

CYCLO- AND CYCLIZED DIENE POLYMERS. XXIII.*
ETHYLALUMINIUM DICHLORIDE AS A CATALYST
FOR POLYMERIZATION OF ISOPRENE

B. MATYSKA^a, I. DOLEŽAL^b and I. KÖSSLER^a

^a *Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

^b *Department of Physical Chemistry,
Charles University, Prague 2*

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Polymerization of isoprene catalysed by ethylaluminium dichloride at room temperature, in the absence of water or some other co-catalysts has been found to be extremely slow. The co-catalytic activities of water, hydrogen chloride and ethanol were positive up to a critical molar ratio of the aluminium organocompound to the co-catalyst employed. The value of this ratio depended on the nature of the co-catalyst. If the content of the co-catalyst exceeded that corresponding to the maximum reaction rate the polymers formed had a lower molecular weight. An efficient catalytic system for cyclopolymerization of isoprene was formed by the reaction of tert-butyl chloride with ethylaluminium dichloride. The course of the polymerization in the medium of non-polar hydrocarbons is explained by the assumption that the active centres formed by the reaction of ethylaluminium dichloride with the co-catalyst are consumed as the polymerization advances. A reaction scheme is proposed from which the dependence of the polymerization rate on the concentrations of the constituents has been derived. The results obtained are in a qualitative agreement with the experimental data.

Various Friedel-Crafts halides are known to catalyse polymerization of isoprene to powdery products¹, the structure of which is similar to that of cyclized natural rubber². Ethylaluminium dichloride was originally considered to be one of the active catalysts of this type³. Subsequent experiments have proved, however, that alkylaluminium halides, and even Ziegler's catalysts are inactive in the polymerization of certain monomers if no traces of water or other proton donors are present in the medium⁴. This finding revealed that a prerequisite for the catalytic activity of ethylaluminium dichloride was the presence of slight quantities of co-catalytic substances. The present paper deals with the effect of reaction conditions on this activity.

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EXPERIMENTAL

Polymerization Components

Isoprene and the solvents were purified in the way previously described⁵, except that the final desiccation was effected by 12 hours' boiling with sodium hydride. Ethylaluminium dichloride was twice distilled *in vacuo*. The purified and dried polymerization components were distilled *in vacuo* into ampoules previously dried by heating. After the distillation the ampoules were sealed under vacuum.

Polymerization

Most experiments were carried out in an apparatus with ground-glass joints. In special cases we employed an apparatus without joints, equipped with high-vacuum valves of stainless steel. This apparatus was dried 72 h by circulation of a solvent, continually dried with sodium hydride. All operations with the solvents, monomer and catalyst were carried out *in vacuo*. The desired quantities of the individual components were charged into the reactor in sealed ampoules, which were then crushed^{2,5}. Gaseous isoprene was brought into the reaction mixture from a thermostatted pressure bottle, connected to the reactor *via* a vacuum stop-cock. The pressure in the isoprene bottle, of a known volume, was read on a mercury manometer; in this way it was possible to calculate the amount of isoprene brought into the reactor at any stage of the polymerization. Another manometer was attached to the reactor. An experiment was started by crushing the ampoule with the solvent. Then, under vigorous stirring, isoprene was brought in until the total pressure over the mixture reached the value corresponding to the desired concentration of the monomer in the solution (employing a calibration plot of the total pressure *vs.* the composition of the liquid phase). When an equilibrium between the liquid and the gaseous phases got established a chosen quantity of a co-catalyst was brought into the mixture and the polymerization was started by crushing the ampoule containing the catalyst. In most experiments the concentration of the monomer in the mixture was kept constant by introducing isoprene from the bottle at a suitable rate, so that the total pressure over the reaction mixture was constant. In this arrangement the quantity of the monomer that had been brought in by a given time equalled the amount of the polymer. In preliminary experiments it had been found that the polymer did not affect the liquid-vapour equilibrium until its concentration exceeded 5% (w./w.). The polymerization, conducted in all cases in 33 ml of a solvent at 21°C, was discontinued by evaporation of the monomer and the solvent at room temperature.

