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Cationic Initiation by Thionyl Chloride/Titanium Tetrachloride. I. Model Reactions

Hung Anh Nguyen^a; Lajos Balogh^b; Tibor Kelen^b; Sándor Holly^c; János Borbély^b

^a Visiting scientist. Laboratoire de Synthèse Macromoléculaire, Université P. et M. Curie, Paris, France ^b

Kossuth Lajos University Institute of Applied Chemistry, Debrecen, Hungary ^c Central Research

Institute of Chemistry of the Hungarian Academy of Science, Budapest, Hungary

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CATIONIC INITIATION BY THIONYL CHLORIDE/TITANIUM TETRACHLORIDE. I. MODEL REACTIONS

HUNG ANH NGUYEN,[†] LAJOS BALOGH, TIBOR KELEN,*
SÁNDOR HOLLY,[‡] and JÁNOS BORBÉLY

Kossuth Lajos University
Institute of Applied Chemistry
4010 Debrecen, Hungary

ABSTRACT

The thionyl chloride/titanium tetrachloride combination is found to be a good cationic initiating system for olefin polymerizations. This paper deals with reactions of tetraphenylethylene (TPE) and 1,1-diphenylethylene (DPE) as models for aromatic monomers, and of 2,3-dimethyl-2-butene (DMB) and 2-methyl-2-butene (MB) as models for aliphatic monomers. Results of FT-IR, ¹³C-NMR, and elemental analyses show that, in the case of TPE, DPE, and DMB, the



main products are symmetric sulfoxide derivatives, R-S-R, where R is a monomer or dimer, depending on the extent of steric hindrance in the starting monomer. With MB (and also with isobutylene) the reaction stops after the cationation step, indicating the effect of the formed allylic-like structure. The ionic character of the system has been shown by conductivity measurements.

[†]Visiting scientist. Permanent address: Laboratoire de Synthèse Macromoléculaire, Université P. et M. Curie, 4 Place Jussieu, 75005 Paris, France.

[‡]Central Research Institute of Chemistry of the Hungarian Academy of Science, POB 17, 1525 Budapest, Hungary.

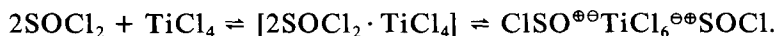
INTRODUCTION

Searching for new initiating systems of olefin cationic polymerizations, we previously found that a class of compounds, i.e., the oxychlorides, can be used as initiators. The compounds studied in this respect are phosphorus oxychloride (POCl_3), vanadyl chloride (VOCl_3), thionyl chloride (SOCl_2), chromyl chloride (CrO_2Cl_2), and phosgene (COCl_2) [1-9].

Generally, these reactants were used alone, and the results varied with the monomers used. Thus, CrO_2Cl_2 polymerizes isobutyl vinyl ether [8] but POCl_3 or SOCl_2 [4-7] does not. SOCl_2 is known to be a potent initiator for the polymerization of *N*-vinylcarbazole [5, 7] but not for styrene. No explanation has been given for why this monomer does not polymerize.

For this reason we thought that it would be interesting to examine activation of the oxychlorides by combining them with coinitiators. The initiation of isobutylene and styrene polymerizations by the combined use of phosgene with Lewis acids was a successful experiment [9]. We found that the combination of SOCl_2 with aluminum chloride or titanium tetrachloride initiates the polymerization of styrene (St). Preliminary results have been presented [10, 11].

According to Spandau et al. [12], SOCl_2 and most of the Lewis acids form complexes which can dissociate into ionic species. Thus, in the case of TiCl_4 , they assume a proportion of 2:1, i.e.,



In order to elucidate the mechanism of the initiation step, we carried out model reactions for which we selected tetraphenylethylene (TPE) and 1,1-diphenylethylene (DPE) as models for styrene, and 2,3-dimethyl-2-butene (DMB) and 2-methyl-2-butene (MB) as models for isobutylene (IB). We used the $\text{SOCl}_2/\text{TiCl}_4$ combination in CH_2Cl_2 solution at -70°C .

EXPERIMENTAL

The vacuum line technique was used for this study.

TPE was recrystallized from toluene solution. DPE, DMB, and MB were purified and dried by vacuum distillation from CaCl_2 before use.

