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$TiCl_4$에 의한 Trioxane의 양이온 중합에 있어서 개시 반응기구

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The Initiation Mechanism in the Polymerization of Trioxane with Titanium Tetrachloride

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요 약. 트리옥산을 니트로벤젠 용매중에서 $TiCl_4$로서 중합시킬때 개시 반응기구를 연구하였다. 중합반응속도를 측정한결과 미량의 물이나 메탄올을 첨가하면 반응속도가 급격히 감소하였으며 중합[illegible]을 개시하는 데는 조촉매로서 다른 물질이 필요 없음이 알려졌다.

유전상수 측정결과에 의하면 중합과정중 양성이온이 생기지 않으며 중합계나 개시제 용액의 전기전도도를 측정한 결과 개시 반응은 니트로벤젠 용매중에서 개시제가 등종간 주고 받기반응에 의하여 생긴 $TiCl_3^{\oplus}$ 양이온에 의하여 일어난다는 것이 판명되었다.

ABSTRACT. The initiation mechanism of trioxane polymerization catalyzed by $TiCl_4$ in nitrobenzene was investigated. The kinetic studies revealed that the rate of polymerization was drastically decreased by the addition of a minute amount of water or methanol. A third substance as cocatalyst was not required for the polymerization. Measurements of dielectric constants gave no evidence for the zwitterionic mechanism of the polymerization. The electric conductivity measurements of the polymerization system and the initiator solution showed that the initiation was started by $TiCl_3^{\oplus}$ cation, formed by a disproportionation of the initiator in nitrobenzene.

1. INTRODUCTION

In the cationic polymerizations of vinyl monomers with Lewis acides, a cocatalyst is generally neccessary in order to initiate the polymerizations[1]. However, few authors have investigated the neccessity for a cocatalyst in the ring opening polymerization of heterocyclic monomers with Lewis acids[2~4].

In the studies on the polymerization of trioxane[2,3], it has been found that the rate of polymerization catalyzed with $SnCl_4$ or BF_3-etherate was accelerated by the addition of a minute amount of water, reaching a maximum rate at a definite ratio of water to catalyst. However, when $TiCl_4$ is the catalyst, the rate was drastically decreased by addition of water[2]. The former catalysts require a cocatalyst, whereas a direct initiation without a cocatalyst seemed to occur in the latter case.

It is interest to elucidate the mechanism for the direct initiation of the cationic polymerization, which is quite different from the conventional initiation by cocatalysis. This paper reports the initiation mechanism of trioxane polymerization catalyzed by $TiCl_4$ in nitrobenzene.

2. EXPERIMENTAL

2.1 Purification of Trioxane and Nitrobenzene.

1, 3, 5-trioxane was purified as follows: 1) To 200 g of trioxane, which was purified by distillation, 20 g potassium and 10 g lithium aluminium hydride were added. This mixture was refluxed five days and fractionated over a 50 cm Vigreux column. 2) Benzophenone (30 g) and potassium (10 g) were added to 200 g of trioxane. The mixture was refluxed under N_2-atmosphere for one day and then fractionated over a 50 cm Vigreux column.

Nitrobenzene (1 *l*) was refluxed over P_2O_5(50 g) for five days and fractionated through a 1.5 m helices-packed column. $TiCl_4$ (98 % up, Titanium Co., Leverkusen) was distilled directly in the dried nitrobenzene.

2.2 Measurement of the Water Content in the Monomer Solution by Gas Chromatograpy.

Water, trioxane and nitrobenzene can be seperated on a Poropak Q column (Gas Chromatograph, A-700, Varian-Aerograph with thermal conductivity detector). A water content of 10 ppm in the monomer solution was evaluated with the aid of a calibration curve, which had a linear relationship and passed through the origin. The water content of the trioxane solution in the nitrobenzene (1 mole/*l*) was found to be 37 ppm, dried by method 1, and 30 ppm, purified by method 2, as mentioned above.

2.3 Polymerization

The trioxane solution in nitrobenzene was added to a round bottom flask which had been previously dried by flamming in vacumm and filled with nitrogen gas. The catalyst solution in nitrobenzene was added by a syringe. The polymerization was carried out under N_2-atmosphere. At the end of the polymerization, a mixture of methanol and acetone was added and the polymer was obtained by centrifugation.

2.4 Measurement of Electric Conductivity.

The specific conductivity was measured with a conductivity meter model LBR (Science and Technical Instrument Co. Weilheim).

