

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Cyclo- and Cyclized Diene Polymers. XXII. Kinetics of Cyclopolymerization of Isoprene with $C_2H_5AlCl_2$ , $TiCl_4$ Catalyst

B. Matyska<sup>a</sup>; H. Antropiova<sup>a</sup>; M. Svestka<sup>a</sup>; N. G. Gaylord<sup>b</sup>

<sup>a</sup> Institute of Physical Chemistry Czechoslovak Academy of Sciences Prague, Czechoslovakia <sup>b</sup> Gaylord Associates Inc. Newark, New Jersey

**To cite this Article** Matyska, B. , Antropiova, H. , Svestka, M. and Gaylord, N. G.(1970) 'Cyclo- and Cyclized Diene Polymers. XXII. Kinetics of Cyclopolymerization of Isoprene with  $C_2H_5AlCl_2$ ,  $TiCl_4$  Catalyst', *Journal of Macromolecular Science, Part A*, 4: 7, 1529 – 1547

**To link to this Article:** DOI: 10.1080/00222337008069368

**URL:** <http://dx.doi.org/10.1080/00222337008069368>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **Cyclo- and Cyclized Diene Polymers. XXII. Kinetics of Cyclopolymerization of Isoprene with $C_2H_5AlCl_2 + TiCl_4$ Catalyst**

B. MATYSKA, H. ANTROPIOVA, and M. SVESTKA

*Institute of Physical Chemistry  
Czechoslovak Academy of Sciences  
Prague, Czechoslovakia*

and

N. G. GAYLORD

*Gaylord Associates Inc.  
Newark, New Jersey 07104*

### **SUMMARY**

The polymerization of isoprene in aromatic solvents, catalyzed by an ethylaluminum dichloride—titanium tetrachloride system, proceeds via a complex of the monomer with the catalyst, chain growth occurring when a monomer cation-radical is formed through the transfer of one electron from the monomer to the catalyst. The deactivation of the active species results from the dissociation of the complex polymer cation-radical to free ions. The over-all reaction is a nonstationary process during which the concentration of free ions increases and the concentration of the active species decreases. A reaction mechanism is proposed which leads to kinetic expressions that quantitatively describe the experimental data.

## INTRODUCTION

A catalytic system consisting of ethylaluminum dichloride and titanium tetrachloride has been found to be very active in the polymerization of isoprene and butadiene to polymers whose proposed structure contains fused rings, e.g., perhydrophenanthrenes [1, 2]. Although changes in the Al/Ti molar ratio within the range 0.1-10 did not affect the structure of the isoprene polymers, wherein the content of linear structural units did not exceed 15%, such changes apparently influenced the structure of the butadiene polymers [2]. In both cases a cation-radical mechanism, capable of explaining essentially all of the experimentally observed phenomena, has been proposed [2-4].

Whereas an earlier paper [1] dealt with a kinetic analysis of the polymerization of isoprene in *n*-heptane, which yields insoluble polymers, the present study describes a more detailed kinetic analysis of the reaction in aromatic solvents, which leads to completely soluble products.

## EXPERIMENTAL

Monomer, catalyst components, and solvents were always handled in vacuo. Their purification has been described earlier [1]. The final drying of isoprene and of all solvents was carried out by refluxing with sodium hydride over a period of at least 2 days. The purity of the solvents was checked by means of mass spectrometry and gas chromatography.

Polymerizations were performed in a preevacuated all-glass apparatus in which all connections including those to the reservoir containing the monomer, to the storage ampoule containing the solvent, and to the high vacuum manifold were made by means of high vacuum stopcocks of stainless steel. Before each run the entire apparatus was dried by prolonged evacuation with simultaneous heating. A known volume of the dry, degassed solvent was then distilled into the reaction vessel in vacuo. Both ethylaluminum dichloride and titanium tetrachloride were charged by magnetically breaking thin-walled ampoules containing the individual compound. The mixture of the catalyst components was allowed to undergo reaction for 1 hr and then the polymerization was started by the introduction of gaseous monomer from the storage vessel. Reaction rates were determined from the pressure drop in the reservoir, while the concentration of isoprene in the reaction medium was kept constant.

In some experiments the electrical conductivity of the reaction mixture

was also followed, using a modified reaction vessel containing platinum electrodes [5].

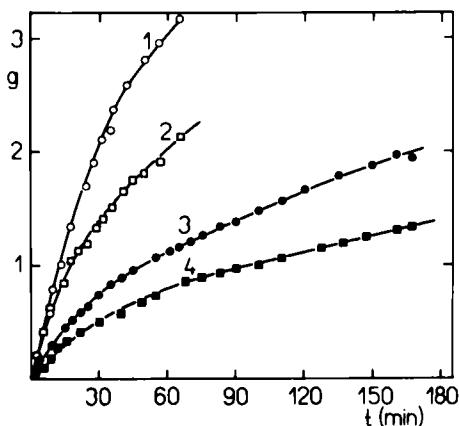
Molecular weights were determined either by light scattering or viscometrically using the Kuhn-Mark equation with the following constants [6]:  $a = 0.22$ ,  $K = 5.25 \times 10^{-3}$  (benzene,  $25^\circ\text{C}$ ).

## RESULTS

### Polymerizations in Benzene

The individual components of the catalyst failed to induce the polymerization of isoprene to solid products either in n-heptane or in benzene, toluene, or p-xylene when complete removal of moisture was achieved. However, when the components were mixed together an active catalyst resulted, leading to rapid polymerization even under extremely dry conditions.

