ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1085–1089. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.P. Zakharov, V.Z. Mingaleev, P.A. Taibulatov, I.A. Ionova, Yu.B. Monakov, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 6, pp. 1028–1032.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Reducing Consumption of Titanium Catalyst in Stereospecific Polymerization of Butadiene

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Received February 10, 2009

Abstract—The possibility of reducing the consumption of titanium catalyst in butadiene polymerization by using a tubular turbulent prereactor of the diffuser–confuser design in the step of mixing the reaction mixture components was examined.

DOI: 10.1134/S1070427209060299

Microheterogeneous Ziegler–Natta catalytic systems are widely used in industrial synthesis of stereoregular polydienes and make a significant contribution to the prime cost of the product [1]. Therefore, one of the ways to decrease the prime cost of stereoregular polymers is finding synthesis procedures allowing the catalyst consumption to be reduced at the expense of enhancing its activity. This approach suggests an increase in the concentration of active centers (ACs) or in the rate constant of the polymer chain propagation [2]. The AC concentration for microheterogeneous catalysts in which the propagation centers are located on the surface of solid phase particles [3] can be increased by modification of the surface structure of the catalytically active precipitate.

The goal of this study was to assess the possibility of reducing the consumption of the microheterogeneous titanium catalytic complex in butadiene polymerization by affecting its surface structure under the conditions of turbulent mixing, and also revealing the causes and relationships of the modification of the catalyst solid phase.

The polymerization was performed on an experimental installation [4, 5] involving a six-section tubular turbulent prereactor of the diffuser–confuser design. The polymerization was performed by two procedures.

Procedure 1. Reaction mixture components (separately prepared titanium catalytic complex and butadiene solution) were mixed directly in a 500 cm^3 flask, with slow stirring with a magnetic stirrer. This procedure simulated the traditional industrial polymerization process [6].

Procedure 2. The preliminarily kept catalytic complex was mixed with a butadiene solution in a tubular turbulent prereactor of the diffuser–confuser design for 2–3 s. After that the reaction mixture was fed to a volume apparatus in which the conditions were similar to those in procedure *1*.

Enhancing the intensity of stirring the reaction mixture in the initial moment of the polymerization process by using a tubular turbulent prereactor leads to an increase in the polymer yield (Fig. 1, curves *1, 3*). Analysis of the kinetic parameters of the process indicates that, as the hydrodynamic mode in the reaction zone is changed (procedure *2*), the AC concentration increases by a factor of 1.7–2 (see the table). At the same time, preliminary turbulization of flows does not noticeably affect the rate constant of the polymer chain propagation. This fact allows the catalyst concentration in the initial reaction mixture to be proportionally reduced.

The most probable cause of the increase in the concentration of polymerization centers in procedure *2* is disintegration of $TiCl_3$ particles bearing ACs on their surface under the action of turbulent pulsations of the solvent. In the approximation of spherical shape of catalytically active particles of the titanium catalyst,

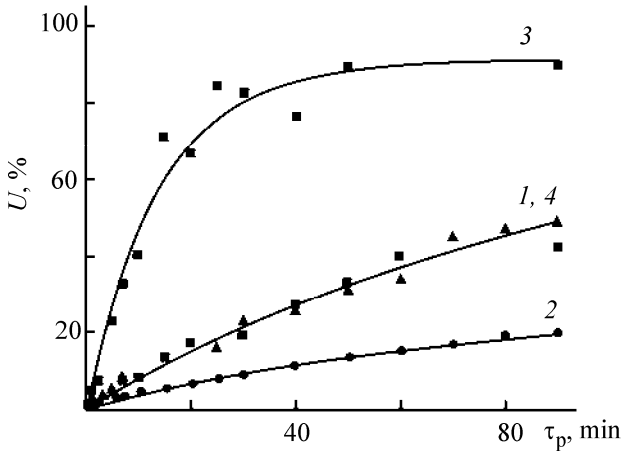

Fig. 1. Yield U of polybutadiene as a function of polymerization time τ_p in the presence of the $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalyst (prepared separately). Toluene, 25°C, Al/Ti = 1.4 (mol/mol), c_M = 1.5 M. Procedure: (*1, 2*) *1* and (*3, 4*) *2*. c_{Ti}, mM: (*1, 3*) 5 and (*2, 4*) 3.

their crushing under the action of a turbulent flow should formally mean a decrease in the particle radius and a change in the particle size distribution function. However, there are data that the specific surface area of microheterogeneous Ziegler–Natta catalysts changes in the initial moment of polymerization under the action of the wedging effect of propagating polymer chains [7]. Therefore, to elucidate physical causes of decrease in the catalyst consumption in procedure *2*, it is appropriate to consider the effect of the hydrodynamic action on the size of catalytically active particles under the conditions of polymer chain propagation on the surface of $TiCl_3$ crystals.

