

## CATIONIC POLYMERIZATION OF ISOPRENE: INITIATION BY COMPLEXES OF TITANIUM CHLORIDE WITH HALOGENOACETIC ACIDS

Bohumír MATYSKA, Ludmila PETRUSOVÁ, Karel MACH and Miroslav ŠVESTKA

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,  
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received May 25th, 1976

Polymerization of 2-methyl-1,3-butadiene (isoprene), initiated by titanium chloride in combination with trifluoro- and trichloroacetic acid and their *t*-butyl esters as coiniciators, was studied in benzene, 1,2-dichlorobenzene and heptane at 20°C. Curves of the dependence polymerization rate *vs* coiniciator concentrations exhibit in the first two media a minimum and a maximum, those in heptane exhibit an inflex only. This is due to the fact that the acids and the esters are partly consumed to carboxylate  $\text{TiCl}_4$  and to form mono- and dicarboxylates of titanium chloride. Other products are either HCl or the corresponding alkylchlorides whose co-catalytic activity is very low. It follows from kinetic data and from electric conductivity and infrared spectra measurements that active centers in the polymerization are complexes of oligoesters of halogenoacetic acids with  $\text{TiCl}_4$  and its carboxylates, in which the ester bond is either considerably polarized or dissociated. Free ions are formed during the polymerization, too, contributing to changes of electric conductivity; however, they do not influence the polymerization rate directly

Initiations by protonization of the monomer are regarded as the best understood steps of cationic polymerizations of various confirmed or postulated mechanisms. The source of protons is usually a strong protonic acid or, more frequently, systems formed by combining a Lewis acid with a suitable protogenous substance, as, *e.g.*, water or a protonic acid. Many authors have regarded as a very suitable system for kinetic studies the system formed in the reaction of  $\text{TiCl}_4$  with  $\text{CCl}_3\text{COOH}$ . This system appeared to be well defined and to have other advantages, as a good solubility in organic solvents, a high activity *etc.* A detailed study of 2-methylpropene polymerization initiated by this system at temperatures about  $-75^\circ\text{C}$  was published by Plesch<sup>1</sup>. This author assumed, when suggesting a reaction mechanism, that both components of the initiation system react mutually to form an equilibrium mixture of a non-active complex  $\text{TiCl}_4 \cdot 2 \text{CCl}_3\text{COOH}$  and an active complex  $\text{TiCl}_4 \cdot \text{CCl}_3\text{COOH}$ . The loss of active molecules during the polymerization process can be partly compensated by their formation in the reaction between the non-active complex and free  $\text{TiCl}_4$ . The same initiation system during the polymerization of some cyclic unsaturated hydrocarbons at about  $-75^\circ\text{C}$  was studied by Imanishi and coworkers<sup>2-5</sup>. They assumed the formation of a complex with the equimolar abundance of both initial components which only in subsequent reactions with the monomer and with the acid transforms to an active center. Mondal and Young<sup>6</sup> studied the polymerization of cyclooctadiene with the same initiator. They found a monotonous decrease of the polymerization rate from the very start of the polymerization reaction. They distinguish a stationary phase and a non-stationary phase on conversion curves. Dependences polymerization rate *vs*  $\text{CCl}_3\text{COOH}$  concentration

passed through a maximum at the molar ratio of both components equal to unity. The decrease of the polymerization rate with the increasing monomer concentration was explained by the formation of stable cyclooctadienyl cations at the terminal positions of the polymer chain. In an analogy with the original ideas of Plesch, Prosser and Young<sup>7</sup> interpreted data on the polymerization of indene and acenaphthylene, assuming an equilibrium between active complexes  $TiCl_4 \cdot CCl_3 \cdot COOH$  and dormant complexes  $TiCl_4 \cdot 2 CCl_3COOH$ .

This study develops the results of Mach and Drahorádová<sup>8</sup> who have shown that  $TiCl_4$  reacts with halogenoacetic acids not only to form simple complexes, but also to form various titanium carboxylates. Their presence prominently influences kinetic dependences in the isoprene polymerization at 20°C so that the concepts of formation of active and non-active complexes, postulated originally by Plesch and essentially taken over by other authors for different conditions, cannot be used in this case to interpret the observed data.

