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Copolymerization of Propylene with 1-Hexene and 4-Methyl-1-Pentene in Liquid Propylene Medium. Synthesis and Characterization of Random Metallocene Copolymers with Isotactic Propylene Sequences

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Summary

Propylene copolymerization with 1-hexene and 4-methyl-1-pentene in liquid propylene medium in presence of MAO-activated C_2-symmetry *ansa*-zirconocene *rac*-$Me_2Si(4\text{-}Ph\text{-}2\text{-}MeInd)_2ZrCl_2$ was studied. Random copolymers of propylene with 1-hexene and 4-methyl-1-pentene content up to 7 mol % were obtained at 60°C. General kinetic characteristics of propylene/higher α-olefin copolymerization were evaluated. The distinct feature of propylene copolymerization with 1-hexene and 4-methyl-1-pentene in liquid propylene medium – the proximity of comonomer relative reactivity ratios ($r_1 \sim r_2 \sim 1$) that indicates azeotropic nature of copolymerization processes in studied conditions. Synthesized copolymers were characterized with the use of IR, ^{13}C NMR, GPC, WAXD, DSC techniques, and uniaxial tensile testing.

Introduction

The development of metallocene catalysts has opened up new possibilities in the processes of α-olefin copolymerization. One can control the copolymer microstructure, vary relative reactivity ratios of comonomers in a wide range, and obtain copolymers with narrow MWD, homogeneous composition and very low content of extractables by using different metallocenes [1].

Nowadays, the researches of propylene copolymerization with higher α-olefins generate great interest in the field of modifying PP properties and synthesis of the new grades of PP-based materials. A lot of recent studies are focused on improving mechanical properties of existing PP-based materials [2]. In the present work we use the specific approach to the synthesis of propylene/higher α-olefin copolymers – propylene copolymerization in liquid propylene medium with the use of highly active isospecific *ansa*-metalocene MAO-activated catalytic system that allows obtaining of copolymers with high yields and high molecular weights. According to the existing literature data [3], metallocene catalytic systems on the base of *rac*-$Me_2Si(4\text{-}Ph\text{-}2\text{-}MeInd)_2ZrCl_2$ represent the attractive combination of high catalyst activity and high isoselectivity with very effective incorporation of α-olefins without sacrificing narrow molecular mass distribution and uniformity, molecular mass independent comonomer incorporation, covering wide copolymer composition range.

The main feature of our experimental approach is that the synthesis of propylene/ higher α-olefin copolymers is carried out in conditions similar to those used in industrial processes (high temperatures and pressures, utilization of liquid propylene as a solvent instead of toluene that is prevalent in laboratory polymerisation experiments). In the present work we are focused on the propylene copolymerization with the small amounts of comonomers (up to 10 mol% of higher α-olefin content). One of the objectives of our investigation was the evaluation of the influence of comonomer structure alteration (linear or branched higher α-olefin) over kinetic features of propylene copolymerisation and properties of the copolymers obtained.

Experimental

Materials

Polymerization grade propylene was kindly donated by Moscow Oil Refining Plant and used in copolymerization experiments without prior treatment. Metallocene catalyst *rac*-$Me_2Si(4\text{-}Ph\text{-}2\text{-}MeInd)_2ZrCl_2$ was purchased from Boulder Scientific Co. MAO as a 10 wt % solution in toluene was purchased from Witco. The comonomers, 1-hexene and 4-methyl-1-pentene, were purified by refluxing over metallic sodium and further distillation in inert atmosphere. The metallocene was pretreated as described in [4,5] and then used in polymerization as a solution in MAO.

Copolymerization

Copolymerization experiments were carried out at a temperature of 60°C and a pressure of 4 MPa in 400 cm^3 stainless steel autoclave reactor equipped with a high speed stirrer. Reactor was first evacuated for 1.5 h at 60°C before copolymerization experiments and then filled with a liquid propylene and comonomer. Next, cocatalyst (MAO) had been added, afterwards a glass ampoule containing metallocene solution in MAO was broken. With the purpose of keeping concentration ratio between comonomers constant, the feed of liquid comonomer was carried out periodically with the use of calibrated stainless steel injector attached to reactor. The comonomer consumption was controlled in the course of all experiments.

