Effect of Polymerization Conditions on Polypropylene Synthesis in Liquid Monomer

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Abstract—The effect of polymerization conditions (temperature, polymerization time, monomer and hydrogen concentrations) on propylene polymerization in the liquid monomer in the presence of a $TiCl_4/DBP/MgCl_2$ + TEA/cyclohexylmethyldimethoxysilane catalyst system is studied. It is shown that the variation of the propylene polymerization conditions in the studied ranges leads to a change in the characteristics of the resulting polypropylene. The kinetic parameters of propylene polymerization in the liquid monomer for the studied catalyst system are determined. Polymerization conditions providing the formation of polypropylene with high polymer yield, isotacticity, and bulk density values are found. The process parameters that make it possible to effectively control the molecular and rheological characteristics of polypropylene are identified.

The leading position in the plastics industry is held by polypropylene (PP); the world production of PP exceeds 60 million tons per year [1]. The overall production of PP is ever increasing, while the range of PP grades is ever expanding. Today, there are hundreds of commercial grades of PP with a variety of properties, and their number continues to increase. A correct choice of the catalyst system and the polymerization reaction conditions provides the formation of materials for use in various applications [2].

Most of the catalyst systems currently used in the commercial production of PP are Ziegler−Natta catalysts of the latest generations, for example, the 4th-generation catalysts with dimethoxysilane external electron donors and the 5th-generation catalysts with diether donors [2]. It was earlier shown [3, 4] that the technology for synthesizing supported titanium−magnesium catalysts (TMCs) developed at Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences provides the formation of a catalyst with a required activity, isotacticity, and morphology, i.e., with properties similar to those of foreign commercial samples, which are imported because they are not produced in Russia [5, 6]. Therefore, to continue the studies on the synthesis of modern domestic catalyst systems for liquid propylene polymerization, works on synthesizing TMCs and studying kinetics of the propylene polymerization in the presence of TMCs are being conducted.

It is known that more than 50% of the PP production capacities in the world are based on liquid-monomer polymerization processes (bulk polymerization). Owing to a high monomer concentration, propylene polymerization in a liquid monomer is characterized by a higher reaction rate than that of slurry polymerization in hexane or heptane [7, 8]; this is a significant advantage in terms of equipment effectiveness. In addition, it is important to determine optimum conditions for propylene polymerization in a liquid monomer in the presence of a TMC in order to control the process and obtain the product with desired characteristics.

This study is focused on the effect of polymerization conditions on the activity and stereospecificity of a TMC and the morphology and rheological and molecular characteristics of the PP powder synthesized in a liquid monomer medium.

EXPERIMENTAL

TMC (IK-8-21 grade) with an average particles size of 47 μm and titanium and magnesium contents of 2.5 and 17.7 wt %, respectively, was synthesized as described in [9]. The catalyst had the following com-
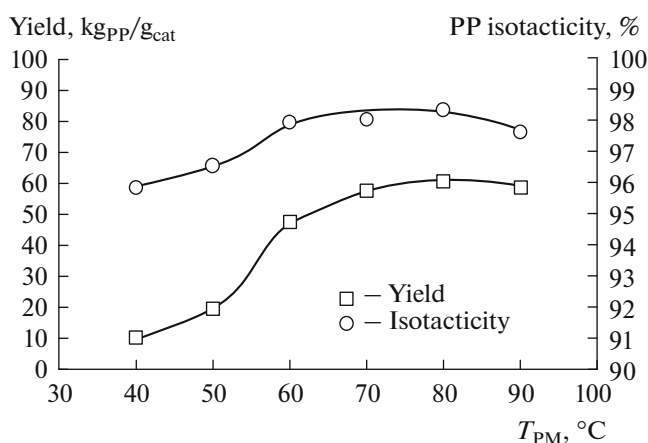
Fig. 1. Dependence of the yield and isotacticity of PP on the polymerization temperature.

position: $TiCl_4/D_1/MgCl_2$, where D_1 is an internal donor, namely, dibutyl phthalate (DBP).

The particles size distribution of the catalyst was determined by laser diffraction on a Malvern Master-sizer 2000 instrument.

