IONIC POLYMERISATION

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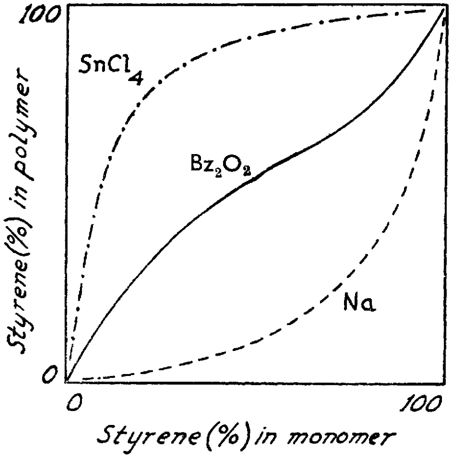
(I) General Introduction

THE study of addition polymerisations initiated by free radicals is now so far developed that it is almost a subject in itself. In contrast, the similar reactions initiated by ions have received very little fundamental investigation, though in a few cases they have been developed technologically to produce important polymers, especially poly*iso*butene and the polyvinyl ethers.

Under appropriate conditions, polymerisation of olefins and vinyl compounds may be induced by three different types of catalyst: (1) Organic peroxides, and other organic compounds or inorganic redox systems yielding free radicals; (2) strong acids and the Friedel–Crafts catalysts (Lewis acids); (3) strong (Lewis) bases, *e.g.*, Na, $NaNH_2$, organometallic compounds. The products in all cases are substantially the same—linear polymers showing only secondary differences—but reaction mechanisms and kinetics are very different. These differences of mechanism may perhaps be most concisely demonstrated by the copolymer composition curves obtained from a given pair of monomers with the different catalysts. The Figure shows such curves for styrene–methyl methacrylate polymerised by stannic chloride, benzoyl peroxide, or sodium in liquid ammonia, constructed from Landler's data.[1] The relative reactivity of the two monomers is clearly very different in the different cases.



Copolymer compositions with different catalysts.

The differences in reactivity become even more marked if monomers are

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[1] *Compt. rend.*, 1950, **230**, 539.

chosen with substituents of more widely different electronegativity. If the substituent group is strongly electrophilic the monomer can be readily polymerised by basic catalysts, but not by acidic, and *vice versa*. The following list shows qualitatively the range of susceptibility to the different catalysts shown by vinyl monomers, $CH_2{:}CHY$:

$$\text{Y} = \overbrace{\underbrace{\text{CN, CO}_2\text{Me, OAc, }\mathrlap{\underbrace{\phantom{\text{CH:CH}_2\text{, C}_6\text{H}_4\text{Cl}(p)\text{, C}_6\text{H}_5\text{, CH}_3\text{, OAlk, C}_6\text{H}_4\cdot\text{OMe}}\vphantom{\underbrace{x}_{\textit{Basic}}}}_{\textit{Acidic}}}\text{CH:CH}_2\text{, C}_6\text{H}_4\text{Cl}(p)\text{, C}_6\text{H}_5}_{\textit{Basic}}}^{\textit{Radical}}\text{, CH}_3\text{, OAlk, C}_6\text{H}_4\cdot\text{OMe}$$

This list refers to the polymerisation of the pure monomers ; in copolymerisation the range of susceptibility to the different catalysts is appreciably extended.

The different reactivities point to different mechanisms, which it is natural to attribute to the three possible ways of opening a double bond to give a reactive intermediate, *viz.* :

$$\begin{array}{llll} R\cdot + CH_2{:}CHY & \longrightarrow & R{\cdot}CH_2{\cdot}CHY\cdot & \text{Radical} \\ A^+ \text{ (from acid)} & \longrightarrow & A{\cdot}CH_2{\cdot}CHY^+ & \text{Cation} \\ B^- \text{ (from base)} & \longrightarrow & B{\cdot}CH_2{\cdot}CHY^- & \text{Anion} \end{array}$$

This identification is supported by the studies to be described below, with the modification that the ionic intermediates are more nearly ion-pairs than free ions, *i.e.*, the polymeric ion is always associated with an oppositely-charged ion derived from the catalyst.

(II) Cationic Polymerisation

(II, 1) **Introduction.**—Examples of the " resinification " of unsaturated compounds by Friedel–Crafts halides or by strong acids have been known since Deville [2] polymerised styrene with stannic chloride in 1839. Systematic investigation, however, really begins with the work of Staudinger's school in the second decade of this century. By the early 1930's it was established that styrene and many derivatives, the terpenes, and the vinyl ethers could give resinous polymers of low to medium molecular weight (up to *ca.* 20,000), and that the lower alkenes also responded to these catalysts, giving very low polymers, mainly dimers and trimers. From this stage, studies of the subject have diverged, according as the aim of the investigator has been to prepare useful products (high polymers, lubricating oils, aviation spirit), or to study the reactions as the ionic analogues of the established radical-chain polymerisations. Different monomers and widely different reaction conditions have been found appropriate for these aims, and as a result there have grown up two rather disparate bodies of information and theoretical ideas which cannot yet be completely integrated.

The various systems show a great variety and complexity of behaviour, but the following generalisations may be made :

(1) Linear addition polymerisation is only one of many simultaneous reactions which can be induced by the powerful catalysts used. The

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[2] *Ann. Chim.*, 1839, **75**, 66.

Friedel–Crafts compounds (*i.e.*, Lewis acids) are more active in this sense than the hydrogen acids, and in general give rise to a greater complexity of product as well as a greater polymer molecular weight.

(2) The different reactions have different temperature dependence, and in most systems all " side " reactions are frozen out at low temperatures. In this region the polymer molecular weight normally increases continuously as the reaction temperature is lowered.

(3) Different monomers show widely different susceptibility to side reactions. The greatest complexity is found with the alkenes, whose reactivity in isomerisation, alkylation, etc., is well known. With these monomers, high polymers are obtained only at very low temperatures (below − 50°, and usually lower). With styrene and its derivatives, and the vinyl ethers, reactivity in side reactions is much less, and linear polymers can be obtained at room temperature, though as a rule only of fairly low molecular weight.

Under the reaction conditions (high temperature, high catalyst concentration) which favour the formation of very low polymers of alkenes, Meier [3] has listed no less than eight side reactions, giving rise to isomers, homologues, paraffins, aromatics, and naphthenes. This congeries of reactions has been termed " conjunct polymerisation " and has recently been reviewed by Schmerling and Ipatieff.[4] The systems are often heterogeneous (solid or insoluble catalysts), or become so by the separation of a highly polar liquid phase—the well-known Friedel–Crafts " tar ". It is not known whether the tar is the site of the reaction or merely one of its products. Studies of these reactions have naturally concentrated on the identification of products, and the explanation of their formation by reaction mechanisms of " small molecule " chemistry.

In the systems chosen for kinetic study of the polymerisation, the above complications are not obviously present, polymer being formed in quantitative yield. The reaction kinetics have been interpreted in the theoretical framework developed for radical-chain polymerisations, and attention has been concentrated on deducing the molecular processes responsible for chain initiation, propagation, termination, etc. As will appear below, this is not a simple task, partly because of ambiguities arising from the effects of trace co-catalysts (promoters) and solvent effects, and partly because the variety of carbonium reactions offers a wide choice of alternative processes for the elementary steps of the chain reaction.

True, as distinct from conjunct, polymerisation has been reviewed in recent years by Heiligmann,[5] Plesch,[6] and Hamann,[7] and in the reports of discussions in Dublin University in 1949,[8] and in the University College of North Staffordshire in 1952.[9]

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[3] *J.*, 1950, 3656. [4] " Advances in Catalysis ", Academic Press, New York, 1950.

[5] *J. Polymer Sci.*, 1949, **4**, 183.

[6] (*a*) *Research*, 1949, **2**, 267 ; (*b*) *J. Appl. Chem.*, 1951, **1**, 269.

[7] *Angew. Chem.*, 1951, *A*, **63**, 231.

[8] Pepper, (*a*) *Nature*, 1949, **164**, 655 ; (*b*) *Sci. Proc. R. Dublin Soc.*, 1950, **25**, 131.

[9] Plesch, (*a*) *Nature*, 1952, **169**, 828 ; (*b*) " Cationic Polymerisation ", Heffer, Cambridge, 1953.

(II, 2) **Catalysts.**—A great many different catalysts have been found effective, but they are all acids in Lewis's generalised sense, *i.e.*, electron acceptors. They include :

Hydrogen acids : H_2SO_4, H_3PO_4, $HClO_4$, $ClSO_3H$; HCl, HBr, HF ; acid silicates, *e.g.*, floridin.

Lewis acids : Metal halides, *e.g.*, $BeCl_2$, $CdCl_2$, $ZnCl_2$, BF_3, BCl_3, BBr_3, $AlCl_3$, $AlBr_3$, $GaCl_3$; $TiCl_4$, $TiBr_4$, $ZrCl_4$, $SnCl_4$, $SnCl_2$, $SnBr_4$; $SbCl_5$, $SbCl_3$, $BiCl_3$, $FeCl_3$, UCl_4.

Cation-forming substances : I_2, $AgClO_4$, CPh_3Cl.

The hydrogen acids have been used mainly to bring about dimerisation and conjunct polymerisation of alkenes, but in a few instances have been used under different conditions (low temperatures, polar solvents) to produce high polymers, *e.g.*, α-methylstyrene–H_2SO_4,[10] styrene–HCl (HBr).[11]

The action of floridin on olefins was studied extensively by Lebedev and Filonenko,[12] who found it to polymerise only the asymmetric di- and tri-substituted ethylenes, and proposed its use for analytical distinction and separation. Vinyl ethers [13] and α-methylstyrene [14] have also been polymerised on acid silicate catalysts of this type.

Of the Friedel–Crafts halides, the most commonly used are BF_3, $AlCl_3$, $AlBr_3$, $TiCl_4$, and $SnCl_4$. Their relative activity in the polymerisation of *iso*butene at $-78°$ has been found by Fairbrother and Seymour [15] to be in the order : $BF_3 > AlBr_3 > TiCl_4 > TiBr_4 > SnCl_4 > BCl_3 > BBr_3$ as judged by the yield of polymer in a given time. The polymer molecular weight decreased in the same order, with the exception of the stannic chloride polymer, which had the lowest molecular weight. This behaviour is in accord with the oft-quoted "rule of thumb" that the most active catalysts also give the highest molecular weight. If the activity of a catalyst is judged by the rate of polymerisation rather than by the yield, then this rule shows many exceptions. Thus with styrene in carbon tetrachloride at 25°,[16] the order of rates with different catalysts decreases in the order $SbCl_5 \gg SnCl_4 > BCl_3$, but the polymer molecular weight shows only small variation and in the reverse order. With styrene in ethylene dichloride,[11] the rate with stannic bromide is some 400 times less than with stannic chloride, but the molecular weight twice as great.

Fairbrother and Seymour's order of catalyst activity follows that found by Bodendorf and Boehme [17] for the racemisation of 1-phenylethyl chloride, and by Dermer and Billmeier [18] for the acetylation of toluene, though it differs in the relative positions of $TiCl_4$ and $SnCl_4$ from the order quoted by Calloway [19] based on a general survey of Friedel–Crafts reactions. However, a unique order of activity in all systems is not to be expected, as specific

[10] Heiligmann, *J. Polymer Sci.*, 1951, **6**, 155.

[11] Pepper and Somerfield, ref. (9*b*), p. 75.

[12] *Ber.*, 1925, **58**, 163.

[13] Reppe, quoted in Schildknecht, "Vinyl Polymers", Wiley, New York, 1952.

[14] Salt, Clay Minerals Bulletin, 1948, **2**, 43.

[15] Thesis, Manchester Univ., 1943.

[16] Williams, *J.*, 1940, 775.

[17] *Annalen*, 1935, **516**, 1.

[18] *J. Amer. Chem. Soc.*, 1942, **64**, 465.

[19] *Chem. Reviews*, 1935, **17**, 327.

interactions with monomer and solvent are likely to play a part—to take an extreme example, the order of activity in Friedel–Crafts depolymerisation of paraldehyde in ether solution [20] is markedly different. Moreover, it has been demonstrated in many systems that in addition to the catalyst another substance—the co-catalyst—is necessary for polymerisation. We must therefore expect activity to depend not on the catalyst alone but on the catalyst–co-catalyst combination.

(II, 3) **Co-catalysts.**—The rates of Friedel–Crafts polymerisations are notoriously irreproducible, and in many cases the variability has been traced to the presence in varying amounts of very small concentrations of promoting substances or co-catalysts, without which the Friedel–Crafts halide is inactive. The present theory of the function of the co-catalyst is that it unites with this halide to form an ionic complex which provides the cation necessary for initiation of polymerisation. Two groups of co-catalysts are now recognised.

(A) *Proton-releasing substances, especially hydroxy-compounds and hydrogen acids.* It has been rigorously demonstrated by Evans and Meadows [21] that the polymerisation of *iso*butene by boron trifluoride does not take place in absence of traces of water. In other systems it has been difficult to obtain unambiguous evidence that such traces are *necessary* as distinct from *ancillary*, because of the exceedingly low concentrations of water which will support reaction (concentrations far below those reached by normal methods of severe drying). But in a number of cases, listed in Table 1 (p. 101), the rates of polymerisation can be markedly decreased by drying, and accelerated by adding traces of water. Other co-catalysts of this type are acetic acid and *tert.*-butanol,[22] and the chloroacetic acids,[23] active in the polymerisation of *iso*butene by boron trifluoride and titanium tetrachloride, respectively. The hydrogen halides also can act as co-catalysts; *e.g.*, hydrogen chloride is necessary in the (low) polymerisation of ethylene by aluminium chloride,[24] and accelerates the polymerisation of styrene by stannic chloride or bromide.[11] Industrial patents [25, 26] state that hydrogen halides " activate " the catalyst, and improve or promote the polymerisation of olefins.

