

1356. *The Kinetics of Ionic Polymerisation. Part XI.* Low-temperature Polymerisation of Isobutyl Vinyl Ether in n-Hexane-Toluene as Solvent*

By G. J. BLAKE and D. D. ELEY

The isotactic polymerisation of isobutyl vinyl ether catalysed by boron trifluoride ether complex in 50:50 n-hexane-toluene solvent is homogeneous over the first 20% of polymerisation at least, and follows $[M]^2[C]$ kinetics. There is a change point around -65° ; below this activation energies are $E = 6.4 \text{ kcal.mole}^{-1}$ for overall velocity and $E_{DP} = +2.6$ for molecular-weight variation with temperature; above -65° $E = 12.5$ and $E_{DP} = -3.5$. It is tentatively concluded that monomer transfer dominates at lower temperatures and spontaneous termination at higher temperatures. However, this interpretation is complicated by the observation that the degree of isotacticity of the polymer (which could only be isolated at 100% polymerisation) decreases with increase in temperature (and also with increase in monomer and catalyst concentration). This may denote some increase in activation energy for propagation with increase in temperature. Also degree of isotacticity of polymer decreases with increases in monomer and catalyst concentration, a result which may be associated with increase in heterogeneity in the system.

THE system isobutyl vinyl ether, boron trifluoride diethyl ether complex, n-hexane-toluene was studied under conditions producing isotactic polymer. Okamura *et al.*¹ have shown that this polymerisation may proceed heterogeneously or homogeneously depending on the order of adding the reagents.

The heterogeneous system was studied by Eley and Johnson² and a rate law of $-d[M]/dt = k[M]^2[C]$ established.† A homogeneous mechanism was proposed and it

* Part X, D. D. Eley and A. F. Johnson, *J.*, 1964, 2238.

† *Nomenclature.*—M is used to denote monomer, M_n dead polymer, and M^* and M_n^* the activated species, and we discontinue the term P_1 for monomer, used in a recent review (The Chemistry of Cationic Polymerisation, ed. P. H. Plesch, Pergamon Press, 1963), and in Parts VIII to X.

¹ S. Okamura, T. Higashimura, and H. Yamamoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1958, 61, 1636.

² D. D. Eley and A. F. Johnson, *J.*, 1964, 2238.

was surmised that the homogeneous and heterogeneous reactions were the same and that the propagation step was homogeneous in each case.

The present Paper considers some details of the true homogeneous reaction where monomer is added to a solution of catalyst. Further evidence is offered supporting isotactic propagation in a homogeneous phase and without the need of a catalyst solid surface.

EXPERIMENTAL

Reaction Velocity.—The technique used was similar to that of Eley and Johnson.² An adiabatic calorimeter similar to that of Biddulph and Plesch³ was used to measure reaction rates. The solvents hexane and toluene were dried over calcium hydride and regularly degassed for 2 weeks. These were cold-distilled into burettes and from there to the calorimeter.

The catalyst was added by metering gaseous boron trifluoride and ether into a bulb of known volume and cold-distilling from these to the calorimeter. Finally, after thorough stirring at the required steady temperature, the reaction was started by breaking a bulb of monomer under the catalyst solution. A vacuum of 10^{-5} mm. Hg was always obtained and maintained for several hours before a run. All taps isolating the reaction system were of the greaseless type. All runs except for activation energy runs were at an initial temperature of -78° and this temperature was achieved by passing air cooled by liquid nitrogen through a large Dewar vessel surrounding the calorimeter.

Molecular Weights.—Samples isolated after activation-energy runs were investigated by osmometry and viscometry and a relationship established, between intrinsic viscosity and number average molecular weight. The graph is shown in the Appendix to Part XII, which follows. All other molecular weights were determined by viscosity. The osmometer employed was of a design by Pinner and Stabin⁴ and measurements were made of polymer in 1, $\frac{1}{2}$, and $\frac{1}{4}$ % concentrations in tetrahydrofuran at $28.50^{\circ} \pm 0.01^{\circ}$. An Ostwald type viscometer was used which could be filled and emptied by means of a syringe. Measurements were made on 1, $\frac{1}{2}$, $\frac{1}{4}$ % concentrations in tetrahydrofuran solution at $28.50^{\circ} \pm 0.05^{\circ}$.