To this end, we prepared the catalytic complex by mixing $TiCl_4$ and $Al(i\text{-}C_4H_9)_3$ solutions in the molar ratio [Al]/[Ti] = 1.4, with the subsequent keeping at 273 K for 30 min. The processes occurring with the catalyst particles in the initial period of polymerization were simulated by adding to the catalytic complex prepared the calculated amount of the monomer (butadiene) in the range of molar ratios [Butadiene]/[Ti] = 0–10. The resulting microheterogeneous systems were subjected to sedimentation analysis in the gravitational field, using a torsion balance [8]. Each value of the [Butadiene]/[Ti] ratio corresponds to a definite moment of time, required for the addition of the preset amount of butadiene to the active centers in the course of the polymerization.

To evaluate the effect of the hydrodynamic mode in the reaction zone on the catalyst particle size in the initial moment of the polymerization, we performed single circulations of the suspensions obtained through a small tubular turbulent apparatus of the diffuser–confuser design. Physical simulation of processes occurring with the catalyst particles in the initial moment (procedure *1*) was performed with slow stirring of the reaction mixture after adding the calculated amount of butadiene to the catalytic complex. Immediately after adding the calculated amount of butadiene to the preliminarily formed catalytic complex, we performed a hydrodynamic action on the reaction mixture in a tubular turbulent apparatus, which corresponded to procedure *2*.

The time in which the preset amount of the monomer is added to AC can be calculated as

$$\tau_i = U/W, \quad (1)$$

where U is the polybutadiene yield (M), and W, initial polymerization rate.

Because of small values of c_M^0 in the initial moment of polymerization, it can be assumed that $U \approx c_M^0$, where c_M^0 is the initial monomer concentration. The degree of polymerization P_p is calculated by the formula

$$P_p = N_B/N_c, \quad (2)$$

where N_B is the number of butadiene (monomer) molecules, and N_c, number of polymer chains in the system.

As the polymerization time simulated is short, the reactions of polymer chain transfer to the monomer and organoaluminum compound can be neglected. Hence, N_p is identical to the number of macromolecule propagation centers.

In synthesis by procedure *1*, about 60 monomeric units are added within 50 s (Fig. 2). This is accompanied by a decrease in the catalyst particle radius from 4.4 to 1.7 μm. At hydrodynamic action on the catalyst particles in a tubular turbulent prereactor (procedure *2*), the disintegration is complete in 20 s, and in this time about 30 monomeric units are added to AC. The particle radius decreases from 1.3 to 1 μm. The time period in which the catalyst particles undergo disintegration under the action of propagating chains in procedure *1* exceeds the residence time of the reactants in a tubular prereactor by a factor of 17–25. Thus, the observed changes in the particle size in going to synthesis procedure *2* are determined by preliminary hydrodynamic action on the catalyst surface structure.

In stepwise addition of the monomer to AC, the catalyst particle radius decreases owing to disintegration under the action of propagating polymer chains. Superposition of the hydrodynamic action on this process (procedure *2*) leads to deeper disintegration of the catalytically active precipitate, which is due to additional disintegration of particles under the action of the kinetic energy of turbulent pulsations. The contribution of the hydrodynamic constituent to the particle disintegration is characterized by a decrease in the mean radius by a factor of 1.7. On the assumption of the spherical shape of microheterogeneous catalyst particles, the specific surface area of the catalytically active precipitate varies in proportion with the particle radius.

Thus, the cause of the enhancement of the catalyst activity on changing the hydrodynamic mode in the reaction zone is particle disintegration under the action of vigorous turbulent mixing. As a result, previously inaccessible to alkylation titanium atoms become accessible, with the subsequent formation of a bimetallic AC, which corresponds to an increase in the AC concentration [9]. An increase in the active center concentration upon hydrodynamic action on the reaction mixture allows the catalyst concentration to be proportionally decreased (under the experimental conditions, by a factor of 1.7: from 5 to 3 mM).