Co-catalysts of this type have been found necessary in many simpler Friedel–Crafts reactions, *e.g.*, water, hydrogen fluoride, or sulphuric acid in the boron trifluoride-catalysed alkylation of benzene with olefins,[27] ethers,[28] and alkyl halides.[29] Many reactions catalysed by aluminium bromide—*e.g.*, isomerisations [30]—are promoted by hydrogen bromide.

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[20] Bell and Skinner, *J.*, 1952, 2955.

[21] *Trans. Faraday Soc.*, 1950, **46,** 327.

[22] Evans, Meadows, and Polanyi, *Nature*, 1947, **160,** 869.

[23] Plesch, *ibid.*, p. 868.

[24] Ipatieff and Grosse, *J. Amer. Chem. Soc.*, 1936, **58,** 915.

[25] Otto, D.R.-P. 504,730.

[26] Palmer, U.S.P. 2,471,890.

[27] Ipatieff and Grosse, *J. Amer. Chem. Soc.*, 1935, **57,** 1616.

[28] Burwell and Elkin, *ibid.*, 1951, **73,** 502.

[29] Hennion and Kurtz, *ibid.*, 1943, **65,** 1001.

[30] Grummitt, *ibid.*, 1945, **67,** 910.

The mode of action of the co-catalysts is formulated in reactions of the type :

$$\begin{aligned} BF_3 + HOR &\longrightarrow BF_3{\cdot}ORH \rightleftharpoons BF_3{\cdot}OR^- + H^+ \\ SnCl_4 + HX &\longrightarrow SnCl_4XH \rightleftharpoons SnCl_4X^- + H^+ \end{aligned}$$

Such complexes are to be regarded as transitory reaction intermediates rather than stable compounds—the stable higher hydrates are inactive, and vapour-pressure measurements show no evidence for the appreciable stability of $HAlCl_4$[31] or $HAlBr_4$.[32] In view of the latter observations, Plesch[6b] suggests that the hydrogen halide co-catalysts react not so much with the catalyst as with a monomer–catalyst complex, for whose existence as π-complexes there is much evidence.

(B) *Carbonium-ion forming substances.* Co-catalysis by alkyl halides was first suggested[33] to account for the apparent absence of water co-catalysis in the stannic chloride polymerisation of styrene in solution in ethylene dichloride. Analogous reactions to those above are postulated, *i.e.*, $RCl + SnCl_4 \longrightarrow R^+SnCl_5^-$, the carbonium ion here taking the place of the proton in initiating the polymerisation chain. Evidence in support of this mechanism has been reported by Plesch,[34] who finds indications of alkyl end-groups in polystyrenes produced by titanium tetrachloride in solution in several alkyl bromides. It is also known that alkyl halides frequently act as promoters in reactions catalysed by aluminium bromide, *e.g.*, the polymerisation of alk-1-enes.[35]

Reactions of this type provide the most plausible mechanism for many simpler Friedel–Crafts reactions, *e.g.*, the addition of halogenated compounds to olefins,[36, 37] the racemisation of 1-phenylethyl chloride,[17] and the isomerisation of *n*-propyl chloride.[38] The existence of such complexes, or of such ionisation processes, has been inferred from a wide variety of phenomena : from vapour-pressure measurements of ethyl and methyl chlorides in presence of gallic chloride ;[39] from the electrical conductivity of aluminium chloride–ethyl chloride solutions ;[40] from the enhancement of dipole moment of aluminium bromide in ethyl bromide ;[41] and from the absorption spectra of triphenylmethyl chloride in presence of stannic chloride[42] and of mercuric chloride.[43] The exchange of halogen which should result from such reactions has been observed between aluminium

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[31] Brown and Pearsall, *J. Amer. Chem. Soc.*, 1951, **73**, 4681.

[32] Fontana and Herold, *ibid.*, 1948, **70**, 2881.

[33] Pepper, *Trans. Faraday Soc.*, 1949, **45**, 404.

[34] Ref. (9*b*), p. 86.

[35] (*a*) Fontana and Kidder, *J. Amer. Chem. Soc.*, 1948, **70**, 3745 ; (*b*) Fontana, Kidder, and Herold, *Ind. Eng. Chem.*, 1952, **44**, 1688 ; (*c*) Fontana, Herold, Kinney, and Miller, *ibid.*, p. 2955 ; (*d*) Fontana, ref. (9*b*), p. 122.

[36] (*a*) Prins and Boeseken, *K. Akad. Wetensch. Amsterdam*, 1911, **13**, 685 ; (*b*) Prins, *Rec. Trav. chim.*, 1932, **51**, 1065.

[37] Schmerling, all refs. in *J. Amer. Chem. Soc.*, 1952, **74**, 2885.

[38] Crowell and Jones, *ibid.*, 1951, **73**, 3506.

[39] Brown, Pearsall, and Eddy, *ibid.*, 1950, **72**, 5347.

[40] Wertyporoch and Firla, *Annalen*, 1933, **500**, 287.

[41] Fairbrother, *J.*, 1945, 503.

[42] Hantzsch, *Ber.*, 1921, **54**, 2573.

[43] Bentley and Evans, *Research*, 1952, **5**, 535.

halides and both alkyl [44] and acyl [45] halides, and even with the relatively unreactive carbon tetrachloride,[46] though here it is suspected that the exchange with aluminium chloride may take place only heterogeneously. The ionic complexes would be expected to have only low stability, and in fact only extreme examples have been isolated, *e.g.*, $CPh_3Br–SnBr_4$[41] and $R·COCl–TiCl_4$.[47] However, even a transitory existence would suffice for initiation of polymerisation.

The effect of nitrobenzene or nitroparaffin solvents in accelerating the polymerisation of styrene by stannic chloride [48, 49] may also be an instance of "solvent" co-catalysis *via* the known complexes of these substances with the chloride.[50, 51] A similar marked effect of nitroparaffin solvents is observed in alkylations.[52]

It will be realised that this theory of co-catalysis shifts the emphasis from the Friedel–Crafts halide to the co-catalyst, since it is the latter which provides the initiating cation. The function of the catalyst becomes merely to facilitate the dissociation of the cation by complexing with and stabilising the anionic residue, *i.e.*, it behaves as an "ansolvo" acid in Meerwein's sense.[53] The effectiveness of a given catalyst–co-catalyst pair in providing a proton will depend on the electrophilic character of the catalyst, and on the donor character of the co-catalyst and its acid strength. These influences have been considered qualitatively by Plesch,[54] for the catalysts boron trifluoride, titanic chloride, stannic chloride with the co-catalysts water, *tert.*-butanol, and the chloroacetic acids. Russell [55] has measured the effect of different co-catalysts on the rate of polymerisation of *iso*butene by stannic chloride in ethyl chloride at − 78° and finds :

$$CCl_3·CO_2H > Cl·CH_2·CO_2H \gg CH_3·CO_2H > EtNO_2 > MeNO_2 > C_6H_5·OH > H_2O$$

a sequence which follows the acid dissociation constants where known. However, other factors must also play an important part, for picric acid, which has the same dissociation constant as trichloroacetic acid, is found not to co-catalyse the system titanium tetrachloride–*iso*butene–hexane.[23] Topchiev [*et al.*][56] have measured the electrical conductivity of a great many complexes of boron trifluoride with hydroxy-compounds, but find no correlation with catalytic activity.

The effectiveness of the chlorinated and other polar solvents is not determined only by their co-catalytic activity ; here the effect is composite, and the general polar character of the solvent—its capacity to solvate the

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[44] Fairbrother, (*a*) *J.*, 1937, 503 ; (*b*) *J.*, 1941, 293.

[45] Korshak and Kolesnikov, *J. Gen. Chem. U.S.S.R.*, 1944, **14,** 435, 1092.

[46] Wallace and Willard, *J. Amer. Chem. Soc.*, 1950, **72,** 5275.

[47] Cullinane and Leyshon, *J.*, 1952, 4106.

[48] Pepper, *Nature*, 1946, **158,** 789 ; *Trans. Faraday Soc.*, 1949, **45,** 397.

[49] (*a*) George, Wechsler, and Mark, *J. Amer. Chem. Soc.*, 1950, **72,** 3891 ; (*b*) George and Wechsler, *J. Polymer Sci.*, 1951, **6,** 725.

[50] Reihlen and Hake, *Annalen*, 1927, **452,** 47.

[51] Plesch, ref. (9*b*), p. 86.

[52] Schmerling, *Ind. Eng. Chem.*, 1948, **40,** 2072.

[53] Meerwein, *Annalen*, 1927, **455,** 227.

[54] Ref. (8*b*), p. 154.

[55] Ref. (9*b*), p. 114.

[56] *Doklady Akad. Nauk. U.S.S.R.*, 1951, **80,** 381.

ions formed—plays a part, as well as the donor character of its molecules. This effect is discussed later.

The relationship of the above postulated catalyst–co-catalyst complexes to the known stable complexes of Friedel–Crafts halides is not yet clearly established. Where strong (and probably covalent) complexes can be formed, *e.g.*, of stannic chloride with ether, alcohol, or acetone, polymerisation in these solvents is completely suppressed.[57] However, even stable complexes of this type may have catalytic activity in other solvents ; *e.g.*, $SnCl_4,2Et_2O$ is active in ethylene dichloride solution,[57] and $BF_3,2Et_2O$ is commonly used as a milder catalyst than boron trifluoride itself. It is not known whether in these instances the ether acts as a co-catalyst, initiating reaction by Et^+,[58] or whether the activity is due to partial hydrolysis. A series of papers and discussions on the subject of Friedel–Crafts complexes has recently been published,[9b] but a detailed consideration is outside the scope of this Review.

(II, 4) **Monomers.**—Well over fifty unsaturated compounds have been reported to give polymeric products with acids or Friedel–Crafts catalysts, and there is a growing number of instances where C=O bonds and hetierocyclic rings may also be opened by these reagents to give polymers. Since the emphasis of this Review is on the comparison of ionic with radcal polymerisations, attention will be confined to the former class of monomers.

It is probably true to say that any monomer whose double bond is not deactivated by strongly electrophilic substituents is capable of initiation by cationic reagents, provided that its structure interposes no gross steric hindrance. However, because of the great reactivity of many monomer carbonium ions, the previously-mentioned " side " reactions may predominate over linear addition. For this reason true high polymers have been obtained in only a few systems, under narrowly defined conditions of temperature, catalyst concentration, etc.

Ethylene at high pressures and above room temperatures can be polymerised by $AlCl_3$–HCl [24, 59] or by H_3PO_4,[60] but the product is a mixture of paraffins, olefins, naphthenes, and aromatics of low molecular weight, *i.e.*, it is a " conjunct " polymerisation in Schmerling's sense. However, low polymers suitable for lubricating oils have been obtained.[61] Under conditions usually found optimum for linear polymerisation—very low temperatures, with BF_3 or $AlCl_3$—ethylene shows so little reactivity that it can be used as a solvent for the polymerisation of *iso*butene.[62]

Propene and the *n*-butenes also normally give conjunct rather than high polymers.[3] Products of molecular weight *ca.* 3000 have been obtained at – 80° only with high catalyst concentrations ($AlCl_3$ in EtCl) and with long reaction times.[63] With $AlBr_3$–HBr in propane solution, Fontana *et al.*[35]

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[57] Devlin and Pepper, ref. (9*b*), p. 24.

[58] Evans and Meadows, ref. (8*b*), p. 138 ; *J. Polymer Sci.*, 1949, **4**, 359.

[59] Waterman and Leendertse, *Trans. Faraday Soc.*, 1936, **32**, 251.

[60] Ipatieff and Pines, *Ind. Eng. Chem.*, 1935, **27**, 1364.

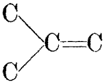
[61] Zorn, *Angew. Chem.*, 1948, **60**, 185.

[62] Thomas and Arey, A.C.S. Louisiana Meeting, 1948.

[63] Thomas and Reynolds, U.S.P. 2,387,784.

have obtained high-molecular-weight (and highly branched) polymers from propene and but-1-ene by the use of special reaction conditions (semi-batch, or semi-continuous processes) with optimum temperatures at −50° and − 35°, respectively.

*iso*Butene by contrast polymerises very readily, and all competing side reactions appear to be frozen out at low temperatures. Molecular weights up to several million are obtainable below − 80° with aluminium chloride or boron trifluoride in solution in ethylene or chlorinated solvents:[62, 64] Co-catalysts are not mentioned, but may be water, or the chlorinated solvents, or traces of hydrogen halides (larger amounts reduce the molecular weight). Little has been published of the research which led to the development of butyl rubber (copolymers of *iso*butene with small proportions of isoprene or butadiene), but kinetic studies have been made of the polymerisation by BF_3,[65] $TiCl_4$,[66] and $SnCl_4$,[67] and the co-catalytic effect of water was first demonstrated with this monomer.[68]

The higher 1-alkenes, mainly pentenes and hexenes, but also even hexadecene,[59] have received some attention. Under the various conditions employed by different authors (H_2SO_4, normal temperature ; [69] $AlCl_3$, − 80° ; [59] $AlCl_3$, room temperature [70]) conjunct rather than simple linear polymerisation was found. From a comparative study of the isomeric pentenes, Leendertse and Waterman [71] concluded that olefins with a  structure reacted faster than those with —C—C=C—. In more recent work, Ruthruff [72] finds a different order of reactivity, placing 3-methylbut-1-ene as the most reactive, and 2-methylbut-1-ene as the most inert. In a patent application [63] rubber-like polymers are reported from the pentenes 3-methylbut-1-ene and pent-2-ene by use of aluminium chloride in ethyl chloride at − 78°, but only low-molecular-weight oils from hexenes.

Styrene shows fewer complications than the alkenes, and polymers of moderate molecular weight—up to about 40,000 according to catalyst and solvent—can be obtained at room temperature. Most of the kinetic studies of cationic polymerisation have been carried out with this monomer, starting with a series of papers by Williams [73] on the polymerisation by stannic chloride in carbon tetrachloride and chloroform. The reaction has been

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[64] Thomas, Sparks, Frohlich, Otto, and Mueller-Conradi, *J. Amer. Chem. Soc.*, 1940, **62**, 276.