## EXPERIMENTAL

Isoprene, titanium chloride, and solvents were purified and the manipulation with them carried out in all-glass evacuated devices described earlier<sup>9</sup>. Final drying of the monomer and of the solvents was done by refluxing for 48 hours with NaH; the purity of these compounds was checked by gas-chromatography. Trichloroacetic acid (Fluka) was re-distilled under nitrogen and its middle fraction used, trifluoroacetic acid (Fluka) was used without further purification. Esters of both acids were synthesized and purified in the same way as in ref.<sup>10</sup>

Polymerizations were carried out in all-glass devices evacuated beforehand to  $1.3 \cdot 10^{-2}$  Pa (ref.<sup>11</sup>). Dosing of the solvents and of the components of the initiator was carried out under vacuo by breaking tips of the ampules containing solutions of these compounds. The last component added was the monomer. Its concentration in the reaction mixture was kept constant; this was achieved by admitting it into the reactor continuously from the reservoir with a rate equal to its rate of consumption in the polymerization process so that the over-all vapour pressure of the reaction mixture did not change. Evolution of hydrogen chloride in the reaction of  $TiCl_4$  with  $CCl_3COOH$  was followed by measuring its partial pressure over 4 ml of a solution in benzene. For several initiator concentrations the amount of evolved HCl was determined by titration after its absorption in 0.1M-NaOH. Infrared spectra of the reaction mixtures were measured in the same manner as described earlier<sup>8</sup>. In electric conductivity measurements the same procedures and devices were used as in the other polymerization experiments; only the reactor was modified in such a way to serve simultaneously as the conductivity cell.

## RESULTS AND DISCUSSION

### *Polymerizations*

Polymerizations of isoprene were investigated in benzene, 1,2-dichlorobenzene, and heptane at 20°C using as the initiator  $TiCl_4$  in combination with trifluoro- and trichloroacetic acid and their t-alkyl esters as co-initiators.

These polymerizations occur very smoothly and lead mostly to cyclic polymers<sup>12</sup> of a very wide distribution of molecular weights. Sec-alkyl esters as co-initiators show

little activity and *n*-alkyl esters are entirely inactive. Titanium chloride or esters alone do not initiate the polymerization. Concentrated acids alone give terpenic oligomers of isoprene and low molecular weight oligoesters of the acid with a low yield.

Conversion curves in all the media and with all the initiation systems studied exhibit a monotonous decrease of the polymerization rate ( $R_p$ ) with time. Their shape depends very little on the type of the acid, medium, and component concentrations, as shown in Fig. 1.

In heptane the polymerization practically stops quite early, even if the free monomer is present in the solution in an unchanged concentration. In the other two media the reaction comes to an end only after a longer period of time. In polar solvents "waves" appear on the curves sometimes; their position and magnitude could not be reproduced and thus their origin cannot be explained at present. It can be seen from

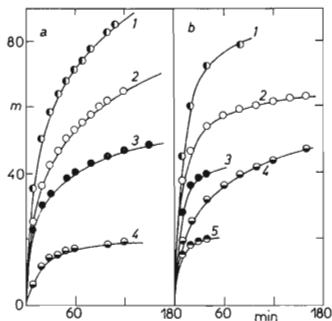


Fig. 1

Conversion Curves of Isoprene Polymerization Initiated by Systems  $TiCl_4$ -Co-Initiator at  $20^\circ C$

Isoprene concentration  $[M] = 0.89$  mol/l,  $[TiCl_4] = 15$  mmol/l. *a* Benzene, various co-initiators C,  $[C] = 15$  mmol/l: 1 C =  $CCl_3 \cdot COOH$ ; 2  $CF_3COOH$ ; 3  $CF_3COOC_4H_9$ ; 4  $CCl_3COOC_4H_9$ . *b* Co-initiator  $CCl_3 \cdot COOH$ . Curves 1, 3, 5 in *n*-heptane, 2, 4 in 1,2-dichlorobenzene,  $[C]$  mmol/l: 1 15; 2 62.5; 3 25; 4 15; 5 12.5; curves 2 and 4 with  $[M] = 0.45$  mol/l. *m* polymerized amount in 40 ml of reaction mixture (mmol).

