	*n*-Butyl	0·774	0·905	4·37	1,800	1·8	0·052
	,,	—	—	2·18	1,800	(1·8)	0·01
	,,	—	—	5·47	1,800	3·0	0·073
5	Ethyl	0·748	0·937	4·37	1,900	3·2	0·09
6	2-Chloroethyl	1·039	1·234	4·37	90	>4·3	>0·007

The order in which the electron-repulsive effect of the side chain decreases is from 1 to 6, so far as can be judged from published data on reactions of ions with aliphatic carbon atoms.

The reactions were stopped at 20—30% of polymerisation, the dilatometer opened, the catalyst destroyed with thiosulphate, and the polymer isolated according to Eley and Richards (*loc. cit.*). The molecular weight was determined from the freezing-point depression Δ in benzene. This was determined at a range of concentrations c, and Δ/c plotted against c so as to allow extrapolation to obtain $(\Delta/c)_{c\rightarrow0}$, which was used in the calculation.

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* Part II, *Trans. Faraday Soc.*, 1949, **45**, 436.

In all experiments, the polymerisations were carried out with diethyl ether as solvent, so as to obviate any marked change in the dielectric constant of the system as the reaction progressed.

Reaction Velocity.—The reaction curve was accurately linear over the first 10% of polymerisation and passed through the origin, showing an absence of any induction period. An example is shown in Fig. 1.

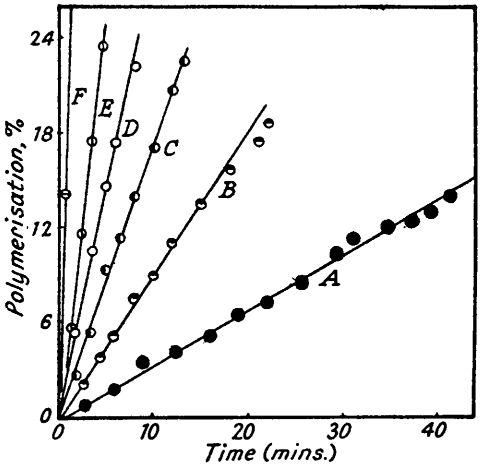


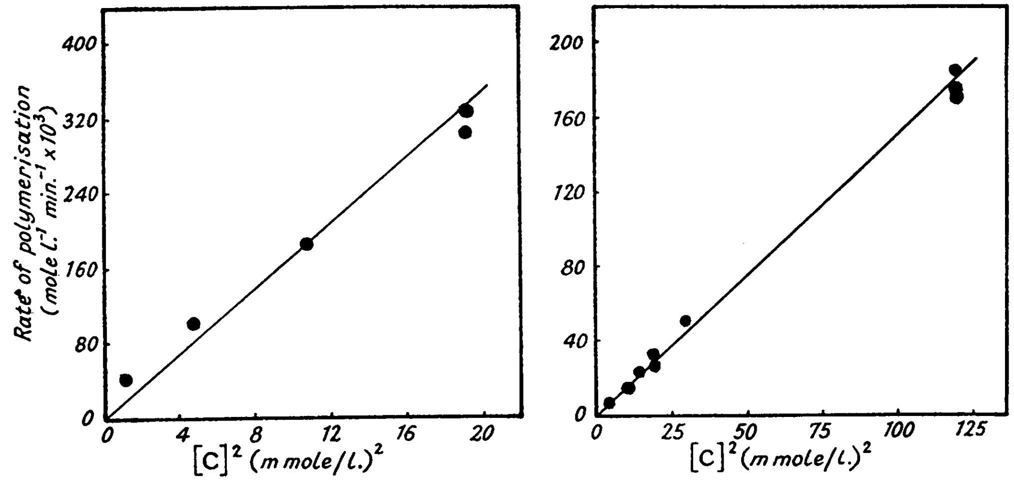
FIG. 1. *Polymerisation–time relationships for* n-*butyl vinyl ether.* ([M] = 0·86 mole/l. Curve *A*, [C] = 1·10; curve *B*, [C] = 2·19; curve *C*, [C] = 3·29; curve *D*, [C] = 3·84; curve *E*, [C] = 5·47, and curve *F*, [C] = 10·95 mmole/l.)