Intensification of stirring of the reaction mixture (procedure *2*) in combination with a decrease in the catalyst concentration allows the process to be performed at essentially the same rate as in procedure *1* (Fig. 1, curves *1, 4*). The molecular characteristics of the synthesized polybutadiene also undergo the corresponding changes (Fig. 3).

The hydrodynamic action, despite a decrease in the catalyst concentration, favors a decrease in the weight-average molecular weight (Fig. 3, curves *1, 2).* Combined effect of an increase in the intensity of turbulent mixing and of a decrease in the catalyst concentration leads to synthesis of polybutadiene with a constant number-average molecular weight in different experiments (Fig. 3, curves *3, 4*). As a result, the molecular-weight distribution of polybutadiene becomes narrower.

One of the causes of broad molecular-weight distribution of stereoregular polymers can be polycentric nature of Ziegler–Natta catalytic systems, manifested in distribution of active centers with respect to reactivity [10, 11]. Solution of the inverse problem of MWD curves showed that, in synthesis by procedure *1*, the distribution curve of ACs of butadiene polymerization on the examined catalytic system is characterized by the presence of four maxima (Fig. 4). Each maximum corresponds to particular types of centers producing a polymer of a definite molecular weight: type I, ln M = 9.2–10.4; type II, ln M = 11.2–11.4; type 3, ln M = 12.9–13.2; and type IV, ln M = 14.1–14.7. The area of each peaks corresponds to the kinetic activity of propagation centers of macromolecules of a definite type, i.e., to the product of the concentration by the rate constant of chain propagation. A decrease in the total catalyst concentration with intensification of turbulent mixing leads to disappearance of type I ACs producing the low molecular weight polybutadiene fraction. In this

Kinetic parameters[a] of butadiene polymerization in the presence of $TiCl_4$–$Al(i\text{-}C_4H_9)_3$

Polymerization procedure	c_{Ti}, mM	$c_a \times 10^4$, mM	k_p, l mol^{-1} min^{-1}
1	5	2.5	56
2	5	4.2	58
1	3	1.1	62
2	3	2.2	64

[a] (c_a) Concentration of active centers and (k_p) rate constant of the polymer chain propagation; the polymerization conditions are given in Fig. 1.

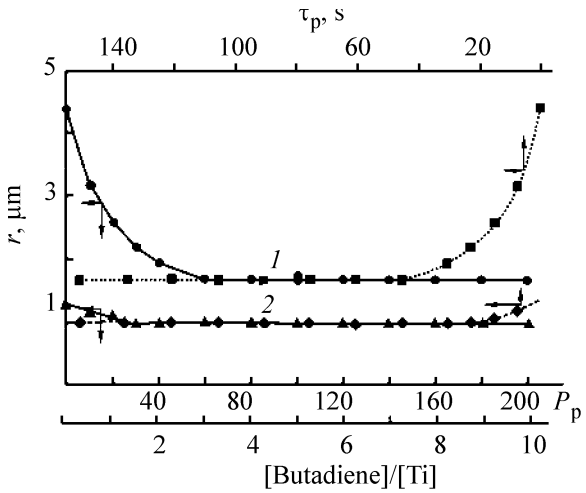

Fig. 2. Dynamics of disintegration of $TiCl_4$–$Al(i\text{-}C_4H_9)_3$ catalyst particles in the initial moment of butadiene polymerization (c_{Ti} = 5 mM). (r) Particle radius, (τ_p) reaction time, and (P_p) degree of polymerization. Procedure: (*1*) *1* and (*2*) *2*.