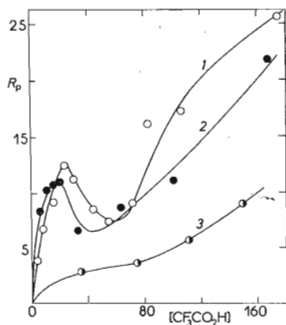


Fig. 2

Dependence of Polymerization Rate ( $R_p$  in mmol/l min) on the Concentration of Trifluoroacetic Acid ( $[CF_3COOH]$  in mmol/l) at  $20^\circ C$

1 Benzene,  $[TiCl_4] = 15$  mmol/l,  $[M] = 0.89$  mol/l; 2 1,2-dichlorobenzene,  $[TiCl_4] = 13.6$  mmol/l,  $[M] = 0.60$  mol/l; 3 heptane,  $[TiCl_4] = 15$  mmol/l,  $[M] = 0.89$  mol/l. The rate measured 30 minutes after the reaction start.

the shapes of the conversion curves obtained (Fig. 1) that several different stages of the reaction, observed with the same initiator by other authors with other monomers<sup>5-7</sup>, can be distinguished with difficulties in this case. This conclusion is further confirmed by the fact that the shape of all conversion curves for times longer than 15 minutes from the reaction start can be formally described by the same function of the type  $m_t/m_0 = c - a \exp(-bt)$  (here,  $m_0$  and  $m_t$  are the amounts of the monomer introduced into the reactor from the reservoir at times  $t = 0$  and  $t$ , respectively; constants  $a, b, c$ , are positive numbers). As it holds  $R_p \approx k_p MP^+$  ( $M$  is the monomer concentration, a constant in our case;  $P^+$  is the concentration of active centers), the decrease of  $R_p$  with time, characterized by the shapes of the conversion curves, reflects the time decrease of the number of active centers during the polymerization. Their concentration is at maximum at the reaction start. The dependences of  $R_p$  on the concentration of isoprene or  $TiCl_4$  have a shape usual for cationic polymerizations, i.e. linear for the monomer and parabolic for  $TiCl_4$ . On the other hand, the dependences of  $R_p$  on the concentrations of co-initiators (acids or esters) exhibit a prominent maximum and a minimum in benzene and 1,2-dichlorobenzene, while in heptane they are monotonous with an inflex (Fig. 2, 3). This shape remains the same for any part of the reaction course (Fig. 4).

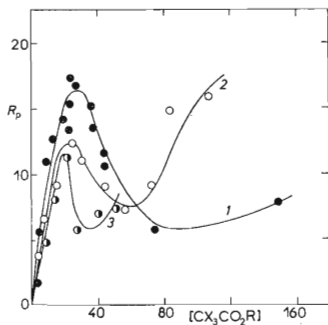


FIG. 3

Dependence of Polymerization Rate ( $R_p$  in mmol/l min) on the Concentration of Co-Initiators ( $[CX_3CO_2R]$  in mmol/l) at 20°C Benzene,  $[TiCl_4] = 15$  mmol/l,  $[M] = 0.89$  mol/l,  $t$  30 min. Substituents: 1 X = Cl, R = H; 2 X = F, R = H; 3 X = F, R =  $t-C_4H_9$  ( $[TiCl_4] = 13.6$  mmol/l).

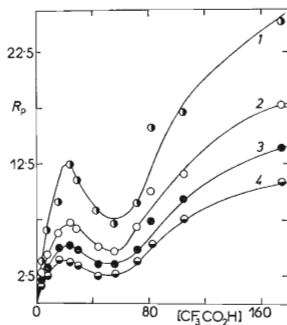


FIG. 4

Dependence of Polymerization Rate ( $R_p$  in mmol/l min) on the Concentration of Trifluoroacetic Acid (in mmol/l) for Various Reaction Times

Benzene, 20°C,  $[TiCl_4] = 15$  mmol/l,  $[M] = 0.89$  mol/l; polymerization times (min): 1 30; 2 60; 3 80; 4 100.

