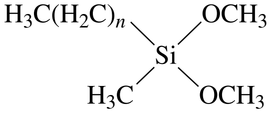
ISSN 0023-1584, *Kinetics and Catalysis*, 2006, Vol. 47, No. 2, pp. 176–185. © MAIK "Nauka/Interperiodica" (Russia), 2006.

Advances in Ziegler–Natta Catalysts for Polypropylene[1]

A. Ferraro, I. Camurati, T. Dall'Occo, F. Piemontesi, and G. Cecchin
Basell Polyolefins, G. Natta Research Center, 44100 Ferrara, Italy
e-mail: giuliano.cecchin@basell.com

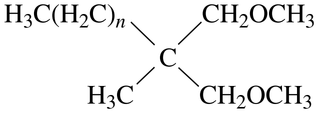
Received July 11, 2005

Abstract—The most advanced catalysts, based on $MgCl_2$-supported $TiCl_4$ and electron donors, are able to provide polypropylenes with an isotacticity higher than 99%. This, together with the continuous progress made in understanding and exploiting the role of electron donors in controlling polymer MW and MWD, has led to polypropylene products having an unprecedented level of stiffness or stiffness/impact balance. On the other hand, other potential fields of application exist where rigidity is not required and, actually, the key property is softness rather than stiffness. As a matter of fact, it has clearly been established that soft polypropylenes can be more attractive from the business standpoint than their stiff counterparts. Generally, these materials are multiphase copolymers obtained via sequential gas-phase copolymerization of propylene and ethylene-propylene mixtures using the morphology-controlled conventional $MgCl_2$–$TiCl_4$ catalysts based on the couple phthalate-silane as internal and external donors. This communication deals with a new class of donors that can be used either as external donors in combination with phthalates (**A**) or as internal/external donors (**B**).



A

$n > 3$



B

When combined with the $MgCl_2$–$TiCl_4$ systems, both donors substantially improve the flexibility and softness of the resulting soft materials while maintaining the operability window of the Catalloy process. This is due to the particular microstructure of the relevant building blocks: the presence of a controlled concentration of stereodefects in the homopolymer fraction, and good comonomer distribution in the copolymer fraction. As compared with the conventional products, the new ones show comparable or better flexibility when the rubber phase is relatively rich in ethylene. This likely opens the door for these products to enter the demanding thermoplastic elastomers (TPE) application field.

DOI: 10.1134/S0023158406020042

Since the beginning, research on Ziegler–Natta catalysis for polypropylene has mainly striven for perfection, e.g., the achievement of perfectly isotactic polymer chains. Nowadays the most advanced catalysts, based on $MgCl_2$-supported $TiCl_4$ and electron donors, are able to provide polypropylenes with an isotacticity higher than 99 mol %. This, together with the continuous progress made in understanding and exploiting the role of electron donors in controlling polymer MW and MWD, has led to polypropylene products having an unprecedented level of stiffness or stiffness/impact balance [1]. On the other hand, other potential fields of application exist where rigidity is not required and, actually, the key property is softness rather than stiffness. As a matter of fact, it has clearly been established that soft polypropylenes can be more attractive from the business standpoint than their stiff counterparts. In this respect, the Catalloy technology, with its soft or supersoft grades [2], has considerably expanded the property envelope of polypropylene and contributed to the shift of this mature product from the commodity to the specialty application areas, enabling it to enter high-margin, value-added application fields such as geomembranes. Generally, these materials are multiphase copolymers obtained via sequential, gas-phase copolymerization of propylene and ethylene–propylene mixtures using the morphology- and porosity-controlled, conventional $MgCl_2$–$TiCl_4$ catalysts based on the couple phthalate–silane as internal/external donors [2].

In this communication, we would like to report on a new class of donors [3] that can be used either as external donors (ED) in combination with phthalates or as internal/external donors (ID/ED):

---

[1] The text was submitted by the authors in English.

$$CH_3(CH_2)_n(Me)Si(OMe)_2 \quad CH_3(CH_2)_n(Me)C(CH_2OMe)_2 \quad n > 3.$$

In particular, we will focus on octylmethyldimethoxysilane (SM1) as an external donor and on 2-octyl-2-methyl-1,3-dimethoxypropane (CM1) as an internal donor (Fig. 1). The catalysts obtained using the new donors have been employed for the homopolymerization of propene, the copolymerization of propene with ethylene, and the in situ synthesis of alloys consisting of the relevant building blocks, with a view to obtaining soft thermoplastic polyolefins (TPO) or thermoplastic elastomers (TPE) having new and improved performances with respect to the existing Catalloy products.

EXPERIMENTAL

Catalysts. The spherical $MgCl_2$ supports and the derived catalysts were prepared according to the general methods described in US Patent nos. 4399054, 4971937, 5221651, and 5236962.

