Influence of Turbulent Mixing on Fast Polymerization Reactions

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ABSTRACT: Investigations on development of a macrokinetics approach were generalized to the analysis of fast chemical reactions, mainly using cationic polymerization of isobutylene as an example, which is a new class of liquid-phase processes. The removal of diffusional constraints on polymer synthesis, by intensification of turbulent mixing in the reaction zone, makes it possible to calculate the kinetic parameters of polymerization and polymer-analogous reactions, to optimize the molecular characteristics of polymeric products obtained, and to control the character of the process as a whole. The laws pertaining to the progression of fast processes are considered for the synthesis of separate polymers, in particular stereoregular polydienes, ethylene–propylene copolymers, and chlorobutyl rubber. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 613–624, 2004

Key words: synthesis; fast processes; cationic polymerization; reactive processing; kinetics (polym.)

INTRODUCTION

In studying the processes of liquid-phase synthesis of high molecular mass compounds, it has been found that many of them occur extremely rapidly (the characteristic time of a chemical reaction is $\tau_{ch} < 0.01$–0.1 s). In this case, even very slow addition of a polymerization initiator, use of dilute reactant solutions, and intense stirring cannot ensure that the process will occur under isothermal conditions. Chemical reactions of this type start well before the moment when the reactants, introduced into the reaction zone, become mixed. They occur in the diffusion region and are determined by the processes of mixing of reactants, primarily by the degree of turbulence in the reaction volume, given that the mixing time of reactants is generally longer than the characteristic reaction time ($\tau_{mx} > \tau_{ch}$).

A review of the literature indicates that this essentially new class of chemical reactions has scarcely been studied, although it encompasses a rather large variety of processes of synthesis of polymeric products. Of these, we can name the electrophilic polymerization of isobutylene, styrene, p-chlorostyrene, and cyclopentadiene; ionic polymerization of formaldehyde; nonequilibrium polymerization; copolymerization of isobutylene with isoprene and styrene; chlorinated butyl rubber synthesis reactions; cationic polymerization of piperylene; the generation of polymerization sites with the use of Ziegler–Natta catalyst systems; and initiation reaction (in particular, in the manufacture of stereoregular isoprene and butadiene rubbers and ethylene–propylene elastomers).

FUNDAMENTAL PRINCIPLES OF OCCURRENCE OF FAST PROCESSES IN POLYMER SYNTHESIS

New approach to studying the specifics of fast reactions

A simple experiment simulating the fast process of electrophilic polymerization of isobutylene in the presence of aluminum trichloride (243 K) showed[1] that the reaction proceeded locally, by 80–95 wt %, immediately at the catalyst feed point in the monomer solution. In this case, the temperature of the reaction mass is different at different points of the reactor and depends on the monomer and catalyst concentrations. In the topochemical aspect, a fast polymerization reaction occurs as a plume with characteristic gradients of temperature and reactant and product concentrations in the reaction-zone coordinates. In shape, the reaction front formed is similar to that observed in a combustion reaction. When fast polymerization processes are carried out in stirred tank reactors, it is practically impossible to maintain the isothermal regime in the reaction zone; and temperature in the bulk of a reactor can vary by tens of degrees under actual conditions. As a result, a characteristic feature of fast processes of polymer synthesis is the impossibility of correct evaluation of kinetic parameters with classical

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techniques; the uncertainty of the molecular structure of the polymeric products and, hence, of their performance characteristics; scatter in values of the molecular parameters [molecular mass and molecular mass distribution (MMD)] of the polymer; and irreproducibility of the experiment.
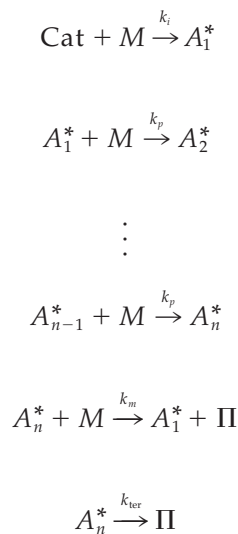
This scenario of fast chemical processes has demanded a search for and the development of new approaches to study the specifics of these reactions. It is necessary to know how to determine the values of rate parameters, to reveal the basic principles of polymer synthesis reactions, and to gain other information from the totality of experimental data obtained under conditions of nonisothermal occurrence of the process, initial concentration of substances, and molecular mass and other parameters of the polymeric product formed. To reveal the kinetic and macroscopic features of fast chemical processes, and basic relationships characteristic of this class of reactions, we propose use of the diffusion model based on the solution of chemical kinetics, diffusion, and heat transfer (macrokinetics) equations with the volume-invariable turbulent diffusion coefficient D_t and heat conductivity λ_t.

