729. *The Kinetics of Ionic Polymerisation. Part VII.* The Polymerisation of Alkyl Vinyl Ethers with the Boron Trifluoride–Ether Complex.*

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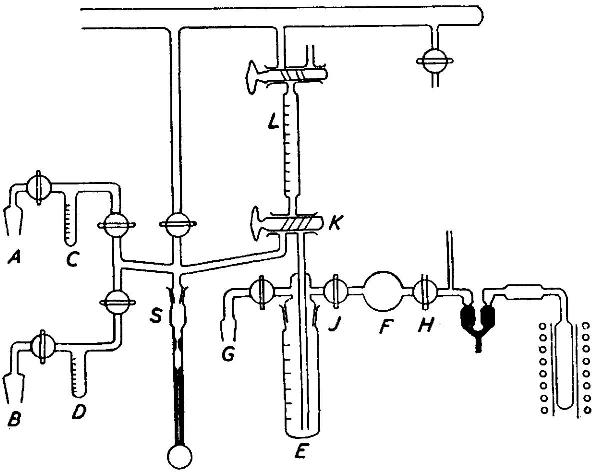
In previous papers [1] the kinetics of the polymerisation of alkyl vinyl ethers with various catalysts were examined and a carbonium-ion mechanism was postulated. The present investigation is concerned with the polymerisation in solution of a pair of vinyl ethers catalysed by a stable co-ordination complex, boron trifluoride–diethyl ether.

EXPERIMENTAL

Reaction Velocity.—The technique used was similar to that of Eley and Richards,[1a] the polymerisations being followed in evacuated sealed dilatometers of 9 c.c. capacity and accurately known stem calibrations of approximately 0·05 c.c. per cm. Except for activation-energy determinations all reactions were carried out at 25°. Solutions for rate determinations were prepared in an all-glass apparatus (Fig. 1) capable of being evacuated to 10^{-6} mm. Hg. Monomer and solvent were outgassed and stored over sodium in vessels attached to *A* and *B* respectively. Immediately before an experiment they were distilled *in vacuo* into the calibrated vessels *C* and *D* and the required volumes finally distilled into the dilatometer. This diluted solution of monomer was cooled and outgassed at least three times.

FIG. 1. *Vacuum apparatus for filling dilatometer.*



The catalyst solution was prepared in vessel *E*. Calcium fluoroborate, dried at 120° for 24 hr. *in vacuo*, was heated to 250° by means of a Nichrome-wound electric furnace. The boron trifluoride evolved by the high-temperature decomposition was passed over sodium fluoride, to remove hydrogen fluoride, and into a 100 c.c. calibrated volume *F*, the pressure in which could be measured with a mercury manometer. At a known pressure a sample was isolated by closing tap *H*, and condensed into *E* with liquid air.

Ethyl ether, outgassed and stored over sodium in a vessel attached to *G*, was condensed on the frozen boron trifluoride and the mixture allowed to warm slowly to room temperature. The volume of the solution was noted. This catalyst solution was outgassed at least three times. Portions were drawn up into the calibrated tube *L* and discharged into the dilatometer,

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* Part VI, *J.*, 1954, 1677.

[1] (*a*) Eley and Richard, *Trans. Faraday Soc.*, 1949, **45**, 425, 436; (*b*) Eley and Saunders, *J.*, 1952, 4167; 1954, 1668, 1672, 1677.

containing frozen monomer solutions, *via* the two-way tap *K*. The frozen dilatometer was evacuated, sealed off, and stored at −180°. In the later experiments it was found possible to simplify this technique, allowing a transference of catalyst solution through the air without in any way altering the results obtained.

Densities (ρ) of monomer (M) and polymer (P) samples were determined at 25° so that initial rates of change of volume could be converted into reaction velocities in moles $l.^{-1}$ $min.^{-1}$. The average values used which agree with those of Eley and Saunders [1b] (*loc. cit.*) and others [2] were: *n*-butyl vinyl ether, $\rho_M = 0{\cdot}7733$ g./c.c., $\rho_P = 0{\cdot}9053$ g./c.c.; 2-chloroethyl vinyl ether, $\rho_M = 1{\cdot}039$ g./c.c., $\rho_P = 1{\cdot}234$ g./c.c.

