1357. *The Kinetics of Ionic Polymerisation. Part XII. Polymerisation of Isobutyl Vinyl Ether at* $-40°$ *in the Solvent* 50 : 50 *n-Hexane–Toluene*

By G. J. Blake and D. D. Eley

The polymerisation of isobutyl vinyl ether at $-40°$ in 50 : 50 n-hexane–toluene solvent gives atactic polymer, with a polymerisation rate $R_p = k[M][C]$, an overall activation energy $E = 12{\cdot}5$ kcal.mole^{-1}, and molecular-weight activation energy $E_{DP} = -3{\cdot}5$ kcal.mole^{-1}. The kinetics are shown to fit a non-stationary mechanism with fast initiation and slow propagation, as deduced earlier by Pepper for sulphuric acid–styrene. In this case the overall activation energy $E = E_p$ for the propagatin step, and it is deduced that the termination activation energy E_t is $16{\cdot}0$ kcal.mole^{-1}. This high value explains why spontaneous termination is supplanted by monomer transfer below $-70°$, but the chemical nature of the termination step is still obscure.

In Part XI [1] the stereopolymerisation of isobutyl vinyl ether at $-78°$ was studied and a steady-state kinetic scheme established. The main chain-terminating mechanism at $-78°$ was shown to be monomer transfer, and a low activation energy of monomer transfer was postulated to explain this phenomenon so that

$$E_t > E_p > E_{tr}$$

It was shown that, at $-40°$, the molecular-weight activation energy was negative. In our pursuit of a connection between the stereoregulation of growing chains at $-78°$ and the observed kinetics, we consider that the study of an analogous system at $-40°$ where mainly atactic polymer is produced is worthwhile as a comparison.

Experimental and Results

Essentially an identical technique was used as that described in Part XI. Since the reaction rates were much greater at $-40°$ than at $-78°$ lower concentrations of reagents were used.

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[1] G. J. Blake and D. D. Eley, preceding Paper.

With low concentrations of monomer, temperature rises were small and single reaction curves could be analysed.

In Part XI we noted that at −40°, the overall activation energy was $E = 12{\cdot}5$ kcal.mole^{-1} and a molecular-weight activation energy

$$E_{\text{DP}} = -3{\cdot}5 \text{ kcal.mole}^{-1}$$

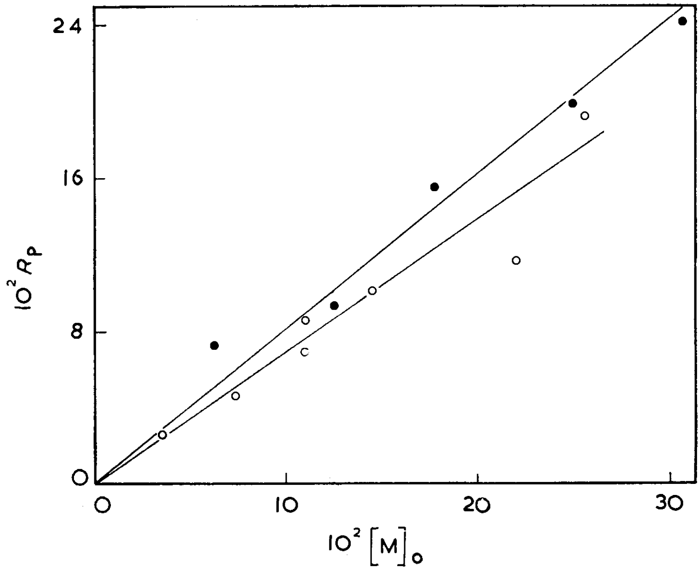

FIGURE 1. Reaction rate as a function of initial monomer concentration $[\text{M}]_0$
● $T = -47°$, $[\text{C}] = 2{\cdot}2 \times 10^{-3}$ mole l.$^{-1}$
○ $T = -40°$, $[\text{C}] = 1{\cdot}425 \times 10^{-3}$ mole l.$^{-1}$