All the polymers were investigated by infrared spectroscopy. The molecular weights of the benzene-soluble polymers were determined by differential ebullioscopy or light scattering. The contents of the double bonds were determined by the iodomonochloride method.

RESULTS

POLYMERIZATION IN HEPTANE

The Effect of Water

The polymerization of isoprene (M) in heptane with ethylaluminium dichloride as catalyst (at a constant concentration of the monomer) ceased after a certain time of the reaction (*cf.*^{3,6}). The total quantity of the reacted isoprene was appreciably dependent on the time (perfection) of desiccation of the individual components.

At concentrations $[\text{AlEtCl}_2]_0 = 0.038 \text{ mol/l}$ and $[\text{M}_0] = 0.4 \text{ mol/l}$ the minimum polymerization in the ground-glass apparatus after a most scrupulous desiccation was 10 to 12 mol of the monomer per mol of the catalyst. By contrast, in the jointless apparatus under the same conditions it was only 4 to 6 mol of isoprene per mol of the catalyst. None of these experiments gave rise to high-molecular-weight polymers; there were only traces of them on the wall of the reactor.

The role of water in the polymerization was elucidated by an experiment in which moist heptane was added to the reaction mixture after the polymerization had come to a halt. Each addition was followed by further consumption of isoprene (Fig. 1). The dependence of the limit (final) consumption of the monomer on the concentration of water, the concentrations of the other constituents being constant, exhibited a peak (Fig. 2). The polymers formed at concentrations of $20 \cdot 10^{-6}$ to $100 \cdot 10^{-6}$ mol of water/l were macromolecular, insoluble in benzene, whereas those formed at higher contents of water than would correspond to the maximum in Fig. 2 were jelly-like to oily and their molecular weights were 300 to 800. In all cases the final yields were rather low. The maximum yield was not obtained at any stoichiometrically significant molar ratio of water to the catalyst (1 : 380).

The Yield in Relation to the Concentrations of the Catalyst and the Monomer

At given concentrations of ethylaluminium dichloride ($3.8 \cdot 10^{-2} \text{ mol/l}$) and water ($< 10^{-5} \text{ mol/l}$), and a constant concentration of isoprene in the reacting mixture

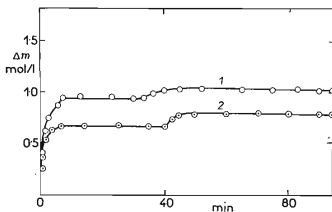


FIG. 1

The Effect of Water on the Polymerization of Isoprene ($[\text{AlEtCl}_2]_0 = 3.6 \cdot 10^{-2} \text{ mol/l}$)
 1 $[\text{M}]_0 = 0.4 \text{ mol/l}$, 2 $[\text{M}]_0 = 0.14 \text{ mol/l}$;
 0.14 mg of water in heptane was added 35 and 40 min after the starts of polymerizations 1 and 2, respectively; Δm denotes the limit consumption of the monomer.

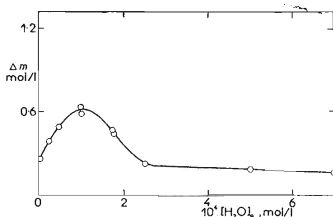


FIG. 2

The Effect of the Increasing Concentration of Water on the Limit Consumption of the Monomer, Δm

Polymerization in heptane, $[\text{M}_0] = 0.14 \text{ mol/l}$, $[\text{AlEtCl}_2]_0 = 3.8 \cdot 10^{-2} \text{ mol/l}$, polymerization time 90 min.

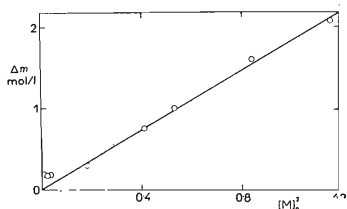


FIG. 3

The Limit Consumption of Isoprene, Δm , in Relation to its Concentration $[M]_0$

Polymerization in heptane, $[AlEtCl_2]_0 = 3.8 \cdot 10^{-2}$ mol/l, polymerization time 60 min.