Note that fast chemical processes should be carried out and studied in a jet in a well-stirred tubular reactor (i.e., in highly turbulent flows).[1] This is reasonable from several vantage points. First, the conduction of fast reactions in a jet confined by a repulsive wall is the most convenient and natural way for their experimental study. Second, when such reactions are carried out in classical stirred tank reactors, it is in principle impossible to provide effective heat and mass transfer within a time comparable to the time of chemical reaction. Third, under the turbulent conditions of moving jets, fast chemical processes can be conducted with the maximum intensity over the minimum period of time and in the minimal volume. Fourth, the study of reactions in a stationary stream with turbulent mixing is theoretically simpler and more effective than their investigation in the single-addition mode under batch conditions. Finally, when a fast reaction is conducted in a jet, it is possible to vary the characteristic mixing time $\tau_{mx} = R^2/D_t$ [R is the radius of the jet (flow) confined by a solid wall] and, in particular, to make it comparable with the characteristic chemical-reaction time $\tau_{ch} = 1/k_{ter}$ (k_{ter} is the rate constant of chain termination in polymerization). By comparison of mixture times and chemical reaction as the criterion, the characteristic time of mixture for a range of wide-scale turbulent pulsations was chosen. The size of turbulent pulsations compared with the sizes of reactor (turbulent length scale at fast chemical reactions requires length equal to the radius reactor R).

A convenient model for studying fast processes of polymer synthesis is the isobutylene polymerization reaction, for which the propagation rate constants $k_p = 10^6$–10^8 L mol^{-1} s^{-1} (243 K) are available from the literature.[3] It is obvious that the approach developed[4] is common for any fast reactions of polymer synthesis with limited heat and mass transfer.

The simulation of isobutylene polymerization is based on the kinetic scheme of the process in which a principal reaction controlling the molecular-mass characteristics of the polymer produced is the reaction of chain transfer to the monomer,[1,3] expressed in the following set of equations:

$$\text{Cat} + M \xrightarrow{k_i} A_1^*$$

$$A_1^* + M \xrightarrow{k_p} A_2^*$$

$$\vdots$$

$$A_{n-1}^* + M \xrightarrow{k_p} A_n^*$$

$$A_n^* + M \xrightarrow{k_m} A_1^* + \Pi$$

$$A_n^* \xrightarrow{k_{ter}} \Pi$$

where k_i and k_m are rate constants of initiation and chain transfer to the monomer, respectively; and A^* is the active site (growing polymer chain). In this case, solving the direct problem results in the relationship[3]

$$\bar{P}_n = \frac{k_p}{k_m + \dfrac{k_{ter}}{[M]}} \qquad (1)$$

However, the number-average degree of polymerization of the polymer formed under conditions provided by modern tank mixers is always lower and the MMD width is always greater than the corresponding calculated values, which parameters are in principle uncontrollable. The mixing of reactants and a chemical reaction in fast polymerization processes are described by diffusion, heat transfer, and chemical-kinetics equations, wherein actual flows must definitely be turbulent. In this case,

$$\frac{\partial[M]}{\partial\tau} = D_t\nabla[M] - k_p[M][A^*] - v\,\text{grad}[M] \quad (2)$$

$$\frac{\partial[A^*]}{\partial} = D_t\nabla[A^*] - k_{ter}[A^*] - v\,\text{grad}[A^*] \quad (3)$$