Propylene polymerization was run in a 5-dm^3 steel autoclave in a liquid monomer medium at a temperature of 40–90°C (typically, 70°C, 30 bar) for 5–120 min (typically, 120 min). Polymerization-grade propylene (PAO Nizhnekamskneftekhim) with a volume fraction of the basic substance of 99.8% was used for polymerization. The following standard conditions were assumed: a propylene weight of $m_{C_3H_6}$ = 1300 g, a catalyst weight of m_{cat} = 0.015 g, molar ratio Al/Ti = 1500, and molar ratio Al/D_2 = 20 (D_2 is cyclohexyl-methyldimethoxysilane used as the external donor). The catalytic complex was prepared by mixing a calculated amount of triethylaluminum (TEA), cyclohexyl-methyldimethoxysilane, and the TMC in *n*-hexane in a glass flask. After stirring for 5 min, the catalytic complex was loaded into the reactor at 20°C. After that, propylene and hydrogen (typically, 0.15 mol) were introduced. The temperature was further increased to the main polymerization temperature.

Polypropylene isotacticity (*XI*) was determined by dissolving a PP sample in *o*-xylene, slowly cooling the solution to 25°C under controlled conditions, separating the solid phase by filtration, evaporating *o*-xylene from the solution, and determining the amount of the atactic PP fraction soluble in xylene (*XS*, wt %); PP isotacticity (*XI*) was determined as $XI = 100 - XS$ (wt %).

The particles size of the PP powder was determined by granulometric analysis on an Octagon Digital sieve shaker in accordance with ASTM D 1921; the bulk density of the PP powder was determined in accordance with GOST 11035.1-93.

The melt flow index (MFI) of the polymer was determined on a Ray-Ran extrusion rheometer in accordance with ASTM 1238 at a temperature of 230°C and a constant load of 2.16 kg.

The molecular characteristics of the PP samples were determined on a Polymer Labs (now Agilent) PL-GPC 220 high-temperature gel-permeation liquid chromatograph at a temperature of 160°C in a 1,2,4-trichlorobenzene eluent at a solvent flow rate of 1 cm^3/min.

RESULTS AND DISCUSSION

The effect of the following polymerization conditions was studied: temperature, polymerization time, and hydrogen and monomer concentrations.

Effect of Polymerization Temperature

Temperature is the most important characteristic of the olefin polymerization process. A variation in temperature has a significant effect not only on the process rate, but also on the micro- and macrostructure of the resulting polyolefins.

The effect of temperature (T_{PM}) on propylene polymerization in the presence of the $TiCl_4/DBP/MgCl_2$ + TEA/cyclohexylmethyldimethoxysilane catalyst system was studied in a range of 40–90°C (Table 1, Fig. 1). The highest catalyst activity, all other polymerization conditions being equal, is achieved in a temperature range of 70–90°C. Thus, at a polymerization temperature of 40°C, the polymer yield is 10 kg_{PP}/g_{cat}, whereas at T_{PM} = 70–90°C, it is at a level of 60 kg_{PP}/g_{cat}. With an increase in T_{PM}, the isotacticity curve exhibits a behavior similar to that of variation in activity; the highest stereospecificity of the catalyst system is achieved at 70 and 80°C. Note that the polymer has a high *XI* value (97.6%) even at 90°C.

The morphology of the PP powder depends on the polymerization temperature as follows (Table 1): the average particles size of PP increases with increasing T_{PM}, i.e., simultaneously with an increase in the PP yield; the largest particles size (more than 1700 μm) is achieved at temperatures of 70–90°C. With an increase in T_{PM}, the content of PP particles with a size of less than 500 μm decreases. Throughout the entire variation in the polymerization temperature, the PP powders synthesized in the presence of the IK-8-21 catalyst are characterized by a narrow particles size distribution and the absence of a dust fraction of PP (with a size of less than 75 μm); under variation in other polymerization conditions, this fraction is not present either. The bulk density of PP powders synthesized at different polymerization temperatures remains at a high level (0.45–0.47 g/cm^3). This fact is also confirmed by the data obtained earlier by the authors of [8], who studied the effect of temperature of

