16. *Developments in the Theory of Cationic Polymerisation. Part IV.*[1] *A General Theory Explaining Discontinuous Variations of the Degree of Polymerisation with the Concentration of the Reagents.*

By P. H. Plesch.

In cationic polymerisations it is commonly found that the degree of polymerisation (D.P.) changes abruptly as the concentration of one of the constituents of the reaction mixture is varied. These variations, especially the very sharp D.P. peaks, have not been explained hitherto in detail. A theory is developed which accounts quantitatively for all forms of D.P. variation in terms of neutralisation, or formation, or both successively, of chain-breaking agents, as the concentration of the relevant reactant is changed. The theory is illustrated by applying it to six examples from the literature.

One of the most characteristic and common features of cationic polymerisation is that, as the concentration of one of the components of the reaction mixture is changed, the degree of polymerisation (D.P.) of the polymers varies in a manner such that the relevant curve shows a more or less abrupt, sometimes even catastrophic, change of direction and cannot be represented simply by the Mayo equation.

It was realised that the phenomenon was probably due to impurities,[2,3d] and Ambroz,

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[1] Part III, Plesch, *Ricerca sci.*, 1955, **25**, 140.

[2] (*a*) Zlamal, Ambroz, and Vesely, *J. Polymer Sci.*, 1957, **24**, 285; (*b*) Vesely, *ibid.*, 1958, **30**, 375; (*c*) Ambroz and Zlamal, *ibid.*, 1958, **30**, 381; (*d*) Ambroz and Zlamal, *ibid.*, 1958, **29**, 595; (*e*) Zlamal, Symposium on Macromolecules, Wiesbaden, 1959, Paper III A 14; (*f*) Zlamal, Ambroz, and Ambroz, *Chem. Listy*, 1955, **49**, 1606; (*g*) Zlamal and Kazda, Symposium on Macromolecules, Moscow, 1960.

[3] Kennedy and Thomas, *J. Polymer. Sci.*, (*a*) 1960, **46**, 481; (*b*) 1961, **55**, 311; (*c*) Thomas Sparks, Frolich, Otto, and Muller-Cunradi, *J. Amer. Chem. Soc.*, 1940, **62**, 276; Kennedy and Thomas, *J. Polymer Sci.*, (*d*) 1960, **46**, 233; (*e*) 1961, **49**, 189.

Kazda, Vesely, and Zlamal[2] investigated from this point of view the polymerisation of isobutene by aluminium chloride. A prominent feature of their results was that with increasing concentration of catalyst the D.P. went through a sharp maximum. Vesely attempted the formulation of a quantitative theory of this phenomenon.[2b] He suggested that the region where the D.P. decreases with the concentration of aluminium chloride is to be explained in terms of chain-breaking by " bases," and that beyond the turning point of the curve 1/D.P. is proportional to $K_e[AlCl_3]$, where K_e was supposed to be a (composite) equilibrium constant governing the concentration of " bases " (especially free anions) in the reaction mixture. Unfortunately the exposition of these interesting ideas is so condensed that the argument is obscure, and the many, apparently *ad hoc*, assumptions make the validity of the conclusions far from obvious. There is also an implication that these ideas could be applied to other types of D.P. variation, but no attempt at elaboration; a more detailed discussion of the work of Vesely and his co-workers has been presented elsewhere.[4]

The object of the present paper is to expound a theory which accounts in an algebraically precise manner for all known forms of D.P. curves. Four general types of such curves are known: (A) The D.P. goes through a maximum. (B) The D.P. rises to a maximum constant value. (C) The D.P. falls to a minimum constant value. (D) The D.P. goes through a minimum. These types are illustrated in Figs. 1, 5—7. In a few systems the D.P. varies in a manner which can be considered as a combination of two of these types.

The variation of the D.P. can be further classified into four categories according to the reagent, the variation of the concentration of which produces the change in the D.P.: (1) Catalyst (metal halide). (2) " Additive," which *may* be a co-catalyst. (3) Monomer. (4) Solvent composition. These Categories are illustrated in Figs. 1—4.

The most striking and also the most enigmatic type of D.P. variation is type A, and it is also the most common in that it occurs in all four categories. For these reasons the theory will be explained in detail with reference to this type, and the other types will then be considered more briefly. After the development of the general theory, some examples of its application to results in the literature will be elaborated.

GENERAL THEORY

Type (A) Variation.—The essence of the theory is that curves such as those shown in Figs. 1—4 are not considered as a whole, but are regarded as made up of two parts. Consider a generalised curve of this type which represents the variation of D.P. with the concentration of a reagent F. Let the concentration of this reagent be f, and let the value of f corresponding to the D.P. peak be g (Fig. 8).