2.5 Measurement of Dielectric Constant

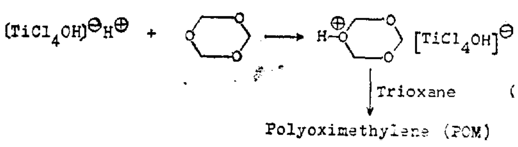
Dielectric constants were measured with a Dipole meter model DMO 1 (Science and Technical Instrument Co.) at a frequency of 2MHz.

3. RESUITS AND DISCUSSION.

3.1 Kinetic Studies of the Polymerization

The kinetic study has been proven to be useful method for the elucidation of cocatalysis mechanisms in cationic polymerization[1]. In the case where a cocatalyst is necessary for cationic polymerization of trioxane with $TiCl_4$, it is expected that 1) the polymerization cannot be started in the absence of a cocatalyst and 2) the rate of polymerization should attain a maximum at a definite ratio between catalyst and cocatalyst. For example, with water as a cocatalyst:

$$TiCl_4 + H_2O \longrightarrow TiCl_4(H_2O) \longrightarrow [TiCl_4OH]^{\ominus}H^{\oplus} \qquad (1)$$



(2)

If the polymerization can be initiated without any cocatalyst, *i.e.*, through a direct initiation between catalyst and monomer, the rate of polymerization should be decreased by the addition of water, since water deactivates the initiator, and it should increase with increasing concentration of initiator.

The conversion of monomer as a function of polymerization time is shown in *Fig.* 1. The polymerization proceeded rapidly for the first few hours and leveled off thereafter, which may be due to either the incorporation of active species into the polymeric crystalls or termination.

Since the rate of conversion during the first few hours is nearly linear, the conversion after one hour of polymerization was taken as a measure of the rate of polymerization. The termination and heterogeneous reaction medium, which become significant at the later stages of polymerization, may be negligible initially.

The rates of polymerization (conversion at one hour) are plotted against the concentrations of water and methanol in *Fig.* 2. The rate of polymerization are drastically decreased by the addition of minute amounts of water and methanol. After injecting the initiator solution, the development of a gas, presumably HCl, was observed. The amount of gas increased with increasing concentration of water in the polymerizing solution, suggesting that $TiCl_4$ might react with water to form $TiOCl_2$, TiO_2 and HCl.

No induction period was observed; the polymerization solution turned turbid immediately after addition of the initiator solution. The turbidity should be associated with the formation af titanium dichloride or titanium dioxide, which were the only insolubee products at the beginning of the polymerization. A decrease in conversion on the addition of methanol is observed, which is smaller in comparison with that by water. The deactivation of catalyst seemed to be more effected by water than by methanol.

Generally, it was assumed that the monohydrate of the metal halide was very active and it could spontaneously initiate the cationic polymerization[1]. Ideally, the maximum conversion could be expected therefore at about equimolar concentrations of water and $TiCl_4$, as was found

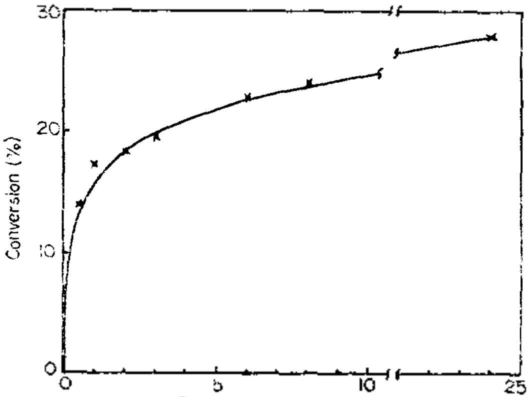


Fig. 1. Conversion as a function of the polymerization time in nitrobenzene at 30 °C; trioxane=9. 15 mole/*l*, $TiCl_4$=0. 03 mole/*l*.