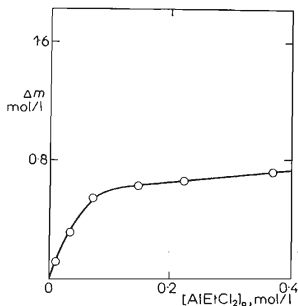


FIG. 4

The Limit Consumption of the Monomer in Relation to the Concentration of Ethylaluminum Dichloride

Polymerization in heptane, $[M]_0 = 0.4$ mol/l, $[H_2O]_0 < 1 \cdot 10^{-5}$ mol/l, polymerization time 60 min.

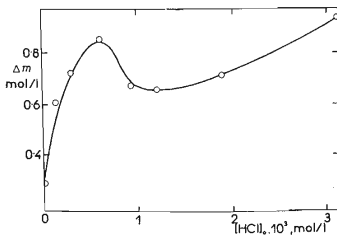


FIG. 5

The Limit Consumption of the Monomer in Relation to the Concentration of Hydrogen Chloride

Polymerization in heptane, $[M]_0 = 0.15$ mol/l, $[AlEtCl_2]_0 = 3.8 \cdot 10^{-2}$ mol/l, polymerization time 90 min.

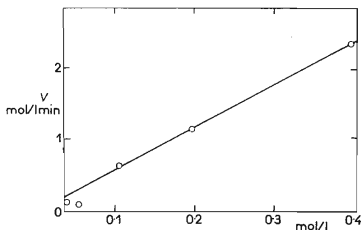


FIG. 6

The Polymerization Rate (V) in Relation to the Concentration of tert-Butyl Chloride

The rate data refer to the 15th minute of polymerization in heptane, $[M]_0 = 0.15$ mol/l, $[AlEtCl_2]_0 = 3.8 \cdot 10^{-2}$ mol/l.

during the experiment the final quantity of the reacted monomer was a linear function of the square of its starting concentration $[M]_0$ (Fig. 3). The effect of the monomer concentration on the reaction rate was difficult to estimate since immediately on crushing the ampoule with the catalyst the monomer rapidly reacted, and as early as 5 minutes later the polymerization ceased. At low concentrations of the monomer (c. 0.2 mol/l) no high-molecular-weight polymer was isolated. At higher monomer concentrations the polymers formed were insoluble in benzene, so that their molecular weights could not be determined.

Also in studying the effect of the catalyst concentration the reaction rate could not be measured since with the experimental technique employed we were unable to determine reliably the starting slopes of the curves expressing the consumption of the monomer. Therefore, we determined only the limit yield after the reaction had stopped. The steep starting increase of the limit consumption of the monomer with the increasing concentration of the catalyst at $[M]_0 = 0.4$ mol/l, $[H_2O]_0 < 10^{-5}$ mol/l and $[AlEtCl_2] \approx 8 \cdot 10^{-2}$ mol/l turned very moderate (Fig. 4).

The Effect of the Co-Catalysts on the Final Yield

The effect of water on the limit consumption of isoprene was similar to that observed with hydrogen chloride, ethanol, or acetylacetone. In all these cases the dependence of the limit consumption of isoprene (after the polymerization had died away) on the concentration of the co-catalyst exhibited a peak, in the case of hydrogen chloride followed by a minimum (Fig. 5). In the presence of hydrogen chloride all polymers had high molecular weights and were insoluble in benzene. In the case of ethanol, at concentrations beyond the point of the maximum, the polymers had relatively low molecular weights, like in the presence of water.

The co-catalytic effect was most marked in the use of tert-butyl chloride and triphenylmethyl chloride (in benzene). In these two cases even the type of the conversion curves was different. Although the polymerization rate gradually decreased it never dropped to zero in the time interval studied. In a typical experiment the very rapid onset of the reaction was followed by a stage of a virtually constant rate, which (e.g.) 15 min after the start of the polymerization was linearly dependent on the concentration of tert-butyl chloride (Fig. 6).

