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

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Gel permeation chromatography (GPC) analysis was carried out at 140 °C with a "GPCV 2000" (Waters) chromatograph equipped with column Styrogel HT 6 E (7,8 x 300 mm) and a refractometer. 1, 2, 4-Trichlorobenzene was used as a solvent. Molecular weights (MWs) of the P/H copolymers were determined using the universal calibration dependence relative to polystyrene standards with a narrow MW distribution.

The microstructure and composition of propylene and 1-hexene copolymers were determined by IR- and ^{13}C NMR spectroscopy.

IR spectra of the polymers were recorded on a Bruker Vertex 70 FTIR spectrometer. The absorbance ratio of 998 and 973 cm^{-1} bands was used as the parameter of PP stereoregularity (macrotacticity).[S1]

^{13}C NMR spectra of polymers (~2-3 wt% solutions in o-dichlorobenzene) were recorded at 99 °C on a Bruker Avance-400 spectrometer (100.614 MHz). The relaxation delay was 15 s, the number of scans varied from 4400 to 7000. The content of 1-hexene in the P/H copolymers (mol%), was calculated from the ^{13}C NMR data. Complex profiles of CH_3 signals in the 21.9 to 22.2 ppm range in the spectra were resolved into signals of stereo-components, pentads mmmm, mmmr, rmmr, mmrr, mmrm, rrmr, mrmr, rrrr. The signal assignment in the spectra was carried out according to Hsieh and Randall.[S2]

The melting point (T_m) and heat of melting (ΔH_m) of PP and copolymers were determined by the DSC method on a Netzsch DSC-209 F1 analyzer for samples weighing 5-9 mg at a scan (heating / cooling) rate of 10 °C/min. The crystallinity degree of PP and the P/H copolymers was calculated from the heat of melting (ΔH_m) as ($\Delta H_m/\Delta H^0_m$) × 100 (%); the ΔH^0_m=165J/g.

Samples for testing the mechanical properties were prepared by pressing polymers at 190 °C and a pressure of 10 MPa at a melt cooling rate of 20 °C/min. The antioxidant Irganox was used as a stabilizer in an amount of 0.5 wt%. Tensile tests were carried out at 20 °C on an Instron 1122 machine on samples with the cross section of 0.75 - 5 mm, base length 35 mm. The test mode: stretching at a speed of 50 mm / min up to breaking of the sample.

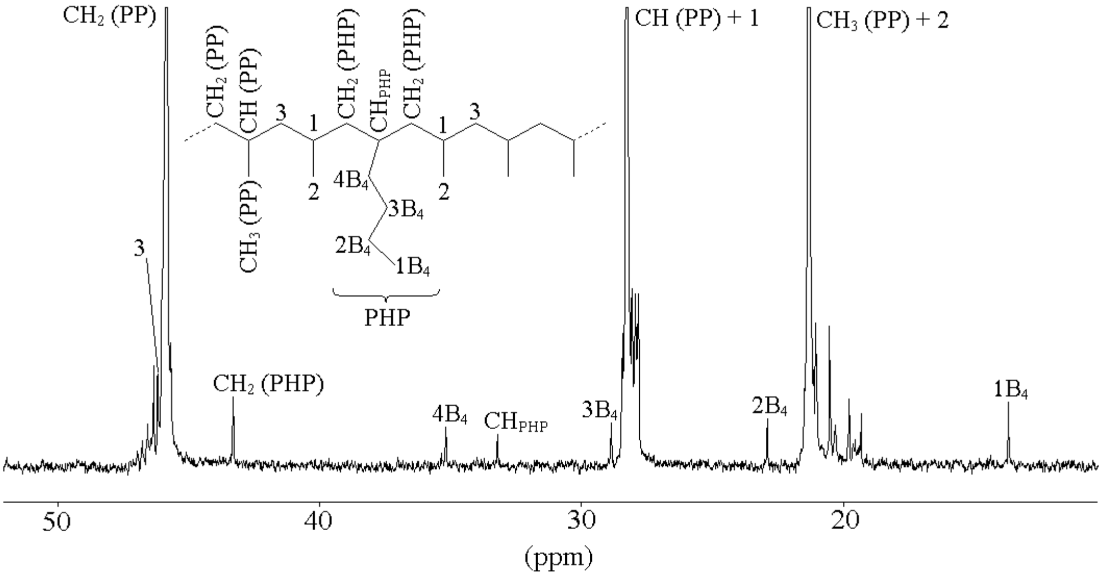

Figure S1 ^{13}C NMR spectrum of the copolymer propylene / 1- hexene N 3 (0.6 mol%)

Table S1 Polymer stereoregularity (0.6 mol % hexene) from ^{13}C NMR

Chem.shift, ppm	Pentades	Integral intensity	% pentades
21.5253	mmmm	0.06	90.07
21.3118		88.93	
21.1266		0.54	
21.0379	mmmr	1.31	2.56
21.0021		1.23	
20.7965	rmmr	0.42	0.42
20.5055	mmrr	2.4	2.41
20.2920	mmrm+rrmr	1.26	1.31
20.1961		0.04	
20.1275	mrmr	0.03	0.19
20.0838		0.11	
20.0043		0.05	
19.7995	rrrr	0.35	1.13
19.7525		0.77	
19.6132	rrrm	0.38	0.89
19.5366		0.36	
19.4627		0.15	
19.3815	mrrm	0.33	1.02
19.3019		0.68	
		99.99	
	Total		100

Table S2 The content of propylene steric triads in copolymers (%)

Entry	mm	mr	rr
1	90.97	5.0	4.05
2	92.28	4.16	3.58
3	93.08	3.91	3.04
4	93.14	3.59	3.26

Activation mechanism was considered in ref. [S3]

The activating effect of 1-hexene during copolymerization of propylene with 1-hexene can be explained as follows.

At the initiation stage, after the secondary incorporation of the propylene molecule (by type 2-1) into the Ti-C or Ti-H bond, Ti-CH(CH_3)$_2$ centers are formed, which have a reduced reactivity, the so-called ‘dormant’ centers.

$Ti–CH_2–CH(CH_3)–[CH_2–CH(CH_3)]_n–R + CH(CH_3)=CH_2 \rightarrow$

$Ti–CH(CH_3)_2 + CH_2=C(CH_3)–[CH_2–CH(CH_3)]_n–R$

The primary incorporation of both propylene and 1-hexene into these centers is difficult for steric reasons, while the secondary incorporation of comonomers seems to be more likely

$Ti–CH(CH_3)_2 + CH(CH_3)=CH_2 \rightarrow Ti–CH(CH_3)–CH_2–CH(CH_3)_2$

$Ti–CH(CH_3)_2 + CH(C_4H_9)=CH_2 \rightarrow Ti–CH(C_4H_9)–CH_2–CH(CH_3)_2$

The β-H elimination reaction in both cases should lead to the formation of a Ti-H bond and the subsequent insertion of propylene into the 1-2 position. This reaction is more favorable in the case of $Ti–CH(C_4H_9)–CH_2–CH(CH_3)_2$ sequence due to the presence of two CH_2 groups in the β-position to the Ti atom, which can lead to the activation of the system with small additions of 1-hexene compared to the homopolymerization reaction of propylene.

References

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S3 L. A. Rishina, N. M. Galashina, P. M. Nedorezova, A. N. Кlyamкina, A. M. Aladyshev, V. I. Tsvetкova, A. O. Baranov, V. A. Optov and Y. V. Kissin, *Polym. Sci., Ser. A,* 2004, **46**, 911.