

Thermooxidative Degradation of Isotactic Polypropylene Prepared on Metallocene Catalyst and Its Sorption Capacity

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ABSTRACT: The sorption capacity and resistance to thermooxidative degradation are comparatively studied for isotactic polypropylene (PP) produced in the medium of the liquid monomer on homogeneous metallocene catalytic systems and on a heterogeneous titanium–magnesium catalyst. These polymers are characterized by different sorption capacities with respect to the phenyl- β -naphthylamine antioxi-

idant and different induction periods of oxidation by molecular oxygen. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 808–811, 2006

Key words: thermooxidative degradation; isotactic polypropylene; metallocene catalyst; sorption capacity

INTRODUCTION

In recent years, there has been a growing interest in polypropylene (PP) synthesized on modern, highly efficient homogeneous metallocene catalysts (MCCs).^{1–4} In contrast to commercial heterogeneous catalysts, MCCs with their identical active sites allow controlled design of the polymer chain microstructure and preparation of PP with a narrow molecular mass distribution. The use of MCCs offers wide prospects for the production of new materials and for broadening the assortment and practical use of polyolefins, including PP.

As compared to commercial isotactic PP produced on heterogeneous titanium–magnesium catalysts, metallocene isotactic PP with its narrow molecular mass distribution and higher crystallinity shows better strength characteristics.²

As is known, the supramolecular structure of PP affects the aging of the polymer. In this work, the resistance to thermooxidative degradation was studied for isotactic PP produced on homogeneous MCCs and on a heterogeneous titanium–magnesium catalyst.

EXPERIMENTAL

Isotactic PP was synthesized by polymerization of propylene in the medium of the liquid monomer at

60°C by using catalytic systems based on *ansa*-metallocenes: *rac*-Me₂Si(4-Ph-2-Me-Indenyl)₂ZrCl₂ and Me₂Si(4-Ph-2-Et-Indenyl)₂ZrCl₂ (*rac* : *meso* = 1 : 2), activated by polymethylaluminum, oxane,^{4,5} as well as in the presence of the heterogeneous TiCl₄/MgCl₂ catalyst containing an internal donor (dibutyl phthalate, D₁) and activated by Et₃Al together with an external donor (silane, D₂).⁶ The samples of isotactic PP were washed from residual catalysts with 10% hydrochloric acid and then repeatedly washed with ethanol.

The molecular mass characteristics of PP were studied by the GPC method on a Waters 150C gel chromatograph at 145°C in *o*-dichlorobenzene at a polymer solution concentration of 0.04%.

The microstructure of the polymers was studied by using the method of IR spectroscopy by analysis of absorption bands D_{998}/D_{973} (macrotacticity), according to refs. ⁷ and ⁸.

The thermophysical characteristics of the polymers (melting point and fusion heat) were measured by the DSC method. To calculate the degree of PP crystallinity, $\Delta H_o = 165$ J/g was used as the reference (standard) fusion heat.⁹ The degree of crystallinity was also estimated for the synthesized polymers by X-ray diffraction analysis.

The data on the stereoregularity, molecular mass, and thermophysical characteristics of the isotactic PP samples are listed in Table I.

To study the sorption of phenyl- β -naphthylamine (PNA) on the samples of isotactic PP prepared on different catalysts, the polymer films were kept in PNA solutions in heptane for 450 h at 40°C; then the

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TABLE I
Characteristics of Samples Based on Isotactic PP

Catalytic system	Sample	$M_w \times 10^{-3}$	$\frac{M_w}{M_n}$	$\frac{D_{998}}{D_{998}}$	T_m (°C)	ΔH_m (J/g)	Degree of crystallinity* (%) (DSC)	Degree of crystallinity (%) (X-ray)
$\text{Me}_2\text{Si}(4\text{-Ph-2-EtInd})_2\text{ZrCl}_2$ (rac : meso = 1 : 2)/MAO	1	660	2.5	0.95	161	104	63	65
rac- $\text{Me}_2\text{Si}(4\text{-Ph-2-MeInd})_2\text{ZrCl}_2$ /MAO	2	770	2.2	0.98	158	93	56	55
$\text{TiCl}_4/\text{MgCl}_2\text{-D}_1\text{-Et}_3\text{Al-D}_2$	3	330	5.0	0.96	161	86	52	48

*This value was estimated as $\Delta H_m/165 \times 100$.

dissolved PNA was extracted with heptane at 40°C and studied by spectrophotometric analysis.

To investigate the resistance to oxidation, the samples of isotactic PP were oxidized in a standard vacuum chamber at 120–150°C. The reaction was studied by numbers at the curves measuring the changes in the oxygen pressure; the volatile oxidation products (water, acetone, etc.) were sorbed with solid KOH.

RESULTS AND DISCUSSION

The samples of isotactic PP prepared under different conditions may be characterized by different stereo- and regioregularity, as well as by different levels of disorder in the macromolecular packing, which determines the content of the amorphous and crystalline polymer phases.