[65] Summarised by Evans, *J. Appl. Chem.*, 1951, **1**, 240.

[66] Plesch, (*a*) *J.*, 1947, 257 ; (*b*) *J.*, 1950, 543 ; (*c*) *J.*, 1952, 3355.

[67] Norrish and Russell, *Nature*, 1947, **160**, 543 ; *Trans. Faraday Soc.*, 1952, **48**, 91.

[68] Evans, Meadows, and Polanyi, *Nature*, 1946, **158**, 94.

[69] Norris and Joubert, *J. Amer. Chem. Soc.*, 1927, **49**, 873.

[70] Asaoka, *J. Chem. Soc. Japan*, 1943, **64**, 541, 612, 804, 931.

[71] (*a*) Leendertse, Tulleners, and Waterman, *Rec. Trav. chim.*, 1934, **53**, 715; (*b*) Waterman, Leendertse, and Klazinga, *ibid.*, 1935, **54**, 79.

[72] A.C.S. Boston Meeting, 1939.

[73] *Nature*, 1937, **140**, 363 ; *J.*, 1938, 246, 1046 ; 1940, 775.

studied with this catalyst in the solvents carbon tetrachloride,[74] ethyl chloride,[75] ethylene dichloride,[33] and nitro-compounds ; [48, 49] with aluminium chloride [76] and boron trifluoride [77] in carbon tetrachloride ; and with titanium tetrachloride in several solvents.[78] Styrene polymerises readily under the influence of hydrogen acids, *e.g.*, sulphuric acid, and with hydrogen chloride or bromide in solvents of high dielectric constant.[79] Most of the above work has been concerned with the mechanism of the reaction, and the conditions for maximum molecular weight have not been explicitly investigated. However, it is generally found to increase with lower reaction temperature, and at – 100° with aluminium chloride in ethyl chloride a polymer suitable for moulding has been obtained,[80] though the molecular weight is not recorded.

α-Methylstyrene was one of the first monomers to be investigated by Staudinger's school, using stannic chloride [81] and other Friedel–Crafts catalysts. More recent workers have used aluminium chloride,[82, 83] stannic chloride,[48a, 84] and sulphuric acid,[10] usually in chlorinated or other polar solvents. Under similar conditions it is usually found to react more rapidly than styrene, but with aluminium chloride in carbon tetrachloride the reverse order is reported. At room temperature only low polymers are formed, which are saturated [81] and show evidence of termination by ring closure, leaving substituted phenylindane end-groups.[84] In the region of – 80° molecular weights of approximately 90,000 have been obtained with $AlCl_3$ in EtCl, and with H_2SO_4 in CH_2Cl_2 (heterogeneous dispersion).

A great many substituted styrenes (*e.g.*, with methyl, methoxy-, or halogen groups, etc.) and other styrene derivatives can be polymerised by cationic reagents, *e.g.*, stilbene, 1 : 1-diphenylethylene, indene, coumarone, phenanthrene, vinylnaphthalenes, acenaphthylene, and other unsaturated hydrocarbons such as *cyclo*hexene, *cyclo*pentadiene, and pinene. The information is mostly qualitative, and its main theoretical interest is that it seems to show that 1 : 2-disubstitution exerts no notable steric hindrance to polymerisation, even when the substituents are joined, *i.e.*, when the double bond forms part of a ring system.

The vinyl ethers constitute the largest single group of related monomers studied in ionic polymerisation. Wislisenus in 1878 [85] discovered that ethyl vinyl ether could be converted into a balsam-like resin by iodine or by sulphuric acid. Chalmers in 1932 [86] examined the polymerisation of the ethyl, 2-chloroethyl, *n*-butyl, and phenyl ethers with the catalysts iodine,

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[74] Dainton, Tomlinson, and Batke, ref. (9*b*), p. 80.

[75] Gantmakher and Medvedev, *J. Phys. Chem. U.S.S.R.*, 1949, **23,** 516.

[76] Jordan and Mathieson, *Nature*, 1951, **161,** 523 ; *J.*, 1952, 611, 621 ; ref. (9*b*), p. 90.

[77] Clark, ref. (9*b*), p. 99.

[78] Plesch, ref. (9*b*), p. 85 ; *J.*, 1953, 1653.

[79] Pepper and Somerfield, ref. (9*b*), p. 77.

[80] Sparks, U.S.P. 2,436,614.

[81] Staudinger and Breusch, *Ber.*, 1929, **62,** 442.

[82] Hersberger, Reid, and Heiligmann, *Ind. Eng. Chem.*, 1945, **37,** 1073.

[83] Jordan and Mathieson, ref. (9*b*), p. 90 ; *J.*, 1952, 2354, 2358, 2363.

[84] Dainton and Tomlinson, ref. (9*b*), p. 80 ; *J.*, 1953, 151.

[85] *Annalen*, 1878, **192,** 106.

[86] *Canadian J. Res.*, 1932, **7,** 113.

antimonic chloride, and stannic chloride. A wide range of polymers, including poly(octadecyl vinyl ether), was produced in the 1930's by the I.G. Farben., some rubber-like, but mainly as waxes and adhesives. The vinyl ethers are very reactive, and to avoid charring and cross-linking, mild catalysts are used, *e.g.*, the complexes of boron trifluoride with ethyl or *iso*butyl ethers, rather than the trifluoride itself. The polymerisation has also been carried out at − 10° in liquid sulphur dioxide, which acts as catalyst as well as solvent.[13] Very mild catalysts, *e.g.*, stannous chloride, ferrous chloride, and zinc chloride, are quoted also by Russian authors.[87, 88] For the different ethers polymerised by boron trifluoride etherate, Schildknecht *et al.*[89] find the order of reactivity $Pr^i > Bu^i > Bu^n > Et > Me$. According to the nature and solubility of the catalyst, the reaction may proceed either homogeneously or as a "polyphase" process, giving rise to polymers of quite different physical properties and intermolecular structure.[89b] The kinetics of polymerisation are described in a series of papers by Eley and his colleagues,[90] dealing with several alkyl vinyl ethers, in different solvents, with the catalysts stannic chloride, silver perchlorate, triphenylmethyl chloride and iodine, mainly the last. In a quantitative comparison of the rates of polymerisation by iodine in ethyl ether solution, Eley and Saunders[90c] find *cyclo*hexyl $\gg$ *iso*butyl $=$ ethyl $>$ *n*-butyl $>$ 2-ethylhexyl $>$ 2-chloroethyl. Phenyl vinyl ether is very unreactive towards iodine,[86] but may be polymerised at − 10° by aluminium chloride or boron trifluoride.[88]

(II, 5) **Mechanisms.**—The mechanisms of the dimerisations and "conjunct" polymerisations have recently been reviewed;[4] attention will be confined here to the macropolymerisations.

That these are normally true chain polymerisations, as distinct from stepwise additions, is demonstrated by the formation of polymer of the full chain-length from the beginning of the reaction—the molecular weight does not normally change greatly over the whole conversion. In one system only—the $AlBr_3$–HBr polymerisation of alk-1-enes[35]—the molecular weight is reported to increase uniformly throughout the reaction, but here the operating conditions are complex, there being continual replenishments with monomer. In some systems, with powerful catalysts and/or very reactive monomers, the polymerisation may be almost explosive, and there are some other indications of non-stationary behaviour (see p. 112), but where moderately slow and uniform polymerisation is achieved there seems no reason to doubt that a stationary chain reaction is established.

Evidence that the chain intermediates are cationic may be seen in the following general characteristics of the reactions: (1) The pronounced effect of polar solvents; (2) the cationic nature of the catalysts, or, when these

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[87] Favorski and Shostakovski, *J. Gen. Chem. U.S.S.R.*, 1943, **13**, 1.

[88] Losev, Fedotova, and Trostanskaya, *ibid.*, 1945, **15**, 353.

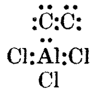
[89] (*a*) Schildknecht, Zoss, and Grosser, *Ind. Eng. Chem.*, 1949, **41**, 2891; (*b*) Schildknecht, *op. cit.*, ref. (13).

[90] (*a*) Eley and Pepper, *Trans. Faraday Soc.*, 1947, **43**, 112; (*b*) Eley and Richards, *ibid.*, 1949, **45**, 425; (*c*) Eley and Saunders, *J.*, 1952, 4167; ref. (9*b*), p. 145.

are covalent, the necessity for some co-catalyst ; (3) the nucleophilic character of susceptible monomers ; (4) inhibition by amines and anions.[49]

The identification of the elementary steps of the chain reaction has proved difficult, and it seems probable that there are several alternatives for each step, according to the system and experimental conditions.

(A) *The Polar-bond Mechanism.*—Until the recognition of co-catalysis, the formulation of a precise mechanism was hampered by the difficulty of envisaging how an ionic reaction could be initiated by a covalent Friedel–Crafts halide. The earliest proposals consequently assumed, not free ions, but polar molecules formed by co-ordination of the electrophilic catalyst. Hunter and Yohe [91] in 1933 suggested that the polymerisation of ethylene and *iso*butene by aluminium chloride was initiated by the donation of a pair of electrons from the double bond to the catalyst, forming the complex (I), the further carbon atom being left with only six electrons, and thereby being capable of addition to further monomer. The implied separation of charge was not explicitly written, but was later emphasised by Price and Ciskowski,[92] who applied this notion to the simple alkylations, and later [93] expanded it into a full chain-reaction scheme for the polymerisation of styrene by stannic chloride. To explain Williams's observed kinetics,[73d] Price assumed the formation of a polar catalyst–monomer complex, as a separate step, preliminary to the chain-initiation process :



$$\begin{array}{c} :\ddot{\mathrm{C}}:\ddot{\mathrm{C}}: \\ \mathrm{Cl}:\ddot{\mathrm{Al}}:\mathrm{Cl} \\ \mathrm{Cl} \end{array}$$

(I)

Complex formation :

$$\mathrm{SnCl_4 + CH_2{:}CHPh \longrightarrow \overset{-}{Cl_4Sn}{\cdot}CH_2{\cdot}\overset{+}{C}HPh}$$

Initiation :

$$\mathrm{\overset{-}{Cl_4Sn}{\cdot}CH_2{\cdot}\overset{+}{C}HPh + CH_2{:}CHPh \longrightarrow \overset{-}{Cl_4Sn}{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}\overset{+}{C}HPh}$$

Propagation :

$$\mathrm{\overset{-}{Cl_4Sn}{\cdot}[CH_2{\cdot}CHPh]_{\mathit{n}}{\cdot}CH_2{\cdot}\overset{+}{C}HPh + CH_2{:}CHPh \longrightarrow \overset{-}{Cl_4Sn}{\cdot}[CH_2{\cdot}CHPh]_{\mathit{n}+1}{\cdot}CH_2{\cdot}\overset{+}{C}HPh}$$

Termination :

$$\mathrm{\overset{-}{Cl_4Sn}{\cdot}[CH_2{\cdot}CHPh]_{\mathit{x}}{\cdot}CH_2{\cdot}\overset{+}{C}HPh \longrightarrow Cl_3Sn{\cdot}[CH_2{\cdot}CHPh]_{\mathit{x}}{\cdot}CH{:}CHPh + HCl}$$

$$\text{or}\quad \mathrm{Cl_3Sn{\cdot}[CH_2{\cdot}CHPh]_{\mathit{x}}{\cdot}CH_2{\cdot}CHPhCl}$$

The " zwitterions " postulated in this scheme are plausible reaction intermediates in small molecules, where the charges are close together or separated by a conjugated chain, but have been criticised as improbable when the charges are separated by a macromolecular saturated chain. Another weakness of this scheme is that it leaves no room for the action of co-catalysts, which have since been found necessary with this catalyst and monomer in a number of solvents (see Table 1). However, the polar-bond mechanism has recently been invoked to explain the polymerisation

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[91] *J. Amer. Chem. Soc.*, 1933, **55**, 1248.

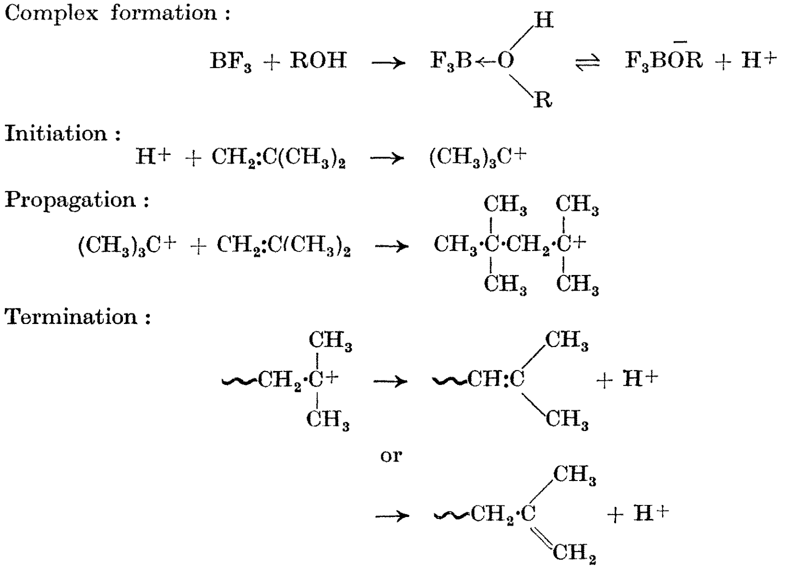
[92] Price and Ciskowski, *ibid.*, 1938, **60**, 2499.

[93] Price, *Ann. New York Acad. Sci.*, 1943, **44**, 368 ; " Reactions at Carbon–Carbon Double Bonds ", Interscience, N.Y., 1946.

of styrene and α-methylstyrene by aluminium chloride in carbon tetrachloride,[77, 83] where no co-catalysis by water or hydrogen chloride was observed.