For the branch of the curve representing values of $f > g$ it is evident that an increase in f is producing an increase in the concentration of a chain-breaking reagent,* which may be F itself, or a compound derived from F, the concentration of which is proportional to $(f - g)$. If the D.P. of the polymer is governed by a number of chain-breaking reactions, the rates of which can be represented generally by terms of the form $k_{x_i}[X_i]^{x_i}[P_n^+]$, where k_{x_i} is the rate constant for the reaction of growing chains of concentration $[P_n^+]$ with the i-th chain breaking agent, X_i, and x_i is the order of that reaction with respect to X_i, and if the rate of propagation is given by $k_p[P_1][P_n^+]$, then we can write the Mayo equation in the form

$$\frac{1}{\text{D.P.}} = \frac{k_f(f-g)}{k_p[P_1]} + \frac{1}{k_p[P_1]} \cdot \sum_i k_{x_i}[X_i]^{x_i}, \qquad (1)$$

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* In the following discussion we shall use the non-committal term " chain-breaker " since it is not possible to determine from studies of D.P. alone whether such a one is a terminator or a transfer agent.

[4] " The Chemistry of Cationic Polymerization," Ed. Plesch, Pergamon Press, London, 1963, Ch. 4.

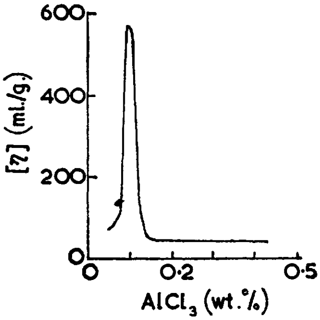

FIG. 1. Variation of the intrinsic viscosity of polyisobutene with concentration of $AlCl_3$.[2a]

Temp. −78°. Solvent: ethyl chloride. [CH_2:CMe_2] = 4·15M.

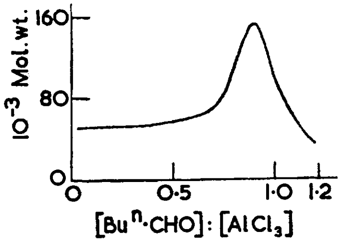

FIG. 2. Variation of the molecular weight of polyisobutene with the ratio [Bu^n·CHO] : [$AlCl_3$].[2c]

Temp. −78°. Solvent: ethyl chloride. [CH_2:CMe_2] = 2M. [$AlCl_3$] = 8·1mM. [Bu^n·CHO] = 0—10 mM.

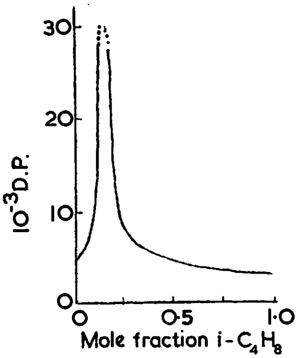

FIG. 3. Variation of D.P. with concentration of isobutene.[3e]

Temp. −78°. Solvent: methyl chloride. [$AlCl_3$] = 3·76 × 10^{-4}M.

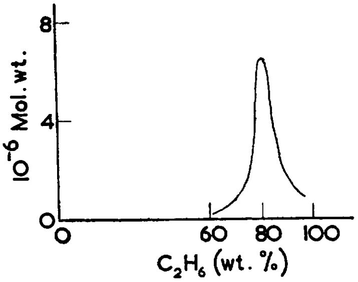

FIG. 4. Variation of the molecular weight of polyisobutene with the composition of the solvent.[2f]

Temp. −80°. Solvent: ethyl chloride + ethane. [$AlCl_3$] = 0·3% by wt. [CH_2:CMe_2] not given.

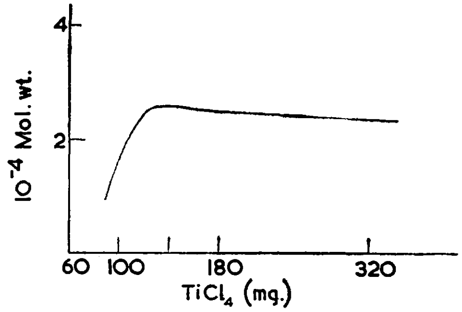

FIG. 5. Variation of the molecular weight of polyisobutene with the concentration of catalyst in the presence of diethyl ether.[2b]

Temp. −78°. Solvent: ethyl chloride. [Et_2O] = 16·2 mM. [CH_2:CMe_2] and vol. of reaction mixture not given.

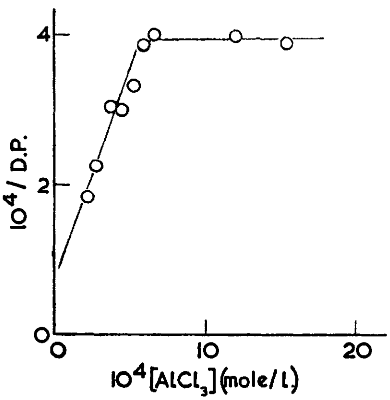

FIG. 6. Mayo plot of 1/D.P. against catalyst concentration for the polymerisation of undiluted isobutene at −78°.[3a]

where k_f is the rate constant for the reaction between growing chains and F, or the compound formed from F. It follows, as is well established, that a plot of 1/D.P. against f gives a straight line from the slope of which k_f/k_p can be found.