$$\frac{\partial T}{\partial\tau} = \chi_t\nabla T + \frac{q}{\rho C_p}k_p[M][A^*] - v\,\text{grad}\,T \quad (4)$$
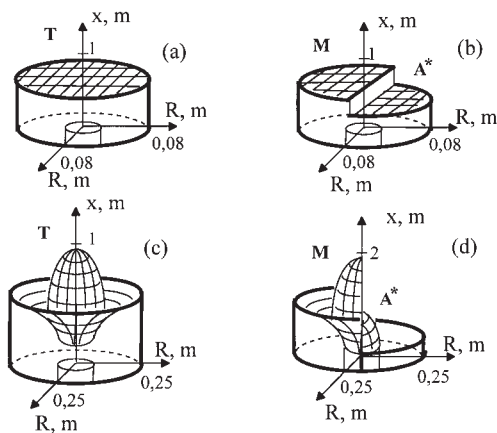
Figure 1 Temperature fields of (a, c) concentration of active sites A^* and (b, d) monomer M formed on fast isobutylene polymerization in a flow with $R = 0.08$ m (a, b) and $R = 0.25$ m (c, d). Monomer conversion (in wt %): (a, b) 99.3; (c, d) 65; ΔT (in K): (a, b) 28; (c, d) 22 ($[M]_0 = 1$ mol/L; $[AlCl_3]_0 = 0.0045$ mol/L, $D_t = 0.025$ m^2/s; $k_p = 10^5$ L mol^{-1} s^{-1}; $k_{ter} = 20$ s^{-1}; $T_0 = 300$ K); (a, b) plane reaction front determining the quasi-isothermal mode in the reaction zone and (c, d) the process occurring in the plume mode.

where $[M]$ and $[A^*]$ are the monomer and catalyst concentrations, respectively; T is the temperature; q is the heat of reaction; ρ and C_p are the average density and heat capacity of the reaction mixture, respectively; v is the linear flow velocity; χ_t is the effective turbulent thermal diffusivity; ∇ is the Hamiltonian; and τ is the time. In the case of turbulence conditions, it may be assumed that $\chi_t = \lambda_t/\rho C_p \approx D_t$ (i.e., it coincides with the turbulent diffusion coefficient).

The macrokinetic model was used to calculate reactant-concentration and temperature fields and the yield, molecular mass, and MMD of a polymer for mixing of two coaxial flows—the monomer solution (outer flow) and the catalyst solution (inner flow)—in the reaction zone of a jet reactor.[4]

Quasi-plug-flow mode in turbulent flows

The plots obtained upon solving the set of eqs. (2)–(4) show that, at process parameters close to realistic quantities, there are considerable gradients of temperature and monomer and catalyst concentrations (Fig. 1). In fact, there is practically local occurrence of fast polymerization, in which the temperature field in the reaction zone is determined by the turbulence scale in the zone, chain propagation rate constant, heat of reaction, and monomer and catalyst concentrations.[5–7] An important result obtained in the analysis of experimental data and solution of the inverse problem in the chemistry of fast polymerization processes is the finding that a macroscopic quasi-plug-flow reaction mode, having no analogues, can be formed in turbulent streams. In the region determined by the strictly defined radii of jet-type reaction zone R_{max} and R_{min},

a plane front of reactant concentrations and temperatures is formed at which the temperature in the reaction zone is virtually constant (i.e., a quasi-isothermal mode of the process is formed). In this case, the effective mixing of reactants and uniform distribution of their concentration and temperature over R takes place in the reaction zone. Allowance for the axial turbulent mixing of the reactants distinguishes this mode from the known plug-flow mode formed in laminar flows. The quasi-plug-flow mode is observed at sufficiently high linear flow velocities of reactants in the reaction zone, which provide a high level of turbulence. One of the most essential factors in this case is the influence of geometry and design of the reaction volume (Fig. 2) on the reactant mixing time τ_{mx} and molecular-mass parameters of the polymeric products (Table I). The conditions of attaining the quasi-plug-flow mode in turbulent flows (plane reaction front) upon fast polymerization are defined by the relationship $\tau_{mx} = R^2/D_t < \tau_{ch} = 1/k_{ter}$ [Fig. 1(a), (b)]. This equation suggests that there is a critical radius R_{cr} characterizing the transition from the quasi-plug-flow mode in turbulent flows to the plume mode:

$$R_{cr} = \sqrt{D_t/k_{ter}} \qquad (5)$$

In particular, if $R > R_{max} = R_{cr}$, there is the transition to the plume mode. At $R < R_{min}$, the same happens because of transition from the turbulent mode of flow to a transient and then to the laminar mode. An increase in the linear velocity of streams v (and, hence, D_t once $D_t \sim v$) extends the admissible domain of parameters determining the occurrence of fast polymerization processes under quasi-isothermal conditions. Thus, the interval between R_{min} and R_{max} increases because R_{min} decreases and R_{max} increases. Consequently, the output of the process can be enhanced considerably if necessary.

To summarize, in the case of fast polymerization processes conducted in the jet mode, the axial motion of reactants is determined by the linear flow velocity v, and the range of reactant concentrations is determined
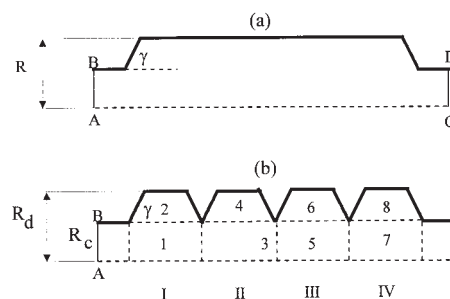

Figure 2 Schematic of the (a) cylindrical and (b) divergent–convergent reaction zone: γ, the divergent angle of a tube; 1–8, regions of the reaction zone; I–IV, divergent–convergent sections.

Reaction mode	R (m)	Conversion, ω (wt %)	$\bar{P}_n$	$\bar{P}_w/\bar{P}_n$	τ_{mx} (s)
		Cylindrical reaction zone ($D_i = 0.025$ m^2/s)			
Quasi-isothermal	0.01	100	43	2	0.004
	0.03	100	43	2.2	0.036
	0.05	99	30	3.1	0.10
Plume	0.10	90	21	3.7	0.40
	0.50	30	17	4.0	10
		Divergent–convergent reaction zone ($D_i = 0.20$ m^2/s)			
	0.03	100	50	2	0.0045
Quasi-isothermal	0.05	100	50	2	0.0125
	0.10	100	48	2.1	0.05
	0.30	94	41	2.8	0.45
Plume	0.50	85	28	3.2	1.25
	1.00	50	20	4.0	5.00

^{a} $K_p = 10^5$ L mol^{-1} s^{-1}, $K_{ter} = 20$ s^{-1}, $[M]_0 = 1$ mol/L, $[A^*]_0 = 0.0045$ mol/L.

by the turbulent diffusion as $\sqrt{D_t}$. At high flow velocities, a fast polymerization process approaches the plug-flow mode because the role of axial diffusion decreases. When v decreases within the limits of the turbulent mode, the temperature "spread" in the reaction zone (attributed to axial turbulent diffusion and heat transfer in the direction reverse to that of flow) leads to the fact that a constant temperature is almost entirely established throughout the reaction volume (quasi-isothermal mode). This makes it fundamentally different from the plug-flow mode. It is also important to note that, if fast polymerization reactions occur at $R_{cr} < R$, the reaction front formed has the plume shape, and the rate parameters of the process and the molecular characteristics of the polymer produced will not agree with those predicted using the plug-flow model. An increase in D_t by increasing v or varying the design of the reaction zone (Fig. 2) leads to a corresponding increase in the conversion of reactants. In this case, the residence time τ_r of reactants in the reaction zone shortens and the reaction zone is contracted (Fig. 3). In addition, the temperature maxima in the reaction zone smooth out, despite the fact that the total yield of the products increases and more heat is evolved.[3]

