Effect of the cocatalyst on the copolymerization of propylene and small amount of ethylene with high activity Ziegler-Natta catalyst

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SUMMARY
The copolymerization of propylene with small amount of ethylene using $MgCl_2$-supported stereospecific catalysts in combination with different Al-alkyls was performed. At least for the particular catalyst used, it resulted that TEA and TIBA are the preferred Al-alkyls; whereas, the mixture TEA/DEAC provides copolymers with a high amount of xylene solubles. Finally, the mixture TEA/DEAI largely decreases catalyst activity, but it provides a copolymer with broad MMD.

INTRODUCTION
Al-alkyls are well known cocatalysts for Ziegler–Natta propylene polymerization; it has been reported that they affect both catalyst activity and polymer isotacticity[1-3]. In particular, it is known[3,4] that diethylaluminumiodide (DEAI) greatly improves the stereospecificity of low yield $TiCl_3$ catalyst, with respect to triethylaluminum (TEA); however, it decreases the polymerization activity. It is also known that diethylaluminumchloride (DEAC) increases stereospecificity of $TiCl_3$, with respect to TEA[1]. In a recent work[5] the effect of different Al-alkyls on ethylene and propylene copolymerization was studied. But, the authors dealt with $MgCl_2$-supported catalyst without any external and/or internal donor and they dealt with the synthesis of polyethylene modified with propylene. The slight modification of polypropylene through random copolymerization with ethylene is a very important polymerization reaction as it affords materials having interesting physico-mechanical properties[6]. In particular, the ethylene insertion in the polypropylene chain decreases melting temperature (Tm) and crystallization temperature (Tc). These features are very important for many applications as, for example, low temperature thermoweldable films[7-9]. The comonomer insertion increases xylene solubility; as a linear relationship between yield stress and xylene solubles has already been established[3] for low-comonomer levels, the solubility measurements can give an information around mechanical behaviour. Thus, an informative and rapid way to

characterize such copolymers is to determine Tm, Tc, xylene solubles and molecular mass distribution (MMD). The copolymerization can be conveniently performed with $MgCl_2$-supported catalysts having both internal and external donor(6). Despite the fact that this reaction has already been described(3,6) there is a lack of information around the effect of Al-alkyls on catalyst behaviour in copolymerization and on copolymer features (xylene solubles, Tm, Tc, MMD). Thus, it seemed of interest to deal about this topic using TEA, triisobutylaluminum (TIBA), tri-n-octyl-aluminum (TNOA), trimethylaluminum (TMA), a 1:1 molar mixture of TEA and DEAC, and a 1:1 molar mixture of TEA and DEAI in combination with a $MgCl_2$-supported catalysts, having both internal and external donor.

EXPERIMENTAL Catalyst. The catalyst synthesis is described in reference 10. Tipically, the spherical adduct $MgCl_2$.nEtOH was reacted at 100°C for two hours with $TiCl_4$ in the presence of diisobutylphthalate (DIBP) (Mg/DIBP=8 molar). The hot liquid was syphoned off and $TiCl_4$ was added to the solid; such a mixture reacted for one hour at 120°C. Again, the liquid was syphoned off and the solid was washed several times with hexane and dried under nitrogen. The chemical composition was Ti= 2.55 %Wt.; DIBP= 9.8 %Wt.. The external donor used was cyclohexylmethyldimethoxysilane and the Al/silane molar ratio was 5. The Al/Ti molar ratio was 400. The concentration of aluminumalkyls was 2 mmol/L.
Copolymerizations. The copolymerizations were carried out in a 4 L stainless steel batch reactor in the following way: the precontacted catalytic complex was first added at 25 °C, then the suitable amount of comonomers mixture was rapidly introduced in the reactor at the same temperature. After that, the temperature was quickly raised to 65 °C and comonomers mixture was fed throughout the run to keep the pressure constant at 32 bar. Copolymer characterization. Intrinsic viscosity of copolymers was measured at 135 °C in tetrahydronaphtalene. The thermograms were recorded at a heating/cooling rate of 10 °K/min with a PERKIN-ELMER DSC-7 apparatus. Molecular mass and molecular mass distribution were measured in o-dichlorobenzene at 135°C with a GPC WATERS Mod. 150. Universal calibration was made using polystyrene monodispersed fractions. Xylene solubility was determined through dissolution of the sample in o-xylene at 135 °C and successive recrystallizaton at 25 °C. The ethylene content was determined by infrared spectroscopy using a NICOLET 20SXC spectrometer; the bands at 13.671 and 13.917 micron were used for the analytical measurements. The ^{13}C-NMR spectra were recorded in 1,1,2,2-tetrachloroethane-d_2 at 120 °C on a Bruker AC-200 spectrometer in the FT mode: pulse width 6 μs; acquisition time 1.6 s; relaxation delay 15 s.

