

CATIONIC POLYMERIZATION OF 1-CHLORO-2,3-EPOXYPROPANE INITIATED BY TRIPHENYLMETHYLHEXAFLUOROANTIMONATE(V)

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The activity of Ph_3CZn in the initiation of polymerization of 1-chloro-2,3-epoxypropane decreases in dependence on ZX_n in the following series $\text{AsF}_6^{(-)} \geq \text{SbF}_6^{(-)} \approx \text{SbCl}_6^{(-)} > \text{AlCl}_4^{(-)} > \text{SnCl}_5^{(-)} > \text{TiCl}_5^{(-)}$. The polymerization initiated by Ph_3CSbF_6 is a first-order reaction both with respect to the monomer and to the catalyst. The following values were determined for the rate constants of initiation, propagation, and termination, respectively: $k_1 = 3 \cdot 10^{-6} \text{ mol}^{-1} \text{ l} \cdot \text{s}^{-1}$; $k_p = 9 \cdot 10^{-2} \text{ mol}^{-1} \text{ l s}^{-1}$; $k_t = 2 \cdot 10^{-4} \text{ mol}^{-1} \text{ l s}^{-1}$. The initiation occurs *via* a hydride-ion transfer from 1-chloro-2,3-epoxypropane to the triphenylmethyl cation. The oxonium ion formed by $\text{Ph}_3\text{C}^{(+)}$ addition on 1-chloro-2,3-epoxypropane presumably does not take part in the initiation; the equilibrium constant of formation of this adduct K_6 is $3 \cdot 0 \cdot 10^{-1} \text{ mol}^{-1} \text{ l}$. Oligomers are *n*-multiples of monomeric epichlorohydrine, and products of \bar{P}_n 4–7 have mostly cyclic structure.

1-Chloro-2,3-epoxypropane (further on epichlorohydrine) can be subjected to cationic polymerization by the action of both Lewis and protonic acids¹. The initiator used in most studies of polymerization and co-polymerization was BF_3 and $\text{BF}_3 \cdot \text{OEt}_2$ (ref.^{2,3}). In studies of elementary steps of the mechanism of cationic polymerization stable triphenylmethyl salts have been used as initiators^{4–7}. Their advantage, besides a considerable inertness towards air and humidity, lies mainly in an easy and accurate spectroscopic determination of the triphenylmethyl cation concentration during the polymerization process. However, the mechanism of the triphenylmethyl cation initiation is not simple and depends on the nature of the monomer. While with vinyl monomers an addition of $\text{Ph}_3\text{C}^{(+)}$ on the monomer takes place⁸, with oxygen-containing heterocycles the main initiation step is a hydride-ion transfer from the monomer to the cation and the formation of triphenylmethane^{4,5}. An important finding concerning the mechanism of epichlorohydrine polymerization initiation was made by Kuntz^{9,10}: the rate of polymerization of tetrahydrofuran (THF) initiated by triphenylmethylhexafluoroantimonate(V) increases strongly, if a co-catalytic amount of epichlorohydrine or epoxypropane is added. Kuntz explained the influence of these co-catalysts by a change of the initiation mechanism: in the presence of these compounds in the initiation no hydride-ion abstraction from THF occurs, but an addition of THF on the oxonium ion, formed by the addition of Ph_3C^+ on the corresponding oxirane.

This contribution aims at elucidating the polymerization mechanism of epichlorohydrine by triphenylmethyl cations. In the detailed study of the initiation mechanism of the epichlorohydrine polymerization Ph_3CSbF_6 was used, because it contains

a stable anion — similarly as Ph_3CAsF_6 — which does not undergo a reduction during the polymerization reaction⁵.

EXPERIMENTAL

Chemicals

Epichlorohydrine (produced by Spolek pro chemickou a hutní výrobu, Ústí n/L) was carefully distilled in the nitrogen atmosphere and then dried by calcium hydride for 10 days; then it was distilled under vacuum into an ampule containing CaH_2 and from there it was distributed after two days by distillation under vacuum into sample ampules equipped with a breakable seal. The ampules were protected against light exposure. Dichloromethane was shaken for three days with sulphuric acid, rinsed by water, dried, and after distillation it was refluxed with CaH_2 ; after 10 days it was distilled into a sample ampule containing CaH_2 ; the ampule was connected to a vacuum line by means of a high-vacuum stopcock. Ph_3CSbF_6 and Ph_3CAsF_6 (Ozark-Mahonig) were purified by a multiple precipitation of the salts from a dichloromethane solution into hexane, and after drying they were kept *in vacuo*. $\text{Ph}_3\text{CSbCl}_6$ was prepared under vacuum from triphenylmethyl chloride and antimony(V) chloride in a CCl_4 solution; after a multiple precipitation from a CH_2Cl_2 solution into hexane and drying the substance was kept under vacuum. Ph_3AlCl_4 was prepared by mixing a nitrobenzene solution of AlCl_3 with Ph_3CCl , the substance was then precipitated several times by hexane from a CH_2Cl_2 solution. $\text{Ph}_3\text{CSnCl}_5$ and $\text{Ph}_3\text{CTiCl}_5$ were prepared, in view of their low stability, in catalytic amounts in the reaction vessel by mixing equimolar amounts of Ph_3CCl with SnCl_4 or TiCl_4 in dichloromethane immediately before being used.