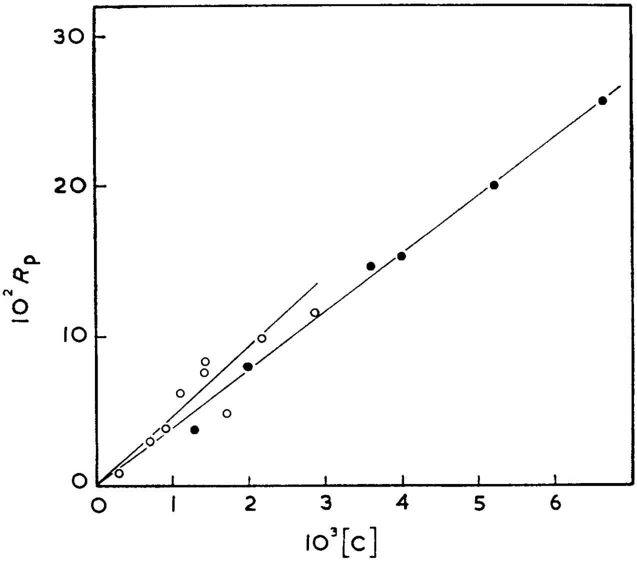

FIGURE 2. Reaction rate as a function of catalyst concentration [C]
● $T = -47°$, $[\text{M}]_0 = 0{\cdot}126$ mole l.$^{-1}$
○ $T = -40°$, $[\text{M}]_0 = 0{\cdot}11$ mole l.$^{-1}$

Reaction Rates.—Using pre-prepared phials of isobutyl vinyl ether in n-hexane solution broken into the boron trifluoride–diethyl ether complex catalyst solution, the reaction appeared to proceed homogeneously at all monomer and catalyst concentrations. Variation of monomer and catalyst concentrations produced reaction curves whose initial slopes led to the expression for the overall kinetics at the beginning of the reaction $R_p = k[M][C]$ at $-40°$ and $-47°$ (see Figures 1 and 2).

Yields of Polymer.—Measurements of yield by weight and from the temperature rise accompanying the overall reaction lead to the conclusion that at low [C]/[M] ratios, the yield is limited. This is shown in Figures 3 and 4.

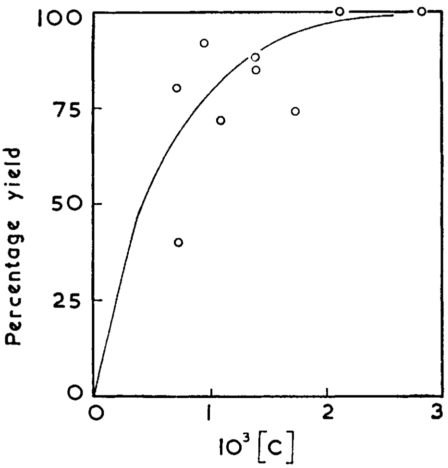

FIGURE 3. Yield of polymer as a function of catalyst concentration [C], at $T = -40°$, $[M]_0 = 0{\cdot}11$ mole l.$^{-1}$

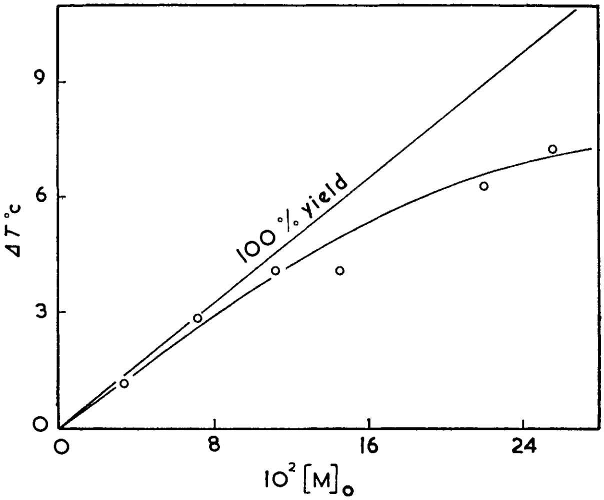

FIGURE 4. Temperature rise as a function of initial monomer concentration $[M]_0$, at $T = -40°$, $[C] = 1{\cdot}425 \times 10^{-3}$ mole l.$^{-1}$

Molecular Weights.—Data for polymers produced at $-40°$ fitted the Staudinger law in distinction to those (Part XI) produced at $-78°$ which obeyed the Mark–Houwink equation. Interpolations from a Staudinger relationship of

$$[\eta] = 1{\cdot}33 \times 10^{-5}\,\overline{M}_n$$

derived from viscometric and osmotic data gave number-average molecular weights (see Appendix). A plot of molecular weight against monomer consumed gave a scatter of points around a linear plot indicative of absence of transfer, as in Figure 5.