Propene polymerization and ethylene/propene copolymerization. A four-liter stainless-steel autoclave was used, equipped with a magnetic stirrer, a manometer, a temperature indicator, a system for feeding the catalyst components, monomer supply lines, and a jacket for thermostatic temperature control. For polypropene polymerization, the reactor was purged with nitrogen flow at 70°C for 1 h; then 75 ml of anhydrous hexane containing 7 mmol of $AlEt_3$, 0.35 mmol of external donor, when used, and 10 mg of solid catalyst component (procatalyst) were introduced in the order under propene flow at 30°C. The autoclave was closed, 1.5 Nl of hydrogen was added, and then 1.2 kg of liquid propene was fed under stirring. The temperature was raised to 70°C after five minutes and the polymerization was carried out at this temperature for 2 h. The unreacted propene was flashed off and the polymer was recovered and dried at 70°C under vacuum for 3 h. For ethylene-propene copolymerization, the autoclave was purged by flushing with ethylene at 80°C for 1 h and then 242 g of hexane was introduced at room temperature. The temperature was brought to 50°C, and then 392 g of propane and the proper amount of hydrogen were introduced into the reactor. Afterwards, a given amount of ethylene and propene, depending on the desired gas-phase composition, was fed into the reactor. The procatalyst, the cocatalyst (triethylaluminum) and, optionally, the external electron donor compound were injected under a pressure of ethylene and the polymerization was started. During the reaction, a proper ethylene–propene mixture (EPM), depending on the desired EPM composition, was fed at constant pressure for the desired polymerization time. The reaction was then stopped and the polymer was recovered and dried under vacuum.

In situ synthesis of elastomeric heterophasic compolymers (case of EPM fractions containing 50 wt % ethylene). A 40-l stainless-steel reactor was used instead of a 4-l reactor, in order to prepare samples big enough for further physical-mechanical characterization. About 0.30 g of catalyst components were reacted in a 250 ml glass flask with 11.4 g of triethylaluminum (TEAL) in about 100 ml of anhydrous hexane. The mixture was fed under propene flow into the autoclave previously purged with gaseous propene for 1 h at 80°C. Subsequently, 12 kg of liquid propene together with 11 Nl of hydrogen were fed at 30°C. The temperature was raised to 60°C and the polymerization carried out for 20 min. Propene was then vented and the reactor brought to room temperature. In the same reactor, 3.9 Nl of H_2, 34 g of ethylene, and 132 g of propene were fed at 30°C; the temperature was then raised to 60°C and the polymerization started again. The composition of the gas-phase was kept constant by feeding a mixture of the two monomers containing 50% by weight of ethylene. Copolymerization was carried out for about 60 min and then stopped. The obtained polymer was dried under vacuum.

NMR characterization. The samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 at 120°C with a 8 wt % concentration and the ^{13}C NMR spectra of both PP and EPR were acquired on a DPX-400 spectrometer operating at 100.61 MHz in the Fourier transform mode at 120°C. The peak of the *mmmm* pentad and of the Sδδ (nomenclature according to [4]) carbon were used as internal reference at 21.8 and 29.9 ppm respectively. Each spectrum was acquired with a 90° pulse, 12 s of delay between pulses, and CPD (WALTZ 16) to remove ^1H–^{13}C coupling. About 2500 for PP and 1500 transients for EPR were stored in 32 K data points using a spectral window of 6000 Hz. The assignments of PP spectra were made according to [5]. The *mmmm* content was obtained by modeling the experimental pentad distribution with the enanthiomorphic site model.

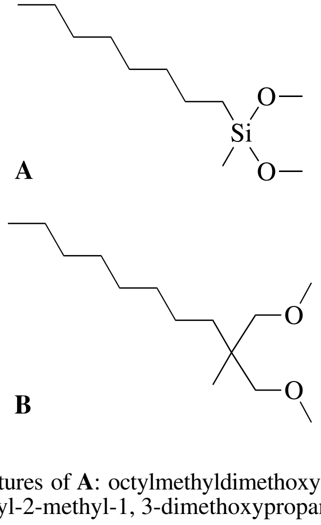


Fig. 1. Structures of **A**: octylmethyldimethoxysilane (SM1) and **B**: 2-octyl-2-methyl-1, 3-dimethoxypropane (CM1).

The assignments of EPR spectra, triad distribution and composition were obtained according to literature [6]. The product of reactivity ratios r_1r_2 was calculated from triads according to [4] as

$$r_1r_2 = 1 + \left(\frac{[\mathrm{PPP}] + [\mathrm{PPE}]}{[\mathrm{EPE}]} + 1\right) - \left(\frac{[\mathrm{E}]}{[\mathrm{P}]} + 1\right)\left(\frac{[\mathrm{PPP}] + [\mathrm{PPE}]}{[\mathrm{EPE}]} + 1\right)^{0.5}.$$

TREF characterization. Temperature Rizing Elution Fraction (TREF) fractionation was carried out by dissolving 1 g of polymer in *o*-xylene at 135°C and slowly cooling the solution (20 h) to 25°C in a column loaded with glass beads. Elution with *o*-xylene (600 ml/h) was first carried out at 25°C to obtain the xylene-soluble ("atactic") fraction. Elution was then continued while increasing the temperature from 25 to 100°C to yield a single fraction mainly consisting of the "stereoblock" fraction. Finally, the temperature was increased from 100 to 120°C at a rate of 3 K/h, collecting individual fractions at temperature intervals of 1 K. The polymer fractions were recovered by precipitation in acetone, filtered on a 0.5 μm PTFE filter, and dried under vacuum at 70°C. All the recoveries were above 97%.

Thermal analysis. Thermoanalytical curves were recorded at a heating rate of 10 K/min using a Perkin-Elmer DSC-7 differential scanning calorimeter calibrated against indium and tin standards. As melting temperature, the peak of the second fusion run was taken.