The dilatometers were opened after 20%—30% polymerisation, the catalyst was destroyed by addition of a 5% solution of sodium hydroxide in water, and the polymer isolated according to the method of Eley and Richards.[1a]

Polymers.—All polymers isolated were transparent viscous liquids, those of *n*-butyl vinyl ether being colourless, and those of 2-chloroethyl vinyl ether pale yellow. Their molecular weights were determined by the Staudinger method. In each case the viscosity of a benzene solution was measured at five or six concentrations and the intrinsic viscosity (or limiting viscosity number) $[\eta]$ determined by extrapolation of the plot η_{sp}/c against c, which was linear in all cases. If c is in base moles per litre then it was found that (cf. Appendix)

$$[\eta] = 3{\cdot}8 \times 10^{-4}M$$

All polymer molecular weights in this paper were calculated from observed viscosity data through the above relation.

Materials.—*Boron trifluoride.* A high-purity sample, kindly given by the National Smelting Co. Ltd. (Avonmouth), was purified by Bistline's method.[3] The diethyl ether complex was purified by Laubengayer and Finlay's method to remove silicon tetrafluoride,[4] and mixed with calcium fluoride (B.D.H. " pure ") and kept for 24 hr. Excess of ether was removed by heating, the sample plugged with glass wool, and the glass vessel sealed to the vacuum apparatus.

Diethyl ether. The B.D.H. product, purified by Taylor and Smith's method,[5] was kept over sulphuric acid for 12 hr., washed, and mixed with saturated potassium permanganate solution containing 20 g. of sodium hydroxide. After standing for 24 hr. it was treated with water, concentrated sulphuric acid, and water again, and dried ($CaCl_2$). The product was distilled from sodium, the middle fraction being collected.

Vinyl ethers. The commercial products, purified by Schildknecht's method,[6] were washed five times with an equal volume of water made slightly alkaline with potassium hydroxide, dried (Na), and distilled *in vacuo*, the middle fraction being collected.

Ethylene dichloride. The commercial product was washed with 5% sodium hydroxide solution, then water, and distilled from phosphoric oxide, the middle fraction being collected.

RESULTS

Reaction Velocity.—The reaction curves were linear up to 10% polymerisation and induction periods were normally absent. In some cases induction periods of a few minutes were found which are attributed to impurities.

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

$$v = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k\,[\mathrm{M}]^2[\mathrm{C}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The results obtained are shown in Fig. 2 and give the overall rate constants, k : *n*-butyl vinyl ether, 16·5; 2-chloroethyl vinyl ether, 4·5 $l.^2$ $mole^{-2}$ $min.^{-1}$.

Overall Activation Energy.—A series of reaction rates were determined at five different temperatures in the range 20—40° with solutions containing constant amounts of monomer