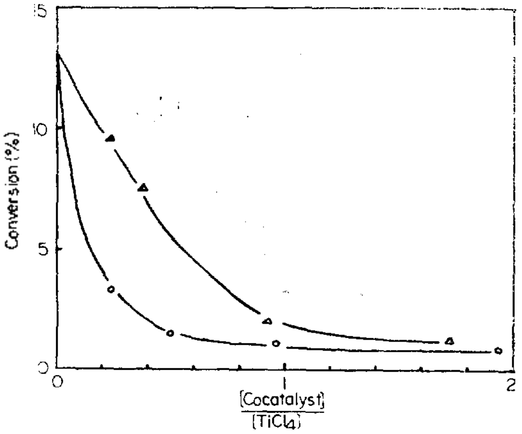


Fig. 2. Polymerization of trioxane (0. 92 mole/*l*) in nitrobenzene at 30 °C with 3. 25 mole % of $TiCl_4$. Conversions after one hour at different concentrations of added water (○) and methanol (△) (mole/mole $TiCl_4$).

Table 1. The optimum mole ratio of cocatalyst to catalyst under various conditions, at which the maximum rate of polymerization was observed.

Monomer	Catalyst	Cocatalyst	Solvent	Temp. (°C)	$\frac{[\text{Cocatalyst}]}{[\text{Catalyst}]}$	Ref.
Styrene	$SnCl_4$	H_2O	Nitrobenzene $+CCl_4$(25 vol%)	25	0.25	5
Styrene	$SnCl_4$	H_2O	Nitrobenzene	0	1	6
Trioxane	BF_3-Etherate	H_2O	Ethylene chloride	—	0.5	3
Trioxane	$SnCl_4$	H_2O	Nitrobenzene	30	1	2
Trioxane	$SnCl_4$	Methanol	Nitrobenzene	30	2	2

in the polymerization of trioxane with $SnCl_4$ in nitrobenzene[2], whereas the ratios for the vinyl polymerization were found to be much lower than one (see *Table* 1). In these experiments, the ratio of water to $TiCl_4$ could not be smaller than 0.03, because the trioxane-nitrobenzene solution, even when purified carefully, contains 35 ppm water. Questions have been raised, as to whether the maximum rate of polymerization could occur at ratios of 0~0.03. The optimum ratios of cocatalyst to initiator, at which the maximum rates of polymerization were observed, are summarized in *Table* 1. Since the ratios are higher than 0.5 in case of trioxane polymerizations, it could scarecely be expected that the ratio in the polymerization of trioxane would occur below 0.03.

The rates of polymerization were measured by increasing the cocnentration of initiator at the two different monomer concentrations (*Fig.* 3). It was shown that the rates increased with the concentration of initiator until ratio $[TiCl_4]/[\text{Trioxane}]=0.07$, after which the conversion diminished. The decrease in conversion at high concentration of initiator can be accounted for by the formation of a high concentration of active species, thus resulting in oligomers, which are soluble in nitrobenzene. The increase in conversion with the concentration of initiator at low catalyst concentration is also consistent with the direct initiation without cocatalyst, since the rate of polymerization in the presence of cocatalyst should be controlled by concentration of cocatalyst according to Eqs. (1) and (2).

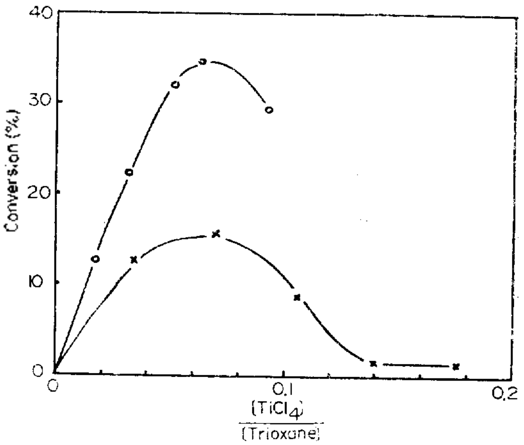
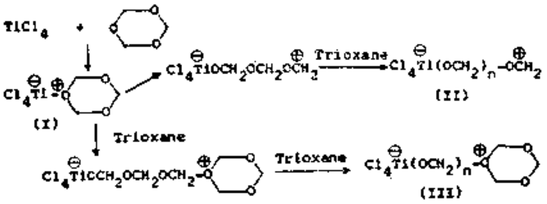


Fig. 3. Conversions after one hour at different concentrations of $TiCl_4$ in the polymerization of trioxane in nitrobenzene at 30 °C with $TiCl_4$; trioxane=2.45 mole/l (○) and 0.92 mole/l (×).

3.2 Possible Mechanisms for a Direct Initiation.

Kinetic studies indicate that the polymerization occur through a direct initiation between catalyst and monomer without any participation of a third substance (cocatalyst). The following two mechanisms might be feasible for the case of a direct initiation of the polymerization.