As there is a linear relationship between  $R_p$  and the concentration of active centers, the curves in Figs 2–4 reflect simultaneously the dependence of the concentration of active centers on the co-initiator concentration. The shape of these dependences is quite unusual and indicates that the concentration of active centers at the reaction start and during its course is determined by a much more complicated set of  $\text{TiCl}_4$ –halogenoacetic acid interactions than one would expect from a simple formation of complexes of both partners. The fact that the character of the dependences is the same in later polymerization stages shows that the initiation (monomer protonization) must be sufficiently fast and that the mechanism of all partial reactions (propagation, termination, transfer) does not change during the reaction. The observation that exchanging the acid for an ester does not change the quality of the kinetic dependences is another indication of a small influence of the protonization on the over-all kinetics. Thus, during the polymerization the active centers are complexes of esters of halogenoacetic acids with  $\text{TiCl}_4$  formed after isoprene addition.

### Electric Conductivity

Dependences of the electric conductivity on the concentration of both acids were measured at a constant  $\text{TiCl}_4$  concentration in the absence of the monomer. In several experiments, conductivity changes were investigated during the polymerization process. Examples of these dependences are shown in Fig. 5 and Fig. 6. It is evident that the concentration of conducting particles in the original system (*i.e.* before the start of the polymerization) depends very substantially both on the type of the solvent and on the acid used. From a qualitative comparison of the dependence polymerization rate–acid concentration in, *e.g.*, benzene (Fig. 3, curves 1 and 2)

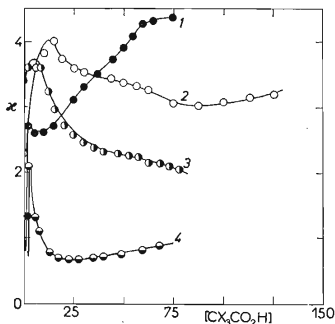


FIG. 5

Dependence of Specific Conductivity  $\kappa(\Omega^{-1} \cdot \text{cm}^{-1})$ , on the Concentration of Co-Initiators (in mmol/l)

$[\text{TiCl}_4] = 15 \text{ mmol/l}$ ,  $25^\circ\text{C}$ . System: 1 benzene,  $\text{CCl}_3\text{COOH}$ ,  $\kappa_0 2.7 \cdot 10^{-12}$ ,  $\kappa \cdot 10^{-11}$ ; 2 1,2-dichlorobenzene,  $\text{CCl}_3\text{COOH}$ ,  $\kappa_0 2.3 \cdot 10^{-7}$ ,  $\kappa \cdot 10^{-7}$ ; 3 heptane,  $\text{CCl}_3 \cdot \text{COOH}$ ,  $\kappa_0 3.4 \cdot 10^{-12}$ ,  $\kappa \cdot 10^{-12}$ ; 4 benzene,  $\text{CF}_3\text{COOH}$ ,  $\kappa_0 5.5 \cdot 10^{-12}$ ,  $\kappa \cdot 10^{-11}$ .

with the analogous dependence of the electric conductivity (Fig. 5, curves 1 and 4) one can see that the free ion concentration exhibits no simple relation to  $R_p$ . Though both types of dependences are curves with a minimum and a maximum, the position of the extremes with respect to the acid concentration is different. The difference between the course of  $\kappa$  and  $R_p$  can be seen even more clearly from Fig. 6. The simultaneous increase of the electric conductivity with the decrease of the reaction rate shows that the polymerization products are at least partly free cations of considerable stability on which a further addition of the monomer does not take place to an appreciable extent. Because the resulting polymer contains a large percentage of cyclic segments<sup>12</sup>, it is probable that these stable cations are homoallylic or bridgehead cations at the end of these segments. Therefore, it follows from the electric conductivity measurements that the over-all concentrations of free ions are not identical with the concentration of active centers.

#### Evolution of Hydrogen Chloride

The reaction of both trifluoro- and trichloroacetic acid with  $TiCl_4$  is accompanied always by hydrogen chloride evolution, according to the equation



A practically equilibrium state is reached as early as after 3–5 minutes after mixing the components. However, if the reaction is followed for several hours, a further small increase of the free HCl can be observed which hangs together with

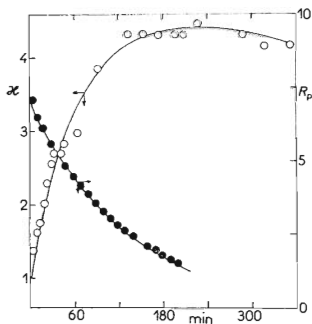


FIG. 6

Dependence of Specific Conductivity,  $\kappa$  ( $\Omega^{-1} \cdot \text{cm}^{-1}$ ), and of Polymerization Rate ( $R_p$  in mmol/l·min) on the Polymerization Time  
 1,2-Dichlorobenzene,  $[TiCl_4] = [CCl_3 \cdot COOH] = 15 \text{ mmol/l}$ ,  $[M] = 0.75 \text{ mol/l}$ ,  $20^\circ\text{C}$ .