Table 1. Test results for the TMC at different polymerization conditions

Parameter	Temperature, °C [a, b]						Amount of hydrogen in the reactor, mol [b,c]				Initial/average propylene concentration in the reactor, g/L [a–c]			Polymerization time, min [a, c]				
	40	50	60	70	80	90	none	0.15	0.21	0.31	93/61[d]	248/172[e]	403	5	10	30	60	120
Yield, kg_{PP}/g_{cat}	10	19	47	57	60	58	36	57	60	56	14	39	57	10	13	21	34	57
MFI (at 2.16 kg/230°C), g/10 min	42.7	13.0	2.4	3.9	4.1	14.5	0.4	3.9	4.8	8.2	57	8.7	3.9	4.3	4.8	4.2	3.8	3.9
Isotacticity (XI), %	95.8	96.5	97.9	98.0	98.3	97.6	97.7	98.0	98.0	98.2	98.1	98.2	98.0	97.3	97.5	97.8	98.1	98.0
Number average molecular mass M_n (×10^{-3}), g/mol	32	40	84	91	81	59	125	91	84	77	38	59	91	77	73	93	92	91
Weight average molecular mass M_w (×10^{-3}), g/mol	190	216	435	390	380	260	660	390	380	345	185	311	390	370	360	380	395	390
Polydispersity index (M_w/M_n)	5.9	5.4	5.2	4.3	4.7	4.4	5.3	4.3	4.5	4.5	4.9	5.3	4.3	4.8	4.9	4.1	4.3	4.3
Bulk density, g/cm³	0.45	0.45	0.47	0.45	0.47	0.46	0.47	0.45	0.45	0.45	0.46	0.46	0.45	0.43	0.43	0.44	0.45	0.45
Average particles size of PP powder, μm	930	1150	1620	1720	1760	1740	1470	1720	1750	1710	1070	1510	1720	940	1030	1230	1440	1720
Content of particles with a size of less than 500 μm, wt %	4.8	1.1	0.4	n/a	n/a	0.4	3.1	n/a	0.4	2.4	3.8	0.8	n/a	2.8	2.4	2.0	0.4	n/a

Conditions: $m_{C_3H_6}$ = 1300 g, m_{cat} = 0.015 g, Al/Si = 20 (mol), and Al/Ti = 1500 (mol). [a] Amount of hydrogen in the reactor is 3.5 L (0.15 mol). [b] t_{PM} = 120 min. [c] T_{PM} = 70°C.
[d] $m_{C_3H_6}$ = 300 g and $m_{C_3H_6}$ = 1000 g. [e] $m_{C_3H_6}$ = 800 g and $m_{C_3H_8}$ = 500 g.
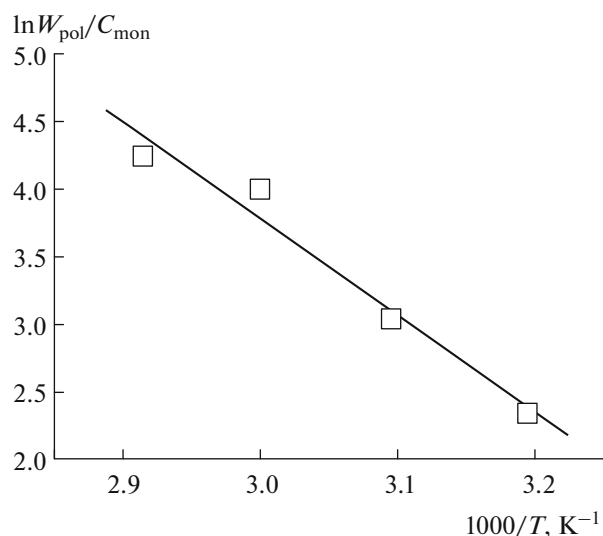
$\ln W_{pol}/C_{mon}$

Fig. 2. Temperature dependence of W_{pol}/C_m in Arrhenius coordinates in a range of 40−70°C.

prepolymerization and main polymerization on the morphology of the PP powder.