Fractionation of ethylene/propylene copolymers. 6 g of an EPR sample divided in small pieces was placed in a flask with 600 ml of a 90 : 10 volume ratio of diethyl ether–acetone mixture. It was heated to solvent reflux for 6 h and left overnight at room temperature to equilibrate between soluble and insoluble. It was then filtered and the soluble part was recovered in a rotary evaporator and then dried under vacuum to constant weight. The insoluble residue was then treated in the same way with diethyl ether, then with diethyl ether/*n*-hexane (volume ratio of 90 : 10), then with *n*-hexane. The final residue is the insoluble part in *n*-hexane.

Preparation of cross-linked EPR samples. l00 g of polymer was impregnated with 30 g of Flexon 876-paraffin oil. This mixture was introduced into an internal mixer of the Banbury type at a temperature of 60°C together with 50 g of carbon black, 5 g of ZnO, 2.5 g of Triallyl cyanurate (TAC) and 6 g of Peroximon F40. The mixtures were molded and cured in a plate press for 10 min at 180°C and then cooled in a second press maintained for 10 min at 23°C.

TPV preparations. Dynamic vulcanizations were carried out in a Brabender mixer plasticorder with coagent and peroxide [7]. The temperature was set a 160°C and speed at 60 rpm. The polymer melt temperature ranged between 185–195°C. The polymer was added at the beginning with the coagent and, after 3 min, with the peroxide. The batch was then mixed for the time necessary to reach a flat torque curve, no less than three minutes.

Cured samples were compression molded in a plate press in plaques 2 mm thick. After 5 min of preheating at 200°C, the sample was held at 100 bars for a further 2 min. Then the plaques were cooled in a second press for 10 min at room temperature.

RESULTS

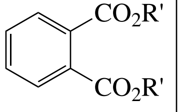
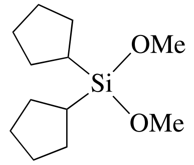
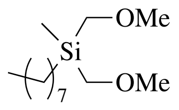
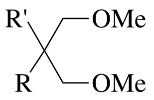
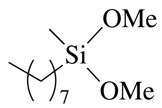
Propene Homopolymerization

The new compounds octylmethyldimethoxysilane and 2-octyl-2-methyl-dimethoxypropane have been used, respectively, as external donors in combination with phthalate-based catalysts, and as internal donors to prepare $MgCl_2/TiCl_4$ catalysts for the homopolymerization of propene in liquid–monomer slurry. Both catalyst families, based either on "standard" (porosity in the 0.10–0.15 cm^3/g range) or "porous" (porosity in the 0.40–0.60 cm^3/g range) spherical $MgCl_2$ supports have been synthesized. They have been tested both in comparison with the corresponding typical stereospecific catalysts based either on the couple phthalate–silane (diisobutylphthalate–dicyclopentlyldimethoxysilane, DIBP/D) or on diethers (typically 2,2-disubstituted 1,3-dimethoxypropanes), and with nonstereospecific, external donor-free DIBP-based catalysts (Table 1). Particular attention was paid to the capability of the catalyst system to generate substantial amounts of what we have defined as "stereoblock" fraction. The presence of this defective fraction (see below for structural details) is important because it has been found to be the key to reducing the stiffness of the polymer without impairing its thermal or optical properties.

The results indicate that, whereas the "conventional" stereospecific catalysts show the expected behaviour (isotacticity in the 97–98 mol % range and stereoblock content in the 10–15 wt % range), the new catalysts are peculiar in that they generate a large amount of stereoblock fraction (about 40 wt %) without producing considerable amounts of amorphous material. Conventional nonstereospecific catalysts are also able to produce large amounts of stereoblock fraction (30–35 wt %) but only at the expense of the generation of huge amounts of amorphous, sticky material (35–40 wt %). This not only would preclude the synthesis of soft polypropylenes via liquid monomer or, and especially, via gas-phase technologies, but would also create problems during the transformation (smoke and odor) and the end use (surface blooming) of the resulting products.

The key advantage of the new catalyst systems over the conventional systems consists exactly in the possibility to generate soft polypropylenes having a controlled amount of defective material while avoiding the

Table 1. Propene polymerization with Ziegler–Natta catalysts from standard and porous $MgCl_2$ supports

Support	ID	ED	ID/Ti, mol/mol	Activity,[a] kg/g	IV,[b] dl/g	XS,[c] wt %	St. block,[d] wt %	$mmmm_{XI}$, wt %	T_m, °C
S1		–	0.7	28	2.1	34.7	27	86.1	158
S2		–	0.4	23	1.0	41.1	35	85.7	157
S1			0.7	64	1.7	1.0	9	97.8	165
S2			0.4	28	1.8	3.4	12	96.9	161
S1			0.7	50	–	7.4	37	88.7	160
S2			0.4	25	–	8.1	38	89.9	159
S1		–	0.7	115	1.9	3.1	12	96.8	163
S2		–	0.1	20	1.3	30.5	28	88.9	159
S1		–	1.1	50	–	9.5	36	88.0	160
S2		–	1.2	30	1.6	11.6	39	88.9	159

Note: S1—Standard support, porosity 0.12–0.16 cm^3/g, surface area 10–14 m^2/g (Hg method). S2—porous support, porosity 0.40–0.60 cm^3/g, surface area 20–50 m^2/g (Hg method).

