MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Synthesis of Polypropylene in the Liquid Monomer in the Presence of a Titanium–Magnesium Catalyst: Effect of Various Internal Donors

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Abstract—The influence of supported titanium–magnesium catalysts with various internal and external donors on the propylene polymerization in the liquid monomer medium and the characteristics of the polypropylene formed were studied. The following internal donors were used: dibutyl phthalate, diisobutyl phthalate, 9,9′-bis(methoxymethyl) fluorene, and diethyl 2,3-diisopropylsuccinate. The catalysts studied allow synthesis of polypropylene with high isotacticity (>96%) and different molecular-mass distribution (M_w/M_n from 3.3 to 6.3). The influence of external donors (alicyclic, amine) in combination with phthalate and nonphthalate electron-donor compounds on the stereo-specificity and activity of the catalysts and on their sensitivity to hydrogen was studied. The optimum catalytic systems for preparing polypropylene for various purposes can be found by varying pairs of internal and external donors.
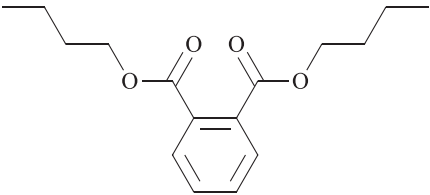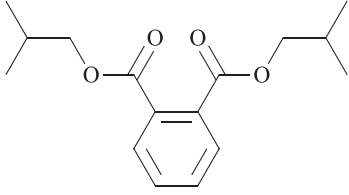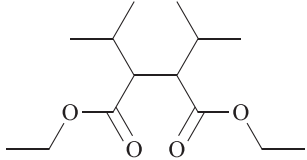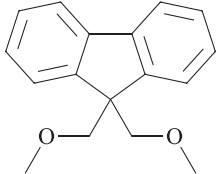
Keywords: titanium–magnesium catalyst, propylene polymerization, electron donors, isotacticity, molecular characteristics, thermal characteristics

Polymerization of propylene in the presence of supported titanium–magnesium catalysts (TMCs) attracts interest owing to high activity and high stereospecificity of the catalytic systems. It is known that the catalytic system based on TMC with internal phthalate donors proved to be effective and in the 2000s was the most widely used catalytic system for commercial production of polypropylene throughout the world [1–5]. These TMCs with phthalate electron-donor compounds in combination with alkoxysilanes were named catalysts of fourth generation. The catalytic system has the general composition $TiCl_4$/ID/$MgCl_2$ + TEA/ED (ID is an internal donor, ED is an external donor, and TEA is triethylaluminum). The mechanism of the action of electron-donor compounds consists in blocking of nonstereospecific active sites, or their conversion to stereospecific active sites, and or an increase in the propagation rate constant for stereospecific active sites [1–3].

Catalytic systems based on phthalate catalysts without external donor exhibit low stereospecificity [5]. This is caused by the fact phtalates are desorbed from the $MgCl_2$ surface after interaction with alkyl-aluminium and require substitution by an external donor (usually alkoxysilane) to preserve high stereo-specificity of the catalytic system. Search for new internal donors led to the discovery of a new family of internal donors belonging to the class of 1,3-diethers (e.g., 2,2′-diisopropyl-1,3-dimethoxypropane), which ensure high stereospecificity of TMC in propylene po-lymerization without external donor [6]. Such catalysts are sometimes named catalysts of fifth generation. The polypropylene obtained is characterized by narrower molecular-mass distribution (MMD) compared to that obtained with phthalate TMCs (M_w/M_n = 3–4 against 4–6, respectively). On the other hand, such internal donors as 2,3-substituted succinates were also found [7]; their use in TMC allowed synthesis of polypropyl-

Table 1. Titanium–magnesium catalysts with different internal donors, used in this study

Catalyst sample	Internal donor	ID structure	Titanium content	Magnesium content	ID content	d_{cat}^{50}, μm
			wt %			
TMC-1	DBP		2.5	17.7	10.2	47
TMC-2	DIBP		2.6	16.7	8.9	55
TMC-3	DEDIPS		2.6	17.0	11.0	41
TMC-4	BMMF		2.9	15.8	14.8	49

ene with high isotacticity and broader molecular-mass distribution ($M_w/M_n > 6$) compared to the polypropylene prepared in the presence of phthalate catalysts [8, 9].

In production processes, phthalate TMCs are now gradually replaced by nonphthalate TMCs because of restrictions of REACH-2015 regulations, associated with the data on harmful effect of phthalates on human health. Consumers prefer more and more frequently nonphthalate polypropylene grades for food packing and storage and for fabrication of children's toys and hygienic means. Therefore, TMCs with 1,3-diethers and succinates as internal donors are of indubitable interest as nonphthalate catalysts. Studies of nonphthalate catalysts are more and more topical, which is confirmed by an increase in the number of patents and publications on this subject [10–14]. New nonphthalate catalysts open possibilities for producing new polypropylene items with improved properties. Systematic studies of pairs

of donors with evaluation of the complete set of physicomechanical properties of polymers, allowing choice of optimum catalytic systems for producing polypropylene for various purposes, are lacking, especially for nonphthalate TMCs.

In this work we studied how various combinations of internal and external donors influence the activity and stereospecificity of titanium–magnesium catalytic systems for propylene polymerization and the characteristics of the polypropylene obtained. Such data would allow successful synthesis of polymers with preset properties and control of their commercial production process.