Degree of Isotacticity.—The method of Okamura, Higashimura, and Sakurada⁵ was employed. Solutions of polymer of $\frac{1}{2}$ % concentration in ethyl methyl ketone were slowly cooled in an alcohol bath by adding solid carbon dioxide. A fairly regular rate of fall of temperature of about $0.2^{\circ}/\text{min.}$ was achieved with practice. The precipitation temperature was noted visually and taken as an index of the degree of isotacticity.

Materials.—*Isobutyl vinyl ether.* The monomer was purified by the method of Schildknecht, Zoss, and McKinley.⁶ The product was then distilled through a column of glass helices equivalent to 30 theoretical plates, and the product was checked for purity by gas chromatography.

Boron trifluoride. The gas from a cylinder supplied by Imperial Smelting Co. (Avonmouth) was passed into diethyl ether cooled in an ice-bath. When no more gas would dissolve the complex was poured into B.D.H. pure calcium fluoride and mixed to a stiff paste. This was dried, pulverised, and pumped to 10^{-5} mm. Hg at 150° then heated to 350° to regenerate the boron trifluoride which was passed through NaF to remove HF and stored in a glass bulb ready for use.

Diethyl ether. The spectroscopically pure product from B.D.H. was used without further purification.

Toluene. Sulphur-free toluene (B.D.H.) was shaken with 10% sulphuric acid then water and finally sodium carbonate solution. After drying (CaCl_2) the product was twice distilled in air and once *in vacuo*.

n-Hexane. The B.D.H. product was shaken with 0.1N-potassium permanganate in 10% sulphuric acid solution, then water, and finally 0.1N-potassium permanganate in 10% sodium hydroxide solution. After drying (CaCl_2) the product was twice distilled in air and once *in vacuo*.

RESULTS

The boron trifluoride–diethyl ether complex as catalyst was completely dissolved in the 50 : 50 : toluene–hexane solvent before the isobutyl vinyl ether monomer was introduced. The

² R. H. Biddulph and P. H. Plesch, *Chem. and Ind.*, 1959, 1482.

³ S. H. Pinner and J. V. Stabin, *J. Polymer Sci.*, 1952, **9**, 575.

⁴ S. Okamura, T. Higashimura, and I. Sakurada, *J. Polymer Sci.*, 1959, **39**, 507.

⁶ C. E. Schildknecht, A. O. Zoss, and C. McKinley, *Ind. Eng. Chem.*, 1948, **39**, 180.

reaction thereafter appeared to proceed homogeneously and precipitation of polymer was not observed until at least 0.1 mole l^{-1} of monomer had polymerised. Thus the initial slopes taken over the first 20% of the time-course plots can be assumed to refer to a truly homogeneous reaction. Some typical reaction curves are shown in Figure 1.

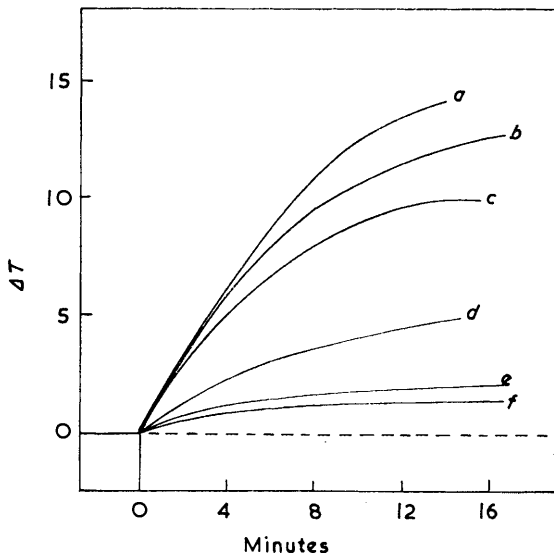


FIGURE 1. Rise in temperature T° as a function of time for $[C] = 6.5 \times 10^{-3}$ mole l^{-1} and -78° and the following values of initial monomer concentration $[M]_0$, in mole l^{-1} : (a) 0.496, (b) 0.435, (c) 0.373, (d) 0.248, (e) 0.186, (f) 0.124.

No attempt was made to derive "internal order" of reaction from these graphs, because of complicating factors, such as temperature rise and heterogeneity, which are apparent at higher degrees of conversion.

Induction Periods.—No induction period was observed when carefully purified reagents were used. Traces of water caused long induction periods but this effect was not studied quantitatively.