Deactivation of the Catalyst in the Course of the Polymerization

To ascertain whether the polymerization stopped soon after its start as a result of deactivation of the catalyst we carried out several experiments ($[AlEtCl_2]_0 = 3.8 \cdot 10^{-2}$ mol/l, $[M]_0 = [M]$, in which 90 min after the start of the reaction the readily volatile compounds were removed from the reactor under reduced pressure. There was left a slight, viscous residue on the bottom of the reactor, in the presence

of which the polymerization was repeated under the original conditions (without the addition of more catalyst). The decrease in the limit consumption of isoprene (Δm) observed in the repeated polymerization (Δm^1) was found to be proportional to the amount of ethylaluminium dichloride recovered after the evacuation in the freeze-trap before the diffusion pump

$[M]_0$, mol/l:	0.15	0.31	0.68	0.95
Δm , mol/l:	0.48	0.87	1.77	2.84
Δm^1 , mol/l:	0.39	0.82	1.57	2.39

Polymerization in Benzene

The polymerization in benzene considerably differed from that proceeding in heptane under otherwise identical conditions. The yields of the polymers were higher, the polymerization rate did not drop as low as zero, but levelled down to a practically constant value; the consumption of isoprene Δm , within a definite time interval was a linear function of concentration of the monomer (Fig. 7), independent (like the molecular weights of the polymers, \bar{M}_n) of the concentration of ethylaluminium dichloride ($[M]_0 = 1.0$ mol/l, reaction time 90 min):

$[AlEtCl_2]_0$, 10^{-2} mol/l:	3.86	12.7	16.2	19.2	28.2	38.6
Δm , 10^{-2} mol/l:	50	49	44	82	89	50
\bar{M}_n :	3 000	4 600	3 700	—	3 500	—

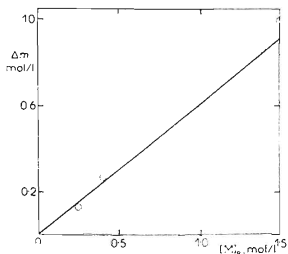


FIG. 7

Polymerization of Isoprene in Benzene

$[AlEtCl_2]_0 = 3.8 \cdot 10^{-2}$ mol/l, $[H_2O]_0 < 1 \cdot 10^{-5}$ mol/l, polymerization time 90 min.

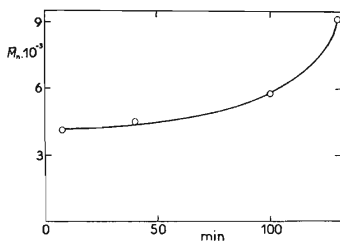


FIG. 8

The Number-Average Molecular Weight in Relation to the Polymerization Time

$[AlEtCl_2]_0 = 3.8 \cdot 10^{-2}$ mol/l, $[M]_0 = 0.64$ mol/l.

In contrast to the medium of heptane, no polymerization was observed in dry benzene after 3 hours in the use of the jointless apparatus.

Structure of the Polymers

Judging by the infrared spectra all the polymers should be practically identical in structure. The spectral bands of the addition forms 1·4 and 3·4 were absent in all cases, so that the polymers were evidently cyclic³. The contents of double bonds in these cyclopolymers related to that of natural rubber (100%) were 15 to 30%.

DISCUSSION

Absolutely dry ethylaluminium dichloride in a nonpolar medium effected no detectable polymerization of isoprene even after several hours. The negligible reaction of isoprene observed in heptane was evidently due to a trace of water, which we did not succeed in removing even from the jointless apparatus. This means that it was the reaction product of ethylaluminium dichloride and water, or some other co-catalyst, that produced a sufficiently rapid polymerization. Water is obviously taken up by the polymerization. Under the conditions given in Fig. 1 one molecule of water brought about polymerization of 100 molecular of isoprene, whereupon the reaction ceased.