(B) *Proton-initiated Carbonium-ion Mechanism.*—The low polymerisations, isomerisations, etc., of olefins by hydrogen-acid catalysts were formulated by Whitmore [94] as reactions of carbonium ions formed by the addition of a proton from the acid (HX) to the olefin double bond. The various products were explained by the various subsequent reactions of the carbonium ions, *e.g.*: (1) Union with the anion X^-, giving the addition product; (2) reversal of first step, *i.e.*, proton expulsion; (3) rearrangement of the carbonium-ion skeleton, followed by expulsion of hydrogen ion, giving a new olefin; (4) addition to further olefin, *i.e.*, polymerisation. To explain the wide variety of products in conjunct polymerisation, further possibilities are now suggested, *e.g.*, disproportionation, capture of H^- or R^-, etc.[3, 95, 96] The polymerisation was not formulated by Whitmore's school as a chain reaction, but it is clear that the above reactions include all the necessary elementary steps.

Their discovery of water co-catalysis in the polymerisation of *iso*butene by boron trifluoride enabled Evans and Polanyi [97] to formulate a similar carbonium-ion mechanism for the reactions induced by the Friedel–Crafts halides. Here the proton necessary for initiation is furnished by an ionic hydrate or similar complex between the catalyst and the co-catalyst:



Complex formation:

$$BF_3 + ROH \longrightarrow F_3B\leftarrow O\begin{smallmatrix}H\\R\end{smallmatrix} \rightleftharpoons F_3B\bar{O}R + H^+$$

Initiation:

$$H^+ + CH_2{:}C(CH_3)_2 \longrightarrow (CH_3)_3C^+$$

Propagation:

$$(CH_3)_3C^+ + CH_2{:}C(CH_3)_2 \longrightarrow CH_3{\cdot}\overset{CH_3}{\underset{CH_3}{C}}{\cdot}CH_2{\cdot}\overset{CH_3}{\underset{CH_3}{C}}{}^+$$

Termination:

$$\sim CH_2{\cdot}\overset{CH_3}{\underset{CH_3}{C}}{}^+ \longrightarrow \sim CH{:}C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix} + H^+$$

or

$$\longrightarrow \sim CH_2{\cdot}C\begin{smallmatrix}CH_3\\CH_2\end{smallmatrix} + H^+$$

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[94] *J. Amer. Chem. Soc.*, 1932, **54**, 3274; *Ind. Eng. Chem.*, 1934, **26**, 94.

[95] Schmerling, A.C.S. Cleveland Meeting, 1951.

[96] Bartlett, Condon, and Schneider, *J. Amer. Chem. Soc.*, 1944, **66**, 1531.

[97] *J.*, 1947, 252.

The general plausibility of this mechanism and its success in linking up the Friedel–Crafts with the acid-catalysed polymerisations has made it generally accepted for the hydrogen-co-catalysed systems. The kinetics of the above reaction are as yet not fully explored, but the validity of the processes postulated is supported by evidence from other sources, *e g.*, (i) the spectroscopic identification of the analogous carbonium ion $Ph_2(CH_3)C^+$ in the system $Ph_2C:CH_2–BF_3,H_2O$;[98] (ii) infra-red evidence of *tert* -butyl and methylene end groups, and of C–D links in polymer from *iso*butene–BF_3–D_2O.[99]

TABLE 1. *Water co-catalysis*

Monomer	Catalyst	Solvent	Slowed by drying	Accel by H_2O	Ref
*iso*Butene	BF_3	*iso*Butene	+	+	21
	$TiCl_4$	,,	+	+	66
	$SnCl_4$	C_2H_5Cl	+	+	67
Propene	$AlBr_3$	Butane		HBr +	35
But-1-ene	,,	,,		,,	
Styrene	BF_3	CCl_4	+	+	77
	$AlCl_3$	,,	—	—	76
	$TiCl_4$	Hexane	+	+	78
	,,	Toluene	+	+	,,
	,,	$(CH_2Cl)_2$	—	+	,,
	$SnCl_4$	Benzene	+	+	100
	,,	C_2H_5Cl	—	H_2O +, HCl +	75
	,,	$(CH_2Cl)_2$	—	H_2O —, HCl +	100
	,,	Ph·NO_2	—		48*b*
	,,	CCl_4	+	H_2O +, HCl —	73, 101
α-Methylstyrene	$AlCl_3$	CCl_4			83
	$SnCl_4$	C_2H_5Cl	+	+	84
Stilbene	$TiCl_4$	Hexane	+	+	102
Octyl vinyl ether	$AgClO_4$	Ether		+	90*b*
	$SnCl_4$	Hexane	—	—	,,

The Necessity for Co-catalysis.—Under the conditions of extreme dryness achieved by Evans and Meadows,[21] boron trifluoride and *iso*butene do not react. The rapid polymerisation normally found is therefore attributed to traces of contaminating moisture. Most of the recent work with other systems, listed in Table 1, has sought to discover whether this is generally true. These results suggest that water (or other hydrogen co-catalyst) is

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[98] Evans and Hamann, ref. (8*b*), p. 139.

[99] Dainton and Sutherland, *J. Polymer Sci.*, 1949, **4**, 37.

[100] Pepper, ref. (9*b*), p. 70.

[101] Colclough, personal communication.

[102] Brackman and Plesch, ref. (9*b*), p. 103.

necessary for hydrocarbon monomers in non-polar solvents, but is not necessary, though sometimes helpful, in polar and especially chlorinated solvents. The results are not entirely unambiguous, since the conclusion to be drawn from the effect of drying depends on the level of dryness actually reached—there is evidence in two systems [77, 101] that the rate may pass through a maximum and then fall with increasing water content. However, it is clear from at least one pair of parallel experiments [100] that methods of drying and manipulation adequate to demonstrate water co-catalysis with styrene–stannic chloride in benzene entirely fail to reveal it in ethylene dichloride.

Carbonium-ion Initiation : Solvent Co-catalysis.—The polymerisation of octyl vinyl ether by triphenylmethyl chloride in ionising solvents,[90b] and the incorporation of alkyl end groups in polymers prepared in solution in alkyl bromides,[78] indicate that polymerisation may be initiated by carbonium ions as well as by protons. Such carbonium ions may be produced by interaction of Friedel–Crafts halides with many organic halides, as described earlier. Interactions of this type, *i.e.*, " solvent co-catalysis ", have been postulated to explain the apparent non-necessity of water co-catalysis in many chlorinated solvents as described in the last section. Nitro-solvents may also act in the same way, though here the precise formulation of ionic complexes is not so simple.

In some systems, *e.g.*, styrene–stannic chloride in ethyl chloride, water and hydrogen chloride do not appear to be *necessary*, but do in fact accelerate the reaction. Presumably, then, in any normal, *i.e.* imperfectly dried mixture, initiation will proceed *via* all three co-catalysts, *viz.*, solvent, water, and hydrogen chloride (from hydrolysis of catalyst). Which process predominates in a given solvent will depend on the relative concentrations of the co-catalysts and their relative affinities for the catalyst, and on the relative carbonium-ion and proton affinities of the monomer. These latter quantities are usually unknown, and present estimates of activity in " solvent co-catalysis " must be based largely on the expected ease of formation of carbonium ions from the halide, *viz.*,

$$\mathrm{Ph_3C{\cdot}Cl > Bu^tCl > Pr^iCl > EtCl > Cl{\cdot}CH_2{\cdot}CH_2Cl > CCl_4}$$

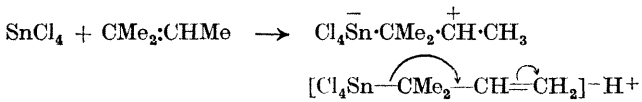
i.e., one would expect solvent co-catalysis to be less, and hydrogen co-catalysis to be more important in the solvents at the lower end of this series. Comparative results are not available, but there is reason to believe that the above is not a unique order of efficacy, and that the general polarity of the solvent plays an important part in deciding whether solvent co-catalysis does or does not take place.

Monomer Co-catalysis.—In some systems where solvent or hydrogen co-catalysis appeared unlikely, it has been suggested that catalyst–monomer complexes could provide initiating ions, *e.g.*, in the stannic chloride polymerisation of vinyl ethers in hexane,[103] and in the dimerisation by stannic chloride of trimethylethylene.[104] In the latter case, it is inferred from the

[103] Hamann, Plesch, and Skinner, ref. (8*b*), p. 141.

[104] Baker, *Nature*, 1948, **161**, 171 ; *J.*, 1950, 1302.

structure of the dimeride that the electrophilic catalyst stabilises one of the hyperconjugation structures of the olefin :



$$SnCl_4 + CMe_2{:}CHMe \longrightarrow Cl_4\overset{-}{Sn}\cdot CMe_2\cdot\overset{+}{C}H\cdot CH_3$$
$$[Cl_4Sn{-}CMe_2{-}CH{=}CH_2]^-H^+$$

General Conclusions on Initiation.—For the above reasons it is now widely believed that the polymerisation always involves ions, rather than polar co-ordination complexes, and that when the catalyst is a Friedel–Crafts halide there must always be a co-catalyst of some sort. These conclusions may be summarised by writing the equation for the initiation reaction with the following generalised symbols :

For acid catalysts (HB) :

$$HB + CH_2{:}CHY \longrightarrow CH_3\cdot\overset{+}{C}HY + B^-$$

For Friedel–Crafts catalysts (MX_n) :

$$MX_n\cdot AB + CH_2{:}CHY \longrightarrow A\cdot CH_2\cdot\overset{+}{C}HY + [MX_nB]^-$$

where AB represents any potentially ionisable compound whose dissociation may be sufficiently enhanced by complexing with the Friedel–Crafts halide.

Ions or Ion-pairs.—The above mechanisms have been written for convenience as reactions of free ions, but it is believed that ion-pairs rather than free ions are involved, *i.e.*, that the carbonium ions remain always in close association with the anions of the catalyst–co-catalyst complex. In organic solvents of relatively low polarity one would expect little solvation of the ions and high energies of charge separation (estimated at 80 kcal. in *iso*butene [58]). Even in the much more polar nitroparaffin solvents, spectroscopic evidence indicates that ion-pairs and not free ions are the predominant species formed from Ph_3CCl and from the complex $Ph_3CCl,HgCl_2$.[43, 105] With $Ph_3CBr,SnBr_4$ in alkyl halides [106] the ionisation constant to ion-pairs is deduced to be 10^5—10^7 times greater than the dissociation constant to free ions. (In the strongly ionising solvent sulphur dioxide, compounds such as Ar_3CClO_4 and Ar_3CCl dissociate appreciably.[107, 108])

However, these considerations do not absolutely exclude the possibility of initiation by free ions, since in a chain reaction the concentration of initiators need only be very small. The decision will probably have to be made on kinetic evidence, which is as yet inconclusive, but to some extent supports ion-pair rather than free-ion mechanisms. If free ions were formed by equilibrium dissociation of the catalyst–co-catalyst complex, then the rate and degree of polymerisation should show a fractional dependence on the concentration of catalyst (or co-catalyst, whichever is limiting) which is not normally found. Another observation, that the probability of monomer transfer is different with different catalysts, suggests that the

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[105] (*a*) Bentley, Evans, and Halpern, *Trans. Faraday Soc.*, 1951, **47**, 711 ; (*b*) Bentley and Evans, *J.*, 1952, 3468.

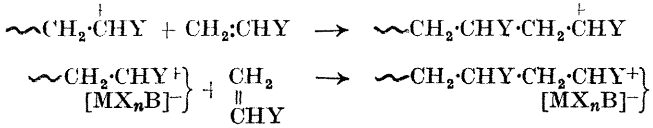
[106] Fairbrother and Wright, *J.*, 1949, 1058.

[107] Ziegler and Wollshitt, *Annalen*, 1930, **479**, 90.

[108] Lichtin and Bartlett, *J. Amer. Chem. Soc.*, 1951, **73**, 5530.

transfer process, or the termination step, or both, are influenced by the proximity of the catalyst anion.

The Propagation Reaction.—This is regarded simply as the addition of a monomer molecule to the growing carbonium ion or ion-pair, *viz.*:



$$\sim\!\mathrm{CH_2}\cdot\overset{+}{\mathrm{C}}\mathrm{HY} + \mathrm{CH_2{:}CHY} \longrightarrow \sim\!\mathrm{CH_2\cdot CHY\cdot CH_2}\cdot\overset{+}{\mathrm{C}}\mathrm{HY}$$

or

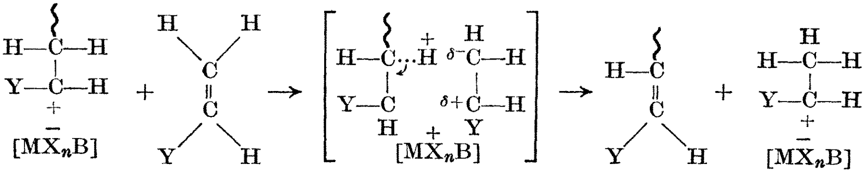
$$\left.\begin{matrix}\sim\!\mathrm{CH_2\cdot CHY^{+}}\\ \mathrm{[MX_{\mathit{n}}B]^{-}}\end{matrix}\right\} + \begin{matrix}\mathrm{CH_2}\\ \Vert\\ \mathrm{CHY}\end{matrix} \longrightarrow \left.\begin{matrix}\sim\!\mathrm{CH_2\cdot CHY\cdot CH_2\cdot CHY^{+}}\\ \mathrm{[MX_{\mathit{n}}B]^{-}}\end{matrix}\right\}$$

In such reactions the monomer molecule will be highly polarised in the transition state, and hence its preferred orientation will be that of maximum polarisibility as determined by the character of its substituents. Since these are normally electropositive groups, we should expect cationic addition to occur always at the least substituted end of the double bond, giving a regular head-to-tail structure to the chain. This has been demonstrated in the case of poly*iso*butene,[64] even though the regular structure has appreciably higher (strain) energy than the head-head-tail-tail structure.[109]

As Dainton [110] has pointed out, the coulombic energy of interaction between the ion, or ion-pair, and the dipole induced in the monomer double bond should reduce the activation energy for propagation below that for propagation of radical chains, and is therefore one reason for the lower overall activation energies found in ionic polymerisations.