Polymerization

Polymerization of epichlorohydrine in CH_2Cl_2 was carried out in a high-vacuum thermostated apparatus. The solution of the triphenylmethyl salt in CH_2Cl_2 and epichlorohydrine were added in this sequence to the distilled amount of CH_2Cl_2 by breaking the breakable seals of the ampules. The reaction mixture was vigorously agitated by a magnetic stirrer during the mixing. The polymerization kinetics was followed by measuring changes of the equilibrium pressure over the polymerization mixture at a constant temperature. An increase of temperature during mixing of the monomer with the catalytic solution at higher catalyst concentrations levelled off during 3–4 minutes and the first measurements were carried out after 5 minutes from the reaction start.

Measurements

The measurements of the specific electric conductivity of the reaction system were carried out in the same vacuum apparatus as the polymerizations. The all-glass conductivity cell with platinum electrodes¹¹ served as the reaction vessel. A semiautomatic bridge Tesla BM 484 was used in the measurements.

Concentration of the triphenylmethyl salt and its decrease during the polymerization was determined by optical density measurements at 430 nm at 20°C ($\epsilon = 3.95 \cdot 10^4 \text{ mol}^{-1} \text{ l cm}^{-1}$). The all-glass cuvette was attached to the mixing cell on the high-vacuum apparatus and after sampling the reaction mixture it was sealed off. A double-beam spectrometer Optica Milano CF 4 DR was used in the measurements.

Fractionation of poly(epichlorohydrine) was carried out by the elution column method. In order to separate oligomers of a mean polymerization degree 2–5, first elution by pentane at 12.5°C

was carried out, then elution by hexane at the same temperature, and finally elution by heptane at 14°C. Thereafter, elution at 25°C by the elution gradient heptane-acetone was carried out; the initial mixture contained 100 vol.% and the final 51 vol.% of heptane. The fractionation yield was 92%. Molecular weights of poly(epichlorohydrine) were measured by the VPO method on a Knauer instrument.

Infrared spectra were measured using a UR 10 spectrometer (Zeiss, Jena) and ¹H-NMR spectra were determined on a Tesla 487 instrument at 80 MHz. Mass spectra were measured with the help of a JEOL JMS-D 100 spectrometer.

RESULTS AND DISCUSSION

Polymerization Activity of Triphenylmethyl Salts

Polymerization of epichlorohydrine in CH₂Cl₂ at 20°C was initiated by a series of triphenylmethyl salts under the same concentration conditions. After adding the monomer into the solution of Ph₃C⁽⁺⁾ salts an increase of temperature was always observed, if the salt concentration was equal or higher than 10⁻² mol l⁻¹. Orange colour of triphenylmethyl salts did not visibly change during the polymerization. The influence of salt anions on the initiation activity of the triphenylmethyl cation is demonstrated by conversion curves for various salts in Fig. 1. Molecular weights of poly(epichlorohydrine) obtained with the most active catalysts are summarized in Table I.

The polymerization activity of the Ph₃C⁺ salts decreases in the series AsF₆⁽⁻⁾ ≥ SbF₆⁽⁻⁾ ≈ SbCl₆⁽⁻⁾ > AlCl₄⁽⁻⁾ > SnCl₅⁽⁻⁾ > TiCl₅⁽⁻⁾. While Ph₃CTiCl₅ exhibited under the given conditions but a negligible initiation activity, Ph₃CsSnCl₅ induced a fast polymerization whose rate, however, decreased during a few minutes practically to zero. Placing the activity of Ph₃CAICl₄ into the series was carried out by comparing yields of block polymerizations after 24 hours of reaction time.

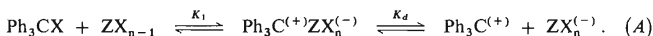
TABLE I

Molecular Weights of Polymers Obtained in Epichlorohydrine (M) Polymerization in CH₂Cl₂ ([M]₀ = 3.2 mol l⁻¹) Initiated by Triphenylmethyl Salts

| Anion | [Ph ₃ CZ _n X _n] ₀ 10 ⁻² mol l ⁻¹ | t h | M _n | Anion | [Ph ₃ CZ _n X _n] ₀ 10 ⁻² mol l ⁻¹ | t h | M _n |
|---------------------------------|--|--------|----------------|----------------------------------|--|--------|----------------|
| SbF ₆ ⁽⁻⁾ | 0.018 | 100 | 1 260 | SbF ₆ ⁽⁻⁾ | 1.8 ^a | 5 | 350 |
| SbF ₆ ⁽⁻⁾ | 1.3 | 3 | 1 180 | AsF ₆ ⁽⁻⁾ | 1.8 | 5 | 810 |
| SbF ₆ ⁽⁻⁾ | 1.8 | 5 | 1 200 | SbCl ₆ ⁽⁻⁾ | 1.8 | 5 | 615 |

^a Polymerization with addition of water, [H₂O]/[Ph₃C⁽⁺⁾] = 13.

