Thermal and material balances of the synthesis of PE block copolymers

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Abstract. The complex two-phase model based on the well-mixed and two-phase models is presented. The profiles of concentrations and temperatures in microparticles are obtained. The average concentrations and temperatures at the active sites of the catalyst are determined. Heat exchange efficiency on the basis of temperature dependence on technological parameters was studied.

The production of block copolymers of propylene and ethylene is environmentally friendly (alternative reaction conditions are solvent-free and in a liquid monomer medium). This process is occurred using the latest technologies, therefore, it is relevant to describe the hydrodynamics of the block copolymerization of propylene and ethylene (BCPE) on a Ti-Mg catalyst and to carry out experiments in order to identify a rational mode of the synthesis process.

As well as many polymers, BCPE has resistance to aggressive environment, heat and frost resistance (unlike polypropylene), high mechanical and dielectric properties. The share of block copolymers produced by the industry in the total volume of polyolefins is raised steadily. In the most dynamically developing Japanese market, the share of consumption of homopolymers is less than 40%, while in Western Europe - 55%, North America - 66%, in Russia - 83%. The increase in polyolefin consumption in Japan in the last decade has been in block copolymers. The block copolymers of propylene and ethylene were synthesized in the late 1950s and now they are produced almost everywhere where polypropylene and ethylene are produced. The current technological scheme of synthesis consists of several main units: reactor unit designed for the synthesis of polypropylene (PP) or copolymer of propylene and ethylene (CPE) (1 -5% of ethylene links). The polypropylene synthesis can be carried out in one or more reactors, in the medium of gaseous or liquid propylene or inert solvent.

The construction of the reactors is also different: fluidized bed reactor, continuously stirred tank reactor, loop reactor. Despite the variety of constructions, their main function is to obtain a necessary amount of polymer of a certain molecular weight per unit of time. Molecular mass is regulated by
hydrogen. If a reactor cascade is used instead of a single reactor, it reduces the dispersion of the catalyst particles in time and provides for a fuller use of the catalyst. In addition, the reactor cascade allows fuller use of propylene and dispense with a degassing unit. However, the reactor cascade increases the cost of equipment and requires a certain pressure difference between reactors for the flow of the reaction mass, which is not always feasible without the installation of pumps.

Polymerization of propylene (stage 1) in a liquid monomer is carried out in tubular loop reactors with a jacket [1-2]. Then the resulting polymer is fed to a gas-phase reactor with a fluidized bed, where the process of copolymerization of polypropylene and ethylene in the gas phase is carried out (figure 1).

![Figure 1. Scheme of polymerization: 1-reaction zone; 2-separation zone; 3-cyclone; 4 – heat exchanger; 5-compressor.](image)

To this day there are a number of technological difficulties, the main of which is the heat removal. The polymerization reaction is highly exothermic and if there is insufficient heat removal, localized overheating points and a violation of the fluidization mode can be formed. The problem of modeling such a process is the need to take into account many interactions between phases. A distinctive feature of the gas-phase polymerization is that the system does not involve the gas phase in the polymerization zone. Polymerization occurs in the boundary layer between the solid catalyst and the polymer matrix. The role of the gas phase is to transport the monomers, mix the polymer particles, and remove the heat of the reaction. These problems cannot be solved without a mathematical modeling tool [3,4].

The complex two-phase model is based on models: well-mixed and two-phase.

The two-phase model of interest is represented by a system of material and thermal balances [5-12]:

\[
C_{bc} = C_{c} \exp \left( \frac{H}{Ub Kbc} \right)
\]

\[
U_c C_0 \cdot C_c = Q \cdot \frac{C_c}{V_0 \rho_p} k_p \rho e^{-RT_0}
\]

\[
C_c X_{kp} \rho_p \left( 1 - \varepsilon_{mf} \right) + \Delta K_{bc} \frac{C_{bc} - C_c}{(1 - \Delta)} = 0
\]

\[
T_{bc} = T_c + \left( T_0 - T_c \right) \left( \frac{Ub \varepsilon_{pg}}{H_{bc} H} \right)
\]
\[ AU_c (1 - \Delta) C_0 e_{mf} c_{pg} (T_0 - T_c) + c_{pg} k_{bc} (c_b - c_c) V_b (T_{bc} - T_c) + \]
\[ + H_{bc} V_b (T_{bc} - T_c) + \Delta H k_{p0} \exp_c^{RT_0} c_c * X_{kt} \rho_c \frac{1 - e_{mf}}{e_{mf}} = 0, \]

where \( c_{pg} \) is the heat capacity of the gas phase, \( \rho_p \) is the density of PE block copolymer, \( U_c \) is the reaction rate in a continuous medium, \( H \) is the height of the reactor, \( K_{fc} \) is the mass transfer coefficient from the boundary layer in the continuous phase, \( K_{bc} \) is the mass transfer coefficient from the bubble phase in the continuous phase.

