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UV ENHANCEMENT OF SURFACE CATALYTIC POLYMERIZATION OF ETHYLENE

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ABSTRACT

The polymerization of ethylene on surfaces sequentially dosed with TiCl_4 and trimethylaluminum was studied by Fourier transform infrared spectroscopy. The polymer film was observed *in situ* as a function of time and under the influence of 254-nm cw radiation. The rate of polymerization and the saturation thickness of the polyethylene are strongly dependent on the order of dosing and the partial pressures of the reactants that form the catalyst. UV enhancement of polymerization was demonstrated to occur through two separate photochemical channels: gas-phase photolysis of the reactants and solid-phase chemical transformation of a noncatalytic thin film.

INTRODUCTION

The UV photodeposition of a thin film of a catalyst is among the more complex photoprocesses from a molecular and structural standpoint. In earlier studies [1,2] it was shown that the 257-nm photolysis of a gaseous mixture of TiCl_4 and trimethylaluminum (TMA) can form an organometallic thin film which, upon subsequent exposure to ethylene (C_2H_4) vapor induces catalytic polymerization at room temperature. This thin film was shown to behave similarly to a Ziegler-Natta catalyst [3-6].

In this paper, we describe an investigation of the mechanisms whereby UV irradiation enhances the catalytic activity of a film formed by dosing surfaces with TiCl_4 and TMA. The study was performed *in situ* with Fourier transform infrared (FTIR) spectroscopy with and without UV stimulation. FTIR spectroscopy, if used in conjunction with an internally reflected element (IRE) can be a powerful surface sensitive technique which allows for the investigation of very thin films on the IRE. It is demonstrated that gas-phase photolysis of TiCl_4 and TMA, as well as solid-state photochemistry contribute to the formation of a catalyst film, which can induce polymerization of ethylene.

EXPERIMENTAL

The experimental setup consists of a vacuum-tight stainless steel cell placed in an FTIR spectrometer, and connected to a gas handling and a pumping system. Pumping is performed with a

mechanical pump to a base pressure ~ 10 mTorr. The IRE and a UV-grade fused silica flat serve as two opposing sides of the cell. UV radiation at 254 nm from a low-pressure mercury lamp is introduced to the cell through the fused silica window.

The experimental procedure consists of sequential dosing of the IRE with TiCl_4 and TMA, and then exposing it to C_2H_4 . Each dosing stage is followed by pumping. The UV lamp is turned on and off at selected times during the experiment. Any polymerization on the surface of the IRE is monitored *in situ* through the absorption spectrum of the growing thin film. A typical example of the polymer spectrum and its temporal evolution is shown in Fig. 1. The sharp double peak at 2851 and 2919 cm^{-1} represents the C-H symmetric and antisymmetric stretching frequencies of polyethylene, respectively [7], and is the signature of a polymer film growing on the surface of the IRE. The procedure of sequential dosing of reactants to form the catalyst is in contrast with the co-dosing in the earlier work [1,2]. It enables the isolation of the effects of several chemical and photochemical processes which would otherwise take place simultaneously.

RESULTS

The thin film formed on the IRE by the sequential dosing described above, has catalytic properties even in the absence of UV irradiation. Its catalytic activity, as determined by polymer growth, strongly depends on experimental conditions. In particular, the order of dosing plays a dramatic role on the formation of the catalyst. If the first dosant is TMA, no subsequent polymerization is seen without UV, even at the highest dosing pressures used in our studies (Fig. 2). When the first dosant is TiCl_4 , however, a catalyst is indeed formed on the surface, as evidenced by polymer growth when the IRE is exposed to C_2H_4 vapor. The initial rate of polymerization and the saturation thickness of the polymeric thin film are complex functions of dosing pressures and pressure ratios, as shown in Fig. 2. In general, the higher the dosing pressures the more pronounced the polymerizing effects of the metalorganic thin film.

UV irradiation at 254 nm can enhance polymer formation, if it is applied at the appropriate stage in the sequence dose-pump-dose-pump-polymerize. Figure 3 shows two such instances. In the first case, TiCl_4 at a pressure of 2 Torr is added to the cell followed by TMA at 9 Torr. UV is turned on during TMA dosing, and in an independent experiment during TiCl_4 dosing. The presence of UV during TMA dosing has no effect, whereas the rate of polymerization of ethylene is considerably enhanced when the UV is on during TiCl_4 dosing (Fig. 3, curves (a) and (b)). In the second case, the role of the UV is studied when dosing with TMA occurs before the dosing with TiCl_4 . As mentioned above, no polymerization without UV takes place in this case.