The conversion curves in benzene (Fig. 1) distinctly show a continuous decrease in the reaction rate with an increase in the time of reaction. Since



**Fig. 1.** Conversion curves in polymerization of isoprene in 30 ml benzene at  $20^\circ\text{C}$ .  $g$  = yield in grams in 30 ml of reaction mixture.  $[\text{EtAlCl}_2] = [\text{TiCl}_4] = 1.33 \times 10^{-2}$  mole/liter [Isoprene], mole/liter: (1) 1.045, (2) 0.635, (3) 0.361, (4) 0.212.

the concentration of isoprene during each experiment was kept constant, this effect may be attributed to the decrease in the number of active intermediates. At any instance of the reaction, the reaction rate depends

linearly on the concentration of monomer (Fig. 2). Changes in the Al/Ti ratio within the range 0.3-3 had no apparent influence on the reaction course as long as the product of the concentration of the catalyst components  $[\text{EtAlCl}_2] \cdot [\text{TiCl}_4]$  was constant.

The dependence of the over-all reaction rate on the concentration of any catalyst component (concentration of the other component being constant) is not linear, as shown in Fig. 3. A dependence of the form  $V_{\text{brutto}} = k \cdot C_{\text{cat}}^n$ , where  $C_{\text{cat}}$  is the concentration of the catalyst component which was varied and  $n$  is any number  $> 0$ , did not satisfactorily describe the observed behavior. The reason for such behavior, however, may be readily understood

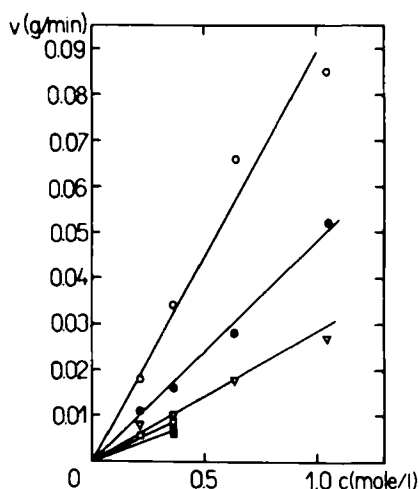
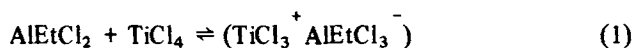


Fig. 2. Dependence of the reaction rate ( $V$ , in g/min in 30 ml of reaction mixture) on the isoprene concentration ( $c$ ) in 30 ml benzene at  $20^\circ\text{C}$ .  $[\text{EtAlCl}_2] = [\text{TiCl}_4] = 1.33 \times 10^{-2}$  mole/liter. Polymerization rate: ( $\circ$ ) at beginning of reaction, ( $\bullet$ ) after 30 min, ( $\nabla$ ) after 60 min, ( $\square$ ) after 100 min, ( $\blacksquare$ ) after 130 min.

by considering that the initiating particle is a complex arising from an equilibrium reaction between ethylaluminum chloride and titanium tetrachloride, e.g.,



which is faster than the reactions in which the complex disappears.

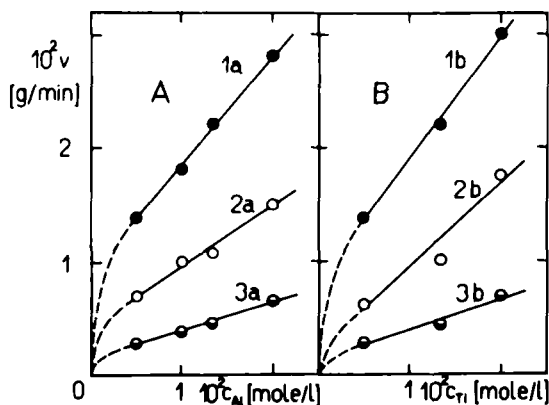


Fig. 3. Dependence of the reaction rate ( $V$ , in g/min in 30 ml of reaction mixture) on the concentration of  $\text{EtAlCl}_2$  (A) and on the concentration of  $\text{TiCl}_4$  (B) in 30 ml benzene at  $20^\circ\text{C}$ . Isoprene concentration maintained constant at 0.212 mole/liter. Polymerization rate: (1a,1b) initial rate, (2a, 2b) after 60 min., (3a,3b) average rate between 120 and 180 min.

Ethylaluminum dichloride may react in the dimeric form so that the structure of the resultant complex may also be different [3].

From the definition of the equilibrium constant and from the material balance in the equilibrium, it follows that the initial equilibrium concentration of the complex particles is given as a root of a quadratic equation of the form:

$$a^2 - a(b + c + 1/K) + (b \cdot c) = 0 \quad (2)$$

where  $a$  = concentration of the complex particles ( $\text{TiCl}_3^+ \text{EtAlCl}_3^-$ ) in equilibrium before the polymerization starts,  $b$  = initial (added) concentration of  $\text{EtAlCl}_2$ , and  $c$  = initial (added) concentration of  $\text{TiCl}_4$ . Consequently, the initial equilibrium concentration of titanium tetrachloride is

$$[\text{TiCl}_4]_{\text{eq}} = c - a \quad (3)$$

The shape of the dependence of the equilibrium concentration of the catalytically active species ( $\text{TiCl}_3^+ \text{EtAlCl}_3^-$ ) on the initial concentration of either  $\text{AlEtCl}_2$  or  $\text{TiCl}_4$  depends on the magnitude of the equilibrium constant  $K$  (presuming that the establishment of the equilibrium is fast). There are two extreme cases when the concentrations in equilibrium are essentially directly proportional to the initial concentrations:

1).  $K \ll 1$ . In this case the equilibrium concentration of the complex is lowered and can be neglected in the material balance so that the equilibrium concentrations of free  $\text{EtAlCl}_2$  and  $\text{TiCl}_4$  are very close to the initial concentrations. Thus,  $a \sim K' \cdot b \cdot c$

2).  $K > 10^4$ . In this case both components react nearly quantitatively to yield the complex. The equilibrium concentration of the complex is then essentially equal to the initially charged concentration of the component which was charged in the lower quantity. This dependence of  $a$  on  $b$  would consequently be  $a \sim K' \cdot b$ , where  $c = \text{constant}$  and  $b \leq c$ .

