

# MECHANISMS OF IONIC POLYMERIZATION

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## INTRODUCTION

As can be seen from a number of the papers submitted to this Symposium, the scope of ionic polymerizations is widening both as regards the variety of catalysts and the number of monomers used. At present, the latter are by no means restricted to compounds with a C=C double-bond. The widening range of monomers and catalysts available has made a deeper understanding of the laws governing these reactions possible. In this lecture I am going to deal in particular with the growth mechanism of ionic polymerizations, which is the principal step in polymer formation. In this connection, I should like to review results recently obtained by our team of workers at the Research Institute of Macromolecular Chemistry in Brno.

## REACTIONS ON FREE IONS AND ION-PAIRS

As regards the reaction mechanism, the growth reaction can take place either on free ions, on ion-pairs in homogeneous solution, or on ion-pairs on the surface of a heterogeneous system.

Let us first consider the conditions under which free ions occur in the polymerizing system. Ionization will be strong if:

- (a) the distance between the centres of charge in the original ion-pair is great;
- (b) if the original ion-pair is strongly solvated and the distance between the centres of charge is increased by solvation; solvation can be secured by any polar component of the system, either solvent, monomer, catalyst or co-catalyst;
- (c) other things being equal, ionization decreases with increasing concentration of the original ion-pair.

Moreover, the formation of ion-pairs in a system is complicated by the fact that many atoms, especially those with a high atomic number, are capable of forming various kinds of complexes. Thus the choice of a catalytic system which does not form complexes, and which is strongly dissociated under the given conditions, is fairly restricted.

Complications due to the formation of various complexes in systems involving stannic chloride and titanium tetrachloride have led a number of authors to believe that growth on ion-pairs is a general mechanism for cationic polymerization<sup>1</sup>. Research carried out in the field of anionic polymerization has also established the mechanism of growth on ion-pairs<sup>2</sup>. On the other hand, our own work on the polymerization of isobutylene in ethyl chloride solution, with an aluminium trichloride catalyst<sup>3</sup>, showed that

free ions play an active part in the growth reaction. Further work on the kinetics of ionic polymerizations led to the conclusion that these reactions take place by different mechanisms under different conditions.

### IONIC POLYMERIZATION ON FREE IONS

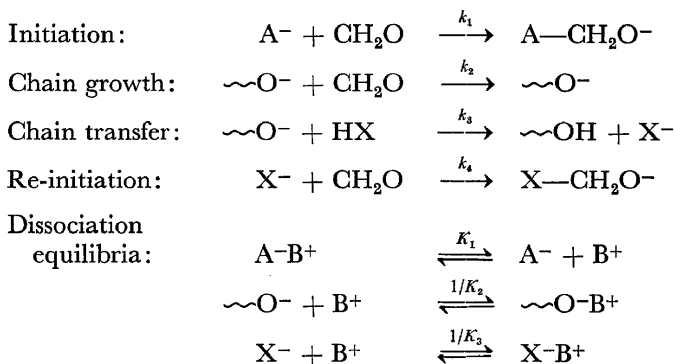
Anionic polymerization of formaldehyde can be cited as an example of ionic polymerization proceeding by means of free ions. This monomer is so very reactive that it is polymerized even by such unreactive anions as the chloride ion. In order to eliminate the effect of the cation, we chose the tetrabutylammonium ion, which is not solvated<sup>4</sup> even in aqueous media, as is borne out by the fact that its radius is identical in both the gaseous and the liquid phase.

It has been shown<sup>5</sup> that the order of reaction with respect to the monomer is 2-3 at the beginning of polymerization. It appears that the monomer is the most polar component of the system. Experiments were made with concentrations of the catalyst in the range  $0.4-200 \times 10^{-6}$  mole/l.

As the conversion is independent of the intrinsic viscosity, the molecular weight is determined only by transfer with water and methanol, which are always present in the reaction mixture in concentrations greater than those of active centres. The dependence of the reaction rate on the catalyst concentration was found to be of the order 0.5-0.8.