Transfer Reactions.—Monomer transfer processes were first recognised in ionic polymerisations by Eley and Richards [111] with octyl vinyl ether and various catalysts. With this monomer and other vinyl ethers [90] and with the 1-alkenes,[3] monomer transfer appears to be the dominant factor in determining the molecular weight at room temperatures. It has also been postulated in the polymerisation of styrene in carbon tetrachloride by aluminium chloride [76] and by boron trifluoride,[77] though it does not seem important with this monomer catalysed by stannic chloride in ethylene chloride.[33] With octyl vinyl ether, transfer takes place to different extents with different catalysts.[90b]

The reaction is regarded as the transfer of a proton from the polymer carbonium ion to a monomer molecule, leaving the " dead " polymer with a terminal double bond. If the process is written with ion-pair structures, then the influence both of the monomer constitution and of the catalyst may be visualised:



The electromeric and inductive effects of the substituent Y may act in

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[109] Evans and Polanyi, *Nature*, 1943, **152**, 738.

[110] Refs. (8*b*), p. 154; (9*b*), p. 150.

[111] *Research*, 1949, **2**, 147.

opposite directions, so that prediction of the effect of different substituents on ease of transfer is not simple.

Solvent transfer processes, so important in radical polymerisations, have so far received little mention in ionic reactions. It has been postulated in the aluminium chloride polymerisation of styrene in carbon tetrachloride,[76] and recently to explain the low molecular weights and *p*-tolyl end groups in polystyrenes produced by $TiCl_4$–$CCl_3{\cdot}CO_2H$ in toluene.[78] In the latter system, Plesch distinguishes four possible types of solvent-transfer reaction, according as the solvent is or is not incorporated in the polymer, and if so, whether it appears in the terminated or the initiated chain or both. Recently Overberger and Endres [111a] have observed that thiophen, anisole, and some other aromatic hydrocarbons act as transfer agents in the polymerisation of styrene by stannic chloride, reducing the chain length in conformity with the quantitative relation discovered for free-radical polymerisation by Mayo.[111b]

All the above transfer processes are proton transfers, and the "dead" polymer is left unsaturated or cyclised. A different type of transfer has been postulated by Meier [3] and by Fontana [35] in the polymerisation of propene and but-1-ene. Here the polymer carbonium ion is thought to capture a negatively charged alkyl group or a hydride ion from a dead polymer molecule or from another polymer carbonium ion, *viz.*, for hydride transfer:

$$\sim\!\sim C^+ + \sim\!\sim CH\sim\!\sim \;\longrightarrow\; \sim\!\sim CH + \sim\!\sim \overset{+}{C}\sim\!\sim$$

or

$$\sim\!\sim C^+ + \sim\!\sim CH\sim\!\sim C^+ \;\longrightarrow\; \sim\!\sim CH + \sim\!\sim \overset{+}{C}\sim\!\sim \overset{+}{C}\sim\!\sim$$

Thus the terminated chain becomes saturated, and the new growth centre is a branched or doubly-charged carbonium ion. Such transfers of H^- or of R^- have been postulated in various alkylation reactions,[96, 112] and are here invoked to explain the formation of highly branched polymers, and as a possible source of the doubly or triply charged carbonium ions which appear to be present in Friedel–Crafts tar.

Termination Reactions.—Several different termination processes have been suggested to account for the overall kinetics of the polymerisation, or for end groups found in the polymer. They include:

(i) *Proton expulsion.* This has been postulated in cases where there is evidence of unsaturation in the polymer, or where many polymer molecules are formed per molecule of catalyst (or co-catalyst), or where there is kinetic evidence of a unimolecular termination step. In the ion-pair formulation, the proton is regarded as lost to the counter-anion:

$$\left.\begin{matrix}\sim\!\sim CH_2\text{—}\overset{+}{C}HY \\ [MX_nB]^-\end{matrix}\right\} \;\longrightarrow\; \sim\!\sim CH{:}CHY + H^+[MX_nB]^- \atop \qquad\qquad (\text{or } MX_n + HB)$$

thus regenerating the initiating complex. For this to be a unimolecular

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[111a] Overberger and Endres, *J. Amer. Chem. Soc.*, 1953, **75**, 6349.
[111b] Mayo, *ibid.*, 1943, **65**, 2324.
[112] Donnell and Kennedy, Int. Congr. Pure and Appl. Chem., 1951.

process, the carbonium ion and its counter anion must be so closely associated as to function as a single kinetic unit. Where this termination process operates it is clear that the relative importance of monomer transfer and of termination is determined primarily by the ratio of the proton affinities of the monomer and the catalyst anion.

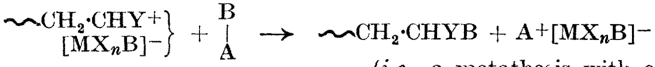
A variant of this process, where the proton is lost from a carbon atom further down the chain or from a substituent benzene ring, has been postulated [84, 102] to explain the cyclised end groups found in low polymers of α-methylstyrene and stilbene.

(ii) *Combination with an anion.* There is evidence in some systems that the counter-anion or some fragment of it may be incorporated in the polymer, *e.g.*, OH^- in *iso*butene–$SnCl_4$–H_2O ; [113] $CCl_3{\cdot}CO{\cdot}O^-$ in *iso*butene–$TiCl_4$–$CCl_3{\cdot}CO_2H$; [114] Br^- in styrene–HBr.[79] The retardation by Cl^- anions of the polymerisation of styrene by stannic chloride [49] and the marked reduction of molecular weight by hydrogen halides in the *iso*butene–BF_3 and styrene–$SnCl_4$ polymerisations may be caused by such a termination process, *e.g.* :

$$\left.\begin{matrix}\sim\!\!\sim CH_2{\cdot}CHY^+\\ [MX_nB]^-\end{matrix}\right\} \rightarrow \sim\!\!\sim CH_2{\cdot}CHYB + MX_n$$

(*i.e.*, a recombination)

or

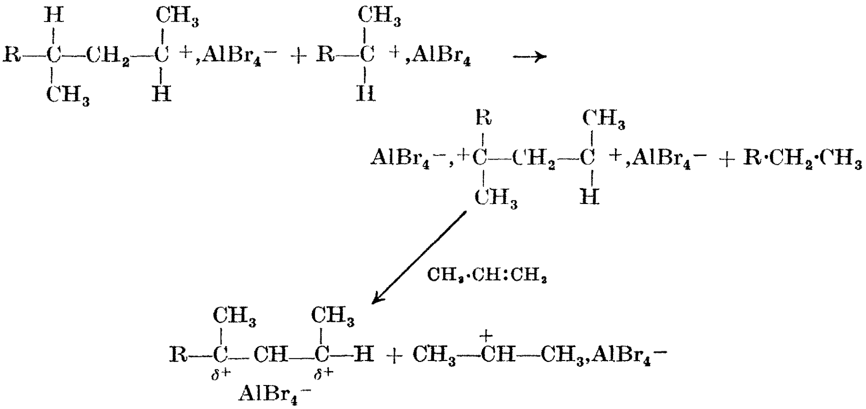


$$\left.\begin{matrix}\sim\!\!\sim CH_2{\cdot}CHY^+\\ [MX_nB]^-\end{matrix}\right\} + \begin{matrix}B\\ |\\ A\end{matrix} \rightarrow \sim\!\!\sim CH_2{\cdot}CHYB + A^+[MX_nB]^-$$

(*i.e.*, a metathesis with cocatalyst)

Traces of tin compounds found in polystyrenes catalysed by tin halides [115, 116] were at first taken as evidence for the polar-bond mechanism of initiation.[93] They could equally well arise from a combination termination process. There is, however, some uncertainty whether the tin is chemically linked to the polymer, or merely physically adsorbed.[117]

(iii) *Resonance stabilisation of multivalent carbonium ions.* This process has been postulated in alkylations by Burk and other authors,[118, 119] and in the polymerisations of 1-alkenes by Meier [3] and by Fontana.[35] When, as a result of hydride-ion transfer, doubly charged carbonium ions are formed, they may react with monomer to form allylic-type carbonium ions so stabilised by resonance as to be incapable of further propagation :



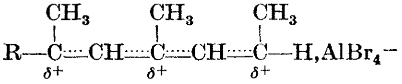
$$R-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}{}^+,AlBr_4^- + R-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}{}^+,AlBr_4 \rightarrow$$

$$AlBr_4^-,{}^+\overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}{}^+,AlBr_4^- + R{\cdot}CH_2{\cdot}CH_3$$

$$\xrightarrow{CH_3\cdot CH:CH_2}$$

$$R-\overset{\overset{CH_3}{|}}{\underset{\delta+}{C}}-\underset{AlBr_4^-}{CH}-\overset{\overset{CH_3}{|}}{\underset{\delta+}{C}}-H + CH_3-\overset{+}{C}H-CH_3,AlBr_4^-$$

For complete inactivation, a further sequence of reactions is envisaged, leading to :



$$\mathrm{R{-}}\underset{\delta+}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}\cdots\mathrm{CH}\cdots\underset{\delta+}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}\cdots\mathrm{CH}\cdots\underset{\delta+}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}\mathrm{{-}H,AlBr_4^-}$$

The existence of complexes of this type in the Friedel–Crafts tar is inferred from the formation of conjugated trienes on hydrolysis of the tar. Although termination reactions of this type may well play a part in the complex behaviour of alkenes, there is as yet no evidence for them in the polymerisation of arylenes and vinyl ethers.

(II, 6) **Kinetics.**—The main kinetic features are now known for a number of systems, though in some cases detailed interpretation is difficult because of uncertainty about the presence or concentration of co-catalysts, and the possible complication of heterogeneous effects.

In some systems, usually with non-polar solvents, behaviour is complex. Lengthy induction periods are observed, followed in some cases by a period of constant rate (zero order), and in others by a rate which falls off rapidly as reaction proceeds (high order). Both these types of behaviour have been found by different observers in the same system, styrene–$SnCl_4$–CCl_4, which is now known to require water as a co-catalyst.[101] Similar behaviour is shown by styrene–BF_3–CCl_4–H_2O,[77] where different orders in monomer concentration were found at different water contents, and a zero-order reaction when the catalyst–co-catalyst was pre-formed on the surface of the reaction vessel. It seems likely that these complexities are associated with heterogeneous reactions on the surface of an insoluble catalytic complex. Heterogeneous polymerisation is, of course, well known on the catalytic silicates, and the BF_3–$CH_3{\cdot}CO_2H$ polymerisation of gaseous *iso*butene has been shown to take place only in presence of crystals of the complex.[22] It may even be found that all water-co-catalysed reactions are heterogeneous, as Skinner [120] has argued that hydrates of the type $BF_3OH^-H^+$ are stable only in the crystalline state.

Dainton [121] has indicated how the proton-initiated mechanism may be applied to a heterogeneous polymerisation : initiation at a " proton site " on the acid crystal surface, propagation in the adsorbed monomer, and termination by loss of a proton to a vacant " proton site ". In such a case, the kinetics may be dominated by the rates of adsorption of monomer and desorption of polymer, though desorption may be facilitated by the locally liberated heat of polymerisation.

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[113] Mark, ref. (5), p. 195.

[114] Flett and Plesch, *J.*, 1952, 543 ; ref. (9*b*), p. 119.

[115] Staudinger, " Die hochmolekularen organischen Verbindungen ", Springer, Berlin, 1932.

[116] Landler, *Rec. Trav. chim.*, 1949, **68,** 992.

[117] Colclough, *J. Polymer Sci.*, 1952, **8,** 467 ; ref. (9*b*), p. 101.

[118] Burk, Lankelma, *et al.*, *J. Amer. Chem. Soc.*, 1945, **67,** 910, 914.

[119] Caviet, van Steenis, and Waterman, *Rec. Trav. chim.*, 1949, **68,** 553.

[120] Ref. (9*b*), p. 28.

[121] Refs. (9*b*), p. 138 ; (8*b*), p. 146.

TABLE 2. *Overall kinetics*

Monomer (M)	Catalyst (C)	Co-catalyst (Co)	Solvent	Rate expression	$\overline{\text{D.P.}}$*	E_R,† kcal.	$E_{D.P}$	Ref.
Propene	$AlBr_3$	HBr	Butane	—	—	10·3	—	35
*iso*Butene	$TiCl_4$	H_2O	Hexane	—	—	8	—	66*b*
		$CCl_3{\cdot}CO_2H$	,,	—	—	− 7·5	− 7·5	,,
	$SnCl_4$	H_2O	EtCl	$k[M][Co]$	$k'[M]/[Co]$	7	—	67
Styrene	$AlCl_3$	?	CCl_4	$k[M][C]$	f([M])	1·2	− 3·8	76
	$TiCl_4$	$CCl_3{\cdot}CO_2H$	Toluene	—	—	− 1·5	—	78
		Solvent	$(CH_2Cl)_2$	$k[M]^2[C]$	—	− 8·5	—	78
	$SnCl_4$	(H_2O ?)	CCl_4	$k[M]^3[C]$	$k'[M]$	3	—	73
		,,	,,	$k[M]^{2-3}[C]$	—	—	—	74
		Solvent ?	EtCl	$\dfrac{k[M]^2[C]}{1 + k''[M]}$	$k'[M]$	4·5	—	75
		Solvent	$(CH_2Cl)_2$	$k[M]^2[C]$	$k'[M]$	—	—	33
α-Methyl-styrene	$SnCl_4$	EtCl ? H_2O	EtCl	$k[M]^{1-2}[C]^{3/2}$	$k'[M]$	− 3·5	− 4·5	84
	$AlCl_3$	,,	EtCl	—	—		− 4 to − 6	82
	H_2SO_4		CH_2Cl_2	—	—		− 6·6	10
Stilbene	$TiCl_4$	$CCl_3{\cdot}CO_2H$	Hexane	$k[M]^2[C][Co]$	—	3·5	—	102
Octyl vinyl ether	$SnCl_4$	Monomer ?	Hexane	$k[M]^2[C]$	$k'[M]$	10	− 3·3	90*b*
	$AgClO_4$	H_2O ?	Ether	,,	Independent	—	—	,,
	Ph_3CCl	—	*m*-Cresol	,,	,,	—	—	,,
	I_2	I_2	Hexane	$k[M][C]^2$	,,	10	− 3·3	,,
	,,	,,	$(CH_2Cl)_2$	,,	,,	16	− 3·3	,,
Other vinyl ethers	I_2	,,	Ether	$k[M][C]^2$	,,	—	—	90*c*

* $\overline{\text{D.P.}}$ = Average degree of polymerisation, *i.e.*, average number of monomer units in the polymer molecule.