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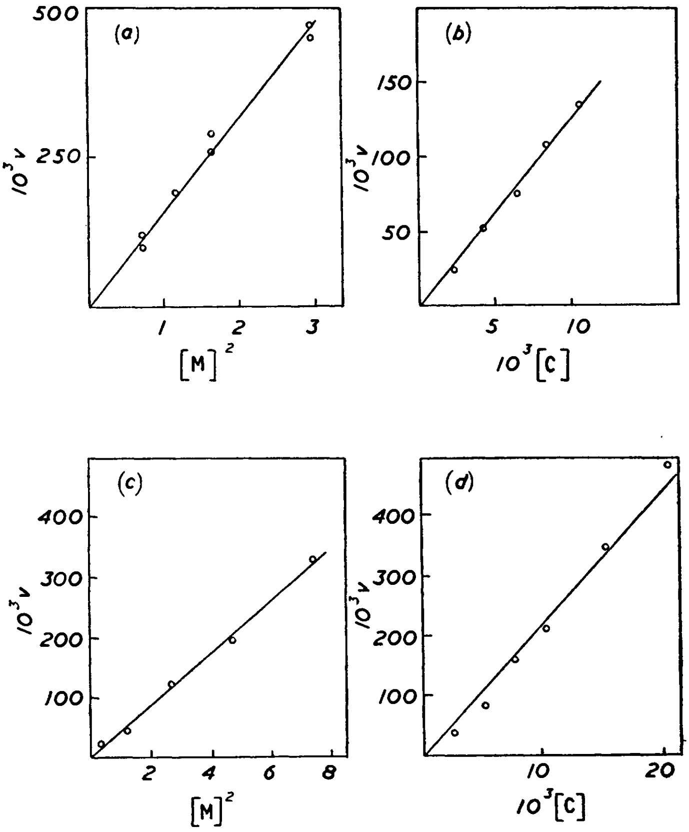
[2] " Monomers," ed. Blout and Mark, Interscience, New York, 1951.
[3] Bistline, *Rev. Sci. Instr.*, 1948, **19**, 846.
[4] Laubengayer and Finlay, *J. Amer. Chem. Soc.*, 1943, **65**, 884.
[5] Taylor and Smith, *ibid.*, 1922, **44**, 2457.
[6] Schildknecht, in ref. 2.

and catalyst. The results shown in Fig. 3 give the overall activation energies, E: *n*-butyl vinyl ether, 6·0 ± 0·5; 2-chloroethyl vinyl ether, E = 6·0 ± 0·2 kcal. mole^{-1}.

Molecular Weight of Poly-(n-*butyl Vinyl Ether*).—Two series of experiments were carried out at 25°. In one the monomer concentration was constant at 2·15 moles l.$^{-1}$ with varying catalyst concentration; in the other the catalyst concentration was 10·2 mmoles l.$^{-1}$ with varying amounts of monomer. The results are shown in Table 1.

FIG. 2. *Order of the reaction.*



(*a*) Effect of [M] with *n*-butyl vinyl ether ([C] = 9·53mM).
(*b*) Effect of [C] with *n*-butyl vinyl ether ([M] = 0·859M).
(*c*) Effect of [M] with 2-chloroethyl vinyl ether ([C] = 10·1mM).
(*d*) Effect of [C] with 2-chloroethyl vinyl ether ([M] = 2·17M).

TABLE 1. *Molecular Weights.*

Varying catalyst, [M] = 2·15M.			Varying monomer [C] = 10·2mM.			Varying monomer [C] = 10·2mM.		
[C] (mM)	$[\eta]$	D.P.	[M] (M)	$[\eta]$	D.P.	[M] (M)	$[\eta]$	D.P.
5·1	1·250	32·9	1·29	0·895	23·6	3·01	1·868	49·2
10·2	1·250	32·9	1·72	1·249	32·0	3·44	1·953	51·4
15·3	1·180	31·0	2·15	1·565	41·2	3·87	2·000	52·6
20·4	1·115	29·3	2·58	1·720	45·3			
25·5	1·111	29·2						

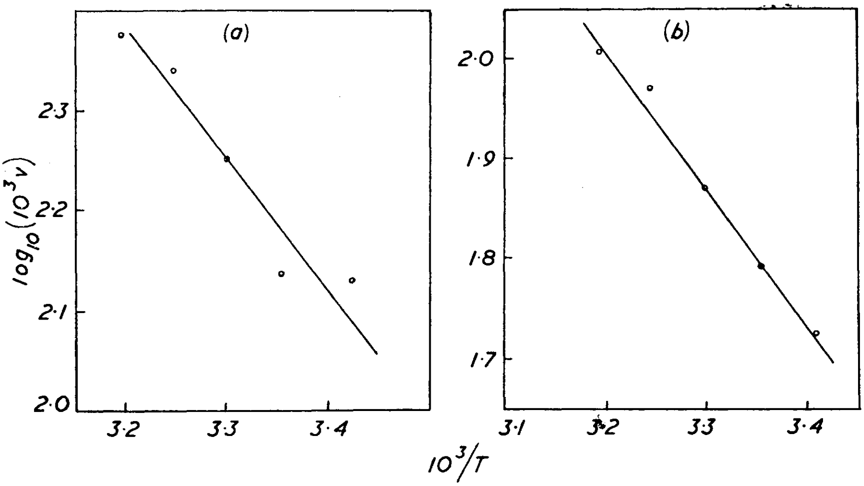
The degree of polymerisation, D.P., is almost independent of [C], and linearly dependent on [M] at low values, reaching a maximum value as the monomer concentration [M] increases, as found earlier with stannic chloride and octyl vinyl ether.[1a]