TABLE 1.

Scheme of chain-breaking (c.b.) reactions for different types of system.

Reaction	F	+	G	→	H
Concn. of reagent when $f < g$	0		$g - f$		f
Concn. of reagent when $f > g$	$f - g$		0		g
C.b. rate-constant	k_f		k_g		k_h

Case no.	Type	k_f	k_g	k_h	Condition	$k_p[P_1]/\text{D.P.} - J_i =$
1	A	+	+	+	$f < g$	$k_g(g - f) + k_hf$
					$f > g$	$k_f(f - g) + k_hg$
2	B	0	+	0	$f < g$	$k_g(g - f)$
					$f > g$	0
3		0	+	+	$f < g$	$k_g(g - f) + k_hf$
					$f > g$	k_hg
4	C	0	0	+	$f < g$	k_hf
					$f > g$	k_hg
Additional reaction H + F → L, L is not c.b.: when $f < g$, $h = f$; when $f > g$, $h = 2g - f$.						
5	D	0	0	+	$f < g$	k_hf
					$f > g$	$k_h(2g - f)$

It is assumed that the formation constants of complexes H and L are very large.
+ denotes that the rate constant is finite.

We next consider the rising branch of the D.P. curve for which $f < g$. This has been the main source of difficulty in understanding these curves. The difficulty is immediately removed if we consider that *as* f *becomes less than* g, *the concentration of a chain-breaking agent* G *increases.* We make the plausible assumption that the total concentration of this agent is g, and that it forms a complex H with F. If this complex contains equimolar quantities of F and G, and if it is very stable, then the concentration of agent which is free is simply $(g - f)$, and the point g represents the exact " neutralisation " of the agent. Let the rate of chain breaking by the agent G be given by $k_g(g - f)[P_n^+]$. Further, it is necessary to assume that the complex H formed can also act as a chain-breaking agent. Let the rate of the corresponding reaction be given by $k_hf[P_n^+]$ for all $f < g$, and $k_hg[P_n^+]$ for $f > g$. These relations are summarised in Table 1; the Mayo equation embodying them takes the following forms:

For $f < g$:

$$1/\text{D.P.} = k_g(g - f)/k_p[P_1] + k_hf/k_p[P_1] + J_i/k_p[P_1], \qquad (2)$$

and for $f > g$:

$$1/\text{D.P.} = k_f(f - g)/k_p[P_1] + k_hg/k_p[P_1] + J_i/k_p[P_1], \qquad (3)$$

where the term J_i represents the summation in the second term of equation (1). Equations (2) and (3) can be transposed to the more useful forms

$$1/\text{D.P.} = [(k_h - k_g)f + k_gg + J_i]/k_p[P_1]; \qquad (4)$$

$$1/\text{D.P.} = [k_ff + (k_h - k_f)g + J_i]/k_p[P_1]. \qquad (5)$$

From equations (4) and (5) it follows that the slope of the left-hand branch of the Mayo plot gives $(k_h - k_g)/k_p$, and that of the right-hand branch gives k_f/k_p. The two branches must meet at $f = g$ at the value of 1/D.P. which we will denote by $1/\text{D.P.}_c$ and is given by the equation

$$1/\text{D.P.}_c = (k_hg + J_i)/k_p[P_1]. \qquad (6)$$

This means that, if a series of groups of experiments is conducted in such a way that in each experiment f is varied over the useful range and g is constant in each group, but is varied from group to group, then eqn. (6) described the variation of $1/\mathrm{D.P.}_c$ with g among the different groups of experiments; in other words, equation (6) describes the locus of the apices of the Mayo plots. A set of results of this type is discussed in detail in example 1 below.

Generalised Treatment.—The analogous argument for types B, C, and D has been set out in detail elsewhere.[4] Here we shall give a more general treatment.

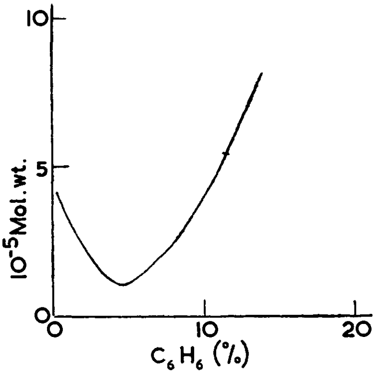

FIG. 7. Variation of the molecular weight of polyisobutene with solvent composition.[2a]

Temp. −78°. Solvent: ethyl chloride + benzene. [$CH_2{:}CMe_2$] and [$AlCl_3$] not given.

