

Molecular characteristics of cis-1.4-polyisoprene on modified titanium catalyst

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Abstract. In the presented paper molecular characteristics of cis-1.4-polyisoprene, synthesized with titanium catalyst, which is modified by electron donor additives, temperature and a hydrodynamic treatment in turbulent flows. In microheterogeneous titanium catalyst, three fractions are marked out, which have different diameter of particles: 0.7-4.5 micron; 0.15-0.68 micron; 0.03-0.13 micron. With a decrease in particle size of a catalyst, molecular masses and a width of a molecular-mass distribution of polyisoprene are reduced. A reduction in a number of fractions and a narrowing of particle size's distribution leads to a synthesis of a polymer with a narrower molecular-mass distribution.

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Introduction

Nowadays, worldwide production volume of synthetic cis-1.4-polyisoprene is more than 700 thousand tons per year, which major part is produced using Ziegler-Natta titanium catalyst. Because of microheterogeneous nature of the catalyst there is a possibility to control a speed of polymerization and molecular characteristics (molecular mass and molecular-mass distribution) of synthesized polymers by changing a particle size distribution of catalytically active particles [1]. A widely used method of modification is a method, comprising an implementation of electron donor additives and a reduction of temperature of a catalyst's formation, which leads to an increase in a concentration of active centers and/or their reactivity [2]. A surface structure of a catalyst can be influenced by a change of a hydrodynamic regime in a reaction zone, mainly, before a start of polymerisation, when there is a small amount of polymer in a reaction mixture [3, 4]. Due to the fact that active centers are located on a surface of a microheterogeneous catalyst, a change in a particle size affects a concentration of macromolecules' growth centers [5]. Moreover, a change of a surface energy during a split of particles causes a change in a reactivity of active centers, which are responsible for a synthesis of a polymer with a varying molecular mass [6, 7].

The purpose of the presented research was to study patterns of a formation of molecular characteristics of synthesized cis-1.4-polyisoprene in a case of titanium catalysts' modification by electron donor additives, temperature and a hydrodynamic treatment in turbulent flows during polymerization on various fractions of a catalyst.

Materials and methods

The titanium catalyst is formed on a basis of TiCl_4 and $\text{Al}(\text{i-C}_4\text{H}_9)_3$ solutions in toluene with a successive addition of electron donor modifiers –

diphenyl oxide (DPO) and 1.3-pentadiene (1,3-PD). A preparation of catalyst was carried out, using different methods.

Method 1. In a sealed reactor calculated amounts of toluene solutions of the catalyst (TiCl_4) and the cocatalyst ($\text{Al}(\text{i-C}_4\text{H}_9)_3$) were mixed. The catalyst's suspension was kept for 30 min with constant mixing at 0°C (-10°C).

Method 2. The catalyst was prepared similarly with method 1, with a following hydrodynamic treatment in a small-sized tubular apparatus of diffuser-confuser design [8, 9]. Duration of a hydrodynamic treatment in a tubular apparatus was about 2-3 seconds. Polymerization of isoprene was conducted in toluene with a concentration of a catalyst of 5 mmol/l and a monomer of 1.5 mol/l and 25°C temperature.

An extraction of the titanium catalyst's fractions was conducted using sedimentation in gravitational field with taking 1.5-2 ml of suspension during a process of particles' deposition. In taken samples a catalyst's concentration was analyzed. Particle's sizes of the catalyst's solid phase were determined by laser diffraction/scattering method using Sald-7101 testing tool. For analyzed catalysts three fractions of particles are marked out, which have different average diameters: fraction I – 0.7-4.5 micron, fraction II – 0.15-0.68 micron, fraction III – 0.03-0.13 micron [10]. Molecular masses (MM) and molecular-mass distribution (MMD) of polyisoprene was determined by gel-penetrating chromatography method using Waters GPC-2000 testing tool.

Results and discussion

A successive modification of titanium catalyst by DPO and 1.3-pentadiene additives leads to an increase of weight average (M_w) and number average (M_n) molecular masses and a reduction of MMD width (table.1). For catalysts $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO}$ and $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$, prepared at 0°C ,

an increase in average molecular masses during polymerization process was detected. With a decrease of a catalyst's preparation temperature to -10°C , in an initial period of polymerization an increase of polyisoprene's average molecular masses was detected (table.1). Further, as polymerization process proceeds, average molecular masses are reduced and their values are approaching the values, which are characteristic for $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-DP}$ catalyst, which was formed at 0°C .