[a] Polymerization conditions: liquid propene, 70°C, 2 h.

[b] Intrinsic viscosity measured in tetrahydronaphtalene at 135°C.

[c] Xylene soluble content at 25°C.

[d] Polymer fraction insoluble in xylene at 25°C and soluble in xylene at 100°C.

formation of those sticky fractions that would both prevent the synthesis and impair the end-use properties of the product. In other words, whereas isospecific catalysts cannot generate, by definition, soft polypropenes and non-stereospecific catalysts cannot produce them under the most common industrial conditions, the new catalysts look to be very promising drop-in candidates for the manufacture of these kind of materials, especially via gas-phase technologies.

Both the catalyst behaviour and the fact that, at least for the diether-based catalyst, the donor is well-incorporated in the solid procatalyst clearly indicate that the new donors are able to interact with the catalyst surface and to alter both the distribution and perhaps also the nature of the active centers, increasing the relative amount of those species that generate the stereoblock fraction.

In order to get a deeper understanding of their microstructure, selected homopolymer samples derived from "porous" $MgCl_2$-based catalysts have been fractionated via TREF and the fractions have been analyzed via solution ^{13}C NMR (Table 2). The samples obtained with the external donor-free DIBP-based catalyst system confirm the presence of large amounts of amorphous material soluble at 25°C, and the absence of those highly stereoregular fractions insoluble at temperatures higher than about 112°C. The isospecific catalyst based on the DIBP/D couple produces very small amounts of both amorphous material and stereoblock material (soluble in the 25–99°C temperature range). On the other hand, this catalyst yields a considerable amount of highly isospecific (*mmmm* > 99 mol %) polymer fractions that are soluble in the 105–120°C temperature range. The new catalysts, either silane- or diether-based, behave very similarly, yielding limited amounts of amorphous fractions (8–15 wt %) and large amounts of stereoblock fractions (about 40 wt %), with the absence of those isospecific fractions insoluble at temperatures higher than 111°C. A typical stereoblock component has been analyzed in some more detail via ^{13}C NMR. The relevant spectrum (Fig. 2) shows that this polymer fraction contains a considerable amount of stereoirregularities, of which the most important are the *mmmr* (about 5 mol %), the *mmrr* (about 5.5 mol %), and the *mrrm* (about 2.5 mol %) pentads. Based on the ^{13}C NMR spectrum, the average isotactic sequence length for this fraction can be estimated to be shorter than 50 monomer units. The microstructure of the homopolymer can also be altered acting on the nature of the donor. For instance, considering the general formula of the silanes **A** (see Abstract), the amount of stereoblock fraction increases from about 25 wt % to about 45 wt % as the value of *n* increases from 2 to 7,

Table 2. TREF of polypropylenes from different catalytic systems: $MgCl_2$–ID–$TiCl_4$/TEA–ED

Temperature, °C	Fractions					
	wt %*	wt %**	*mmmm*, mol %	wt %***	*mmmm*, mol %	wt %****
25	42.8	1.0		8.1		14.6
25–99	27.3	3.7	86.55	40.1	87.02	38.3
100	0.9	0.3		1.1		0.8
101	1.3	0.4		1.6		1.5
102	1.6	0.8		2.0		2.1
103	1.9	0.9		2.8		2.7
104	2.3	1.0		3.8		3.5
105	3.1	1.1		4.9	95.53	4.6
106	4.6	1.5	99.22	5.9		6.1
107	4.3	1.6		6.9		7.6
108	4.3	1.8		7.7		7.7
109	4.0	1.9		7.7	96.98	6.7
110	0.7	2.1		5.3		3.8
111	0.9	2.6		1.8		
112		3.3				
113		5.7	99.41			
114		12.4				
115		22.5	99.57			
116		18.0				
117		10.9				
118		4.8				
119		1.6				

* Catalytic systems: $MgCl_2$–DIBP–$TiCl_4$/TEA.
** Catalytic systems: $MgCl_2$–DIBP–$TiCl_4$/TEA–D.
*** Catalytic systems: $MgCl_2$–DIBP–$TiCl_4$/TEA–SM1.
**** Catalytic systems: $MgCl_2$–CM1–$TiCl_4$/TEA.

Table 3. Fractionation of DIBP/D and CM1-based EPMs: Ethylene content and product of reactivity ratios by ^{13}C NMR

Solvent	$MgCl_2$/DIBP/$TiCl_4$/D				$MgCl_2$/CM1/$TiCl_4$			
	fraction, wt %	IV, dl/g	C_2^-, wt %	r_1r_2	fraction, wt %	IV, dl/g	C_2^-, wt %	r_1r_2
Et_2O/Acetone 90/10	27.3	2.4	32.5	1.42	25.7	2.3	42.0	1.01
Et_2O	27.3	2.9	45.8	1.27	25.4	2.8	48.8	0.88
Et_2O/Hexane 90/10	11.1	–	58.3	1.16	15.3	3.0	58.4	0.99
Hexane	12.1	3.2	68.6	1.75	17.2	3.4	65.9	1.74
Insolubile	22.2	3.5	83.0	3.55	16.4	3.9	77.0	2.90
Raw copolymer	100	2.9	54.7	–	100	3.1	55.5	–

while the amount of amorphous fraction remains generally below 8 wt %.