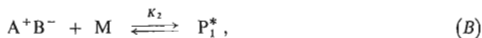
The positive effect of slight concentrations of water on the activity of the catalyst is also apparent from the dependence of the limit consumption of isoprene on the concentration of water in the reaction mixture (Fig. 2). However, even at negligible concentrations of water side reactions occurred, which reduced the total conversion. Examples of these reactions are hydrolysis of ethylaluminium dichloride and the formation of inactive higher hydrates ($\text{AlEtCl}_2 \cdot n \text{H}_2\text{O}$). The yield of the polymerization is further reduced by termination of the growing chains by molecules of water, which conclusion can be deduced from the decrease in molecular weights of the polymers at higher concentrations of water. Fig. 2 shows that these reactions predominate on exceeding the molar ratio $\text{AlEtCl}_2/\text{H}_2\text{O} = 380$.

The course of the curve relating the limit consumption of isoprene to the concentration of ethylaluminium dichloride in heptane (Fig. 4), and the independence of the yield and molecular weights of this concentration in benzene (see Results) suggest that so long as the side reactions do not occur (*i.e.* at very low concentrations of water) the reaction of ethylaluminium dichloride with water goes to an equilibrium. By increasing the concentration of the dichloride at a constant concentration of water the content of the active complex is increased until all water is bound to the catalyst, so that further increasing the concentration of the latter enhances the polymerization very little. Since benzene is easier to dry than heptane the complete binding of the remaining water is attained at much lower concentrations of ethylaluminium di-

chloride than in heptane, so that the polymerization rate proves independent of increasing the dichloride concentration much sooner. Under these conditions the number of the active centres is given exclusively by the content of water.

The cationic polymerizations, characterized by a rapid start soon followed by a complete stop, have been the subject of many communications⁷. The formal kinetics of such polymerizations, based on the assumption that the end of the reaction is caused by depletion of the catalyst, was advanced by Tobolsky⁸ (the so-called dead-end polymerization). Non-stationary polymerizations were treated by Burton and Pepper⁹, Chiang and Hermans¹⁰ and others.

The polymerization described in this paper took a course fitting Burton and Pepper's kinetic description: after a very rapid initiation the number of active centres rapidly dropped to zero. Consequently, the reaction discussed is a typically non-stationary one completely stopped by the depletion of the catalyst^{9,10}. In the simplest case, assuming monomolecular termination and the absence of transfer reactions, the following reaction scheme can be considered



The adduct $\text{AlEtCl}_2 \cdot \text{H}_2\text{O}$ behaves as an ionic pair and in reaction (B) it is designated as A^+B^- ; P_n^* denotes the number of active centres at a given time (these centres represent ionic pairs, too). Reaction (B) or some analogous preceding reaction must occur; it produces a complex of the monomer with the catalytic components, but this complex is not a growth centre yet. The existence of complexes of this type follows from measuring the conductances of solutions of various Lewis acids, which substantially change by the addition of monomers even in cases where no polymerization is initiated¹¹.

If reactions (A) and (B) proceed very rapidly to equilibrium, compared to the other reactions, and the reactivity of the active particles is independent of their polymerization degree, then (since $[\text{M}] = [\text{M}]_0$) reactions (C) to (E) represent a set of normal, monomolecular consecutive reactions. Provided that at zero time ($t = 0$) it holds $[\text{P}_1^*] = [\text{P}_1^*]_0$ and $[\text{P}_n^*] = 0$, the time courses of concentrations of the primary centres, $[\text{P}_1^*]$, and the growth centres, $[\text{P}_n^*]$, are given by the well-known equations

$$[\text{P}_1^*] = [\text{P}_1^*]_0 e^{-k_1[\text{M}]t}, \quad (I)$$

$$[P_n^*] = \frac{k_i[M][P_1^*]_0}{k_t - k_i[M]} (e^{-k_i[M]t} - e^{-k_t t}). \quad (2)$$