A series of polymers were prepared in the temperature range 15—35° from a solution containing 2·15M-*n*-butyl vinyl ether and 9·35mM catalyst. The results obtained, shown in Fig. 4, give an " activation energy " $E_{\text{D.P.}} = -3{\cdot}0 \pm 0{\cdot}5$ kcal. mole^{-1}.

Dielectric Constant.—A series of molecular-weight and rate determinations were carried out on solutions containing fixed amounts of monomer and catalyst, but varying amounts of ethylene dichloride. Ethylene dichloride was chosen since it would not be expected to form a complex with boron trifluoride. Booth and Martin [7] found no evidence for compound formation between HCl and BF_3, and Booth and Frary [8] were unable to prepare a mixed boron trihalide. This is consistent with Meier's observation [9] that boron trifluoride in methyl chloride does not polymerise *n*-butene.

The results obtained at 25° are shown in Table 2.

FIG. 3. *Overall activation energy.*



(*a*) *n*-Butyl vinyl ether ([M] = 0·859M), (*b*) 2-chloroethyl vinyl ether ([M] = 1·084M).

FIG. 4. *The " activation energy " for D.P. for poly-*(n-*butyl vinyl ether*).

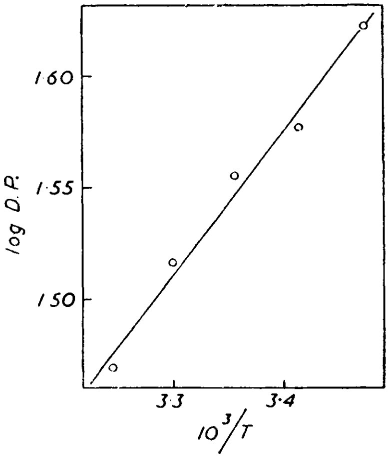
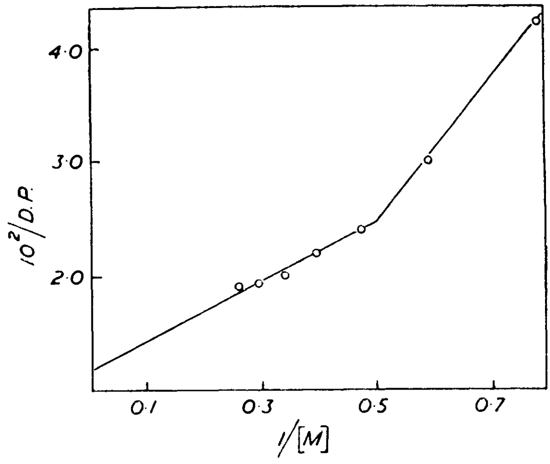


FIG. 5. *The effect of monomer concentration on D.P. of poly-*(n-*butyl vinyl ether*).



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[7] Booth and Martin, *J. Amer. Chem. Soc.*, 1942, **64**, 2198; *Chem. Rev.*, 1943, **33**, 57.

[8] Booth and Frary, *J. Amer. Chem. Soc.*, 1943, **65**, 1836.

[9] Meier, quoted by Plesch, *J. Appl. Chem.*, 1951, **1**, 269.