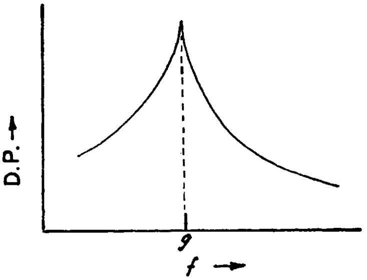

FIG. 8. Schematic representation of a type (A) variation of D.P. with concentration f of a reagent F.

Consider that the concentration h of the complex H is governed by an equilibrium, so that

$$h = K(f - h)(g - h). \qquad (7)$$

If F, G, and H (or substances originating directly from them) are (potential) chain-breakers, the D.P. will be governed by a Mayo equation of the form:

$$k_p[P_1]/\mathrm{D.P.} - J_i = k_f(f - h) + k_g(g - h) + k_h h \qquad (8)$$

$$= (k_h - k_g - k_f)h + k_g g + k_f f, \qquad (9)$$

and $$h = \tfrac{1}{2}(K^{-1} + g + f) - \tfrac{1}{2}[(K^{-1} + g + f)^2 - 4gf]^{\frac{1}{2}}.$$

The minimum in the Mayo plot will now no longer be at $f = g$, but will be displaced in a direction and by an amount determined by the magnitude of K. Moreover, the more stable the complex, the more abrupt will be the change of slope of the D.P. curve. For the case of strong complexing (K great) and F, G, and H all chain-breakers, equation (9) reduces to equation (4) or (5). The forms which the right-hand side of equation (9) takes in various other cases (but all with large K) are set out in Table 1, and the corresponding phenomena are explained below.

Type (B). D.P. growing to Maximum, Constant Value.—The behaviour shown in Fig. 5 indicates that the system contains a chain-breaker G at a concentration g and that reagent F, which is not itself a chain-breaker, combines with it, so that at for $f > g$ the concentration of chain-breaker is constant. If the complex H formed from the chain-breaking agent and reagent F is not itself a chain-breaker, we have case 2; if it is a chain-breaker, we have case 3 of Table 1.

Type (C). D.P. falling to Minimum, Constant Value.—In this case (Fig. 6) there is present in the system a reagent, G (at a concentration g), which itself may or may not be a chain-breaker but forms a (more effective) chain-breaking reagent (complex) H with F, whilst F itself is not a chain-breaker (case 4 of Table 1).

Type (*D*). *D.P. passes through Minimum.*—This pattern, illustrated in Fig. 7, can be interpreted on the supposition that as the concentration, f, of reagent F is increased the concentration of chain-breaking agent H increases. Since this does not continue indefinitely as f increases, it follows that the chain-breaking agent H is formed from F by reaction with a constituent of the reaction mixture, the concentration of which is g. When $f > g$, the excess of f reacts with the chain-breaking complex H to give a further complex L which is either not a chain-breaker or a much less effective one than H (see case 5 of Table 1). An instance of this behaviour is discussed in example 6 below.

Generalised Stoicheiometry.—The treatment can be generalised further by considering the formation of other than binary complexes, as illustrated in the equation:

$$x\mathrm{G} + y\mathrm{F} = z\mathrm{H}$$

In this case, if the formation constant K of H is very great

$$H = zf/y \text{ when } yg > xf,$$

and

$$h = zg/x \text{ when } yg < xf.$$

If K has an intermediate value, it is given by the equation:

$$K = h^z/(f - yh/z)^y(g - xh/z)^x$$

A detailed treatment of results obtained with systems of the kind discussed in examples 5 and 6 may require the use of equations of this type.

Spurious Correlations.—If the reagent F which is, or which may form, or may react with, a chain-breaking agent, is contained as an impurity in the solvent, then increasing the monomer : solvent ratio will decrease f; if it is contained in the monomer, the reverse will happen. In this way a spurious variation of D.P. with monomer concentration may arise, which will be superposed upon the normal effects due to variations in the rate of monomer transfer and solvent transfer with changing monomer concentration. Such effects can only be elucidated by the use of monomer and solvent specimens purified in different ways, as has been demonstrated very effectively by Zlamal, Ambroz, and Vesely (see example 1).

Fontana-Kidder Propagation.—If the propagation is not the normal bimolecular reaction, but unimolecular, as first found by Fontana and Kidder in the polymerisation of propene, the rate of the propagation is given by

$$V_p = k'_{\mathrm{p}}[\mathrm{P}_n{}^+].$$

The rate of chain-breaking is made up of the rates of unimolecular termination and monomer transfer, $k_{\mathrm{t}} + k_{\mathrm{m1}} = J_{\mathrm{o}}$, say, and the rate of bimolecular chain-breaking by various reagents, J_{i}. Thus

$$k_{\mathrm{p}}'/\mathrm{D.P.} = J_{\mathrm{o}} + J_{\mathrm{i}},$$

so that the D.P. is independent of monomer concentration, ***provided*** that J_{i} does not contain a term involving $[\mathrm{P}_1]$.