As expected and desired, the flexural moduli of the obtained polymer samples decrease dramatically as the amount of their stereoblock content increases. On the other hand, their melting point is only slightly affected (Fig. 3). This translates into the possibility of achieving a considerable degree of softness without substantially impairing the thermal performance of the material.

Ethylene-Propene Rubbers

A number of ethylene-propene copolymerization experiments have been conducted in slurry in order to

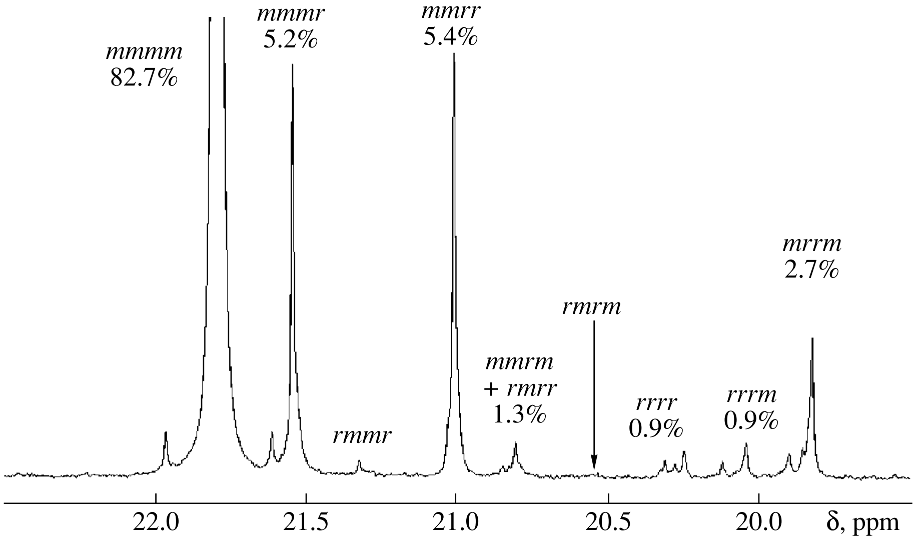


Fig. 2. ^{13}C NMR spectrum (methyl pentad region) of a typical Stereoblock fraction.

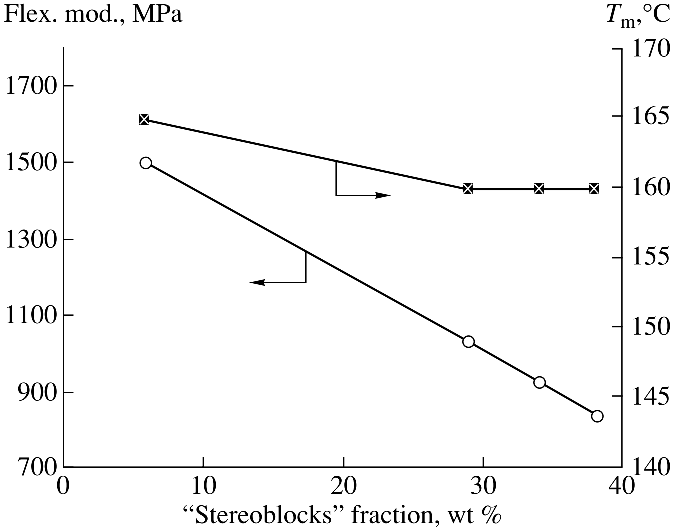


Fig. 3. Flexural moduli (ASTM D-790) and melting points of polypropene homopolymers as a function of their content in Stereoblock fraction.

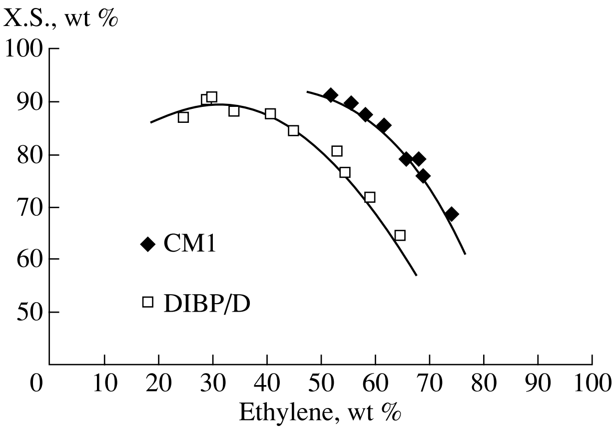


Fig. 4. Pure EPMs synthesized via DIBP/D- or CM1-based catalysts: xylene-soluble substances as a function of their ethylene content.

compare the copolymerization behaviour of the new donors vis a vis the conventional, isospecific catalyst systems for polypropene and to characterize the resulting EPM copolymers. The "porous" version of $MgCl_2$ support has been used and CM1 has been selected as a catalyst modifier (internal donor) because of its better overall performance in comparison with SM1, especially for this application. Fractionation data of the copolymers obtained via CM1 show, in comparison with those obtained using the conventional isospecific catalyst, better intermolecular homogeneity (more homogeneous distribution of the comonomers among the different fractions) and also better intramolecular homogeneity (product of the reactivity ratios constantly lower within the corresponding fractions) (Table 3).