The initial concentrations of the catalyst components can be substituted into the rate equations only in these cases. If, however, the value of  $K$  lies within the indicated limits, the entity  $a$  calculated according to Eq. (2) should be used. Unfortunately the correct value of  $K$  is not readily accessible and, in addition, would undergo considerable change in the presence of monomer due to solvation effects. The equilibrium (1) would be expected to shift to the left in the absence and to the right in the presence of monomer.

It can be shown that the experimental data from Fig. 3, when plotted in the form  $V_{\text{brutto}}$  vs.  $a$ , concentration of the complex which was calculated according to Eq. (2), show a linear relationship when the constant  $K$  is of the order  $10^2$ – $10^3$ , the best results being obtained for  $K = 5 \times 10^2$  (at a monomer concentration of 0.212 mole/liter, and under the assumption that all reaction partners are solvated by monomer without chemical reaction). Since the equilibrium concentration  $a$  of the complex particles depends on the concentrations of both ethylaluminum dichloride and titanium tetrachloride, all the data from Fig. 3 can be plotted in a single relationship, as shown in Fig. 4. The reaction rate apparently depends linearly on the catalyst concentration but this concentration must be expressed as the equilibrium concentration of the intermediate complex. It should be noted, however, that deviations from linearity occur at a higher excess of any of the catalyst components, apparently the result of the distortion of the equilibrium by several postreactions which lead to the reduction of the complex [1].

At such concentrations, also, high conversions are attained in relatively short reaction times so that the increased viscosity of the reaction medium becomes important.

When all side reactions of the catalyst which can be suppressed by the choice of suitable reaction conditions and also all high conversion effects are neglected, the reaction course can be described by the empirical equation:

$$V_{\text{brutto}} = f(t) \cdot M_0 \cdot a \quad (3)$$

where  $M_0$  is the monomer concentration,  $a$  is the equilibrium concentration of the true catalyst at the beginning of the polymerization, and  $f(t)$  is a time-dependent empirical factor that involves a combination of the equilibrium and velocity constants from all reaction steps with variable  $t$ . Therefore, for a given  $t$ ,  $f(t) = \text{constant}$ . Consequently, the product  $f(t) \cdot a$  represents the product of  $K_p$  times the concentration of active centers at any instant of the reaction.

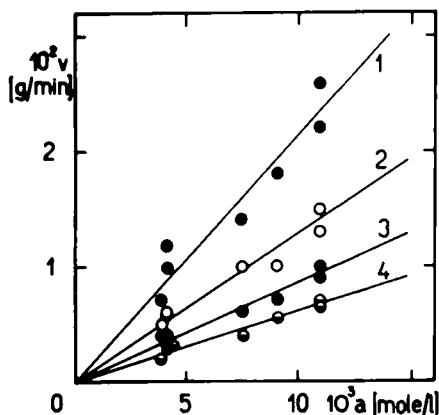


Fig. 4. Dependence of the reaction rate ( $V$ , in g/min in 30 ml of reaction mixture) on the concentration of the intermediate complex  $a$ , calculated according to Eq. (2). Experimental conditions as given in Fig. 3. Polymerization rate: (1) after 10 min, (2) after 30 min, (3) after 60 min, (4) after 100 min.

The time dependence of the factor  $f(t)$  was obtained by plotting the slopes of the lines from Figs. 2 and 4, divided by the corresponding  $a$  in the first case and by  $M_0$  in the latter case, versus time. This dependence is shown in Fig. 5 in coordinates  $\log f(t)$  vs.  $t$ . Analysis of the shape of the curves leads to a formal expression describing the changes of  $\ln f(t)$  with  $t$ , i.e.,

$$\ln f(t) = K \cdot e^{-\gamma t} - \alpha_1 t + B \quad (4)$$

where  $K$ ,  $\gamma$ ,  $\alpha_1$ , and  $B$  are characteristic constants whose meaning will be discussed later.



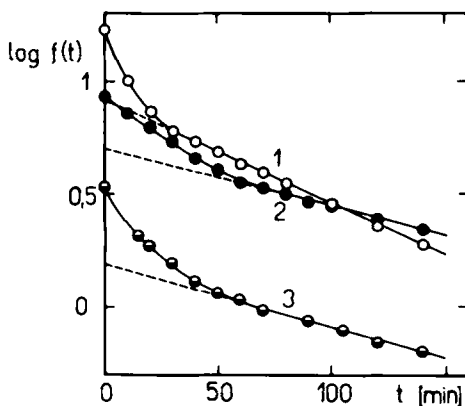


Fig. 5. Dependence of  $\log f(t)$  on time: (1) benzene, (2) toluene, (3) p-xylene.