DETERMINATION OF RATE PARAMETERS OF FAST PROCESSES IN POLYMER SYNTHESIS

Polymerization of isobutylene

Carrying out fast polymerization processes in the turbulent-flow mode (plane reaction front) allowed a novel method for determining some kinetic constants—in particular, k_p and k_{ter}—to be developed.[8] The flow mode is characterized by the interrelation of the apparent monomer and catalyst residence times in the reaction zone $\tau_r = (L/v)_{app}$ (defining the length of reaction zone L at which the polymer yield reaches

90% of the limiting value) with the rate constants of the process,[9] as follows:

$$\left(\frac{L}{v}\right)_{app} = -\frac{1}{k_{ter}} \ln\left\{1 + \frac{k_{ter}}{k_p[A^*]_0} \times \ln\left[0.1 + 0.9 \exp\left(-\frac{k_p[A^*]_0}{k_{ter}}\right)\right]\right\} \quad (6)$$

In this case, each catalyst concentration $[A^*]_0$ corresponds to its own value of the apparent residence time of reactants in the apparatus. For example, at large amounts of an isobutylene polymerization catalyst, we have $\tau_r = 0.005 \pm 0.0005$ s ($v = 2.5$ m/s, $k_p = 10^5$ L mol^{-1} s^{-1}, $k_{ter} = 10$ s^{-1}). If the catalyst concentration is low and polymerization does not go to completion for this reason, τ_r may vary over a wide range (by more than an order of magnitude). Upon analyzing eq.
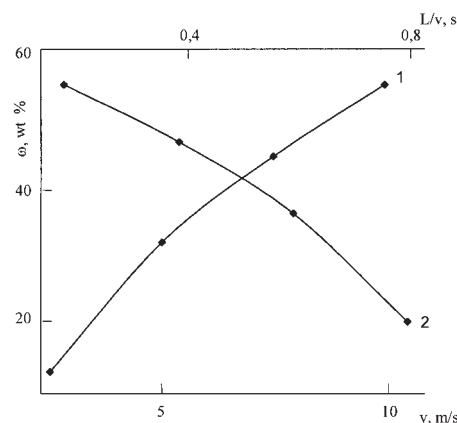

Figure 3 Experimentally measured conversion ω for polyisobutylene as a function of (1) linear velocity of reaction mixture and (2) characteristic time of chemical reaction L/v at $L = 2$ m, $[M]_0 = 2$ mol/L, $[AlCl_3]_0 = 0.0045$ mol/L, $R = 0.25$ m, and $T_0 = 300$ K.

(6), we find that the polymer yield tends to become quantitative at high catalyst concentrations. In this case, the relationship $k_{ter}/(k_p[A^*]_0) \ll 1$ holds and

$$(L/v)_{app} \cong 2.3/k_p[A^*]_0 \qquad (7)$$

At low catalyst concentrations, $k_{ter}/(k_p[A^*]_0) \geq 1$ and

$$(L/v)_{app} \cong 2.3/k_{ter} \qquad (8)$$

The study of variation in the polymer yield along the reaction-zone length L or depending on the linear flow velocity v at different catalyst concentrations and at $R_{cr} > R$ allows the rate constants of some elementary reactions of fast polymerization of isobutylene to be experimentally determined. For example, it was found (for 243 K) that $k_p = 10^6$ L mol^{-1} s^{-1} and k_{ter} = 17.5 ± 5 s^{-1}.[8] Note that the value of k_p obtained generally agrees with the published data[1] and that of k_{ter} is the first value ever determined.

Chlorination of butyl rubber

Using the experimentally determined characteristic residence time τ_r, the rate constant for the fast reaction of chlorination of butyl rubber with molecular chlorine in the manufacture of chlorinated butyl rubber was determined.[10] This polymer-analogous reaction was carried out in a tubular turbulent apparatus, of the divergent–convergent design with a diffuser radius of $R_d = 0.025$ m, a confuser radius of $R_c = R_d/2$, and a length of $L = 2$ m (the reactor volume of 0.004 m^3), filled with a special Teflon packing.