The better homogeneity of the CM1-based copolymers with respect to those based on the DIBP/D couple is also confirmed by their solubility in xylene (X.S.) at room temperature (Fig. 4): for the same composition, e.g, 50–60 wt % ethylene, the former have a soluble content in the 85–95 wt % range whereas the latter have a soluble content in the 70–80 wt % range. These results are also confirmed by thermal analysis of selected samples via DSC: copolymers obtained via conventional catalyst and containing 42–45 wt % ethylene clearly show the presence of an endothermic melting peak at about 130°C; this peak is almost absent in the corresponding copolymer obtained via CM1 (Fig. 5). All this would indicate that, using the new donor, one can obtain ethylene/propene copolymers

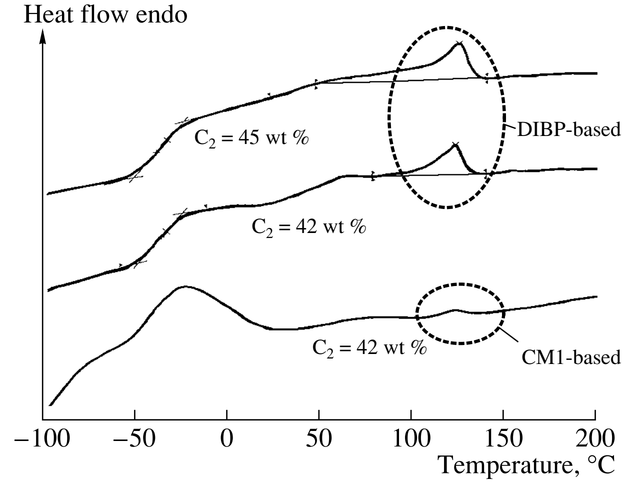


Fig. 5. Pure EPMs synthesized via DIBP/D- or CM1-based catalysts: DSC endothermic plots (second run).

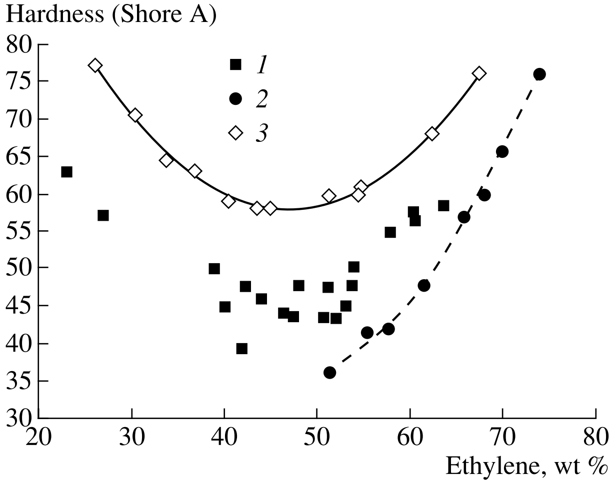


Fig. 6. Pure EPMs synthesized via DIBP/D- or CM1-based catalysts: hardness (Shore A) as a function of composition. *1*—CM1 based catalyst, *2*—CM1 based modified catalyst, *3*—DIBP/D based catalyst.

that are more “rubbery” than those obtained using the conventional donors. Figure 6 shows that this is indeed the case, since the hardness (Shore A) versus composition correlation clearly indicates that the CM1-based EPMs are substantially softer than the corresponding DIBP/D-based EPMs.

As can be seen, an additional reduction in hardness can be achieved by acting on the nature of the procatalyst, but this is beyond the scope of the present communication.

The pure EPM samples, obtained either from CM1-based or DIBP/D-based catalysts and containing 50 wt % ethylene have also been used as starting components for the preparation of cross-linked materials using a typical vulcanization recipe for saturated ethylene-propene rubbers. Based on the stress/strain behaviour, as well as the compression set values of the resulting materials, it can be concluded that CM1-based EPMs have interesting elastomeric properties (Table 4). In particular, their behaviour is intermediate between those of the corresponding EPM from DIBP/D and a typical EPM obtained with Vanadium-based catalysts.

Soft Heterophasic Copolymers

The results reported above prompted us to explore the possibility of synthesizing in situ improved soft heterophasic copolymers using as building blocks the homopolymers and copolymers prepared via CM1-based catalysts instead of via DIBP/D. To this end, a series of experiments have been made in batch (propene homopolymerization in liquid monomer and sequential ethylene/propene copolymerization in the gas phase), using a porous $MgCl_2/TiCl_4$ catalyst in combination with either of the mentioned donor types. Table 5 shows the results concerning copolymers containing about 70 wt % of ethylene-propene rubbers having either about 30 or about 60 wt % ethylene. The former, a propene-rich rubber component is typically used to prepare the so-called Supersoft copolymers, whereas the latter, an ethylene-rich rubber, at least in principle, is a more convenient starting point to obtain the particular class of thermoplastic elastomers (TPEs) called thermoplastic vulcanizates (TPVs). As can be seen, at the same rubber amount and composition, CM1-based materials are considerably softer and more ductile than the DIBP/D-based ones. The difference is particularly evident in the area of products containing ethylene-rich rubbers.