Molecular weights plotted against initial catalyst concentration showed that the molecular weight decreased with increasing catalyst concentration, as in Figure 6.

Effect of Co-catalyst Concentration.—An increase of diethyl ether co-catalyst concentration beyond that of the boron trifluoride concentration leads to a decrease in initial reaction rate and molecular weight, as shown in Figure 7.

DISCUSSION

The main features apparent from the results are: (*a*) kinetic law of $R_p = [M][C]$; (*b*) limited yields of polymer; (*c*) the molecular weight of polymer is dependent on catalyst concentration. None of these points are compatible with a stationary-state mechanism and a close similarity with the non-stationary kinetics of Burton and Pepper[2] is apparent. Adopting their reaction scheme

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[2] R. E. Burton and D. C. Pepper, *Proc. Roy. Soc.*, 1961, *A*, **263**, 58.

$$M + C \longrightarrow M^+ \qquad k_i$$
$$M^+ + M \longrightarrow M_2^+,\ \text{etc.},\ k_p$$
$$M_n^+ \longrightarrow M_n = P \quad k_t \text{ with } k_i \gg k_p$$
$$\text{then } R_p = k_p\,[M][M^+]$$

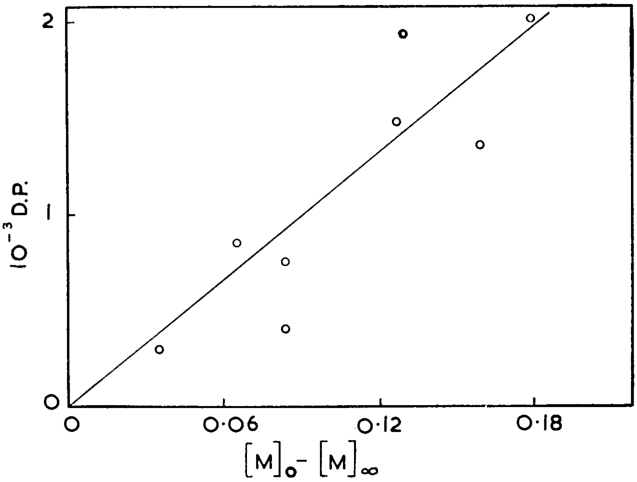

FIGURE 5. The degree of polymerisation of the product, DP, as a function of the concentration of monomer consumed in the polymerisation

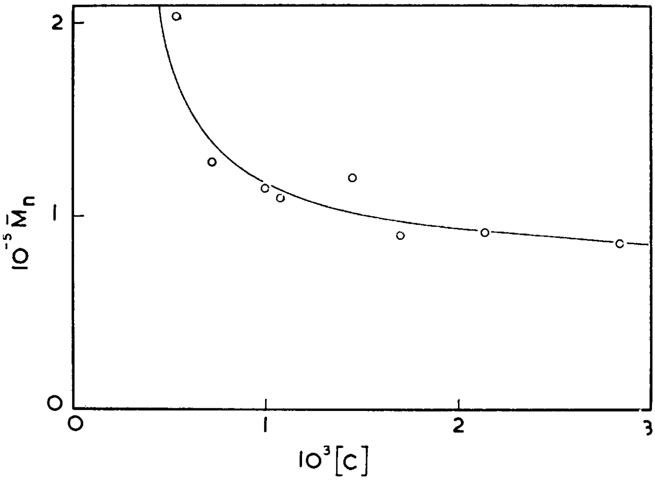

FIGURE 6. The degree of polymerisation of the product, DP, as a function of catalyst concentration

Since at the beginning of the reaction $[M^+]_0 = [C]_0$, the initial reaction rate is given by

$$R_p = k_P[M]_0[C]_0$$

which agrees with the observed kinetics of Figures 1 and 2, so that

$$k = k_p = 500 \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Single Reaction Curve Analysis.—Since the temperature rise involved in a run is small, only 3—4°, the single reaction curves can be analysed. If, in polymerisation, the only possible mode of chain stopping is true termination, *i.e.*, anion recombination, then

$$-\mathrm{d}[\mathrm{M}^+]/\mathrm{d}t = k_\mathrm{t}[\mathrm{M}^+]$$

and

$$[\mathrm{M}^+] = [\mathrm{M}^+]_0\exp(-k_\mathrm{t}t)$$

Since $[\mathrm{M}^+]_0 = [\mathrm{C}]_0$, a single reaction curve would then be given by

$$R_\mathrm{p} = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{M}]_t[\mathrm{C}]_0\exp(-k_\mathrm{t}t)$$

assuming no rate increase through temperature rise. Thus

$$\log(R_\mathrm{p}/[\mathrm{M}]_t) = \log_e k_\mathrm{p}[\mathrm{C}]_0 - k_\mathrm{t}t.$$