The increased order of reaction at the lowest catalyst concentrations can be explained by the high ionization of the system when the catalyst concentration approaches the value of the dissociation constant. The data indicate that growth takes place on free ions.

Let us assume that the system undergoes the following elementary processes:



Let us further assume that the difference between the dissociation constants  $K_1$ ,  $K_2$  and  $K_3$  is negligible, and let us replace them by a single constant  $K$ . Then, for a catalyst concentration  $[Cat]_0$  greater than  $K$ , the following relation will hold:

$$[O^-]_0 = K^{\frac{1}{2}}[Cat]_0^{\frac{1}{2}}$$

where  $[O^-]_0$  is the concentration of all anions present.

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In view of the fact that there is no termination involved in the scheme, we may assume that a static concentration of growing chains  $[O^-]$ , given by the expression  $K^{\frac{1}{2}}[Cat]^{\frac{1}{2}}$ , is quickly built up, with the result that we need not take into account any initiation reactions unless they are extremely slow.

In the presence of a transfer agent, some of the polymer chains are transformed into anions  $X^-$  which possess a reactivity differing, in general, from that of  $\sim O^-$ . Then the following relationship holds:

$$[O^-]_0 = [O^-] + [X^-]$$

A stationary state is reached between both kinds of anions which is expressed by the relation:

$$\frac{d[X^-]}{dt} = k_3[O^-][HX] - k_4[X^-][M] = 0 \quad (1)$$

The expression for the over-all rate of reaction is:

$$-\frac{d[M]}{dt} = k_2[O^-][M] = \frac{k_2 K^{\frac{1}{2}} [Cat]_0^{\frac{1}{2}} [M]}{1 + \frac{k_3 [HX]}{k_4 [M]}} \quad (2)$$

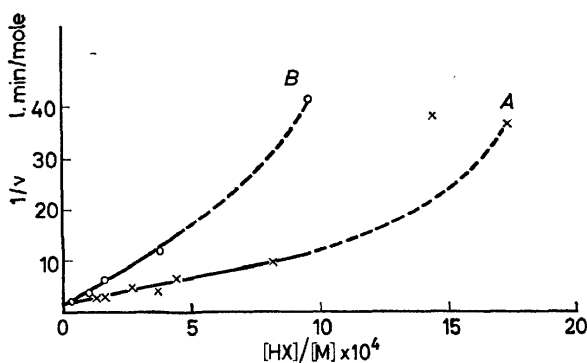
The reciprocal of the rate of reaction in the presence of an impurity HX is given by the following expression, which is derived from the previous one:

$$\frac{1}{v} = \frac{1}{v_0} \left( 1 + \frac{k_3 [HX]}{k_4 [M]} \right) \quad (3)$$

where

$$v_0 = k_2[O^-][M].$$

Relationships found for two typical retarders, namely formic acid and carbon dioxide, are shown in *Figure 1* and *Table 1*.



*Figure 1.* Dependence of the reciprocal of the rate of polymerization on the concentration of chain-transfer agent

*A:* Influence of formic acid (formaldehyde concentration = 4.65 moles/l.; dibutylamine concentration =  $8.65 \times 10^{-6}$  moles/l.; temperature =  $-59.3^\circ\text{C}$ )

*B:* Influence of carbon dioxide (formaldehyde concentration = 3.60 moles/l.; tetrabutylammonium laurate concentration =  $1.5 \times 10^{-6}$  moles/l.; temperature =  $-59.3^\circ\text{C}$ )

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The reciprocal of the degree of polymerization will be given by:

$$\frac{1}{P_n} = \frac{k_3}{k_2} \frac{[\text{HX}]}{[\text{M}]} \quad (4)$$

In the absence of accurate knowledge of the relationship between the intrinsic viscosity and the average degree of polymerization, the dependence of the reciprocal of the reduced viscosity,  $1/\eta_{\text{red}}$ , on the ratio  $(1 + X)/[\text{M}]$  was plotted and the value of:

$$\frac{1}{\eta_{\text{red}}} = C'_{\text{HX}} \frac{[\text{HX}]}{[\text{M}]}$$

was obtained, as is shown in *Table 1*.