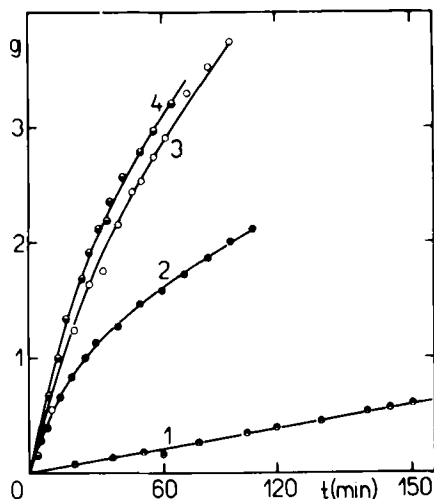
The over-all activation energy for the initial stage of the polymerization in benzene was found to be  $E_{\text{brutto}} = 18$  kcal/mole, whereas the value  $E_{\text{brutto}} = 3$  kcal/mole was obtained for the slow reaction (120-180 min after the start of the reaction).

#### Polymerization in Toluene, p-Xylene, and n-Heptane

In both aromatic hydrocarbons the conversion curves have the same shape as in benzene, i.e., the reaction rate decreases as the reaction proceeds. The dependence of the reaction rate on the monomer concentration and on the equilibrium concentration of the complex particles ( $\text{TiCl}_3^+ \text{EtAlCl}_3^-$ ), calculated in the same manner as in the case of benzene, are also linear. Deviations from the linear path occur, however, at shorter reaction times. Nevertheless, in both cases when the times at which the deviations become serious are omitted, the velocity is again expressed by the same form of the rate Eq. (3) as in benzene. The plot of  $\log f(t) \sim t$  is shown in Fig. 5.

The conversion curves obtained in n-heptane and in the aromatic solvents are compared in Fig. 6. It follows that in aromatic solvents the more basic the solvent the slower the polymerization. This is in contrast with the situation when pure  $\text{AlEtCl}_2$  in the presence of moisture was used as the catalyst [7].

The character of the reaction in n-heptane medium differs substantially from that in aromatic solvents because, under condition comparable with those used in aromatic solvents, the reaction rate is nearly constant over a



**Fig. 6.** Conversion curves in polymerization of isoprene in 30 ml solvent at 20°C. g = yield in grams in 30 ml of reaction mixture. Isoprene concentration maintained constant at 1.045 mole/liter.  $[\text{EtAlCl}_2] = [\text{TiCl}_4] = 1.33 \times 10^{-2}$  mole/liter. Solvent: (1) n-heptane, (2) p-xylene, (3) toluene, (4) benzene.

long time period. This indicates that the concentration of the intermediate complex particles must also be constant for a considerable reaction period and therefore the reaction proceeds under steady-state conditions. The comparison with the course of the reaction in aromatic solvents where, from the very beginning of the polymerization, the reaction rate decreases (and consequently the concentration of the catalytically active complex also decreases) leads to the conclusion that the aromatic molecules are involved in all reactions of the active centers. They apparently promote the polymerization as well as the consumption of the original complex. Therefore, the reaction rates in aromatic solvents are higher than in n-heptane but, on the other hand, the rates decrease with time.

### Electrical Conductivities

The specific conductivity of a  $3 \times 10^{-2}$  M solution of ethylaluminum dichloride in n-heptane at 21°C is  $\kappa = 2.5 \times 10^{-13} \Omega^{-1} \text{ cm}^{-1}$  and that of a solution of titanium tetrachloride under the same conditions and of the same concentration  $\kappa = 3.0 \times 10^{-14} \Omega^{-1} \text{ cm}^{-1}$ . When the solution of

TiCl<sub>4</sub> is added to the solution of AlEtCl<sub>2</sub> in n-heptane the specific conductivity increases to a maximum and then decreases (Fig. 7). The conductivities in benzene and toluene are by several orders of magnitude higher than those in n-heptane, e.g., a  $3 \times 10^{-2}$  M solution of AlEtCl<sub>2</sub> in benzene at 21°C has the specific conductivity  $\kappa = 1.0 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ . The time dependence of the specific conductivity during the reaction AlEtCl<sub>2</sub> + TiCl<sub>4</sub> in benzene and toluene also differs from that in n-heptane, showing a

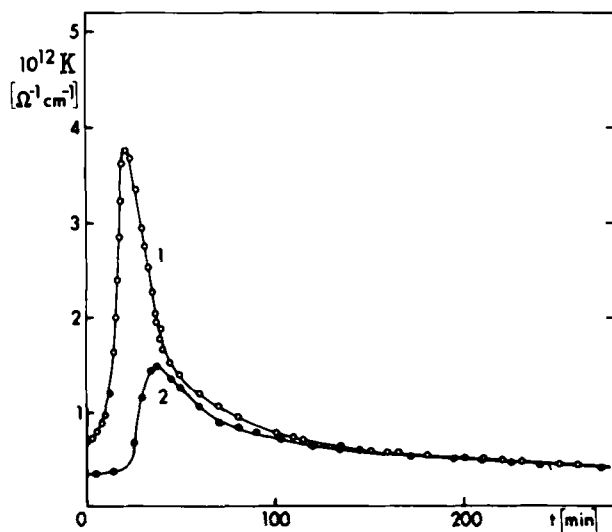
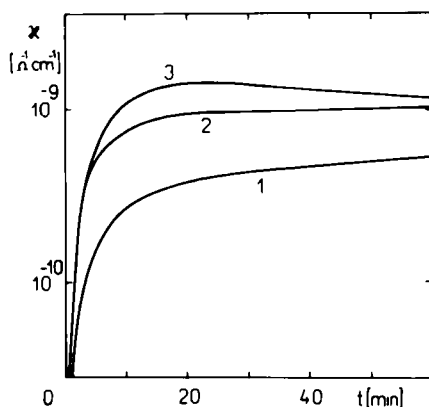


