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Polymerization of Isobutylene by Glow-Discharge and UV Light in the Presence of $TiCl_4$

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Introduction

In the course of our fundamental studies on the mechanism of isobutylene polymerization need arose for highest purity monomer, $TiCl_4$ and solvents e.g., methylene chloride and hexane. During the preparation of these materials in high-vacuum it was observed that glow-discharge and UV light in the presence of $TiCl_4$ readily induced the polymerization of isobutylene. These observations were further explored to determine the scope of the phenomena and to provide an explanation for them. This communication concerns some initial experiments; a full account will be given in forthcoming publications (KENNEDY, DIEM 1978).

Experimental

All experiments including material transfers, dosage, etc. were carried out in an all glass (Teflon stopcocks) assembly under high vacuum (better than $\sim 10^{-5}$ Torr). Details of the vacuum line and purifications will be described elsewhere (KENNEDY, DIEM 1978).

The polymerization reactor was a 25 ml graduate cylinder (7740 Pyrex) onto which was spliced at the top a 0.2 ml calibrated glass tube for $TiCl_4$. First 0.01 to 0.025 ml $TiCl_4$ was distilled into the side tube and cooled to -78^0. Then 3.0 to 12 ml isobutylene and solvent were condensed into the reactor cooled with liquid N_2. The charged assembly was sealed off and removed from the vacuum line. At the start of the glow-discharge experiment the coolant was removed from the $TiCl_4$ side-tube, and while the $TiCl_4$ was distilling into the reactor, 15-25 seconds bursts

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of glow-discharge were applied to the vapor phase in the reactor. The glow-discharge was produced by a BD-20 model Electro-Technic high frequency generator ("Tesla coil"). As soon as the Tesla coil was activated a brown precipitate ($TiCl_3$) started to form on the walls of the reactor. Finally the liquid N_2 coolant was removed and the system thawed by applying a Dry-Ice-methanol bath.

For the UV experiment the charging of the ingredients into the reactor and side tube was essentially the same. After the reactor was sealed off from the vacuum line and heated to the desired temperature, the system was submerged in a quartz Dewar flask with circulating methanol as a coolant and irradiated for 30 minutes with a 450W medium pressure Hanovia Hg lamp from a distance of 10 cm.

The reaction was terminated by methanol, the precipitated polymers redissolved in hexane and reprecipitated with methanol (twice), finally the products were dried in vacuo at 30^0.

Polyisobutylene (PIB) molecular weights were determined by gel permeation chromatography using THF solutions and a Waters Assoc. Model 440 instrument equipped with 5 columns (calibrated for PIB). The molecular weight distributions were monomodal. Due to uncertainties in the PIB calibration curve, $\bar{M}_W$ data are accurate to $\pm$ 10%.

Results and Discussion

In the course of a high-vacuum distillation of $TiCl_4$ during which a routine leakage check was performed using a Tesla coil, a rapid decomposition of $TiCl_4$ to a brown precipitate ($TiCl_3$) was observed. This glow-discharge induced reduction of $TiCl_4$ was very similar to the UV light induced decomposition of $TiCl_4$ observed earlier in our laboratory (KENNEDY, DIEM 1978). These observations were followed up by experiments designed to elucidate the phenomena. Table I summarizes the results.

First it was determined that even with highly purified $TiCl_4$ in the dark (equipment wrapped with aluminum foil) limited amount of PIB was produced. Conversions remain > 20% even under the most favorable conditions i.e., neat monomer at -78^0. In polar or nonpolar solvents at higher temperatures (BIDDULPH,

TABLE I

Polymerization of Isobutene by Glow Discharge and UV Light in the Presence of $TiCl_4$

Exp.	$TiCl_4$ $M \times 10^3$	Isobutylene M	Solvent	Temp. ^0C	Yield %	$\overline{M}_w \times 10^{-3}$
Experiments under darkness						
D-1	6.10	1.52	CH_2Cl_2	-78	8.6	540
D-2	5.72	1.49	CH_2Cl_2	-40	9.0	93
D-3	5.60	1.57	Hexane	-78	11.0	340
D-4	5.30	1.50	Hexane	-40	3.0	-
D-5	5.20	12.34	Bulk	-78	22.1	630
D-Cl*	2.52	1.52	Hexane	-78	16.3	150
Glow-Discharge Experiments						
G-0	-	12.38	Bulk	-78	0.0	-
G-1	6.7	1.50	Ch_2Cl_2	-78	45.0	125
G-3	5.4	1.50	Hexane	-78	17.0	95
G-4	5.0	1.61	Hexane	-40	11.0	37
G-5	6.2	12.34	Bulk	-78	61.0	350
Experiments with UV Light						
L-01	-	12.38	Bulk	-78	0.0	-
L-02**	-	1.75	CH_2Cl_2	-78	0.0	-
L-1	4.6	1.52	CH_2Cl_2	-78	54.2	890
L-3	4.2	1.48	Hexane	-78	21.4	710
L-4	5.1	1.50	Hexane	-40	23.6	190
L-5	6.5	12.34	Bulk	-78	94.6	very broad bimodal