Triphenylmethyl salts are dissociated in solutions



The value of the dissociation constant K_d , $2.5 \cdot 10^{-4} \text{ mol l}^{-1}$ (CH_2Cl_2 , 20°C), is practically independent of the type of the anion¹², values of K_1 differ for various anions considerably (benzoyl chloride, 20°C): for $\text{SbCl}_6^{(-)}$ – 10^4 , $\text{SnCl}_5^{(-)}$ – 300, $\text{TiCl}_5^{(-)}$ – 58, $\text{AlCl}_4^{(-)}$ – 1.5 (ref.¹³). The activity of $\text{Ph}_3\text{CAlCl}_4$ is given evidently, when considering the low value of K_1 , by the activity of free aluminium chloride. Similarly, in the initiation scheme for $\text{Ph}_3\text{CSbCl}_6$ a partial dissociation of the anion to $\text{Cl}^{(-)}$ and SbCl_5 is considered, where SbCl_5 is easily reduced to Sb(III) (ref.^{6,7}). The catalytic activity of the $\text{Ph}_3\text{C}^{(+)}$ salts is not given only by the rate of initiation by the $\text{Ph}_3\text{C}^{(+)}$ cation, but also by the electron-acceptor strength of the Lewis acid and by the stability of the anion. A dependence of the activity on the type of the triphenylmethyl salt anion was found in the polymerization of THF (ref.¹), 1,3-dioxolane⁵, and vinyl monomers¹⁴, too. Therefore, the mechanism of the initiation effect of the $\text{Ph}_3\text{C}^{(+)}$ cation in the polymerization has been studied on the Ph_3CSbF_6 salt; it can be assumed about the anion of this salt that it will not take part in reactions with the monomer.

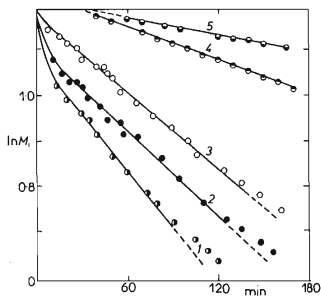


FIG. 1

Polymerization of Epichlorohydrine ($[\text{M}]_0 = 3.2 \text{ mol l}^{-1}$, CH_2Cl_2 , 20°C) Initiated by Ph_3CZnX_n ($[\text{Ph}_3\text{CZnX}_n]_0$ in mol l^{-1})

1 $[\text{Ph}_3\text{CAsF}_6]_0 = 1.82 \cdot 10^{-2}$; 2 $[\text{Ph}_3\text{CSbF}_6]_0 = 1.82 \cdot 10^{-2}$; 3 $[\text{Ph}_3\text{CSbCl}_6]_0 = 1.82 \cdot 10^{-2}$; 4 $[\text{Ph}_3\text{CSnCl}_5]_0 = 3.4 \cdot 10^{-2}$; 5 $[\text{Ph}_3\text{CTiCl}_5]_0 = 3.4 \cdot 10^{-2}$.

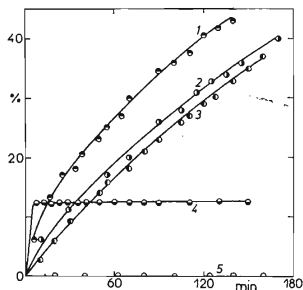


FIG. 2

Semilogarithmic Plot of Conversion Curves during Epichlorohydrine Polymerization ($[\text{M}]_0 = 3.2 \text{ mol l}^{-1}$, CH_2Cl_2 , 20°C) Initiated by Ph_3CSbF_6 ($[\text{Ph}_3\text{CSbF}_6]_0$ in $10^{-3} \text{ mol l}^{-1}$)

1 48; 2 27; 3 18; 4 63; 5 1.08.

Polymerization of Epichlorohydrine Initiated by Ph_3CSbF_6

Semilogarithmic plots of the polymerization curves for various concentrations of Ph_3CSbF_6 are given in Fig. 2. With catalyst concentrations of the order of 10^{-3} mol l^{-1} and smaller, induction periods were observed whose length increased with the decreasing concentration of the catalyst. The polymerization rate decreases with decreasing catalyst concentration. With the initial Ph_3CSbF_6 concentrations of the order of 10^{-4} mol l^{-1} , suitable for measuring the $\text{Ph}_3\text{C}^{(+)}$ concentration diminution by visible spectroscopy, the polymerization rate was so small that it could not be continuously followed in a quantitative way. With these catalyst concentrations the triphenylmethyl salt was completely consumed and the polymerization stopped before reaching the 100% conversion.