Studies of the molecular and viscosity characteristics of PP revealed that their temperature dependence exhibits a complex behavior: in the case of weight average molecular mass (M_w) and MFI, the curves have a maximum and a minimum in a temperature range of 60−80°C, respectively. In general, with a decrease in temperature from 90 to 60°C, an increase in M_w and, accordingly, a decrease in MFI are observed. This finding is consistent with many data on an increase in M_w with a decrease in T_{PM} during the slurry polymerization of olefins in the presence of various catalysts. However, with a further decrease in T_{PM} to 40°C, against expectations, a decrease in M_w and an increase in MFI are observed (Table 1). The cause of this behavior of the system is unclear and requires additional studies. Parallel tests of this catalyst system in slurry polymerization of propylene in heptane at 70 and 40°C showed MFI values of 8.8 and 4.4 g/10 min, respectively, i.e., a conventional decrease in MFI with decreasing T_{PM}. Despite significant changes in M_w and MFI as a function of T_{PM}, the polydispersity index (M_w/M_n, where M_n is the number average molecular mass) varies only slightly: M_w/M_n is 4.3−4.7 at 70−90°C and slightly increases—from 5.2 to 5.9—with a decrease in T_{PM} from 60 to 40°C. The data on the effect of T_{PM} make it possible to determine the Arrhenius dependence of the average polymerization rate W_{pol} on temperature (Table 1). Note that, with a variation in T_{PM}, the monomer concentration C_m also changes and thereby additionally affects W_{pol}. This additional effect of temperature on the polymerization rate can be excluded by relating the average polymerization rate W_{pol} to monomer concentration C_m and
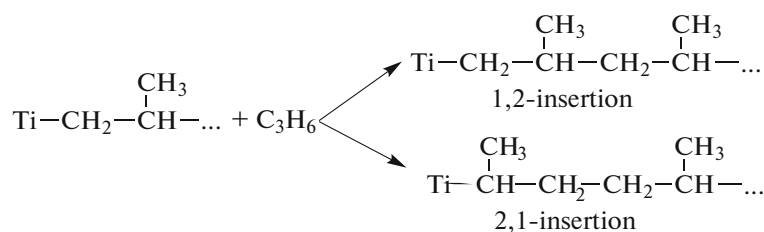
assuming the first order of the polymerization rate with respect to the monomer concentration (see the respective section below). The densities of liquid propylene at 40−80°C were taken from [7] to use as C_m; the density value at 90°C was calculated by a similar procedure.

The average polymerization rate related to monomer concentration W_{pol}/C_m significantly increases in a range of 40−70°C and slightly increases above 70°C. For the range of 40−70°C, the activation energy E_a for the chain propagation reaction was determined (Fig. 2). It is 59.6 kJ/mol, or 14.2 kcal/mol. This value is close to the published data. For instance, the authors of [7], according to data on variation in the initial polymerization rate in liquid propylene as a function of temperature in a range of 40−80°C, found the E_a values of 52.2−77.7 kJ/mol depending on the amount of hydrogen in the reactor. Note that the cited authors observed a slight increase in the polymerization rate with an increase in temperature from 70 to 80°C.

Effect of Hydrogen Concentration

To determine the effect of hydrogen on the polymerization process and the properties of the synthesized polymer, a set of tests in the presence of hydrogen in the reaction medium in an amount of 0.15, 0.21, and 0.31 mol and without hydrogen was conducted. The data (Table 1) show that, in the absence of hydrogen in the polymerization system, the TMC exhibits a low activity; in the presence of hydrogen, the activity significantly increases. Thus, in the absence of hydrogen, the polymer yield is 36 kg_{PP}/g_{cat}, whereas after the introduction of 0.15 mol of H_2 into the polymerization medium, the activity increases by ~40% (to 57 kg_{PP}/g_{cat}). With a further increase in the hydrogen content in the system to 0.21 mol, the activity achieves a maximum value (60 kg_{PP}/g_{cat}), while an increase in the amount of hydrogen to 0.31 mol leads to a slight decrease in the catalyst activity. No change in the isotacticity of PP with a variation in the amount of hydrogen is observed. This dependence of activity on C_{H2} is confirmed by published data [7, 10] for on the bulk polymerization of propylene.