Table 4. Properties of cross-linked EPMs

Catalyst type	Ethylene, wt %	IV,* dl/g	E 100,** MPa	E 200,** MPa	Stress at break,** MPa	Elongation at break,** %	Tension set** 200% 1'+1', %	Compression set*** (22 h, 70°C), %
$MgCl_2/TiCl_4$/DIBP/D	51	2.8	2.3	4.6	8.5	350	30	30
$MgCl_2/TiCl_4$/CM1	50	2.9	2.0	4.6	12	380	18	21
Vanadium based	58	2.1	1.4	4.4	12.5	400	6	11

* Intrinsic viscosity measured in tetrahydronaphtalene at 135°C.
** ASTM D-412.
*** ASTM D-395, method B.

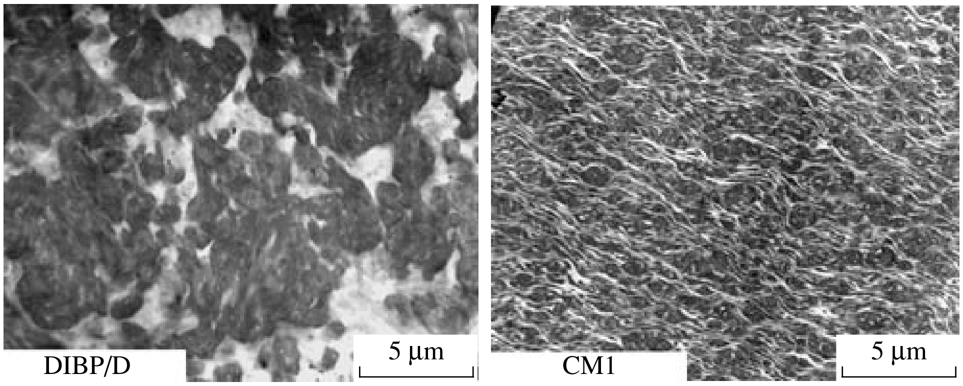
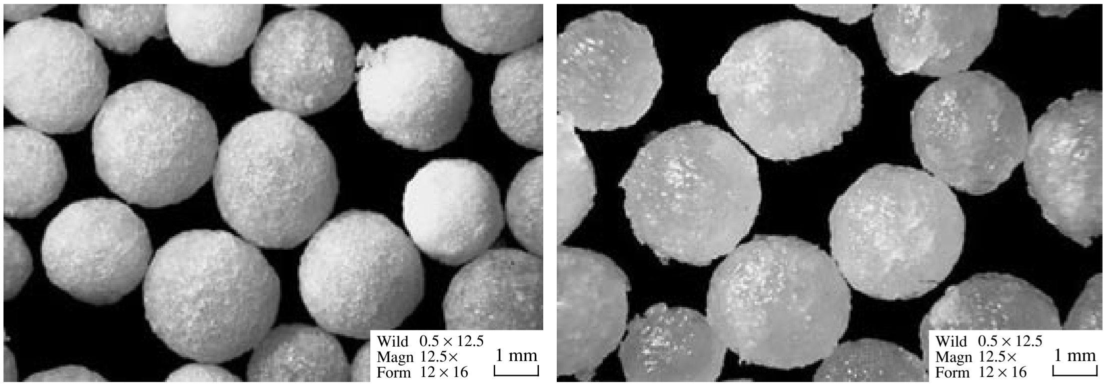


Fig. 7. Morphology (TEM) of sections of supersoft copolymers (molded specimens) synthesized via DIBP/D- or CM1-based catalysts (EPM = 70 wt %, ethylene in EPM = 60 wt %).



EPM C_2^-, 65 wt % EPM C_2^-, 48 wt %

Fig. 8. Morphology (optical microscopy) of the particles of in situ supersoft copolymers synthesized via CM1-based catalysts (EPM = 70 wt %).

Actually, with respect to DIBP/D-based materials, the CM1-based ones exhibit considerably lower flexural modulus and hardness and considerably higher strength and elongation at break. CM1-based materials containing rubbers having an intermediate ethylene content (45 wt %) show better stress/strain behavior, coupled once again with a better softness compared to DIBP/D-based offsets.

The superiority of the soft copolymers derived from CM1 is obviously related to the enhanced rubbery behavior of its ethylene–propylene block, likely coupled with the "defective" nature of the homopolymer block. However in our case, and especially for the products containing ethylene-rich rubbers, this is accompanied and "boosted" by an additional important factor: the compatibility between the rubber phase and the

Table 5. Soft heterophasic copolymers containing either propene- or ethylene-rich EPM fractions

ID	ED	XI, wt %	EPM		Mechanical properties				
			C_2^-, wt %	ethylene-propylene rubber, wt %	flexural* modulus, MPa	strength* at break, MPa	elongation* at break, %	hardness** shore	
								A	D
CM1	–	29	29	70	55	9.1	620	80	21
DIBP	D	36	28	70	83	9.8	500	90	33
CM1	–	31	61	70	34	6.4	438	73	15
DIBP	D	48	60	70	280	3.9	140	–	40

* ASTM D-412.

