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Effect of 1-hexene on the propylene polymerization with supported phthalate-free titanium–magnesium catalyst

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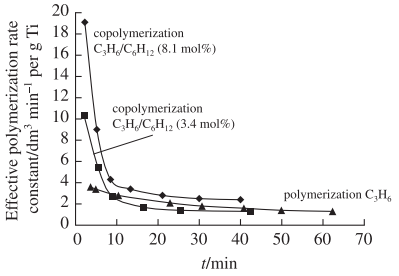
The polymerization of propylene with small amounts of 1-hexene in the presence of supported titanium–magnesium catalyst containing two internal non-phthalate donors was accomplished. Polypropylene modification with small amounts of 1-hexene affects the thermophysical properties and molecular weight characteristics of the polymers. The activation mechanism of the reaction is described; the introduction of small amounts of 1-hexene causes an increase in activity by a factor of 1.5.



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Heterogeneous Ziegler–Natta catalysts occupy the leading position in the field of industrial olefin polymerization. Supported titanium–magnesium catalysts (TMC) containing phthalates as the internal donors were the most widely used for the synthesis of isotactic polypropylene (PP). However, in the early 80's it was discovered that phthalates were harmful to humans due to their toxic effects. Further studies showed that these compounds, gradually turned into metabolites in the human body, might negatively affect different organs.[1,2] Teratogenic and mutagenic effects of several phthalates were also discovered.[3] For this reason, the use of phthalate-containing PP was limited, especially in the food and toy industries. Hence, the need for phthalate-free TMC catalysts stimulated research on the synthesis and the use of the new generation of supported catalysts based on diethers and succinates as internal donors in the polymerization reactions. The effect of these systems on the properties of the synthesized polymers was described.[4–8]

Copolymerization of propylene with small amounts of α-olefins is widely used to improve the properties of PP. Therefore, it is important to study new phthalate-free catalysts for the synthesis of copolymers of propylene with α-olefins. Since most of the published research in this field are patents, information on the copolymerization process and the properties of the polymers is not well defined.

The aim of this work was to investigate propylene polymerization reactions carried out in the medium of liquid propylene with small amounts of 1-hexene. The catalyst system was a TMC, containing the mixture of dialkyl succinate and 1,3-diether [bis(methoxy)methylfluorene] as an internal donor. The Ti content in the catalyst was 3.5 wt%. Triethylaluminum was used as a cocatalyst and cyclohexylmethyl-dimethoxysilane contributed as an external donor. Polymerization experiments were carried out at 50 °C in a 200 cm^3 stainless steel autoclave reactor at a constant pressure of the reaction mixture. The propylene concentration was 11.4 mol dm^{-3}. The content of 1-hexene in the monomer mixture varied from 3.4 to 8.1 mol%.

The obtained polymerization results are presented in Table 1 and Figure 1. As can be seen from Table 1, the introduction of 1-hexene into the reaction medium causes an increase in the catalytic system activity from 100 to 165 kg h^{-1} per g of Ti.

Figure 1 shows the polymerization kinetics at different 1-hexene concentrations in the reaction medium. The kinetic curves demonstrate that the addition of the comonomer leads to the increase in the initial effective polymerization rate constant.

According to the published data, the molecules of higher α-olefins can modify growth centers, significantly changing their

Table 1 Propylene/1-hexene copolymerization reactions data.[a]

Sample	1-Hexene in comonomer mixture (mol%)	Yield/ kg h^{-1} per g Ti	1-Hexene in copolymer (mol%)	D_{998}/D_{973}[b]	$M_w \times 10^{-3}$	M_w/M_n
1	0.0	100	0.00	0.896	1430	6.7
2	3.4	154	0.14	0.894	1800	6.6
3	6.9	165	0.60	0.862	1480	6.3
4	8.1	164	0.80	0.861	1140	5.8

[a] Reaction conditions: [Ti] ≈ 2×10^{-2} mmol; Al : Ti molar ratio, 100–140 : 1; Al : ext. donor molar ratio, ~20 : 1. [b] D_{998}/D_{973} – macrotacticity parameter of PP, obtained from IR spectra.

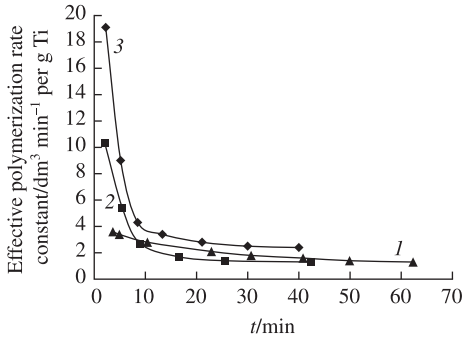

Figure 1 Time dependences of the specific propylene polymerization rate in the presence of TMC in the liquid propylene medium at 50 °C of (*1*) propylene homopolymerization; (*2*) and (*3*) propylene/1-hexene copolymerization with (*2*) 3.4 and (*3*) 8.1 mol% of 1-hexene.

