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MODERN VIEWS ON THE MECHANISM OF THE CATIONIC POLYMERISATION OF VINYL MONOMERS

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I. INTRODUCTION

Since the basic principles of the theory of cationic polymerisation were laid down in monographs dealing with the general chemistry of polymers [1-5] and in review articles [6-8], in particular Pepper's outstanding review [6], there have been many new publications which have barely found mention in the more recent review literature [9,10]. Moreover, many recent investigations have broadened the earlier concepts and make it necessary to review the existing theories on the mechanism of formation, propagation, and termination of chains in cationic polymerisation. The present review is intended to focus attention on these studies. The existence of the earlier sources (especially Pepper and Plesch [6,8,9]) covering the literature extremely fully makes a long introduction unnecessary here, and we limit ourselves to the following brief notes.

Because of the considerable individuality of each polymerisation system, it is impossible to set out a universal mechanism for cationic polymerisation such as is possible for polymerisation by a radical mechanism. Nevertheless, there are some features of cationic polymerisation which are general. The initiation step can be formulated in terms of equations:

for acid catalysis

$$HX + \overset{|}{C}{=}\overset{|}{C} \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + X^-, \qquad (1)$$

for catalytic complexes of the proton-donor–Lewis acid type such as $BF_3.H_2O$

$$H^+[AB]^- + \overset{|}{C}{=}\overset{|}{C} \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AB]^-. \qquad (2)$$

and for catalytic complexes of the carbonium ion-donor–Lewis acid type such as $SnCl_4.C_4H_9Cl$

$$R^+[AX^-] + \overset{|}{C}{=}\overset{|}{C} \rightarrow R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AX]^-. \qquad (3)$$

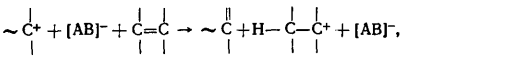
The most widely held view is that the monomeric cations formed by one of these reactions and the growing macrocations are not kinetically independent entities, but exist as ion–counterion pairs held together by electrostatic forces. The growth of the chain is then considered as the entry of a monomer molecule into the interaction zone of the components of such pairs:

$$\sim\overset{|}{C^+} + [AB]^- + \overset{|}{C}{=}\overset{|}{C} \rightarrow \sim\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AB]^-.$$

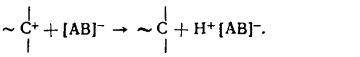
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The universality of this theory was open to doubt[6] and was disproved by later work which showed that free macrocations could exist under certain conditions[11-13]. However, the concept of the growing chain as an ion pair is more general, particularly with media of moderate polarity.

The most important feature of the process under review is the absence of kinetic termination as a necessary and unavoidable step in the reaction. In the overwhelming majority of cases the growing chains are terminated either by transfer of the chain to the monomer:

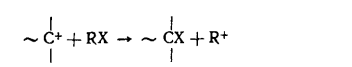


or by regeneration of the catalytic complex:

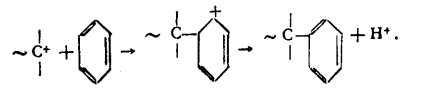


The role played by these reactions at the normal temperatures for radical polymerisation; *i.e.* 20°–30° above room temperature, is so great that the production of high-molecular-weight polymers by cationic polymerisation under these conditions is practically excluded. A substantial reduction of temperature causes, in Pepper's phrase[6], "freezing out" of these processes, and so increases the degree of polymerisation. In radical polymerisation lowering the temperature increases the chain length only in the limited temperature range where a reduction in the contribution of the reaction involving chain transfer to the monomer predominates. Transition to a lower temperature necessarily decreases the molecular weight of the polymer because of increased chain termination in comparison with chain propagation, as is clearly shown, for example, in the radical polymerisation of vinyl acetate[14].

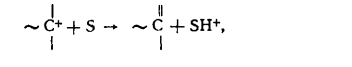
In the presence of a solvent or other additive other types of chain transfer are possible (see Plesch[8] for more detail), of which the most important are apparently anion capture[15]:



and alkylation of an aromatic nucleus by the growing chain[16,17]:



Chain transfer by proton transfer:



the low probability of which was noted by Plesch[8], must be considered, for example, in systems such as $SnCl_4$–styrene–vinyl acetate, where the known transfer of the chain to vinyl acetate[18] can hardly be explained by any other mechanism.

Suppression of chain termination and transfer steps in cationic polymerisation by lowering the temperature sometimes increases the overall rate of the process as well as the degree of polymerisation. In some systems the rate constant for chain propagation in cationic polymerisation has comparatively little temperature dependence[19], but may vary considerably with the nature of the reaction medium[20-22]. In a polar medium a marked increase in the dielectric constant together with a reduction in temperature can even make the rate constant of the propagation reaction vary inversely with temperature[19], which is apparently one of the reasons for the often observed negative value of the overall activation energy of the low-temperature cationic polymerisation of various monomers[2,6,23].

In this review we shall consider mainly work relating to the fundamental steps of cationic polymerisation, generally of isobutene, monomers of the styrene series, and vinyl ethers, on which most of the fundamental investigations have been made.

II. FORMATION AND NATURE OF ACTIVE CENTRES

For a long time the greatest problem in the mechanism of initiation of cationic polymerisation, if initiation by protic acids is ignored, was the problem of co-catalysis. After the discovery of co-catalysis in the polymerisation of isobutene in the presence of boron fluoride and traces of water[24,25], there was a tendency to extend this type of mechanism to other systems, where, however, it cannot always be proved. It was long thought that with certain monomer–catalyst pairs the presence of a co-catalyst is not essential for cationic polymerisation, but work is still being published which proves the opposite. An example is the styrene–aluminium chloride system, for which the co-catalytic action of water and the absence of polymerisation in absolutely dry conditions have been very recently established by Jordan[26], who had previously assumed that initiation took place in this case through a monomer–catalyst complex without the participation of a co-catalyst[27]. Sinn and coworkers[28] have recently shown that H_2O or HCl must be present as co-catalysts in the polymerisation of various monomers under the influence of alkyl aluminium halides†. Particular difficulties arise with a process carried out in a polar medium, where the observed acceleration effects can be ascribed to the increase in the dielectric constant as well as to the co-catalytic action of the solvent. Closely related to this is the question of the actual nature of the catalytic complexes, and hence of the initiating ions, which is often in doubt.

The known cases of initiation of cationic polymerisation can be divided into the following types, distinguished by the components of the primary initiating ions: (a) the catalyst (without participation of the monomer); (b) a catalytic complex of catalyst and co-catalyst (without participation of the monomer); (c) catalyst + monomer; and (d) a catalytic complex of catalyst and co-catalyst + monomer.

Initiation by protic acids (1) belongs to the first type, and initiation by complexes of Lewis acids with proton donors (2) or (if the process takes place in media of sufficiently high polarity) with alkyl halides (3) to the second. The third type includes the polymerisation of monomers which can act as co-catalyst, that is vinyl ethers and oxygen- and nitrogen-containing compounds which are not vinylic: oxides, carbonyl derivatives, cyclic imines, etc. Polymerisation under the influence of catalyst–monomer π-complexes also belongs to this type. The fourth type is characteristic of polymerisation in media of low dielectric constant, in which ionisation of the catalytic complexes is only possible with participation of the monomer as well. Polymerisation under the influence of iodine in polar media where, according to Eley and Richards[29], I^+ ions are produced by the bimolecular reaction

$$2I_2 \rightleftarrows I_3^- + I^+, \qquad (4)$$

† It has also been established that these monomers (isoprene, styrene, etc.) do not polymerise under the influence of complex Ziegler catalysts if all traces of moisture are excluded[28].

in which one of the iodine molecules fulfils the function of co-catalyst, can be related to the second type. In non-polar media the possibility of formation of primary ions *via* iodine–monomer π-complexes must be considered, as suggested by Gantmakher and Medvedev[30]:

$$2MI_2 \rightleftarrows MI^+ + I_3^- + M.$$

This classification has been made possible mainly by recent investigations, amongst which those of Colclough and Dainton[31–35] on the polymerisation of styrene in various media under the influence of stannic chloride deserve mention. They were able to distinguish clearly between the effects of co-catalysis and acceleration of polymerisation due to the polarity of the medium. Using highly purified monomer and solvents, they showed that in CCl_4 and nitrobenzene, which have very different dielectric constants (2.2 and 36.0 respectively‡), reaction proceeds only in the presence of added co-catalysts. Water and alkyl halides are suitable in nitrobenzene, and only water in CCl_4. The reason for this difference must be that the complexes formed between the catalyst and an alkyl halide, *i.e.* compounds of the type $RSnCl_5$, require a certain minimum dielectric constant for their ionisation, and they remain unionised in CCl_4 solution. On the other hand the catalytic complex formed in the presence of water, which is thought to be trichlorostannic acid monohydrate, is able to ionise in CCl_4. From the order of the rate of polymerisation with respect to the monomer, it follows that in the latter case the monomer takes part in the formation of the initial active centres, *i.e.* in the ionisation of the catalytic complex (5), while in nitrobenzene the ionisation proceeds without the participation of the monomer (6):

$$\text{rate of polymerisation in carbon tetrachloride } K[M]^3[C], \quad (5)$$

$$\text{rate of polymerisation in nitrobenzene } K[M][C]. \quad (6)$$

Thus the large difference in the rates of polymerisation in these two media is wholly explained by the difference in their polarities.