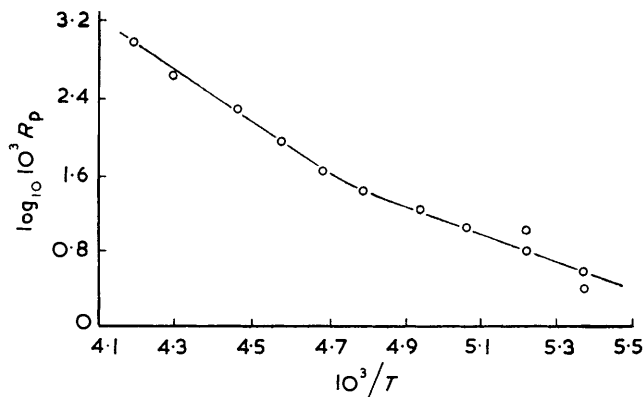


FIGURE 2. Activation-energy plot for $[C] = 6.55 \times 10^{-3}$ mole l^{-1} and $[M] = 0.248$ mole l^{-1} .

Yields.—The yield of polymer was invariably 100% based on initial monomer concentration. This applied to the whole range of monomer, catalyst, and temperature variations.

Reaction Rates.—Using the adiabatic calorimeter, we measured rates at a fixed monomer and catalyst concentration between -40 and -85° . Figure 2 shows variation of overall velocity R_p with initial temperature and an overall activation energy of 6.4 kcal.mole $^{-1}$ is calculated for the reaction occurring within the temperature range -65 to -85° . In the range -65 to -40° , E is 12.5 kcal.mole $^{-1}$. Figure 2 indicates a rather abrupt change point at -65° , but this may be fictitious to some extent, since the kinetics change from $[M]^2[C]$ at -78° to $[M][C]$ at -40° (see Part XII). It may be that the true change point is higher than -65° , or that there

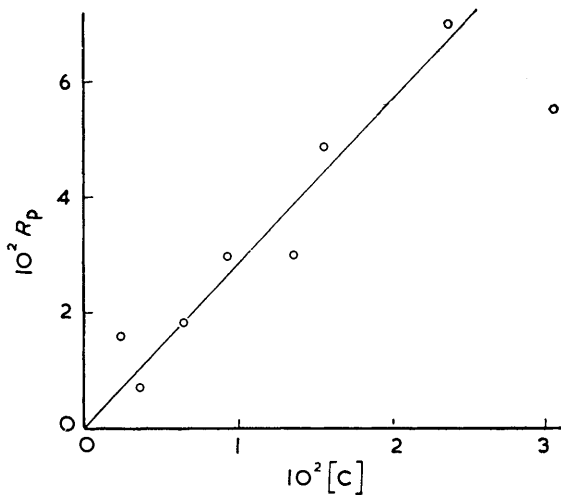


FIGURE 3. Dependence of rate on $[C]$, for $[M]_0 = 0.22$ mole l^{-1} at -78°

FIGURE 4. Dependence of rate on $[M]_0^2$ for $[C] = 6.5 \times 10^{-3}$ mole l^{-1} at -78°

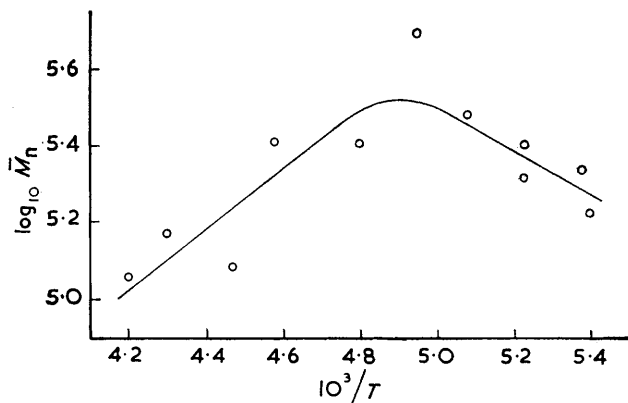
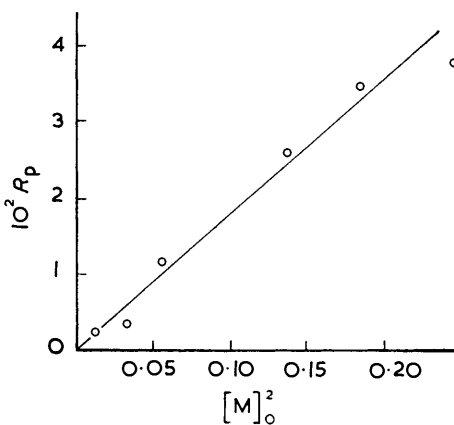


FIGURE 5. Activation-energy for molecular weight

is a gradual region of change over from say -70 to -50° . Overall velocities of polymerisation R_p were examined as a function of monomer and catalyst concentrations at -78° . The results shown in Figures 3 and 4 lead to

$$R_p = -d[M]/dt = k[M]^2[C] \text{ at } -78^\circ$$

where k is evaluated at 0.67 $l.^2$ mole $^{-2}$ sec. $^{-1}$.