If, however, the monomer contains as impurity the reagent F, then the D.P. will show a dependence on monomer concentration, the form of which will be determined by the nature of F, and hence its reactions.

Effect of Temperature.—Another aspect of this matter is the effect of temperature on the pattern of the D.P. curves. One would expect the dissociation constant of the complexes involved to decrease with increasing temperature. In agreement with this expectation one finds quite generally that at higher temperatures, say between +30° and −30°, all the D.P. curves are much more rounded than in the temperature region below about −50°. Unfortunately, only two systems have been investigated over a wide temperature range (—30° to —125°), but the results show the effect very well; this is discussed in example 5.

Electrical Conductivity.—A further topic which needs to be considered is the correlation found by Zlamal, Ambroz, and Vesely[2] between the specific conductivity of solutions (mainly in ethyl chloride) of aluminium chloride containing various quantities of a polar compound (acetonitrile, butyraldehyde, ethanol, etc.) and the D.P. of the polyisobutenes formed in these solutions. Over a certain range of concentrations there is an inverse correlation between the specific conductivity, which has a sharp minimum when the ratio $[AlCl_3]/[\text{Additive}] = 1$, and the D.P., which at the same composition shows a sharp maximum.

This evidence indicates that the principal chain-breakers in these solutions are free ions and that the 1 : 1 complexes which are formed are much less ionised and are much less effective chain-breakers than the compounds (probably 2 : 1 and 1 : 2 complexes) which are prevalent on either side of the neutralisation point. This matter is discussed further in example 5 below. The authors concluded from their results that the propagating species is also a free ion rather than an ion-pair. However, whilst this may be true, it does not follow from this evidence, since the cation in an ion-pair may well be able to react with a free anion.

One further point needs to be made which has not been expounded previously and is essential to an understanding of these experiments:

Since there is a very close correlation between the specific conductivity of the catalytic solutions, *e.g.*, $AlCl_3$,EtOH in ethyl chloride, and the D.P. of polyisobutenes obtained when isobutene is added to these solutions, it follows that the electrical condition of the solutions before and after the addition of the monomer must be essentially the same. This means that the number of solute molecules involved in the initiation of polymerisation must be negligibly small compared with the total. This is amply borne out when one calculates the number of polymer molecules formed in typical systems; it is several powers of ten smaller than the " catalyst concentration."

APPLICATIONS OF THE THEORY

The literature contains a large number of examples of the patterns of D.P. variation which have been discussed above. A list of most of the examples available is given in Tables 2—5.

The Tables include only those systems in which the D.P. variation shows a turning point or discontinuity, so that it must be classed as " abnormal " and is not amenable to analysis by the simple Mayo equation. It is, of course, impossible to discuss each in detail and those selected for such treatment in the following pages are marked in the Tables by an asterisk.

Example 1. *Type* (*A*). *Category* 1.—Zlamal, Ambroz, and Vesely have reported[2a] that, when isobutene is polymerised by aluminium chloride at —78° in ethyl chloride, the D.P. of the polymer passes through a maximum as the concentration of aluminium chloride is increased, and they showed that with progressive purification of the ethyl chloride the maximum D.P. increased and the concentration of aluminium chloride at which it occurred decreased. This concentration is to be identified with our g, and it is reasonable that it decreases with progressive purification of the solvent. The senior author later[2b] presented the same results in the form of Mayo plots, 1/D.P. against $[AlCl_3]$, and these agree with the predictions of our theory inasmuch as (*a*) all the left-hand branches and all the right-hand branches of the plots are approximately parallel, and (*b*) the points of intersection of each pair of branches increase linearly with the aluminium chloride concentration, g, at which they occur, thus confirming equation (6). A similar set of results, for polymerisations in methyl chloride, present essentially the same picture.[2b]

Vesely[2b] concluded that since the value of 1/D.P. obtained (by extrapolation) at $[AlCl_3] = 0$, was approximately the same as that obtained from Norrish and Russell's results with stannic chloride,[5] the fundamental mechanism of polymerisation by both catalysts must be the same. Whilst this may be so, it does not follow from this evidence, because the extrapolations are

[5] Norrish and Russell, *Trans. Faraday Soc.*, **1951**, **48**, 91.

TABLE 2.

Isobutene.