The apparatus was fed with 0.21 m^3/h of a 10% butyl rubber solution in the hexane fraction and 2.1 m^3/h of 5 : 1 (by volume) nitrogen–chlorine mixture. These rates determined the linear flow velocity of reactants that, without account for the volume occupied by the packing, is $v_d = 0.33$ m/s in the broad part of the reactor (diffuser) and $v_c = 1.31$ m/s in the confuser [Fig. 2(b)]. Thus, it follows that the characteristic residence time τ_r is 6 s (300 K). Because molecular chlorine was absent from the effluent gas (N$_2$ + HCl), it might be assumed that its conversion was at least 99%. Thus, it follows that the minimal value of the butyl rubber chlorination rate constant k in the chlorinated butyl rubber manufacturing process is equal to 225 L mol^{-1} s^{-1} and, correspondingly, the chemical-reaction time is $\tau_{ch} = 1/k[c]_0 \sim 0.1$ s, where $[c]_0$ is the initial concentration of chlorine.

On the other hand, according to the published data,[1] the residence time of the reaction mixture upon chlorination of butyl rubber in stirred tank reactors, over the range 290–325 K, is 5–20 s; in the particular case of chlorination of a 15–16 wt % butyl rubber solution in methyl chloride with molecular chlorine (3–3.5 wt % of the butyl rubber mass), $\tau_r = 7.5 \pm 2.5$ s.

According to the relationship

$$k = \frac{1}{\tau_{ch}} \cdot \frac{x}{c_0(c_0 - x)} \qquad (9)$$

where x is the concentration of the product, this gives (at $c_0 = 0.05$ mol/L and a chlorine conversion of 99%) $k \sim 150 \pm 50$ L mol^{-1} s^{-1}, which is almost the same as the butyl rubber chlorination rate constant determined experimentally for the reaction in a turbulent flow confined by a solid wall.[10]

Thus, the chlorination reaction of butyl rubber with molecular chlorine in a tubular reactor should also be grouped with the new class of fast chemical reactions.[2]

ENHANCEMENT OF TURBULENCE IN THE REACTION ZONE AS A KEY TO OPTIMIZING FAST POLYMER SYNTHESIS PROCESSES

New type of reactors for fast polymer synthesis processes

When fast polymer synthesis processes are carried out in classical stirred tank reactors, in which such processes generally occur in the diffusion region ($\tau_{ch} < \tau_{mx}$), it is problematic to arrange the highly effective mixing of reactants and, as a result, the performance characteristics of the product are deteriorated. Processes of this type, as has been noted earlier, must be carried out in a flow confined by a repulsive wall, that is, in tubular turbulent jet reactors[5,11] (Fig. 2). In these apparatuses, the mixing efficiency depends, to a considerable extent, on a relative change in the turbulent diffusion coefficient D_t along the axis of the reaction zone.

The mixing efficiency can be increased not only by increasing the linear flow velocity v but also by stabilizing D_t at a certain level along the direction of the flow. This can be achieved through the formation of circulation zones in the reaction volume, in particular, by varying the geometry of the reaction zone, as well as by changing the reactant feed mode.[12] Tubular turbulent reactors with geometrically identical elements of the divergent–convergent design repeated along the axis [Fig. 2(b)] turned out to be effective in this respect because they provide a significant (by an order of magnitude and greater) increase in D_t and allow a high level of flow turbulence to be maintained along the reaction zone of any length.[6,7,11] Their distinctive feature is the possibility of reaching a required intensity of mixing and heat transfer at significantly (a few times) lower flow velocities. They also differ in an extremely high efficiency in operation with highly viscous fluids (in particular, with polymer solutions) and allow the problems of increasing the production capacity (by a factor of 10–100) to be solved. In addition, turbulent reactors are very effective in operation with multiphase systems, especially with liquid–liquid and gas–liquid systems.[10] Creation of a high level of turbulence, attributed to the geometry of the diver-
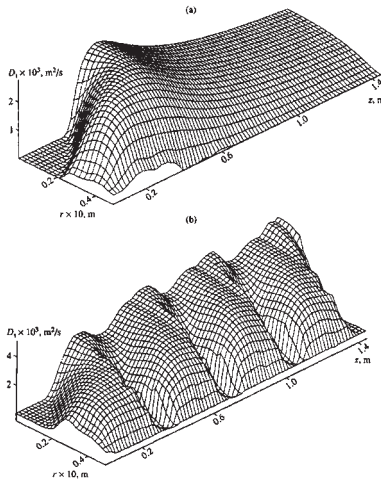
Figure 4 Distribution of turbulent diffusivity D_t in the (a) cylindrical and (b) divergent–convergent reaction zone: Re $= 2 \times 10^5$, $R_c = 0.025$ m, $v = 4$ m/s, $\rho = 1000$ kg/m^3, where r and z are the radial and axial coordinates, respectively.