Polyisoprene with a wide MMD was synthesized in a presence of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalyst, which was formed at 0°C using method 1 (table.1). In that case, there was a decrease in MMD width accompanied by an increase of polymer's output. An introduction DPO and 1.3-pentadiene in the catalytic system leads to a reduction of polyisoprene's MMD. A formation of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$ catalyst at -10°C determines a possibility of a polyisoprene's synthesis with even narrower MMD ($M_w/M_n = 2.4\text{-}2.5$), which width is practically independent from a conversion (table.1).

Table 1. Molecular characteristics of polyisoprene

Catalyst	Polymerization time t, min	$M_w \cdot 10^{-4}$		$M_n \cdot 10^{-4}$		M_w/M_n	
		Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ (0°C)	3	19.3	25.6	3.8	4.2	5.1	6.1
	7	27.4	35.5	5.6	5.1	4.9	6.9
	10	29.1	37.6	6.8	6.5	4.3	5.8
	20	35.5	44.9	8.2	7.1	4.3	6.3
	60	38.0	45.7	9.1	8.6	4.2	5.3
$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO}$ (0°C)	3	39.4	45.3	9.4	9.2	4.2	4.9
	7	39.8	44.9	9.9	10.7	4.0	4.2
	10	30.5	37.6	7.0	8.8	4.4	4.3
	20	36.7	42.7	8.8	11.0	4.2	3.9
	60	38.2	46.0	8.5	9.8	4.5	4.7
$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-DP}$ (0°C)	3	45.0	52.0	12.1	13.4	3.8	5.9
	7	46.7	50.0	12.9	13.4	3.6	3.7
	10	47.5	50.4	13.2	13.8	3.6	3.7
	20	48.3	52.6	13.6	14.6	3.5	3.6
	60	41.4	45.3	11.5	11.7	3.8	3.9
$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$ (-10°C)	3	50.0	53.0	13.6	14.7	3.7	3.6
	7	50.0	51.3	14.0	14.9	3.6	3.4
	10	54.8	56.0	14.3	15.3	3.6	3.7
	20	54.8	53.0	16.6	16.2	3.3	3.3
	60	54.0	55.8	18.3	18.2	3.3	3.4
$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$ (-10°C)	3	54.5	54.5	16.0	16.1	3.2	3.4
	7	76.8	67.5	24.5	21.6	3.1	3.1
	10	72.0	64.2	23.1	19.4	3.2	3.5
	20	66.5	59.0	22.4	18.8	2.9	3.1
	60	62.2	52.6	22.2	18.1	2.8	2.8
$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$ (-10°C)	3	62.2	50.9	20.5	16.7	3.0	3.0
	7	62.7	51.3	21.7	18.3	2.9	2.8
	10	62.0	50.9	20.6	18.0	3.0	2.8
	20	62.0	50.9	20.6	18.0	3.0	2.8
	60	62.0	50.9	20.6	18.0	3.0	2.8

During a formation of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$, $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO}$, $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$ catalysts at 0°C using method 2, there was a slight increase of polyisoprene's average molecular masses. A level of molecular masses' increase subsides in a row of catalysts, prepared at 0°C : $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3 \rightarrow \text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO} \rightarrow \text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$.

$\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-DP}$ catalytic system, prepared at -10°C temperature using method 2, leads to a synthesis of polyisoprene with average molecular masses, comparable with those of method 1.

An influence of titanium catalyst's particle size on molecular mass characteristics of polyisoprene was examined. As a basic example a $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalytic system was studied, which was prepared using method 1 at 0°C and contained all 3 fractions of particles. For 3 fractions of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalyst, which are different in size, same trend in a change of molecular masses is characteristic. In a case of isoprene polymerization on a catalyst, which consists of fractions I, weight average and number average molecular masses increase with an increase of polymer's output, reaching limiting values. In contrast to fraction I, in a

case of isoprene's polymerization on fraction II, average molecular masses increase linearly. In a case of isoprene polymerization on a fraction, which consists of the smallest particles of a catalyst (fraction III), average molecular masses of a polymer almost does not depend on time of polymerization (fig.1).

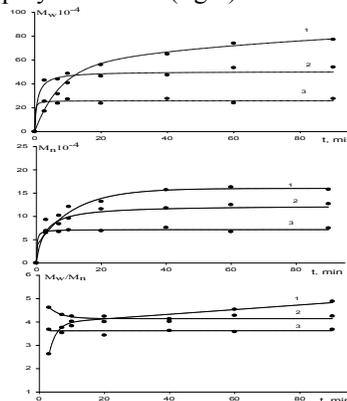


Fig. 1. Dependence of weight average (M_w), number average (M_n) molecular masses of polyisoprene and its polydispersity (M_w/M_n) from polymerization time t at various fractions of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalyst. Fractions: I(1), II(2), III(3). Formation at 0°C , method 1.