RESULTS AND DISCUSSION
Catalyst behaviour. The experimental results are collected in Tab. 1 and the kinetic profiles are shown in figs. 1,2. The type of Al-alkyl affects catalyst performance, at least for

Tab. 1 - Structural characterization of propylene-ethylene random copolymers synthesized with different Al-alkyls.

	TEA	TNOA	TIBA	TMA	TEA/DEAC	TEA/DEAI
Activity (Kg/g h)	31.8	33.7	37.8	27.7	38	1
C2- (%Wt.)	3.8	4.2	4.1	3.6	4.5	3.6
XS (%Wt.)	8.3	9.6	9.6	8.5	18.4	7.5
XI (%Wt.)	91.7	90.4	90.4	91.5	81.6	92.5
Tm (oC)	143.3	141.1	142	144	139.5	144
Tc (oC)	99.3	99.2	100	100.5	96.6	100.5
Mn	61513	53202	50128	46278	38223	35018
Mw	315991	318090	269544	312672	230661	350380
Mz	732234	825746	589968	854064	587861	1676203
MMD (Mw/Mn)	5.1	6.0	5.4	6.8	6.0	10.0
Mz/Mw	2.3	2.6	2.2	2.7	2.5	4.8
Morphology	Spheres	Powder	Spheres	Spheres	Spheres	Spheres

Both mixtures TEA/DEAC and TEA/DEAI were 1:1 molar
Copolymerization conditions: T= 65 C; P=32 bar (liquid monomer); Ethylene=0.76 bar; H2=0.131 bar;
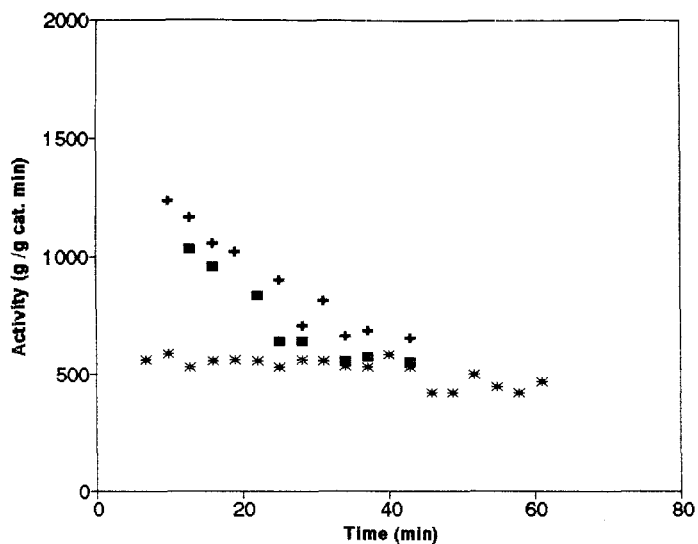
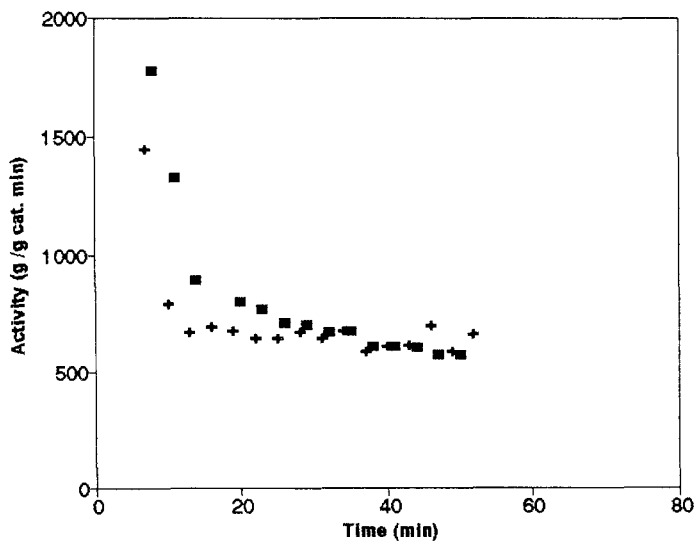FIG. 1 - Effect of different Al-alkyls: ■ TEA; * TMA; + TIBA.

FIG. 2 - Effect of different Al-alkyls: ■ TEA/DEAC; + TNOA.

the particular catalyst we used. When TIBA (fig. 1) was used a slight increase of catalytic activity with respect to TEA was noticed, the kinetic profile being almost unchanged. The TMA (fig. 1) lowers catalyst activity and stabilizes the kinetic profile. It might suggest that TMA does not activate very active but unstable catalytic sites. On the contrary, when TNOA (fig. 2) was used a higher initial polymerization rate was observed; this alkyl may create some sites having high reactivity but, low stability. The mixture TEA/DEAC (fig. 2) allowed slightly higher activity than pure TEA: it could be due to the lower reducing power of cocatalytic mixture that leaves still active some centers. The mixture TEA/DEAI provided very low catalyst activity (see Tab. 1); as an exchange reaction occurs between iodine atoms of DEAI and chlorine atoms of $TiCl_4(11)$, such a variation of the nature of active sites may account for the low activity.