EXPERIMENTAL

Data on the composition and morphology (average particle size, d_{cat}^{50}) of the titanium–magnesium catalysts studied are given in Table 1. TMC-1 and TMC-4

Table 2. Properties of polypropylene synthesized on the catalytic system $TiCl_4/ID/MgCl_2$ + TEA/CHMDMS with different internal donors (70°C, 2 h)

Catalyst sample	Internal donor ID	Isotacticity I.I., %	Activity, kg PP/g cat	Melt flow index, g/10 min	Weight-average molecular mass M_w, kg mol^{-1}	Polydispersity, M_w/M_n
TMC-1	DBP	98.0	57	3.9	390	4.3
TMC-2	DIBP	96.8	50	7.0	300	4.1
TMC-3	DEDIPS	97.5	45	2.0	450	6.3
TMC-4	BMMF	98.3	46	8.0	280	3.1

catalysts were prepared according to [15]. TMC-3 was a commercial catalyst; data for TMC-2 were obtained previously [5]. Titanium–magnesium catalysts TMC-1, TMC-2, TMC-3, and TMC-4 contain internal donors: dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), diethyl 2,3-diisopropylsuccinate (DEDIPS), and 9,9′-bis(methoxymethyl)fluorene (BMMF), respectively.

We used propylene and hydrogen produced by PJSC Nizhnekamskneftekhim. To remove polymerization catalytic poisons, propylene and hydrogen were subjected to deep purification on heterogeneous catalysts with chemical sorption promoters and on molecular sieves 3A and 4A. TEA cocatalyst (PJSC Nizhnekamskneftekhim) with no less than 96% main substance content was used.

The following external donors were used (main substance content no less than 98%): cyclohexylmethyldimethoxysilane (CHMDMS, Wacker ChemieAG), dicyclopentyldimethoxysilane (DCPDMS, USI Chemical), and diethylaminotriethoxysilane (DEATES, Toho Titanium Company).

The procedures for catalytic complex preparation, propylene polymerization in the liquid monomer, and stabilization of the polypropylene (PP) powder obtained were similar to those described in [5]. The catalyst activity was evaluated by the polymer yield (kg PP/g catalyst).

The molecular characteristics of polypropylene samples were analyzed with a Polymerlab 220 high-temperature gel permeation chromatograph [5]. The polymer melt flow index (MFI) was determined in accordance with ASTM 1238 with a Ray-Ran extrusion plastometer. The polypropylene isotacticity index

(I.I.) was determined by dissolution of the sample in o-xylene, followed by slow cooling of the solution to 25°C under controllable conditions, separation of the solid phase by filtration, o-xylene evaporation from the solution, and determination of the relative content of xylene-soluble atactic polypropylene fraction (X.S., wt %); I.I. was determined as I.I. = 100 – X.S. (wt %). Polypropylene samples were studied by differential scanning calorimetry (DSC) under argon with a DSC 204F1 Phoenix device in accordance with ASTM D 3418 [5]. The degree of crystallinity was calculated by the formula $\chi = (\Delta H_m/\Delta H_{100\%}) \times 100\%$, where χ is the degree of the sample crystallinity (%); $\Delta H_{100\%}$, enthalpy of melting of fully crystalline isotactic PP ($\chi = 100\%$) (J g^{-1}); and ΔH_m, enthalpy of melting of the given sample (J g^{-1}).

The following elastic, strain, and strength characteristics of cast polypropylene samples were determined: bending elastic modulus E (according to ASTM D 790), tensile strength σ_t, relative elongation at break ε_b (both according to ASTM D 638), and Charpy notch impact strength at +23°C $A_{23°C}$ (according to ASTM D 256).

RESULTS AND DISCUSSION

The following electron-donor compounds were used as internal donors: dibutyl phthalate, diisobutyl phthalate, diethyl 2,3-diisopropylsuccinate (diethyl ester of substituted succinic acid), and 9,9′-bis(methoxymethyl)fluorene (1,3-diether).

Table 2 shows that the stereospecificity of the catalytic system $TiCl_4/ID/MgCl_2$ + TEA/CHMDMS in

propylene polymerization decreases depending on the internal donor in the following order:

ID	BMMF		DBP		DEDIPS		DIBP
I.I., %	98.3	>	98.0	>	97.5	>	96.8

The polypropylene formed under the action of titanium–magnesium catalysts with different internal donors in the presence of an external donor (CHMDMS) has high isotacticity (>96%). The isotacticity is the highest (98.3%) for the polypropylene synthesized on TMC-4 with fluorene internal donor and the lowest (96.8%) for the propylene synthesized in the presence of TMC-2 with DIBP, in agreement with the results of experiments with 1,3-diethers [16, 17].

Without external donor, the stereospecificity of the catalytic system for the propylene polymerization decreases in the following series of internal donors:

ID	BMMF		DEDIPS		DIBP
I.I., %	96.7	>	93.6	>	66.3

As can be seen, the TMC with DIBP exhibits low stereospecificity because of removal of phthalate from the catalyst under the action of TEA in the course of polymerization. High isotacticity of polypropylene obtained in the presence of BMMF agrees with the published data, according to which the 1,3-diether as an internal donor ensures high stereospecificity without external donor. This is caused by the fact that the 1,3-diether, in contrast to phthalates, is not removed from the catalyst under the action of TEA. The isotacticity of the polypropylene obtained in the presence of TMC with succinate is lower than in the case of the 1,3-diether but considerably higher than in the case of DIBP. These data allow a conclusion that the sensitivity of catalysts to external donors will be maximal in the case of phthalates and minimal in the case of the 1,3-diether. Table 3 shows that the polypropylene isotacticity varies in the series of external donors DCPDMS, CHMDMS, and DEATES as follows: 98.1, 96.8, and 95.3% with DIBP, 97.8, 97.5, and 97.5% with the succinate, and 98.5, 98.3, and 98.4% with BMMF, respectively. That is, the sensitivity of the TMC stereospecificity to the external donor is noticeable in the case of the phthalate and insignificant in the case of the 1,3-diether and succinate. Slightly lower isotacticity of polypropylene in the case of the succinate compared to BMMF (~97.6 against ~98.4%) is consistent with

the results of the polypropylene polymerization without external donor.