Although the data should be considered as preliminary (owing to the use of reduced viscosity instead of true  $P_n$ ), interesting results were obtained. It may be seen from *Table 1* that there is a direct relation between the ease

*Table 1*

| <i>Substance</i>   | $C'_{\text{HX}}$<br>(g/100 ml) | <i>Retardation efficiency</i><br>( $k_3/k_4$ ) |
|--------------------|--------------------------------|--|
| H <sub>2</sub> O   | 18.2                           | None   |
| CH <sub>3</sub> OH | 56.0                           | None   |
| HCOOH              | 395                            | $3 \times 10^3$                                |
| CO <sub>2</sub>    | 415                            | $1.9 \times 10^4$                              |
| H <sub>2</sub> S   | 440                            | None   |
| HCl                | Reacts with the catalyst       | Inhibits the polymerization                    |

of proton liberation, namely "acidity", and the reactivity (basicity) of a given anion in a series of compounds with a common principal atom (*e.g.* oxygen).

However, if hydrogen sulphide is considered, it may be seen that, although the acidity of its hydrogen atom is considerable, and even comparable with that of a moderately strong acid such as formic acid, the anion HS<sup>-</sup> is very reactive when compared with HCOO<sup>-</sup>. This demonstrates the considerable importance of the electronegativity of the principal atom.

Analogous behaviour has also been observed when sulphur-containing substances participate in free-radical polymerizations, where they induce a strong chain-transfer and cause only a slight retardation. These data show that the constants of transfer,  $k_3$ , and re-initiation,  $k_4$ , are independent quantities.

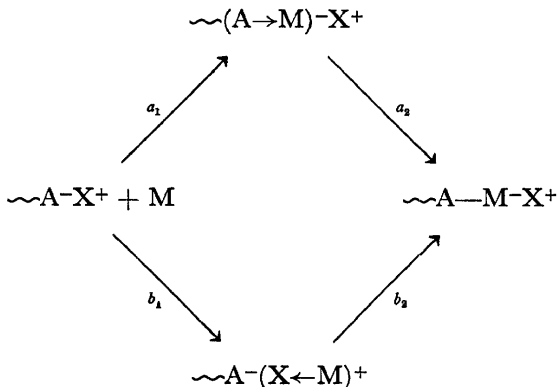
I should like to stress again that formaldehyde, as a simple and highly reactive monomer, permits a far wider study of ionic polymerization than less reactive monomers, for which one has to choose catalytic systems from a rather restricted range of very strong bases or acids.

### IONIC POLYMERIZATION ON ION-PAIRS

The growth of polymer on an ion-pair cannot be viewed as a single elementary step, but rather as an over-all reaction which can, in principle,

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take various courses. Such mechanisms as those given below can be visualized, for instance in the case of the anionic polymerization of the C=C double-bond:

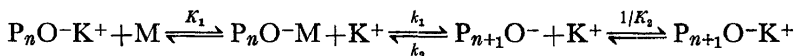


Course *a* does not differ, in principle, from the reaction which involves free ions. As an example, let me cite the anionic polymerization of the cyclic tetramer of dimethylsiloxane<sup>10</sup> on an  $\sim O^-K^+$  ion-pair. Kinetic studies have shown<sup>11</sup> that the over-all rate of reaction is given by:

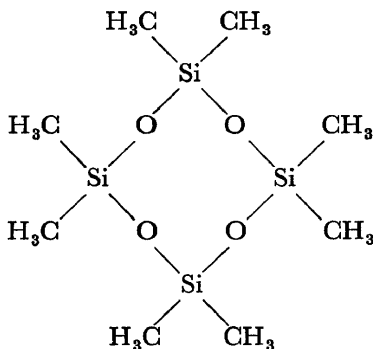
$$-\frac{d[M]}{dt} = [\text{Cat}]^{\frac{1}{2}}(k_1'[M]^{\frac{1}{2}} - k_2'[M]^{-\frac{1}{2}}) \quad (5)$$

where  $[\text{Cat}]$  is the concentration of the catalyst,  $k_1' = k_1K_1^{\frac{1}{2}}$  and  $k_2' = k_2K_2K_1^{-\frac{1}{2}}$ .