gent–convergent channel, leads to excellent dispersion of phases and formation of fine uniform emulsions, as well as to a noticeably higher (by an order of magnitude or greater) rate of dissolution of gases in a liquid than upon bubbling or using mechanical stirrers in stirred tank reactors.[10]

The distribution of the turbulent diffusion coefficient throughout the reaction-zone space in divergent–convergent devices was compared with a corresponding distribution in a cylindrical reactor of the type shown in Figure 4.[6] These results follow from the theoretical consideration of the process.[7]

Theoretical description of turbulent mixing in the divergent–convergent reaction zone

The theoretical description was based on the assumptions that the medium is Newtonian and incompressible and the flow is axially symmetric and nonswirling. Turbulent flow was described by the standard model with such parameters as the specific turbulence kinetic energy K and its dissipation rate ε. The turbulent diffusivity D_t was considered to be equal to the kinematic turbulent viscosity: $D_t = \nu_t = \mu_t/\rho$. In terms of the accepted assumption, the following mathematical-model equations can be written in the cylindrical coordinate system.

The continuity equation expressing the law of conservation of mass:

$$\frac{1}{r}\frac{\partial(ru)}{\partial r} + \frac{\partial v'}{\partial z} = 0 \tag{10}$$

Reynolds-averaged momentum transfer equations:

$$\frac{\rho}{r}\frac{\partial(ruu)}{\partial r} + \rho\frac{\partial(uv')}{\partial z} = -\frac{\partial p}{\partial r} - \left[\frac{1}{r}\frac{\partial(r\tau_{11})}{\partial r} - \frac{\tau_{33}}{r} + \frac{\partial\tau_{21}}{\partial z}\right] \tag{11}$$

$$\frac{\rho}{r}\frac{\partial(ruv')}{\partial r} + \rho\frac{\partial(v'v')}{\partial z} = -\frac{\partial\rho}{\partial z} - \left[\frac{1}{r}\frac{\partial(r\tau_{12})}{\partial r} + \frac{\partial\tau_{22}}{\partial z}\right] \tag{12}$$

where the stress tensor components are given by

$$\tau_{12} = -2\mu\frac{\partial u}{\partial r}, \quad \tau_{22} = -2\mu\frac{\partial v'}{\partial z}, \quad \tau_{33} = -2\mu\frac{u}{r} \tag{13}$$

and

$$\tau_{12} = \tau_{21} = -\mu\left(\frac{\partial v'}{\partial r} + \frac{\partial u}{\partial z}\right) \tag{14}$$