No.	Additive	Solvent	Type	Category	Ref.
1		CH_3Cl	A	3	3*e*
2		C_2H_5Cl	A	3	3*e*
3		CH_2Cl_2	A	3	3*c*
4		C_2H_3Cl	A	3	3*e*
5		n-C_5H_{12}	A	3	3*d, e*
6 *		C_2H_5Cl	A	3	3*b*
7 *		C_2H_3Cl	A	3	3*b*
8 *		None	C	1	3*a*
9 *		CH_3Cl	C	1	3*a*
10 *		C_2H_5Cl	A	1	2*a*
11 *		CH_3Cl	A	1	2*b*
12	$C_3H_7{\cdot}CHO$ †	C_2H_5Cl	A	2	2*c*
13	$(C_2H_5)_2O$	C_2H_5Cl	A ‡	1	2*d*
14	$CH_3{\cdot}O{\cdot}C_6H_5$	C_2H_5Cl	A ‡	1	2*d*
15	C_2H_5OH	C_2H_5Cl	A	1	2*e*
16		$C_2H_6 + CH_3Cl$	A	1	2*f*
17		$C_2H_6 + CH_3Cl$	A	4	2*f*
18		$C_2H_6 + C_2H_5Cl$	A	4	2*f*
19		$C_6H_6 + C_2H_5Cl$	D	4	2*g*
20 *		C_2H_5Cl	B	1	5, 6
21 *	$(C_2H_5)_2O$	C_2H_5Cl	B	1	2*b*
22		CH_2Cl_2	A	2	§

Catalysts: In systems 1—19 the catalyst was $AlCl_3$; in no. 20 it was $SnCl_4$; in nos. 21 and 22 it was $TiCl_4$.

Co-catalysts: In systems 1—19 and 21 the co-catalyst is unknown. It may have been adventitious water, solvent (not in nos. 5 and 8), or the additive or an impurity contained therein; in systems 21 and 22 it was water.

Temperature: For systems 6 and 7 the temperature range was −55° to −125°; for system 22 the temperature was −13°; for all other systems it was −78° to −80°.

† In this paper another 18 compounds are mentioned which as additives gave type (A) curves.

‡ These curves are unlike the normal type (A) curves in that the maximum is flanked closely by a minimum on each side.

§ Biddulph, Plesch, and Rutherford, Symposium on Macromolecules, Wiesbaden, 1959, Paper III A 10.

TABLE 3.

Styrene.

No.	Co-cat.	Solvent	Type	Category	Ref.
23	Bu^tCl	$(CH_2Cl)_2$	B	2	*a*
24	Bu^tCl	$(CH_2Cl)_2$	B	1	*a*
25	H_2O	$(CH_2Cl)_2$	A	2	*a*
26	Bu^tCl	$C_6H_5{\cdot}NO_2$	A	2	*b*
27	Pr^iCl	$C_6H_5{\cdot}NO_2$	A	2	*b*
28	Unknown	SO_2	A	3	*c*
29	Unknown	SO_2	C	1	*c*

In all experiments included in this Table the catalyst was $SnCl_4$, the temperature 25°.

a, Colclough and Dainton, *Trans. Faraday Soc.*, 1958, **54**, 894. *b*, *Idem*, *ibid.*, p. 898. *c*, Azami and Tokura, *J. Polymer Sci.*, 1960, **42**, 545.

afflicted by considerable uncertainty and, moreover, it is now known that the transfer coefficients which determine the intercept depend on the nature of the catalyst.

Example 2. *Type* (*B*). *Category* 1.—It was found by Vesely [2b] that, when isobutene was polymerised by titanium tetrachloride in ethyl chloride at −78° in the presence of diethyl ether, the D.P. rose with increasing concentration of titanium tetrachloride until a maximum value was reached at $[TiCl_4]/[Et_2O]$ approximately unity; thereafter it declined very slightly and then remained constant. Unfortunately the paper does not contain sufficient information to allow the calculation of k_g/k_p and J_l/k_p.

Example 3. *Type* (*C*). *Category* 1.—Kennedy and Thomas [3a] showed that when isobutene was polymerised by aluminium chloride in ethyl chloride at −78° the D.P. decreased with increasing concentration of the catalyst up to a certain concentration, and at higher concentrations remained constant. This means that the system contained an impurity which reacted

TABLE 4.

Alkyl vinyl ethers, $RO{\cdot}CH{:}CH_2$.

No.	R	Solvent	Type	Category	Ref.
30	Bu^i	$n\text{-}C_6H_{14} + CH_3{\cdot}C_6H_5$	A	4	*a*
31	Bu^i	$n\text{-}C_6H_{14} + CH_3{\cdot}C_6H_5$	A	4	*b*
32	Pr^i	$n\text{-}C_6H_{14} + CH_3{\cdot}C_6H_5$	A	4	*b*
33	Et	$n\text{-}C_6H_{14} + CH_3{\cdot}C_6H_5$	C	4	*c*
34	Et	$n\text{-}C_6H_{14} + CH_2Cl_2$	C	4	*c*

TABLE 5.

α-Methylstyrene.