The activity of the catalytic system in polypropylene polymerization depends on the internal and external donors as follows:

	Activity, kg PP/g cat.		
ED\ID	DIBP	DEDIPSC	BMMF
No ED	34	58	63
DCPDMS	56	50	47
CHMDMS	50	45	46
DEATES	40	36	40

As can be seen, the activity of the phthalate catalyst is low without external donor (34 kg PP/g cat.) and significantly increases in the presence of an external donor: to a greater extent with DCPDMS (56 kg PP/g cat.) and to a lesser extent with DEATES (40 kg PP/g cat.). Enhancement of the activity of the catalytic system based on phthalate catalysts on introducing an external donor agrees with the data of [18, 19]. The external donor also significantly enhances the stereospecificity of the catalytic system (from 66 to 95–98%). The activity of nonphthalate catalysts, on the contrary, is maximal without external donor (58 and 63 kg PP/g cat. in the case of the succinate and 1,3-diether, respectively) and noticeably decreases in the presence of an external donor: to 47–50 kg PP/g cat. with DCPDMS and to 36–40 kg PP/g cat. with DEATES. The stereospecificity of the catalytic system slightly increases (from 93.6 to 97.5% and from 96.7 to 98.4% in the case of the succinate and 1,3-diether, respectively). In the case of phthalate TMC, the external donor substitutes the removed phthalate and supports high activity and high stereospecificity of the active sites. In the case of internal donors that are removed to a small extent, the external donor can be partially adsorbed on the active sites, reducing the activity of the catalytic system.

The melt flow index of polyolefins is one of the most important parameters of the polymer rheology, related to the weight-average molecular mass M_w. The MFI values of PP obtained by propylene polymerization on the catalytic system with different internal and external donors are compared, as the hydrogen sensetivity of TMCs, below (data from Table 3):

Table 3. Properties of polypropylene synthesized on the catalytic system $TiCl_4/ID/MgCl_2$ + TEA/ED with different internal and external donors

Catalyst sample	Ixternal donor ED	Isotacticity I.I., %	Activity, kg PP/g cat	Melt flow index, g/10 min	Weight-average molecular mass M_w, kg mol^{-1}	Polydispersity, M_w/M_n	Melting point T_m, °C	Crystallization point T_{cr}, °C	Crystallinity χ, %
TMC-2 (DIBP)	No ED	66.3	34	50	180	4.2	161.9 156.0	109.9	27.5
	DCPDMS	98.1	56	2.0	441	4.3	170.5	116.9	47.0
	CHMDMS	96.8	50	7.0	300	4.1	169.1	118.0	46.6
	DEATES	95.3	40	30	200	4.5	167.0	117.6	49.4
TMC-3 (DEDIPS)	No ED	93.6	58	2.7	490	7.2	165.7	112.7	45.2
	DCPDMS	97.8	50	2.0	500	5.7	171.7	117.7 111.2	47.8
	CHMDMS	97.5	45	2.0	450	6.3	170.0 154.9 148.7	109.5	48.3
	DEATES	97.5	36	3.3	410	5.9	172.5 154.2 148.1	111.7	47.1
TMC-4 (BMMF)	No ED	96.7	63	12.0	240	3.4	165.2 154.6 148.7	113.2	46.3
	DCPDMS	98.5	47	5.1	360	3.3	170.7	110.5	48.5
	CHMDMS	98.3	46	8.0	280	3.1	169.7	109.8	48.8
	DEATES	98.4	40	6.0	350	3.6	169.3	110.0	46.1

		Melt flow index, g/10 min	
ED\ID	DIBP	DEDIPS	BMMF
No ED	50	2.7	12.0
DCPDMS	2.0	2.0	5.1
CHMDMS	7.0	2.0	8.0
DEATES	30	3.3	6.0

As can be seen, in the case of the phthalate catalyst the MFI values for polypropylene depend significantly on the internal donor (from 2 to 30 g/10 min), whereas for nonphthalate TMC with the 1,3-diether and succinate as internal donor the MFI values depend on the external donor insignificantly (5.1–8.0 and 2.0–3.3 g/10 min, respectively). When replacing DCPDMS as external donor by the amine (DEATES), MFI sharply increases (by a factor of 15) in the case of the phthalate TMC and only slightly changes for the nonphthalate TMCs. As already noted, this is associated with high sensitivity of phthalate TMCs, compared to nonphthalate TMCs, to external donors.

The width of the molecular-mass distribution depends on the TMC internal donor. Table 2 shows that M_w/M_n is 4.1–4.3 for phthalate TMCs, 6.3 for TMC-3 with the succinate donor (i.e., the polydispersity becomes higher), and 3.1 for TMC-4 with the fluorene donor (i.e., the molecular-mass distribution, on the contrary, becomes narrower). The shape of the curves in Fig. 1 confirms the effect of the internal donor on the width of the molecular-mass distribution.

Variation of external donors does not lead to significant changes in the polydispersity index (Table 3, Fig. 2). As with CHMDMS, with DCPDMS and DEATES as external donors the M_w/M_n values for polypropylene are determined by the kind of the internal donor used in TMC. In particular, with different external donors the M_w/M_n values are in the interval 4.1–4.5 for phthalate (Fig. 2a), 5.7–6.3 for the succinate (Fig. 2b), and 3.1–3.6 for the 1,3-diether (Fig. 2c).