Initiation by Formation of Zwitterions. Reaction between $TiCl_4$ and trioxane might result in complex (I). A heterogeneous ring opening of the trioxane molecules would lead to the formation of zwitterions, the cationic ends being either a carbonium or *tert*-oxonium ion, from which the propagation proceeds.

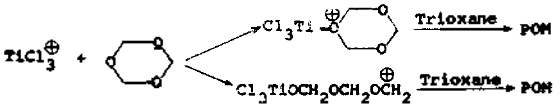


(3)

This type of mechanism has been proposed in the cationic polymerization of cyclic ethers with Lewis acids *i. e.*, trioxane with BF_3[7] and $AlCl_3$[8], dioxolane with BF_3[9] and tetrahydrofuran with BF_3[10].

Initiation by $TiCl_3^{\oplus}$-Ions. It has been found that the disproportionation of $TiCl_4$ occurs in ethylene chloride according to Eq. (4).[11] The initiation of polymerization may be achieved by the attack of titanium trichloride cation on trioxane. The initiation by $TiCl_3^{\oplus}$-ion has been found in several polymerization systems *i. e.*, isoprene with $TiCl_4$ in nitrobenzene,[12] isoprene with $C_2H_5AlCl_2$–$TiCl_4$[13] and isobutylene with $AlBr_3$–$TiCl_4$ in heptane[14].

$$2TiCl_4 \rightleftharpoons [TiCl_3^{\oplus}TiCl_5^{\ominus}] \rightleftharpoons TiCl_3^{\oplus} + TiCl_5^{\ominus} \qquad (4)$$



(5)

3.3 Measurements of Electric Conductivity

The measurements of electric conductivity have been shown to be useful for the investigation of ionic polymerizations. However, they have also had some disadvantages: 1) the nature of the ions, which cause the electric conductivity in the polymerization system, cannot be determined. Various kinds of ions may be formed in the polymerization initiated by metal halide, 2) the conductivity is associated only with free ions, but not with ion pairs, which participate significantly in the propagation of ionic polymerizations.

The solution of $TiCl_4$ in nitrobenzene shows a substantial conductivity, which increases with the concentration of $TiCl_4$ (*Fig.* 4). At 0.1 mole/*l* $TiCl_4$, the specific conductivity (λ) was found to be 2.8×10^{-5} ohm^{-1}cm^{-1}. This conductivity might be due to the ionization of $TiCl_4$ according to Eq. (4). The dissociation constant (K) of $TiCl_4$ can be evaluated by the Eq. (6)[11,15].

$$\lambda = A_T\sqrt{K}[TiCl_4] \qquad (6)$$

Where λ is the specific conductivity, $[TiCl_4]$ is the concentration at equilibrium and A_T is a constant dependent on viscosity of solvent, ion radii and ion charges. By consideration of these factors, A_T was estimated to be of the order of 100 for both ions in nitrobenzene[16]. K was found to be of the order of 10^{-6} and the degree of dissociation was found to be 10^{-3} by applying the initial concentration of $TiCl_4$ in the Eq. (6), since dissociation occurs only to a small extent.

The changes in λ as a function of water concentration at constant concentration of $TiCl_4$ at 25 °C are shown in *Fig.* 5. The conductivity increases proportionally with the concentration of water, and reaches a maximum at the ratio

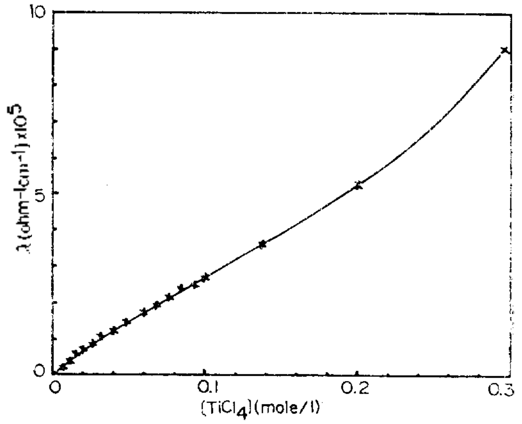


Fig. 4. Specific conductivity (λ) as a function of $TiCl_4$ concentration in nitrobenzene at 25 °C.

$[H_2O]/[TiCl_4]=0.6$, which is contrary to the formation of monohydrate according to Eq. (1). The conductivity, however, is related to the free ions formed in the system and the maximum conductivity could not be ascribed only to the monohydrate.