The experimental data show that the introduction of hydrogen provides an increase in activity by ~40%. Most probably, this increase in activity is a result of the activation of the sites deactivated by the regioirregular 2,1-insertion with hydrogen:

$$\text{Ti}-\text{CH}_2-\overset{\overset{\displaystyle CH_3}{|}}{\text{CH}}-\ldots + \text{C}_3\text{H}_6 \Big\langle$$

$$\text{Ti}-\text{CH}_2-\overset{\overset{\displaystyle CH_3}{|}}{\text{CH}}-\text{CH}_2-\overset{\overset{\displaystyle CH_3}{|}}{\text{CH}}-\ldots$$
1,2-insertion

$$\text{Ti}-\overset{\overset{\displaystyle CH_3}{|}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\overset{\overset{\displaystyle CH_3}{|}}{\text{CH}}-\ldots$$
2,1-insertion

After the regular 1,2-insertion of propylene into the Ti−C bond, the sites remain in the active state, whereas in the case of the 2,1-insertion, the active sites pass into the inactive "dormant" state owing to the steric hindrances between the propylene and the methyl group of the growing chain end at the titanium atom. After the transfer of the chain of these sites, hydrogen forms Ti−H bonds, which form active Ti−C bonds upon the subsequent insertion of propylene. As a consequence, in the presence of hydrogen, the site passes from the dormant to active state.

An increase in the hydrogen concentration in the system leads to the expected decrease in the molecular mass of the PP and, accordingly, an increase in the MFI values owing to the occurrence of chain transfer with hydrogen (Table 1). Thus, in the absence of hydrogen in the polymerization medium, the M_w and M_w/M_n values are 660 kg/mol and 5.3, respectively, whereas after the introduction of 0.15 mol of hydrogen, the M_w and M_w/M_n values become lower, namely, 390 kg/mol and 4.3, respectively; an increase in the amount of H_2 to 0.31 mol leads to a further decrease in M_w (to 345 kg/mol), while the polydispersity index does not change significantly and remains at a level of 4.5. In the absence of hydrogen in the system, the MFI of the polymer is 0.4 g/10 min; at a hydrogen content in the reactor of 0.31 mol, the MFI is 8.2 g/10 min.

Analysis of the morphology of the PP powder formed at different hydrogen concentrations showed that the average particles size of the PP powder in the absence of hydrogen in the reaction system is 15% lower (1470 μm) than that of the PP samples synthesized in the presence of hydrogen (more than 1700 μm). At a hydrogen content of 0.15 mol, the amount of small-size fractions of the PP powder (less than 500 μm) in the polymerization system is the lowest.

The dependence of the M_n values on hydrogen concentration can be used to determine the order of the chain transfer reaction with respect to hydrogen concentration (n) and the rate constant of chain transfer with hydrogen $\left(k_{tr}^H\right)$ using the well-known equation

$$42/M_n - 42/M_{n0} = k_{tr}^H C_{H_2}^n / k_p C_m,$$

where M_{n0} is the molecular mass of PP in the test without hydrogen; k_p is the chain propagation rate constant; and C_m and C_{H_2} are the monomer and hydrogen concentrations in the equation, respectively.

Figure 3 shows the dependence of the determined M_n values on hydrogen concentration according to the above equation in logarithmic coordinates, which gives a fractional value of the reaction order of $n = 0.7$.

A fractional order of the chain transfer reaction with respect to hydrogen concentration was previously observed for polymerization in heptane and discussed in detail earlier in [11]. To determine the k_{tr}^H values in this case, it is correct to use the dependence of $42/M_n − 42/M_{n0}$ on hydrogen concentration in reciprocal coordinates according to the following equation:

$$\left(42/M_n - 42/M_{n0}\right)^{-1} = k_p C_m \left(k_{migr}\right)^{-1} + k_p C_m \left(k_{tr}^H C_{H_2}\right)^{-1},$$

where M_n and M_{n0} is the number average molecular mass of PP in the presence and absence of hydrogen, respectively; k_p is the chain propagation rate constant; k_{migr} is the rate constant of migration of the growing chain end; and k_{tr}^H is the rate constant of the chain transfer with hydrogen.