Molecular Weights.—All runs went to 100% yield and no success was achieved in stopping the reaction at 20%. Molecular-weight measurements therefore refer to the whole range of monomer,

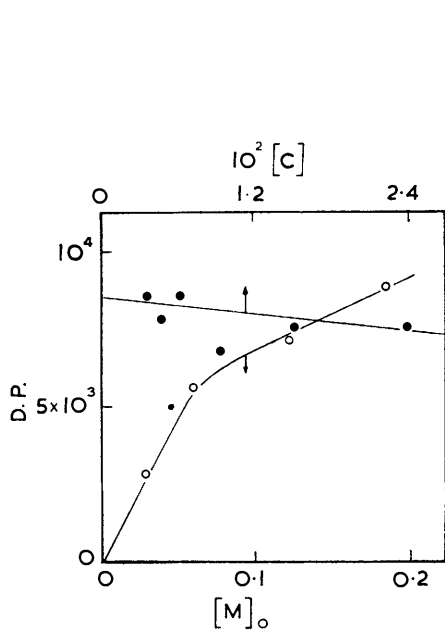


FIGURE 6. Dependence of degree of polymerisation DP on $[C]$ and $[M]_0$

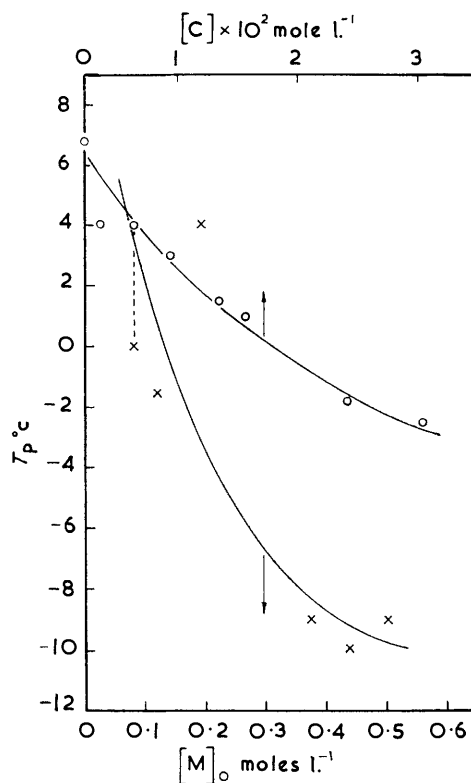
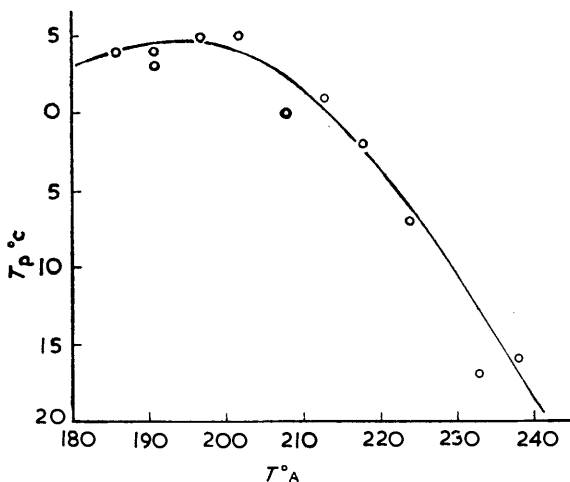


FIGURE 7. Dependence of precipitation temperature T_p on $[C]$ and $[M]_0$

FIGURE 8. Dependence of precipitation temperature T_p °C of product on the polymerisation temperature T_A



catalyst, and temperature variation in a single run. The temperature rise was constant except for runs where monomer concentration was varied. In this case samples for molecular-weight determination were prepared in a thermostatted vessel instead of the calorimeter. Even so,

at high monomer concentrations, the temperature rose about 10° , which was a complicating factor in the interpretation of the results.