A value of R_p can be obtained from the slope of the tangent to the reaction curve at time t. The temperature rise at this point was related to the amount of monomer consumed and thus to $[\mathrm{M}]_\mathrm{t}$. From the plots of log $R_\mathrm{p}/[\mathrm{M}]_t$ against t values of k_p and k_t can be obtained. Some reaction curves are shown in Figure 8 with their analysed plots in Figure 9, the derived values of k_p and k_t being shown in the Table.

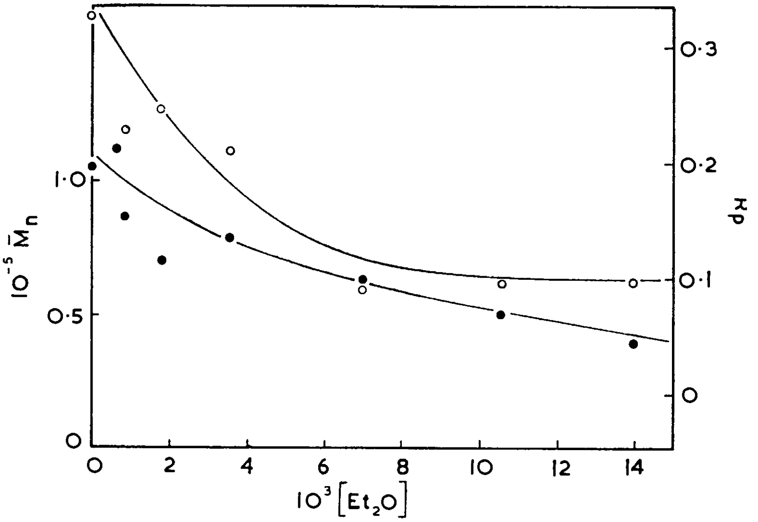

FIGURE 7. Reaction rate (○) and molecular weight (●) as function of the excess concentration of co-catalyst, at $T = -40°$, $[\mathrm{M}]_0 = 0{\cdot}11$ mole l.$^{-1}$ and $[\mathrm{C}] = 0{\cdot}425 \times 10^{-3}$ mole l.$^{-1}$

k_p and k_t at $-40°$, $[\mathrm{M}]_0 = 0{\cdot}11$ mole l.$^{-1}$

Curve	$10^3[\mathrm{C}]_0$ (mole l.$^{-1}$)	k_p (l. mole^{-1} min.$^{-1}$)	k_t (min.$^{-1}$)	Curve	$10^3[\mathrm{C}]_0$ (mole l.$^{-1}$)	k_p (l. mole^{-1} min.$^{-1}$)	k_t (min.$^{-1}$)
a	5·70	456	0·253	*e*	1·07	470	0·390
b	2·85	420	0·253	*f*	1·71	203	0·230
c	2·14	460	0·460	*g*	0·29	650	0·300
d	1·43	550	0·550				
					Average	458	0·348

These average values lead to $k_\mathrm{p}/k_\mathrm{t} = 1316$ l. mole^{-1}.

Yields.—From the total temperature rise, a rough value of the yield was obtained. From the general equation

$$-\mathrm{d}[\mathrm{M}]_t/\mathrm{d}t = k_\mathrm{p}[\mathrm{M}]_t[\mathrm{C}]_0\exp(-k_\mathrm{t}t)$$

$$\int_{[\mathrm{M}]_0}^{[\mathrm{M}]_\infty}\mathrm{d}[\mathrm{M}]_t/[\mathrm{M}]_t = \int_0^\infty k_\mathrm{p}[\mathrm{C}]_0\exp(-k_\mathrm{t}t).\mathrm{d}t$$

Since yield $Y = 1 - ([M]_\infty/[M]_0)$

$$2{\cdot}303 \log_{10}(1 - Y) = -(k_p/k_t)[C]_0$$

A plot of log $(1 - Y)$ against $[C]_0$ as in Figure 10 should give the ratio k_p/k_t. However, the scatter of points in Figure 10 is much too large for an accurate value, so we have drawn a line through the points with the slope $k_p/k_t = 1316$ l. mole^{-1}, which was independently derived earlier from the rates. It is seen that this line is at least consistent with the observed results on yields.