* Cl_2 was used as an initiator, $TiCl_4/Cl_2 = 1.1$

** Radiation time 120 minutes

PLESCH, 1965), conversions are < 10%. Past extensive experience acquired in these laboratories and a variety of reports by others (CHERADAME, SIGWALT 1970, VAIRON, SIGWALT 1971) have shown that a complete absence of polymerization (i.e., 0% conversion) cannot be obtained in "stopping experiments" with isobutylene/$TiCl_4$ systems even after most arduous purification efforts. Evidently, traces of unscavengable cationogenic impurities remain strongly sorbed on surfaces, or diffuse out of the bulk of glass vessels during baking of the apparatus, etc. The first set of five "control runs" in Table I (D1 to D5) give conversions obtained under various conditions. The data reflect the averages of two experiments with ± 2%.

Under essentially the same conditions as with experiments D1 to D5 except under the influence of glow-discharge (Expts. G-0 to G-5) conversions increase by a factor of 2-3. In these experiments $TiCl_3$ precipitates during glow-discharge which may be due to the reduction of $TiCl_4$ in the vapor phase. The reproducibility of these duplicate experiments was ± 4%. In the absence of $TiCl_4$, glow-discharge does not produce polymer (G-0 replicate experiments).

Similarly, Expts. L-1 to L-5 show that UV light in the presence of $TiCl_4$ even more markedly increases conversions; in the absence of $TiCl_4$ polymerization does not occur (L-01, L-02).

Consistently, throughout these experiments highest conversions were obtained with mulk monomer, and polar solvent and low temperatures also tended to increase conversions (compare D, G and L experiments). Temperature does not seem to affect conversions significantly obtained under glow-discharge or UV light.

As expected, the lowering of temperature and the use of polar solvent tend to increase the molecular weight. Interestingly, while glow-discharge produces lower molecular weights, UV light yields somewhat higher molecular weight products than the "controls" (D-1 to D-5). The reason(s) for this is unknown.

It is proposed that the polymerization of isobutylene by glow-discharge or UV light in the presence of $TiCl_4$ is due to the reduction of $TiCl_4$ to $TiCl_3$ plus $Cl^\cdot$; the chlorine radical may recombine to Cl_2 or, in the presence of an organic compound, it may rapidly abstract an $H^{\cdot}$ to produce HCl which in combination with $TiCl_4$ gives rise to the very active cationic initiator system $HCl/TiCl_4$:

$$
\begin{aligned}
&TiCl_4 \xleftrightarrow{h\nu \text{ or glow-discharge}} TiCl_3 + Cl^{\cdot} \\
&Cl^{\cdot} + -\overset{|}{\underset{|}{C}}H \longrightarrow HCl + -\overset{|}{\underset{|}{C}}^{\cdot} \\
&HCl + TiCl_4 \longrightarrow H^{\oplus}\ TiCl_5^{\ominus} \\
&H^{\oplus} + \text{olefin} \longrightarrow \text{polymer}
\end{aligned}
$$

Direct and circumstantial evidences substantiate this hypothesis. Thus we found that pure $TiCl_4$ starts to decompose in the vapor phase within seconds under the effect of glow-discharge and produces a brown precipitate ($TiCl_3$). Similar experiments using UV light gave almost identical results. These observations are not too surprising in view of the very low (26 ± 2 kcal/mole) Ti-Cl bond energy (EDWARDS, FRANKLIN 1971). In the presence of an organic compound, be this a solvent or isobutylene molecule, $TiCl_4$ under the influence of UV light of glow-discharge may produce HCl and $TiCl_3$. ESR studies showed a signal at $g = 1.95$ which developed upon UV-radiation and was assigned to the unpaired electron on $TiCl_3$. While we failed to obtain an ESR signal for organic radicals, chlorinated products probably arising by radical chlorination in UV-irradiated hexane/Cl_2/$TiCl_4$ systems have been detected.

That $HCl/TiCl_4$ is an efficient initiator system for olefin polymerization has been well documented (BOURNE BRANCHU et al. 1969, CHERADAME 1969), and that $Cl_2/TiCl_4$ is also an active combination has been shown in an experiment (D-Cl) in which 16.3% conversion was obtained even at a low (2.52×10^{-3}M) $TiCl_4$ concentration in the dark.

Our results and proposition are different from those of (MAREK, TOMAN 1972, MAREK 1977) who have studied visible light induced polymerization of isobutylene; the reason(s) for this discrepancy will be discussed later (KENNEDY, DIEM 1978).

In sum, it is proposed that the very low isobutylene conversions obtained in the presence of highly purified $TiCl_4$ can be markedly increased by applying glow-discharge or UV radiation to the systems and that the active initiator is the $HCl/TiCl_4$ (or perhaps

$Cl_2/TiCl_4$) combination. The cationogen HCl is produced in situ by the decomposition of $TiCl_4$ to $TiCl_3$ plus $Cl^{\cdot}$, where the latter either recombines to Cl_2 or, in the presence of an organic molecule, gives rise to HCl.

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