A typical time dependence of the triphenylmethyl salt concentration, the specific electric conductivity (κ) and the conversion in the polymerization system at $[\text{Ph}_3\text{CSbF}_6]_0 \leq 2.3 \cdot 10^{-4}$ mol l^{-1} are summarized in Fig. 3. After the monomer was added to the catalyst solution, an immediate decrease of the electric conductivity (mainly because of the dilution) and of the $\text{Ph}_3\text{C}^{(+)}$ ion concentration occurred. The concentration loss of $\text{Ph}_3\text{C}^{(+)}$ observed was larger than that one corresponding to the mere dilution by epichlorohydrine. This loss is due to the addition of $\text{Ph}_3\text{C}^{(+)}$ on the monomer leading to the formation of the colourless oxonium cation. The polymerization proceeds after a long induction period, during which both the $\text{Ph}_3\text{C}^{(+)}$ concentration and the value of κ do not change. The constant value of $\text{Ph}_3\text{C}^{(+)}$ concentration during the induction period shows that there occurs no process in the system of an appreciable rate in which either $\text{Ph}_3\text{C}^{(+)}$ ions or oxonium ions would take part. Therefore, from the known values of the initial concentration of $\text{Ph}_3\text{C}^{(+)}$ and its stationary concentration after the monomer (M) addition as measured during the induction period it was possible to calculate the equilibrium constant of the oxonium ion

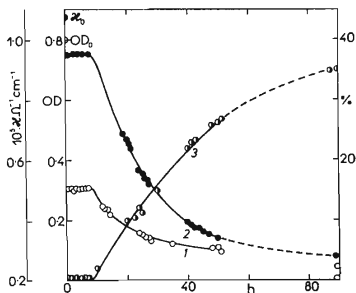


FIG. 3

Time Dependence of Ph_3CSbF_6 Concentration (1 O.D. — Optical Density), Specific Electric Conductivity (2 κ in $\Omega^{-1} \text{cm}^{-1}$) and Conversion (3 %) during Epichlorohydrine Polymerization ($[\text{M}]_0 = 3.2$ mol $\cdot \text{l}^{-1}$, CH_2Cl_2 , 20°C , $[\text{Ph}_3\text{CSbF}_6]_0 = 1.7 \cdot 10^{-4}$ mol l^{-1})

formation (K_e). The value of $K_e \cdot 3.0 \cdot 10^{-1} \pm 0.021 \text{ mol}^{-1}$ was found for $[M]_0 \leq 1.2 \text{ mol l}^{-1}$, $[\text{Ph}_3\text{SbF}_6]_0 \leq 2.8 \cdot 10^{-4} \text{ mol l}^{-1}$, CH_2Cl_2 and 20°C . The equilibrium constants of the oxonium ion formation for a series of cyclic ethers and acetals were determined by Slomkowski and Penczek¹². A comparatively lower value of K_e for epichlorohydrine corresponds well to its lower basicity with respect to the measured oxygen-containing compounds.

The polymerization reaction of epichlorohydrine, starting after the induction period, is accompanied by a decrease of the triphenylmethyl salt concentration and a decrease of the specific conductivity of the system (Fig. 3). Therefore, it may be assumed that in the reaction leading to the disappearance of the triphenylmethyl cation a particle is formed which initiates the polymerization of epichlorohydrine, and that the rate of $\text{Ph}_3\text{C}^{(+)}$ disappearance may be regarded as the initiation rate of the polymerization. The rate constant of the initiation k_1 , obtained by measuring spectroscopically the decrease of the $\text{Ph}_3\text{C}^{(+)}$ concentration has a value of approximately $3 \cdot 10^{-6} \text{ mol}^{-1} \text{ l s}^{-1}$.

If the catalyst concentration was increased to $10^{-2} \text{ mol l}^{-1}$, a suitable value for following the polymerization kinetics, an observable temperature effect takes place upon the monomer addition and the induction period disappears. In the region of lower conversions the polymerizations proceed as reactions of the first order with respect both to the monomer (Fig. 2) and to the catalyst (Fig. 4). The course of the polymerization can be formally described by the relation

$$\ln([M]_{t_1}/[M]_{t_2}) = k't = k[\text{Ph}_3\text{SbF}_6] t. \quad (1)$$

The value found for the rate constant k was $2.1 \cdot 10^{-3} \text{ mol}^{-1} \text{ l s}^{-1}$. In the region of higher conversions the polymerization rate decreases faster than expected from

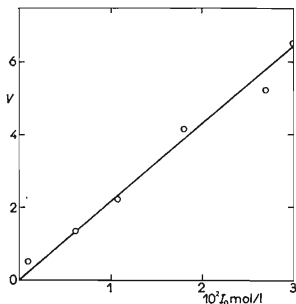


FIG. 4
Dependence of Reaction Rate ($v = \ln \cdot ([M]_{t_1}/[M]_{t_2})/t_1 - t_2$) on Catalyst Concentration ($[M]_0 = 3.2 \text{ mol l}^{-1}$, CH_2Cl_2 , 20°C)

the decrease of the monomer concentration; a deviation from the linear dependence of $\ln [M]_t$ vs time takes place. A heating of the system during mixing of the monomer with the catalyst solution resulted in a higher consumption of the monomer in the first minutes of the reaction (Fig. 2, curve 1 and 2). After reaching the 100% conversion, there is still a high concentration of the triphenylmethyl salt in the polymerization system. Repeated addition of the monomer leads to further polymerization which proceeds with almost the same rate as at the start of the first polymerization.