Figure 4 shows the dependence of $(42/M_n − 42/M_{n0})^{-1}$ on $C_{H_2}^{-1}$ and provides the determination of the k_{tr}^H and k_{migr} constants.

According to Fig. 5 and the above equation, we obtain

(i) $k_p C_m \left(k_{tr}^H\right)^{-1} = 147$; in this case, assuming that $k_p = 2500$ L/(mol s) [11] and $C_m = 9.6$ mol/L, we obtain $k_{tr}^H = (2500 \times 9.6)/147 = 163$ L/(mol s), which is significantly lower than k_p, and

(ii) $k_p C_m (k_{migr})^{-1} = 1790$; in this case, $k_{migr} = (2500 \times 9.6)/1790 = 13.4$ s^{-1} (versus about 4 s^{-1} in the case of polymerization in heptane).

Effect of Monomer Concentration

In tests with a low monomer concentration, the volume of the liquid phase in the reactor was maintained constant by adding propane (Table 1). With an increase in the propylene concentration, the catalyst productivity increases and exhibits a plateau. Thus, at an average monomer concentration of 61 g/L, the
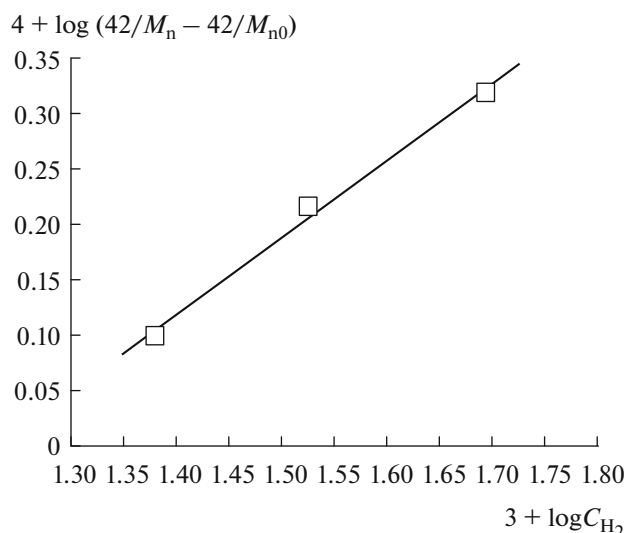
Fig. 3. Dependence of $42/M_n - 42/M_{n0}$ on C_{H_2} in logarithmic coordinates.

Fig. 4. Dependence of $(42/M_n - 42/M_{n0})^{-1}$ on $C_{H_2}^{-1}$.

yield is 14 kg_{PP}/g_{cat}, whereas at $C_m = 172$ g/L, the yield is 39 kg_{PP}/g_{cat}; at $C_m = 403$ g/L, the yield increases to 57 kg_{PP}/g_{cat}. It is evident that, up to the average monomer concentration of 172 g/L, the PP yield increases linearly with an increase in C_m; i.e., the first order of polymerization rate with respect to monomer concentration is observed. With a further increase in C_m, the increase in the PP yield slows down. At the same time, the *XI* value of PP remains at a high level (98.0–98.2%) regardless of the propylene concentration in the reactor. With an increase in the monomer concentration, the average particles size increases from 1130 to 1720 μm (Table 1), while the amount of the PP fraction smaller than 500 μm, conversely, decreases. With a decrease in the monomer concentration, the M_w value decreases (from 390 to 185 kg/mol), while the MFI value increases (from 3.9 to 57 g/10 min). This finding is attributed to an increase in the C_{H_2}/C_m concentration ratio, because C_{H_2} is constant and C_m decreases. In this case, the M_w/M_n values vary insignificantly (from 4.3 to 5.2).

Effect of Polymerization Time

Table 1 shows results of tests with varying polymerization time. An increase of polymerization duration from 5 to 120 min leads to an increase in the polymer yield from 10 to 57 kg/g cat, the *XI* value from 97.3 to 98.0%, the bulk density from 0.43 to 0.45 g/cm³, and the particles size of the PP powder from 940 to 1720 μm and to a decrease in the fraction of particles smaller than 500 μm from 2.8 to 0%.