Differential scanning calorimetry is a simple and informative method for studying the supramolecular structure of polypropylene. Isotactic PP has several polymorphic modifications: $\alpha_1, \alpha_2, \beta$, and γ [20, 21]. Such polymorphic structures of polypropylene can be readily revealed by DSC in several heating–cooling cycles. It is well known [22] that samples of highly stereoregular
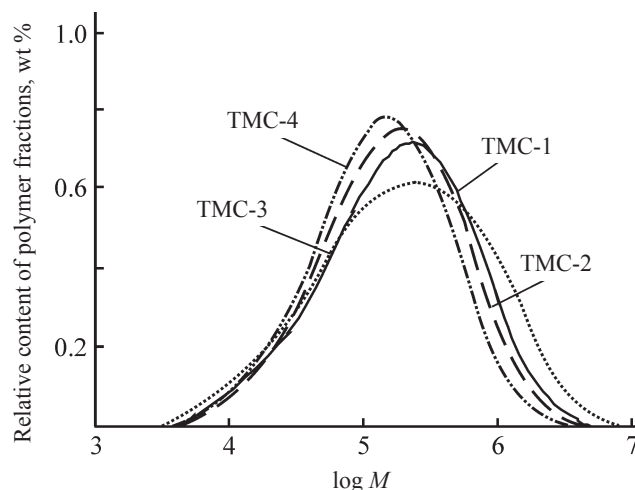

Fig. 1. Gel chromatograms of polypropylene samples obtained on catalysts with different internal donors (TMC-1, DBP; TMC-2, DIBP; TMC-3, DEDIPS; TMC-4, BMMF).

isotactic polypropylene at common crystallization rates form mainly crystallites of α_1-modification.

The results of calorimetric measurements of polypropylene samples obtained using various external and internal donors are presented in Figs. 3–6 and in Tables 3 and 4.

Table 4 shows that the thermal properties of polypropylene synthesized on the catalytic system $TiCl_4/ID/MgCl_2$ + TEA/CHMDMS vary depending on the internal donor as follows:

ID	DBP		DIBP		DEDIPS		BMMF
T_m, °C	169.3	~	169.1	≤	170.0 154.9 148.7		~ 169.7
T_{cr}, °C	116.7	~	118.0	>	109.5		~ 109.8
χ, %	46.9	~	46.6	≤	48.3		~ 48.8

As can be seen, the polypropylene samples prepared on nonphthalate catalysts with CHMDMS external donors are characterized by higher values of T_m and crystallinity but lower crystallization points compared to the polymers prepared on phthalate catalysts.

Analysis of the DSC melting curves at second heating shows that the polypropylene samples synthesized on TMC-1, TMC-2, and TMC-4 are characterized by a single phase transition in the range from 169 to 170°C. The use of catalysts with the phthalate and 1,3-diether as internal donors leads to the formation of polypropylene

Table 4. Thermal properties of polypropylene synthesized on the catalytic system $TiCl_4/ID/MgCl_2$ + TEA/CHMDMS with different internal donors

Catalyst sample	Internal donor ID	Melting point T_m, °C	Enthalpy of melting ΔH_m, J g^{-1}	Extrapolated crystallization onset temperature $T_{cr.onset}$, °C	Crystallization point T_{cr}, °C	Difference between the temperatures of the crystallization onset and crystallization point $T_{cr.onset} - T_{cr}$, °C	Difference between the melting and crystallization points $T_m - T_{cr}$, °C	Enthalpy of crystallization ΔH_{cr}, J g^{-1}	Crystallinity χ, %
TMC-1	DBP	169.3	98.1	121.1	116.7	4.4	52.6	99.8	46.9
TMC-2	DIBP	169.1	97.3	122.0	118.0	4.0	51.1	106.1	46.6
TMC-3	DEDIPS	148.7 154.9 170.0	101.0	118.6	109.5	9.1	60.5	113.0	48.3
TMC-4	BMMF	169.7	102.0	119.4	109.8	9.6	59.9	111.5	48.8

with the α_1-modification of the crystalline phase. However, when using the succinate as an internal donor (TMC-3), additional low-temperature melting peaks at 148.7 and 154.9°C, corresponding to melting of the less stable β-modification [23], appear in the DSC curve (Fig. 3). The temperature characteristics (T_m, T_{cr}) can be clearly subdivided into two groups corresponding to the phthalate donors (TMC-1 and TMC-2) and succinate and fluorene donors (TMC-3 and TMC-4). Similar pattern is observed for the crystallinity of the polypropylene samples. It is clearly seen that the polypropylene samples synthesized on TMC-4 and TMC-3 exhibit the highest crystallinity (on the level of 48.8%) and the crystallinity of the polypropylene samples synthesized using phthalate donors (TMC-1, TMC-2) is slightly lower (46–47%).

The polypropylene samples can also be characterized by the crystallization curves. These data supplement the melting curve data. For example, the crystallization parameters given in Table 4 demonstrate noticeable difference in the crystallization onset temperature between the polypropylene sample synthesized using TMC-3 (succinate) and the samples synthesized using the other TMCs (118.6 against 121–122°C). The former sample is also characterized by low crystallization ability ($\Delta T = T_m - T_{cr} = 60.5$°C is maximal) and minimal crystallization point ($T_{cr} = 109.5$°C). Furthermore, the crystal-

lization peak for the polypropylene sample prepared on TMC with the succinate is broader than the crystallization peaks of the other polymer samples studied. These differences are due to factors influencing the crystallite formation, such as the stereoregularity of the polymer chain and molecular-mass characteristics. In this case, at high isotacticity of the polypropylene sample (TMC-3), an increase in its polydispersity (to $M_w/M_n = 6.3$, Table 2) and viscosity (MFI = 2 g/10 min) leads to a decrease in the crystallization rate (decrease in T_{cr}) and favors the formation of crystals of different thicknesses. This is manifested in the DSC thermogram in the appearance of the melting peak of β-modification crystals [17]. The same phenomenon was noted in [18, 22]. The polypropylene samples synthesized in the presence of phthalate catalysts (TMC-1 and TMC-2) are characterized by high crystal growth rate [$\Delta(T_{cr.onset} - T_{cr}) = 4$°C], maximal intensity of crystallization peaks (Fig. 4, cooling curves, $T_{cr.onset} = 121$–122°C), and maximal crystallization point (Table 4). The PP samples prepared on TMC-4 with the 1,3-diether and on TMC-3 are characterized by slightly lower temperatures (on the level of 109°C) and heights of the crystallization peaks.