A detailed analysis of the kinetics of this reaction has revealed that the rate-determining step is the opening of the cyclic anion ( $k_1$ ), and that the growth and depolymerization reactions are governed by these elementary reactions:



where M is the cyclic tetramer of dimethylsiloxane:



The dielectric constant of the medium was increased by the addition of nitrobenzene; and, consequently, ionization was enhanced to such a degree that the electrical conductivity could be measured directly, and approximate values of the individual constants could be assessed. During the course of these experiments, the tetramer of dimethylsiloxane itself was found to act as a strong solvating agent.

The size of the cation is a most important factor in the reactions under investigation. As the rate of reaction increased considerably in the sequence  $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ , it is apparent that the counter-ion only affects the equilibrium constant  $K_1$ , and, consequently, the concentration of the initial free ions  $\text{P}_n\text{O}^-$ .

The reaction course designated  $b$  in the above scheme is really catalytic, *i.e.* the counter-ion adds to the monomer more easily than the free ion does. This mechanism seems to be of great importance in stereo-specific polymerizations (*e.g.*, this is how Korotkov<sup>6</sup> explains LiR-induced polymerizations). The situation is further complicated by the fact that the rate-determining step is either the reaction  $b_1$ , as in the case of monomers which are slowly adsorbed on the corresponding counter-ion (*e.g.* simple monomers with C=C double-bond), or reaction  $b_2$ , as in the case of easily adsorbed monomers (*e.g.* dienes).

As we shall see later, the above mechanism holds for the heterogeneous polymerization involving Ziegler catalysts as well.

This same group of reactions also comprises the cationic polymerization induced by titanium tetrachloride<sup>7</sup>, stannic chloride<sup>8</sup> and sulphuric acid<sup>9</sup> where, despite considerable dissociation, the kinetic data indicate that growth takes place on ion-pairs.

The formation of a dative bond with the counter-ion is a pre-requisite.

### HETEROGENEOUS SYSTEM: TITANIUM TRICHLORIDE- TRIETHYLALUMINIUM

Our kinetic study of the polymerization of propylene has shown<sup>12</sup> that the over-all rate of polymerization is given by:

$$V_{\text{pol}} = \frac{k_p K_M K_A [S][M][A]}{(1 + K_M [M] + K_A [A] + \Sigma K_i [i])^2} \quad (6)$$

where  $K_M$ ,  $K_A$ ,  $K_i$  are the equilibrium constants of chemisorption of the monomer, triethylaluminium, and inhibitor respectively at the titanium trichloride surface,  $[S]$ , and  $[A]$  is the triethylaluminium concentration.

In terms of this relation, the polymerization process involves the reaction of adsorbed components (triethylaluminium and monomer). The dependence of the rate of reaction on the triethylaluminium concentration goes through a maximum. This is not in agreement with other authors<sup>13, 14</sup> who found that the rate of reaction was independent of the triethylaluminium concentration.

Let us now examine equation (6), for a pure system where  $\Sigma K_i [i] = 0$ , in more detail.