Fig. 7. The change in the specific conductivity  $\kappa$  of the EtAlCl<sub>2</sub> + TiCl<sub>4</sub> system in n-heptane at 21°C with time. [TiCl<sub>4</sub>] =  $3.66 \times 10^{-2}$  mole/liter. Al/Ti mole ratio: (1) 2.9/1, (2) 0.64/1.

much slower increase with time. However, the change in the specific conductivity during the reaction of the pure catalyst components is evidently not of great importance for an understanding of the polymerization mechanism, because the time dependence of  $\kappa$  in a polymerizing system, i.e., in the presence of isoprene, differs profoundly from the cases shown in Fig. 7. After the admission of isoprene, the specific conductivity in n-heptane increases rapidly within the first 30 min to a nearly constant value which depends on the concentrations of all of the components and which is by 3 orders of magnitude higher than the value before the addition of the monomer (Fig. 8). The increase of  $\kappa$  is slower in benzene and it

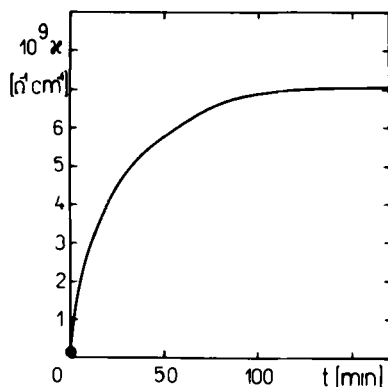


**Fig. 8.** The change in the specific conductivity  $\kappa$  during the polymerization of isoprene with the  $\text{EtAlCl}_2 + \text{TiCl}_4$  catalyst system in *n*-heptane at  $21^\circ\text{C}$ . Isoprene concentration maintained constant at 1.00 mole/liter.  $[\text{EtAlCl}_2] = 2.54 \times 10^{-2}$  mole/liter.  $\kappa$  before addition of isoprene  $1.0 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$ . Al/Ti mole ratio: (1) 1/6.8 (catalyst aged 300 min), (2) 1/10 (catalyst aged 300 min), (3) 1/10 (catalyst freshly prepared).

reaches the limiting value after longer reaction times. The absolute values, however, are much higher than in *n*-heptane (Fig. 9).

### Molecular Weights

The molecular weights of all polymers prepared in benzene are higher than those prepared in toluene and *p*-xylene, telomers being the main product from reactions in the latter solvents. Only insoluble polymers are formed in *n*-heptane. It is evident that the solvent molecules participate extensively in the chain transfer in a similar manner to that which already has been observed in other cases [8], thus indicating the cationic nature of the propagation step. In all cases, the molecular weights increase with increasing concentrations of both catalyst and monomer. However, because the conversion simultaneously increases it is very probable that this effect can be attributed to chain transfer with polymer. Table I shows the dependence of the molecular weights on the duration of the polymerization and on the yield at constant catalyst and monomer concentration. The increase in the molecular weights with the time of the reaction is exponential, as is common in cross-linking reactions. The importance of the chain transfer with polymer is also supported by very high values of the heterogeneity coefficient  $\beta = M_w/M_n = 100$  and by the appearance of microgel.



**Fig. 9.** The change in the specific conductivity  $\kappa$  during the polymerization of isoprene with the  $\text{EtAlCl}_2 + \text{TiCl}_4$  catalyst system in benzene at  $21^\circ\text{C}$ . Isoprene concentration maintained constant at 0.212 mole/liter.  $[\text{EtAlCl}_2] = [\text{TiCl}_4] = 1.33 \times 10^{-2}$  mole/liter.  $\kappa$  before addition of isoprene  $1.93 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ .

**Table 1.** Dependence of the Molecular Weights of Cyclopolyisoprenes on the Polymerization Time<sup>a</sup>

| Polymer yield (g) | Polymerization time (min) | Molecular weight $\times 10^4$ |
|-------------------|---------------------------|--------------------------------|
| 1.05              | 50                        | 20                             |
| 1.40              | 80                        | 31                             |
| 1.65              | 120                       | 67                             |
| 2.05              | 170                       | 210                            |

<sup>a</sup>Polymerization in 30 ml benzene at  $20^\circ\text{C}$ , isoprene concentration, 0.361 mole/liter;  $[\text{EtAlCl}_2] = [\text{TiCl}_4] = 1.33 \times 10^{-2}$  mole/liter.

### Aromatic Residues in Polymers

Due to the fact that aromatic hydrocarbons are very susceptible to electrophilic attack, chain transfer with solvents is very important and leads to the incorporation of solvent residues in the polymer chain [2-4]. The aromatic moieties in the cyclopolyisoprenes increase with increasing concentration of monomer. Table 2 shows the results of the infrared analyses of