For the same internal donors, we performed a series of experiments with variation of the external donors (Table 3).
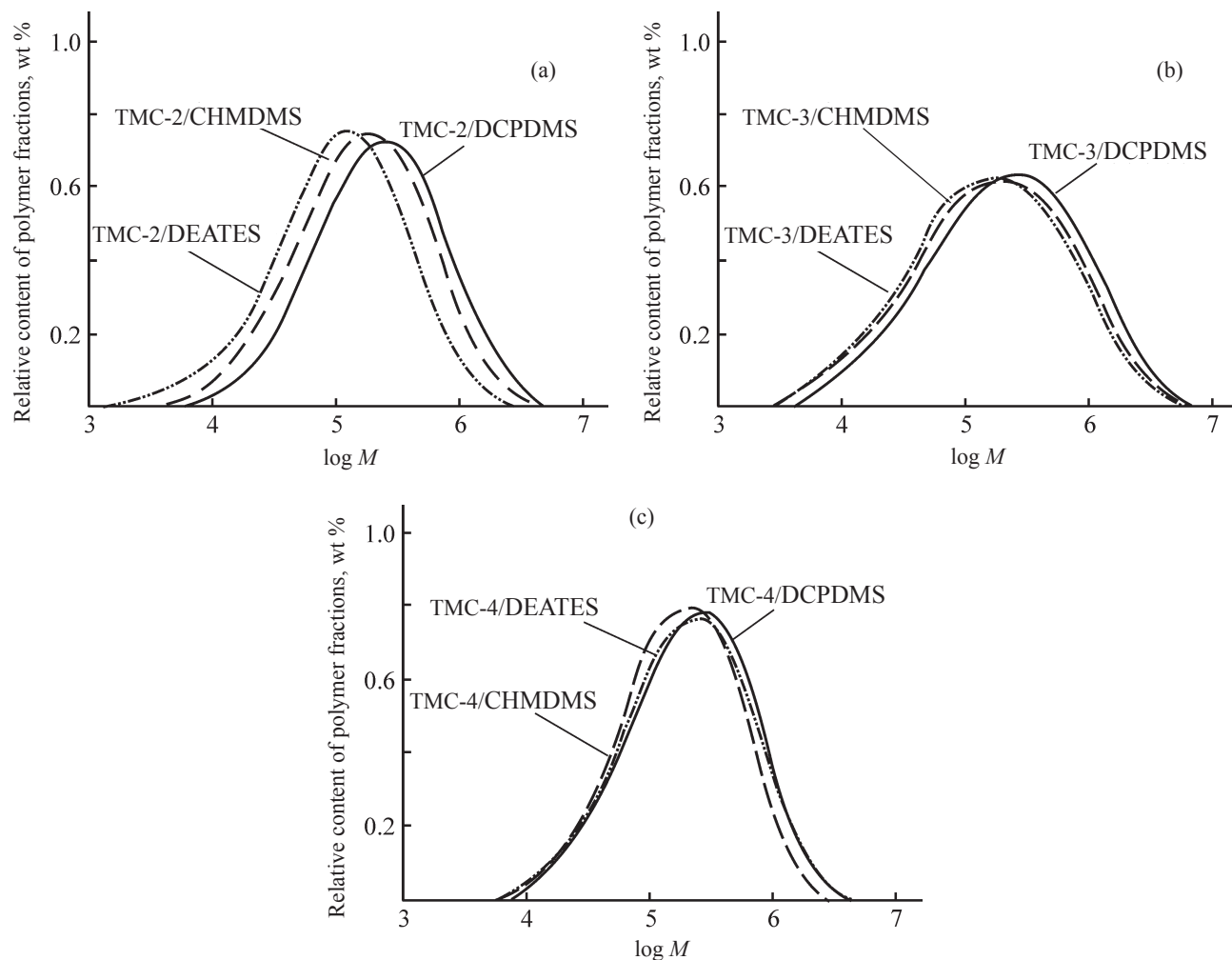
Fig. 2. Gel chromatograms of polypropylene samples obtained on catalysts with different internal and external donors. Internal donor: (a) DIBP, (b) DEDIPS, and (c) BMMF.
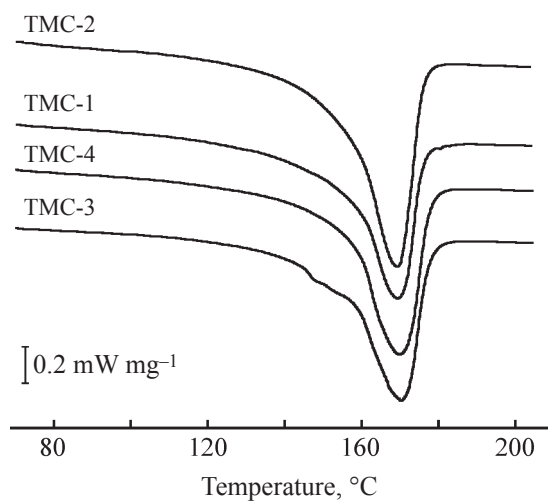