The absence of co-catalytic influence in nitrobenzene makes it useful as a medium for evaluating the relative activities of certain alkyl halides as co-catalysts: dichloroethane was found to have an activity of only 0.007 of that of t-butyl chloride[35]. Despite this, in the absence of nitrobenzene and any specially introduced co-catalysts, polymerisation in dichloroethane proceeds at a definite, reproducible rate, which is of second order with respect to the monomer. Hence a high concentration of a polar agent, even if its dielectric constant is relatively low (ϵ of dichloroethane is 10.4), ensures ionisation of the catalytic complex formed from it; the monomer must, however, participate in the ionisation step. Comparison of the polymerisation of styrene under the influence of the $SnCl_4$–t-C_4H_9Cl system in nitrobenzene and dichloroethane shows the overall rate of the process to be lower in the second case by a factor of 70, which was thought to be due to a lower rate of initiation. This cannot be considered an incontrovertible conclusion, however, since recent data indicate that the polarity of the medium has a very considerable influence on the rate constant of the propagation reaction in cationic polymerisation[20–22]. The corresponding values will be given below.

‡ Here and later the values of ϵ are taken from Ref. 23 if no other reference is given.

The features of the process proceeding under the influence of RCl–$SnCl_4$ complexes in the various media, as established by Colclough and Dainton, can be represented by the following equations:

in nitrobenzene

$$RCl + SnCl_4 \rightarrow R^+SnCl_5^- \xrightarrow{M} RM^+ + SnCl_5^-.$$

in dichloroethane

$$RCl + SnCl_4 \rightarrow RSnCl_5 \xrightarrow{M} RM^+\ SnCl_5^-.$$

These results confirm Pepper's earlier suggestions[6,36] of the possible co-catalytic action of alkyl halides and the associated deduction that polymerisation is initiated by the carbonium ion of the catalytic complex (as by the proton produced from complexes incorporating the hydroxyl-containing co-catalysts water, alcohols, and acids). Direct proof of this mechanism of initiation was obtained by Kennedy and Thomas[37], who established the presence of labelled carbon in polyisobutylene formed under the influence of aluminium chloride in labelled methyl chloride. Since in cationic polymerisation the chain transfer and termination processes can occur only by capture of an anion by the growing chain or by expulsion of a proton from it, the appearance of labelled carbon in the polymer can only occur in the initiation step. The formation of the primary ions is formulated as follows[37]:

$$^{14}CH_3Cl + AlCl_3 \rightleftarrows {}^{14}CH_3^+[AlCl_4]^- \rightleftarrows {}^{14}CH_3^+ + [AlCl_4]^-.$$

These workers later suggested[15] that the labelled carbonium ion might be produced by the reaction

$$\sim\overset{|}{\underset{|}{C}}{}^+[AlCl_4]^- + {}^{14}CH_3Cl \rightleftarrows \sim\overset{|}{\underset{|}{C}}Cl + {}^{14}CH_3^+[AlCl_4]^-,$$

but from the point of view with which we are here concerned this does not affect the essential features of the mechanism.

Initiation by a carbonium ion is also possible in another type of system, in which polymerisation takes place under the influence of Lewis acid etherates. Eley[38] showed that when boron trifluoride etherate is used, the initiating agent is the $C_2H_5^+$ ion; this was also demonstrated later[39], using labelled atoms, in the polymerisation of vinyl ethers with $BF_3.O(^{14}C_2H_5)_2$. The detection of labelled carbon in the polymer indicates that the initiation process is

$$^{14}C_2H_5^+[BF_3.O^{14}C_2H_5]^- + CH_2{=}CH(OR) \rightarrow {}^{14}C_2H_5CH_2{-}\overset{+}{C}H(OR)[BF_3.O^{14}C_2H_5]^-.$$

It may be assumed that in the absence of added co-catalysts the initiation of polymerisation of vinyl ethers proceeds in an analogous manner, *i.e.* by way of the etherate formed by the monomer itself:

$$BF_3O(R)CH{=}CH_2 \rightarrow R^+ + [BF_3{\cdot}OCH{=}CH_2]^-. \quad (7)$$

It has also been suggested that with vinyl ethers the sources of the initial active centres are catalyst–monomer π-complexes[40] and not the coordination complexes (7). There is no doubt that such π-complexes can be formed; their existence has been proved experimentally in systems containing iodine[20,21,41], stannic chloride[41,42], and trichloroacetic acid[43] as catalysts for the polymerisation of vinyl ethers and styrene monomers. However, most workers have rejected the idea of initiation by π-complexes, which has been considered for the systems iodine–vinyl ethers[44], titanium tetrachloride–styrene[19,45] and isobutene[46], and aluminium chloride-styrene[26]. In a recent study Okamura and coworkers[20] dealt with this question in the iodine-catalysed polymerisation of various monomers, and suggested that the formation of a π-complex should be

included as a separate fundamental stage in the usual mechanism of cationic polymerisation. They established the existence of π-complexes in the systems which they studied: they investigated the possible types of initiation, and found that the observed kinetics would fit mechanisms in which monomer–catalyst π-complexes either did or did not participate in the initiation. In calculating the rate constant for chain propagation, however, they took the second alternative, clearly considering it the more probable. It must be emphasised that iodine-containing systems can hardly be considered suitable for evaluating the role played by π-complexes, since the co-catalytic effect produced by the catalyst itself (4) very probably occurs in such systems, and this could mask the weaker effect due to π-complexes. For this reason, the initiating action of the latter can only become evident in systems where other catalytic effects are precluded.

The concept that cationic polymerisation can occur with a particular type of initiation involving monomer–catalyst π-complexes is due to Gantmakher, Medvedev, and coworkers[47,48], who studied the stannic chloride polymerisation of various monomers[47,49-51]. From the donor–acceptor properties of catalyst and monomer, they concluded that the catalyst in solution in the monomer is present as a π-complex, and that initiation occurs by reaction of this complex with another molecule of monomer, which produces an ion pair[47,48]. The kinetics of the separate polymerisation of styrene[30] and isoprene[49] and of the polymerisation of styrene in the presence of small amounts of more active monomers in the $SnCl_4$–C_2H_5Cl system[40,51-53] have been considered on the basis of initiation mechanisms involving a π-complex. The observed sharp increase in the rate of initiation when small amounts of isoprene, isobutene, or α-methylstyrene are added to the styrene is ascribed to the formation of π-complexes of various compositions and hence of varying activity. This is in agreement with the absence of accelerated polymerisation when small amounts of H_2O or HCl are added, since these are more active than the monomers in their complexing action on the catalyst. Higashimura and Okamura[54] assume the formation of active centres by direct reaction between catalyst and monomer in the stannic chloride polymerisation of styrene in benzene solution; they have shown the existence of an induction period even when the reagents are very pure. It is significant that the induction period is less in the presence of a previously polymerised reaction mixture, but the rate and degree of polymerisation are the same as in its absence. The participation of the π-complex $SnCl_3OH.H_2O.CH_2{=}CHC_6H_5$ in the initiation has been used[35] to explain the observed third order kinetics (with respect to monomer) of styrene polymerisation in the $SnCl_4$–H_2O–CCl_4 system, where the monomer is thought to participate in the ionisation

$$M\cdot SnCl_3OH\cdot H_2O + M \rightarrow HM_2^+[SnCl_3(OH)_2]^-.$$

Zlámal and Kazda[55] have said that aromatic monomers can act as co-catalysts in cationic polymerisation.

Pepper has remarked[9] that in systems containing ethyl chloride the formation of a catalytic complex with the solvent cannot be excluded, since the activity of ethyl chloride, despite its low dielectric constant, may be sufficient to produce ionised complexes§.

The difficulties associated with theories of the mechanism of initiation of cationic polymerisation in the presence of alkyl halides become apparent when several systems of this type are compared. Thus the papers previously cited[32-35] indicate that the stannic chloride polymerisation of styrene in alkyl halides proceeds at dielectric constants as low as 7, as demonstrated for reaction in CCl_4–$C_2H_4Cl_2$ mixtures. On the other hand, the titanium tetrachloride polymerisation of styrene[19] or even such an active monomer as isobutene[46] in methylene chloride solution will only proceed in the presence of water, *i.e.* the alkyl halide, of dielectric constant 8.9, cannot here act as co-catalyst. The possibility of initiation of cationic polymerisation in alkyl halides without these acting as co-catalysts must therefore be borne in mind. The effect of the properties of the medium on the influence of various agents which might act as co-catalysts has also been noted[56]; thus the addition of HCl increases the rate of polymerisation of styrene in the $SnCl_4$–C_2H_5Cl system, but reduces it if the reaction is carried out in a less polar solvent (cyclohexane).

When we come to consider initiation of polymerisation by complexes involving water and other oxygen-containing compounds, we find that these can form a number of adducts with metal halides, unlike alkyl halides, which usually give 1:1 complexes¶. These adducts may differ considerably in their catalytic activity, as was shown long ago for BF_3[6] and more recently for $SnCl_4$,[35] $AlCl_3$,[11] and $TiCl_4$.[12] As we noted above, Colclough's studies[32,35] show that the actual catalytic agent in the styrene–$SnCl_4$–H_2O–CCl_4 system is trichlorostannic acid monohydrate, while the stannic chloride mono- and di-hydrates, which are also present, are almost inactive. This is shown by the existence of a maximum on the curve relating the rate of polymerisation to the concentration of water in the region corresponding to the ratio $H_2O:SnCl_4 = 2$, and by the gradual increase in the rate before it reaches the maximum value.