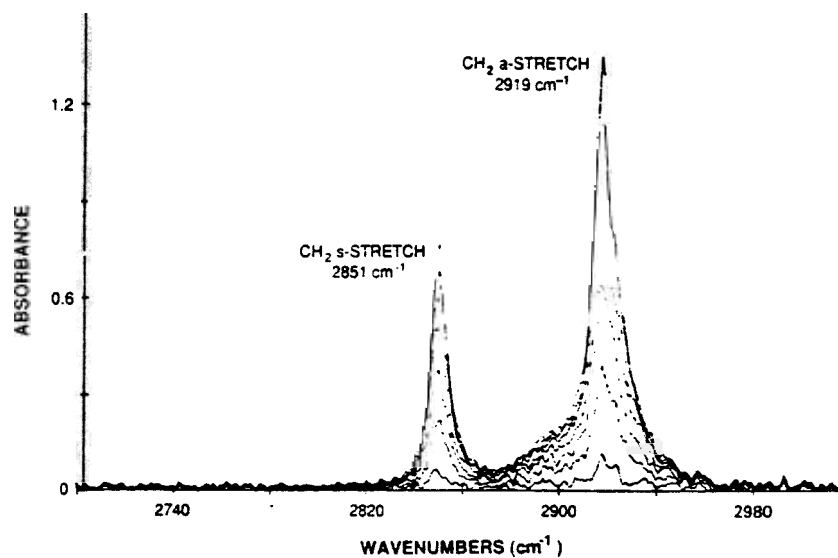


Fig. 1 Representative IR absorption spectra in the 2700- to 3020-cm⁻¹ range taken at 10-min intervals. The double peaks at 2851 and 2919 cm⁻¹ indicate the presence of polyethylene on the IRE surface. The growth of the polymer film is manifested by the increasing amplitude of these peaks. From independent measurements, an absorbance value of 1.0 correlates with a film thickness of 0.45 μm .

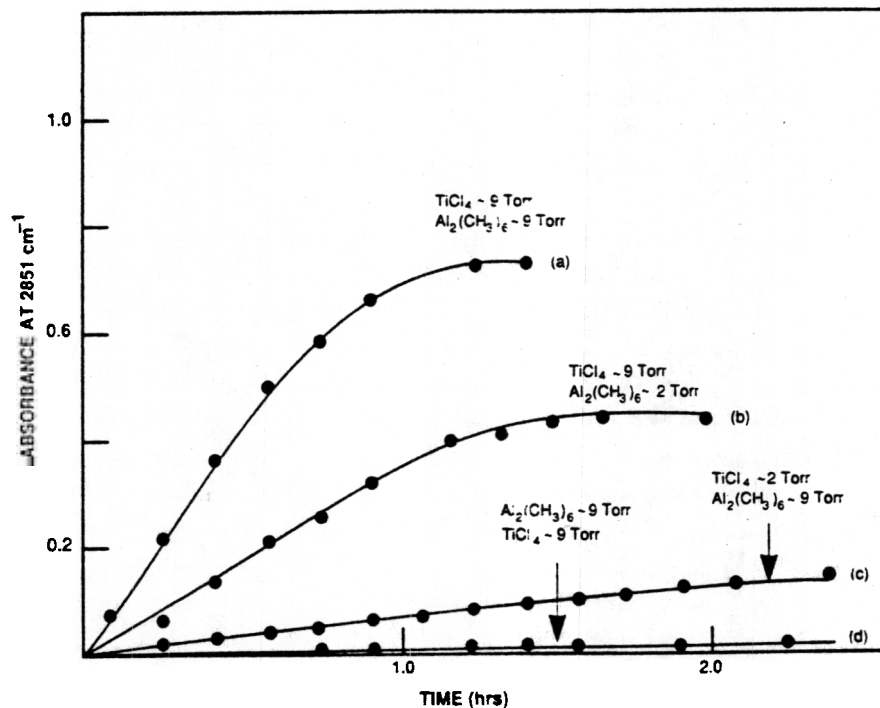
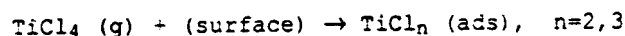


Fig. 2 The growth of polyethylene as a function of time for various different experimental conditions without the presence of UV. Curves (a)-(c) represent the growth when TiCl_4 was the first dosant whereas curve (d) indicates the growth when TMA was the first dosant.

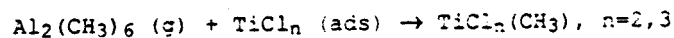
The UV is turned on during the presence of ethylene in the chamber, that is after the formation of a thin film. As gaseous ethylene does not absorb at 254 nm, any effect on the polymerization must occur due to photochemistry of the film. As seen in curve (c) of Fig. 3, polymerization does occur after the UV is turned on; this indicates UV enhanced surface effects. Further experiments where the UV is turned on during TMA and $TiCl_4$ dosing shows similar effects as observed earlier, i.e., there is no enhancement if the UV was turned on during TMA dosing but there is significant enhancement if the UV is turned on during $TiCl_4$ dosing.