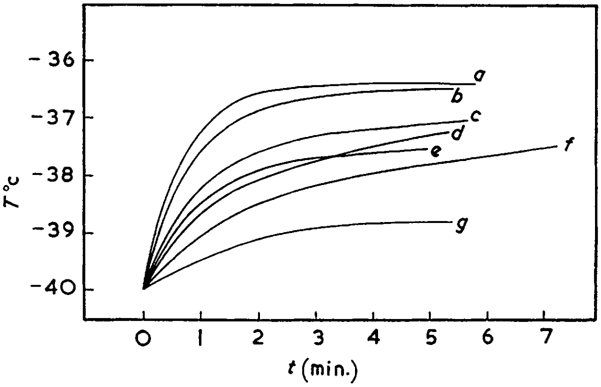

FIGURE 8. Some typical reaction curves for initial monomer concentration $[M]_0 = 0{\cdot}11$ mole l.$^{-1}$, and a catalyst concentration $10^3[C] = 2{\cdot}85$ (*a*); $2{\cdot}14$ (*b*); $1{\cdot}425$ (*c*); $0{\cdot}93$ (*d*); $1{\cdot}07$ (*e*); $0{\cdot}715$ (*f*); $0{\cdot}29$ (*g*); all in mole l.$^{-1}$

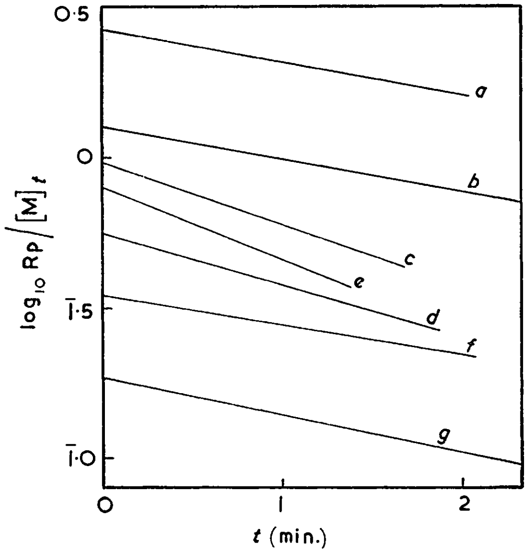

FIGURE 9. Plots of $\log_{10} R_p/[M]_t$ against time (calculated from recorder tracings in Figure 8)

The suggested mechanism so far explains the reaction rate and yield, but fails to fully account for the observed molecular weights. The theory would predict for the degree of polymerisation of the product

$$DP = ([M]_0 - [M]_\infty)/[C]_0$$

absence of transfer being assumed.

A plot of DP against $[M]_0 - [M]_\infty$ shows a large scatter, as in Figure 5, but so far as one can judge, corresponds to a straight line through the origin. However, the plot of DP against $[C]_0^{-1}$ is linear, with an intercept (Figure 11), so that taken together, the results fit the general formula

$$DP = 10^4 + \frac{4}{[C]_0}([M]_0 - [M]_\infty)$$

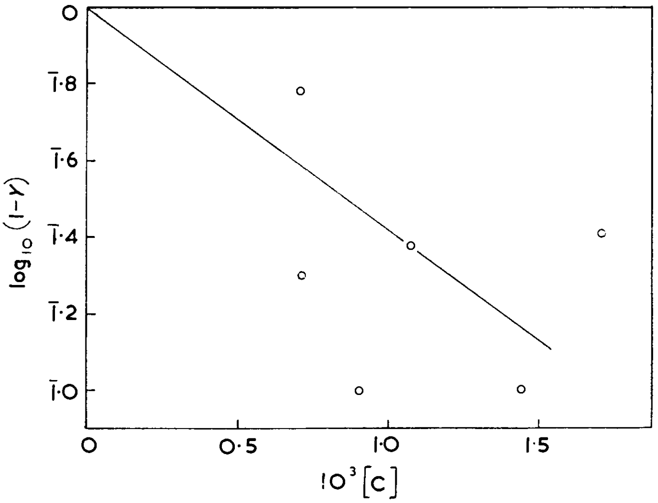

FIGURE 10. Plot of $\log_{10}(1 - Y)$ (Y = yield) against catalyst concentration [C], at $T = -40°$, $[M]_0 = 0{\cdot}11$ mole $l.^{-1}$