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On differentiating with respect to  $K_A[A]$ , the concentration of triethylaluminium for the maximum reaction rate is expressed by:

$$K_A[A]_{\max} = K_M[M] + 1 \quad (7)$$

By analogy, the dependence of the reaction rate on the monomer concentration will reach a maximum which is expressed by the relation:

$$K_M[M]_{\max} = K_A[A] + 1 \quad (8)$$

Substituting from equation (7) in equation (6), for the maximum reaction rate, the following relation will hold:

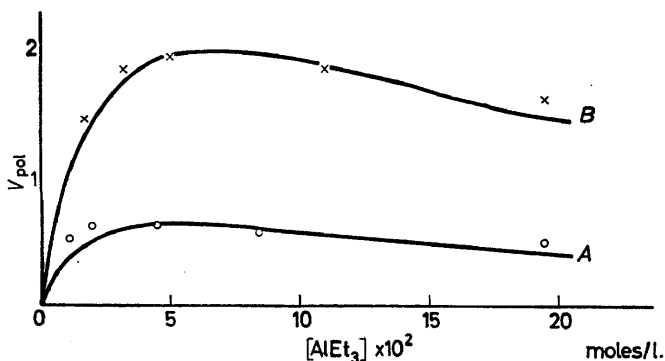
$$V_{\max} = \frac{K_M[M]}{4(K_M[M] + 1)} \quad (9)$$

The value of  $V_{2.3}/V_{0.58} = 3.16$  was obtained experimentally for the relation between the maximum reaction rates at two monomer concentrations (*Figure 2*). The value of  $K_M = 0.163$  was obtained by inserting this value in equation (9). The experimental value  $[A] = 6.5 \times 10^{-2}$  mole/l. for the maximum reaction rate was substituted in equation (7), giving the value of  $K_A = 21.2$ .

From the values given, the dependence of the reaction rate on the concentration of triethylaluminium shown in *Figure 2*, and the dependence on the concentration of the monomer shown in *Figure 3*, were determined.

It is clear from the data given that the assumption that the reaction rate bears a linear relationship to the concentration of the monomer, but is independent of the concentration of triethylaluminium, as has been observed by other authors, is valid only over a limited range of concentrations.

A retardation was observed (*Figure 4*) when impurities were present by determining the influence of different substances on the reaction rate and



*Figure 2.* Theoretical and experimental dependence of the rate of propylene polymerization on triethylaluminium concentration, for various monomer concentrations

A: Monomer concentration = 0.58 moles/l. (temperature = 50°C)

B: Monomer concentration = 2.3 moles/l. (temperature = 50°C)

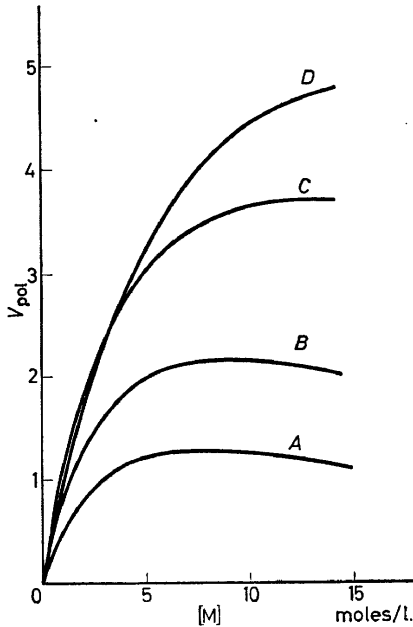


Figure 3. Theoretical dependence of the rate of propylene polymerization on monomer concentration, for various triethylaluminum concentrations

- A: Triethylaluminum concentration = 0.01 moles/l.  
 B: Triethylaluminum concentration = 0.02 moles/l.  
 C: Triethylaluminum concentration = 0.05 moles/l.  
 D: Triethylaluminum concentration = 0.10 moles/l.