The reaction velocity was examined as a function of monomer concentration [M] and catalyst concentration $[I_2]$. At low monomer concentrations, the initial velocities v fit the equation

$$v = -d[M]/dt = k[M][I_2]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in agreement with Eley and Richards (*loc. cit.*). All the results are presented graphically for convenience. Figs. 2*a* and 2*b* show that the reaction velocity is proportional to $[I_2]^2$ in two cases, confirming the work of Eley and Richards on the 2-ethylhexyl ether.

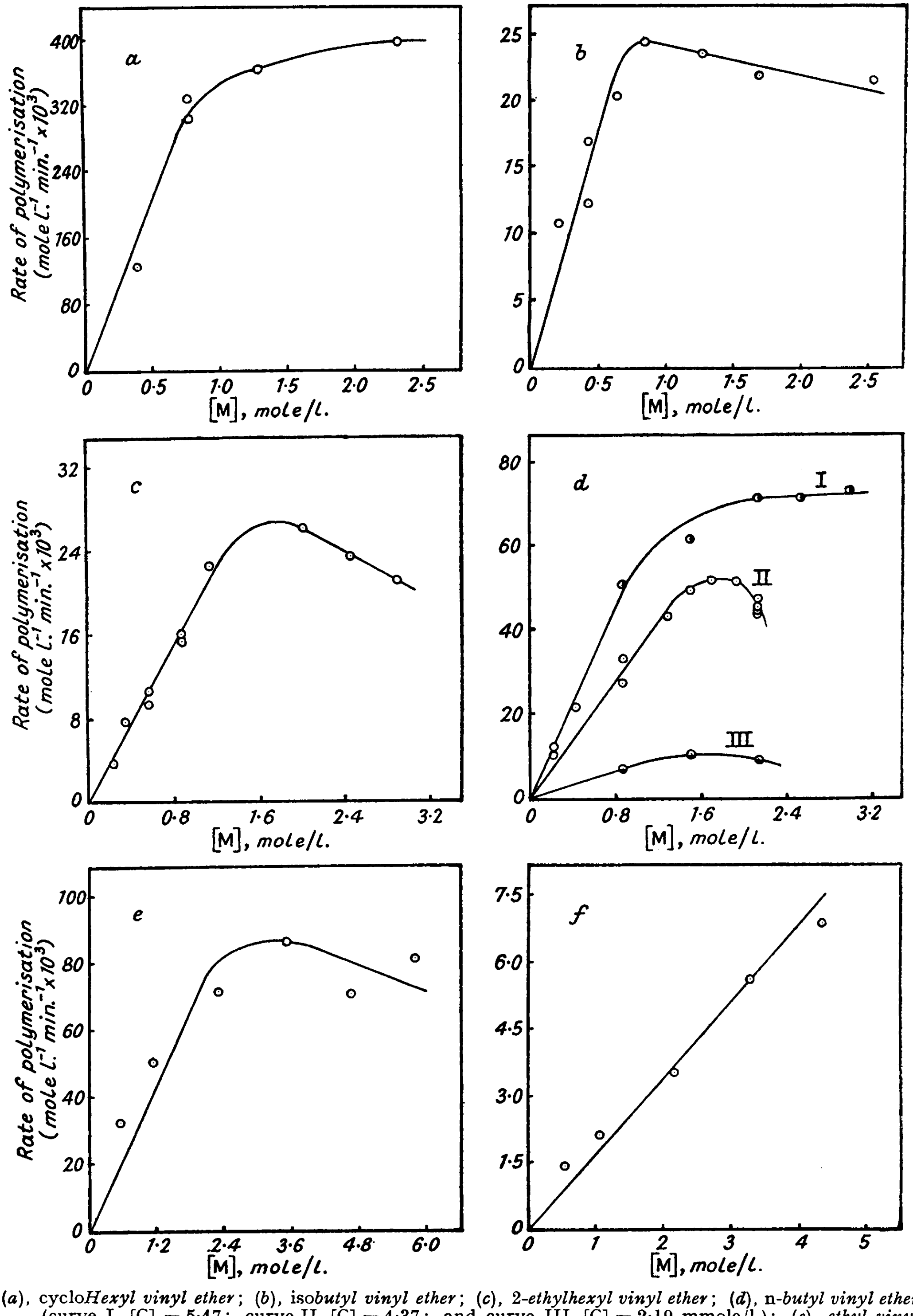
FIG. 2*a–b*. *Rate of polymerisation–catalyst concentration relationships.*



(*a*) cyclo*Hexyl vinyl ether* ([M] = 0·774 mole/l.). (*b*) n-*Butyl vinyl ether* ([M] = 0·86 mole/l.).