It is assumed that the reaction

$$SnCl_4\cdot 2H_2O \rightarrow SnCl_3OH\cdot H_2O + HCl$$

takes place during this period, and that the reduced rate of polymerisation is due to formation of HCl†. The initiation process yields the unionised monomer complex $M.SnCl_3OH.H_2O$, which forms with a second monomer molecule the first active centre capable of further propagation, $HM_2^+[SnCl_3(OH)_2]^-$. From the absence of an induction period with the same system in dichloroethane, it is thought that initiation is here accomplished by the dihydrate, but with participation of the monomer in the formation of the primary polymerisation centres:

$$SnCl_4\cdot 2H_2O + M \rightarrow HM^+ + [SnCl_4OH]^- + H_2O.$$

Overberger and coworkers showed[58] that in the same system in the presence of nitrobenzene the maximum rate in a solvent consisting of 30% nitrobenzene and 70% CCl_4 corresponds to $H_2O:SnCl_4 = 1$. They take the initiating agent here to be stannic chloride monohydrate.

Zlámal[11] has established the presence of four catalytic complexes of different compositions, with the general formula $nAlCl_3.mROH$, where R is an alkyl (from methyl

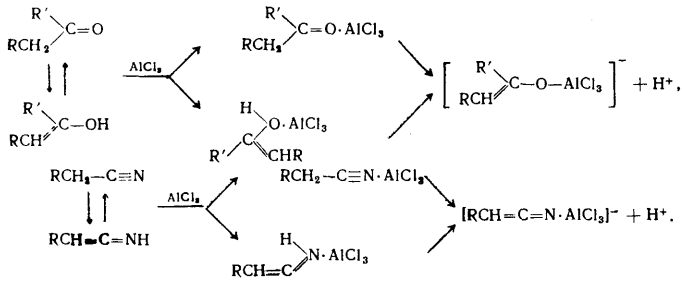
§ Pepper[9] quoted a value for the dielectric constant of C_2H_5Cl which was low, it was later shown[22] to be 10.

¶ Zlámal and Ambrož showed[57] that higher complexes such as RAl_2Cl_7 may be formed in Lewis acid–alkyl halide systems.

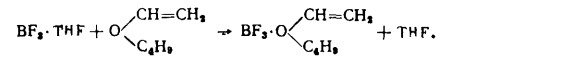
† Under the given conditions HCl as initiator gives only low-molecular-weight products, and this effect is almost unobservable dilatometrically.

to butyl). In each instance the 1 : 1 complexes were the most active in the polymerisation of isobutene dissolved in ethyl chloride. Zlámal and Ambrož[57] found a similar effect with a large number of different oxygen-, sulphur-, and nitrogen-containing compounds: in the polymerisation of isobutene under the influence of complexes of aluminium chloride with aldehydes, ketones, esters, water, hydrogen sulphide, acetonitrile, and other compounds the 1 : 1 complexes showed the greatest catalytic effect. The difficulty in interpreting these data is that in such systems a change in the co-catalyst : catalyst ratio not only yields a complex of new composition, but also permits an actual change in the role of the co-catalyst. Beyond a certain ratio, usually 2 or 3, the latter becomes a termination agent, as is particularly well known for water and alcohols. The same is said to be the case with the above-mentioned compounds[57]. The double action of agents of this type (methanol, organic acids) was noted by Higashimura and Okamura[59] in the stannic polymerisation of styrene. The dependence of the efficiency of a system on the concentration of one component of the catalytic complex does not always therefore have a unique interpretation. This is particularly clearly seen when considering the relationship between the composition of the complex and the degree of polymerisation, which will be dealt with in the following section.

The nature of the ions produced from these complexes was not considered, but the ionisation is more readily visualised as due to the expulsion of a proton than of a carbonium ion:



These mechanisms have not been verified experimentally, and are based solely on the observed initiation of cationic polymerisation by the catalyst–co-catalyst pairs. On the other hand, the absence of styrene polymerisation in the presence of the complex formed between boron fluoride and tetrahydrofuran (THF)[60] shows just as clearly that the BF_3.THF complex does not ionise under the conditions used (30° in benzene solution). Since this complex does produce polymerisation of vinyl butyl ether, it is concluded that the initiation is preceded by an exchange reaction between the initial complex and the monomer:



It is a curious fact that tetrahydrofuran can itself be polymerised under the influence of BF_3.THF to a polymer of molecular weight up to 400 000, but this requires a catalyst concentration at least 5% of the monomer[61].

In addition to the well-known arguments in favour of these polymerisation processes proceeding through cations as intermediates (nature of the catalysts, the nucleophilic character of the monomers, inhibition by anions, etc.), there have recently been direct proofs of their existence. Previously ions could only be identified in certain model systems, such as the $(C_6H_5)_2C=CH_2-BF_3.H_2O$ pair[2], but not under polymerisation conditions, so that the actual nature of the monomeric ions had not been confirmed by direct experimental facts. Jordan and Treloar[62,63] used a spectroscopic method to establish the presence of $\sim CH_2\overset{+}{C}HC_6H_5$ ions in the aluminium chloride or stannic chloride polymerisation of styrene in dichloroethane and carbon tetrachloride. They also concluded that in the sulphuric acid polymerisation of styrene the primary monomeric ions $CH_3\overset{+}{C}HC_6H_5$ are converted, because of the presence of water, into $CH_3(C_6H_5)CHOH_2^+$ ions, the basis for their conclusion being the proximity of the absorption bands of a solution of styrene in sulphuric acid to those obtained with 1-phenylethyl alcohol, which ionises in accordance with the equation

$$CH_3(C_6H_5)CHOH + H_2SO_4 \rightleftarrows CH_3(C_6H_5)CHOH_2^+ + HSO_4^-.$$

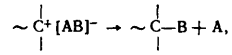
Metz[64] studied the conductivity of the styrene–$SnCl_4$–$C_2H_4Cl_2$–CCl_4 system and established the presence of ions only when catalyst and monomer are both present. This effect illustrates the kinetic results[35] referred to above regarding the participation of the monomer in the ionisation of the catalytic complex in media of low polarity.

The results investigated indicate that the study of the mechanism of initiation of cationic polymerisation should be considered not so much from the point of view of establishing a general approach to any system, but rather of establishing the limits within which a given type of excitation applies, to the case under investigation.

III. PROPAGATION AND LIMITATION OF CHAIN GROWTH

Most of the questions which arise when considering the propagation and termination of chains in cationic polymerisation are associated with the question of the actual nature of the growing chain, which may take the form of a free ion, an ion pair, or an undissociated complex capable of reversible ionisation. The probable coexistence of these states and their mutual overlap is one cause of the complicated kinetics and the difficulty of their elucidation.

A characteristic feature of termination reactions in cationic polymerisation, as we noted in the Introduction, is that they are only extremely rarely associated with irreversible disappearance of the active centres. In most chain growth limitation reactions either the active centres themselves are regenerated or the catalytic complexes from which they are obtained. In this sense such steps should be considered as chain transfer to the counterion rather than as kinetic termination. Of all the possible types of reaction leading to cessation of chain growth (for more detail, see Pepper[9]), excluding direct inhibition by added materials, only one can be classed as a kinetic termination, namely capture of an anion combined with decomposition of the catalytic complex:



where B is a hydroxy-group or an acid residue. Such instances are rather rare, but are observed, for example, in the polymerisation of isobutene under the influence of the complexes $SnCl_4.H_2O$, $TiCl_4.CCl_3COOH$,[6] and $TiCl_4.H_2O$[13] and in the polymerisation of vinyl phenyl ether under the influence of $SnCl_4.C_6H_5OH$,[65] as is shown by the presence of the corresponding groups in the polymer. Termination of

this type is also possible when protic acids are used as catalysts; the effect in non-polar media is then so great that the polymerisation is practically completely suppressed[23,66]. The most frequent type of termination — regeneration of the active centre — in systems which do not contain additional ion sources is predominantly due to reaction of the growing ion with the counterion. The usual assumption that the growing chain–counterion ion pair is held together by electrostatic interaction implies that the reaction between them is monomolecular, and this is confirmed by results which show that the degree of polymerisation is independent of the catalyst concentration[6,8]. However, as Zlámal, Ambrož, and Veselý have shown[11,12,57,67], in some instances the molecular weight of the polymer depends on the concentration of the catalytic complex, although there are wide ranges over which the degree of polymerisation remains almost constant when the catalyst concentration is varied[67]. From this it was concluded[11] that the concept of monomolecular termination arose simply because the process had been studied in just these specific regions, and had been generalised rather prematurely. The correctness of this view is shown by the results obtained in the polymerisation of isobutene under the influence of various complexes nROH.mAlCl$_3$ in ethyl chloride[11]. The effect of varying the ROH : AlCl$_3$ ratio on the molecular weight of the polymer and the conductivity of the system showed the maximum molecular weight to correspond with the minimum conductivity, the latter occurring with an equimolar ratio of the components. However, as already mentioned, a number of complexes of different compositions exist in this system, namely 4ROH.AlCl$_3$, 2ROH.AlCl$_3$, ROH.AlCl$_3$, and ROH.2AlCl$_3$, so that with ROH : AlCl$_3$ > 1 there is no free co-catalyst present, since any excess over the 1 : 1 ratio will lead to the formation of other complexes having other degrees of ionisation. It was therefore concluded[11] that the lower molecular weight of the polymer formed at higher alcohol concentrations is due to the increased concentration of anions from a more ionised complex. From this viewpoint the termination is considered to be the direct consequence of the formation of free anions:

$$\mathrm{ROH \cdot AlCl_3 + ROH \rightarrow 2ROH \cdot AlCl_3 \rightleftarrows [ROH_2]^+ + [AlCl_3OR]^-},$$

and not the result of interaction between the growing chain and the co-catalyst:

$$\sim\overset{|}{\underset{|}{C}}{}^{+} + \mathrm{ROH} \rightarrow \sim\overset{|}{\underset{|}{C}}{=} + [\mathrm{ROH_2}]^+.$$

By maintaining the relative proportions of the components of the catalytic complex constant and allowing for the effects of very small amounts of impurities which can act as terminating agents, Zlámal[11] demonstrated the inverse proportionality between the concentration of the complex and the molecular weight of the polymer, showing that termination proceeds by a bimolecular mechanism, *i.e.* by reaction of the growing cation with free anions. In laying the foundations for his concept of the growth of free macrocations, Veselý[12] shows that the main arguments in favour of the growth of ion pairs (their low degree of dissociation and the absence of a fractional order in the dependence of the rate and degree of polymerisation on the catalyst concentration) are open to objection. According to his calculations[12], there should be considerable ionisation under the normal conditions of cationic polymerisation, *i.e.* a catalyst concentration 0.0001–0.001 M and a dielectric constant of about 9 or higher. Secondly, kinetic data in the literature occasionally indicate deviations in the rate and degree of polymerisation from first order dependence on the catalyst; these are usually ignored. He cites the work of Norrish[68] and Brown[69] on the polymerisation of isobutene who respectively obtained reaction orders of 0.8 and 1–3.5 with respect to the co-catalyst. Deviations of this type have also been noted in other instances, for example in the polymerisation of styrene[60,70].

