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The Effect of Light on the Cationic Polymerisation of Isobutene by $TiCl_4$
Some Comments on Two Papers by Kennedy and Diem

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SUMMARY: Several objections are raised regarding the mechanistic conclusions drawn by Kennedy and Diem in two recent papers dealing with the effect of light on the polymerisation of isobutene and its dimer by titanium tetrachloride. In particular, the process of photogenerated cocatalysis and the attempted explanation of condensation polymerisation by that mechanism are critically discussed.

Kennedy and Diem (1,2) recenty reported that daylight, laboratory diffuse light and light from a medium-pressure mercury arc promote the photolysis of $TiCl_4$, both undiluted and in methylene chloride or hexane solutions. They postulated that the homolytic fission of a Ti-Cl bond is the primary step of this photodecomposition which leads to the precipitation of $TiCl_3$ (and some $TiCl_2$) and the formation of chlorine and/or hydrogen chloride. Although similar observations had already been made (3-5), these authors decided to study their implications on two typical cationic polymerisation systems.

In a first series of experiments with isobutene in bulk and in CH_2Cl_2 or hexane solutions, Kennedy and Diem (1) compared the catalytic activity of $TiCl_4$ in the dark and with irradiation from a 450 W medium-pressure Hg arc (30 min. at about 10 cm from the reactor). Under all the conditions tested, the runs in the presence of uv light gave higher, but not complete, yields, an effect which was attributed to the in situ photogeneration of cocatalytic species (HCl and/or Cl_2) which accelerated the polymerisation process. In a second publication (2), the same authors described another comparative test in which illumination came from a "daylight bulb" placed at an unspecified distance from the reactor. They observed that while the limiting prepolymerisation yield was essentially the same in the dark and with one-hour illumination, in CH_2Cl_2 at -52°C, the subsequent polymerisation by condensation (6) gave a much higher yield under illumination (no DP's reported). Note that, due to a misprint, the $TiCl_4$ concentrations given for these experiments (Table 1, ref.2) should be two orders of magnitude lower. Kennedy and Diem (2) speculated that these results might offer a rationalisation of the intriguing phenomenon of polymerisation by condensation discovered more than a decade ago by Cheradame and Sigwalt (6).

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They argued that vapour-phase photolysis of $TiCl_4$ during the distillation of the volatile components after prepolymerisation gives rise to some HCl which acts as a cocatalyst for the reinitiation of polymerisation upon condensation in the collecting vessel. In the same paper (Table 3, ref.2) the dimerisation of 2,4,4-trimethylpentene-1 by very high concentrations of $TiCl_4$ was also studied as a function of the nature and intensity of irradiation. The yield of dimer was found to be high in the run conducted in darkness and to increase little with all forms of irradiation used.

We wish to make the following comments on the above observations and speculations:

- While it seems well established that the uv photolysis of $TiCl_4$ produces $TiCl_3$, the overall mechanism of this process remains to be ascertained and probably depends on the specific conditions of the photolysis, viz. solvent, $TiCl_4$ concentration, wavelength, etc. Diem and Kennedy did not search for any product other than $TiCl_3$ and their speculations about HCl and/or Cl_2 formation must await direct experimental verification. Note in this context that the photolysis of $TiCl_4$ cannot be induced by "visible light" (ref.2, p.1368), since this compound is totally transparent from 400 to 800 nm, unless impure. Obviously, its decomposition by daylight and "visible" lamps is due to the near-uv emission components of these sources.

- Even if HCl and/or Cl_2 were indeed obtained in the photolysis of $TiCl_4$ in CH_2Cl_2, hexane or isobutene, as claimed by Kennedy and Diem (1), it remains to be proved that these substances are effective cocatalysts for the polymerisation of isobutene in the specific conditions used in that work (Table 1, ref.1). Hydrogen chloride is only a weak cocatalyst in the system isobutene-$TiCl_4$-CH_2Cl_2 at -70°C but not at -30°C (7). It has also been shown to be inactivein the similar systems isobutene-$TiCl_4$ -hexane (8) and -heptane (9), and is most probably inactive in the absence of a solvent. As for chlorine, the only information available is the test carried out by Kennedy and Diem (Table 1, ref.1) which, contrary to the authors' conclusions, suggests to us that this compound is not a cocatalyst, at least in hexane. Indeed, an increase in polymer yield from 11% (no chlorine) to 16.3% (chlorine added to give $[TiCl_4] / [Cl_2] = 1.1$) can hardly be taken as evidence of cocatalytic activity, even if the $TiCl_4$ concentration in the second run was about a half of that used in the first. These considerations cast serious doubts as to the validity of the generalised mechanism proposed by Kennedy and Diem (1).