Copolymer Structure

By using the catalyst system that we prepared according to ref. 10, we observed that the Al-alkyls TIBA, TNOA and TMA seem to leave almost unaltered the copolymer features; whereas TEA/DEAC and TEA/DEAI mixtures significantly affect copolymer characteristics (Tab. 1). In the former case the copolymer with the highest xylene solubility was obtained; it is worth reporting that the semicrystalline xylene insoluble fraction of the copolymer synthesized with pure TEA shows a signal at 28-29 ppm having a lineshape and particular details that come from a richer stereoregular sequences distribution than the one obtained with TEA/DEAC. No evidence around a significantly different comonomer distribution appeared from these measurements: the reactivity ratios product is 1.6 for the copolymer fraction obtained with TEA and it is 1.4 for the copolymer fraction obtained with the mixture. The NMR measurements on xylene solubles do not show substantial differences: both the copolymer fractions have low stereoregularity and almost the same comonomer distribution (the reactivity ratios product is 2.4 for the copolymer fraction obtained with TEA and it is 2.3 for the copolymer fraction obtained with the mixture). These findings seem to suggest that the mixture TEA/DEAC activate a larger number of aspecific sites than pure TEA does. It is likely due to the higher Lewis acid strength of DEAC which may form very stable complexes with the silane donor; in this way DEAC could hinder the stereoregulation effect due to the external donors. Using the mixture TEA/DEAI a copolymer with a very broad molecular mass distribution was synthesized: Mw/Mn=10, when TEA/DEAI was used and Mw/Mn=5 when pure TEA was used; also the ratio Mz/Mw increased from 2.3 with pure TEA up to 4.8 with the mixture. Furthermore, one can observe that Mw stays almost constant for the two copolymers, whereas both Mn and Mz change substantially going from pure TEA to the mixture: Mn decreases and Mz increases. This suggests that the observed broadening of MMD is symmetrical and it is not merely due to low molecular weight tails. As an exchange reaction occurs between iodine of DEAI and chlorine of $TiCl_4(11)$, new active sites containing one or more iodine

atoms could be generated on the catalyst. So, one of the possible explainations is the following: the modification of the nature of active sites may induce a widening of Kp/Ktr range and, as a consequence, the broadening of molecular mass distribution. Finally, from table 1 it appears that melting and crystallization temperatures are related, within the experimental error, to the comonomer content; in the copolymer synthesized with TEA/DEAC also the lower stereoregularity can contribute to the lowering of melting and crystallizzation temperatures.

CONCLUSIONS
On the basis of the data obtained with a high activity Ziegler-Natta catalyst(10) it is possible to conclude that, at least for the particular catalyst used, TEA and TIBA are the preferred Al-alkyls for the random copolymerization of propylene with small amount of ethylene. The mixture TEA/DEAC allows copolymers with an increased xylene solubillity. It is worth noting that the mixture TEA/DEAI largely decreases catalyst activity, but it provides a large broadening of MMD. Further work is in progress aiming to exploit this unexpected behaviour.

REFERENCES
1) Barbè P.C., Cecchin G., Noristi L. (1987), Adv. Polym. Sci. 81: 1 and references therein.
2) Hsu C.C., Yang C.B., (1993) Makromol. Chem. Rapid Commun. 14: 387
3) S. van der Ven (1990) Polypropylene and other polyolefins. Elsevier, Amsterdam Oxford New York Tokyo, and references therein
4) Natta G., Pasquon I., Zambelli A., Gatti G., (1961) Journal of Polym. Sci. 51: 387
5) Seppala J.V., Koivumaki J., Kuutti L., (1992) Polym. Bull. 29: 185
6) Simonazzi T., Cecchin G., Mazzullo S., (1991) Prog. Polym. Sci. 16: 303
7) Galli P., (1980) IUPAC International Symposium on Macromolecules, Florence, Italy.
8) Avella M., Martuscelli E., Della Volpe G., Segre A., Rossi E., Simonazzi T., (1986) Makromol. Chem. 187: 1927
9) Guidetti G., Busi P., Giulianelli I., Zanetti R., (1983) Eur. Polym. J. 19: 757
10) EP-A 395083; HIMONT Inc.; Invs.: Sacchetti M., Govoni G., Ciarrocchi A.
11) Kissin Y.V. (1985) Isospecific polymerization of olefins. Springer-Verlag, New York Berlin Heidelberg Tokyo and references therein