Polymerizations were carried out for 60 min and then quenched by adding ethanol. Synthesized polymers were treated with a dilute solution of hydrochloric acid in ethanol, washed many times with water and ethanol, and dried to constant weight in vacuum at 60°C.

4-Methyl-1-pentene and 1-hexene homopolymerizations were carried out in a monomer bulk at 60°C and 0.1 MPa in a 100 cm^3 glass reactor equipped with magnetic stirrer in the atmosphere of a pure argon.

Sample characterization

The composition and structure of the propylene/1-hexene and propylene/4-methyl-1-pentene copolymers were studied by IR and ^{13}C NMR spectroscopy. The IR spectra of polymer samples were measured on a Perkin-Elmer FTIR spectrometer. The composition of propylene/1-hexene copolymers was preliminarily determined from the ratios of absorbances of IR bands at 725 cm^{-1} and 1460 cm^{-1} as described in [6] and then specified by ^{13}C NMR spectra analysis. The composition of propylene/4-methyl-1-pentene copolymers was calculated only via ^{13}C NMR spectra.

The ^{13}C NMR spectra of 5% copolymer solutions in o-dichlorobenzene were recorded at 120°C on a Bruker DPX-250 spectrometer operated at a frequency of 62.895 MHz. On the basis of the ^{13}C NMR spectra, the content of steric pentads, the composition of copolymers, the reactivity ratio r_1, and the reactivity ratio product r_1r_2 were calculated. The assignment of chemical blocks in the spectra of propylene copolymers was made according to [6, 7]. The reactivity ratios of comonomers (r_1, r_1r_2) were estimated by ^{13}C NMR analysis according to the literature [6, 8, 9].

Molecular weights and molecular weight distribution were determined by GPC in a Waters 150C at 130°C with the use of the linear μ-styragel HT columns. 1,2,4-Trichlorobenzene was used as a solvent. Molecular weights were determined with reference to a polystyrene calibration curve.

The wide angle X-ray diffraction analysis (WAXD) of nascent polymers had been performed at room temperature on a DRON-3M diffractometer (CuK_α-irradiation). The observed 2Θ scanning range was 8 - 32°, with a pointwise increment $\Delta 2\Theta = 0.04°$ and a storage time $\tau = 10$ sec.

The melting temperature T_m of polymers was estimated by DSC using Mettler DSC30 analyzer; the scan rate was 10°C /min, and 3-8 mg samples were used in measurements. The temperature scale was graduated relative to indium. The melting curves obtained from the second heating were analyzed.

The uniaxial tensile testing of polymers was performed at 20°C on an Instron 1122 machine. The samples used for mechanical testing were prepared by compression molding of polymers at a temperature of 190°C and a pressure of 10 MPa; the rate of melt cooling was 16°C/min. The Irganox anti-oxidizing agent (0.5 wt %) was used as a stabilizer. As a measure of elastic properties, we used the value of residual strain $\varepsilon_{100} = (L_1-L_0)/L_0\times100\%$, where L_0 - initial length of specimen, L_1 – specimen's length after stretching at 100% and a following stress relief.

Results and Discussion

Propylene/1-hexene copolymerization

Propylene copolymers containing 0.5, 1, 2, 4 and 7 mol % of 1-hexene units were obtained. The corresponding data on the catalyst activity in relation to comonomer concentration ratio is listed in Table 1.

There is the considerable decrease of catalyst activity corresponding to the increase of 1-hexene concentration in a feed observed. As the concentration of 1-hexene increases in the reaction medium, the extent of comonomer incorporation into the polymer chain also increases. Synthesized copolymers show extreme molecular weight dependence: we see the sharp M_w growth for the copolymer with insignificant 1-hexene content (0.5 mol %), and subsequent M_w reduction for the copolymers with larger 1-hexene content.