Number average molecular weights \bar{M}_n were compared with the intrinsic viscosity by using a Mark-Houwink relationship (see Appendix to Part XII)

$$[\eta] = 1.6 \times 10^{-3} \bar{M}_n^{0.6}$$

Molecular weight of the product as a function of temperature is shown in Figure 5 and as a function of monomer and catalyst concentration in Figure 6. Tetrahydrofuran was chosen as a solvent for molecular-weight studies because of its good solvent power. Benzene, carbon tetrachloride, chloroform, acetone, ethyl methyl ketone, and n-hexane all failed to dissolve the highly isotactic polymers.

Degree of Isotacticity.—Unfortunately there is no indication that precipitation temperature varies linearly with degree of isotacticity so that absolute values of the latter could not be

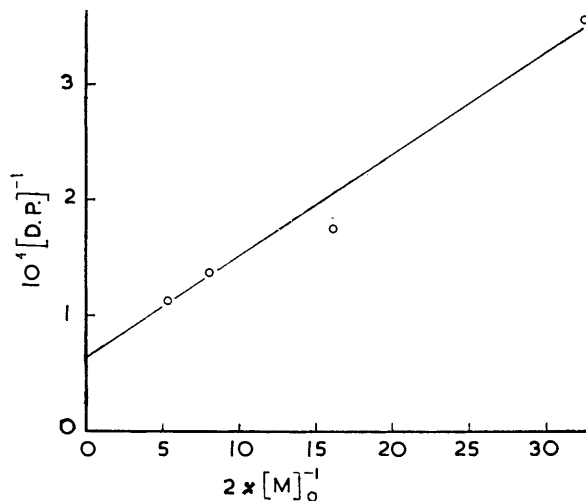


FIGURE 9. Gregg-Mayo plot showing dependence of degree of polymerisation DP on initial monomer concentration $[M]_0$

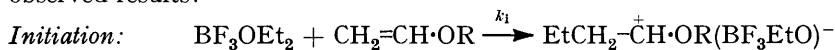
calculated. Also it seems that there is doubt as to what precipitation temperatures correspond to 0 and 100% isotacticity. Approximate values of -40 and $+10^\circ$ have been suggested for these respectively.⁵ Precipitation temperatures as a function of initial monomer concentration, initial catalyst concentration, and initial reaction temperature are shown in Figures 7 and 8.

Effect of Co-catalyst.—Variations in rate with co-catalyst concentration showed that with a ratio $(BF_3) : (Et_2O) > 1$ the rate was very much faster than with $(BF_3) : (Et_2O) = 1$, which in turn was slightly faster than with $(BF_3)_2 : (Et_2O) < 1$. This indicates that the ether has some retarding effect on the reaction when in excess. Excess of boron trifluoride probably complexes with traces of water to give a very active catalyst (cf. Eley and Johnson²) and this causes the marked increase in rate.

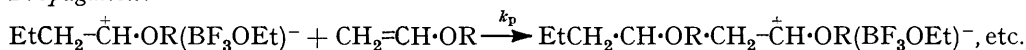
The molecular weight passes through a maximum around -65° , with values for the apparent activation energy for degree of polymerisation $E_{DP} = +2.6 \text{ kcal.mole}^{-1}$ at -78° and $E_{DP} = -3.5 \text{ kcal.mole}^{-1}$ at -40° .

DISCUSSION

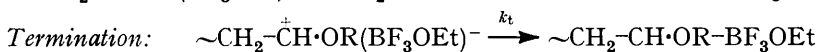
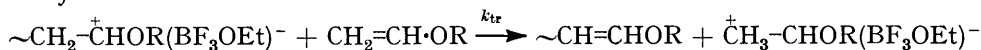
From the kinetic law established above, it appears that the normal steady-state approximation applies. A simple kinetic scheme can therefore be suggested to account for the observed results:



Propagation:



Transfer:



If it is assumed that

$$d[\text{M}^{\oplus}_n]/dt = 0, \text{ then } R_p = -d[\text{M}]/dt = \frac{k_p k_i}{k_t} [\text{M}]^2 [\text{C}]$$

and $\text{DP} = \frac{k_p [\text{M}]}{k_t + k_{\text{tr}} [\text{M}]}$; thus $\text{DP}^{-1} = \frac{k_t}{k_p [\text{M}]} + \frac{k_{\text{tr}}}{k_p}$ (see Figure 9)