a deeper carboxylation of titanium<sup>8</sup>. Fig. 7 shows dependences of the amount of evolved HCl on the concentration of trichloroacetic acid and  $\text{TiCl}_4$ , always for a constant concentration of the second component, in benzene. The reaction was investigated under model conditions, *i.e.* in 4 ml of benzene at relatively high concentrations of the components for 5–25 minutes. In both cases there is a break on the curves at about the molar ratio  $\text{CCl}_3\text{COOH}/\text{TiCl}_4 \approx 2$ ; the break is not very prominent in the acid dependence. It corresponds in both cases to a release of 1 mol of HCl from 1 mol of  $\text{TiCl}_4$ , *i.e.* on the average to the monocarboxylation of  $\text{TiCl}_4$ . Increasing the acid excess leads to a deeper carboxylation of titanium, though to a much lesser extent. For example, a four-fold excess of the acid with respect to  $\text{TiCl}_4$  leads to the formation of only 40% of the dicarboxylate bis(trichloroacetyl)titanium dichloride.

The interval of values of the equilibrium constant of the carboxylation reaction was estimated from the dependence of the evolved HCl on concentration of both components under the conditions, when the formation of dicarboxylate was negligible (*i.e.*  $\text{CCl}_3\text{COOH}/\text{TiCl}_4 \leq 1$ ). The estimated value of the constant is  $6 > K > 1$ . The breaks on the curves in Fig. 7 indicate that the analogous value of  $K$  for the formation of dicarboxylate is still much smaller.

### Infrared Spectra

Additions of isoprene lead to appreciable changes in intensities of the adsorption bands characteristic for the reaction mixture  $\text{TiCl}_4$ -halogenoacetic acids<sup>8</sup>. Fig. 8 shows, as an example, infrared spectra of the system  $\text{TiCl}_4$ - $\text{CCl}_3\text{COOH}$  for various molar ratios of both reaction components and changes of the spectra after an addition of isoprene.

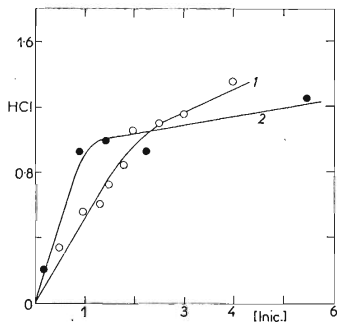


FIG. 7

Dependence of Released Amount of HCl (in mmol) on the Concentrations of the Initiator Components in Benzene at 20°C  
 1  $\text{TiCl}_4$  1 mmol, init. =  $\text{CCl}_3\text{COOH}$  (mmol); 2  $\text{CCl}_3\text{COOH}$  1.9 mmol, init. =  $\text{TiCl}_4$  (mmol), total volume 4 ml.

It can be seen that after the start of the polymerization there is an immediate decrease of the intensity of both the free  $\text{TiCl}_4$  band ( $\nu(\text{Ti}-\text{Cl})$  at  $490\text{ cm}^{-1}$ ) and the free acid bands ( $\nu(\text{C}=\text{O})$  of the dimer at  $1755\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{O})$  of the monomer at  $1784\text{ cm}^{-1}$ ). The bands may even disappear, if the concentration of the given component in the initial mixture was lower than the concentration of the other component (*cf.* Fig. 8, curve 1 and 2 and curves 6 and 7). The characteristic band of the complex  $\text{CCl}_3\text{COOH}\cdot\text{TiCl}_4$  ( $\nu(\text{C}=\text{O})$  at  $1705\text{ cm}^{-1}$ ) decreases considerably or even disappears (in an excess of  $\text{TiCl}_4$  in the initial mixture, curve 7). On the contrary, the band of titanium chloride carboxylates ( $\nu(\text{C}=\text{O})$  at  $1610$  and  $1630\text{ cm}^{-1}$ ), originally a doublet, considerably increases in all cases and changes to an apparent singlet, rather asymmetric, very intense, with a maximum at about  $1620\text{ cm}^{-1}$ . The decomposition of the reaction mixture by ethanol leads to a release of the ester, characterized by a new band ( $\nu(\text{C}=\text{O})$  at  $1765\text{ cm}^{-1}$ ). This band occurs in the spectra of all polymers prepared using an excess of the acid with respect to  $\text{TiCl}_4$ , too.