The rates of both polymerisations increase exponentially with the dielectric constant of the solution, although the molecular weight is decreased. Eley and Richards [1a] found a similar rate increase for octyl vinyl ether.

Water.—The effect of water on the rate of polymerisation of a solution of 2-chloroethyl vinyl ether and the molecular weight of *n*-butyl vinyl ether polymers was examined. The results are shown in Table 3.

TABLE 2. *Dielectric constant.*

	2-Chloroethyl vinyl ether	*n*-Butyl vinyl ether	
	[M] = 1·084M	[M] = 0·859M	[M] = 1·289M
D	10^3 Rate (moles $l.^{-1}$ $min.^{-1}$)	10^3 Rate (moles $l.^{-1}$ $min.^{-1}$)	D.P.
4·34	34·99	195·1	26·71
4·70	59·00	439·0	—
5·08	78·62	609·0	15·95
5·50	100·9	794·3	—
5·92	140·3	1070	12·29
6·72	—	—	12·89

TABLE 3. *Effect of water.*

2-Chloroethyl vinyl ether		*n*-Butyl vinyl ether	
[M] = 1·08M; [C] = 25·58mM		[M] = 1·72M; [C] = 19·2mM	
[H_2O] (mM)	10^3 Rate (moles $l.^{-1}$ $min.^{-1}$)	[η]	D.P.
0	133·4	1·250	32·9
8·33	126·3	0·890	23·4
16·66	139·7	0·621	16·3
25·00	125·3	0·485	12·8
33·33	131·0	0·418	11·0
41·66	—	0·361	9·5

Although the addition of water does not affect the rate, it causes marked induction periods which increased with increasing water concentration. Induction periods of up to 50 min. were found. During the polymerisation of *n*-butyl vinyl ether in the presence of water the solutions turned deep brown and the polymers isolated were pale yellow. The intensity of these colours increased with increasing water concentration.

DISCUSSION

Kinetics.—Equation (1) is consistent with the following kinetic scheme. The numbering of constants is the same as used previously in this Series.

$$\begin{array}{rlr} \mathrm{M} + \mathrm{C} \longrightarrow \mathrm{M}^* & \quad . \quad . & k_2 \\ \left.\begin{array}{r} \mathrm{M}^* + \mathrm{M} \longrightarrow \mathrm{M}_2{}^* \\ \mathrm{M}_{n-1}{}^* + \mathrm{M} \longrightarrow \mathrm{M}_n{}^* \end{array}\right\} & \quad . \quad . & k_3 \end{array} \qquad \begin{array}{rlr} \mathrm{M}_n{}^* \longrightarrow \mathrm{M}_n & \quad . \quad . \quad . & k_4 \\ \mathrm{M}_n{}^* + \mathrm{M} \longrightarrow \mathrm{M}_n + \mathrm{M}^* & \quad . & k_5 \end{array}$$

The last reaction, chain transfer, is suggested to account for the observation that the molecular weight of the polymer, although proportional to [M] at low monomer concentrations, becomes independent of it at higher values (see Table 1).

Normal stationary-state conditions being assumed, $v = -d[M]/dt = (k_2k_3/k_4)[M]^2[C]$ and D.P. $= k_3[M]/(k_4 + k_5[M])$. It is found that if D.P. is plotted against [M] the relation is initially linear ($k_4 \gg k_5[M]$), giving a slope $k_3/k_4 = 18{\cdot}7$ l. mole^{-1}, and reaches a maximum where transfer becomes dominant ($k_5[M] \gg k_4$). This is clearly similar to the results found by Eley and Richards [1a] for stannic chloride. Alternatively, the equation may be put into the reciprocal form $1/\text{D.P.} = k_5/k_3 + k_4/(k_3[M])$.

In Fig. 5 1/D.P. is plotted against 1/[M] and it is seen that there is not a perfect fit to this relation. There is a discontinuity at low values of the monomer concentration (<2 M), which corresponds to a kind of threshold value which must be exceeded before transfer can set in. The reason for this behaviour is obscure, but it may be connected with the effects of traces of water in the solvents. Above this monomer concentration there is a straight-line relation for 5 points, with a slope k_4/k_3 which is the reciprocal of the value 18·7 quoted above, and an intercept on the 1/D.P. axis which gives $k_5/k_3 = 1{\cdot}1 \times 10^{-2}$.