† E_R and $E_{D.P.}$ symbolise the activation energies for overall rate (R) and degree of polymerisation defined by

$$\log R \text{ (or } \log \text{D.P.)} = \text{Constant} - \frac{1}{2{\cdot}3\boldsymbol{RT}} E_R \text{ (or } E_{D.P.})$$

They are composite quantities, *i.e.*, algebraic functions of the activation energies of the elementary steps of the chain reaction, and hence may have negative values under certain conditions (see p. 111).

There has been no detailed study of explicitly heterogeneous polymerisations, but related carbonium-ion chain reactions on solid surfaces have been discussed by Rijnders and Schuit,[122] and the acid strength of surfaces by Walling.[123]

The kinetic expressions and activation energies for the systems so far investigated are collected in Table 2. With the exception of those cited under refs. 66*b*, and perhaps 73 and 74, these systems appear homogeneous. It can be seen that in many systems the overall kinetic relations correspond to :

$$\text{Rate} = k[\text{M}]^2[\text{C}] \quad \text{or} \quad k[\text{M}]^2[\text{Co}], \text{ according as catalyst or co-catalyst is limiting}$$

$$\overline{\text{D.P.}} = k'[\text{M}], \text{ independent of } [\text{C}]$$

Comparison of these with the theoretical steady-state relations shown in Table 3 suggests that in these systems the initiation process is bimolecular (first order in monomer and catalytic complex), and the termination process unimolecular, *i.e.*, it does not involve reaction with monomer, catalyst, or a second polymer ion.

In the polymerisation of vinyl ethers by iodine quite different relations are found. They can be explained if initiation takes place via an iodine cation formed by the reaction $2I_2 = I_3^- + I^+$. If this reaction is slow and a stationary concentration of I^+ becomes established, the initiation rate becomes effectively independent of monomer concentration, and the overall kinetics are as found (see Table 3, case II). A complication found with the vinyl ethers is that they tend to form an inactive complex with iodine, thereby reducing its effective concentration and leading to a maximum in the rate–[M] relation at high values of [M].[90c] The virtual independence of molecular weight on monomer concentration is attributed to a predominance of monomer transfer over the normal termination process.

One of the obvious differences from the kinetics of radical polymerisations is the absence of square-root dependences. These arise in the radical case as a result of the predominantly mutual termination of polymer radicals. Mutual termination of oppositely charged polymer ions has once been suggested,[67a] but is not now believed tenable, since the conditions for stability of carbonium ions and carbanions are so different. Exponents of $\frac{1}{2}$ could in principle arise in another way, *viz.*, if initiation were brought about by free cations formed by equilibrium dissociation of the catalyst–co-catalyst complex (Table 3, Çase I, B, ii). There is no evidence as yet that this occurs. Non-integral exponents may be expected if the catalyst–co-catalyst complex has other than 1 : 1 stoicheiometry, as may be the case in Dainton and Tomlinson's experiments with α-methylstyrene–$SnCl_4$–H_2O in ethyl chloride.[84]

The fact that the molecular weight of the polymer is always found to be independent of catalyst concentration is usually taken as evidence for a spontaneous termination process. It must be remembered, however, that most of the present results refer only to the concentration of the Friedel–Crafts halide, and that the concentration of the co-catalyst, and hence of

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[122] Ref. (9*b*), p. 134.

[123] *J. Amer. Chem. Soc.*, 1950, **72**, 1164.

the initiating complex, is usually unknown. In the few cases where the co-catalyst concentration is known it is found to have an inverse effect on the molecular weight of the polymer. Further study of this effect is much needed, to test present speculations about the rôle of the co-catalyst as a termination or transfer agent.

TABLE 3. *Theoretical expressions for overall kinetics*

Rate constants: k_1, initiation; k_p, propagation; k_{tr}, monomer transfer; k_t, termination.

A stationary chain reaction being assumed, different expressions result according to the termination process postulated, and also according as the rate-determining step in initiation is the ionisation process itself, or the reaction of monomer with the ion (or ion-pair). Some of the relevant cases are as follows:

I. Monomer initiation rate-determining

A. Initiation by ion-pair complex formed in equilibrium:

$$C + Co \overset{K_1}{\rightleftharpoons} \text{Complex}$$

Termination	Overall rate	D.P.
(i) Spontaneous . . .	$\frac{k_1k_p}{k_t}[M]^2K_1[C][Co]$	$\frac{k_p[M]}{k_{tr}[M] + k_t}$
(ii) 1st-Order recombination with anion	,,	,,
(iii) 2nd-Order metathesis with co-catalyst	$\frac{k_1k_p}{k_t}[M]^2K_1[C]$	$\frac{k_p[M]}{k_{tr}[M] + k_t[Co]}$

B. Initiation by free cation from $\text{Complex} \overset{K_2}{\rightleftharpoons} \text{Ions}$:

Termination		
(i) Spontaneous . . .	$\frac{k_1k_p}{k_t}[M]^2(K_1K_2[C][Co])^{1/}$	$\frac{k_p[M]}{k_{tr}[M] + k_t}$
(ii) Combination with free anion	$\frac{k_1k_p}{k_t}[M]^2$	$\frac{k_p[M]}{k_{tr}[M] + k_t(K_1K_2[C][Co])^{1/2}}$

These equations hold for the initial concentrations [C] and [Co] only if K_1 is small and $K_2 \ll K_1$. If K_1 is large, then $K_1[C][Co] = [C]$ or [Co], whichever is smaller.

II. *Ionisation rate-determining, e.g.*, $C + Co \xrightarrow{k} \text{Ions}$

Termination		
Spontaneous	$\frac{kk_p}{k_t}[M][C][Co]$	$\frac{k_p[M]}{k_{tr}[M] + k_t}$

The temperature dependence of rate and degree of polymerisation is usually fairly simple, and linear log rate–$1/T$ and log $\overline{\text{D.P.}}$–$1/T$ relations are often found. (This is not always true; with alk-1-enes–$AlBr_3$–HBr a pronounced maximum in molecular weight is found in the region $-35°$ to $-50°$,[35] and with vinyl ethers–iodine[90b] and α-methylstyrene–$AlCl_3$[82] the normal decrease of molecular weight with temperature steepens sharply at high temperatures.) The derived activation energies are listed in Table 2, and their low, and sometimes negative, values emphasise the difference from radical-polymerisation kinetics. It seems clear that the activation energy for rate of a given monomer varies widely according to catalyst, co-catalyst, and solvent, but that $E_{\mathrm{D.P.}}$ is less affected.

In several radical polymerisations the rate constants and activation energies of all the elementary steps (initiation E_{i}, propagation E_{p}, termination E_{t}, and transfer E_{tr}) have been evaluated. It is found that all except E_{i} are very small, *i.e.*, the overall activation for polymerisation is dominated by the energy of formation of radicals. In ionic polymerisations no method has yet been found to determine the individual rate constants, but it is possible on general grounds to make the following tentative analysis of the activation energies.

Since no fractional exponents appear in the kinetic relations, the overall activation energies are given simply by: $E_{\mathrm{R}} = E_{\mathrm{i}} + E_{\mathrm{p}} - E_{\mathrm{t}}$ and $E_{\mathrm{D.P.}} = E_{\mathrm{p}} - E_{\mathrm{t}}$ (or $E_{\mathrm{p}} - E_{\mathrm{tr}}$ if transfer predominates). There is reason to believe[110] that E_{p} is even smaller in ionic than in radical polymerisations and therefore $E_{\mathrm{p}} \sim 0$. Hence $E_{\mathrm{i}} = E_{\mathrm{R}} - E_{\mathrm{D.P.}}$, and $E_{\mathrm{t}} \sim -E_{\mathrm{D.P.}}$. On these assumptions, the results in Table 2 give values of E_{i} in the region 0—5 kcal./mole for *iso*butene, styrene, and α-methylstyrene, and higher values, 13—16, for the vinyl ethers, and values of E_{t} (or E_{tr}) all in the region 3—7 kcal./mole. Thus it would appear that ionic are similar to radical polymerisations in that the overall activation energy is dominated by E_{i}, and that the low overall values usually found are a consequence of relatively low values of E_{i}, rather than of high values of E_{i} coupled with high values of E_{t}. Similarly, it appears that the variations of E_{R} with different catalysts, etc., are associated more with variations in E_{i} than in E_{t}. This is to be expected, since the activation energy for initiation by different catalyst–co-catalyst complexes will differ widely according to the proton (or carbonium-ion) affinities and solvation energies of the catalyst–co-catalyst anion.

It is not yet possible to identify with certainty the process responsible for the normal decrease of molecular weight with temperature. Strictly, $E_{\mathrm{D.P.}}$ is a composite function to which E_{t} and E_{tr} contribute differently at different temperatures, *i.e.*, the log $\overline{\mathrm{D.P.}}$–$1/T$ plot should change slope with rising temperature as the higher-activation-energy process becomes more important. A linear relation therefore indicates either that only a single chain-stopping process operates, or that E_{t} and E_{tr} are approximately equal.

There are thus three possible cases :

(*a*) $E_{\mathrm{tr}} \gg E_{\mathrm{t}}$, and hence $E_{\mathrm{D.P.}} \sim -E_{\mathrm{t}}$
(*b*) $E_{\mathrm{tr}} \ll E_{\mathrm{t}}$, ,, ,, $E_{\mathrm{D.P.}} \sim -E_{\mathrm{r}}$
(*c*) $E_{\mathrm{tr}} \sim E_{\mathrm{t}} \sim -E_{\mathrm{D.P.}}$

Case (*a*) has been postulated by Eley and Richards for the polymerisation of octyl vinyl ether by stannic chloride, where there is no evidence for monomer transfer at room temperature, and where the normal $E_{\mathrm{D.P.}}$ increases sharply at higher temperatures. Case (*b*) would seem to apply to the polymerisation of the same monomer with iodine, where monomer transfer is said to be predominant yet $E_{\mathrm{D.P.}}$ is only $-3{\cdot}3$ kcal./mole.

Depropagation processes have been suggested by Dainton [110] as an alternative explanation of the decrease of molecular weight at high temperatures. Such reactions have relatively high activation energy ($E_{\mathrm{dep.}} = E_{\mathrm{p}} + \Delta H_{\mathrm{p}}$) and are responsible for " ceiling-temperature " effects in several radical copolymerisations.[124] However, such effects have not yet been observed in ionic polymerisations.

Non-stationary Conditions.—The above discussion is based on the normally accepted assumption that the reactions are stationary chain reactions to which the conventional steady-state analysis can be applied. For most systems this assumption is probably valid, but under some conditions kinetic anomalies are observed—sigmoid reaction–time curves, growth of molecular weight during reaction, etc.—which are suggestive of non-stationary conditions. It is clear that some of the reaction mechanisms postulated earlier may lead under suitable conditions not to chain reactions but to stepwise growth of the polymer molecule. Fontana and Kidder's mechanism [35] is one such, and the proton-initiated mechanism may also in principle give this result. If the polymer is left with a terminal double bond, then it may be reactivated by proton addition and continue to grow. In consequence, the proton-expulsion termination is strictly not a true cessation step, but a dissociation equilibrium :

$$\sim\!\sim\mathrm{CH_2{\cdot}\overset{+}{C}HY} \underset{k_i}{\overset{k_t}{\rightleftharpoons}} \sim\!\sim\mathrm{CH{:}CHY} + \mathrm{H^+}$$

where the back reaction is similar to the original initiation process. If both k_t and ki were large and comparable with k_p, this dissociation equilibrium would be established at all stages of chain growth :

$$\begin{array}{lclcl}
\mathrm{M} + \overset{+}{\mathrm{H}} & \underset{k_t}{\overset{k_i}{\rightleftharpoons}} & \overset{+}{\mathrm{P}}_1 & \xrightarrow[\mathrm{M}]{k_p} & \overset{+}{\mathrm{P}}_2 \\
\mathrm{P}_2 + \overset{+}{\mathrm{H}} & \rightleftharpoons & \overset{+}{\mathrm{P}}_2 & \longrightarrow & \overset{+}{\mathrm{P}}_3 \\
\mathrm{P}_n + \overset{+}{\mathrm{H}} & \rightleftharpoons & \overset{+}{\mathrm{P}}_n & \longrightarrow & \overset{+}{\mathrm{P}}_{n+1}
\end{array}$$

In such circumstances it would be meaningless to speak of a kinetic chain length, and the polymer molecular weight would grow continuously throughout the reaction by a stepwise succession of unit additions of monomer.

Even where there is a true termination process, stationary conditions become rapidly established only when the rate of propagation $\gg$ initiation $=$ termination rate. Recent calculations by Benson [125] show that in order to establish a stationary state early in the reaction (*e.g.*, at a fraction

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[124] Dainton and Ivin, *Nature*, 1949, **163**, 424 ; *Proc. Roy. Soc.*, 1952, *A*, **212**, 207.