As was shown earlier,¹⁰ isothermal crystallization of PP leads to a more regular structure and higher degree of crystallinity; as a result, the induction period of polymer oxidation increases.

As follows from Table I, the main parameters (molecular mass, degree of isotacticity, and melting point) of the studied samples of metallocene isotactic PP are similar to those of PP prepared on the titanium–magnesium catalyst. The principal differences are the following: a narrower molecular mass distribution and higher values of fusion heat and degree of crystallinity. As is known, the macromolecule packing density increases with increasing degree of crystallinity and the dimensions of amorphous regions, in which oxidation takes place, accordingly decrease. This should lead to a longer induction period, which is defined as the time corresponding to absorption of 0.025 mole of oxygen per kilogram of polymer.

Figure 1 and Table II present the results of thermo-oxidative degradation of isotactic PP samples. As is seen, the induction period for the samples synthesized on MCCs is much longer than that of the PP sample prepared on the heterogeneous catalyst. The increase in the induction period among the metallocene PP samples with different degrees of crystallinity may be related to changes in the degree of ordering for samples synthesized on different types of MCCs. The ac-

tivation energy of the oxidation of metallocene isotactic PP was estimated to be equal to 107 kJ/mol. Close values were obtained for the activation energy of the oxidation of PP synthesized on traditional catalysts.¹⁰ As follows from Figures 1 and Table II, as the degree of crystallinity decreases, the rate of PP oxidation also increases. The greatest difference is observed at low oxidation temperatures. These data agree with our

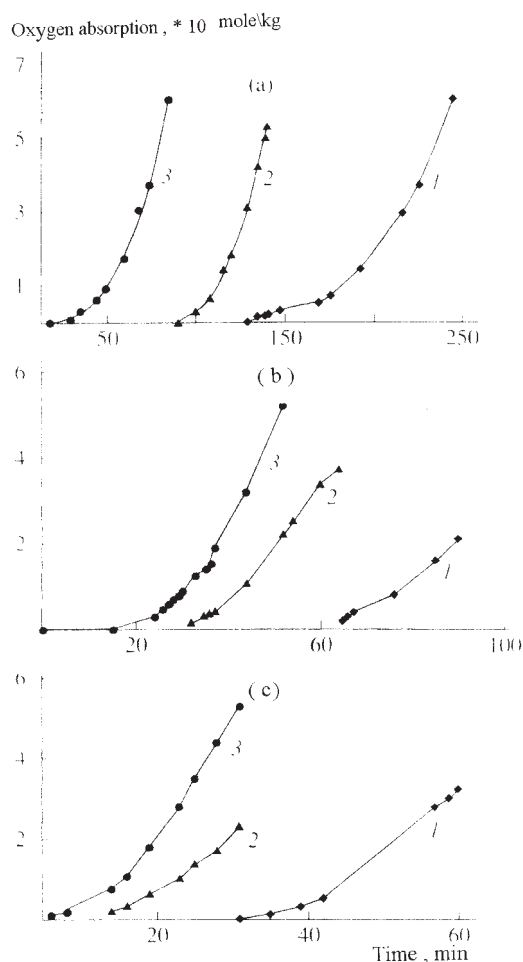


Figure 1 Kinetic curves of oxidation of isotactic PP at (a) 130, (b) 140, and (c) 150°C; oxygen pressure is 300 mmHg. The numbers correspond to Table I.

TABLE II
Induction Period τ and Oxidation Rate w at Different Temperatures for Samples 1–3 of Isotactic PP
(oxygen pressure is 300 mmHg)

Temperature (°C)	τ_1 (min)	τ_2 (min)	τ_3 (min)	w_1 [mol/(kg s)]	w_2 [mol/(kg s)]	w_3 [mol/(kg s)]
120	400	—	—	—	—	—
130	147	116	25	0.00004	0.000035	0.000133
140	66	35	20	0.00013	0.000125	0.000145
150	39	16	10	0.00022	0.00019	0.00031

earlier conclusion concerning the role of PP crystallites in the termination of kinetic chains of the oxidation reaction.¹¹ The PNA sorption also confirms the increased degree of ordering in the samples of metallocene polymers. Figure 2 presents the PNA sorption isotherms for isotactic PP samples. The curves have a complex pattern: while the concentration in solution remains below $[\text{PNA}]_{\text{sol}} = 0.01$ mol/kg, the PNA sorption is small; above this concentration, the curve is convex with saturation at $[\text{PNA}]_{\text{sol}} \approx 0.02$ mol/kg. The mechanism of this sorption was considered in ref. 12, where this shape of the sorption isotherm was explained by a rearrangement of sorption sites at high osmotic pressures of PNA dissolved in the polymer. As follows from Figure 2, the concentration of sorption sites, which are represented by various entanglements of polymer chains, is ≈ 2 times higher in PP prepared on the heterogeneous catalyst than that in the MCC-synthesized PP samples.