Equation (2) shows that $[P_n^*] = f(t)$ is a function that should exhibit a maximum. However, its position on the time axis depends on the rate constants of initiation (k_i) and termination (k_t), and may not be discernible. If the termination rate is much lower than the initiation rate ($k_t \ll k_i[M]$), the termination becomes the rate-controlling step and the polymerization rate can be expressed by

$$V = - \frac{dm}{dt} = k_p[M][P_n^*] = k_p[M][P_1^*]_0 e^{-k_t t}. \quad (3)$$

After substitution for $[P_1^*]_0$, according to reaction (B), we obtain

$$V = k_p K_2 [M]^2 [A^+B^-]_{or} e^{-k_t t}, \quad (4)$$

where $[A^+B^-]_{or}$ designates the original equilibrium concentration of ionic pairs formed from the complex $AlEtCl_2 \cdot H_2O$ at $t = 0$, i.e. when no polymerization started yet but the equilibria of reactions (A) and (B) had already got established; m designates the amount of the monomer in the pressure bottle (in mol or g), which must be distinguished from the concentration of the monomer in the solution, $[M]$ (m is variable, but $[M]$ is a constant). Integration for $t = 0 \Rightarrow m = m_0$ and for $t = \infty \Rightarrow m = m_\infty$ leads to an expression for the limit consumption of the monomer Δm :

$$\Delta m = m_0 - m_\infty = \frac{K_2 k_p}{k_t} [M]^2 [A^+B^-]_{or}. \quad (5)$$

Equation (4) shows that the polymerization rate decreases with time to zero, so that the consumption of the monomer from the pressure bottle increases to a limit value given by equation (5). This value, as the equation shows, is in a linear relation to the square of the concentration of isoprene, which was experimentally corroborated in heptane (Fig. 3). In benzene, by contrast, we have found a linear dependence of Δm on $[M]$. The decrease in the order of the reaction in respect to the monomer can be explained in one way only — by the excluded or limited participation of the monomer in the formation of the primary complex, P_1^* . In reaction (B) monomer is replaced by one molecule of benzene, and the particle P_1^* is then represented by an ion-pair, whose cation is the benzenium ion. Such interactions between aromatic hydrocarbons and Lewis acids in the presence of water and acids have been described in many papers^{12,13}. The only difference that it makes in equations (4) and (5) is a changed meaning of the equilibrium constant K_2 and a decrease in the order of the reaction in respect to the monomer by one degree, in accordance with the experiments in benzene.

According to equation (5), the limit consumption of isoprene, Δm , is in a linear relation to the concentration of the catalytic complex, $[AlEtCl_2 \cdot H_2O]$, present in the form of ionic-pairs A^+B^- . This concentration could be expressed in Eq. (5) in terms of the concentrations of water and ethylaluminium dichloride, employing the relation for the equilibrium constant K_1 . However, the concentrations occurring in the expressions for Δm and the reaction rate would have to be the equilibrium values, which cannot be determined unless the value of K_1 is known. For this reason we present only a qualitative discussion of the extreme cases.

Considering the mass balance for water and the catalyst, at a very low K_1 the equilibrium concentration of $[AlEtCl_2 \cdot H_2O]$ will also be very small and the equilibrium concentrations of the catalytic constituents will be practically equal to their analytic (starting) concentrations. Consequently, the product $K_1 [AlEtCl_2]_0 [H_2O]_0$ should be substituted for $[A^+B^-]_{or}$ in equation (5). The reaction rate and Δm would then be linearly dependent on the concentration of either constituent, the concentration of the other one being constant. This conclusion is at variance with experiment in Figs 2 and 4, but agrees with it very well if tert-butyl chloride as co-catalyst was employed instead of water. In the latter case the polymerization rate was much greater than in the presence of water (Fig. 2). This, however, was due to the concentration of butyl chloride, which was four orders of magnitude higher than the usual concentrations of water, thus compensating for the low value of K_1 .