[125] *J Chem. Phys.*, 1952, **20**, 1605.

α of total conversion) the ratio of initiation to propagation rates must always be less than α and usually less than $\alpha/4$. Where long-chain polymer is formed, this criterion is clearly satisfied. There are, however, many systems where the degree of polymerisation at room temperature or higher is quite low, and in some cases as little as 3—10. If the degree of polymerisation is determined by chain termination rather than by transfer, this means that in the latter cases the propagation rate is only about an order of magnitude greater than the termination (= initiation) rate. We should not therefore expect stationary conditions to be established until the reaction had proceeded some 10—40%. Of course, if transfer processes are active, the ratio of propagation to initiation rates will be greater than indicated by the polymer molecular weight, and stationary conditions may be established even when only very low polymer is formed. But it is clear that individual scrutiny should be given to each system before the stationary-state assumptions are applied.

Solvent Effects.—The marked accelerating effect of polar solvents, especially halogeno- and nitro-compounds, has already been mentioned. Two different types of effect must be distinguished, first the solvent co-catalysis described earlier, and secondly the more general effect of the polarity of the solvent on the ionic processes in the polymerisation. The latter effect has been discussed by the Reviewer [48] and by George, Wechsler, and Mark [49] in terms of the effect of the dielectric constant of the medium on simple ionic reactions. Unequivocal quantitative data are still too scanty to warrant attempts at precise theory, but qualitatively it is clear that the dielectric and dipolar properties of the medium will influence the energies of charge separation, and affect the solvation energies of ions or ion-pairs.

It is usually found that as the dielectric constant of the solvent is increased the rate of polymerisation is markedly increased, but the molecular weight only moderately. Hence it seems that it is the initiation process that is most affected. In two systems, octyl vinyl ether–iodine in hexane and in ethylene dichloride, and styrene–stannic chloride in carbon tetrachloride and in ethyl chloride, there is evidence that the overall rate is greater in the solvent of higher dielectric constant, despite the fact that the overall activation energy is also greater. This fact, together with the previous conclusion, suggests that the major effect of high solvent polarity is to increase the concentration of initiating ions or ion-pairs. Recent measurements by Bentley and Evans [105] show that the ionisation constant of triphenylmethyl chloride (to ion-pairs) increases more than 100-fold in going from 2-nitropropane ($\varepsilon = 19$) to nitromethane ($\varepsilon = 39$).

In a given system it is often difficult to distinguish between the two solvent effects, especially where, as with nitro-compounds, the details of the initiation process are not yet clearly understood. In many halogenated solvents it appears that both effects are present ; the solvents are potential co-catalysts, *i.e.*, can form ionising complexes with the catalyst, but only act appreciably as such if they are sufficiently polar. Thus with stannic chloride, carbon tetrachloride ($\varepsilon = 2$) seems not to act as a co-catalyst, whereas ethyl chloride ($\varepsilon = 5$) and ethylene dichloride ($\varepsilon = 10$) do. The polymerisation of styrene by stannic chloride is more rapid in the latter than in the former, though ethyl chloride should be intrinsically the stronger co-catalyst.

The polar effect without complication by solvent co-catalysis can be seen in the polymerisation of styrene by hydrogen chloride and bromide.[11] In the following solvents of low dielectric constant, CCl_4, $CHCl_3$, $C_2H_4Br_2$, no polymerisation has been observed at 25°, and only very little in PhCl ($\varepsilon = 5{\cdot}9$) and in Bu^nCl ($\varepsilon = 7{\cdot}3$). But in methylene chloride, ethylene dichloride, nitroethane, and nitromethane ($\varepsilon = 8{\cdot}9$, 10, 29, and 39, respectively) rapid polymerisation occurs, accompanied by simple addition to the double bond. In carbon tetrachloride, Williams found hydrogen chloride to inhibit the polymerisation of styrene by stannic chloride, and took this as evidence that the addition and polymerisation reactions were independent and initiated by different mechanisms. In recent work with styrene–hydrogen chloride in ethylene dichloride,[126] the addition and polymerisation are found to be associated and complementary. In this system therefore, the same process—proton addition—serves to initiate both reactions, and the polymerisation can be regarded as an addition reaction in which monomer addition has intervened between the first and the second stage of the hydrohalogenation. Polymerisation can occur appreciably only when the second stage—recombination with the halide anion—is made slower, as would be expected in media of high dielectric constant.

(III) Anionic Polymerisation

Polymerisation of olefins by basic catalysts has been reported at intervals since 1899, *e.g.*, of styrene by sodiomalonic ester,[127] of ethyl crotonate by sodium ethoxide,[128] of nitro-olefins by water [129] and by aqueous alkalis,[130] of allyl cyanide by sodium, sodium ethoxide, and ethylmagnesium bromide,[131] not to mention the intensive study of the sodium polymerisation of isoprene and butadiene for the industrial preparation of synthetic rubbers in Germany and Russia.[132] But until recently the only detailed studies of mechanism were those of Ziegler and his collaborators [133] with butadiene catalysed by various metals and metal alkyls, and of Abkin and Medvedev [134] on the kinetics of polymerisation of gaseous butadiene on similar catalysts. In the last few years, however, the range of monomers has been extended to

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[126] Pepper and Somerfield, *Chem. and Ind.*, 1954, 42.

[127] Hermann and Vorlander, *Chem. Zentr.*, 1899, **70**, 730.

[128] Pechmann, *Ber.*, 1900, **33**, 3329.

[129] Wieland and Sakellarios, *Ber.*, 1919, **52**, 898.

[130] Schmidt and Rutz, *Ber.*, 1928, **61**, 2142.

[131] Bruylants, *Bull. Soc. chim. Belge*, 1923, **32**, 317.

[132] Talalay and Magat, " Synthetic Rubber from Alcohol ", Interscience, New York, 1945.

[133] Ziegler, many papers summarised in *Chem. Ztg.*, 1938, **62**, 125 ; *Annalen*, 1950, **567**, 43.

[134] (*a*) *Trans. Faraday Soc.*, 1936, **32**, 286 ; *J. Phys. Chem. U.S.S.R.*, 1939, **13**, 705 ; (*b*) Mamontova, Abkin, and Medvedev, *Acta Physicochim. U.R.S.S.*, 1940, **12**, 269.

include most of the commoner vinyl compounds with electrophilic substituents.

These polymerisations are now regarded as the anionic counterparts of the cationic Friedel–Crafts polymerisations, *i.e.*, as initiated by the anion of the basic catalyst. Thus, copolymerisation studies reveal their difference from both radical and cationic reactions, and lead to a qualitative order of monomer reactivity :

Acrylonitrile > Methacrylonitrile > Methyl methacrylate > Styrene > Butadiene

which is the expected order of susceptibility to nucleophilic reagents. The same order has been found [135b] in the susceptibility of different monomers to catalysts of different base strength. By this latter standard, the nitro-olefins,[136] α-cyanosorbic acid,[137] and vinylidene cyanide [89b] should appear at the head of the above order of reactivity, since they are the only monomers so far reported to be initiated by the relatively weak base OH^-.

The first formulation of the mechanism as explicitly ionic seems to have been made by Price,[93b] discussing Ziegler's work.[133] An anionic chain mechanism was postulated by Beaman [138] for the polymerisation of methacrylonitrile by Grignard reagents and by sodiotriphenylmethane, where polymer end groups were identified characteristic of the anion of the catalyst. Similarly, amino-end groups have been found by Sanderson and Hauser [139] in polystyrenes catalysed by sodamide in liquid ammonia.

The anionic character of the reaction is not so evident in the systems studied earlier, *viz.*, dienes polymerised by metal alkyls or by sodium. The metal alkyls are largely covalent, and the reactions are nowadays regarded as heteropolar largely by analogy with the similar polymerisation brought about by the definitely ionic sodiotriphenylmethane and potassiodimethylphenylmethane. Ziegler at first formulated these polymerisations as a series of classical addition reactions, and, as will be seen later, under his conditions—high concentrations of relatively covalent catalysts—these reactions do show considerable kinetic differences from the true ionic-chain reactions.

The polymerisation of butadiene by sodium was concluded by Bolland [140] to be a free-radical reaction, and although this is now excluded by copolymerisation experiments,[141] there is still some obscurity about the mechanism. Ziegler [142] has recently advanced reasons against an anionic mechanism in that the polymer differs in structure (ratio of 1 : 2- to 1 : 4-addition) from those produced by anionic (metal alkyls) or radical catalysts. It seems possible, however, that these structural differences could arise from different degrees of chain branching. With potassium in liquid ammonia,

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[135] Higginson and Wooding, (*a*) *J.*, 1952, 760 ; (*b*) *ibid.*, p. 774 ; (*c*) *ibid.*, p. 1178.

[136] Blomquist, Tapp, and Johnson, *J. Amer. Chem. Soc.*, 1945, **67**, 1519.

[137] Hamann, *Angew. Chem.*, 1948, *A*, **60**, 61.

[138] *J. Amer. Chem. Soc.*, 1948, **70**, 3115.

[139] *Ibid.*, 1949, **71**, 1595.

[140] *Proc. Roy. Soc.*, 1941, *A*, **178**, 24.

[141] Walling, Briggs, Cummings, and Mayo, *J. Amer. Chem. Soc.*, 1950, **72**, 48.

[142] Personal communication.

the polymerisation of styrene [135c] is believed to be an ionic reaction initiated by NH_2^- anions formed as follows:

$$2K + CH_2{:}CHPh + 2NH_3 \longrightarrow 2K^+ + CH_3{\cdot}CH_2Ph + 2NH_2^-$$

Kinetics.—Only one detailed study of the kinetics in solution has so far been published. For styrene polymerised by potassamide in solution in liquid ammonia, Higginson and Wooding [135a] find

$$\text{Rate} = k[NH_2^-][\text{Styrene}]^2 \quad \text{and} \quad \overline{\text{D.P.}} = k'[\text{Styrene}]$$

The polymer contains one amino-group per molecule, and there is no evidence of consumption of potassamide. They conclude the polymerisation to be a chain reaction initiated by NH_2^-, and terminated by proton transfer from the solvent ammonia, *viz.*:

Initiation:

$$NH_2^- + CH_2{:}CHPh \longrightarrow NH_2{\cdot}CH_2{\cdot}\overline{C}HPh$$

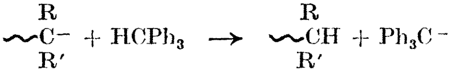
Propagation:

$$NH_2{\cdot}CH_2{\cdot}[CHPh{\cdot}CH_2]_n{\cdot}\overline{C}HPh + CH_2{:}CHPh \longrightarrow NH_2{\cdot}CH_2{\cdot}[CHPh{\cdot}CH_2]_{n+1}{\cdot}\overline{C}HPh$$

Termination:

$$\sim\!\sim\overline{C}HPh + NH_3 \longrightarrow \sim\!\sim CH_2Ph + NH_2^-$$

With methyl methacrylate polymerised by sodiotriphenylmethane in ether solution, where a similar solvent termination cannot occur, these authors find that the polymer molecular weight is greatly reduced by addition of the conjugate acid of the catalyst base, *i.e.*, here also the chains are terminated by H^+:



$$\sim\!\sim\overset{R}{\underset{R'}{C}}{}^- + HCPh_3 \longrightarrow \sim\!\sim\overset{R}{\underset{R'}{C}}H + Ph_3C^-$$

A similar anionic chain terminated by proton capture has been suggested by Hamann for the polymerisation of α-cyanosorbic acid by aqueous alkalis. Here the initiation is envisaged, not as addition of OH^-, but as the abstraction of a proton from the monomer by OH^-.

With weaker bases as catalysts, and in the absence of ionising solvents, different kinetic features appear. From butadiene with large concentrations of metal alkyls (R·M) Ziegler isolated simple addition compounds $R{\cdot}[CH_2{\cdot}CH{:}CH{\cdot}CH_2]_n{\cdot}M$ where n is small. The following series of steps was postulated:

$$\begin{array}{lrcl} (1) & R{\cdot}M + C_4H_6 & \longrightarrow & R{\cdot}C_4H_6{\cdot}M \\ (2) & R{\cdot}C_4H_6{\cdot}M + C_4H_6 & \longrightarrow & R{\cdot}[C_4H_6]_2{\cdot}M \\ (3) & R{\cdot}[C_4H_6]_n{\cdot}M + C_4H_6 & \longrightarrow & R{\cdot}[C_4H_6]_{n+1}{\cdot}M \end{array}$$

and the polymerisation was described as a " continuous series of metal-organic syntheses ". According to the relative rates of the first and subsequent steps, this scheme can give rise to quite different overall kinetics. With lithium alkyls and potassiodimethylphenylmethane the catalyst was found to be rapidly consumed, and short-chain products could be isolated. Ziegler therefore concluded [133a] that in these systems the first addition of catalyst to monomer was faster than the subsequent growth reaction.

Under these conditions, then, the additions take place stepwise, and the polymerisation is kinetically analogous to a polycondensation. With sodium or sodiotriphenylmethane the polymerisation was found to be much faster, with little catalyst consumed. Short chains could not be isolated, except by the addition of so-called "interceptor agents", *e.g.*, triphenylmethane, fluorene, and especially amines, which react with the chain intermediates. With these catalysts, therefore, the growth reaction is faster than the initiation, and a chain reaction becomes possible. In the absence of the above "interceptor agents" there would seem to be no true termination process, and the reaction corresponds to a "polycondensation of the second kind" as described by Bauer and Magat [143] and discussed earlier as a possibility under certain conditions in cationic polymerisation. The interceptor agents terminate by proton transfer, as demonstrated by Ziegler by the isolation of intermediates of the type $R{\cdot}[C_4H_6]_n{\cdot}H$, and as found later by Higginson and Wooding with methyl methacrylate.