The infrared spectra show that further carboxylation of Ti occurs in the reaction mixture after isoprene addition. Oligoesters and polymeric esters of the acids are formed, bound mostly to  $\text{TiCl}_4$  and its carboxylates; the esters can be released from these complexes after terminating the reaction by ethanol.

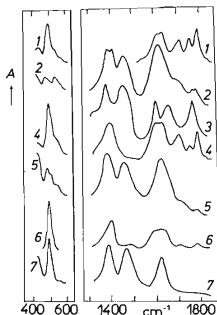
### Active Centers

It follows from the experimental data reported in this paper that the reaction between  $\text{TiCl}_4$  and halogenoacetic acids yields a rather complicated mixture of various products whose concentrations are mutually dependent through equilibrium reactions. The reaction mixture of the initial components can be characterized by the

Fig. 8

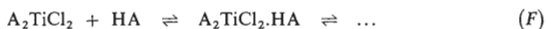
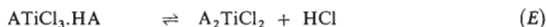
Infrared Absorption Spectra of the Mixtures  $\text{TiCl}_4$ — $\text{CCl}_3\text{COOH}$ —Isoprene in Benzene at  $20^\circ\text{C}$

1 System A:  $[\text{TiCl}_4] = 36.5\text{ mmol/l}$ ,  $[\text{CCl}_3\text{COOH}]/[\text{TiCl}_4] = 3.5$ ; 2 A + 10 mmol I (I = isoprene); 3 A + I +  $\text{C}_2\text{H}_5\text{OH}$  (5 mmol); 4 system B:  $[\text{TiCl}_4] = 110\text{ mmol/l}$ ,  $[\text{CCl}_3\text{COOH}]/[\text{TiCl}_4] = 1.15$ ; 5 B + 10 mmol I; 6 system C:  $[\text{TiCl}_4] = 110\text{ mmol/l}$ ,  $[\text{CCl}_3\text{COOH}]/[\text{TiCl}_4] = 0.35$ ; 7 C + 5 mmol I. Doses of I and  $\text{C}_2\text{H}_5\text{OH}$  added to 10 ml of the reaction mixture.





following reactions ( $CX_3COOH = HA$ )



Besides that there could be present in the reaction mixture also complexes of HCl with  $TiCl_4$  and its carboxylates. However, because it was proved that in aliphatic hydrocarbons HCl does not form complexes with Lewis acids<sup>13</sup> and also because their existence in 1,2-dichlorobenzene is not probable, we do not have to consider contributions of these complexes to the concentration of active centers in these solvents. Experiments in which hydrogen chloride was added to  $TiCl_4$  and to its mixture with  $CCl_3COOH$  in the polymerization of isoprene in these solvents did not show any co-catalytic influence of HCl. On the other hand, Lewis acids form with protonic acids in benzene sigma-complexes in which the aromatic hydrocarbon participates<sup>13</sup> and these complexes may partly play a role in the initiation. The formation of these complexes might also explain the increase of electric conductivity with the addition of trichloroacetic acid in benzene (Fig. 5, curve 1). Indeed, in benzene a slow polymerization of isoprene was observed, when the system  $TiCl_4 + HCl$  was used as the initiator; the rate of this polymerization decreased to zero after 25 minutes.

After introducing isoprene a fast addition of protons to the monomer occurs and thus a transformation of protonic complexes  $TiCl_4 \cdot HA$ ,  $ATiCl_3 \cdot HA$ , and  $A_2TiCl_2 \cdot HA$  (originally both dissociated and non-dissociated) to analogous complexes of esters derived from isoprene,  $TiCl_4A-MH$ , takes place. Similarly as in the complexes of acids, the complexes of esters are ionized to ionic pairs and free ions, too. A considerable increase of electric conductivity upon addition of the monomer shows that the over-all degree of ionization of the latter complexes is appreciably higher than that one of the complexes of acids. The corresponding equilibria are again characterized by reactions (B)–(F) with organic cations or radicals replacing protons; however, values of the complexity constants and the ionization constants are different. The values of both these constants evidently depend to a large extent on the structure of the terminal ester segment. If this segment is a group bound to the acid carbonyl through a primary carbon (*e.g.*, n-alkyl), the corresponding ester is not ionized even if bound in a complex. Such an ester does not have the ability of adding further molecules of the monomer, as indicated by the inability of n-alkyl esters to act

