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Ethylene Polymerisation with New Catalysts: Et_2AlCl-Organotitanium Compounds

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Summary

A brief kinetic study is reported of the polymerisation of ethylene catalysed by four aluminium-titanium chloro-organic complexes, three of which are new. These systems proved efficient both in terms of polymerisation rate and of the linearity of the high polymers obtained. A comparison is made with previous work in this field.

Introduction

The use of soluble coordination catalysts for the polymerisation of ethylene and other olefins has been the subject of many studies essentially aimed at a better understanding of the mechanism by which linear and stereoregular macromolecules are formed (HENRICI-OLIVE and OLIVE, 1969). Most of these studies involved the classical combination of an alkylaluminiumchloride with dicyclopentadienyltitaniumdichloride (Cp_2TiCl_2), although some other organotitanium compounds have also been tested (HENRICI-OLIVE and OLIVE, 1967; WATERS and MORTIMER, 1972). The recent synthesis and characterisation of several new dicyclopentadienyltitanium derivatives (TIROUFLET et al., 1973; LE MOIGNE et al., 1973) prompted us to carry out a study of their efficiency in the polymerisation of ethylene, when coupled with diethylaluminiumchloride (Et_2AlCl). In order to have a reference system to which the new results could be related, we also carried out polymerisations with the well-known catalyst pair, Et_2AlCl - Cp_2TiCl_2.

Experimental

Et_2AlCl (Alfa Inorganics) was purified following Zakharkin and Khorlina's method (1960) and distilled into breakable phials which were then sealed off under nitrogen. Solutions of this compound in dry toluene were made up shortly before use in a nitrogen glove box. The following dicyclopentadienyltitanium derivatives were used as second catalyst: -dichloride, naphthoxychloride ($Cp_2TiONaphtCl$), -di(orthoisopropyl, paramathylphenoxy) ($Cp_2Ti(OPh)_2$) and -triphenylsiloxychloride ($Cp_2TiOSiPh_3Cl$). They were synthesised in Prof. Tirouflet's laboratory at Dijon University (TIROUFLET et al., 1973; LE MOIGNE et al., 1973) and stored and handled under nitrogen in a glove box. Ethylene (Air Liquide, high purity) was taken without further treatment from the commercial cylinder. Toluene (Prolabo) was purified according to conventional techniques, redistilled with a few drops of

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AlEt$_3$ and collected in pressure bottles where it was stored under about 2000 Torr of dry nitrogen. Polymerisations were carried out in a cylindrical glass reactor (1.2 l) provided with magnetic stirring (800 rpm) and thermostatted at 25±1 °C. The reaction vessel was equipped with metal valves for the introduction of nitrogen, solvent, monomer and the solution of Et$_2$AlCl, and for evacuation. It was furthermore connected to a mercury manometer to allow the monitoring of monomer pressure during the reaction. Polymerisation rates were thus obtained,from plots of the ethylene pressure drop as a function of time. The standard procedure adopted for all experiments was as follows: The titanium compound was introduced into the previously dried reactor and the system was then evacuated ($\sim 10^{-2}$Torr)for 3 hours at 85°C. The vessel was then allowed to cool down to 25°C, 100 ml of toluene were added and the mixture stirred for 30 minutes. At that point the Et$_2$AlCl solution was injected and the resulting catalyst solution allowed to "age" for 5 minutes. Finally, the monomer was quickly introduced to give an initial pressure of about 1500 Torr. From that moment pressure readings were taken. Once a polymerisation had reached a conversion of about 90%, a second rapid injection of ethylene was carried out and the new rate of polymerisation monitored. This cycle was often repeated for a third time. The polymer precipitated during the reaction. It was isolated by pouring the final suspension into an excess of methanol and by filtering. It was then washed with a 10% HCl solution in methanol, with pure methanol, and vacuum dried to constant weight at 60°C.

Results and Discussion

The Table summarises the results obtained with the four catalyst combinations used in this work. It must be emphasised that provided the experimental procedure described above was followed the reproducibility was always satisfactory. The course of a typical triple polymerisation is shown in Fig. 1, while Fig.2 shows the influence of the aluminium-to-titanium molar ratio on the initial rate of polymerisation for the four catalyst pairs. The following general conclusions can be drawn from an examination of the present results:

1. No induction period was ever observed if the reaction vessel was conditioned as described in the experimental section. All initial rates reported in the Table are therefore maximum rates. In previous reports dealing with Cp$_2$TiCl$_2$ and similar catalysts (HOCKER and SAEKI, 1971; WATERS and MORTIMER, 1972) the maximum rate of polymerisation was often observed after an acceleration period. It seems clear now that such a phenomenon is not an intrinsic mechanistic feature of these systems but rather an artifact related to operational procedures, most probably the drying of the reaction vessel. In other words, the active species formed in the interaction of the two catalytic components are at their best potential when ethylene is introduced and do not require activation by the latter. The absence of acceleration in all

TABLE

Conditions and results for some typical polymerization expériments.