Clearly this concept, which is based on the experimental results of Czech workers, could be extended to other systems, and would require observance of the conditions indicated above, *i.e.* a constant catalyst–co-catalyst ratio and exclusion of chain-terminating agents. It is as yet difficult to estimate how far this type of treatment can be applied to different examples of cationic polymerisation, because even quite similar systems show substantial differences, as Veselý himself remarked[12]. Thus in the polymerisation of isobutene in ethyl chloride solution under the influence of titanium tetrachloride etherate, a change in the ratio of the catalyst components only affects the molecular weight of the polymer if $Et_2O : TiCl_4 > 1$. With excess $TiCl_4$ the conductivity of the system does not vary and so the number of ions remains constant; therefore the molecular weight of the polymer is independent of the $TiCl_4$ concentration under these conditions. On the other hand, in isobutene polymerisation under the influence of aluminium chloride monoetherate, which is very little ionised, excess of either component leads to the formation of more highly dissociated complexes, as shown by conductivity data, and to a sharp decrease in the molecular weight of the polymer (Fig. 1).

A qualitatively similar situation is observed in the isobutene–ethyl chloride–AlCl$_3$–benzene system studied by Zlámal and Kazda[55]. Here the specific conductivity passes through a maximum and the molecular weight of the polymer through a minimum at a $C_6H_6 : AlCl_3$ ratio of about 400; no such relationships are observed if the aluminium chloride is replaced by its complex with ethanol, when the conductivity of the reaction mixture and the molecular weight of the polymer decrease with increasing benzene concentration. This difference was shown to be due to the relative basicity and polarity of the polymerisation components. The increased conductivity of the catalytic complex in the absence of ethanol can be explained by the reaction

$$\mathrm{C_6H_6 + EtAlCl_4} \rightleftharpoons \left[\text{C}_6\text{H}_6\text{Et}\right]^+ + [\mathrm{AlCl_4}]^-,$$

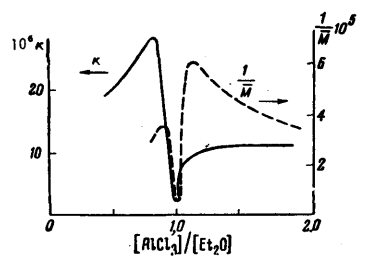


Fig. 1. Dependence on the AlCl$_3$/Et$_2$O ratio of the specific conductance at 25° of the solution and of the molecular weight of the polyisobutylene (polymerised at -78.5°); solvent – ethyl chloride.

in which benzene acts as an electron donor. However, benzene cannot displace ethanol from the $AlCl_3$.EtOH complex; the addition of benzene only reduces the dielectric constant. This conclusion is confirmed by the effect of hexane under analogous conditions: hexane does not form complexes, and its presence reduces the conductivity of the system for each complex. An interesting fact is that the molecular weight of the polymer is affected differently in each case: dilution of the isobutene–ethyl chloride–$AlCl_3$ system with hexane increases the molecular weight of the polymer, which can be explained as chain termination by free anions, the concentration of which falls with decreasing polarity of the medium. This is not found with the $AlCl_3$.EtOH complex.

It thus becomes clear that the suggestion of Veselý and coworkers provides a termination mechanism which may predominate under certain conditions. This is particularly probable for catalyst–co-catalyst systems which can form several catalytic complexes of markedly different degrees of ionisation.

The related studies by Kennedy and Thomas [15,37,71-74] of the polymerisation of isobutene, are of particular interest because of the unusual kinetic relationships found and their interpretation. Aluminium chloride in various media [73,74] gave a degree of polymerisation which varied inversely with the concentration of monomer. Only at low concentrations was there a direct relationship (Fig. 2).

The explanation given was that propagation, like initiation, only occurs when the ion pair is dissociated [Eqns. (8) and (9)], while transfer to the monomer proceeds by reaction of the latter with an undissociated ion pair [Eqn. (10)]:

$$M_n^+A^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} M_n^+ + A^- \text{ (slow)}, \qquad (8)$$

$$M_n^+ + A^- + M \xrightarrow{k_2} M_{n+1}^+A^- \text{ (very fast)}, \qquad (9)$$

$$M_n^+A^- + M \xrightarrow{k_4} P + M^+A^-, \qquad (10)$$

where K_1 is the dissociation constant, k_2 the rate constant of propagation, k_4 the rate constant of chain transfer to the monomer, and P the polymer. The inclusion of these steps in the usual kinetic treatment of the steady state in cationic polymerisation gives the relationship

$$\bar{P} = \frac{K_1 k_2 [M]}{(k_2[M] + K_{-1})(k_3[X] + k_4[M])},$$

where k_3 is the rate constant of the termination reaction and X the termination agent. If $K_{-1} \ll k_2[M]$, it agrees with the experimental data described.

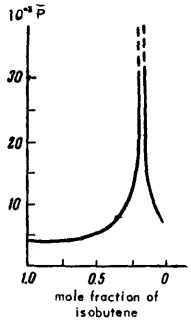


Fig. 2. Influence of monomer concentration on the degree of polymerisation of isobutene at -78°; catalyst — $AlCl_3$; solvent — methyl chloride.

From this point of view the reason for the inverse dependence of $\bar{P}$ on [M] is that at relatively large monomer concentrations an increase in the concentration increases only the rate of chain transfer to the monomer but does not affect the propagation reaction, since the rate of the latter is determined by the slow ionisation of the complex M^+A^-. With low [M], $k_2[M] \ll K_1$ and $\bar{P}$ varies directly with [M].

There are certain objections to this suggested mechanism. Even if it is allowed that there is a distinction between the steps of propagation and transfer to the monomer (8) and (10), it still does not follow that transfer is excluded for the dissociated ion pair, and it is even more difficult to consider that transfer according to Eqn. (10) predominates. Nevertheless there is no other satisfactory explanation of the fact established by Kennedy and Thomas. For example, the role of the dielectric constant in cationic polymerisation, where it usually affects the separation of the ion pair, *i.e.* the rate and degree of polymerisation, suggests a different interpretation of the above results, for when the process is conducted in a polar medium a decrease in the monomer concentration necessarily increases the dielectric constant. However, this idea must be rejected in view of the results of the same investigators for the polymerisation of isobutene in ternary mixtures of monomer, alkyl halide, and CS_2 [73] where the similar dielectric constants of CS_2 and isobutene make it possible to hold the solution at a given dielectric constant while varying the monomer concentration. In this system the degree of polymerisation varied with the monomer concentration in the same way as before. Decreasing [M] from 3 to 1 mole per litre produced a substantial increase in the degree of polymerisation, while further decrease of [M] reduced it. To reconcile the contradictions between literature data on the influence of the dielectric constant and their own results, they introduced the concept of "effective dielectric constant". The process is treated in a specific topochemical fashion, according to which it is assumed that a difference exists between the overall dielectric constant throughout the reaction volume and that in the solvate sheets surrounding discrete sectors in which the fundamental steps of the polymerisation occur. It can then be further assumed that even a small amount of a polar solvent is sufficient to produce a high dielectric constant around the growing centre. Further increase in the concentration of the polar material will then increase the dielectric constant in the main bulk of the solution without affecting the "effective dielectric constant". This approach explains why there is no increase in the molecular weight of polyisobutylene when the dielectric constant of the medium is increased by increasing the concentration of methyl chloride [72]. According to Kennedy and Thomas [73], the amount added with the catalyst (aluminium chloride in solution in methyl chloride was used) creates the necessary "effective dielectric constant".

Another very important conclusion reached by Kennedy and Thomas in their investigation of isobutene polymerisation relates to the temperature variation of the dependence of the degree of polymerisation on the monomer concentration. They found [15] that plots of the degree of polymerisation

against the reciprocal of the temperature have different slopes with different monomer concentrations, and intersect in a single point. Special experiments at the temperature corresponding to this point of intersection showed that the degree of polymerisation is in fact independent of monomer concentration under these conditions. When the degree of polymerisation is plotted against monomer concentration at different temperatures, distinct regions occur in which $\bar{P}$ is independent of [M] over approximately the same concentration range at the various temperatures. The further course of the curves depends on the polymerisation temperature: a lower temperature gives an inverse relationship, and a higher temperature a direct relationship (Fig. 3). On this basis the concept of the inversion temperature is introduced, *i.e.* the temperature at which the dependence of $\bar{P}$ on [M] changes sign. The inversion temperature depends on the medium: in methyl chloride, vinyl chloride, and ethyl chloride it is -42°, -52°, and -55° respectively.