If the initiation occured by the cocatalysis *via* Eq. (1), the maximum rate of polymerization would be expected to coincide with the maximum conductivity, which is, however, not the case (*Fig.* 2). This observation indicates that the start of the polymerization would not occur by cocatalysis but by a direct initiation.

By extrapolating the linear part of the curve to zero water concentration, λ was found to be 1.2×10^{-4} ohm^{-1} cm^{-1}, the specific conductivity of the $TiCl_4$ solution seems to be due mainly to the disproportionation of $TiCl_4$ (Eq. 4). Assuming that λ is due only to the reaction of water and $TiCl_4$, the initial linear part of the curve was extrapolated to the abscissa. The water content of the $TiCl_4$ solution (100 mmole/*l*) was found to be higher by a factor of 30 than that of the $TiCl_4$ solution (2.8 mmole/*l*) measured by gas chromatography. This result gives additional evidence for the ionization of $TiCl_4$ (Eq. 4).

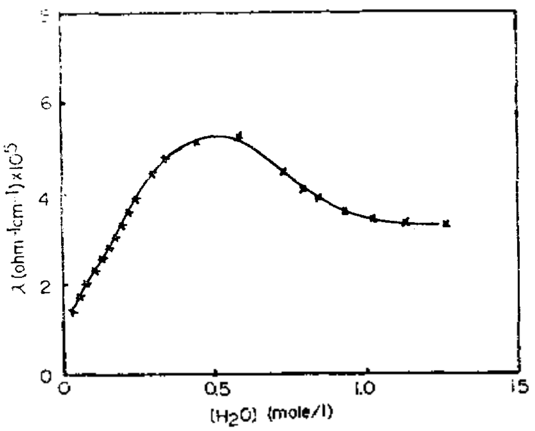
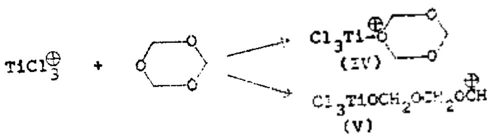


Fig. 5. The changes in specific conductivity as a function of water concentration at constant concentration of $TiCl_4$ (0.7 mole/*l*) in nitrobenzene at 25 °C.

The changes in λ were measured during the polymerization (*Fig.* 6). Immediately after the addition of the initiator solution, λ was found to be 4.38×10^{-6}ohm^{-1}cm^{-1} (*Fig.* 6). Compared with the conductivity of $TiCl_4$ solution (*Fig.* 4), this drastic decrease in λ might be due to the reaction between $TiCl_3^{\oplus}$ ion and trioxane. The velocity of the ions (IV) and (V) formed should be much lower than that of the $TiCl_3^{\oplus}$-ion, resulting in a lower specific conductivity.



(7)

3.4 Measurement of the Dielectic Constants (D.C.)

The macrozwitterions can have several conformations in solution. If the chain ends form ion pairs, either the polymer molecules are cyclized to form loops or intermolecular aggregation of several zwitterionic polymer molecules may occur at high polymer concentrations. At low polymer concentration in a highly polar solvent, separation of the ion pairs could result to form free ions. In the case that macrozwitterions occur as free ions in random coils, they should have very high dipole moments. The increase in the D.C. of the polymerization

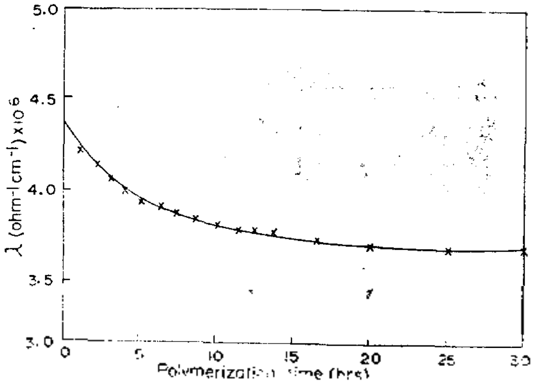


Fig. 6. Specific conductivity (λ) during the polymerization of trioxane at 25 °C in nitrobenzene; trioxane = 0.91 mole/*l*, $TiCl_4$ = 0.064 mole/*l*.

solution which was observed in the polymerization of β-propiolactone with triethylamine in dimethylsulfoxide, has verified that the polymerization proceeds through a zwitterionic mechanism.[17]