Fig. 3. DSC thermograms (heating curves) of polypropylene samples obtained on catalysts with different internal donors (TMC-1, DBP; TMC-2, DIBP; TMC-3, DEDIPS; TMC-4, BMMF).
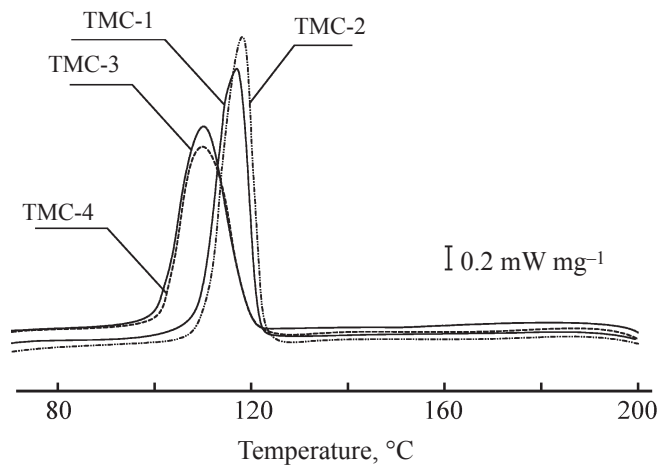
Fig. 4. DSC thermograms (cooling curves) of polypropylene samples obtained on catalysts with different internal donors (TMC-1, DBP; TMC-2, DIBP; TMC-3, DEDIPS; TMC-4, BMMF).
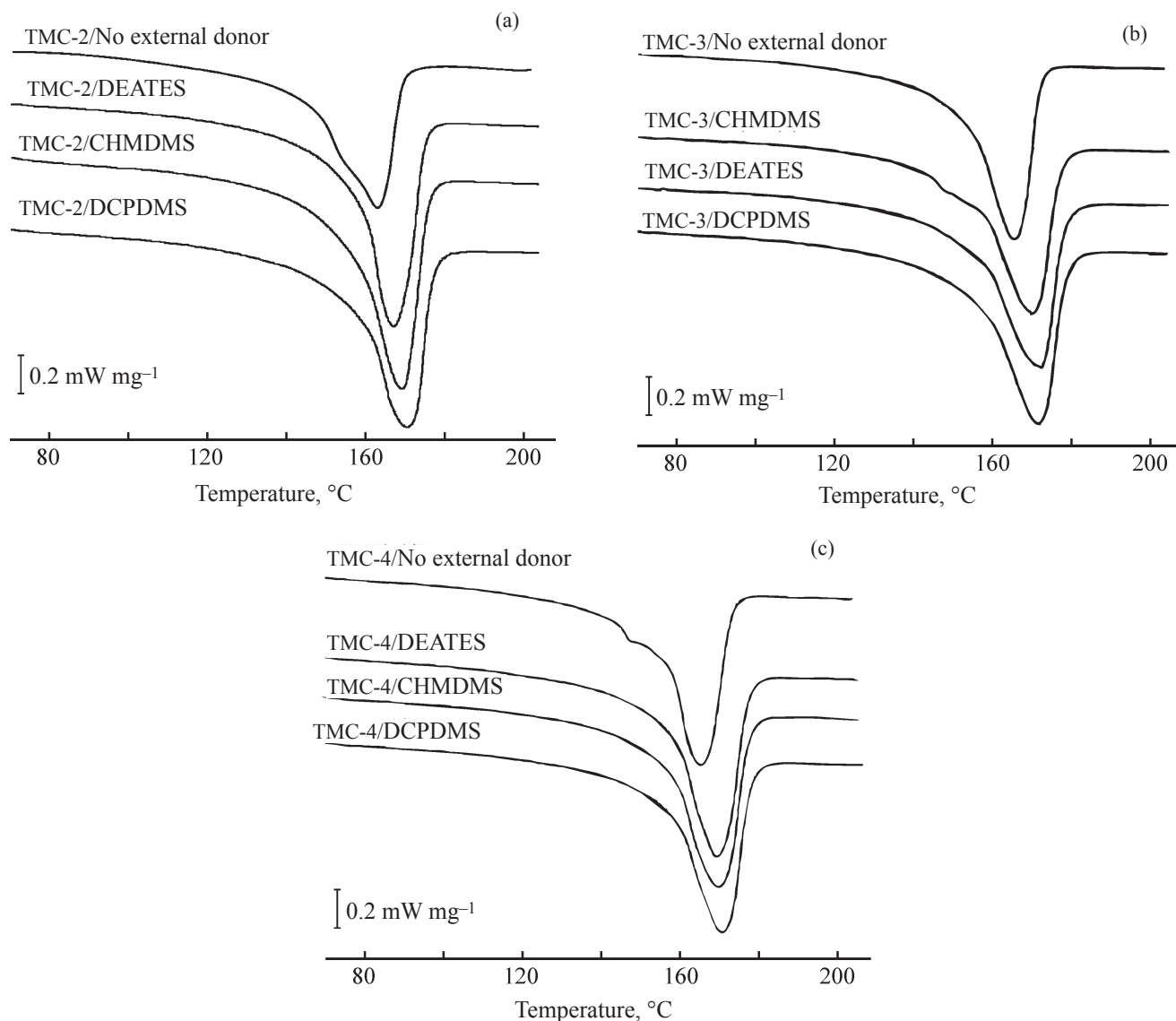
Fig. 5. DSC thermograms (heating curves) of polypropylene samples obtained on catalysts with different internal and external donors. Internal donor: (a) DIBP, (b) DEDIPS, and (c) BMMF.

For the TMCs with different internal donors (phthalate, succinate, fluorene), dicyclopentyldimethoxysilane as an external donor exhibits the highest stereoregulating ability. Table 3 and Figs. 5 and 6 show that the polypropylene samples obtained on the phthalate catalyst with different external donors have the crystallinity of 46.6–49.4% with T_m = 167–170.5°C (Figs. 5a, 6a). The polypropylene samples obtained on the succinate catalyst with different silanes have the crystallinity of 47.1–48.3% with T_m = 170–172.5°C (Figs. 5b, 6b). The polypropylene samples obtained on the catalyst with the 1,3-diether and external donors have the