T = 25 °C. Solvent = 100 ml of toluene. $|Ti| = (2.0 \pm 0.1) \times 10^{-3}$ mol l^{-1}.

The initial monomer pressure was always 1450 ± 50 Torr.

t_i and t_f are the monomer injection time and the final time of each polymerization.

R_o and R_f are the initial and final rates of monomer consumption for each injection.

P_f is the final ethylene pressure after each polymerization (before further injection).

Organic titanium Compound	$\frac{\lvert Al\rvert}{\lvert Ti\rvert}$	monomer injection	t_i/min	R_ox10^2/ mol. $l^{-1}min^{-1}$	t_f /min	P_f/torr	R_fx10^2/ mol. $l^{-1}min^{-1}$	external order in monomer
$TiCp_2Cl_2$ (2)	3.0	1	0	5.7	60	84	0.12	1.0
		2	60	2.4	120	416	0.33	
	3.9	1	0	7.3	60	280	0.11	
	7.6	1	0	32.4	15	56	0.61	1.1
		2	15	21.6	49	64	0.18	1.2
		3	50	7.7	110	170	0.26	
	5.8	1	0	30.0	15	40	0.16	1.0
		2	15	6.9	75	168	0.27	
	15.3	1	0	35.6	16	40	0.31	1.2
		2	18	23.3	52	48	0.05	1.4
		3	52	5.7	113	164	0.26	
$TiCp_2(ONapht)Cl$ (1)	5.8	1	0	18.8	30	80	0.51	1.3
		2	30	20.7	56	104	0.06	
	8.0	1	0	21.3	16	64	0.70	1.0
		2	16	16.5	50	56	0.14	1.2
		3	50	6.9	110	200	0.28	
	15.7	1	0	44.0	15	32	0.13	1.3
		2	15	22.0	50	72	0.17	1.3
		3	50	10.1	110	90	0.15	
$TiCp_2(OSiPh_3)Cl$ (4)	6.0	1	0	16.7	40	56	0.24	1.3
		2	40	15.8	100	72	0.05	
	7.9	1	0	15.7	40	72	0.36	1.1
		2	40	11.1	100	112	0.29	
	15.6	1	0	26.6	40	72	0.20	1.4
		2	40	14.8	100	224	0.22	
$TiCp_2(OPh)_2$ (3)	7.7	1	0	20.7	31	232	0.46	1.9
		2	31	14.1	92	168	0.16	
	15.8	1	0	33.0	35	104	0.25	1.6
		2	35	18.1	95	254	0.20	

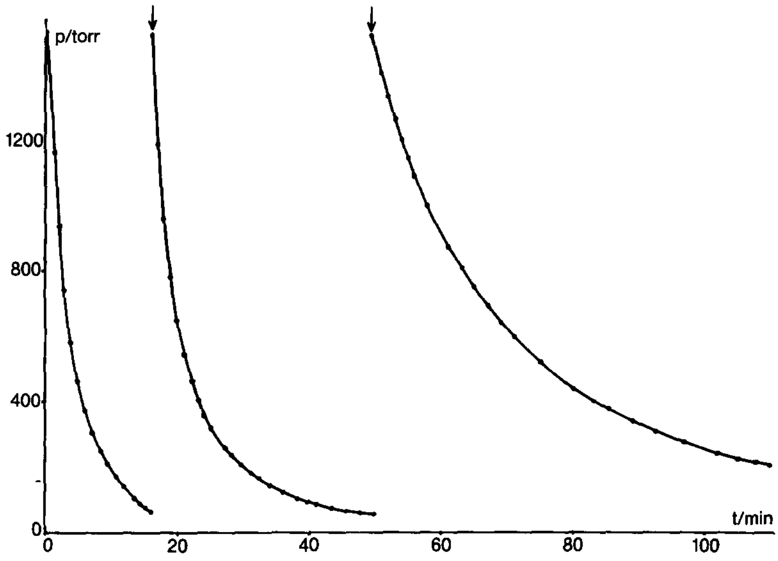

Fig.1. A typical triple polymerisation with $CP_2TiONaphtCl$, Al/Ti = 8 (see Table). The arrows indicate the times at which ethylene was reintroduced into the reactor.

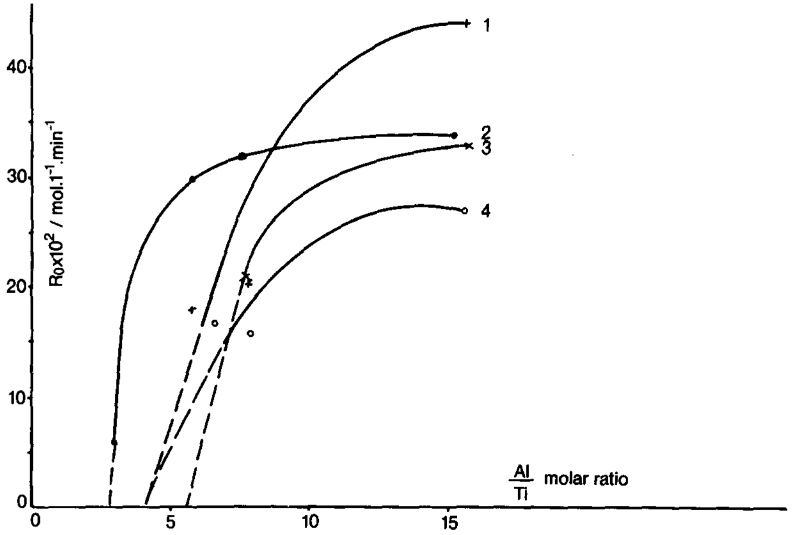

Fig.2. The effect of Al/Ti on the initial rate of polymerisation. The curves are numbered for the different catalyst combinations, as in the Table.