The time dependence of the specific conductivity (κ) of the polymerization systems parallels the course of the polymerization (Fig. 5a). In the systems exhibiting an induction period the specific conductivity is, after an initial decrease due mainly to the dilution, almost constant (Fig. 5b). After the induction period the conductivity decreases proportionally to the increasing conversion. An attempt was made to estimate the value of the dissociation constant of the oxonium salt Ph_3CSbF_6 -monomer from the values of the specific conductivity measured in the polymerization system with $[M]_0 = 3.2 \text{ mol l}^{-1}$, $[\text{Ph}_3\text{CSbF}_6]_0 K_d = 2.5 \cdot 10^{-4} \text{ mol l}^{-1}$, CH_2Cl_2 , 20°C . Before the monomer addition $\kappa = 1.08 \cdot 10^{-5} \Omega^{-1} \text{ cm}^{-1}$, and this value is given by the number of free ions $\text{Ph}_3\text{C}^{(+)}$ and $\text{SbF}_6^{(-)}$. If we use the published¹² value of the dissociation constant of Ph_3CSbF_6 , $K_d = 2.5 \cdot 10^{-4} \text{ mol l}^{-1}$ (CH_2Cl_2 , 20°C), and then calculate the number of free ions in the solution, the value of the equivalent conductivity is 80, in good agreement with the published¹⁵ value 84. After the mono-

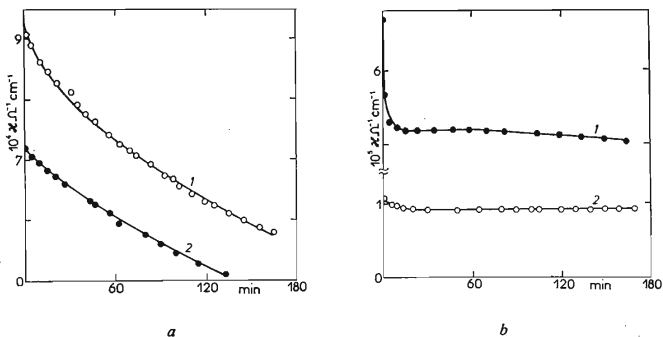


FIG. 5

Time Dependence of Specific Electric Conductivity (κ , $\Omega^{-1} \text{ cm}^{-1}$) during Epichlorohydrine Polymerization ($[M]_0 = 3.2 \text{ mol l}^{-1}$, CH_2Cl_2 , 20°C) Catalyzed by Ph_3CSbF_6 . $[\text{Ph}_3\text{CSbF}_6]_0$ in $10^{-3} \text{ mol l}^{-1}$

a) 1 27.1, 2 18.0; b) 1 2.08, 2 0.17.

mer addition the specific conductivity is $0.95 \cdot 10^{-5} \Omega^{-1} \text{cm}^{-1}$ and this value includes the contribution of the corresponding oxonium ion. The equivalent conductivity of the solution calculated with the use of the value of the dissociation constant K_d for Ph_3CSbF_6 (corrected for the change of the dielectric constant of the system after the monomer addition) is 79. This result shows that the dissociation constant of the oxonium salt is approximately equal to the value of K_d of the triphenylmethyl salt.

After addition of the monomer into the triphenylmethyl salt solutions of $[\text{Ph}_3\text{CSbF}_6] \approx 10^{-2} \text{mol l}^{-1}$ a sharp decrease of the specific conductivity takes place due mainly to the dilution effect. Thereafter, proportionally to the monomer conversion, the specific conductivity slowly and monotonously decreases. After the 100% conversion is reached the conductivity is still quite high and further on it does not change with time (Table II). As the values of the dissociation constants of both the triphenylmethyl salt and the oxonium salt are approximately equal, the decrease of conductivity accompanying the polymerization reaction is caused by an increase of the diameter of conducting particles, by a decrease of the mobility of particles due to an increased viscosity of the medium, and – mainly – by a decrease of the ion concentration due to the termination reaction.

Though it was not possible to measure quantitatively by means of the spectroscopic techniques the decrease of the $\text{Ph}_3\text{C}^{(+)}$ concentration in the reaction mixture at the catalyst concentration $10^{-2} \text{mol l}^{-1}$, measurements in diluted solutions after completing the polymerization showed a very small consumption of $\text{Ph}_3\text{C}^{(+)}$ during the polymerization. Therefore, it may be assumed that in the region of higher catalyst concentrations the initiation rate constant is of the same order of magnitude as k_i measured at $[\text{Ph}_3\text{CSbF}_6]_0 = 10^{-4} \text{mol l}^{-1}$. The polymerization kinetics shows that the increase of the number of active centers with time must be compensated by the termination reaction. The most likely termination reaction in the case of a stable anion as $\text{SbF}_6^{(-)}$ and cyclic ethers is a degrading transfer to the polymer¹⁶.