Table 2. Molecular Weights and Amounts of Toly! Groups in Cyclopolyisoprenes Prepared under Various Conditions<sup>a</sup>

| Al/Ti<br>molar ratio | [TiCl <sub>4</sub> ]<br>× 10 <sup>2</sup> | Tolyl group content<br>(wt%) | Molecular weight<br>× 10 <sup>-4</sup> |
|----------------------|---|------------------------------|--|
| 1/1                  | 0.667                                     | 6.1                          | 3.2                                    |
| 1/1                  | 1.33                                      | 7.7                          | 7.5                                    |
| 1/1                  | 2.65                                      | 9.1                          | 220.0                                  |
| 0.33/1               | 1.33                                      | 6.8                          | 6.7                                    |
| 0.67/1               | 1.33                                      | 8.6                          | 11.5                                   |
| 1.50/1               | 1.33                                      | 8.2                          | 14.5                                   |
| 1/0.33               | 0.445                                     | 12.8                         | 1.3                                    |
| 1/0.67               | 0.885                                     | 9.5                          | 7.0                                    |
| 1/1.5                | 2.0                                       | 8.9                          | 24.0                                   |

<sup>a</sup>Polymerization in 30 ml toluene at 20°C; isoprene concentration, 1.045 mole/liter; reaction time, 180 min; catalyst aged 60 min.

the contents of tolyl moieties in cyclopolyisoprenes prepared under various conditions. When comparing the aromatic residue content with molecular weight it is seen that one polymer molecule must contain more than one aromatic nucleus, in accordance with previous results [3, 4]. Thus, in addition to chain transfer with the solvent, other reactions leading to the incorporation of the solvent residues into the macromolecule also occur. The mechanism of such reactions has already been proposed [3, 4].

## DISCUSSION

The reaction of ethylaluminum dichloride with titanium tetrachloride is rather complex and has already been the subject of several studies [9-11]. Arlman and de Jong [9] investigated the rate of formation of titanium trichloride at 80°C in isooctane. Adema, Bartelink, and Smidt [10] used the ESR method to follow the reaction course in n-heptane and assigned the ESR signal to two types of paramagnetic particles which were formed during the reaction. The concentration of the first type increased with time to a limiting constant value while that of the other type underwent a steady increase with constant rate after a rapid initial stage. Bestian and Clauss [11] showed that the reaction of titanium tetrachloride with methylaluminum dichloride is an equilibrium reaction in which alkyltitanium chlorides are formed.

The conductivity measurements indicate that after the mixing of both catalyst components an intermediate is formed which dissociates to free ions. The concentration of free ions reaches a maximum due to the fact that the primary reaction product (a complex which is either in a dissociated or undissociated form) undergoes further decomposition (Fig. 7). The reaction scheme of Adema and co-workers [10] seems to represent satisfactorily the complexity of the reactions taking place in the system. The non-ionic nature of the paramagnetic particles found by Adema et al. is confirmed by the comparison of the time dependence of the ESR signal [10] and the specific conductivity, the latter showing a sharp maximum (Fig. 7). The irreversible nature of the over-all reaction does not exclude, however, the reversibility of some individual steps. As has been postulated previously [1], and as was also proposed by Adema et al., free, excess ethylaluminum dichloride and titanium tetrachloride take part in the decomposition reactions of the intermediate complex, leading to the final unreactive products such as  $\text{TiCl}_3$ ,  $\text{AlCl}_3$ , etc.

In benzene medium the ions are solvated by the solvent molecules which cause higher degrees of dissociation but the reactions of the solvated particles with excess original components are slower so that the decomposition reactions leading to the disappearance of ions and to the decrease of electric conductivity are evident after longer reaction times.

In the presence of monomer the course of the specific conductivity  $\kappa$  in the  $\text{AlEtCl}_2 + \text{TiCl}_4$  system is quite different from that in its absence (Figs. 8 and 9). In *n*-heptane, under the experimental conditions,  $\kappa$  increases rapidly to a nearly constant value which decreases very slowly in later stages. At the same time the reaction rate is practically constant. During the polymerization polymer slowly precipitates from the reaction medium due to its insolubility in *n*-heptane. The fact that the concentration of active centers in this case remains nearly constant over a considerable period of the reaction shows that the active centers are regenerated in the termination step of the chain growth. The concentration of free ions is closely related to the concentration of the active particles, probably through a dissociation equilibrium. It is also evident that the reactions of free catalyst components with the intermediate complex or with ions formed therefrom, leading to the decomposition of the complex and finally to the reduction of titanium tetrachloride according to the reaction scheme of Adema et al., are less important in the presence of monomer. The final result of the polymerization is also the reduction of titanium tetrachloride; however, the actual reducing agent in this case is isoprene. In fact, it has been observed that the formation of the solid

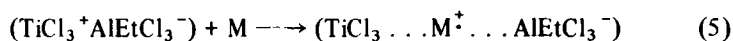
$\text{TiCl}_3$  in the system  $\text{TiCl}_4 + \text{AlEtCl}_2$  is highly accelerated in the presence of isoprene and that there is a close parallel between the appearance of  $\text{TiCl}_3$  and the start of the polymerization.

In aromatic solvents there is no parallel between the rate of the polymerization and the change in the specific conductivity, both showing opposite time dependence, i.e., the concentration of ions increases with the simultaneous decrease of the reaction rate (compare Figs. 1 and 9). Due to the maintenance of the monomer concentration at a constant level during the reaction, the decrease in the reaction rate with time must be connected with the disappearance of the active centers. The simultaneous increase of the conductivity, however, indicates that free ions are not identical with active centers and also that during polymerization active centers are finally converted to stable free ions.

Taking all the experimental data into consideration, the principal features of the polymerization mechanism can be summarized as follows:

- 1). The reaction of ethylaluminum dichloride with titanium tetrachloride leads to a product that is active as the catalyst either as an undissociated complex or as an ion pair. This complex or ion pair is in equilibrium with free ions which are unreactive.
- 2). The solvation of the complex with monomer protects it against further reaction with excess catalyst components.
- 3). The active complex is consumed during the polymerization with a simultaneous increase in the concentration of free ions.
- 4). Titanium tetrachloride is reduced during the polymerization process to the trivalent state.