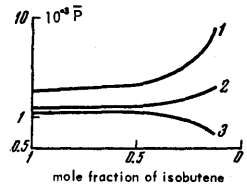


Fig. 3. Degree of polymerisation of isobutene as a function of monomer concentration at various temperatures: 1) -78°; 2) -50°; 3) 30°; catalyst — $AlCl_3$; solvent — methyl chloride.

The existence of the inversion temperature demonstrates the existence of a region in which there is a balance between the two tendencies — the direct ("normal") and inverse ("anomalous") dependence of the degree of polymerisation on the monomer concentration. This novel and extremely interesting fact is closely related to the dependence of the chain limitation reactions on the experimental conditions, mainly temperature and monomer concentration. Clearly, the key role is played by transfer and not termination reactions; this follows from the invariance of the extent of conversion in the polymerisation of isobutene over the temperature range -35° to -180°: a reduction in temperature only increases the degree of polymerisation[15,71] ‡.

Similar effects, namely the existence of a maximum on the plot of $\bar{P}$ against temperature, the invariance of $\bar{P}$ with [M] at low temperatures, and the increase of $\bar{P}$ with decreasing [M] in a definite concentration range had been observed previously[77-79], but in most cases the workers had restricted themselves to a statement of the facts. However, Biddulph and Plesch[78] also concluded that chain transfer to the monomer plays the decisive role in the titanium tetrachloride polymerisation of isobutene with various co-catalysts. They observed no variation of $\bar{P}$ with [M] in ethyl chloride at -70° and in ethyl bromide below -60°, the co-catalyst being trifluoroacetic acid in the first case and water in the second. The mechanism of the isobutene polymerisation in both systems is thus seen to be the same.

For other initiating systems or other monomers under the same polymerisation conditions there is often a considerable change in the specific contribution of a particular step in the process. In this respect it is relevant here to compare the above results[78] with those of Norrish and Russel[23,68] for the polymerisation of isobutene under the influence of $SnCl_4$–H_2O complexes at -78°, which differ greatly: the latter workers found $\bar{P}$ to vary directly with [M], with the process proceeding at an incomparably lower rate and the molecular weights of the polymers being much lower. It is perfectly clear that in this case transfer to the monomer is not the determining factor. From an analysis of the differences, it was concluded[78] that here the main reaction limiting the chains is termination by stannic chloride monohydrate. This fact and the low rate of initiation give relationships which are different in principle from those occurring in polymerisation under the influence of titanium or aluminium halides, where initiation is rapid and termination is slow§.

Of great interest are the differences established by Plesch and coworkers in the polymerisation of isobutene and styrene by the $TiCl_4$–H_2O system in methylene chloride under comparable conditions. With isobutene[46] 100% conversion is only attained in the presence of a certain quantity of water which is fixed for each temperature and each concentration of monomer. A process which has stopped because of a deficiency of co-catalyst can be restarted by adding further water. If $[H_2O]_C$ is the amount of water required for 100% conversion, it has been shown that when $[H_2O] < [H_2O]_C$ the initial rate of the process increases with the amount of water present, but when $[H_2O] > [H_2O]_C$ it is independent of it. For a monomer concentration of 0.1 M, $[H_2O]_C$ lies within the limits 1×10^{-5}–3×10^{-4} M in the temperature range -90° to +25°. The dependence of the initial rate on the monomer concentration is of first order above -30° and of zero order below -60°. A full interpretation of these facts is difficult, but there is no doubt that a fast termination reaction involving water occurs. The study of the polymerisation of styrene between -90° and -30° has established[19] that $\bar{P}$ is independent of [M], that the initial rate is of second order with respect to the monomer, and, most important, that there is no kinetic termination reaction such as was observed with isobutene. Moreover, the active centres do not disappear when the reaction ceases because of exhaustion of the monomer; if more monomer is added, the reaction starts up again, and this was considered to be the first instance in which "live" polymers had been shown to exist in cationic polymerisation. On this basis Plesch supposes that whereas with isobutene, in the polymers of which hydroxy as well as

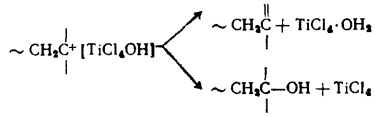
‡ Further development of these investigations has shown[75,76] that an inversion temperature is only observed in polar media. A more complete interpretation of the effects described is given. The expression for the degree of polymerisation is converted into the form

$$\bar{P} = \frac{K_1}{(k_4 - k_3)NS - k_3 L},$$

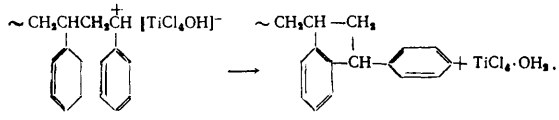
where N and S are the mole fractions of monomer and solvent respectively and L is the total number of moles of monomer and solvent. From this expression it is possible to find the boundary conditions corresponding to the experimental results referred to above, and to explain the different form of the variation of $\bar{P}$ with [M] in polar and non-polar media.

§ Biddulph and Plesch[46] also give previously unpublished results obtained by Russel.

vinylidene end-groups have been detected[46], both the termination reactions



occur, with styrene[19] the most probable termination reaction is cyclisation, with regeneration of the catalytic complex:



The formation of indane rings in the cationic polymerisation of styrene, α-methylstyrene, and stilbene is well established[6,23], but according to Pepper's results[80-82] this type of chain limitation reaction is not the predominant one. It was shown very recently[82] that in styrene polymerisation the indane rings arise as a result of transfer of the chain to the monomer; termination with regeneration of the catalyst leads to the formation of unsaturated end-groups.

Analogous differences — the presence and absence of irreversible kinetic termination — have been established by Pepper in the polymerisation of a single monomer, styrene, under the influence of different protic acids. With sulphuric acid[83,84] the rapid reaction may be broken off before exhaustion of the monomer, because of the insufficiency of catalyst. Addition of acid allows the process to go to completion. This leads to the suggestion that the reaction

$$\sim CH_2\overset{+}{C}H(C_6H_5)[H_2SO_4]^- \rightarrow \sim CH_2CH(C_6H_5)OSO_3H,$$

occurs. In the $HClO_4$ polymerisation of styrene[22] the effect found by Plesch in the styrene–$TiCl_4$ system[19] is observed, *i.e.* the reaction is not broken off. We shall return later to Pepper's studies of the polymerisation of styrene by protic acids.

Although the process continues when further monomer is added to the reaction mixture, it still does not follow that we are dealing with "live" polymers in the sense in which this term is used in anionic polymerisation. In the latter the retention of the activity by the reaction mixture after complete monomer consumption is associated with the theoretical continuity of the process, and is the result of the existence of "live" macroanions or polymers with end-groups of the type $C^- - M^+$ which are able to dissociate. In cationic polymerisation the activity of the system can also be retained in the absence of "live" macrocations, since here the absence of kinetic termination does not preclude the existence of chain limitation reactions involving regeneration of the active complex; it is clear that the renewal of the reaction on addition of extra monomer may be due to the presence in the system of the catalytic complex recovered from this process. In the general case, allowance must be made for the possibility of equilibrium between the polymer chain and the catalytic complex after all the monomer has been consumed. If there is no isomerisation of the macrocations into less active forms, this equilibrium would result in "indestructibility" of the live chains. A direct indication of the existence of "live" macrocations would be an increase in the molecular weight of the polymer after adding a further portion of monomer, or the synthesis of block copolymers such as has been achieved in anionic polymerisation using "live" polymers. However, such evidence has as yet not been obtained in cationic polymerisation. In addition to the studies referred to above, certain indications of the existence of "live" macrocations have been obtained by Asami and Tokura[85,86] in their investigation of styrene polymerisation in the systems $SnCl_4-SO_2$ and $BF_3.OEt_2-SO_2$ at temperatures from 0° to 25°. They found a linear relationship between the degree of polymerisation and the monomer : catalyst ratio; this had not previously been observed in cationic polymerisation, and could not be explained by the usual mechanisms postulated for the process. It was further shown that liquid sulphur dioxide, which in this instance acts as the co-catalyst, can, because of its polar nature (ϵ = 15.6 and 13.7 at 0° and 25° respectively), strongly solvate the growing cations and counterions, which virtually prevents the termination reaction, as is shown by the rapid and quantitative polymerisation, producing polystyrene of unusually high molecular weight for a cationic process, reaching, in the case of $SnCl_4$, 90 000¶. All this supports the propagation of polymerisation by "live" chains. The following mechanism was suggested for the formation of the initial active centres:

$$2SO_2 \rightleftarrows SO_3^{2-} + SO^{2+},$$

$$2SnCl_4 + 2SO_2 \rightarrow 2[SnCl_4{}^1/_2SO_3]^{2-} + SO^{2+}.$$

The important part played by solvation of the growing chains in cationic polymerisation had previously been convincingly demonstrated by Szwarc and coworkers[66] in the polymerisation of styrene in the presence of trifluoroacetic acid, where the order of adding the reaction components play a key role. Adding the acid to the monomer gives only the product of addition of the elements of the acid to the double bond of the styrene, since the low polarity of the medium completely excludes the possibility of polymerisation. When the styrene is added to the acid, it polymerises immediately and quantitatively to give a polymer of molecular weight above 20 000.