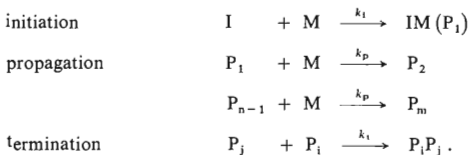
TABLE II

Time Dependence of Specific Electric Conductivity κ and Conversion during Epichlorohydrine (M) Polymerization

Conditions: $[\text{Ph}_3\text{CSbF}_6]_0 = 1.8 \cdot 10^{-2} \text{mol l}^{-1}$; $[\text{M}]_0 = 3.2 \text{mol l}^{-1}$; CH_2Cl_2 , 20°C .

| | | | | | | | |
|--|-----|-----|-----|-----|-----|-------|-------|
| t , min | 0 | 50 | 100 | 200 | 300 | 1 440 | 6 000 |
| $10^6 \kappa$, $\Omega^{-1} \text{cm}^{-1}$ | 497 | 360 | 312 | 281 | 260 | 210 | 197 |
| Conversion, % | — | 20 | 35 | 48 | 55 | 100 | 100 |

A simple kinetic scheme of the epichlorohydrine polymerization initiated by triphenylmethylhexafluoroantimonate (initiator I) includes initiation, propagation, and termination



A mathematical solution of this problem, assuming a negligible consumption of the monomer (M) during the initiation stage in comparison with its consumption during the propagation step, leads to¹⁶

$$\begin{aligned}
 -d \ln [M]_t / dt &= k_p [I]_0 \left\{ 1 - \exp \left(-k_i \int_{[M]_0}^{[M]_t} [M] dt \right) \right\} - \\
 &- k_t \{ [M]_0 \ln [M]_0 / [M]_t - ([M]_0 - [M]_t) \}
 \end{aligned}$$

Average values of k_p and k_t obtained by solving this equation for the particular time intervals using $k_i = 3 \cdot 10^{-6} \text{ mol}^{-1} \text{ l s}^{-1}$ are $9 \cdot 10^{-2} \pm 0.02 \text{ mol}^{-1} \text{ l s}^{-1}$ and $2 \cdot 10^{-4} \pm 0.0001 \text{ mol}^{-1} \text{ l s}^{-1}$, respectively.

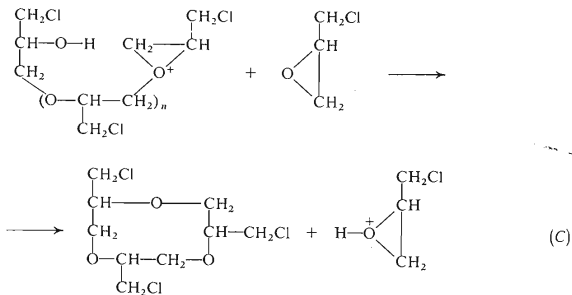
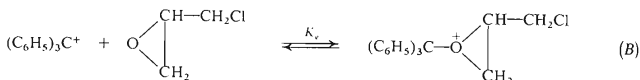
Characterization of Products

Molecular weights of polymers are independent of the triphenylmethyl salt concentration (Table I). The mean polymerization degree lies between 12–14, while the theoretical maximum ought to have much higher values. From the experiments in which a complete consumption of Ph_3CSbF_6 during the polymerization took place one obtains for the propagation reaction rate a value 14 times larger than for the monomer transfer (assuming that each catalyst molecule initiates a growth of one chain). For example, following data were obtained for concentrations $[\text{Ph}_3\text{CSbF}_6]_0 = 1.8 \cdot 10^{-4} \text{ mol l}^{-1}$, $[M]_0 = 3.2 \text{ mol l}^{-1}$: conversion 35%, kinetic chain length $\bar{v} = v_p/v_i = 5740$, measured mean numerical polymerization degree 14.

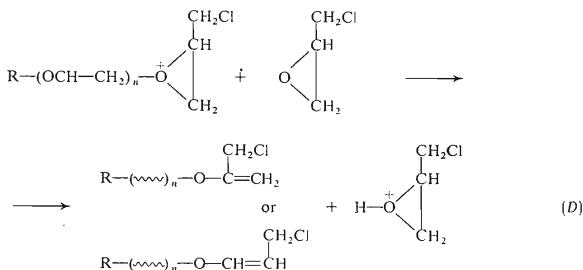
The value 3.4 of the index M_w/M_n calculated from the fractionation data shows a considerable polydispersity of the sample, mainly because of the low-molecular-weight region of the distribution curve. This value is only informative, as it gives a lower limit for the value of the real polydispersity index¹⁷. The distribution curve shown in Fig. 6 exhibits two maxima; the first one in the region of $P_n = 4$ corresponds to a large extent to cyclic products. Similarly as in this study, Entelis³ found a bimodal distribution by the GPC analysis of products of the cationic oligomerization

of epichlorohydrine catalyzed by BF_3 . On the ground of a quantitative determination of OH groups and $\text{C}=\text{O}$ bonds he assumed the formation of cyclic products (mainly of the tetramer) in the region of the first maximum. The polydispersity index, assuming that no cyclization process takes place, would be $M_w/M_n \approx 1.6$.