Activation Energies.—The overall activation energy, E, for the reaction has the same value, 6·0 kcal. mole^{-1}, for each monomer. Now $E = E_2 + E_3 - E_4$, where E_2, E_3, and E_4 are the activation energies associated with the individual steps; E_2 may or may not be composite. The molecular-weight "activation energy," $E_{\text{D.P.}}$, is equal to $E_3 - E_4$ and for *n*-butyl vinyl ether has the value $-3{\cdot}0$ kcal. mole^{-1}. Thus E_2 for *n*-butyl vinyl ether is equal to 9·0 kcal. mole^{-1}. The overall rate constant for this monomer, 16·5 l.^{2} mole^{-2} min.$^{-1}$, is equal to k_2k_3/k_4. Using the value of k_3/k_4, 18·7 l. mole^{-1}, from molecular-weight data above, we find that k_2 is 0·88 l. mole^{-1} min.$^{-1}$.

These values of the rate constant and the activation energy for the initiation provide an estimate of the entropy of activation equal to -35 ± 5 e.u. mole^{-1} in the standard state of 1 mole l.$^{-1}$. This high negative value must involve the creation of an ion-pair in solution and may be compared with the value found[10] for the Menschutkin reaction $Et_3N + EtBr \longrightarrow Et_4N^+Br^-$ in acetone–benzene of about -40 e.u. mole^{-1}.

A similar calculation can be made by using published data for the system stannic chloride–octyl vinyl ether–light petroleum.[1a] Here $k_2k_3/k_4 = 24$ l.^{2} mole^{-2} min.$^{-1}$ * and $k_3/k_4 = 117$ l. mole^{-1}, and the activation energy $E_2 = 13{,}300$ cal. Hence it may be calculated that $\Delta S_2^{\ddagger} = -27{\cdot}2$ e.u., suggesting that here also we are concerned with the creation of an ion-pair. In this case the ion-pair probably arises from the interaction of the stannic chloride with the vinyl ether monomer acting as cocatalyst.[11]

Initiation.—The absence of half-powers of [C] in the rate expression and the low dielectric constant of diethyl ether solvent (4·3) exclude the possibility of free ions' being the active species. The polar but un-ionised $BF_3{\cdot}OEt_2$ molecule, or the ion-pair $Et^+BF_3OEt^-$, must be considered as the effective initiator. The ion-pair $Et^+BF_3OEt^-$ is likely to be solvated to an oxonium compound $Et_3O^+BF_3{\cdot}OEt^-$, the solvation energy more than compensating for the small loss of Coulombic attraction energy attendant upon the greater charge separation involved.

A sample of ethoxonium fluoroborate, $Et_3O{\cdot}BF_4$, prepared by Meerwein's method[12] was found to polymerise a sample of *n*-butyl vinyl ether instantaneously.

Termination.—The anionic fragment $BF_3O{\cdot}Et^-$ cannot form a co-ordinate bond with the carbonium ion, and proton extraction from the latter must be the operative termination mechanism. This is confirmed by the observation that polymers prepared in the region where transfer was unimportant rapidly decolorised a solution of bromine in carbon tetrachloride. The polymer did not contain boron. Further evidence is provided by the observation that one catalyst molecule could initiate several polymer chains, again in a region where little transfer was occurring.

Dielectric Constant.—The results of Table 2 show that increasing the dielectric constant of the solution leads to a logarithmic increase in reaction rate, but a decrease in the molecular weight of the polymer formed. Eley and Richards[1a] found a similar increase in rate with no increase in molecular weight when investigating octyl vinyl ether.

In view of Overberger and Endres's observation[13] that it is the net electron-donating character of a transfer agent that determines its efficiency, it is unlikely that ethylene dichloride is acting in this capacity. It must be concluded that the decrease in molecular weight is a dielectric effect.