The unusual kinetic features of cationic polymerisation often throw doubt on the correctness of the interpretation of a particular case from the point of view of the quasi-steady state. The vigorous development of the reaction and its rapid completion in many cationic systems have led to the process being regarded, as non-steady state, as was originally suggested by Pepper[6,9] who, together with his school, later developed this idea[21,83,84,88-90]. The first point to be considered in resolving this question is the relative rate constants of the separate stages, especially that of the initiation reaction. Polymerisation may be said to take place under steady-state conditions if the rate constant for initiation is small compared with that of the propagation reaction (with the termination reaction also occurring, of course), as in radical polymerisation, where these rate constants differ by 6 or 7 powers of ten. However, in the actual examples investigated by Pepper, *i.e.* the polymerisation of styrene by strong acids in polar media, the relative values are clearly quite different: thus the reaction is explosive in the styrene–sulphuric acid–dichloroethane system[82]. Reduction of the rate of polymerisation by decreasing the monomer concentration to $[M] \leqslant 0.35$ M and the catalyst concentration to $[C] \leqslant 3 \times 10^{-3}$ M

¶ High-molecular-weight polystyrene can also be obtained in other systems, but this requires a low temperature. Thus the sulphuric acid polymerisation of styrene in methylene chloride solution at -78° produces a polymer with M = 85 000; at 0° the molecular weight of the polymer is 4500.[87]

enabled the process to be studied under isothermal conditions, when it was found that the reaction breaks off sharply before complete consumption of the monomer (Fig. 4). This effect is a consequence of the non-steady-state nature of the polymerisation of styrene in the given system, which, it is thought, is due to the exceptionally high rate of initiation, with $k_1 \gg k_2$ (where k_1 is the rate constant of the initiation reaction) and a relatively fast termination reaction† determining the duration of the overall process, the half-life at 25° being about 2 min. Analogous effects were observed in the polymerisation of styrene in dichloroethane in the presence of several other acids[83]. There was a substantial difference with perchloric acid[22], where, while the inequality $k_1 \gg k_2$ is retained, there is no irreversible termination reaction and the reaction taking place before the complete disappearance of the monomer is (up to a degree of conversion of 95% or more) of first order with respect to monomer and has a rate constant proportional to the initial acid concentration. In this system there is instantaneous appearance of the absorption bands at 4100 Å observed in the polymerisation of styrene under the influence of $AlCl_3$ and $SnCl_4$ [62] and ascribed to a carbonium ion, the intensity of the bands not changing with time. In the given case, therefore, the rapid initiation and the absence of termination produce an immediate constant concentration of active centres equal to the initial acid concentration, and in this sense the process is a steady-state one. As Pepper and Reilly remark[22], the main conclusion from this investigation is in agreement with the results obtained by Okamura and coworkers[20,21], who showed, for quite different systems, namely iodine–vinyl ethers and iodine–*p*-methoxystyrene, that the concentration of active centres is 30–90% of the total catalyst content. Hence even with this catalyst whose activity is fairly low, the initiation must be very rapid.

The results discussed serve as a basis for considering certain other processes from the same point of view, for instance the low-temperature polymerisation of isobutene, which under certain conditions shows features similar to those of the polymerisation of styrene under the influence of protic acids. For isobutene polymerisation we could also take $k_1 \gg k_2$, which would mean that steady-state conditions are only possible in the absence of kinetic termination. This approach seems more applicable to this process than does Kennedy's mechanism[73], with propagation represented by a two-stage reaction the rate of which is determined by the slow dissociation of an ion pair, each successive addition of a monomer molecule again producing an undissociated species [see Eqns. (8) and (9)]. This question clearly requires further study.

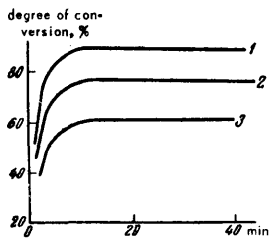


Fig. 4. Kinetics of the H_2SO_4 polymerisation of styrene at 25° in dichloroethane. Concentration of catalyst (10^{-3} M): 1) 3.4; 2) 1.7; 3) 0.81.

The investigations of Pepper and his collaborators have paved the way for a reappraisal of the energetics of cationic polymerisation. Until recently before the absolute rate constants were available for the separate stages of the process, the predominant view was that the rate constant of propagation in cationic polymerisation must be considerably higher than the corresponding value in radical polymerisation, because of the lower activation energy of the propagation reaction in the former, and this was apparently supported by the known negative temperature variation of the overall rate of the process. In the $HClO_4$ polymerisation of styrene, the absence of termination and the existence of the inequality $k_1 \gg k_2$ enabled Pepper[22] to take the experimental overall rate constants of the polymerisation to be the absolute rate constants of the propagation reaction, and the overall energy of activation to be the energy of activation of the propagation reaction: for the temperature range -30° to +25° and with dielectric constant ~ 10 this value was 8.3 kcal mole^{-1}. Reduction of the dielectric constant by changing the concentration of monomer or by using different reaction media led to an increase in the energy of activation, which with $\epsilon = 5.16$ reaches 13.0 kcal × × mole^{-1}. Taking the energy of activation for propagation in the H_2SO_4 polymerisation of styrene as 8.5 kcal mole^{-1}, on the basis of the results obtained with $HClO_4$, Pepper[84] obtained the following values for the activation energies (in kcal mole^{-1}) of the various stages for the styrene–H_2SO_4–dichloroethane system; irreversible termination 13.5, reversible termination with regeneration of catalyst 12.5, and transfer to monomer 16.0‡. The values found were quite different from what had been expected on the basis of the corresponding values for radical polymerisation. For the propagation reaction in cationic polymerisation a slightly higher rather than lower activation energy was obtained (in the radical polymerisation of styrene the activation energy for propagation is 6.9–7.8 kcal mole^{-1} [91,92]), while for the other reactions the activation energy was considerably higher than was expected. These results are also of interest in that they provide a simple explanation of the negative overall energy of activation and the high overall rates of the process, which had earlier often been related to a low activation energy for propagation. With $k_1 \gg k_2$ the concentration of active centres is close to the initial concentration of catalyst, and in the absence of irreversible termination is equal to it, *i.e.* it is of the order of 10^{-3} M, while in radical polymerisation the usual concentration of active centres is only 10^{-8} M. Thus even when the rate constants of the propagation of these processes are similar the difference in the total rates of polymerisation should be very large.

It is very desirable to estimate the extent to which the quantitative data given and the conclusions drawn from

† Irreversible termination is intended.

‡ For the rate constants of the corresponding reactions at 25°, the following values were obtained[84]: propagation 7.6 litre mole^{-1} × × sec^{-1}, irreversible termination 6.7 × 10^{-3} sec^{-1}, reversible termination 0.049 sec^{-1}, and transfer to monomer 0.12 litre mole^{-1} × × sec^{-1}.

them are applicable to other systems. The idea that the values obtained by Pepper may be reasonably accurate for other cases is also supported by the similarity between the quantity $E_3 - E_2 = 4.2$ kcal mole^{-1} found by him in the work cited and the values obtained by Imanishi and coworkers[93] for isobutene polymerisation under the influence of $TiCl_4$ and $SnCl_4$ (4.0 and 4.3 kcal mole^{-1} respectively, in hexane and 4.0 and 3.4 kcal mole^{-1} in chloroform). In an attempt to generalise these results, we may regard it as probable that when the overall activation energy of a cationic polymerisation process is negative (or positive but very small), the relationship between the activation energies of the separate stages will be about the same as was found for the H_2SO_4–styrene system. On the other hand, with cationic polymerisation in systems characterised by a relatively high positive overall activation energy, it is probable that the activation energy of the initiation reaction makes a substantial contribution. Of course, this throws no light on the absolute values of the activation energies of the other fundamental stages in the reaction.

TABLE 1. Absolute constants for the propagation reaction in cationic polymerisation.

Monomer	Catalyst	Solvent	t, °C	k_2, litre × × mole^{-1} × × sec^{-1}	References
Isobutene*	$TiCl_4 \cdot H_2O$	CH_2Cl_2	−30	14.3	20
	$TiCl_4 \cdot H_2O$	CH_2Cl_2	−60	11.3	20
	$TiCl_4 \cdot H_2O$	CH_2Cl_2	−90	12.8	20
p-Methoxystyrene	I_2	$C_2H_4Cl_2$	30	15.66	21
	I_2	CCl_4	30	0.13	21
Isobutyl vinyl ether	I_2	$C_2H_4Cl_2$	30	6.50	21
	I_2	CCl_4	30	0.04	21
Styrene	$HClO_4$	$C_2H_4Cl_2$	25	17.0	22
	$HClO_4$	$C_2H_4Cl_2$	−30	0.7	22
	$HClO_4$	$C_2H_4Cl_2+CCl_4$ (55 : 40)	25	0.4	22
	H_2SO_4	$C_2H_4Cl_2$	25	6.7	22
	$SnCl_4$	$C_2H_4Cl_2$	30	0.4	41
	I_2	$C_2H_4Cl_2$	30	0.003	41

* Plesch[17] has recently reported preliminary results in which k_2 for isobutene is of the order of 10^4 litre mole^{-1} sec^{-1}. The experimental conditions are not given.