crystallinity of 46.1–48.8% with T_m = 169.3–170.7°C (Figs. 5c, 6c). On the whole, the T_m values are relatively close and maximal in the case of the succinate; the polypropylene crystallinity is close in the cases of the phthalate and succinate and slightly lower in the case of the 1,3-diether. Without external donor, the crystallinity of the polypropylene obtained with the phthalate, succinate, and 1,3-diether as internal donors is 27.5, 45.2, and 46.3%, and T_m of the polymer is 159, 165.7, and 165.2°C, respectively. The maximal T_{cr} is reached when using DCPDMS as an external donor on TMC with the phthalate and succinate internal donors. It suggests high
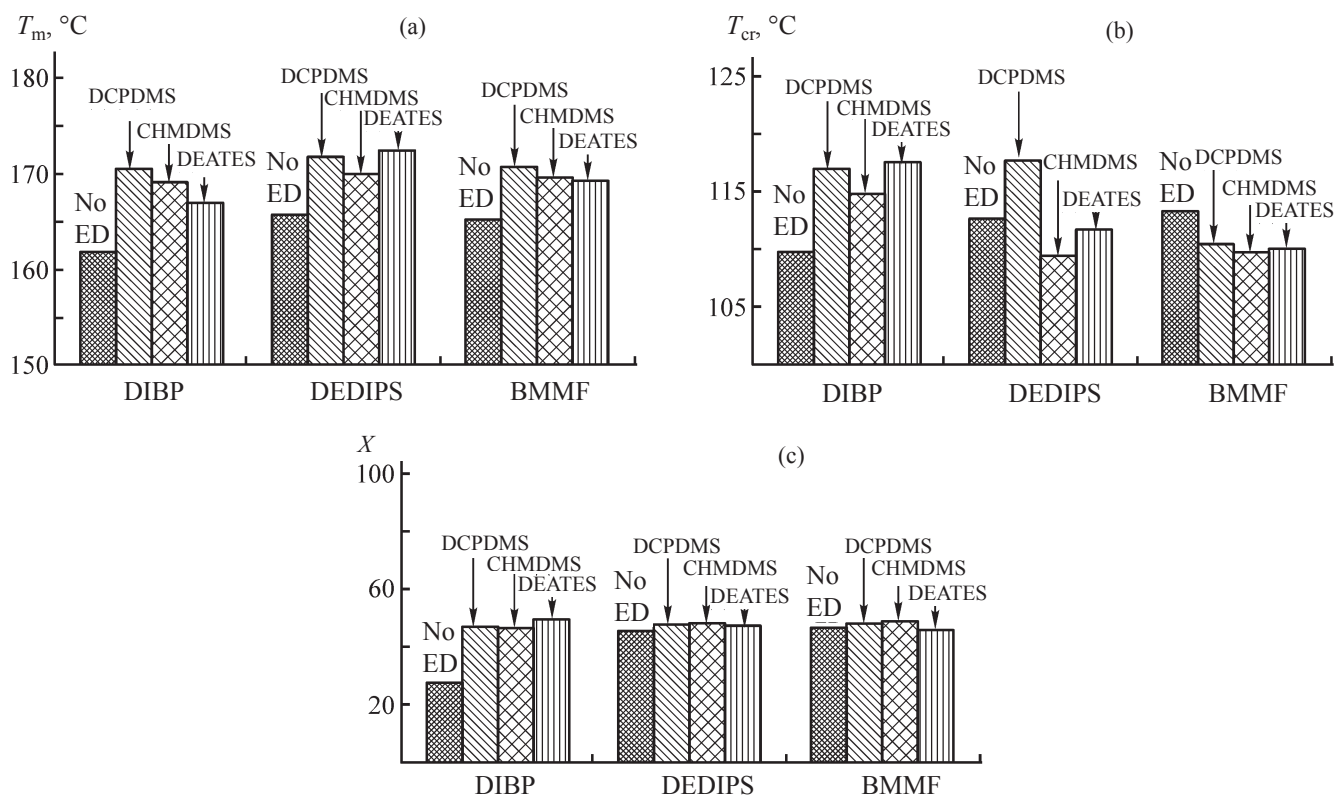
Fig. 6. (a) Melting point, (b) crystallization point, and (c) crystallinity of polypropylene samples obtained on catalysts with different internal and external donors.

stereoregularity of the polypropylene samples studied. As can be seen, variation of T_m and crystallinity (Figs. 6a, 6c) show that the TMCs with the phthalate internal donor are more sensitive than the nonphthalate TMCs to the chemical structure of the external donor. In the case of the succinate internal donor, high values of T_m, T_{cr}, and crystallinity are reached simultaneously only with DCPDMS as an external donor (Fig. 6).

It can also be noted that, for all the TMCs studied with different internal donors, the maximal values of the isotacticity, degree of crystallinity, and molecular characteristics of polypropylene samples are reached when using DCPDMS as an external donor (with two cyclopentyl substituents and two methoxy groups). For the polypropylene samples obtained using the internal donor based on the 1,3-diether, the kind of the external donor (among those we studied) does not significantly influence the properties of the polymer obtained.

Thus, according to the DSC data, the polypropylene samples prepared on the succinate catalyst with external donors exhibit high crystallinity (47–48%) and the highest T_m. The polymers prepared on TMC with the

1,3-diether and different external donors have somewhat lower values of the crystallinity and T_m. In the case of the phthalate catalyst, the values of T_m and crystallinity depend on the external donor.