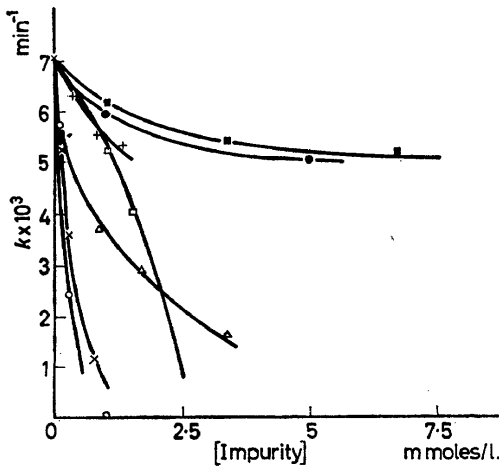


Figure 4. The influence of impurities on the rate of propylene polymerization (monomer concentration = 2.33 moles/l.; triethylaluminum concentration =  $3.5 \times 10^{-2}$  moles/l.; titanium trichloride concentration = 0.77 g/l.; temperature =  $50^\circ$ )

- $\circ$  : COS;  $\times$  :  $CS_2$ ;  $\triangle$  :  $Me_2S$ ;  $\bullet$  : EtSH;  $\blacksquare$  :  $H_2S$ ;  $\square$  : CO;  $+$  :  $H_2O$



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from equation (6). Values for  $K_1$  were obtained. The values of different adsorption constants are illustrated in *Table 2*.

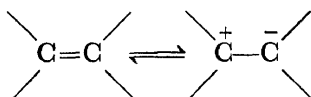
*Table 2*

| <i>Substance</i>              | <i>K</i>          |
|-------------------------------|-------------------|
| COS                           | $2.4 \times 10^3$ |
| CS <sub>2</sub>               | $1.7 \times 10^3$ |
| Me <sub>2</sub> S             | $4.1 \times 10^2$ |
| H <sub>2</sub> O              | $1.3 \times 10^2$ |
| H <sub>2</sub> S              | 50                |
| AlEt <sub>3</sub>             | 21.2              |
| C <sub>3</sub> H <sub>6</sub> | 0.16              |

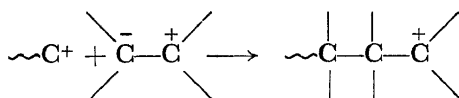
It follows from what has been said that this case is analogous to the case (b) of growth on ion-pairs, that is, the reaction of the monomer with counter-ions occurs as an intermediate step in the growth reaction.

### DISCUSSION

The majority of authors who have dealt with ionic polymerization have failed to analyse the growth reaction itself. Such questions were only discussed<sup>15, 16</sup> for the purpose of calculating the energy necessary to split the monomer double-bond heterolytically as follows:

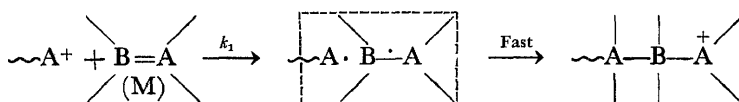


In the case of isobutylene, for instance, such a fission requires an energy of 201 kcal/mole. That is why a high solvation energy must be assumed. This consideration follows from the assumption that, in cationic polymerization, for instance, which takes place on the free cation  $\sim\text{C}^+$ , the heterolytically split monomer donates two electrons to form a new link according to the scheme:



The mechanism postulated would require a very high activation energy of the growth reaction.

Let us assume, as Szwarc<sup>17</sup> does in the case of initiation by alkali metals, that, even during the growth reaction, the rôle of active intermediates is played by ion-radicals which are formed by the transfer of a single electron between the active centre and the monomer. Then we may write the growth reaction as follows:

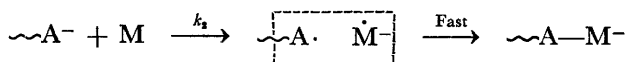


The activation energy of this reaction will be expressed by:

$$\Delta E_1 = I(M) - A(A^+) + S(A^+) - S(M^+) \quad (10)$$

where  $I(M)$  is the ionization potential of the monomer;  $A(A^+)$  is the electron affinity of the cation;  $S(A^+)$  is the solvation energy of the polymer cation; and  $S(M^+)$  is the solvation energy of the ion-radical formed from the monomer.