The ratio k_3/k_4, from the molecular-weight results, must be decreased at higher dielectric

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* The third-order constants k quoted in Eley and Richards's[1a] paper, Table 1, p. 429; Fig. 5, p. 432; and p. 440 are in fact values of 10^6k. The necessity for this correction invalidates a remark by Eley made at the Dublin Symposium (*Sci. Proc. Roy. Dublin Soc.*, 1950, **25**, 137).

[10] Wynne-Jones and Eyring, *J. Chem. Phys.*, 1935, **3**, 492.

[11] Hamann, Plesch, and Skinner, *Sci. Proc. Roy. Dublin Soc.*, 1950, **25**, 131.

[12] Meerwein, *J. prakt. Chem.*, 1939, **154**, 83.

[13] Overberger and Endres, *J. Polymer Sci.*, 1955, **16**, 283.

constant and this is doubtless due to an increase in k_4 since the reaction (proton extraction) involves a concentration of electrostatic charge. The overall rate constant k_2k_3/k_4 is increased however. Thus k_2, the initiation reaction, is the step most affected, as is to be expected since this is the only reaction involving the actual creation of charges in solution.

The initiation reaction would be expected to obey Kirkwood's equation.[14] Non-electrostatic forces being neglected,

$$\log k_2 = \log k_0 - \frac{1}{kT} \cdot \frac{D-1}{2D+1}\left[\frac{\mu_C^2}{r_C^3} + \frac{\mu_M^2}{r_M^3} - \frac{\mu^2}{r^3}\right]$$

where $k_0 = \alpha kTK_0/h$. Here $K_0^\ddagger$ is the equilibrium constant between the activated complex and the initial reactants, D is the dielectric constant, μ_C and μ_M are the dipole moments of catalyst and monomer respectively and μ that of the activated complex, and r's similarly apply to the molecular radii. Thus a plot of log k_2 against $(D - 1)/(2D + 1)$ should be linear, with a slope of $-(1/kT)[(\mu_C^2/r_C^3) + (\mu_M^2/r_M^3) - (\mu^2/r^3)]$. Individual values of k_2 are not known, but since this is the reaction predominantly affected the error in using values of the overall rate constant $k = k_2k_3/k_4$ should not be prohibitive.

FIG. 6. *The effect of solvent dielectric constant (Kirkwood theory) on the rate of polymerisation for (A)* n-*butyl vinyl ether and (B)* 2-*chloroethyl vinyl ether.*

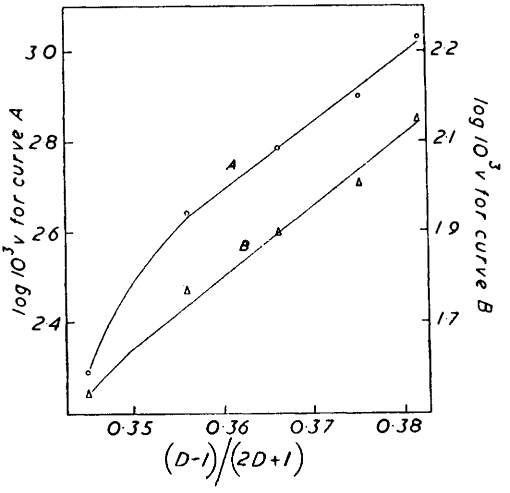
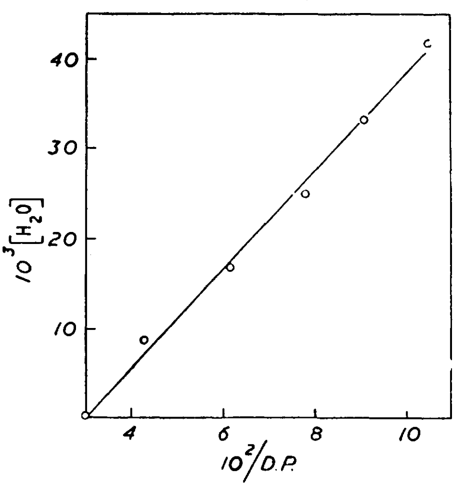


FIG. 7. *Effect of* [H₂O] *on D.P. of poly-*(n-*butyl vinyl ether*).