Infrared spectra of ail oligomers, regardless of the polymerization degree, show the presence of small amounts of OH groups (3400 cm^{-1}), $\text{C}=\text{C}$ (1640 cm^{-1}), and of a negligible amount of $\text{C}=\text{O}$ (1740 cm^{-1}). Neither in infrared nor in NMR spectra triphenylmethyl groups bound to the polymer could be detected. Mass spectrometric analysis showed that the oligomers of $P_n = 4-7$ are pure n -multiples of monomer units. Their structure is cyclic and the cyclization occurs with a proton release:



A pure substance confirming the presence of products of this type was isolated: the cyclic dimer 2,5-dichloromethyldioxane. Its formation in the cationic polymerization of epichlorohydrine was observed as early as in 1950 by Meerwein^{18,19}. The detection of terminal groups OH and $\text{C}=\text{C}$ by means of PMR spectroscopy was not successful ($< 3\%$), as well as an attempt of the H—D exchange in the OH groups and the mass spectrometric detection. Nonetheless, the detection of OH and $\text{C}=\text{C}$ groups by infrared spectroscopy confirms that a certain small amount of linear oligomers is formed (according to (D)), namely of those of a higher molecular weight:



Initiation Mechanism

In the initiation of polymerization of cyclic ethers and acetals two mechanisms are considered which may play a role⁵: a reversible formation of the oxonium ion according to (B) followed by the monomer addition (see (E)), or the hydride ion transfer from the monomer to the triphenylmethyl cation with the formation of triphenylmethane (see (F)). The presence of Ph₃C-groups in the products is characteristic of the former initiation mechanism, while the presence of triphenylmethane in the reaction mixture confirms the latter mechanism.

From the polymerization mixtures terminated by undried methylalcohol triphenylmethane, triphenylmethyl ether, and triphenylcarbinol was successfully isolated and the compounds were identified by means of infrared, NMR, and mass spectrometry. The latter two products are formed in reactions of non-consumed Ph₃CSbF₆ as shown by a blank experiment in the absence of epichlorohydrine. As triphenyl-

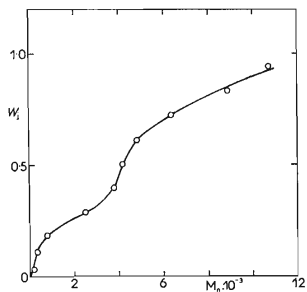


FIG. 6

Integral Distribution Curve of Molecular Weights of Poly(Epichlorohydrine)

Polymerization conditions: $[M]_0 = 3.2 \text{ mol l}^{-1}$, $[\text{Ph}_3\text{CSbF}_6]_0 = 1.7 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$, CH_2Cl_2 , 20°C , reaction time 5 h, conversion 60 %.

methane was extracted by sublimation from a non-terminated reaction mixture, the abstraction of hydride by the triphenylmethyl cation can be regarded as the main initiation mechanism of epichlorohydrine polymerization. The absence (within the framework of detection limits of infrared and NMR spectroscopy) of Ph_3C -groups in the oligomers of epichlorohydrine is not, however, a proof that the initiation by the oxonium ion does not take place at all: a very slow initiation coupled with a very fast transfer of the polymerization chain by the monomer may result in a very low concentration of the fraction of oligomers containing Ph_3C -groups, not detectable by the methods employed. The oxonium ion formed from $\text{Ph}_3\text{C}^{(+)}$ and epichlorohydrine, stabilized by charge delocalization, is able — as shown by Kuntz^{9,10} — to initiate the polymerization of THF or 1,3-dioxolane; however, the initiation rate of the epichlorohydrine polymerization by this particle is evidently much smaller than the initiation

rate by the ion $\text{O}^+ \begin{array}{l} \text{CH}-\text{CH}_2\text{Cl} \\ | \\ \text{CH}_2 \end{array}$.

The question of the co-catalytic effect of trace amounts of water in the initiation of epichlorohydrine polymerization by triphenylmethyl salts was elucidated in a special

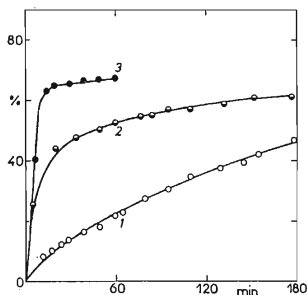


FIG. 7

Influence of Water on Polymerization of Epichlorohydrine (M) Initiated by Ph_3CSbF_6

Conditions: $[\text{M}]_0 = 3.2 \text{ mol l}^{-1}$, $[\text{Ph}_3\text{CSbF}_6]_0 = 1.82 \cdot 10^{-2} \text{ mol l}^{-1}$, CH_2Cl_2 , 20°C ; $[\text{H}_2\text{O}]_0/[\text{Ph}_3\text{C}^{(+)})_0$: 1 0, 2 2, 3 13.