In the case of anionic polymerization on a free ion:



the activation energy will be given by:

$$\Delta E_2 = I(A^-) - A(M) + S(A^-) - S(M^-)$$

where the symbols are analogous to those given above.

There is at present little experimental data available on ionization potentials of monomers and electron affinities of cations<sup>18</sup>. But even this limited information indicates that the difference between the two values for a given monomer is less than 1 eV.

A term which corresponds to the difference between the solvation energy of a cation and of an ion-radical formed from the monomer, is likely to be of minor importance.

Even less experimental data are available for a calculation of the activation energy of anionic polymerization. The electron affinity is usually determined from quantum-mechanical calculations. As has already been shown by Szwarc<sup>19</sup>, the polarographic half-wave potential can be taken as a measure of the electron-affinity of the monomer provided that the reaction is reversible. A number of published polarographic half-wave potentials<sup>20</sup> of monomers shows that the reactivity of monomers in anionic polymerization decreases in the same order.

### REACTION ON ION-PAIRS

As has already been indicated, the polymerization on ion-pairs can take two different courses.

(a) Course without catalytic activity of the counter-ion: This case is quite similar to that of growth on free ions, the difference is that the growth reaction is made more difficult by the low dissociation of the ion-pair. Consequently, such reactions often proceed with measureable speed at high temperatures only.

(b) Course with catalytic activity of the counter-ion: As is known from the theory of catalysis this course may be energetically so favourable that it may be even easier than the reaction on free ions.

I should like to take this opportunity to point out that reaction-kinetics data<sup>7, 9, 21, 22, 23</sup> have frequently indicated that a reaction with titanium tetrachloride, stannic chloride and sulphuric acid proceeded *via* ion-pairs even though a relatively high concentration of free ions was present<sup>3</sup>, as

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calculated from Bjerrum's equation which has been verified experimentally by Fuoss and Kraus<sup>24</sup>.

A strictly analogous mechanism can also be regarded as valid for a Ziegler polymerization.

Kinetic data referred to above show, without ambiguity, that chemisorption is the decisive process which decreases the activation energy of growth to such an extent that even a monomer with as little reactivity as ethylene can be made to polymerize in this way. In the growth reaction proper, the adsorbed components react in their ion-radical form.

## CONCLUSIONS

All of the above-mentioned mechanisms of ionic polymerizations can be described as stepwise reactions on the basis of the reaction kinetics data. There is no stationary state of equilibrium between initiation and termination, such as is known to exist in the field of free-radical chain reactions, since the active centres cannot disappear by mutual termination. Although these reactions are of one single type, the rates of growth reactions can vary within a very wide range. These differences are characteristic for the individual systems, *i.e.* for the type of active centre, for the monomer and for the solvent.

For further development of the theory of ionic polymerizations, it is necessary to develop a wide experimental basis, *i.e.* more exact kinetic measurements should be performed on as wide a series of monomers, catalysts and solvents as possible.

## Summary

Research on the mechanism of ionic polymerizations has been made possible only on the basis of extensive knowledge of the mechanism of chain polymerization of the free-radical type. Laws governing both types of polymerization mechanisms are essentially similar. However, ionic polymerization can proceed with growth taking place according to various reaction schemes. The growth reaction can assume either a chain-like or step-wise character, or both mechanisms may combine.

While the radical-induced polymerization is limited to a narrow choice of monomers, a wide variety of substances can undergo ionic polymerization. A selection of a few monomers has been made to demonstrate the influence of the ionization potential and of the electron affinity of reacting components on the growth reaction. Whether growth proceeds through ion-pairs or through free ions has been examined in this light.

Ionization potential and electron affinity data of reaction components are also the fundamental quantities governing the growth reaction on solid surfaces.

All samples referred to can be explained in terms of a generally valid mechanism of the growth reaction in which ion-radicals are produced as intermediate products. The amount of energy necessary for the formation of an ion-radical is the decisive quantity from the viewpoint of the rates of the growth reactions and of the transfer reactions with other substances in the system.

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