In order to prove the formation of a trioxane-TiCl$_4$ complex (I) in nitrobenzene, the D.C. of the solution containing equimolar concentration of TiCl$_4$ and trioxane was measured (*Fig.* 7). Since the dipole moments of trioxane (μ=2.18 D) and TiCl$_4$ (μ=0 D) are lower than that of solvent (nitrobenze, μ=3.9 D), addition of both compounds lowers the D.C. of the solution as expected. After sufficient reaction time, a decrease in the D.C. of the equimolar TiCl$_4$-trioxane solution was observed, hence evidence for the formation of complex (I) could not be obtained. This result implies that the reaction (4, 5) should occur rather than the formation of complex (I).

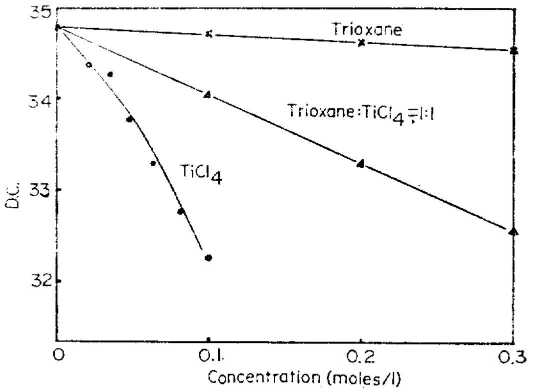


Fig. 7. Dielectric constants of nitrobenzene solution containing trioxane(×), TiCl$_4$(○) and trioxane-TiCl$_4$ equimolar mixture (△) at 25 °C.

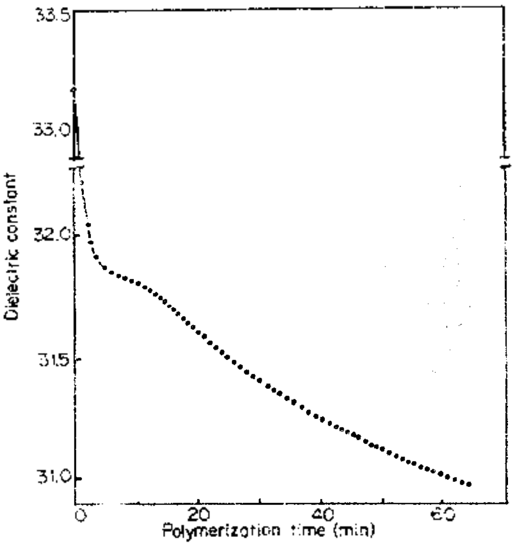


Fig. 8. Changes in D.C. during the polymerization of trioxane with TiCl$_4$ at 25°C: trioxane=1.2 mole/*l* and TiCl$_4$=0.1 mole/*l*.

Trioxane was polymerized with TiCl$_4$ as catalyst in the cell of dipole meter and the D.C. was determined by continuous capacity measurements (*Fig.* 8). The D.C. decreased repidly as the polymerization proceeded. The dipole moment of trioxane is nearly twice that of the monomeric unit in polyoxymethylene. The decrease in the D.C. during the polymerization is attributed to the ring opening of the trioxane. In this investigations, no evidence for the formation of zwitterions during the polymerization could be obtained.

4. CONCLUSION

The rate of polymerization decreased drastically by the addition of a minute amount of water or methanol. Measurements of electric conductivity showed that the highest conductivity was observed at a ratio of [H$_2$O]/TiCl$_4$]=0.6. This ratio is about one order of magnitude at least higher than the ratio, at which the maximum rate of polymerization was measured. These results lead to the conclusion that the cocatalysis with water seems to be improbable.

During the polymerization, the D.C. of polymerizing solution is decreased. Hence, there are no evidence for the formation of zwitterions by a direct initiation and for the presence of macrozwitterions having random coils with free ion end groups.

The solution of $TiCl_4$ in nitrobenzene without trioxane showed disproportionation of $TiCl_4$ into $TiCl_3^{\oplus}$ and $TiCl_5^{\ominus}$ ions. The electric conductivity decreased dramatically at the beginning of the polymerization, which may be due to the direct reaction between $TiCl_3^{\oplus}$ and trioxane.

Based on these results, we may conclude that the initiation is started by the $TiCl_3^{\oplus}$ cation and that the polymerization proceeds *via* Eq. (5), the active species being either *tert*-oxonium or carbonium ions.

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