Table 1. Copolymerization of propylene with 1-hexene in liquid propylene medium[a)]

1-Hexene in feed, (mol %)	Catalyst activity (kg/(mmol Zr h))	1-Hexene in copolymer (mol %)	M_w	M_w/M_n
0	238	0	750000	2.3
0.4	63	0.5	1269400	2.6
0.8	29	1	722500	2.3
1.7	18	2	610300	2.4
6.4	16	7	299500	2.3
100 [b)]	1.5	100	40700	2.4

[a)] polymerization conditions: $[Zr]=7\cdot10^{-7}$ mol·l^{-1}; molar MAO/metallocene ratio = 9000 for all runs, except 1-hexene homopolymerization: 2500; reaction temperature = 60°C; polymerization time – 60 min.

[b)] polymerization in a bulk of 1-hexene; polymerization time – 180 min.

We determined the equality of comonomer relative reactivity ratios: $r_1=r_2=1$ ($r_1r_2=1$) that indicates the pure random distribution of comonomer units in macromolecules of the synthesized copolymers.

WAXD profiles of synthesized copolymers are shown in Figure 1.

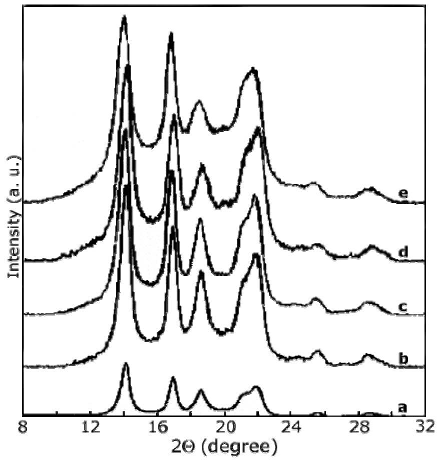

Figure 1. WAXD profiles of (a) iPP, and propylene random copolymers with (b) 0.5 mol % of 1-hexene, (c) 1 mol % of 1-hexene, (d) 2 mol % of 1-hexene, (e) 4 mol % content of 1-hexene units.

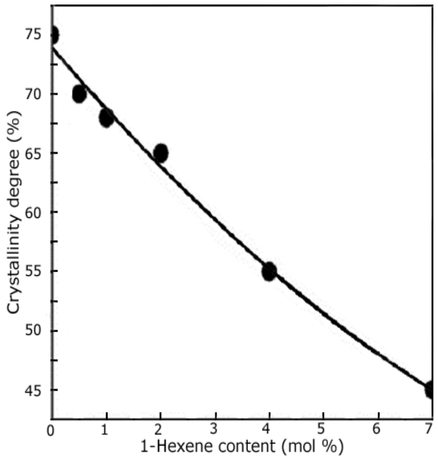

Figure 2. Relationship between the degree of copolymer crystallinity and copolymer composition.

The analysis of X-ray diffraction patterns shows that the degree of copolymer crystallinity gradually decreases with an increase of 1-hexene content (Figure 2). All the copolymers contain predominantly pure α-modification of isotactic polypropylene. DSC curves of the synthesized copolymers are displayed in Figure 3 and show typical melting behavior of random copolymers with isotactic propylene sequences. The melting point of copolymer drops down according to the increase of the extent of comonomer units incorporated. That arises from the copolymer crystallinity lessening and the growth of the crystalline phase distortion.

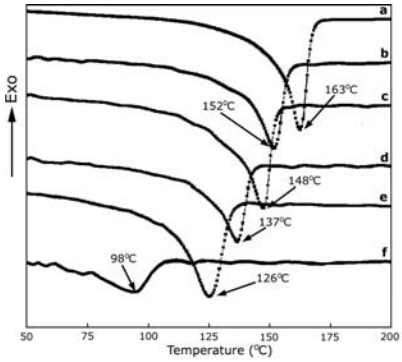

Figure 3. DSC curves of (a) iPP, and propylene copolymers containing (b) 0.5 mol % of 1-hexene; (c) 1 mol % of 1-hexene; (d) 2 mol % 1-hexene; (e) 4 mol % of 1-hexene; (f) 7 mol % of 1-hexene.

Mechanical characteristics of propylene/1-hexene copolymers obtained by the uniaxial tensile testing are summarized in Table 2. Incorporation of even small amounts of 1-hexene units into polypropylene chain leads to the noticeable modification of polypropylene's mechanical properties. The increase of comonomer content results in the reduction of the Young modulus and yield stress of material, and the increase of its tensile strain. Tensile strength of copolymer is actually not affected by the amount of incorporated 1-hexene units for the examined range of copolymer composition: despite the significant decrease of Young modulus, synthesized copolymers retain nearly the same values of tensile strength as compared with iPP. There is considerable strengthening observed for the copolymers containing more than 4 mol % of 1-hexene.