SOCl_2 and TiCl_4 were twice distilled before use. The initiator solution (I) was a 1:2 mixture of $\text{SOCl}_2:\text{TiCl}_4$ in CH_2Cl_2 (the TiCl_4 concentration was 1 mol/L). The ratio 1:2 was chosen to prevent an excess of TiCl_4

(which could polymerize St by direct initiation) and to render bifunctionality of the initiating species possible.

The reactions were carried out as follows. The monomer solution (M) was introduced into an all-glass reactor, equipped with a magnetic stirrer. After cooling to -70°C , the initiator solution was added. After 30 min at -70°C , the reaction was stopped by introducing a small amount of CH_3OH . The solution was washed several times with water, dried over CaCl_2 , and filtered. The solvent was removed by evaporation.

The polymerization process was followed by conductivity measurement with equipment designed and constructed in our laboratory [13].

The final product was analyzed by ^{13}C and ^1H NMR (Bruker 200 SY, CDCl_3 solvent, TMS reference), by FT-IR (Nicolet 170 SX, KBr pellet or C_6H_6 solution), and by elemental analysis.

RESULTS AND DISCUSSION

The results obtained with aromatic and aliphatic vinyl compounds (monomers and models) are shown in Table 1.

TABLE 1. Reaction of Various Monomers with $\text{SOCl}_2/\text{TiCl}_4$ in $\text{CH}_2\text{Cl}_2^{\text{a}}$

	[M], mol/L	[I], mol/L	Conversion, %	Elemental analysis, % ^b				
				C	H	S	Cl	O ^c
TPE	0.12	0.12	3	92.8	6.1	1.7	1.5	
DPE	0.28	0.05	95	86.9	6.1	4.5	0	2.5
				<u>87.7</u>	<u>6.0</u>	<u>4.2</u>	<u>0</u>	<u>2.1</u>
St	1	0.01	95	—	—	—	—	—
DMB	1	0.1	20	48.7	7.0	12.7	27.8	3.8
				<u>50.1</u>	<u>8.6</u>	<u>11.2</u>	<u>24.7</u>	<u>5.4</u>
MB	1	0.1	0	—	—	—	—	—
IB	1	0.01	0	—	—	—	—	—

^aT = -70°C , 30 min reaction time.

^bUnderlined: calculated data.

^cPercentage obtained by subtraction from 100.

1. Aromatic Vinyl Compounds: TPE, DPE, St

The first analytical results obtained by ^{13}C NMR and by dispersive IR seemed to show that TPE does not react with the $\text{SOCl}_2/\text{TiCl}_4$ system since the spectra of TPE and of TPE + $\text{SOCl}_2/\text{TiCl}_4$ were found to be identical.

However, elemental analysis indicated the presence of sulfur and chlorine in the product of the TPE + $\text{SOCl}_2/\text{TiCl}_4$ reaction. For this reason, measurements by FT-IR seemed to be necessary in order to improve the S/N ratio and to subtract the TPE spectrum from the TPE + $\text{SOCl}_2/\text{TiCl}_4$ one. Figure 1 shows the difference spectra of the product of the TPE + $\text{SOCl}_2/\text{TiCl}_4$ reaction and TPE. We found the following characteristic bands: 1) $-\text{OH}$ at 3511 and 3412 cm^{-1} , corresponding to tertiary and aromatic $\text{C}-\text{OH}$ bonds; 2) >S=O at 1090 cm^{-1} of $\text{R}_2\text{S=O}$ and at 1016 cm^{-1} of $\text{R}\text{>S=O}$ in intramolecular H-bridges between >S=O and aromatic $\text{C}-\text{OH}$ groups [14]; 3) disubstituted phenyl rings in *para* and *ortho* positions at 850 and 730 cm^{-1} ; 4) monosubstituted phenyl rings at 1442 and 755 cm^{-1} ; 5) $\text{>C}-\text{Cl}$ tertiary chlorine at 590 cm^{-1} .