Since the reaction goes to 100% conversion, we crudely approximate $[\text{M}]$ by $[\text{M}]_0/2$, the usual procedure. At -78° the available results give

$$k_t/k_p = 0.88 \times 10^{-5} \text{ mole l.}^{-1} \text{ and } k_{\text{tr}}/k_p = 0.6 \times 10^{-4}$$

and the ratio of transfer to termination velocities is

$$R_{\text{tr}}/R_t = -6.8[\text{M}].$$

Thus, transfer is dominant at $T = -78^\circ$ and $[\text{M}] \geq 1 \text{ mole l.}^{-1}$. It is also apparent that (cf. p. 7408)

$$k_p k_i/k_t = 0.67 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1} \text{ at } -78^\circ$$

and hence $k_i = 0.67 \times 0.88 \times 10^{-5} = 5.9 \times 10^{-6} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at -78° .

Energetics.—For $T = -78^\circ$ approximately, the overall activation energy is

$$E = E_p + E_i - E_t = 6.4 \text{ kcal.mole}^{-1}$$

and for degree of polymerisation of the polymer

$$E_{\text{DP}} = +2.6 \text{ kcal.mole}^{-1}$$

The initial monomer concentration used for activation energy runs is $[\text{M}]_0 = 0.25 \text{ mole l.}^{-1}$, therefore

$$R_{\text{tr}}/R_t = 1.7$$

and transfer is predominating, but not to an overwhelming extent at this monomer concentration. So we cannot identify the observed activation energy for degree of polymerisation with either $E_p - E_t$ or $E_p - E_{\text{tr}}$ and the result may be discussed only qualitatively. A positive energy of activation for molecular weight has not been observed previously. We can explain this result by assuming that the activation energy of true termination is greater than the activation energy for transfer. This is the reverse of what is usually observed but support for our postulate comes from Kennedy⁷ who showed that at -78° , using catalyst and monomer concentrations similar to ours, 99.3% of the chains were initiated by transfer and only 0.7% by direct catalytic initiation. From studies outside the scope of this Paper we have evidence⁸ that monomer transfer is largely absent at -40° . It is likely, then, that the observed activation energy for molecular weight at -78° , $E_{\text{DP}} = E_p - E_{\text{tr}}$.

Finally, if this steady-state mechanism exists at -40° , then the activation energy for molecular weight is indeed $E_p - E_t$ and this would correspond with the negative value of -3.5 kcal.mole .

Thus, if $E_{\text{DP}} = E_p - E_t = -3.5$, it follows that $E_i = 9.9 \text{ kcal.mole}$ and, combining this value with the observed rate constant for initiation at -78° , $k_i = 5.9 \times 10^{-6} \text{ l. mole}^{-1} \text{ sec.}^{-1}$, we calculate a value for the entropy of initiation at -78° of $\Delta S_i^\ddagger = -32.8 \text{ e.u.}$

The assumption that the result shown in Figure 5 is due only to the change from termination to transfer as we lower the temperature below -65° can be true only to a first approximation because it assumes that E_p is constant over the whole temperature range.

⁷ J. P. Kennedy, *J. Polymer Sci.*, 1959, **38**, 263.

⁸ J. D. Coombes and D. D. Eley, *J.*, 1957, 3700.

In support, however, by analogy with the radical polymerisation of methyl methacrylate,⁹ we may assume that although the activation energy for atactic propagation E_{pa} will be larger than for isotactic propagation E_{pi} , the difference $E_{pa} - E_{pi}$ is likely to be less than 1 kcal.mole⁻¹, hardly sufficient to account for the observed change in E at -65° . It follows, however, that there is some uncertainty in the values of E_i and ΔS_i^\ddagger calculated above assuming a constant value of E_p .

A further difficulty is that while the isotactic character of the polymer decreases with rising temperature, it also decreases with monomer and catalyst concentration. One possible explanation of the effect of increase in catalyst concentration is that it decreases tacticity of the product by making the system partially heterogeneous (cf. ref. 10). Another possible explanation involved two distinct propagation mechanisms, the usual one involving the growing chain and monomer for isotactic propagation, and a new one between the growing chain and a monomer-catalyst complex for atactic propagation, with spontaneous termination in both cases as before. However, on this mechanism, the DP of the atactic polymer should increase with catalyst concentration, which is not the case. This, therefore, causes us to favour the former explanation involving heterogeneity, but the matter is still obscure.

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⁹ F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, 1960, **44**, 173.

¹⁰ S. Okamura, T. Higashimura, and T. Kodama, *Kobunshi Kagaku*, 1960, **17**, 179.