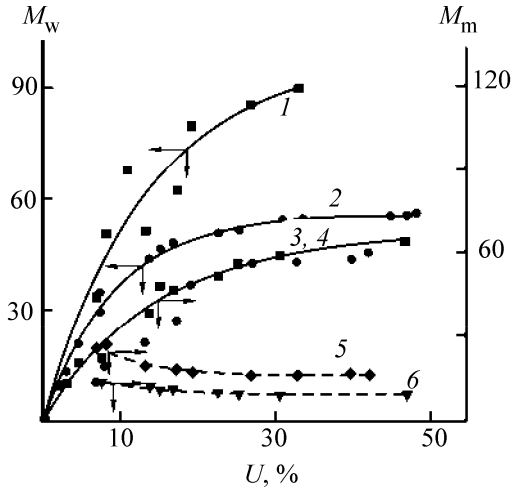

Fig. 3. (*1, 2*) Weight-average (M_w) and (*3, 4*) number-average (M_n) molecular weights and (*5, 6*) polydispersity of polybutadiene. c_{Ti}, mM: (*1, 3, 5*) 5 and (*2, 4, 6*) 3. Procedure: (*1, 3, 5*) *1* and (*2, 4, 6*) *2*.

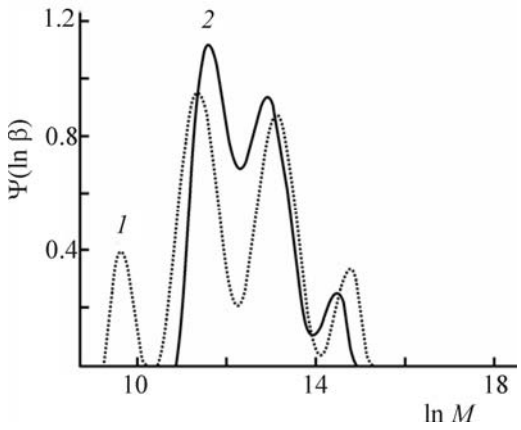

Fig. 4. Distribution of active centers of polybutadiene polymerization with respect to reactivity (U = 1–2%). c_{Ti}, mM: (*1*) 5 and (*2*) 3. Procedure: (*1*) *1* and (*2*) *2*.

case, the concentration of type II centers somewhat increases and that of type IV centers decreases. The latter fact may be responsible for a decrease in the weight-average molecular weight of polybutadiene (Fig. 3).

Variation of the number-average degree of polymerization is described by the equation [12]

$$P = \frac{c_M^0[1 - \exp(-k_p c_a \tau)]}{c_a + \frac{k_t^M}{k_p} c_M^0[1 - \exp(-k_p c_a \tau)] + k_t^A c_A \tau_A}, \quad (3)$$

where k_t^M and k_t^A are the rate constants of polymer chain transfer to the monomer and organoaluminum compound, respectively; k_p, rate constant of chain propagation; c_A, concentration of the organoaluminum compound; and c_a, AC concentration.

Analysis of Eq. (3) shows that, owing to low rate of polymer chain transfer to the organoaluminum compound, in the initial moment of polymerization the last term in the denominator does not noticeably affect the number-average degree of polymerization, including the case of decreased concentration of the cocatalyst (triisobutylaluminum). Taking into consideration the constancy of k_t^M and k_p in procedure *2* (this was shown in [12]), this fact accounts for stabilization of the number-average molecular weight of polybutadiene when the polymerization procedure is changed and the catalyst concentration is decreased (Fig. 3).

Thus, an increase in the AC concentration occurs in the initial moment of the polymerization process under the action of wedging effect of propagating polymer chains. This effect is enhanced upon superposition of the hydrodynamic action on the reaction mixture by using a tubular turbulent prereactor, with short vigorous stirring of the reactants. The suggested synthesis scheme with a tubular turbulent prereactor in the step of formation of the reaction mixture allows the consumption of the titanium catalyst to be reduced in proportion with an increase in the AC concentration. The polybutadiene synthesized in the process has a narrower MWD owing to redistribution of ACs with respect to reactivity.

CONCLUSIONS

(1) With a tubular turbulent prereactor used in the step of formation of the reaction mixture of butadiene polymerization in the presence of $TiCl_4$–$Al(i\text{-}C_4H_9)_3$, disintegration of catalytically active particles is complete in 20 s, and about 30 monomeric units are added to active center. The process rate is 2–3 times higher compared to the traditional polymerization procedure.

(2) The use of the prereactor allows the catalyst consumption to be reduced by a factor of 1.7. In the process, the polydispersity coefficient of polybutadiene decreases owing to a decrease in the weight-average and stabilization of the number-average molecular weight.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 08-03-99005) and by the Foundation for Support of Leading Scientific Schools (garnt no. NSh-2186.2008.3).

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