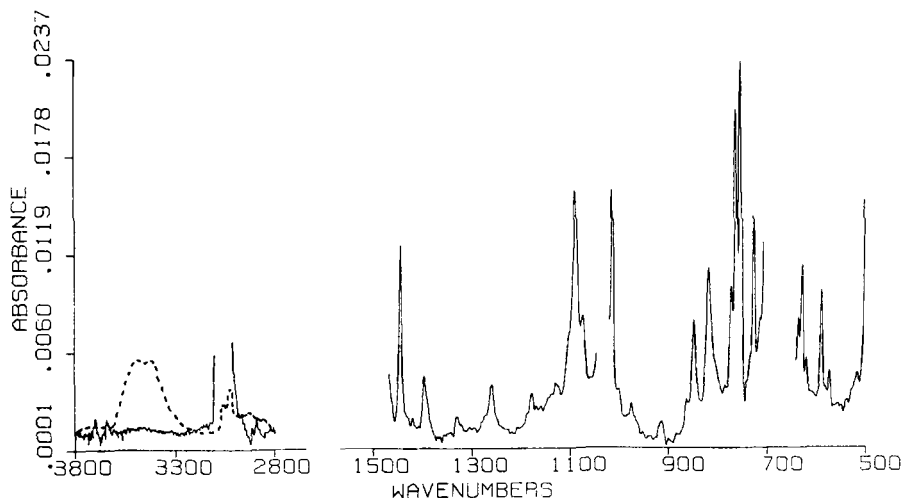
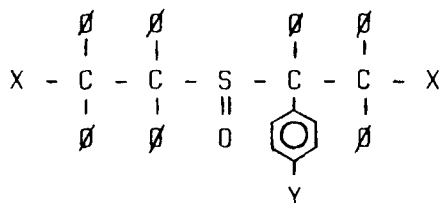


FIG. 1. IR difference spectra of TPE and TPE with $\text{SOCl}_2/\text{TiCl}_4$ in benzene (continuous line) and in KBr (dotted line). The reaction was carried out at -70°C in CH_2Cl_2 .

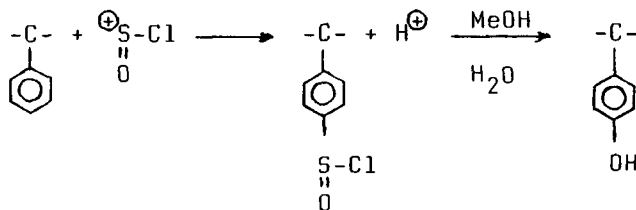
These results, together with composition calculations, make a mixture of products probable which possess the same main skeleton of the bis(tetraphenylethyl)sulfoxide type:



where $X = \text{OH}$ or Cl , $Y = \text{OH}$.

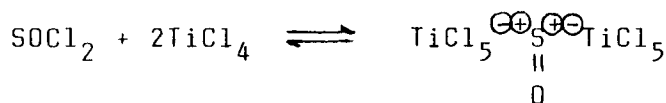
The existence of Cl end groups may be explained, e.g., by a "transfer to the gegenion" type reaction. The tertiary OH groups might have originated by the stopping reaction with MeOH .

The presence of OH in *para* and *ortho* positions is probably due to the high concentration of the initiator (see Table 1), so that a Friedel-Crafts reaction may occur as a side reaction, giving rise to chlorosulfoxyl pendent groups, which are sensitive to hydrolysis, e.g.,



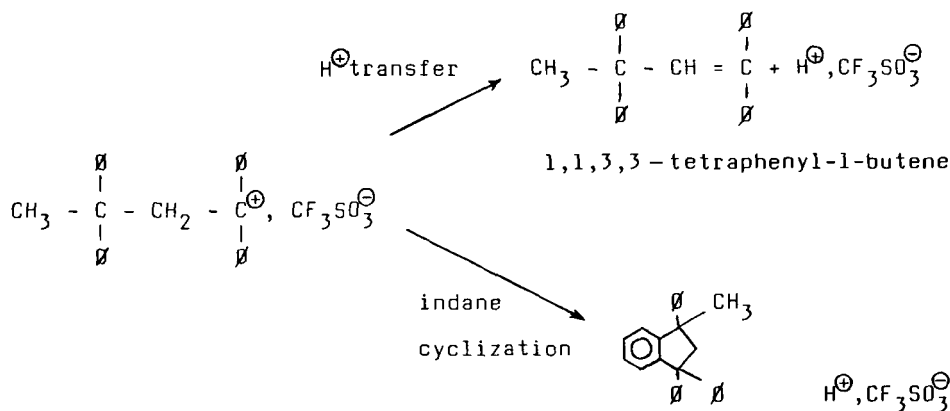
We do not know the exact amount of the disubstituted phenyl rings and of the OH and Cl end groups per molecule. The elemental analysis results are not accurate enough (see Table 1) to calculate exact compositions.