IV. ROLE OF THE COUNTERION

The concept of the growing chain as an ion pair must be considered from yet another viewpoint, namely the influence of the counterion on the rate of growth of the chain and its microstructure. This question is of great interest for at least two reasons. Firstly, it is associated with the problem of regulating the rate of the reaction and the structure of the elementary units of the polymer chain, and, secondly, it is an approach to the investigation of the true nature of the growing chain in the sense referred to at the beginning of this section, since the parameters indicated should be independent of the nature of the catalyst when the active centres are the free macrocations. Despite the large amount of information on the relationship between the nature of the catalyst and the features of cationic polymerisation, only in a limited number of cases can it be used for quantitative evaluation of these effects. In dealing with the influence of the counterion on the rate of the propagation reaction (we shall deal first with this side of the process), it is necessary to consider the high sensitivity of cationic polymerisation to changes in the polarity of the medium, and particularly the fact that it can affect the various fundamental stages to different extents. It is thus extremely difficult to maintain the other conditions constant when passing from one counterion to another, especially when using cationic catalysts of different types (for instance Lewis acids and protic acids) for which the comparison would be particularly valuable. These considerations are based on recent data on the rate constant for propagation in cationic polymerisation in certain systems and its variation with the polarity of the medium. The temperature does not always affect this constant to any substantial extent (Table 1).

Okamura and coworkers[93-96] carried out special investigations of the effect of the counterion on the kinetics of polymerisation of styrene, α-methylstyrene, isobutene, and methyl vinyl ether, in which the ratios of the rate constants k_3/k_2 and k_4/k_2 for different catalytic complexes were compared. The results (some of which are given in Table 2) show that there are distinct differences between these ratios for different catalysts, especially with isobutene. This is an important finding, which demonstrates that the characteristics of a counterion may be clearly expressed in terms of kinetic data. However, no general

TABLE 2. Influence of the catalyst and solvent on the ratios of the constants for the fundamental reactions in the polymerisation of various monomers.

Monomer	Catalyst	Co-catalyst	Solvent	t, °C	$10^4(k_3/k_2)$	$10^4(k_4/k_2)$	References
Styrene	$TiCl_4$	H_2O	C_6H_6 + 30% by vol. of $C_2H_4Cl_2$	30	32	150	94
	$SnCl_4$	H_2O		30	62	108	94
	BF_3	$(C_2H_5)_2O$		30	78	80	94
α-Methylstyrene	BF_3	$(C_2H_5)_2O$	n-C_6H_{14}	−50	6.4	91.0	95
	BF_3	$(C_2H_5)_2O$	CH_2Cl_2	−50	35.5	25.9	95
Isobutene	$TiCl_4$	CCl_3COOH	n-C_6H_{14}	−50	0.8	2.0	93
	$SnCl_4$	CCl_3COOH	n-C_6H_{14}	−50	10.5	17.0	93
	$TiCl_4$	CCl_3COOH	CH_2Cl_2	−50	0.56	5.68	93
	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−50	9.0	36.0	93
	$TiCl_4$	CCl_3COOH	CH_2Cl_2	−20	1.3	26.9	93
	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−20	54.0	60.0	93
Methyl vinyl ether	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−50	29.2	15.2	96
							96
	$SnCl_4$	CCl_3COOH	CH_2Cl_2	−20	44.0	32.0	96
	BF_3	$(C_2H_5)_2O$	CH_2Cl_2	−50	12.4	6.4	96
	BF_3	$(C_2H_5)_2O$	CH_2Cl_2	−20	14.4	31.2	96

regularities could be established. For instance, the ratio k_3/k_2 is very sensitive to a change from hexane to methylene chloride with the system $BF_3 \cdot Et_2O$–α-methylstyrene, but is very little different when isobutene is polymerised in the same media under the influence of $TiCl_4$ or $SnCl_4$.

An unexpected feature is that differences in the values of k_3/k_2 for different catalysts are not evened out as the polarity of the medium is increased. An increase in the dielectric constant would be expected to suppress the effect of the counterion characteristics, because the ion–counterion bond is weakened, and so levels off the values of k_3/k_2 when the other experimental conditions are maintained constant. However, the ratio changes to approximately the same extent with both the above initiators in the case

of isobutene polymerisation in solution in hexane and in methylene chloride. Working with ratios of rate constants and not with their absolute values introduces substantial difficulties into the interpretation of these results. It is natural to suppose that a difference in the nature of the counterion may become evident in chain propagation and termination reactions to very different extents, and this will apply both to data for different catalysts under the same conditions, and to the results for a single catalyst in different media or at different temperatures. This is well illustrated by the complex relationships established in the polymerisation of α-methylstyrene under the influence of $BF_3.Et_2O$ (Fig. 5)[95]. Table 3 gives the polarities of the reaction media corresponding to the curves of Fig. 5.

It is no less difficult to explain the direction and extent of the changes in the rate constant of chain transfer to the monomer k_4/k_2 on passing from one medium to another but with the same catalyst in each case (Table 3). Irrespective of the temperature, the rate constant of chain transfer to the monomer during polymerisation in the system α-methylstyrene–$BF_3.Et_2O$–solvent passes through a minimum at a dielectric constant of 5 to 7; [95] this only indicates the substantial difference between the ways in which k_4 and k_2 change when the polarity of the medium is varied.

The possible existence of a connection between the microstructure of the polymer and the nature of the catalyst in cationic polymerisation was pointed out by Flory[2] in his discussion of certain consequences of the concept of propagation by ion pairs. He dealt only with differences in the structure of the unit in polymers of diene hydrocarbons by analogy with the polymerisation of dienes under the influence of alkali metals or their organic derivatives, where the proportions of the different types of elementary unit in the polymer are determined by the nature of the metal. This question has been very little studied in the field of cationic polymerisation, apparently because the polymerised diene hydrocarbons produced in this case are not of practical interest. In the only published work on this subject, Ferington and Tobolsky[97] compared the structure of the polybutadienes obtained at -78° in the presence of various cationic catalysts. For catalysts such as aluminium chloride or bromide in ethyl chloride solution, and boron trifluoride etherate in the absence of solvent, the ratio of 1,4-*trans*/1,2-units is 4.0–4.6, irrespective of the nature of the catalyst, over a wide range of reagent concentrations and for different degrees of conversion (in no case were 1,4-*cis*-units observed). There was some deviation with titanium tetrachloride, which in ethyl chloride solution gave a value of 3.1–3.4, and somewhat larger deviations on passing to the highly polar media nitroethane and nitrobenzene, where for aluminium chloride the ratio of 1,4-*trans*/1,2-units is 2.8 and 2.0 respectively.

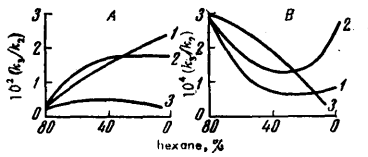


Fig. 5. Influence of the polarity of the medium on the ratio k_2/k_3 in the $BF_3.Et_2O$ polymerisation of methylstyrene: *A*) at -20°; *B*) at -70°; monomer concentration 20 vol.%. Reaction media: 1) chloroform–hexane; 2) methylene chloride–hexane; 3) toluene–hexane.

TABLE 3. Dielectric constant of solutions of α-methylstyrene in various media[95].

Components, vol.%					Dielectric constant	
α-methylstyrene	n-hexane	toluene	chloroform	methylene chloride	-20°	-70°
100	—	—	—	—	2.65	2.77
20	80	—	—	—	2.09	2.17
20	—	80	—	—	2.50	2.62
20	—	—	80	—	5.03	6.27
20	—	—	—	80	9.30	12.31

In general the normal tendency of cationic catalysts to produce diene polymers of predominantly 1,4-*trans*-structure is retained in all cases. In the investigation cited, the content of such units lies within the fairly narrow limits 66–82%, which creates the impression that the structural differences in the polymerisation of dienes by the cationic mechanism are considerably less than in their polymerisation by alkali metals and their derivatives, where the microstructure of the diene polymers is considerably affected by altering the metal or the medium. There are no real grounds, however, for making far-reaching conclusions on this basis, as to the difference in principle between the roles of the counterions in the propagation by the ion pairs $\sim \overset{|}{\underset{|}{C^+X^-}}$ and $\sim \overset{|}{\underset{|}{C^-M^+}}$. The results for the polymerisation of isoprene by alkali metals indicate that true stereospecificity has been established only for lithium, which can give a polymer constructed wholly of 1,4-*cis*-units. All the other alkali metals give polyisoprenes composed mainly of 1,4-*trans*- and 3,4-units, the ratio of these varying little with the metal used[98] (Table 4).

It is thus possible to refer only to a substantial difference between lithium and the other alkali metals in this respect§. The variations in the microstructure of the polyisoprene obtained with the metals sodium to caesium are fully comparable with those established by Ferington and Tobolsky[97] in the polymerisation of butadiene by various cationic catalysts. It is also necessary to point out that a high stereospecificity can be attained in the cationic polymerisation of diene hydrocarbons: thus Rinehart[100] obtained polybutadiene with up to 99% of 1,4-*trans*-units by using rhodium salts [$Rh(NO_3)_3.2H_2O$ and $RhCl_3.3H_2O$] as catalysts. There are also reports of the production of stereoregular poly(tetramethylbutadiene) using cationic catalysts[101]. It is difficult to compare these results with Ferington's[97], since the polymerisation was effected under quite different conditions, but it can be said that it is not by any means futile to consider the possibility of controlling

§ Organolithium compounds occupy a similar unique position in the stereospecific polymerisation of methyl methacrylate[99].

TABLE 4. Microstructure of polyisoprene produced under the influence of alkali metals in pentane solution[98].

Metal	Units, %			
	1,4-		3,4-	1,2-
	cis-	trans-		
Li	94.4	0	5.6	0
Na	0	43	51	6
K	0	52	40	8
Rb	5	47	39	8
Cs	4	51	36	8

the microstructure of diene polymers in cationic polymerisation and to discuss the role of the counterion in the propagation of the macrocation.