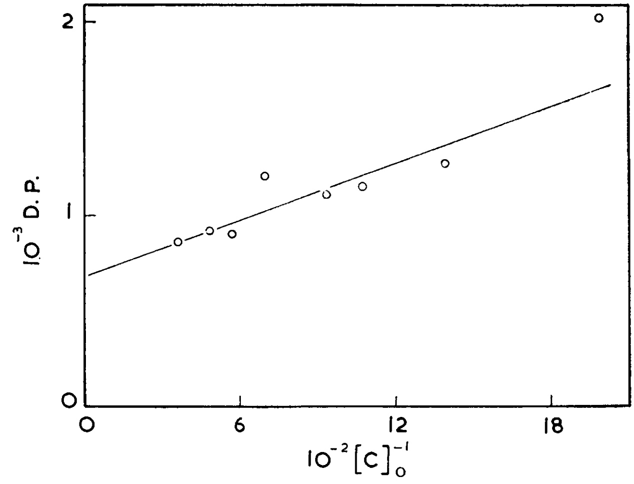

FIGURE 11. Plot of degree of polymerisation DP against reciprocal catalyst concentration $[C]^{-1}$ at $T = -40°$ and $[M]_0 = 0{\cdot}11$ mole $l.^{-1}$

The DP is clearly a composite of terms independent and dependent on catalyst concentration, respectively, indicating the possibility of two mechanisms; (*a*) a steady-state mechanism as observed at lower temperatures leading to an independence of molecular weight from catalyst concentration; (*b*) a non-steady state mechanism as described in this Paper contributing a term to the molecular-weight equation with inverse dependence on catalyst concentration.

This suggestion does not completely account for the observed molecular weights because in the catalyst-dependent term the non-steady state mechanism predicts a numerical value for DP

$$\mathrm{DP} = ([\mathrm{M}]_0 - [\mathrm{M}]_\infty)/[\mathrm{C}]_0$$

and the observed molecular weights are about four times this prediction. To account for this fact, a number of further suggestions can be made: (*a*) The catalyst involved in the steady-state component is removed from the reaction mixture, so reducing the effective concentration of catalyst. (*b*) Some association of the polymer molecules leads to an erroneously high molecular weight of the product. (*c*) The catalyst as introduced is not effective itself but furnishes an effective catalyst through an equilibrium reaction with the monomer. The concentration of the effective catalyst would then need to be about a quarter of the introduced catalyst concentration in order to explain the observed results. (*d*) The initiation step is not completely instantaneous, but is of comparable speed with the propagation step so that the two proceed simultaneously during most of the reaction. In this way some of the catalyst would not be involved in polymerisation at all.

Effect of Co-catalyst.—The lowering of reaction rate and molecular weight with increasing co-catalyst concentration is thought to be due to the lowering of the non-steady state reaction rate and the steady-state molecular weight. The lowering in molecular weight is probably due to an additional chain-stopping mechanism which does not affect the reaction rate in its initial stages. The lowering in reaction rate is due to the effective lowering of catalyst concentration, either by complexing or solvation or if raw boron trifluoride is the effective catalyst, diminishing its concentration in the equilibrium

$$\mathrm{BF_3} + \mathrm{Et_2O} \rightleftharpoons \mathrm{BF_3Et_2O}$$

Since the same reaction producing isotactic polymer at —78° has a steady-state character, it is highly probable that some steady-state character will still exist at —40°.

Energetics.—The overall activation energy is found in Part XI of $E = 12{\cdot}5$ kcal.mole^{-1} must correspond to the activation energy of propagation, E_{p}. This value is rather higher than would be expected in view of the predictions made by Dainton,[3] but agrees well with recent results of Hayes and Pepper [4] for styrene polymerised by sulphuric and perchloric acids in ethylene dichloride.

The molecular-weight activation energy at —40° was found in Part XI to be $E_{\mathrm{DP}} = 3{\cdot}5$ kcal.mole. If the degree of polymerisation were given by the simple equation $\mathrm{DP} = ([\mathrm{M}]_0 - [\mathrm{M}]_\infty)/[\mathrm{C}]_0$, then substitution for $[\mathrm{C}]_0$ gives

$$\mathrm{DP} = \frac{[\mathrm{M}]_0 - [\mathrm{M}]_\infty}{k_{\mathrm{t}}/k_{\mathrm{p}}\ln[\mathrm{M}_0]/[\mathrm{M}]_\infty}$$

and

$$E_{\mathrm{DP}} = E_{\mathrm{p}} - E_{\mathrm{t}}$$

Since the steady-state component of the molecular-weight law would give the same equation for degree of polymerisation the values so obtained can be quoted with confidence.