As shown in refs. 13 and 14, macromolecular packing in the crystalline phase is more regular for metallocene isotactic PP than for isotactic PP prepared on a heterogeneous catalyst. The melting curves of nascent samples (samples 1 and 3) clearly show that the melting peak of titanium-synthesized PP is wider than the narrow melting peak of metallocene isotactic PP (Fig. 3). This evidence suggests a marked difference in the distributions of stereodeflects and regiodeflects in the polymer chains of isotactic PP samples synthesized on heterogeneous and homogeneous catalysts.

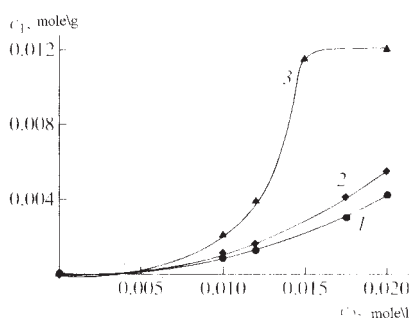


Figure 2 Sorption isotherms describing PNA sorption from heptane by samples of isotactic PP. $T = 40^\circ\text{C}$. C_1 and C_2 stand for the concentrations of PNA in the isotactic PP film and in the solution, respectively. The numbers at the curves correspond to the numbers of the samples in Table I.

MCCs with homogeneous active sites ensure the synthesis of isotactic PP with a narrow molecular mass distribution and a uniform distribution of defects in polymer chains. In the case of heterogeneous catalysts, their multicenter character leads to isotactic PP with a wide molecular mass distribution and a wide range of polymer chains of different stereoregularity; at the same time, fractions with a lower molecular mass are characterized by a higher content of stereodeflects.¹⁴ As a result of wider molecular mass and stereocomposition distributions, this polymer shows a wider melting peak. As known, oxidation primarily takes place in the amorphous phase of polymers. One may

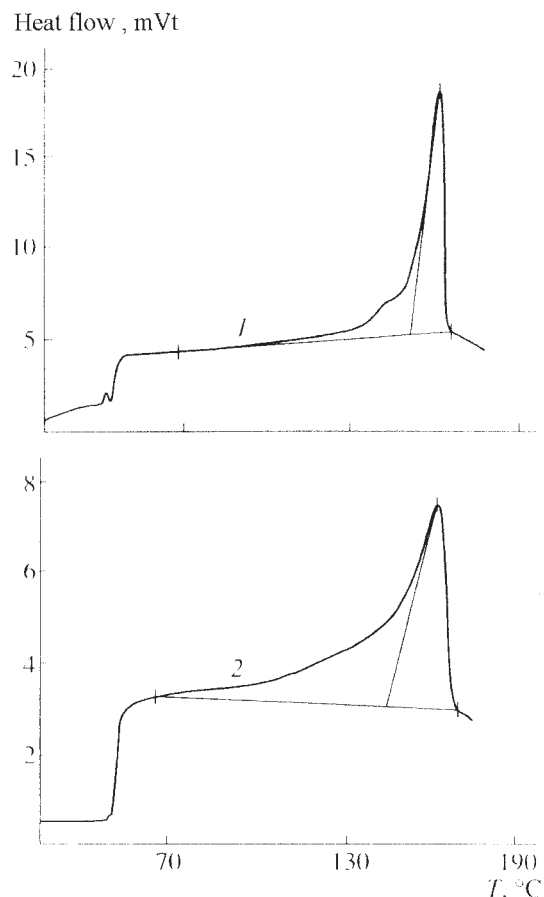


Figure 3 Melting curves of nascent samples of isotactic PP prepared on (1) homogeneous and (2) heterogeneous catalysts. Heating rate is 10 K/min.

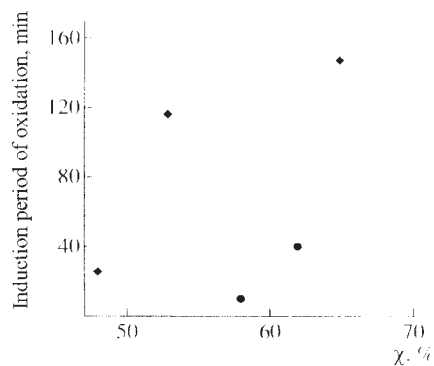


Figure 4 Induction period of oxidation of isotactic PP at 130°C versus degree of crystallinity χ : (1) our results and (2) data from ref. [10].

expect that, because since the metallocene isotactic PP is characterized by a more homogeneous structure of its crystalline regions and hence by a more uniform structure of intercrystalline tie chains, its amorphous phase is less accessible both for PNA sorption and for the oxidation reaction.

Evidently, the sorption characteristics and oxidation induction periods must be different for isotactic PPs prepared on homogeneous and heterogeneous catalysts. Therefore, samples having close degrees of crystallinity but synthesized on different catalysts may have significantly different induction periods of oxidation (Fig. 4).

Thus, depending on the type of the catalyst (homogeneous or heterogeneous), the samples of isotactic PP

are characterized by different structures of their crystalline and amorphous regions. Therefore, they differ both by their sorption capacity with respect to PNA and by their resistance to the action of air oxygen.

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