reactions, including those involving further monomer additions, also indicates that the equilibration of ethylene between the gas and the liquid phase is much faster than the process of polymerisation, i.e., diffusion phenomena do not interfere with the kinetics of monomer consumption.

2. The reference catalyst pair chosen in this work gave polymerisation rates comparable to, or higher than, those obtained in previous studies under similar conditions (CHIEN, 1959; HENRICI-OLIVE and OLIVE, 1967; HOCKER and SAEKI, 1971). Moreover, reproducibility was always satisfactory. These facts suggest that we were able to optimise the performance of a catalyst which had been used for many years (see also 1.) and that the comparisons between that system and the new catalyst are all the more valid since we were using a reference at its highest standard.

3. In all reactions a (slow) depletion of active species was observed. This is clearly shown in the experiments involving second and third addition of ethylene to restore the original pressure. Lower rates of monomer consumption were obtained after these additions and they were the lower, the longer the time elapsed from the beginning of the experiment (see Table and Fig.1). This termination reaction can be rationalised either in terms of a true deactivation of some chain carriers by chemical destruction, or by their physical occlusion into the precipitated polymer. The first hypothesis seems more plausible in the light of some experiments we carried out with a very large excess of Et_2AlCl (not in the Table). Under those circumstances the activity of the catalyst solution remained unchanged for several days and successive additions of ethylene resulted in the same rate of polymerisation. It seems that the termination reaction is due to the formation of inactive complexes which can only be reactivated if an excess of Et_2AlCl is available. Thus, occlusion of titanium compounds in the precipitated polymer did not occur to any serious extent. We noticed that good stirring made the polymer coalesce in very fine grains and it seems therefore likely that the active species could return into the solution during or soon after the precipitation.

4. The thermograms of all polymers produced showed that these were in fact high-molecular weight polyethylene, given their facile crystallization and sharp transition at 139°C. While these observations had already been made in the case of the reference catalyst pair, it is interesting to note that substitution of one or both chlorine atoms in the titanium compound with more bulky organic groups did not alter the quality of the catalysts in terms of their capacity to induce linear growth.

5. The new catalyst combinations studied in the present work displayed remarkable activity, since they behaved similarly to, and sometimes better than, the one used as reference (see Table), as long as a suitable amount of Et_2AlCl was employed. Considering that the reference pair is among the strongest homogeneous catalysts known for the polymerisation of ethylene, it was gratifying to observe such powerful performances with the new systems. Some experiments with $Cp_2TiPhCl$ - Et_2AlCl (not in the Table) indicated

that this catalyst is also very active in the polymerisation of ethylene.

6. A comparison of the polymerisation rates immediately before and after the second and the third addition of ethylene allowed us to make an approximate calculation of the external order in monomer, since in the small time interval between the two measurements the concentration of active species did not vary appreciably. The values of these orders are shown in the Table. They tend to be higher than unity, particularly at the higher Al/Ti ratios. We tentatively interpret these results as evidence for two types of active species, one favoured by an excess of Et_2AlCl and requiring perhaps two molecules of monomer in the propogation step, the other needing only one. The fractional order in ethylene would thus be the reflection of two distinct modes of monomer addition, one monomolecular, the other bimolecular. The range of orders encountered would result from the relative population of the two distinct chain carriers.

7. The study of the effect of the ratio Al/Ti upon the polymerisation rate (Table and Fig.2) provided some interesting information. First, all the initial rates increased as that ratio was increased in the four systems studied. This general tendency was very pronounced for small ratios and then levelled off gradually (Fig.2). It seems that for a given concentration of titanium compound the number of active species increased with the excess of Et_2AlCl until saturation was reached. The second and more important point is the observation that the amount of Et_2AlCl required to obtain appreciable polymerisation rates varied with the titanium compound used and more specifically with the number of chlorine atoms it contained. Thus for example, for $Al/Ti < 6$, the system with one chlorine atom bound to the titanium compound gave very low rates (see Table), while the reference system (two Cl atoms) already worked well with Al/Ti=3. In the case of $Cp_2Ti(OPh)_2$, the situation is even more drastic, since an excess of Et_2AlCl of 8 was necessary to obtain substantial rates. The existence of critical values of Al/Ti below which the polymerisation proceeds with difficulty, a value which increases with decreasing Cl content of the titanium component, suggests that only those complexes which contain a sufficient number of Cl atoms are active chain carriers for the polymerisation of ethylene.

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