No.	Solvent	Type	Category	Ref.
35	$n\text{-}C_6H_{14} + CHCl_3$	A	4	*d*
36	$n\text{-}C_6H_{14} + CH_3{\cdot}C_6H_5$	A	4	*d*

Notes to Tables 4 *and* 5.

The catalyst in systems 30—36 was BF_3,Et_2O; the co-catalyst is unknown, but was probably adventitious water; the temperature was −78°.

a, Okamura, Higashimura, and Sakurada, *J. Polymer Sci.*, 1959, **39**, 507. *b*, Okamura, Higashimura, and Yamamoto, *J. Chem. Soc. Japan, Ind. Chem. Section*, 1958, **61**, 1636. *c*, Higashimura, Sunaga, and Okamura, *Chem. High Polymers (Japan)*, 1960, **17**, 257. *d*, Okamura, Higashimura, and Imanishi, *Chem. High Polymers (Japan)*, 1959, **16**, 69.

with aluminium chloride to give a chain-breaking agent. For experiments with an isobutene concentration of ~9·5 mole/l., the results do not permit precise determination of *g*, but this is probably in the region of $1{\cdot}2 \times 10^{-3}$ mole/l., whereas at a monomer concentration of about 4·6 mole/l., it is about 5×10^{-4} mole/l. Hence it is reasonable to suppose that the main source of the impurity was the monomer. This is borne out by the fact that other experiments recorded in the same paper, show *g* for undiluted monomer to be $\sim 7 \times 10^{-4}$ mole/l.

In a later paper [3b] Kennedy and Thomas reported that, when undiluted isobutene was polymerised at −78° with aluminium chloride as catalyst, with the same range of concentrations as in the previous study, the D.P. was independent of the catalyst concentration. They did not comment on this discrepancy, but it can now be understood on the supposition that in the later work the monomer was so pure that *g* was lower than the lowest catalyst concentration used ($\sim 1{\cdot}5 \times 10^{-4}$ mole/l.), so that all experiments fell into the " plateau " region.

These experiments are *prima facie* identical with those reported by Vesely [2b] and discussed in example 1. However, the range of aluminium chloride concentration is very different, and so indeed is the behaviour of the D.P. Whereas the concentrations used by Vesely ranged from ~0·02 to 0·2 mole/l., those used by Kennedy and Thomas lay in the range $(2\text{—}20) \times 10^{-4}$ mole/l. We must conclude that the materials used by Kennedy and Thomas were probably very much purer than those used in Vesely's work.

Example 4. *Type C. Category* 2.—It was found by Norrish and Russell [5] that when isobutene was polymerised by stannic chloride in ethyl chloride at −78° the D.P. of the polymer fell rapidly with increasing water concentration until the ratio $[H_2O]/[SnCl_4]$ was about unity, and remained approximately constant at all higher water concentrations. These results have been analysed and interpreted in detail.[6] It was concluded that the principal chain-breaking agent is a species whose concentration was proportional to that of stannic chloride monohydrate, and at first it was identified with the monohydrate itself, but a consideration of the kinetic information available subsequently led to the conclusion that the chain-breaking agent is the anion derived from stannic chloride monohydrate by loss of a proton, and that the reaction of this with the growing carbonium ion is a termination.[4]

Example 5. *Type A. Category* 3.—The first reported instance of the " peak phenomenon," by Thomas *et al.*[3c] concerns the variation of the D.P. of polyisobutene with the concentration of monomer in reactions catalysed by aluminium chloride in an alkyl halide solvent at low temperatures. Subsequent, more detailed studies confirmed the existence of the phenomenon for reactions in pentane, methyl chloride, ethyl chloride, vinyl chloride, and methylene dichloride. It was also shown [3b] that for any one solvent the shape of the curve relating the D.P. to the

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[6] Biddulph and Plesch, *J.*, 1960, 3913.

monomer concentration depended on the temperature, in that the peak was the more prominent the lower the temperature; near $-50°$ it was very small and near $-30°$ it was absent, the D.P. increasing steadily with the monomer concentration to the value characteristic of polymers obtained from undiluted monomer. These findings agree with our theory according to which the sharpness of the peak is related to the magnitude of an equilibrium constant which diminishes with increasing temperature.

The shape of the curve obtained at $-78°$ was the same for all the solvents and shows a steep rise in the D.P. with increasing monomer concentration up to a maximum at a relatively low monomer concentration, followed by a more gradual fall to the D.P. characteristic of polymers obtained from undiluted monomer. The monomer concentration at which the D.P. maximum occurs varied from one solvent to another, as did the height of the D.P. peak.