Polydispersity of polyisoprene, produced on fraction I, increases with an increase of polymerization time from 2.5 to 4 (fig. 1). At the same time, MMD width of polyisoprene, which was synthesized on fractions II and III practically does not depend on duration of polymerization. At the same time, a polymer obtained in a presence of fractions III, has narrower MMD ($M_w/M_n \approx 3.5$).

A catalyst's modification by DPO additives causes an increase of average molecular masses of polyisoprene, which was synthesized in a presence of fractions I, not affecting those values for a polymer, which was produced on fractions II and III. In a case of polyisoprene synthesis on a catalyst, containing DPO, MMD width of polyisoprene is not different from one for $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalyst.

A hydrodynamic treatment (method 2) of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalyst leads to increased M_w of polyisoprene, whereas the M_n practically does not change, as compared with method 1 (fig. 2). In that case, linear dependence between M_w and M_n from polymerization time continues to exist. Molecular-mass distribution of polyisoprene, produced on fraction II and formed using method 2, is wider than one obtained using method 1 (fig. 1, 2). It can be explained by the fact that fraction II of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalyst after a single hydrodynamic treatment in a turbulent reactor consists of a mixture of particles, which originally were a part of a catalyst and particles, which were formed as a result of a split of big particles of fraction I during a turbulent motion. Because of a different origin of

particles of the same size, active centers, located at their surfaces are different in their nature.

During a formation of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO}$ catalyst in turbulent flows, an increase of weight average and number average molecular masses of polyisoprene during its synthesis on fraction II is detected. Polyisoprene in that case is characterized by narrower MMD. Narrowing of polyisoprene MMD, produced on fraction II, in that case, can be explained by the fact, that produced as result of a hydrodynamic treatment active centers of fraction I are close, in a context of reactivity, to the centers that contain DPO. That leads to a decrease of differences in kinetic characteristics of active centers, located on particles of fraction II, which, by definition, leads to a reduced distribution by molecular masses.

Also, in a same manner as a hydrodynamic treatment in turbulent flows, an introduction of 1,3-pentadiene leads to a formation of a catalyst from fractions II and III. A presence of DPO and 1,3-pentadiene in a catalytic system in a case of polymerization on particles of fraction II leads to an increased average molecular mass of polyisoprene and narrowing of its MMD, as compared with $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3$ catalyst (method 1). In that case, there is something in common between an influence of 1,3-pentadiene and a hydrodynamic treatment (method 2) on large particles of a catalyst. Those factors lead to an acceleration of particles breaking to sizes of fraction II, which is, in a case of DPO presence, leads to an increase of reactivity of that faction during isoprene polymerization.

A hydrodynamic treatment of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$ catalyst leads to an increased uniformity of fraction II and does not cause changes in average molecular masses of polyisoprene and its polydispersity, as compared with a formation of a catalyst using method 1. A formation of $\text{TiCl}_4\text{-Al}(\text{i-C}_4\text{H}_9)_3\text{-DPO-1.3-PD}$ catalyst using method 1 at -10°C causes an increase of uniformity in particles' size of fraction II and an increase of polyisoprene average molecular mass accompanied by narrowing of MMD.

Regardless of the titanium catalyst' conditions of a formation on fraction III (electron donor additives, temperature of a formation, a hydrodynamic treatment), low-molecular polyisoprene with polydispersity equal to 3.0-3.5 is synthesized.

It is worth mentioning, that polyisoprene polydispersity is quite sensitive to a particle's diameter of the titanium catalyst. For catalysts, consisting of particles of three fractions, polydispersity varies in a range of 2.5-6.0. A decrease in a number of factions by a transition of fraction I in fraction II, as well as an increase of a uniformity of fraction II, leads to a 7/9/2014

reduced MMD and in that case polydispersity varies between 3.2-3.5. Obviously, that fact is determined by functioning of several types of active centers, located on a surface of a catalyst particle of various diameters, i.e. kinetic heterogeneity of titanium catalytic system.

Conclusion

Depending on a composition (modifying additives diphenyl oxide and 1,3-pentadiene) and conditions (temperature, hydrodynamic treatment in turbulent flows) of titanium catalyst 3 factions, which differ in a diameter of particles are marked out: 0.7-4.5 micron; 0.15-0.68 micron; 0.03-0.13 micron. With a decrease in particle size of a catalyst, molecular masses and a width of a molecular-mass distribution of polyisoprene are reduced. A decrease in a number of factions and narrowing of particle sizes distribution within one faction leads to a formation of a polymer with a narrower molecular-mass distribution ($M_w/M_n = 3.0\text{-}3.5$).

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