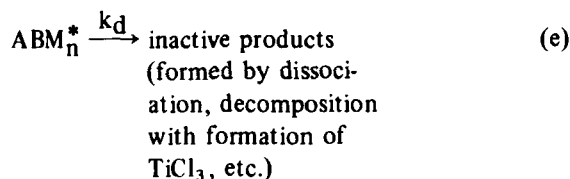
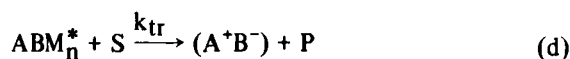
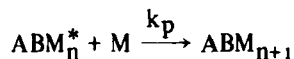
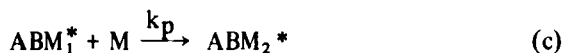
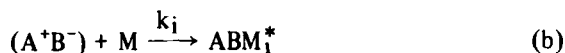
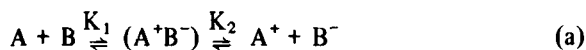
Therefore, the reaction scheme proposed by Adema et al. in the absence of monomer should be modified by considering all ions and ion-pairs as solvated by the monomer molecules which are the most basic species in the reaction system, and by replacing the reactions of the intermediate complex with excess catalyst components with its reaction with monomer. The reaction of isoprene with the intermediate complex (existing probably as an ion-pair) may be the actual initiation step leading to the formation of an active monomer cation-radical, as proposed by Gaylord et al. [3, 4]. The cation-radical is closely associated with its counterion so that the electron transfer takes place inside of a donor-acceptor complex. Reaction (1) is thus followed by the initiation step:





The actual form of the  $(\text{TiCl}_3)$  moiety is unknown. It may represent one of the possible forms proposed earlier [3]. The chain growth proceeds through the addition of further monomer to the complexed monomer cation-radical. By chain transfer with the solvent or with polymer, e.g., with internal double bonds, the active catalyst is regenerated from the complex polymer cation-radical which is the prevailing termination reaction in heptane. Termination of the chain growth may also occur as a result of the dissociation of the complexed polymer cation-radical due to the effect of steric factors in the voluminous polymeric mass. Another possibility is that the polymer cation-radical eliminates a portion to form the inactive  $\text{TiCl}_3$ , the slightly active  $\text{H}^+\text{AlEt}_2\text{Cl}_5^-$ , and the polymer chain bearing a radical. The polymer radical either recombines or, before combination, grows by addition of further monomer molecules to produce linear segments, or abstracts hydrogen from the solvent. A complete description of the proposed mechanism has been published elsewhere [3, 4].

The whole process is certainly more complicated than previously considered; however, the rate controlling steps may be those discussed above. The following reaction scheme is thought to describe satisfactorily the principal reactions:



where  $\text{A} = \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ ,  $\text{B} = \text{TiCl}_4$ ,  $\text{S} = \text{solvent}$ , and  $\text{ABM}_1^*$ ,  $\text{ABM}_2^*$ , . . . ,  $\text{ABM}_n^*$  = cation-radical.

Assuming that the rate of the establishment of the equilibrium (a) is high, the following set of differential equations describe the process:

$$\frac{d[(A^+B^-)]}{dt} = -k_i[M]_0[(A^+B^-)] + k_{tr}[S][ABM^*]$$

$$\frac{d[ABM^*]}{dt} = k_i[M]_0[(A^+B^-)] - (k_d + k_{tr}[S])[ABM^*]$$

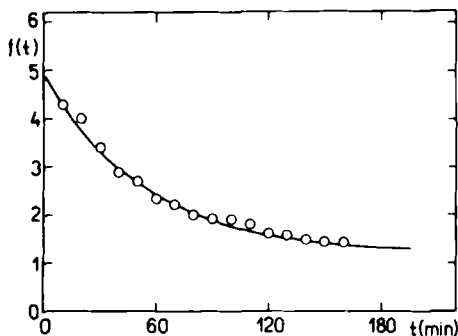
$$\frac{+d[M]}{dt} = -k_i[M]_0[(A^+B^-)] - k_p[M]_0[ABM^*]$$

Because the concentration of isoprene  $[M]_0$  was kept constant, the system is linear and homogeneous. Solution of the first two equations for the initial conditions  $t = 0$ ,  $[(A^+B^-)] = a$ ,  $[ABM^*] = 0$ , and substitution in the third equation (in which the first term on the right side is neglected) yields:

$$\frac{dM}{dt} = a \cdot [M]_0 (C_1 \cdot e^{-\alpha_1 t} + C_2 \cdot e^{-\alpha_2 t}) \quad (6)$$

Constants  $C_1$ ,  $C_2$ ,  $\alpha_1$ , and  $\alpha_2$  involve the rate constants  $k_i$ ,  $k_p$ ,  $k_{tr}$ ,  $k_d$ , and the concentration of isoprene  $[M]_0$ . Their explicit forms are rather complicated so that they are not of practical use in the determination of the individual rate constants.