The explanation which we propose is that the solvents contained one or more impurities, the nature and concentration of which depended on the nature of the solvent and may have differed from one batch of solvent to another, and that these impurities reacted with, and thus rendered ineffective (" neutralised "), a chain-breaking agent present in all the reaction mixtures. Thus the region where the D.P. rises from the value characteristic of polymers obtained from the undiluted monomer to its maximum can be described more logically as " an increase of D.P. with increasing diluent concentration " rather than as " a decrease of D.P. with increasing monomer concentration." This effect is superposed on two others: the " normal " change of D.P. with monomer concentration which shows itself in the region of lowest monomer concentrations, and an increase of D.P. as the decrease of the diluent concentration reduces the rate of chain-transfer by the diluent.

A detailed analysis of the curves is further complicated by the fact that the magnitude of all the rate constants and any equilibrium constants involved may be affected by the change in the electrical properties of the medium with changing monomer : diluent ratio (except for the reactions in pentane). However, the experiments with pentane as diluent, and others, showed that the change of medium—at least in terms of bulk dielectric constant— was not by itself responsible for the peak.[3b]

The question now arises as to the origin and nature of the ubiquitous chain-breaking impurity. The clue to this is given by the experiments of the same authors discussed in example **3**. Our analysis shows that the monomer contained a substance which combines with aluminium chloride to give a chain-breaking agent. Let this be denoted by G, and let the active impurity in the solvent be G′. We propose that in the absence of solvent the ternary complex Al_2Cl_6,G predominates, and that this is an efficient chain-breaker, but that the binary complexes $AlCl_3$,G and $AlCl_3$,G′, which we suppose to be formed on addition of solvent, are very much less effective. As the ratio of solvent to monomer is increased, more of the ternary complex will be converted into the binary complexes, so that there is a progressive neutralisation of the most efficient chain-breaker.

This suggestion would be no more than an *ad hoc* hypothesis were it not that the most likely impurities are water and other oxygen-containing compounds (alcohols, ethers); and that Zlamal had found that for isobutene in ethyl chloride at $-78°$ the chain-breaking activities, given in our notation by k_h/k_p, of the complexes of aluminium chloride and ethanol had the values:

	Al_2Cl_6,EtOH	$AlCl_3$,EtOH	$AlCl_3$,2EtOH
k_h/k_p	$1{\cdot}5 \times 10^{-2}$	$7{\cdot}4 \times 10^{-5}$	$1{\cdot}6 \times 10^{-3}$

Thus, when G is ethanol, the ternary complex is two-hundred times more effective than the binary complex and, moreover, the second ternary complex, $AlCl_3$,2G is also a much more efficient chain-breaker. It seems very likely that for other oxygen compounds the situation is similar, since probably, not the complexes themselves, but anions from them are the true chain-breakers.

The fall of the D.P. from the peak as the solvent : monomer ratio becomes very great (very low monomer concentration) may be at least partly due to the progressive formation of the ternary complexes of the type $AlCl_3$,2G which are efficient chain-breakers.

Example 6. *Type D. Category* 4.—Zlamal and Kazda[2g] have reported that, when isobutene was polymerised by aluminium chloride at $-78°$ in a mixture of ethyl chloride and benzene, the D.P. of the polymers went through a minimum when the solvent contained about 5% by weight of benzene. In conformity with the ideas developed in the previous example, we interpret this effect as being due to an impurity, G, in the benzene which reacts with aluminium chloride to form two complexes, thus:

$$Al_2Cl_6 + G \longrightarrow Al_2Cl_6,G$$
$$Al_2Cl_6,G + G \longrightarrow 2\ AlCl_3,G$$

The supposition, made in the discussion of the previous example, that the ternary complex which is formed at first is a much more efficient chain-breaker than the binary complex which is formed subsequently, is adequate to explain the observed behaviour.

In these experiments the concentration of aluminium chloride was 2 × 10^{-3} mole/l. In further experiments,[2g] with the complex $AlCl_3$,EtOH at a concentration of 24·6 × 10^{-3} mole/l. Zlamal and Kazda found that the D.P. of the polyisobutenes did not change significantly as the proportion of benzene in the solvent was raised from 0 to 15%. This is entirely in agreement with expectation based on our theory.

Zlamal and Kazda attempted to explain these results and the differences between them and others, obtained with a mixed solvent containing hexane instead of benzene,[2g] on the supposition that the benzene itself forms a complex with $C_2H_5^+$ ions derived from the reaction of ethyl chloride and aluminium chloride, thus enhancing the dissociation of ion-pairs, and leading to a simultaneous increase in specific conductivity and decrease in D.P. While the formation of $C_2H_5^+$ ions under the relevant conditions is highly unlikely, the idea that they could form a complex with benzene rather than a $C_2H_5,C_6H_6^+$ ion seems rather odd. However, ions of this type would serve the theory equally well, the criticism of which must therefore be based on the point that there is no evidence that benzene as such has a major effect on the D.P. and that the presence of active impurities in it at concentrations of the order of $10^{-3} - 10^{-2}$ mole/l. seems very likely.

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