However, in spite of the low conversion and uncertain analysis, we can point out the paramount fact of the formation of disubstituted sulfoxide products. This supports an ionic mechanism:

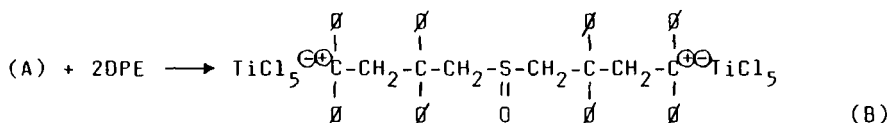
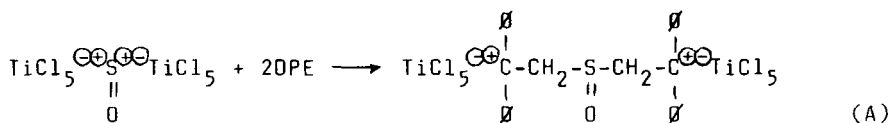


Contrary to Spandau's proposition, we assume a 1:2 ratio of SOCl_2 : TiCl_4 .

In the case of DPE, the steric hindrance is less important than with TPE; thus the conversion is higher. Sigwalt et al. [15–17] studied the cationic dimerization of DPE in detail. They found that, depending on experimental conditions and the initiating systems used, DPE easily reacts and forms either a linear head-to-tail or a cyclic dimer or a mixture of both. Thus, with triflic acid as initiator, the following dimers can be obtained from termination reactions:



On the base of these results, we assume that the sulfoxonium dication can react with DPE to give a dimer dication (A) and/or a tetramer dication (B).



The ^{13}C -NMR spectrum indicates a mixture of several products. Attempts to fractionate, separate, or purify these products failed. With the help of the "attached-proton test" (APT) technique applied in the 100–160 ppm region, we can identify, beside the remaining monomer, three products possessing the following structures:

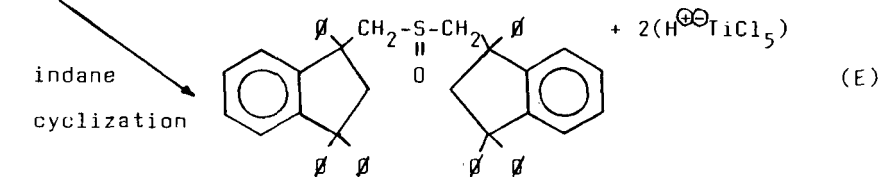
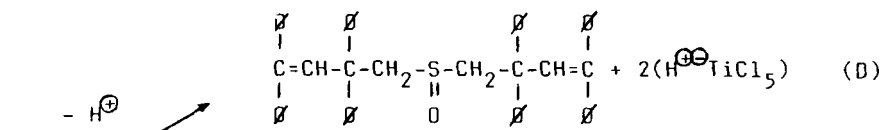
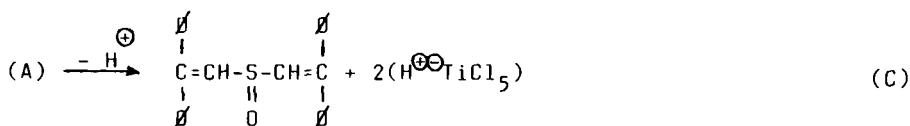


Figure 2 shows the APT ^{13}C -NMR spectrum of the products of the DPE + $\text{SOCl}_2/\text{TiCl}_4$ reaction. Based on this spectrum, using the assignments proposed by Masure for DPE dimers [18] and by Nguyen for indene and indane derivatives [19], we identified the main products as (D) and (E). The presence of the indane derivative (E) is a proof of the existence of the tetramer dication (B). A calculation of the composition, assuming that only (D) and (E) isomers are present, gives values (underlined in Table 1) which are in good agreement with the experimental data.