The dependence of the polymer yield and the PP isotacticity on the polymerization time (t_{PM}) is shown in Fig. 5. It can be seen from Fig. 5 that the PP yield
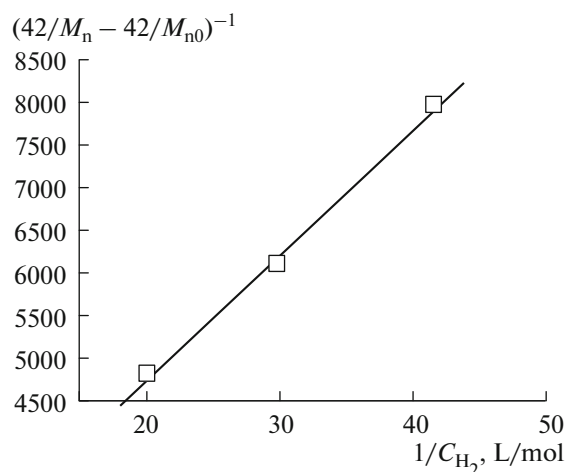
linearly increases with increasing t_{PM}. This fact suggests that the catalyst activity is stable throughout the polymerization time. Simultaneously with an increase in the PP yield, the average particles size of the PP powder increases and the amount of the small-size fraction of the PP powder decreases (Table 1).

With an increase in t_{PM}, the M_w value slightly increases (from 370 to 390 kg/mol), the MFI value of PP slightly decreases (from 4.3 to 3.9 g/10 min), and the molecular mass distribution slightly narrows (Table 1).

CONCLUSIONS

The effect of polymerization conditions (temperature, polymerization time, and monomer and hydrogen concentrations) on propylene polymerization in a liquid monomer in the presence of a
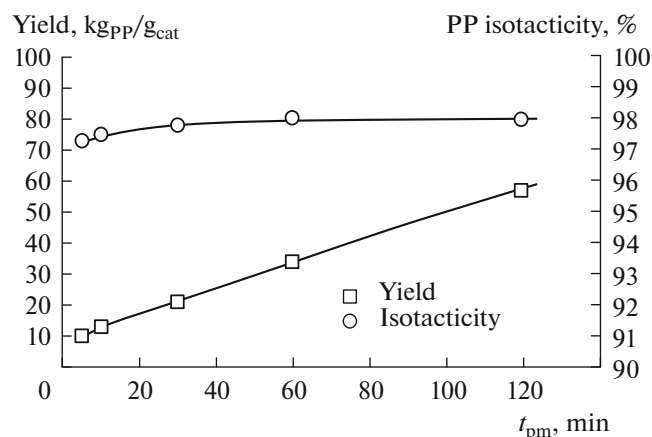

Fig. 5. Dependence of the PP yield and isotacticity on the polymerization time.

TiCl$_4$/DBP/MgCl$_2$ + TEA/cyclohexylmethyldimethoxysilane catalyst system has been studied. It has been shown that the variation of the propylene polymerization process conditions in the studied ranges leads to a change in the activity of the TMC and the characteristics of the resulting PP. The kinetic parameters of propylene polymerization in a liquid monomer for the studied catalyst system have been determined.

The highest activity of the catalyst system is observed at temperatures of 70−90°C and a monomer concentration of 403 g/L in the presence of hydrogen (0.15 mol under the studied conditions). Under these polymerization conditions, the PP powder has optimum characteristics in terms of bulk density and morphology, i.e., a high average particles size and the absence of a fine fraction. The PP isotacticity slightly increases with an increase in temperature, hydrogen concentration, and polymerization time. Concerning the molecular characteristics of the synthesized PP, it has been found that a decrease in the process temperature and the hydrogen content and an increase in the polymerization time and the monomer concentration lead to an increase in the average molecular mass; in this case, the MFI value, conversely, decreases. With an increase in temperature, process time, and hydrogen concentration, the molecular mass distribution of the PP samples slightly narrows.

The results of this study make it possible to select optimum conditions for synthesizing PP in a liquid monomer in the presence of the studied catalyst system; the determined process parameters provide an efficient control of the molecular and rheological characteristics of the PP.

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