The effect of monomer concentration is considered for all the cases examined in Figs. 3*a*—*f* inclusive. It is seen that, for the 2-chloroethyl vinyl ether, $v \propto [M]$ over the whole range up to [M] = 4·3 mole/l. For the other ethers, there is a fairly definite value of [M], designated $[M]_t$, at which the reaction velocity reaches a maximum value, v_t. In the case of 2-ethylhexyl ether, Eley and Richards failed to reach a high enough [M] value to find the maximum velocity. We

FIG. 3. *Rate of polymerisation–monomer concentration relationships.* [C] = 4·37 *millimole per litre throughout, except in* (*d*).



(*a*), cyclo*Hexyl vinyl ether*; (*b*), iso*butyl vinyl ether*; (*c*), *2-ethylhexyl vinyl ether*; (*d*), n-*butyl vinyl ether* (curve I, [C] = 5·47; curve II, [C] = 4·37; and curve III, [C] = 2·19 mmole/l.); (*e*), *ethyl vinyl ether*; (*f*), *2-chloroethyl vinyl ether*.

have confirmed two of their results at low values of [M], and made further experiments at high values of [M] to establish the curve shown.

In the first place, all the results on effect of [M] were obtained at the catalyst concentration, $[I_2] = 4{\cdot}37$ millimole/l. Subsequently, in one case, that of *n*-butyl vinyl ether, experiments on the maximum velocity were made at two other catalyst concentrations. In the table, ρ_m and ρ_p are the densities at 25° of monomer and polymer, respectively; $[I_2]$ is the total iodine added, in millimoles $l.^{-1}$; k, the third-order velocity constant, in $l.^2$ $mole^{-2}$ $min.^{-1}$; $[M]_t$ the monomer concentration, in moles $l.^{-1}$, for maximum velocity; and $[v]_t$ the maximum velocity, in moles $l.^{-1}$ $min.^{-1}$.

The Polymers.—Most of the polymers were transparent viscous fluids, varying from colourless to orange, as found previously for 2-ethylhexyl vinyl ether. The *cyclo*hexyl vinyl ether gave a range of products from colourless liquids through colourless non-tacky solids to almost black solids.

Systematic work on cryoscopic molecular weights was carried out with *n*-butyl vinyl ether, *cyclo*hexyl vinyl ether and 2-chloroethyl vinyl ether, and the results are presented in Table 2 as degree of polymerisation (D.P.). The solid polymers are distinguished in the Table. There is a fair scatter in the cryoscopic results, but the following comments and conclusions seem warranted:

(*a*) The *n*-butyl vinyl ether was carefully investigated for the effect of monomer and catalyst concentration, and there would seem to be no systematic effect of either of these variables on degree of polymerisation of the product; the average value of D.P. is 9·8.

(*b*) The average D.P. of 4·6 for the 2-chloroethyl ether is not systematically changed by a four-fold change in monomer concentration.

(*c*) If we except the three lowest values of D.P., which relate to the viscous liquid product, the poly*cyclo*hexyl vinyl ethers are all solids with an average D.P. of about 16, not systematically affected by a ten-fold change in catalyst concentration or a four-fold change in monomer concentration. The rather high values of D.P. obtained may not be entirely comparable with those of the other two monomers, as the polymer could only be isolated at a later percentage polymerisation of monomer.

(*d*) The average D.P. of the product for the 2-chloroethyl ether is 4·6, and that for the *cyclo*hexyl ether is 16. This increase by a factor of 3—4 may be neglected in comparison with the observed 244-fold increase in overall velocity of polymerisation.

One sample of each of these polymers was tested for the presence of iodine with negative results, in agreement with Eley and Richards.

TABLE 2. *Molecular-weight data* (ca. 20% *polymerisation*).