as co-initiators. A similar situation occurs for segments bound to the ester group through a secondary carbon (a negligible co-initiation activity of sec-alkyl esters). Therefore, each addition of the monomer leading to the formation of groups of the above mentioned two types means a termination, essentially a cation-anion recombination. However, if the terminal segment is bound to the carbonyl through a tertiary carbon, the ester bond in the complex is polarized or even dissociated and the chain growth can proceed. The same activity series  $n\text{-alkyl} < \text{sec-alkyl} < \text{tert-alkyl}$  was found in the alkylation of benzene by esters of organic acids in the presence of  $\text{TiCl}_4$  (ref.<sup>10</sup>). However, terminal segments of growing chains may have "active" structures of other types, too, e.g. allyl groups of various kinds. The presence of segments containing condensed five- or six-membered rings in the macromolecular cation gives besides that a possibility of forming structures in which the resulting cations are very stable. Ester groups of this type are ionized to a large extent, up to free ions unable of further propagation.

The concentration of primary initiation centers (*i.e.* protons in ion pairs or free protons) is determined by equilibrium reactions (B)–(F). (In benzene there are in addition the reactions of formation of sigma-complexes with the aromatic hydrocarbon.) The dependence of this concentration on the amount of the halogenoacetic acid added, expressed by means of the equilibrium constants with regard to the material balance of both initial components, is given by an equation of the sixth order. If one can assume that protonization of the monomer is fast and that establishing the equilibria is faster than the propagation, the same curve describes also the course of the concentration of active centers of the ester type at the reaction start ( $t = 0$ ), however, with other values of the constants. By a suitable choice of the coefficients of the particular exponents of the acid concentration (besides a combination of equilibrium constants a proportionality constant between the active center concentration and  $R_p$  was included) it was indeed possible to fit a theoretical curve through the experimental points in Fig. 3.

The above mentioned data do not allow to make conclusions about the very nature of the propagating particles (free ions or ion pairs). However, it can be said that typical features of pseudocationic polymerizations<sup>14</sup> were not observed.

#### REFERENCES

1. Plesch P. H.: J. Chem. Soc. 1950, 543.
2. Imanishi Y., Kohiya S., Momiyama Z., Higashimura T.: Kobunshi Kagaku 23, 119 (1966).
3. Kohiya S., Imanishi Y., Higashimura T.: J. Polym. Sci., Part A-1, 9, 747 (1971).
4. Kohiya S., Imanishi Y., Okamura S.: J. Polym. Sci., Part A-1, 6, 809 (1968).
5. Imanishi Y., Matsuzaki K., Kohiya S., Okamura S.: J. Macromol. Sci., Chem. A3, 237 (1969).
6. Mondal M. A. S., Young R. N.: Eur. Polym. J. 7, 523 (1971).
7. Prosser H. J., Young R. N.: Eur. Polym. J. 11, 403 (1975).

8. Mach K., Drahorádová E.: *This Journal* 40, 326 (1975).
9. Matyska B., Mach K., Vodehnal J., Kössler I.: *This Journal* 30, 2569 (1965).
10. Mach K., Drahorádová E.: *This Journal* 41, 2878 (1976).
11. Matyska B., Antropiusová H., Švestka M., Gaylord N. G.: *J. Macromol. Sci., Chem.* 44, 1529 (1970).
12. Drahorádová E., Doskočilová D., Matyska B.: *This Journal* 36, 1301 (1971).
13. Brown H. C., Pearsal H. W., Eddy L. P., Wallace W. J., Grayson M., Nelson K. LeRoi: *Ind. Eng. Chem.* 45, 1462 (1953).
14. Plesch P. H. in the book: *Progress in High Polymers*, Vol. 2 (J. C. Robb, F. W. Peaker, Eds), p. 137. Iliffe Books, London 1968.

Translated by Z. Herman.