Table 2. Mechanical characteristics of propylene/1-hexene copolymers

1-Hexene content (mol %)	E[a] (MPa)	σ_y[b] (MPa)	ε_y[c] (%)	σ_{br}[d] (MPa)	ε_{br}[e] (%)	ε_{100}[f] (%)
0	1570	40.3	7.2	29.1	200	88
0.5	1430	31.4	8.9	24.4	250	90
1	1182	31.3	10.0	34.8	522	90
2	979	26.3	10.0	30.0	563	91
4	698	18.1	10.2	30.6	612	90
7	304	11.0	12.2	30.5	680	74

[a] Young modulus
[b] yield stress
[c] yield strain
[d] breaking strength (tensile strength)
[e] strain at break
[f] residual strain after stretching at 100%

Propylene/4-methyl-1-pentene copolymerization

Copolymers containing 1, 2, 3 and 6 mol % of 4-methyl-1-pentene units were synthesized. Table 3 provides data on catalyst activity in relation to comonomer concentration ratio.

Table 3. Copolymerization of propylene with 4-methyl-1-pentene in liquid propylene medium[a)]

4-Methyl-1-pentene in feed, (mol %)	Catalyst activity (kg/(mmol Zr h))	4-Methyl-1-pentene in copolymer (mol %)	M_w	M_w/M_n
0	100	0	750000	2.0
0.8	160	1	301200	2.0
1.7	21	2	236800	2.0
3.7	13	3	233000	2.0
6.9	4	6	115500	2.5
100 [b)]	0.1	100	-	-

[a)] polymerization conditions: $[Zr]=2.6\cdot10^{-6}$ mol·l^{-1}; molar MAO/metallocene ratio = 6000 for all runs, except homopolymerization of 4-methyl-1-pentene: 4400; reaction temperature = 60°C; polymerization time – 60 min.
[b)] polymerization in a bulk of 4-methyl-1-pentene; polymerization time – 180 min.

Introduction of small amounts of 4-methyl-1-pentene into reaction medium leads to the evident increase of catalyst activity (second monomer activation effect; this effect is generally attributed to the regeneration of dormant sites $Zr\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}R$, which form as result of a secondary insertion (2-1 type) of propylene into $Zr\text{-}CH_2CH(CH_3)\text{-}R$ bond, by the incorporation of α-olefin [10]). Addition of the higher amounts of comonomer results in the significant decrease of catalyst activity. We observe the exponential decrease of copolymer molecular weight according to the growth of 4-methyl-1-pentene content.

Values of the relative comonomer ratios ($r_1=r_{C3H6}=1.2$, $r_2=r_{C6H12}=0.8$; $r_1r_2\sim1$) show random distribution of comonomer units in macromolecules of the obtained copolymers.

The results of X-ray diffraction analysis for propylene/4-methyl-pentene copolymers (WAXD patterns shown in Figure 4) are similar to those obtained for propylene/1-hexene copolymers: crystallinity degree drops down with an increase of 4-methyl-1-pentene content. Synthesized copolymers contain predominantly pure α-modification of isotactic polypropylene - only trace amounts of γ-form of iPP were observed in copolymers containing more than 2 mol % of 4-methyl-1-pentene units.

As expected from previously obtained data, the melting behavior of propylene/4-methyl-1-pentene copolymers corresponds to that of propylene/1-hexene copolymers. Table 4 summarizes data on copolymer crystallinity and melting temperature in relation to comonomer content.

Mechanical characteristics of propylene/4-methyl-1-pentene copolymers are listed in Table 5. By varying copolymer composition in a relatively limited range (comonomer content up to 6-7 mol %), we can synthesize a broad spectrum of PP-based materials differ in mechanical characteristics.