[M], mole/l.	$[I_2]$, mmole/l.	D.P.	[M], mole/l.	$[I_2]$, mmole/l.	D.P.	[M], mole/l.	$[I_2]$, mmole./l.	D.P.	[M], mole/l.	$[I_2]$, mmole/l.	D.P.
n-Butyl vinyl ether						*cyclo*Hexyl vinyl ether *					
0·86	1·095	5·5	0·215	4·37	10·5	0·774	1·092	3·6	0·774	19·7	11·5 *s*
,,	2·19	11·0	0·43	,,	12·5	,,	2·185	6·7	,,	39·4	22·5 *s*
,,	3·29	9·5	1·288	,,	10·5	,,	3·278	16 *s* †	0·387	4·37	11·5 *s*
,,	3·84	12·5	1·504	,,	12·0	,,	4·37	21 *s*	1·548	,,	13·5 *s*
,,	4·37	7·5	1·717	,,	11·5	,,	4·37	18·2 *s*	2·322	,,	5·5
,,	,,	6·5	1·933	,,	9·0						
,,	5·47	10·0	2·149	,,	6·5	2-Chloroethyl vinyl ether					
,,	10·95	11·0	,,	,,	7·5	1·084	4·37	6·0	3·252	4·37	3·2
,,	,,	13·0				2·168	,,	4·2	4·336	,,	5·2

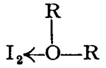
* Owing to speed of reaction, polymer could only be isolated at 60—80% polymerisation.

† *s* denotes solid polymer.

DISCUSSION

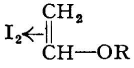
The Kinetics.—The equation (1) may be deduced from Eley and Richards's kinetic scheme (*loc. cit.*). To account for the observed maximum velocity at a certain monomer concentration $[M]_t$, the scheme requires an addition.

The nature of the interaction of molecular iodine with donor groups is not fully understood. In the first place, it seems very likely that it forms a weak co-ordinate link with ether oxygen (Kleinberg and Davidson, *Chem. Reviews*, 1948, **42**, 601). This is suggested by the brown colour, and by the fact that its solubility is somewhat in excess of that calculated for a regular solution (Hildebrand, Benesi, and Mower, *J. Amer. Chem. Soc.*, 1950, **72**, 1017). This complex is (I). In addition, we postulate a complex with the ethylenic bond of the vinyl ether (II), by analogy with the complex $I_2 \ldots C_6H_6$ found spectroscopically for benzene by Benesi and Hildebrand (*ibid.*, 1949, **71**, 2703). Finally, we postulate a carbonium ion formed by addition of I^+ at one side of the double bond (III) in accordance with Eley and Richards's scheme.



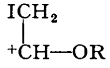
$\mathrm{I_2{\leftarrow}\overset{\displaystyle R}{\overset{|}{O}}{-}R}$

(I)



$\mathrm{I_2{\leftarrow}\overset{\displaystyle CH_2}{\overset{\|}{CH}}{-}OR}$

(II)



$\mathrm{\overset{\displaystyle ICH_2}{\overset{|}{{}^{+}CH}}{-}OR}$

(III)

There is no further need to consider (I) since all molecules present, monomer, solvent, and polymer, contain ether oxygen groups. We, therefore, have a more or less constant environment of oxygen donor atoms in space and time, and (I) may be assumed to be the normal state of all iodine not bound in (II) or (III) or as I_3^-. If the bond in (I) were at all strong, we should expect diethyl ether to be a slower solvent than light petroleum, whereas the reverse is the case. We may compare the addition of pyridine to the system, which *does* form a strong donor link to iodine and, according to our observations (to be published), completely inhibits the polymerisation.

We further assume that iodine bound in complex (II) is removed from the sphere of reaction, and is not free to ionise and hence form (III) and initiate reaction.