The utility of Eq. (6) in the description of the polymerization process, however, was verified by comparison of experimental curves of the dependence of the polymerization rate on time with model curves representing Eq. (6), by means of an analog computer using various values of  $C_1$ ,  $C_2$ ,  $\alpha_1$ , and  $\alpha_2$ . Figure 10 shows, for one example in benzene, that experimental



**Fig. 10.** Dependence of  $f(t)$  on time. (—) Theoretical curve obtained on analog computer for the values of the constants given in Table 3. (o) Calculated values of  $f(t)$  from the experimental points in Curve 2 in Fig. 1.

$$f(t) = \frac{-d[M]}{dt} / [M]_0 \cdot a$$

points (circles) fit the theoretical curve (drawn line). Values of the constants  $C_1$ ,  $C_2$ ,  $\alpha_1$ , and  $\alpha_2$  correctly describing the time dependence of the reaction rate in benzene, toluene, and p-xylene obtained from the computer are summarized in Table 3. It is also seen that for any given time  $t$  the reaction rate depends linearly on  $M_0$  and  $a$ , as was found experimentally.

Comparing Eq. (6) with the empirical Eq. [3]:

$$f(t) = C_1 \cdot e^{-\alpha_1 t} [1 + C_2/C_1 \cdot e^{-(\alpha_2 - \alpha_1)t}]$$

Table 3. Values of Constants from Eq. (6)

| Solvent  | Analog computer <sup>a</sup> |       |                      |                      | Experimental <sup>b</sup> |       |                      |
|----------|------------------------------|-------|----------------------|----------------------|---------------------------|-------|----------------------|
|          | $C_1$                        | $C_2$ | $\alpha_1$           | $\alpha_2$           | $C_1$                     | $C_2$ | $\alpha_1$           |
| Benzene  | 3.86                         | 7.95  | $2.9 \times 10^{-3}$ | $3.3 \times 10^{-2}$ | 5.3                       | 5.5   | $7.1 \times 10^{-3}$ |
| Toluene  | 4.8                          | 3.8   | $5.0 \times 10^{-3}$ | $3.6 \times 10^{-2}$ | 5.1                       | 2.7   | $5.8 \times 10^{-3}$ |
| p-Xylene | 1.2                          | 4.0   | $8.4 \times 10^{-4}$ | $4.5 \times 10^{-2}$ | 1.5                       | 1.2   | $6.5 \times 10^{-3}$ |

<sup>a</sup>Values obtained by fitting the model curves to experimental time dependence of  $f(t)$  vs. time (Fig. 10) in conversion Curve 2 of Fig. 1.

<sup>b</sup>Values obtained from the dependence of  $\log f(t)$  vs.  $t$  from Fig. 5.

After converting to logarithmic form and expansion of the logarithm of the expression in parenthesis:

$$\ln f(t) = \ln C_1 - \alpha_1 t + C_2/C_1 \cdot e^{-(\alpha_2 - \alpha_1)t} \quad (7)$$

which is identical with Eq. (4) derived by the graphical analysis of the experimental curves in Fig. 5. The validity of Eq. (7) is limited by the condition

$$-1 < C_2/C_1 \cdot e^{-(\alpha_2 - \alpha_1)t} < 1$$

and by the fact that from the expansion series only the first member was taken into account. In spite of these simplifications, the equation describes the experimental data satisfactorily. The meaning of the constants in Eq. (4) is now evident. From the time dependence of  $\log f(t)$  represented in Fig. 5 it is possible to determine the constant  $C_1$ ,  $C_2$ , and  $\alpha_1$  according to Eq. (7) using the limiting case  $t = 0$  and  $t = \infty$ . The values of the constants obtained in this manner are also included in Table 3.

Chain transfer to polymer is probably responsible for the increase of the molecular weight with the time of reaction. Its existence, however, cannot be distinguished from kinetic measurements of the total reaction rate because it would only change the magnitude of the rate constant  $k_{tr}$ .

## REFERENCES

- [1] B. Matyska, K. Mach, J. Vodehnal, and I. Kössler, *Collect. Czech. Chem. Commun.*, **30**, 2569 (1965).
- [2] N. G. Gaylord, I. Kössler, and M. Štolka, *J. Macromol. Sci.-Chem.*, **A2**, 1105 (1968).
- [3] N. G. Gaylord, B. Matyska, I. Kössler, and K. Mach, *J. Polym. Sci., Part A-1*, **6**, 125 (1968).
- [4] N. G. Gaylord, I. Kössler, and M. Štolka, *J. Macromol. Sci.-Chem.*, **A2**, 421 (1968).
- [5] B. Matyska, M. Švestka, and K. Mach, *Collect. Czech. Chem. Commun.*, **31**, 659 (1966).
- [6] V. Boháčková, J. Poláček, and H. Benoit, *J. Chim. Phys.*, **66**, 197 (1969).
- [7] I. Kössler, M. Štolka, and K. Mach, *J. Polym. Sci., Part C*, **4**, 977 (1964).
- [8] P. H. Plesch, *J. Chem. Soc.*, **1953**, 1662; C. G. Overberger, G. F. Endres, and A. Monaci, *J. Amer. Chem. Soc.*, **78**, 1969 (1956); T. Higashimura and S. Okamura, *Kobunshi Kagaku*, **13**, 431 (1956).
- [9] E. J. Arlman and J. P. de Jong, *Rec. Trav. Chim. Pays-Bas*, **79**, 910 (1960).
- [10] E. H. Adema, H. J. M. Bartelink, and J. Smidt, *Rec. Trav. Chim. Pays-Bas*, **81**, 73 (1963).
- [11] H. Bestian and K. Clauss, *Angew. Chem. Int. Ed.*, **2**, 704 (1963).

Accepted by editor January 8, 1970

Received for publication March 16, 1970