A plot of $\log_{10}k$ against $(D - 1)/(2D + 1)$ is shown for both monomers in Fig. 6. The slopes are equal and positive, showing that $\mu > (\mu_M + \mu_C)$, as is to be expected where the final products are ionised.

Effect of Water.—As seen from Table 3, water lowers the molecular weight of the polymer but does not affect the rate of the reaction. Quantitatively this molecular-weight lowering may be expressed by Mayo's chain-transfer equation:

$$1/(\text{D.P.})_n = 1/(\text{D.P.})_0 + (k_6/k_3)([\text{R}]/[\text{M}])$$

where we have a transfer step $\text{M}^* + \text{R} \longrightarrow \text{M} + \text{R}^*$ . . . . k_6

Here D.P. is the molecular weight in presence of transfer agent, $(\text{D.P.})_0$ that in its absence, and [R] the concentration of transfer agent.

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[14] Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.

A plot of 1/D.P. against [H_2O] is shown in Fig. 7, giving a value $k_6/k_3 = 3{\cdot}1$.

Using the data of Eley and Richards [1a] and Eley and Pepper [16] we can calculate values of k_6/k_3 for other systems as follows:

Vinyl ether	Catalyst	Transfer Agent	k_6/k_3
n-Butyl	$SnCl_4$	BuOH	7·2
n-Butyl	$BF_3{\cdot}OEt_2$	H_2O	3·1
Octyl	I_2	BuOH	34·8

Butyl alcohol is a more efficient transfer agent than water, in accord with its greater electron availability. The anomalous value obtained with iodine as catalyst is probably due to the catalyst itself acting as a transfer agent. This is supported by the observation [1a] that iodine gave only low-molecular-weight polymers in contrast to those obtained with other catalysts.

APPENDIX

Viscosity Molecular Weights.—The molecular weights *M* were determined cryoscopically for 6 specimens of poly-(*n*-butyl vinyl ether). For each specimen a range of concentrations in benzene was examined, and the molecular weights evaluated from the extrapolated values of $(\Delta/c)_{c\rightarrow 0}$, where Δ is the depression and *c* the concentration. The limiting viscosity number [η] was determined with an Ostwald viscometer. The results are shown in Fig. 8., from which is derived the Staudinger relation $[\eta] = 3{\cdot}8 \times 10^{-4}M$ when *c* is in base moles per litre.

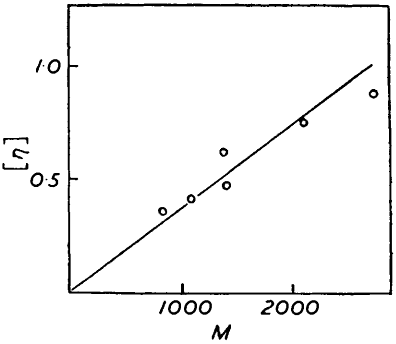

FIG. 8. *Relation between [η] and cryoscopic molecular weight, M.*

It is noted that the range of *M* taken is only 832 to 2702 while in the kinetic work the method was used for polymers up to *M* = 5260 (D.P. = 52·6). However, the earlier results of Eley and Richards [1a] support the validity of the relation to *M* = 5000 for poly-(2-ethylhexyl vinyl ether) where a Staudinger constant of $5{\cdot}0 \times 10^{-4}$ was found for light petroleum (b. p. 60—68°) as solvent.

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THE UNIVERSITY, NOTTINGHAM. [*Received, April 1st,* 1957.]

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[15] Mayo, *J. Amer. Chem. Soc.*, 1943, **65**, 2324.
[16] Eley and Pepper, *Trans. Faraday Soc.*, 1947, **43**, 112.