- Our main concern focusses on the attempted explanation of the phenomenon of polymerisation by condensation (2). If one-hour illumination was insufficient to produce any meaningful increase in the prepolymerisation yield with respect to the experiment conducted in the dark, the claim that the same weak source could become photolytically active upon $TiCl_4$ in the vapour phase seems untenable. The authors state (2) that it took about 2.5 minutes for the volatile components of the quiescent prepolymerised mixture to distil into the second vessel. This implies a residence time of a few seconds at the most for any $TiCl_4$ molecule in the vapour phase. During this short exposure to the weak illumination of a "daylight bulb" it cannot be conceived that these molecules could suffer a photolytic feat (i.e. formation of HCl with the solvent) which they failed to undergo after a whole hour illumination of the solution containing all the $TiCl_4$. A further piece of evidence reported but not discussed by Kennedy and Diem goes against their interpretation. In Fig.6 of their second paper (2) it is shown that $TiCl_3$ formation from the photolysis of $TiCl_4$ solutions ($\geqslant$ 1 M) with a strong uv source occurs with an induction period of at least 10 minutes. In the condensation experiments the uv intensity was very much lower ("daylight bulb"), the actual $TiCl_4$ concentration in the vapour phase was several orders of magnitude smaller and the exposure time was no more than a few seconds for each $TiCl_4$ molecule. If no detectable photolysis occurred in 10 minutes of drastic irradiation of a concentrated solution, it cannot be possibly claimed that any photodecomposition would accompany the distillation in the mild conditions used. In fact, the daylight bulb was such a weak source that it failed to produce any cocatalyst during one hour illumination of the prepolymerising solution.

- The sensitivity of $TiCl_4$ solutions to fairly long exposures to daylight is well known. Plesch (5) discussed its possible implications to cationic polymerisation in 1972 after pointing out that Puxeddu had first reported it in 1929 (3). According to Plesch's experience (4,5) solutions of $TiCl_4$ in hexane were stable for weeks in a laboratory situated in a dark basement, i.e. illuminated artificially, but showed some $TiCl_3$ precipitation within a day when exposed to a south-facing window. Cheradame and Sigwalt (10) observed similar phenomena for CH_2Cl_2 solutions. The reports of Kennedy and Diem are also similar (2), but the time required for $TiCl_3$ to appear after exposure to daylight is alternatively said to be hours (p.1360) or days (p.1368). It should be noted that if a cocatalyst such as HCl and/or Cl_2 were produced by a moderate illumination of $TiCl_4$ solutions, no reproducibility would be expected in polymerisations using this initiator. All past experience shows that this is not the case. Among the condensation polymerisations reported by Cheradame and Sigwalt (6), one was carried out in the absence of light. Kennedy and Diem (2) quoted it, but argued that some residual illumination might have caused the high polymer yield obtained. We wish to point out that in this experiment, as in those conducted by Kennedy and Diem, darkness was guaranteed by working at night, the only light available being artificial street illumination diffusing into the laboratory. In view of the considerations developed above, we are confident that under such tenuous illumination, the possibility of $TiCl_4$ photolysis during the distillation of the volatile components can be entirely ruled out. Therefore, the fact that this experiment gave a yield similar to those of obtained under normal laboratory light (6) excludes the possibility that the phenomenon of polymerisation by condensation of isobutene be due to the photodecomposition of $TiCl_4$ in the vapour phase. It must also be noted that several experiments of this type (10) were conducted in daylight but using a condensation vessel internally coated with a sodium mirror. Since moreover this vessel was plunged into a dewar, the amount of laboratory light reaching the reagents' vapours must have been extremely low. Despite this, all those experiments gave once again high yields of poly(isobutene) upon condensation.

- It remains to be explained why in the work reported by Kennedy and Diem (2) the condensation experiment with light (2 runs, Table 1) gave higher yields than that carried out in the dark (1 run, Table 1). The single control experiment conducted in the dark by these authors gave a surprisingly low yield compared with previously reported data (6,11,12). It is well known that reproducibility in this extremely delicate context is difficult to achieve and that occasional strong yield variations are not uncommon (6,11). Sigwalt's group recently reported some relevant observations concerning condensation experiments with the system 1,1-diphenylethylene -$TiCl_4$ -CH_2Cl_2 (13). When the reactants were condensed simultaneously from the quiescent solutions, the yield of carbenium ions was very high, but if they were condensed one after the other, negligible or extremely low amounts of active species were formed. Thus, simultaneous condensation of monomer and initiator seems to be an important requirement for the efficiency of this type of polymerisation. The large difference in vapour pressure between $TiCl_4$ and 1,1-diphenylethylene allowed the clear observation of this phenomenology, but similar features had already been noticed with isobutene (10,11), although to a lesser degree.It is also likely that the condensation temperature might play an important role in determining the extent of polymerisation. We think that one or several of the specific features enumerated above might have been responsible for the low yield obtained by Kennedy and Diem in their single control experiments. We prefer this interpretation to one based on light-enhanced yields arising from the photoproduction of a cocatalyst. Since we have shown that this reaction cannot take place in the vapour phase during distillation, such an interpretation would imply that the cocatalyst is formed in the liquid phase during illumination of the prepolymerising mixture and that for some unknown reason its action is impeded until distillation takes place. This complicated hypothesis could in principle explain the behaviour of these systems but we feel that it lacks reasonable experimental or mechanistic support.

- Gandini and Cheradame (14) recently put forward a general interpretation of the phenomenon of polymerisation by condensation based on direct initiation by the Lewis acid in competition with deactivation due to the homoconjugation of counterions with the initiator. The fact that Kennedy and Diem could not reduce the yield of 2,4,4-trimethylpentene-1 dimer in reactions conducted in the dark with high $TiCl_4$ concentrations even after repeated and thorough purification procedures (2) suggests to us that direct initiation and not residual cocatalytic impurities played an important role in that system.

In conclusion, three major objections can be raised to the two papers under discussion (1,2): (i) the mechanism of $TiCl_4$ photolysis was not fully established, but partly inferred; (ii) the general scheme of photogenerated cocatalysis is in conflict with both previous experience and some of the results reported in these very studies; (iii) the attempted photochemical explanation of the phenomenon of polymerisation by condensation is questionable.

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