In the other extreme, if K_1 is very high (and only a small portion of the catalyst is utilized for the formation of active centres) it holds that

$$[A^+B^-]_{or} = K_1 [AlEtCl_2]_{or} [H_2O]_{or} = \{ [AlEtCl_2]_0 - [A^+B^-]_{or} \} \cdot \{ [H_2O]_0 - [A^+B^-]_{or} \} \cdot K_1 \quad (6)$$

where the subscripts *or* and *0* designate the equilibrium and the starting (analytical) concentrations, respectively. If $[AlEtCl_2]_0 \gg [A^+B^-]_{or}$, which is the case, *e.g.*, at low concentrations of water, we arrive at the relation

$$[A^+B^-]_{or} \approx [AlEtCl_2]_0 [H_2O]_0 / (1/K_1 + [AlEtCl_2]_0) \quad (7)$$

This approximative equation reveals that at sufficiently great concentrations of the catalyst the concentration of the active complex and the value of Δm are no longer dependent on the concentration of the catalyst and the concentration of the active complex equals the concentration of water. This deduction accords with the data in Fig. 4. An analogous consideration would be valid for an excess of water, but the hydrolytic reactions, occurring even at relatively low concentrations of water, prevent the formation of the active complex. For this reason equation (5) applies only to the starting, steep part of the curve in Fig. 2.

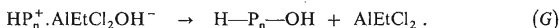
With the simplifications introduced, the proposed reaction scheme qualitatively covers the behaviour of the system under study. The neglecting of the transfer reactions does not alter the character of the curves relating the reaction rate to the concentrations of the components.

The actual mechanism of the initiation is not known and cannot be derived from the kinetic data. A plausible hypothesis seems to be that the complex $[\text{AlEtCl}_2 \cdot \text{H}_2\text{O}]$ is most active when dissociated into an ionic-pair, since the conductivity and the polymerization rate in relation to time took reverse courses¹¹ (in other words an increase in the content of free ions was associated with a decrease in the polymerization rate). There must be a number of types of ionic pairs in the solution, differing in the distance between the two ions. In addition, part of the complex is fully dissociated to free ions and another part fully associated (polymeric salts of the hypothetical acid $\text{HAiEtCl}_2\text{OH}$). If, however, the reactions leading to equilibria are rapid, all these inactive particles decrease in number at the same rate as the active centres, so that they need not be considered in the kinetic scheme.

A monomolecular mechanism of termination, quite common in cationic polymerizations, may be elimination of proton from a growing polymeric ion:



Then, however, the original catalyst would be regenerated, so that the polymerization should go on. This reaction may be responsible for the more moderate decrease of the reaction rate in benzene. Another case of monomolecular termination is rearrangement of the hydroxyl group within the ionic pair:



The water originally present in the system is irreversibly taken up and the inactive catalyst is liberated. This mechanism accounts for the experimental finding that water is consumed during the polymerization, whereas ethylaluminium dichloride is not.

The effect of hydrogen chloride as co-catalyst on Δm (Fig. 5) seems to be more complex than that of the other co-catalysts studied. Since no interaction of hydrogen halides and aluminium halides is known to occur in the medium of aliphatic hydrocarbons¹² the catalytic activity of the system cannot be attributed to simple protonation of isoprene by a hypothetical strong acid HAiX_4 . On the other hand, hydrogen chloride is known to form π -complexes with olefins¹⁴. Hence it can be assumed that interaction of ethylaluminium dichloride with this complex gives rise to an active ion-pair, where the function of the dichloride itself reduces to that of an acceptor of the chloride ion. As for the trough on the curve relating Δm to the concentration of hydrogen chloride, no explanation can be advanced on the basis of our experiments.

As was demonstrated previously⁶, in addition to the rapid polymerization initiated by the interaction product of ethylaluminium dichloride and water there may proceed a slow polymerization initiated by the dichloride alone. However, the rate of this secondary polymerization is orders of magnitude lower than that of the polymerization initiated by the system ethylaluminium dichloride-co-catalyst, so that it need not be considered in the above reaction scheme.

The experimental growth of molecular weights with the reaction time (Fig. 8) is to be ascribed to the transfer by the polymer, which is considerably operative at higher conversions. The high content of a gel in the polymers supports this explanation.

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