The system is completed by equations for finding the average values of the concentration and temperature of the monomer, as well as equations of material and thermal balances for a single bubble:

\[ \bar{C}_b = C_c + \exp \left( \frac{K_{bc} * H}{U_b} \frac{U_b}{K_{bc} * H} \right) \]

\[ \bar{T}_b = T_c + (T_0 - T_c) \left( \frac{U_b C_{pg}}{H_{bc} H} \right) \left[ 1 - \exp \left( \frac{-H_{bc} * H}{U_b * H} \right) \right] \]

\[ T_b = T_c + \exp \left( \frac{U_b C_b * c_{pg}}{K_{bc} * H} \right) \]

\[ C_b = C_c + \exp \left( \frac{K_{bc} * H}{U_b} \right) \]

where \( C_b \) is the concentration of the gaseous monomer in the bubble phase, \( C_c \) is the concentration of the gaseous monomer in the continuous phase, \( H_{bc} \) is the heat transfer coefficient from the bubble phase in the continuous phase, \( H \) is the height of the reactor, \( U_b \) is the velocity of the bubble phase, \( c_{pg} \) is the heat capacity of the gas phase, \( T_0 \) is the inlet gas temperature, \( T_c \) the temperature in the continuous phase.

**Figure 2.** Dependence of the monomer temperature on the height of the solid phase in the apparatus at \( T_0=340, T_{01}=350, T_{02}=360, C_0=20 \text{ kg/m}^3, U_0=0.34 \).

**Figure 3.** Dependence of the monomer concentration on the height of the bubble phase in the apparatus at \( T_0=340, T_{01}=350, T_{02}=360, C_0=20 \text{ kg/m}^3, U_0=0.34 \).
The temperature dependences on the height of the fluidized bed of the reactor are obtained for different input velocity of gas and monomer input temperature (figure 2 and figure 3).

The system of equations of the two-phase model was solved by the Runge-Kutta method of 4 orders. Profiles of concentrations and temperatures in microparticles were obtained and the average concentrations and temperatures at the active centers of the catalyst were determined.

The result of the research is necessary to reduce the temperature of the copolymerization stage to 60°C by reducing the heat removal efficiency of stage 2 by about 45% relative to the stage, while the line performance will not change and the PE block copolymer will contain at least 15 wt%.

Variable parameters of synthesis:

- the temperature of the second stage is 50, 60 or 70°C;
- hydrogen concentration at the first stage;
- the ratio of the catalytic system components;
- the composition of the mixture of ethylene and propylene fed to the reactor;
- time of homo- and copolymerization stages and the yield of the statistical copolymer.

The influence of the main significant technological parameters on the composition and properties of the block copolymer of propylene and ethylene (BCPE) is assessed. Experiments were carried out, changing one of the parameters when all others are constant.

- Donor concentration. With the decrease of Si/Ti ratio in the studied range, there is an increase in the copolymerizing ability of the catalyst (the ethylene contents in BCPE and the amount of soluble fraction in heptane increase).
- Duration of the homopolymerization stage. When the duration of the homopolymerization stage is reduced from three to two hours, the copolymerization capacity of catalyst increases, as evidenced an increase of the weight part of CPE in the block copolymer up to 6.8 wt% and a higher ethylene contents in BCPE.
- Effect of hydrogen concentration. To regulate the length of the polymeric chain of the block copolymer, hydrogen supplied at the first stage was used. In the secondary reactor hydrogen is not dosed due to technological problems. The analysis of experimental data showed that in the studied range of hydrogen concentrations (up to 6.9 v%) the increasing H2 concentration leads to an increase in titanium-magnesium catalyst activity at the stage of homo- and copolymerization at H2 concentration up to 4 v% and a slight decrease in catalyst activity with further increase in hydrogen concentration. Accordingly, the ratio of polypropylene that is received at the first stage and CPE that is received at the second phase changes.
- Effect of the duration of the copolymerization stage. Using a mixture, containing 75 v% of ethylene, the synthesis of BCPE that is differed only in the time of the copolymerization stage (1.5 and 2.0 hours) is carried out. The results show that it is possible to increase the ethylene contents by prolonging the copolymerization stage. However, the maximum performance of the catalyst is observed in the first 2÷3 hours. As a result, using this technology, BCPE samples with the ethylene contents up to 15 wt% can be obtained using titanium-magnesium catalyst.

The calculations show that the average values of molecular masses increase and the polydispersion index decreases with the increase in the number of blocks in the chain. Both tendencies are expected because longer chains will have a higher probability of beginning the active center transformation stage than shorter chains. The effect on $K_{wa}$ is a simple consequence of selection of an narrower fraction of polymers: single-block chains follow the statistics of Flory with $K_{wa}=2$ and chains with two, three or more blocks will have narrower molecular-weight distribution, as they are selected from a narrower fraction with an increasing molecular mass.
The influence of the donor type can also be studied by changing the values of the coefficient of transformation of active centers by the donor \( k_{12} \) and \( k_{21} \). The use of the best donors reduces the mass part of stereoblock chains, as the transformation of isotactic centers into atactic centers is less likely during the lifetime of the polypropylene chain.

Analogously, the effect of changes of hydrogen concentration on polypropylene microstructure is studied. Molecular mass decreases with increasing hydrogen concentration. Changes in hydrogen concentration also affect the proportion of stereoblock chains: polymer chains become shorter with an increase in hydrogen concentration and thus the probability of transformation of active centers occurring during the growth time of polymer chains decreases. Therefore, when the hydrogen concentration increases, the proportion of stereoblock chains decreases.

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