Detailed kinetic studies of sodium polymerisation are hampered by the heterogeneous nature of the reaction—in pure liquid butadiene, the polymer grows out from the sodium surface as a swollen gel.[134a] Even in the apparently homogeneous polymerisation by potassiodimethylphenylmethane in ether solution, surface effects are important.[134b]

(IV) Ionic Copolymerisation

Ionic initiators, like their free-radical counterparts, may bring about true copolymerisation of two (or more) monomers, *i.e.*, the polymer chain contains both monomer species, in proportions determined by the monomer concentrations and their reactivity with the ionic chain. The kinetics of such copolymerisations have the complications associated with four simultaneous propagation steps, and have not yet been investigated in the ionic reactions. However, valuable information about monomer reactivities in ionic reactions has been obtained from studies of the *composition* of copolymers prepared at different monomer ratios, by use of the equation developed by Alfrey [144] and by Mayo and Walling,[145] *viz.*,

$$\text{Ratio of monomers in copolymer} = \frac{\mathrm{d}[M_1]/\mathrm{d}t}{\mathrm{d}[M_2]/\mathrm{d}t} = \frac{[M_1]}{[M_2]}\left\{\frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}\right\}$$

where M_1 and M_2 represent the two monomers, and r_1 and r_2 are the ratios of propagation rate constants for each type of polymer ion with the pair of monomers, *viz.* :

$$\begin{array}{lll}
\sim\!\sim M_1 + M_1 \xrightarrow{k_{11}} \sim\!\sim M_1M_1 & & \\
 & & r_1 = \dfrac{k_{11}}{k_{12}} \\
\sim\!\sim M_1 + M_2 \xrightarrow{k_{12}} \sim\!\sim M_1M_2 & & \\
\sim\!\sim M_2 + M_2 \xrightarrow{k_{22}} \sim\!\sim M_2M_2 & & \\
 & & r_2 = \dfrac{k_{22}}{k_{21}} \\
\sim\!\sim M_2 + M_1 \xrightarrow{k_{21}} \sim\!\sim M_2M_1 & &
\end{array}$$

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[143] *J. Chim. phys.*, 1950, **47**, 841.

If for steric or other reasons the monomers cannot add to chains ending in their own type, then the monomer units alternate in the copolymer chain and $k_{11} = 0 = k_{22}$, *i.e.*, $r_1 = r_2 = 0$. At the other extreme, monomers may add equally readily to chain ends of either type, in which case $k_{11} = k_{21}$ and $k_{22} = k_{12}$, *i.e.*, $r_1 = 1/r_2$. All cationic and several anionic copolymerisations so far studied approximate to the latter behaviour, and it therefore becomes possible to derive from the values of r_1 and r_2 a relative order of reactivity of the different monomers to carbonium ions or carbanions.

Cationic Copolymerisation.—Mayo and Walling[145] compiled such an order of reactivity to carbonium ions for 17 monomers, though much of the data then available referred to copolymers prepared at only a single monomer composition. Subsequent work has largely borne out their conclusions, but has also raised some uncertainty whether a unique order of reactivity can be expected, and in particular whether the relative reactivities are influenced by the nature of catalyst and solvent. Thus, the reactivity ratios found by Landler[146a] for vinyl acetate, methyl acrylate, and methyl methacrylate with styrene catalysed by stannic bromide in benzene and nitrobenzene are much greater than those found previously in solventless monomer mixtures.[145] Florin also,[147a] with *o*-chlorostyrene copolymerised with 3 : 4-dichlorostyrene by aluminium chloride finds different reactivity ratios in carbon tetrachloride and in nitrobenzene. On the other hand, with styrene and *p*-chlorostyrene copolymerised by stannic chloride, Overberger *et al.*[148a] find no effect of solvent in the above solvents and their mixtures, and negligible effects of catalyst concentration and of traces of water.

Specific influences of different Friedel–Crafts catalysts have been reported by Florin,[147b, c] who found values of r_1 varying from 2·8 with aluminium chloride to 7·2 with titanium tetrachloride in the copolymerisation of styrene and 3 : 4-dichlorostyrene in carbon tetrachloride. However, Florin's later values[147a] for these monomers in nitrobenzene showed a smaller variation, and those for styrene and *o*-chlorostyrene hardly any difference with different catalysts. Some authors[148c] have therefore preferred to attribute the earlier reported variation to anomalies caused by heterogeneity and by variable chlorine substitution from the solvent. Recently Overberger[148d] has shown that the reactivity ratios for the monomer-pair styrene–*p*-chlorostyrene are independent of the nature of the catalyst, but may be affected by heterogeneity.

The values of reactivity ratios reported up to the end of 1952 are collected in Table 4. They reveal little tendency to alternation (*i.e.*, $r_1 \times r_2 \approx 1$ in all cases), and the following order of carbonium-ion reactivity at 0—20°

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[144] " Copolymerisation ", Interscience, New York, 1952.

[145] *Chem. Reviews*, 1950, **46**, 112.

[146] (*a*) *Compt. rend.*, 1950, **230**, 539; (*b*) *J. Polymer Sci.*, 1952, **8**, 64.

[147] (*a*) Int. Congr. Pure Appl. Chem., 1951; (*b*) *J. Amer. Chem. Soc.*, 1949, **71**, 1867; (*c*) *ibid.*, 1951, **73**, 4468.

[148] (*a*) Overberger, Arnold, and Taylor, *ibid.*, p. 5541; (*b*) Overberger, Arond, Tanner, Taylor, and Alfrey, *ibid.*, 1952, **74**, 4848; (*c*) Overberger, ref. (9*b*), p. 106; (*d*) Overberger, Ehrig, and Tanner, *J. Amer. Chem. Soc.*, 1954, **76**, in the press.

TABLE 4 *Reactivity ratios in cationic copolymerisation*

M_1	M_2	Temp	Catalyst	Solvent	r_1	r_2	Ref
Styrene	*p* Methoxy styrene	0°	$SnCl_4$	$\left\{\begin{matrix}NO_2Ph\\CCl_4\end{matrix}\right\}$	(0 01)	(100)	148*b*
	m Methoxy styrene	0	,,	,,	0 9∓0 15	1 1+0 15	,,
	Methyl acrylate	20	,,	C_6H_6	2 2∓0 2	0 4	146*b*
	p Chlorostyrene	32	,,	CCl_4	2 2∓0 3	0 35∓0 05	149
		0	,,	,,	2 5∓0 4	0 3 ∓0 03	148*a*
		−20	,,	,,	2 5∓0 4	0 3 ∓0 03	,,
	m ,,	0	,,	$\left\{\begin{matrix}CCl_4\\NO_2Ph\end{matrix}\right\}$	3 3∓0 4	0 3 ∓0 05	,,
	o ,,	0	Various	CCl_4	1 6 −3 8	0 54 −0 35	147*a*
		0	,,	NO_2Ph	3 2 −3 8	0 25 −0 30	,,
		23	$AlCl_3$	CCl_4	1 82	0 68	,,
		23	,,	NO_2Ph	3 1	0 38	,,
	3 4 Dichloro styrene	0	Various	CCl_4	2 8 −7 2	0 45 −0 1	147*c*
		0	,,	NO_2Ph	5 0 −6 2	0 07 −0 12	147*a*
	Vinyl acetate	20	$SnBr_4$	NO_2Ph	8 25	0 015	146*a*
	Methyl methacrylate	20	,,	,,	10 5	0 1	,,
	2 5 Dichloro styrene	0	$AlCl_3$	C_2H_5Cl	14 8∓2	0 34∓0 2	147*b*
	Chloroprene	−18	BF_3Et_2O	C_6H_{12}	15 6	0 24	150*a*
	m Nitrostyrene	0	$SnCl_4$	$\left\{\begin{matrix}CCl_4\\NO_2Ph\end{matrix}\right\}$	20∓4	0 03	148*b*
α Methyl styrene	*p* Dimethyl aminostyrene	0	$SnCl_4$	$\left\{\begin{matrix}CCl_4\\NO_2Ph\end{matrix}\right\}$	0 035∓0 015	31∓19	,,
	p Methoxy styrene	0	,,	,,	0 3∓0 1	15∓5	,,
	m Methoxy styrene	0	,,	,,	5∓1	0 3∓0 1	,,
	p Chlorostyrene	0	,,	None	28∓2	0 12∓0 03	151
p Chloro styrene	*p* Methylstyrene	0	$SnCl_4$	CCl_4	0 22∓0 05	4 5∓0 7	148*b*
	m Methoxy styrene	0	,,	,,	0 38∓0 05	2 6∓0 4	,,
	p Bromostyrene	0	,,	,,	1 0∓0 1	1 0∓0 1	,,
o Chloro styrene	Anethole	0	,,	,,	18∓3	0 03∓0 005	152
*iso*Butene	Butadiene	−103	$AlCl_3$	C_2H_5Cl	115∓15	0 01∓0 01	153
	Isoprene	,,	,,	,,	2 5∓0 5	0 4∓0 1	,,
	Vinylacetylene	−100	BF_3		8	0 13	154

may be derived, together with the approximate magnitude relative to that of styrene.

p-Dimethylaminostyrene	*p*-Methoxystyrene	α-Methylstyrene	Anethole	*p*-Methylstyrene	*m*-Methoxystyrene
190	20–100	7	4–11	1·8	1·2

Styrene	Methyl acrylate	*p*-Chlorostyrene	*p*-Bromostyrene	*m*-Chlorostyrene	*o*-Chlorostyrene	3 : 4-Dichlorostyrene
1·00	0·45	0·45	0·45	0·3	0·2–0·6	0·14–0·35

Vinyl acetate	Methyl methacrylate	2 : 5-Dichlorostyrene	Chloroprene	*m*-Nitrostyrene
0·12	0·095	0·07	0·06	0·05

Reactivity ratios are not yet available for the copolymerisation of *iso*butene and the dienes with any of the monomers in the above series, and they cannot strictly be given their places in the sequence. However, if we follow Mayo and Walling in considering *iso*butene about as reactive as α-methylstyrene, then the relative reactivities of *iso*butene, isoprene, vinylacetylene, and butadiene would be approximately 7, 2·5, 1, and 0·07 respectively on the above scale. [Note added in proof. Since the above was written, results have been reported for the monomer-pair styrene–*iso*butene.[155] The values are variable (r_1 = 0·2—2·0 ; r_2 = 1·7—9·0) but suggest that the reactivity of *iso*butene may be somewhat less than the above estimate.]

The above sequence differs from that of Mayo and Walling in the positions assigned to methyl acrylate, vinyl acetate and methyl methacrylate, which were earlier reported to have much lower reactivity. The higher values appear to be associated with the use of a solvent. The uncertainties in the positions of anethole, *o*-chlorostyrene and 3 : 4-dichlorostyrene arise from the variable results reported for the last two monomers with different catalysts and solvents—the more consistent results obtained in nitrobenzene appear to justify the lower positions actually assigned. Despite these individual uncertainties, the results as a whole bear out the earlier conclusions based on results at a single monomer composition, and reveal the expected trend of reactivity with the electronegativity and orientation of substituents. Overberger [148b, c] has shown that the effect of substituents on the reactivity ratios is parallel to their effect on other cationic reactions, as measured by Hammett's sigma constant, though the dimethylamino- and methoxy-groups show an enhanced effect.

Anionic Copolymerisation.—Quantitative studies of copolymerisation by basic catalysts are uncommon and only a few reactivity ratios have been reported (see Table 5). From these values, and from the qualitative evidence

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[149] Alfrey and Wechsler, *J. Amer. Chem. Soc.*, 1948, **70**, 4266.

[150] Foster, (*a*) *J. Polymer Sci.*, 1950, **5**, 369 ; (*b*) *J. Amer. Chem. Soc.*, 1950, **72**, 1370 ; (*c*) *ibid.*, 1952, **74**, 2299.

[151] Smets and de Haes, *Bull. Soc. chim. Belge*, 1950, **59**, 13.

[152] Alfrey, Arond, and Overberger, *J. Polymer Sci.*, 1949, **4**, 539.

[153] Thomas and Sparks, U.S.P. 2,356,128.

[154] Denoon, U.S.P. 2,384,731.

[155] Rehner, Zapp, and Sparks, *J. Polymer Sci.*, 1953, **11**, 21.

that styrene is more reactive than butadiene,[156] the following qualitative order of carbanion reactivity can be drawn up :

Acrylonitrile > butyl vinyl sulphone > methyl acrylate > methacrylonitrile > methyl methacrylate > vinyl acetate > styrene > butadiene

This sequence is less securely established than the corresponding order of reactivity to carbonium ions, but the general trend is quite clear, and is in the opposite direction, as expected. A quantitative comparison is not yet possible, and an inspection of Table 5 suggests that the reactivity of a given monomer is not always the same towards all carbanions. In two cases, styrene–vinyl acetate and acrylonitrile–butyl vinyl sulphone, the product $r_1 \times r_2$ is considerably less than unity, indicating a tendency to alternation.

TABLE 5. *Reactivity ratios in anionic copolymerisation*

M_1	M_2	Temp	Catalyst	Solvent	r_1	r_2	Ref
Methyl methacrylate	Methyl acrylate	30°	$NaNH_2$	NH_3	0.1	4.5 ± 0.5	146*b*
	Acrylonitrile	"	"	"	0.25	7.9	"
	Methacrylonitrile	– 55	Na	"	0.61 ± 0.02	5.2 ± 1.0	150*b*
	Vinyl acetate	– 30	$NaNH_2$	"	3.2 ± 1.1	0.4	146*b*
	Styrene	– 30	Na	"	6.4	0.12	146*a*
Styrene	Vinyl acetate	– 30	Na	"	0.01	0.1	"
Acrylonitrile	Butyl vinyl sulphone	– 55	Na	"	1.1 ± 0.2	0.2 ± 0.1	150*c*

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[156] Schulze and Crouch, *J. Amer. Chem. Soc.*, 1948, **70**, 3891.