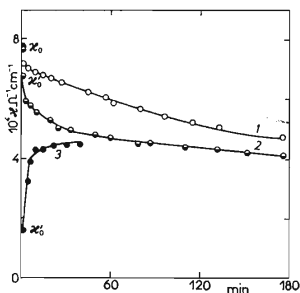
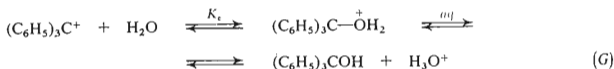
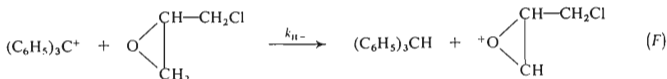
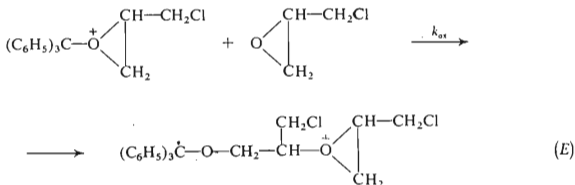


FIG. 8

Time Dependence of Specific Electric Conductivity ($\kappa, \Omega^{-1} \text{ cm}^{-1}$) during Polymerization of Epichlorohydrine (M) with Additions of Water in CH_2Cl_2 at 20°C

$[\text{Ph}_3\text{CSbF}_6]_0 = 1.82 \cdot 10^{-2} \text{ mol l}^{-1}$;
 $[\text{H}_2\text{O}]_0/[\text{Ph}_3\text{C}^{(+)})_0$: 1 0, 2 2, 3 13; κ_0 specific conductivity before water addition, κ'_0 specific conductivity after water addition.

set of experiments. Additions of co-catalytic amounts of water to the polymerization system increased several times the initial polymerization rate (Fig. 7) and decreased the specific electric conductivity (Fig. 8). With the ratio $[\text{H}_2\text{O}]_0/[\text{Ph}_3\text{CSbF}_6]_0 = 13$ a fast drop of κ occurs even before the addition of the monomer; this is because of the formation of hydrolytic products whose built-up can be visually observed. Upon the monomer addition dissolving of the hydrolytic products takes place and the value of κ increases (Fig. 8, curve 3). Water reacts with $\text{Ph}_3\text{C}^{(+)}$ to form the corresponding protonated alcohol and hydroxonium ions according to (G); the value of K_e is high: $K_e = 62 \text{ l mol}^{-1}$, CH_2Cl_2 , 25°C (ref.¹²).



The oxonium ion formed by epichlorohydrine protonation is very reactive. As a result, a larger amount of active centers is formed than in the triphenylmethyl cation initiation; low molecular weights of products correspond to this situation (Table I). However, it follows from the measured induction periods in thoroughly dried polymerization systems that water does not take part as a co-catalyst in the initiation and that the conclusions obtained on the mechanism of epichlorohydrine polymerization are in this respect entirely correct.

REFERENCES

1. Paquin A. M.: *Epoxyverbindungen und Epoxydharze*. Steinkopff, Berlin, 1958.
2. Entelis G., Korovina G. V.: *Makromol. Chem.* **175**, 1253 (1974).
Estrin J. J., Entelis G.: *Vysokomol. Soedin. A* **13**, 1654 (1971).
3. Yamashita J., Tsuda T., Okada M., Imatsuti S.: *J. Polymer Sci. A* **4**, 2121 (1966).
4. Ledwith A.: *Makromol. Chem.* **175**, 1117 (1974).
Ledwith A.: *Advan. Chem.*, Ser. **91**, 317 (1969).
5. Penczek S.: *Makromol. Chem.* **175**, 1217 (1974).
6. Kubisa P., Penczek S.: *Makromol. Chem.* **144**, 169 (1971).
7. Penczek S., Kubisa P.: *Makromol. Chem.* **165**, 121 (1973).
8. Bawn C. E. H., Fitzsimmons C., Ledwith A., Penfold J., Sherington D. C., Weightman J. A.: *Polymer* **12**, 119 (1971).
9. Kuntz I., Melchior M. T.: *J. Polymer Sci. A* **1**, 7 (1959) (1969).
10. Kuntz I.: *Trans. N. Y. Acad. Sci.* **33**, 592 (1971).
11. Švestka M., Matyska B.: *Chem. Listy* **61**, 245 (1967).
12. Slomkowski S. A., Penczek S.: *J. Chem. Soc., Perkin Trans. 2*, 1718 (1974).
13. Gutman V.: *Coordination Chemistry in Non-Aqueous Solutions*. Springer Verlag, Wien 1968.
14. Smith B. J. K., Dodd J. A., Instone A. T., Partridge D. B.: *J. Polymer Sci. B* **5**, 625 (1976).
15. Burns F. W., McCarthy B., O'Connor R. M., Pepper D. C.: *IUPAC International Symposium on Macromolecules, Helsinki 1972*, Preprints Vol. 1—30, 183.
16. Penczek S., Kubisa P.: *Makromol. Chem.* **130**, 186 (1969).
17. Poláček J., Boháčková V., Pokorná Z., Sinkulová E.: *This Journal* **41**, 2510 (1976).
18. Meerwein H., Eisenmenger U., Mathiae H.: *Justus Liebigs Ann. Chem.* **566**, 150 (1950).
19. Tanaka J.: *J. Macromol. Sci. Chem. A* **1**, 1059 (1967).

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