It is very tempting to correlate the nature of the counterion with another distinguishing feature of the unit structure of the polymer chain, namely the differences in tacticity in vinyl polymers. As with diene hydrocarbons, the number of facts at our disposal in this field is small, although the first isotactic polymers [poly(alkyl vinyl ethers) and polystyrene] were in fact obtained by cationic polymerisation, long before the idea of the stereoregularity of vinyl polymers was introduced. The data on the production of stereoregular polymers by cationic polymerisation and views on the possible nature of this effect have recently been compiled in a monograph by Gaylord and Mark[102]. Several new publications have recently appeared in this field, dealing mainly with vinyl ethers[103-113]; in these, as in the earlier investigations, the dependence of stereoregularity in polymers on the experimental conditions has been treated mainly from the viewpoint of the phase state of the system, the order of introduction of the components, and the polymerisation temperature. Only in some of these studies is there an indication that the nature of the catalyst has a substantial influence on the stereospecificity of the process. For example, in the polymerisation of vinyl isobutyl ether by $BF_3.Et_2O$ or $SnCl_4.CCl_3COOH$ the former catalyst gives the more stereoregular polymer[105]. It must be emphasised that the formation of stereoregular poly(alkyl vinyl ethers) under the influence of boron trifluoride etherate has been noted especially often. It has been thought[102] that the stereospecificity of this catalyst is due to the propagation process involving the formation of a coordination complex:

$$BF_3 \cdot O(C_2H_5)_2 \xrightarrow{CH_2=CHOR} BF_3 \cdot O(R)CH=CH_2,$$

which precedes the addition of the next monomer unit to the growing chain. It has recently been shown[108] that polymers of vinyl isobutyl ether which are more stereoregular than those obtained at low temperatures by boron trifluoride etherate can be prepared by using other cationic catalysts, which are complexes of sulphuric acid with aluminium, magnesium, or chromium sulphates. A selective stereospecificity in the polymerisation of vinyl ethers has been established for certain alkyl aluminium halides[104,110]. Polymers with a high degree of stereoregularity can be obtained by the cationic polymerisation of α-methylstyrene[112] and 3-methylbut-1-ene[113].

The limited data available and the high sensitivity of chain formation to various influences have so far prevented the determination of the actual part played by the counterion in the steps determining the microstructure of the polymer. The possible existence of such a connection has been touched upon when introducing this question.

While noting a connection between the effects considered in this section and the problem of the propagation of ion pairs and the role of the counterion, it must be said that the creation of an objective picture of cationic polymerisation would be much helped by an evaluation not only of the characteristics of a given ion pair, but of the macrocation also. It is relevant to recall here Szwarc's remark[114] about the useful information which may be gleaned from a systematic investigation of cationic polymerisation initiated by radiation, since ion pairs are apparently then absent, and it is free macrocations which grow. In this sense radiation-initiated cationic polymerisation is a very valuable method for investigating the mechanism of the process, since it should promote the appearance of features specific to the monomeric cations in the free state. Strictly speaking, the study of the reactivity of the growing chains in cationic polymerisation requires the macrocation to be in just this state, since the presence of the counterion substantially modifies the process, as the data given above (Tables 2 and 3) indicate. From this point of view, it is convenient to return to the problem of cationic copolymerisation. It had earlier been assumed that the counterion and the polarity of the medium were factors which could affect the copolymerisation constants, but until recently there were very few data on this point. It was known[115] that there were marked variations in the copolymerisation constants in the case of the pair styrene–3,4-dichlorostyrene when different catalysts were used, but with the pair styrene–*p*-chlorostyrene different cationic catalysts and variation of the dielectric constant from 2.2 to 29.7 hardly affected the copolymerisation constants[116,117]. Among more recent studies of the copolymerisation of various pairs of monomers by cationic catalysts[118-124], only a few deal specifically with this point[118,120,122,126]. Table 5 gives some results illustrating the substantial parts played by the catalyst and the medium.

As Overberger points out[126], the possibility of selective solvation of the active centres by one of the monomers

TABLE 5. Influence of catalyst and polarity of medium on the copolymerisation constants in cationic copolymerisation at 0°.

M_1	M_2	Catalyst	Solvent	r_1	r_2	References
Styrene	3,4-dichlorostyrene	$AlCl_3$	CCl_4	2.8	0.45	115
		$BF_3.Et_2O$	CCl_4	5.9	0.27	115
Isobutene	*p*-chlorostyrene	$AlBr_3$	*n*-hexane	1.01	1.02	120
			nitrobenzene	14.7	0.15	120
			nitromethane	22.5	0.7	120
Styrene	*p*-methoxystyrene	$SnCl_4$	nitrobenzene – CCl_4 (1 : 1)	0.04	19	124
		$AlCl_3$		0.34	11	124
		$TiCl_4$		0.12	14	124
		$TiCl_4$	CCl_4	0.05	46	124
		$TiCl_4$	nitrobenzene	0.48	5.6	124
Styrene	chloroprene	$AlBr_3$	benzene	6.9	0.04	126
		$AlBr_3$	nitrobenzene	16.0	0.06	126

must also be considered in cationic copolymerisation. For example, conditions may be more favourable for chain propagation by the more polar monomer even if it is less reactive than the other. Of course, such an effect would be more likely in the absence of stable solvation shells, *i.e.* in non-polar media. In particular, this view finds confirmation in the results obtained for the pair isobutene–*p*-chlorostyrene.

Results of studies on cationic polymerisation under the influence of γ-radiation began to appear in 1957. The results for copolymerisation obtained in this way, mainly by Abkin and coworkers[127-133], do not yet allow us to decide whether deviations from the values known for ordinary cationic polymerisation occur¶. Of course, differences in the copolymerisation constants determined by the presence, absence, or nature of the counterion are only possible with relatively similar monomers; in other cases, the possible effects of this type will always be hidden by differences in the polarities of the double bonds, which must occur not only with such pairs as styrene–methyl methacrylate, but also in less extreme cases.

It is thus clear that the whole problem of explaining the connection between the nature of the counterion in cationic polymerisation and the effects associated with it — the kinetics of the process, the relative contributions of the fundamental steps, and changes in the microstructure of the polymer chain — is in a very early stage of development. All these questions merit further study.

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CHELATE POLYMERS

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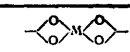
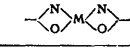
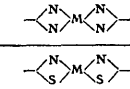
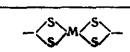
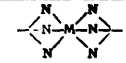
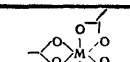
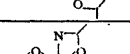
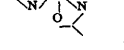
I. INTRODUCTION. SOME PROBLEMS OF TERMINOLOGY

Interest in macromolecular compounds containing metals has grown considerably during recent years. Such compounds are often termed "chelate polymers", and several reviews of work on their synthesis and properties have appeared in the Soviet and foreign literature[1-5]. Most of these, however, either do not cover the whole of the literature or else are already considerably out of date. The aim of the present review is to survey the literature on the preparation and properties of chelate polymers up to May 1962.

We must consider briefly some problems of the terminology of these compounds. The name "chelate compound" which we use is based on the term "chelate" ($\chi\eta\lambda\eta$), a claw or talon, proposed by Morgan and Drew[6]. The expressions "inner complex" and "clawlike compound" also are often employed in Soviet chemical literature. In several cases we use the nomenclature recommended by the International Union of Pure and Applied Chemistry[7].

The term "chelatophore" has been proposed[3] for a group which is capable of forming chelate rings. In our view, however, it is more appropriate to use the term "chelate ligand". Terent'ev and Rukhadze[8] proposed the name "analytical loops" for the cyclic groups formed by the addition of chelate ligands to a central atom. Later we suggested calling such cyclic chelate groups "chelate loops"[9]. The accompanying Table lists some possible chelate loops and the names and symbols which we employ for them.

Some possible chelate loops.

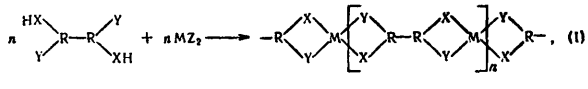
Coordination No. of metal (M)	Name of chelate	Schematic formula of chelate*	Shortened formula of chelate
4	**bisdioxa**		2(O, O) — M
4	**bisazaoxa**		2(N,O) — M
4	**bisdiaza**		2(N, N) — M
4	**bisazathia**		2(N, S) — M
4	**bisdithia**		2(S, S) — M
6	bistriaza		2(N, N, N)—M
6	trisdioxa		3(O, O) — M
6	trisazaoxa		3(N, O) — M

* In several actual cases the schematic formula can be still further simplified by representing N, O, and S atoms as points.

II. METHODS OF PREPARATION AND STRUCTURE

Chelate polymers can be synthesised in three fundamentally different ways.

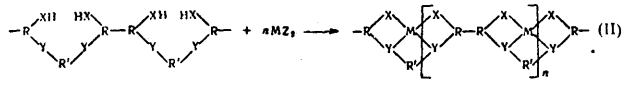
Firstly, by the metal forming donor–acceptor bonds with donor atoms in molecules which usually† contain at least two pairs of donor groups:



(I)

where X and Y are donor groups, and M is a metal.

Secondly, by entry of a metallic ion into an existing polymer chain in which the monomeric unit contains at least two pairs of donor groups:



(II)

Polymers of types (I) and (II) can be formed also by the method of nascent reagents[10,11].

† In some rare cases polychelates may be formed when a chelate ligand possesses less than two pairs of donor groups, an example being provided by the hydroxo-bridged compounds. This question will be discussed in greater detail later.