Let $[I_2]$ denote the total concentration of molecular iodine as added initially, [M] the total initial concentration of monomer, and x the concentration of inactive complex (II). We assume an equilibrium

$$\text{(I)} + \mathrm{RO{\cdot}CH{:}CH_2} \rightleftharpoons \text{(II)} + \text{ether}$$

which for the reason above we write simply as

$$\mathrm{I_2 + RO{\cdot}CH{:}CH_2} \rightleftharpoons \text{(II)}$$

and

$$x/[\mathrm{M}]([\mathrm{I_2}] - x) = K_c \ (\mathrm{l.\ mole^{-1}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where we neglect the concentration of iodine bound in the reactive complex (III). Therefore the concentration of iodine free to initiate polymerisation, $[I_2]_f$, is

$$[\mathrm{I_2}]_f = [\mathrm{I_2}] - x = [\mathrm{I_2}]/(1 + K_c[\mathrm{M}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The kinetic scheme is

$$\begin{array}{rcll} 2\mathrm{I_2} & \longrightarrow & \mathrm{I^+ + I_3^-} & k_1 \\ \mathrm{I^+ + M} & \longrightarrow & \mathrm{I^+M} = \text{(III)} & k_2 \\ \mathrm{I^+M + M} & \longrightarrow & \mathrm{M_2^*} & \multirow{2}{*}{} \\ \mathrm{M_{n-1}^* + M} & \longrightarrow & \mathrm{M_n^*} & \left.\right\} k_3 \\ \mathrm{M_n^*} & \longrightarrow & \mathrm{M_n} & k_4 \\ \mathrm{M_n^* + M} & \longrightarrow & \mathrm{M_n + M^*} & k_5 \end{array}$$

Assuming stationary concentrations of I^+ and M_n^*, we obtain as before (Eley and Richards, *loc. cit.*) a third-order equation, but with $[I_2]_f$ written in place of the total iodine concentration $[I_2]$. The two concentrations are related by equation (3). Hence

$$v = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_1k_3[\mathrm{I_2}]_f^2[\mathrm{M}]/k_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\mathrm{D.P.} = k_3[\mathrm{M}]/(k_4 + k_5[\mathrm{M}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Equations (4) and (5) account satisfactorily for our results, since $[I_2]_f \sim [I_2]$, according to (3), at low monomer concentrations where $K_c[M] \ll 1$.

As the monomer concentration rises, we expect increasing amounts of iodine bound as the inactive complex (II). According to equation (2), the amount bound will depend on the mass-action constant K_c. This constant may be obtained from the monomer concentration for maximum velocity $[M]_t$, which by differentiation of the rate equation (4) and substitution for $[I_2]_f$ according to equation (3), is found to be

$$K_c = 1/[\mathrm{M}]_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus we arrive at the values of K_c given in Table 3.

TABLE 3. *Equilibrium constant for inactive complex.*

No.	Side chain	$[I_2]$, mmole l.$^{-1}$	K_c, l. mole^{-1}
1	*cyclo*Hexyl	4·37	1·25
2	*iso*Butyl	4·37	1·25
3	2-Ethylhexyl	4·37	0·67
4	*n*-Butyl	4·37	0·5
	,,	2·18	(0·5)
	,,	5·47	0·33
5	Ethyl	4·37	0·31
6	2-Chloroethyl	4·37	$<$0·23

These values of K_c are rather larger than the iodine–benzene equilibrium constant given by Benesi and Hildebrand (*loc. cit.*), when converted into l. mole^{-1}.

In the case of the *n*-butyl ether, reference to Fig. 3 shows that the value of $[M]_t$ increases as the catalyst concentration increases so that the K_c value varies somewhat. There are not sufficient points accurately to define the shallow maximum at $[I_2] = 2·18$ mmole l.$^{-1}$ so the K_c value is put in parentheses.

Effect of the Side Group R.—The side chains 1—6 in Tables 1 and 3 are numbered in order of their decreasing electron-repulsive effect. We are here concerned with the inductive effect, *i.e.*, the effect of the side chain on the reactivity of an aliphatic carbon atom to a positive (or negative) ion, and a survey of the literature of reactions of this type was made to establish the order for all common side chains. It seems clear that the overall reaction velocity constant k is much increased by an electron-repelling side chain, as we go from 2-chloroethyl (6) to *cyclo*hexyl (1). The exact order of groups 2—5, which lie rather close together so far as their inductive effect goes, may be influenced by the steric factor.