Since $E_{\mathrm{DP}} = -3{\cdot}5$ and $E_{\mathrm{p}} = 12{\cdot}5$ we can calculate that $E_{\mathrm{t}} = 16{\cdot}0$ kcal.mole^{-1}.

This high value for E_{t} explains why true termination is frozen out at very low temperatures and monomer transfer still exists with the very high molecular weights of 500,000. Nevertheless, it is difficult to predict a mechanism of termination which would have so high an activation energy. It has been assumed that termination is by anion recombination but this is apparently normally a simple process not requiring much activation energy. However, it is possible that the large size of the gegenion $\mathrm{BF_3OEt^-}$ leads to great stability through delocalisation of the electron, and the species would then be reluctant to form a covalent bond with the carbonium ion.

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[3] F. S. Dainton, *Sci. Proc. Roy. Dublin Soc.*, 1951, **25**, 148.

[4] M. J. Hayes and D. C. Pepper, *Proc. Roy. Soc.*, 1961, *A*, **263**, 63.

APPENDIX

Viscosity–Molecular Weight Relations.—In Part XI, the following relationship was used between intrinsic viscosity $[\eta]$ and number average (osmometric) molecular weight $\bar{M}_n$, for poly(isobutyl vinyl ether) specimens produced by boron trifluoride–diethyl ether complex in n-hexane–toluene, at high conversions at −78°;

$$[\eta] = 1\cdot6 \times 10^{-3}\, \bar{M}_n^{0\cdot6}$$

The data on which this is based are shown in Figure 12.

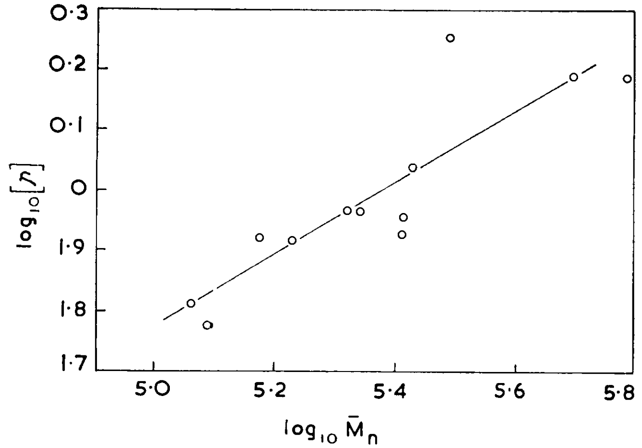

FIGURE 12. The viscosity–molecular weight relation for polymers produced at −78°

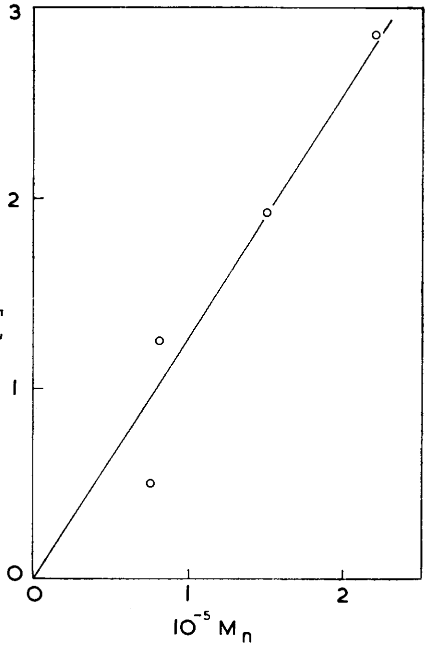

FIGURE 13. The viscosity–molecular weight relation for polymers produced at −40°

In Part XII the relationship used, for polymers produced by the same system, but at −40°, above the point (*ca.* −65°) at which there is a change from the stationary to non-stationary mechanisms, is

$$[\eta] = 1\cdot33 \times 10^{-5}\, \bar{M}_n$$

This is based on the data shown in Figure **13**, which clearly can only be regarded as approximate, in view of the small number of points.

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