The ionic character of the initiating species is well demonstrated by conductivity measurements. Thus, the conductivity of the DPE solution showed an instant increase when the $\text{SOCl}_2/\text{TiCl}_4$ solution was introduced (details will be published elsewhere [13]).

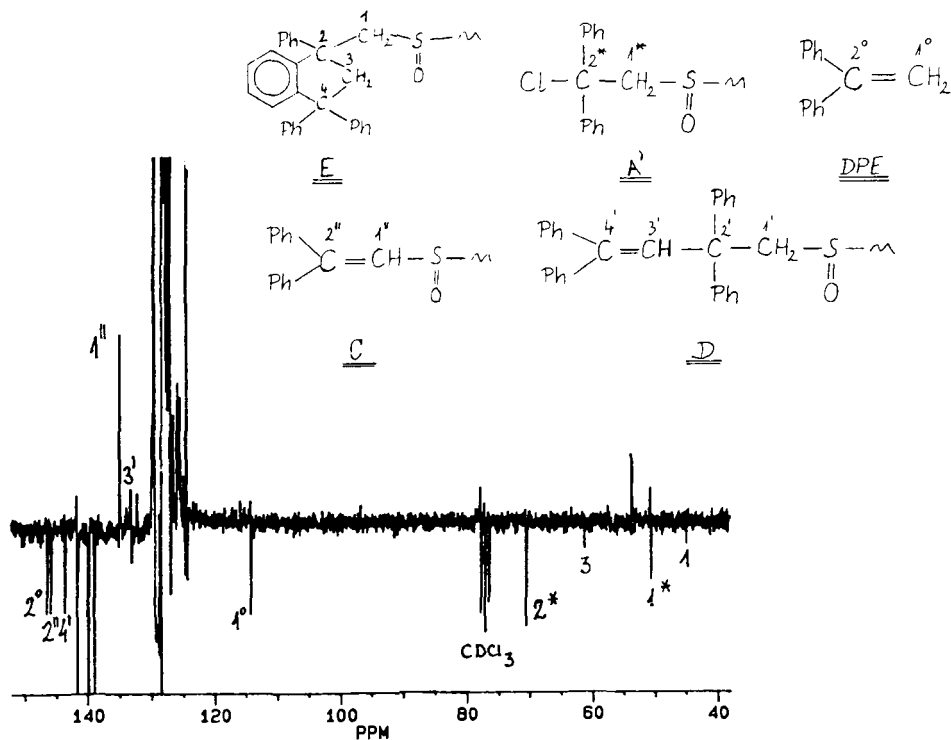


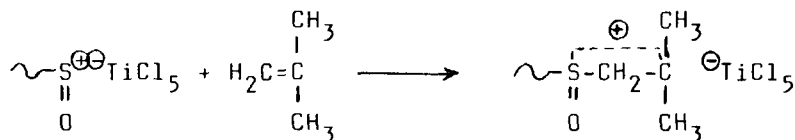
FIG. 2. APT ^{13}C -NMR spectrum (CDCl₃) of the products of the reaction of DPE with SOCl₂/TiCl₄ at -70°C in CH₂Cl₂ solution (A': same as A with Cl end group).

In the case of styrene we found that the combination of thionyl chloride with titanium chloride is an efficient initiator. Details of these polymerizations will be published as Part II of this work [20].

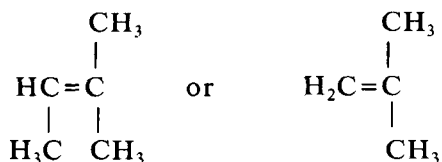
2. Aliphatic Vinyl Monomers: DMB, MB, IB

Several experiments were carried out with MB and IB using the SOCl₂/TiCl₄ initiating system, but no polymers or oligomers were found. However, conductivity measurements always showed a large jump when monomer and initiator solutions were brought together. This phenomenon may be explained by the effect of the allylic-like structure formed: the