Table 2 The content of propylene steric pentads in polymers (%).[a]

Sample	mmmm	mmmr	rmmr	mmrr	mmrm + rrmr	mrmr	rrrr	rrrm	mrrm
1	87.8	2.90	0.27	3.04	1.77	0.19	1.72	1.07	1.26
2	89.9	2.20	0.18	2.58	1.35	0.23	1.42	0.91	1.25
3	90.1	2.56	0.42	2.41	1.31	0.19	1.13	0.89	1.02
4	89.2	3.50	0.44	2.28	1.14	0.17	1.24	0.87	1.15

[a] m denotes meso dyads, r denotes racemic dyads.

catalytic properties.[9–12] There is an assumption[12] that the polymer chain growth constant increases as a result of a specific solvation of active center by 1-hexene molecules, thus facilitating the incorporation of propylene molecules into the Ti–C bond. Another activation mechanism was considered in our earlier work.[13] An increase in the polymerization rate due to the comonomer introduction was attributed to the 1-hexene activation of the 'dormant' centers, which are formed *via* the 2,1-insertion of a propylene molecule into the growing polymer chain. A detailed explanation of the activation mechanism by 1-hexene is presented in Online Supplementary Materials.

To determine the copolymerization constant $r_1 = k_{11}/k_{12}$ (1 is propylene, 2 is 1-hexene), we used the simplified Mayo–Lewis equation $f \approx r_1 F$, where F and f are the ratios of molar concentrations of comonomers in the reaction medium and in the copolymer, respectively. The value of the copolymerization constant r_1 is 12.3, which indicates the predominant incorporation of propylene into the polymer chain as compared to 1-hexene.

The introduction of small amounts of 1-hexene into the PP polymer chains affects their molecular weight characteristics (see Table 1). The average molecular weight M_w of the copolymer increases by a factor of ~1.25 at the 1-hexene content of 0.14 mol%. A further increase of the 1-hexene content in the copolymer leads to a slight decrease of the M_w and molecular weight distribution; this occurs due to the chain transfer reaction with 1-hexene.

The width of the molecular weight distribution depends on the nature of the internal donor in a TMC.[5] Our catalyst with the mixture of non-phthalate donors produces polymers with higher values of the width of the molecular weight distribution M_w/M_n (5.8–6.7, see Table 1) in comparison with the known TMC containing phthalate donors (M_w/M_n ~4.5–5.5).[14,15] It was shown recently[5] that the M_w/M_n values are in the range of 5.7–6.3 for succinate-containing TMC and 3.1–3.6 for 1,3-diether-containing TMC. In the catalyst under study, the succinate has the predominant effect on the formation of the active sites, which leads to the production of PP and copolymers with wider molecular weight distribution.

The introduction of small amounts of 1-hexene into the polymer chain leads to the decrease in the macrotacticity parameter, which characterizes the proportion of propylene in polymer blocks with a length of at least 10–11 monomer units, and thus indicates the change in the microstructure of the PP chain (see Table 1).

The content of steric propylene pentads, calculated from ^{13}C NMR spectra, is given in Table 2. The assignment of chemical shifts for different sequences in the spectra of PP and propylene/1-hexene copolymers was carried out according to the publication.[16]

Table 3 Properties of PP and propylene/1-hexene copolymers.[a]

Sample	1-Hexene in copolymer (mol%)	T_m/°C	χ (%)	E/MPa	σ_y/MPa	σ_{br}/MPa	ε_{br} (%)
1	0.00	164.9	55.3	951	34.0	25.8	120
2	0.14	161.6	53.2	974	31.3	31.9	397
3	0.60	156.8	49.7	873	31.6	35.3	435
4	0.80	154.7	50.2	808	29.8	25.8	355

[a] E is tensile modulus, σ_y is yield strength, σ_{br} is strength at break, ε_{br} is elongation at break. Test speed 50 mm min^{-1}. χ is degree of crystallinity, determined as $\chi\% = (\Delta H_m/\Delta H_0) \times 100$, where $\Delta H_0 = 165$ J g^{-1}.

The content of stereo-propylene pentads in the copolymers remains quite high (see Table 2), which implies that the nature of the stereoregularity of the investigated phthalate-free TMC is maintained in propylene/1-hexene copolymerization reactions.

Thermophysical properties of the obtained copolymers, *viz.* melting temperature T_m (the second heating), the degree of crystallinity χ and the stress-strain data, are given in Table 3.

The changes in the microstructure of the polymer chains are reflected in the decrease in the melting point and the crystallinity degree. A small number of 1-hexene units can be considered as structural defects in the polymer chains, they lead to disruptions in the length of regular PP sequences. As a result, a decrease in the content and degree of perfection of the crystalline phase is observed with an increase in the content of 1-hexene units.

The obtained stress–strength characteristics of the copolymers indicates that the insertion of a small quantity of 1-hexene into a PP chain leads to a slight decrease in the elastic modulus, a decrease of the stress at the yield point, and a noticeable increase in the deformation characteristics.

In conclusion, the introduction of small amounts of 1-hexene in the bulk propylene polymerization reaction with TMC containing two internal non-phthalate donors results in the significant modification of the active centers. The catalytic activity of the system increases by 50% and the improvement in the deformation characteristics of the polymers is achieved. Further study of propylene polymerization reactions with phthalate-free TMC under conditions close to industrial production of polyolefins is promising for obtaining polypropylene with the specified properties.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.037.

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