** ASTM D-2240.

Table 6. Properties of TPVs from soft copolymers via dynamic vulcanization

ID	ED	EPM, wt %	Compression set* (22 h, 70°C), %	Hardness** Shore A
DIBP	D	85	50	77
DIBP	D	70	41	84
CM1	–	70	36	75
Dutral CO 038 + Moplen PP		70	35	84

* ASTM D-395, method B.
** ASTM D-2240.

homopolymer matrix. It is known that propene-rich rubbers are fairly compatible or, better, mixable, with the homopolymer due to the fact that their solubility parameters are quite close. Actually, for this noncritical rubber composition, the micromorphologies of both CM1- and DIBP/D-based supersoft materials are very similar, as expected. The situation is much more critical when dealing with ethylene-rich rubbers. In this case, the micromorphology of the obtained supersoft products is clearly different: again very good dispersion of the rubber domains within the host homopolymer matrix is seen for CM1-based materials but gross separations of the phases and extremely poor dispersion of the rubber domains within the matrix is evident for DIBP/D materials (Fig. 7). This accounts well for the already mentioned difference in the performance of the relevant products containing ethylene-rich copolymer fractions. As for the reason why homopolymers from CM1-based catalysts are particularly compatible with their corresponding ethylene/propene copolymers, one can assume that this is due to the particular microstructure of the relevant building blocks: the presence of a controlled concentration of stereodefects in the homopolymer fraction and quite good intra- and intermolecular distribution of comonomers in the rubber fraction. It is important to stress that the above-reported materials can be obtained as free flowing spherical particles, like the conventional supersoft products ex Catalloy (Fig. 8). The new catalysts based on CM1 can thus be considered as drop-in systems for the preparation of new and improved in situ supersoft materials via gas-phase technologies. These products, especially those containing ethylene-rich EPMs, may in turn constitute a promising starting material for the preparation of TPVs.

Towards TPEs–TPVs

The preparation of thermoplastic elastomers and, in particular, thermoplastic vulcanizates starting from polyolefinic building blocks such as polypropene and ethylene/propene rubbers is well known in the art and entails a stage where the components are at the same time mixed in the melt and treated with vulcanizing agents such as peroxides and co-agents. During this treatment (dynamical vulcanization), the rubber phase tends to cross-link and to form fine spherical droplets which are intimately dispersed within the homopolymer matrix. These added-value materials are peculiar in that they posses fairly good elastomeric properties with the advantage and possibility, in contrast with the conventionally vulcanized pure rubbers, to be transformed and (re)processed like plastomers. The properties of TPVs are strictly related to both the amount and nature of their components and, especially, to the quality of the rubber phase in terms of the following: sufficiently high ethylene content for effective cross-linking (EPMs with less than 40–50 wt % ethylene tend to degrade); good inter- and intramolecular comonomer distribution for optimum elastomeric properties; and, finally, compatibility with the polypropylene matrix. Based on the above-reported experimental results, it can be concluded that only the CM1-based catalysts can provide the right amount and quality of building blocks required for the effective preparation of TPVs.

Of course, these materials cannot be manufactured in situ but, once the in situ supersoft products have been achieved, the step between supersoft materials and TPVs is quite straightforward. Actually, supersoft copolymers contain both the right amount and, in principle, the right composition of the components. The key point is the composition and the quality of the rubber phase and the compatibility between the components that CM1-based catalysts are able to provide.

Starting from these considerations, we performed some experiments using, as starting materials for TPVs, supersoft copolymers containing about 70 wt % of ethylene-rich rubbers. Table 6, which shows some preliminary results, indicates that TPVs from CM1 are clearly superior with respect to the corresponding TPVs from DIBP/D in terms of softness (lower Shore A hardness) and elastomeric properties (lower compression set). It is interesting to note that the new materials are similar to or better than those obtained starting from a typical ethylene-rich, vanadium-based rubber normally used to prepare this kind of products.

CONCLUSIONS

A new class of donors has been identified and used for the preparation of $MgCl_2$-supported catalyst systems for the (co)polymerization of propene. These donors can be either silanes or diethers characterized by the presence of a relatively long, linear hydrocarbyl radical. When combined as external or internal donors, respectively, with the $MgCl_2/TiCl_4$ system, they are able to provide homopolypropenes characterized by a controlled amount of stereodefects and ethylene-propene copolymers having a fairly good comonomer distribution and, thus, elastomeric properties. These special homopolypropene and ethylene-propene fractions have been used as building blocks for the preparation of supersoft materials via in situ sequential polymerization of propene and ethylene-propene mixtures. It has been found that the resulting products, either as such or employed as starting materials for the preparation of TPVs, considerably improve the elastomeric properties of polypropene-based products, enabling them to enter the added-value TPE application area.

These findings point out once again the vitality and versatility of traditional Ziegler-Natta catalysts and the key role electron donors play in the relentless tuning of their performance.

REFERENCES

1. Cecchin, G., Morini, G., and Pelliconi, A., *Macromol. Symp.*, 2001, vol. 173, p. 195.
2. Cecchin, G., *Macromol. Symp.*, 1994, vol. 78, p. 213.
3. Int. Pat. Appl. WO 03/106514, 2003.
4. Carman, C.J., Harrington, R.A., and Wilkes, C.E., *Macromolecules*, 1977, vol. 10, p. 563.
5. Resconi, L., Cavallo, L., Fait, A., and Piemontesi, F., *Chem. Rev.*, 2000, vol. 100, p. 1253.
6. Kakugo, M., Naito, Y., and Mizunuma, K., *Macromolecules*, 1982, vol. 15, p. 1150.
7. Bacci, D., Marchini, R., and Scrivani, M.T., *Polym. Eng. Sci.*, 2005, vol. 45, p. 336.