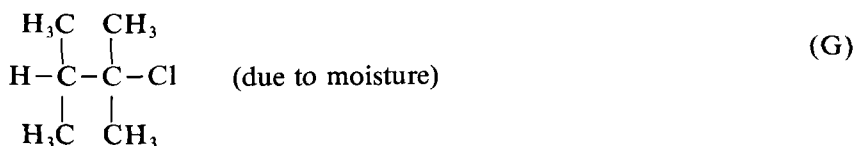
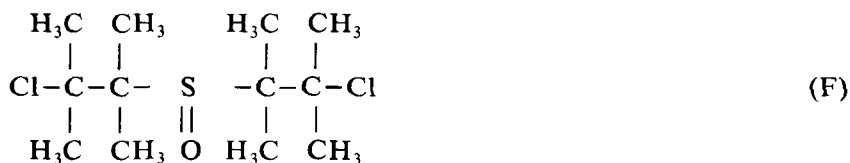
built-in S=O group activates the hydrogen attached to the neighboring C-atom ("allyl activation"). The result of this activation is that the positive charge becomes distributed, and the reactivity of the cation decreases:



This "stabilization by allyl activation" occurs only when the attacked C-atom of the double bond is linked to H atom(s) like in MB or IB:



In contrast, the species formed by the reaction of SOCl₂/TiCl₄ with DMB (no H is linked to the attacked C atom of the double bond) react easier, but steric hindrance prevents attainment of high conversion. Essentially two products can be identified on the basis of the APT ¹³C-NMR spectrum of the reaction products (Fig. 3):



A calculation of the composition on the assumption that only (F) is present (underlined in Table 1) indicates that (F) is the main product.

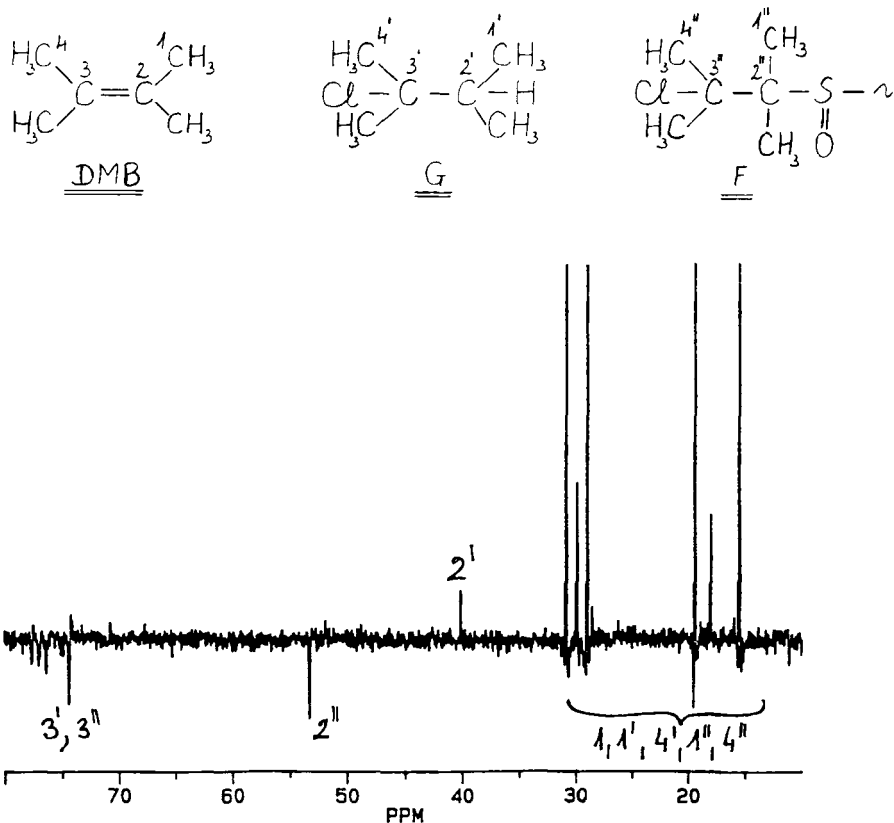


FIG. 3. APT ¹³C-NMR spectrum (CDCl₃) of the products of the reaction of DMB with SOCl₂/TiCl₄ at -70°C in CH₂Cl₂ solution (A': same as A with Cl end group).

Conductimetric measurement shows a sudden increase when SOCl₂/TiCl₄ solution is added to DMB solution, again indicating the ionic character of the initiating species.

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