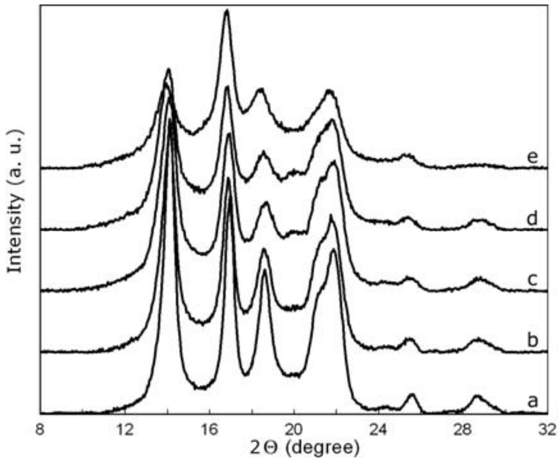

Figure 4. WAXD profiles of (a) iPP, and propylene/4-methyl-1-pentene copolymers with: (b) 1 mol % of 4-methyl-1-pentene, (c) 2 mol % of 4-methyl-1-pentene, (d) 3 mol % of 4-methyl-1-pentene, (e) 6 mol % of 4-methyl-1-pentene.

Table 4. Crystallinity degree and melting temperature of propylene/4-methyl-1-pentene copolymers

4-Methyl-1-pentene in copolymer (mol %)	Crystallinity degree [a]	Melting temperature [b]
0	75	163
1	70	148
2	65	140
3	60	129
6	55	99

[a] obtained from WAXD
[b] obtained from DSC

Table 5. Mechanical characteristics of propylene/4-methyl-1-pentene copolymers

4-Methyl-1-pentene content (mol %)	E[a] (MPa)	σ_y[b] (MPa)	ε_y[c] (%)	σ_{br}[d] (MPa)	ε_{br}[e] (%)	ε_{100}[f] (%)
0	1570	40.3	7.2	29.1	200	88
1	1310	29.9	9.0	31.4	400	96
2	1300	33.1	9.0	22.1	500	92
3	1020	27.0	9.7	25.0	510	89
6	300	9.8	12.8	26.8	660	72

[a] Young modulus
[b] yield stress
[c] yield strain
[d] breaking strength (tensile strength)
[e] strain at break
[f] residual strain after stretching at 100%

As reported above, the unexpected proximity of comonomer reactivity ratios (r_1~r_2~1) for the examined pairs of comonomers (propylene/1-hexene and propylene/4-methyl-1-pentene) had been observed that indicates virtually azeotropic (ideal) nature of propylene copolymerization in liquid propylene medium in presence of *rac*-Me_2Si(4-Ph-2-MeInd)$_2ZrCl_2$/MAO catalyst system (the character of propylene/4-methyl copolymerization slightly differs from ideal, but it virtually corresponds to the case of azeotropic process). That is also illustrated by copolymer composition versus feed composition chart (Figure 5). Azeotropic nature can be considered as a distinctive feature of propylene copolymerization with selected higher α-olefins in liquid propylene medium that is not typical for propylene/higher α-olefin copolymerization in toluene [6]. This rare effect was also described with reference to propylene copolymerization with 1-butene and 1-octene [11]. The mechanism of this phenomenon will be the point of our further investigation.

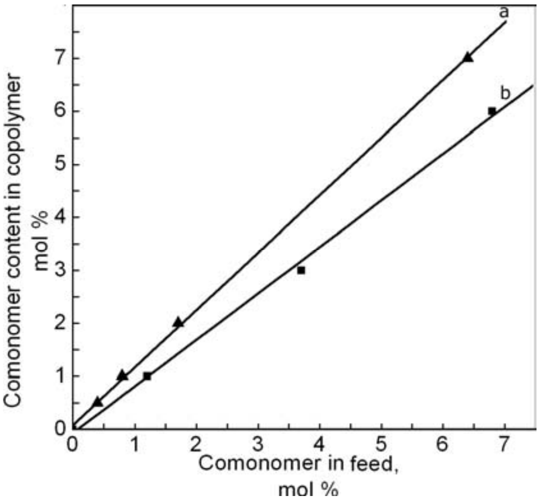

Figure 5. Copolymer composition in relation to comonomer concentration in feed
(a) 1-hexene
(b) 4-methyl-1-pentene

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