DISCUSSION

The experimental observations presented above are interpreted within accepted models of Ziegler-Natta type catalysts and the photochemical properties of the precursors $TiCl_4$ and TMA. Specifically, UV enhancement of polymerization can occur via two separate channels: gas-phase photolysis of $TiCl_4$ (absorption cross section $\sim 5 \times 10^{-19} \text{ cm}^2$ at 254 nm), and solid state photochemistry of a titanium chloromethyl thin film. Because the effects studied here are partly heterogeneous reactions, information on the chemical nature of any adsorbates is also of importance. Therefore we observed the spectrum of the adsorbed species following $TiCl_4$ dosing, but before exposure to TMA. The characteristic Ti-Cl stretch frequency of gaseous $TiCl_4$, around 500 cm^{-1} , is reduced by $\sim 20 \text{ cm}^{-1}$ in the adsorbate. We interpret this result as indicative of partial dechlorination [8,9], possibly as a result of chemical reactions with surface contaminants such as residual water:



The addition of gaseous TMA to this adsorbate probably yields a titanium compound of the form shown below.



The compound indicated in Eq. (2) has been shown to be a catalyst by Gray et al. [6] and thus polymerization takes place as shown in Fig. 2, curves (a)-(c). The enhancement of catalyst formation by UV irradiation during $TiCl_4$ dosing (compare Fig. 3, curves (a) and (b)), is interpreted as a result of photolytic dechlorination of gaseous $TiCl_4$, and the formation of additional $TiCl_2$ and $TiCl_3$ on the surface. The absence of any noticeable UV enhancement during TMA dosing is similarly understood as the result of negligible photochemical decomposition of TMA vapor ($\sigma < 5 \times 10^{-21} \text{ cm}^2$).

When dosing with TMA occurs first, TMA is stripped of methyl radicals and an unsaturated aluminum compound resides on the surface [10,11]:

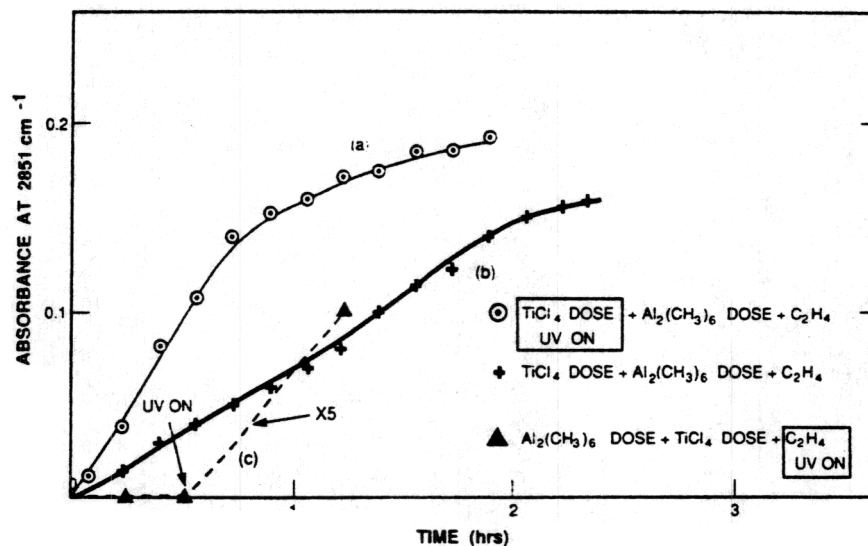
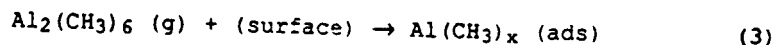
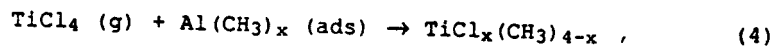


Fig. 3 The effects of UV on polymer growth. Curves (a) and (b) represent the growth with and without UV on during TiCl_4 dosing, respectively. Curve (c) shows the formation of the polymer in the case when dosing by TMA was first. Here, the UV was off for the first 0.5 hrs, during which no polymerization was observed; the lamp was then turned on (see arrow), and growth of the polymer film was noted.



Upon exposure of this adsorbate to TiCl_4 , a surface Ti compound may be formed, in which the Ti has fully saturated bonds, and which therefore does not have catalytic properties as evidenced by the absence of polymer formation in Fig. 2 curve (d):



with $x = 1-3$. In the presence of UV that has been turned on after the formation of this non-catalyst, a solid-phase photochemical reaction apparently takes place, which results in the formation of a catalytically active, coordinatively unsaturated Ti compound, and UV enhanced surface polymerization takes place (Fig. 3, curve (c)).

SUMMARY

Polymerization of ethylene due to catalytic action of a thin film formed by sequential dosing of TiCl_4 and TMA was observed with and without UV radiation. Catalytic activity was shown to depend strongly on the order of dosing and gas pressures. UV enhancement of the rate of polymerization was seen to occur through gas phase decomposition of TiCl_4 and by surface photochemistry of a non-catalytic film. However, UV irradiation of gaseous or adsorbed TMA alone had no effect upon the subsequent activity of the film.

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