To supplement the above, we have the early observations that iodine will not catalyse the polymerisation of phenyl vinyl ether (Chalmers, *loc. cit.*) or divinyl ether. We should expect the vinyl group to be No. 7 in the list and markedly more electron-attractive than 2-chloroethyl. Thus, we should expect little or no reactivity for divinyl ether, but the phenyl group would be expected to give a somewhat more rapid polymerisation than 2-chloroethyl, as we should expect to fit it in between Nos. 5 and 6. The lack of activity to iodine may in part be explained by the co-ordination of the iodine to the phenyl ring, with a $K_c \sim 10^{-1}$ l. mole^{-1}, according to the work of Benesi and Hildebrand (*loc. cit.*). The phenyl vinyl ether may be polymerised with metallic halides and boron trifluoride (Favorskii and Shostakovskii, *J. Gen. Chem. U.S.S.R.*, 1943, **13**, 1; Losev, Fedotova, and Trostyanskaya, *ibid.*, 1945, **15**, 353).

The electron-repulsive effect of R in raising k may be due to either (*a*) rise in k_1, (*b*) rise in k_3, or (*c*) decrease in k_4. Since the vinyl ether does not enter into step 1, we can rule out (*a*). We have not specified the termination step 4, but this probably involves the expulsion of a positive ion, I^+ or H^+, and thus would be restrained by an electron-repulsive group as suggested. We may certainly expect (*b*) to operate, *i.e.*, the electron-repulsive group in the monomer will favour its reaction with a carbonium ion. We conclude that the effect observed is at any rate most probably due to a change in the ratio k_3/k_4.

It is also understandable that an electron-repulsive group R will raise the formation constant K_c for the inhibiting complex (II), and this is what is found (Table 3).

The Polymer.—The random variation in molecular weight values is somewhat larger than that found by Eley and Richards (*loc. cit.*), possibly owing to our use of the cryoscopic rather than the viscometric method. It seems clear that the observed D.P. is independent of catalyst and monomer concentrations, which agrees with equation (5) when one makes the proviso that transfer is important, so that $k_5[M] > k_4$, as found previously for the 2-ethylhexyl ether. This seems to hold not only for the case of *n*-butyl vinyl ether, but also for the extremely rapidly polymerising *cyclo*hexyl vinyl ether and the extremely slow 2-chloroethyl ether.

Since the D.P. is given by k_3/k_5, we can understand why a change in R from 2-chloroethyl to *cyclo*hexyl only increases the D.P. by at most a factor 4, while accelerating the overall rate 240-fold. The reaction k_5 is a reaction of active polymer with monomer, just as is k_3. We may, therefore, expect a similar effect of electron-repulsion in the side chain R on both reactions, leaving the ratio and therefore the D.P. almost unaffected.

Where spontaneous termination is active in ending the polymer chains, *i.e.*, $k_4 > k_5[M]$, it might be expected that for given conditions the *cyclo*hexyl vinyl ether will give a much higher molecular weight polymer than the 2-chloroethyl ether, since the ratio k_3/k_4 will be increased. We have considered that this condition holds for stannic chloride as catalyst, and the corollary is worth experimental test. It is clear from this discussion that, in any event, experiments on the effect of R may help to throw light on the question of termination mechanisms in controversial cases.

The polymer was isolated by destroying the catalyst with thiosulphate and removal of solvent and monomer under reduced pressure at 65—70°. Eley and Richards showed that the polymeric 2-ethyl hexyl vinyl ether so isolated did not contain any iodine and we confirm this for the *n*-butyl and the *cyclo*hexyl vinyl ether. By isolation at room temperature, a polymer containing roughly 0·5 double bond and 1·4 atoms of iodine was obtained. We take this to mean that the polymer probably contains one double bond per molecule, and that some iodine is held rather loosely, *e.g.*, possibly as di-iodide formed after the reaction, or a type (II) complex with a terminal double bond. Since transfer is operative, we should only expect one iodine atom in every $k_5[M]/k_4$ chains, even if an iodine atom were not lost in the termination step k_4. The results scarcely allow us to be definite at present, but since all the iodine dissociates easily from the polymer, it seems unlikely that any iodine is chemically bound, apart from the possibility of di-iodide formation by subsequent addition of iodine to a terminal double bond. This would mean that I^+ ions are lost in the termination step k_4, and if this is so, in order not to disturb our kinetic scheme, we need to postulate that $k_1[I_2]_f^2 \gg k_4[M_n^*]$. This seems a reasonable assumption.

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