The results of studying the elastic, strain, and strength characteristics of polypropylene samples synthesized on the catalytic systems $TiCl_4/ID/MgCl_2$ + TEA/ED with different internal and external donors are given in Table 5. As can be seen, when comparing catalysts with different internal donors, the highest values of the bending elastic modulus of polypropylene were reached when using the succinate catalyst with DCPDMS and CHMDMS ($E = 1260$ and 1210 MPa, respectively) as external electron donors. The lowest values of the elastic modulus were obtained when using the fluorene catalyst with DEATES as an external donor ($E = 1080$ MPa). In the case of the phthalate catalyst with different external donors, the E values are close (1140–1160 MPa). Without external donor, E decreases slightly for nonphthalate TMCs ($E = 975$–1000 MPa) and sharply for the phthalate catalyst ($E = 270$ MPa), which is associated with a sharp

Table 5. Physicomechanical properties of polypropylene synthesized on the catalytic system $TiCl_4/ID/MgCl_2$ + TEA/ED with different internal and external donors

Catalyst sample	External donor ED	Flexural modulus E, MPa	Charpy impact strength at +23°C $A_{23°C}$, kJ m^{-2}	Tensile at break σ_b, MPa	Elongation at break ε_b, %
TMC-2 (DIBP)	No ED	270	19.0	15.9	670
	DCPDMS	1150	8.7	10.5	63
	CHMDMS	1140	7.9	17.9	76
	DEATES	1160	5.3	22.4	270
TMC-3 (DEDIPS)	No ED	975	8.7	14.7	122
	DCPDMS	1260	6.0	20.8	43
	CHMDMS	1210	6.1	11.4	67
	DEATES	1100	5.5	13.6	44
TMC-4 (BMMF)	No ED	1000	6.2	18.5	613
	CHMDMS	1100	5.7	16.2	90

decrease in the PP isotacticity and crystallinity in the latter case.

The Charpy impact resistance of the polypropylene samples obtained with different donors correlates to a greater extent with the polymer molecular mass than with its crystallinity. In the case of TMC with DIBP, polypropylene with different levels of impact resistance depending on the molecular mass range is formed, with the highest value reached when using the phthalate catalyst with DCPDMS (8.7 kJ m^{-2} at M_w = 441 kg mol^{-1}), and the lowest, with DEATES (5.3 kJ m^{-2} at M_w = 200 kg mol^{-1}). In the case of the succinate, the impact resistance of the polypropylene samples obtained with DCPDMS, CHMDMS, and DEATES as external donors was close (6.0, 6.1, and 5.5 kJ m^{-2}, respectively), with the molecular mass being also close (M_w = 500, 450, and 410 kg mol^{-1}, respectively). In the case of the TMC with the 1,3-diether in the presence of CHMDMS as an external donor, the impact resistance of polypropylene was 5.7 kJ m^{-2}, being lower than for the polypropylene samples obtained on the catalysts with DIBP (7.9 kJ m^{-2}) and DEDIPS (6.1 kJ m^{-2}).

The relative elongation of polypropylene at break also significantly depends on the kind of internal and external donors. In the case of DIBP with DCPDMS and CHMDMS as external donors, the relative elongation of the polypropylene samples at break is 63–76%, and with DEATES as an external donor ε_b is 3.5–4 times higher, 270%. With the succinate catalyst, the polypropylene synthesized in the presence of DCPDMS and DEATES as external donors has the lowest ε_b (43–44%), and that synthesized in the presence of CHMDMS, the highest ε_b (67%). As for the tensile strength, the maximal value (22.4 MPa) is reached on TMC-2 catalyst with DEATES as an external donor.

Apparently, with an increase in the molecular mass of polypropylene and with a decrease in the relative content of the low-stereoregularity fraction, the elastic modulus and impact resistance of the polymer increase, but the polymer becomes rigid and less elastic (more brittle), which is manifested when using the succinate irrespective of the kind of the external donor. An increase in the amorphous phase content of the polymer favors an increase in the relative elongation at break.

The results of the elastic, strength, and strain studies of polypropylene samples show that the polymers obtained have different values of the bending elastic modulus, impact resistance, strength, and relative elongation at break depending on the combinations of the internal and external donors in the TMC. The data obtained allow the polypropylene properties to be controlled in a wide

range by varying electron-donor compounds of different structures, and optimum TMC-based catalytic systems can be chosen for preparing polymers for different purposes. For example, polypropylene with narrow molecular-mass distribution, prepared on TMC with the diether internal donor, is more suitable for producing fibers and threads, whereas polypropylene with broad molecular-mass distribution, formed on TMC with the succinate donor, is preferred by producers of plastic pipes.

CONCLUSIONS

Our study shows that the structure of the internal electron-donor compound as a component of the titanium–magnesium catalyst largely determines the course of the propylene polymerization and the final characteristics of the polypropylene formed. A study of the influence exerted by phthalates, 1,3-diether, and substituted succinate as internal donors in the titanium–magnesium catalyst on the polypropylene synthesis in the liquid monomer revealed trends in the stereospecificity and activity of the catalytic system and in the melt flow index, polydispersity, and thermal properties of the polymer. The use of the titanium–magnesium catalysts with diethers and diesters as internal donors leads to the formation of polypropylene samples with different values of isotacticity and melt flow index and different molecular-mass distribution. In particular, the polypropylene synthesized using the titanium–magnesium catalyst with the succinate or 1,3-diether has broader or narrower molecular-mass distribution, respectively, than the polymer synthesized on the phthalate catalyst. Introduction of external donors (alicyclic, amine) into the polymerization system containing the catalysts studied leads to the formation of catalytic systems with different levels of activity and sensitivity to hydrogen.

Data on the bending elastic modulus, Charpy impact resistance, and relative elongation at break of the polypropylene samples obtained on the titanium–magnesium catalyst with different internal donors show that the physicomechanical properties of polypropylene largely correlate with its degree of crystallinity and weight-average molecular mass. The nonphthalate catalysts compared to phthalate catalysts are characterized by weaker influence of the kind of external donor on the properties of the polypropylene obtained.

Thus, variation of the internal donors based on diethers and diesters (1,3-diether, substituted succinate, phthalate) in the titanium–magnesium catalyst formulation allows control of the isotacticity, molecular and thermal characteristics, and impact resistance of the polypropylene obtained. The results of experiments on variation of combinations of internal and external electron donors in the catalyst are useful for finding catalytic systems for the production of polymers with the required properties.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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