Equations for the transfer of turbulence kinetic energy and its dissipation:

$$\frac{\rho}{r}\frac{\partial(ruK)}{\partial r} + \rho\frac{\partial(v'K)}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{\mu}{\sigma_K}\frac{r\partial K}{\partial r}\right) + \frac{\partial}{\partial r}\left(\frac{\mu}{\sigma_K}\frac{\partial K}{\partial z}\right) + \mu_T G - \rho\varepsilon \tag{15}$$

$$\frac{\rho}{r}\frac{\partial(ru\varepsilon)}{\partial r} + \rho\frac{\partial(v'\varepsilon)}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{\mu}{\sigma_E}\frac{r\partial\varepsilon}{\partial r}\right) + \frac{\partial}{\partial z}\left(\frac{\mu}{\sigma_E}\frac{\partial\varepsilon}{\partial z}\right) + \mu_T C_1 G\varepsilon/K - C_2\rho\varepsilon^2/K \tag{16}$$

$$G = \frac{1}{\mu^2}\left[\frac{1}{2}\left(\tau_{11}^2 + \tau_{22}^2 + \tau_{33}^2\right) + \tau_{12}^2\right] \tag{17}$$

$$\mu_T = \rho\frac{C_\mu K^2}{\varepsilon} \tag{18}$$

where p is the pressure; r and z are the radial and longitudinal coordinates; u and v' are the axial and radial velocity components, respectively; μ is the apparent dynamic viscosity; and μ_T is the dynamic turbulent viscosity. The standard values for the constants of the turbulence model: $C_1 = 1.44$, $C_2 = 1.92$, $C_\mu = 0.09$, $\sigma_c = 1.0$, and $\sigma_E = 1.30$, are used.

The flow of a liquid with a dynamic viscosity of $\mu = 0.001$ Pa s^{-1} and a density of $\mu = 1000$ kg/m^3 was considered. Boundary conditions represented the symmetry conditions along the z-axis and conditions of the liquid adhering to solid wall surfaces.

A schematic of the reaction zone for cylindrical and divergent–convergent channels is shown in Figure 2. Pressure was preset at the reactor outlet (line CD), and a linear flow velocity of $v = 5$ m/s was preset at the reactor inlet (line AB) along the symmetry axis.

The lengths of the inlet and outlet regions were many times greater than their diameter ($L \gg 2R$), thus allowing the influence of entrance and exit turbulence parameters on the characteristics of turbulent flow in the divergent–convergent channel, which are the subject matter of study, to be eliminated.

The best results for the efficiency of mixing of liquid flows is given by a reaction zone of the divergent–convergent design [Fig. 2(b)] with a divergent angle γ of 30–85°. In this case, the convection velocity on the periphery of the reaction zone is much lower than that in its central part (i.e., all transport processes are attributed to turbulent exchange). This dramatically decreases τ_{mx}, which is important in realization of fast chemical processes and, as shown experimentally,[13] in the case of mass-transfer physical processes. As a result, a sufficiently uniform field of the turbulent diffusion coefficient D_t is established in the divergent–convergent reaction zone. High numerical values of D_t are retained over a wide range of the divergent angle ($\gamma \sim$ 30–85°).

Thus, carrying out fast chemical processes in flow, especially in the synthesis of polymeric products, divergent–convergent reactors have considerable advantages over cylindrical reactors (Fig. 2). The divergent–convergent channel allows high-turbulence parameters to be maintained over the entire reaction-zone length, whereas these parameters in a constant–cross section reaction zone sharply decrease with reactants traveling from the inlet by a distance as small as two–three channel diameters (Fig. 4). In addition, the turbulent mixing intensity in the constant-diameter reaction zone depends on the reactant feed mode and geometry,[12] whereas the turbulence characteristics in a divergent–convergent reaction zone are primarily determined by the geometry of the channel itself.[14] This is seen from the figure, which shows a change in the turbulent kinetic energy and its dissipation rate depending on the channel geometry. Based on this concept, a new type of reactor (tubular devices that operate in the high-turbulence plug-flow mode[5,11] and are used with extremely high cost performance and engineering advantages in the manufacture of polymeric products) was designed.

SELF-SIMILAR LIQUID FLOW

The divergent–convergent shape of the reaction zone has another important advantage, especially in the solution synthesis of polymers, for example, isobutylene polymers, butyl rubber, and chlorinated butyl rubber. In some cases, the viscosity of high-turbulence flow does not affect the flow parameters of the bulk of the reaction medium. In this case, the flow is said to be self-similar with respect to viscosity. The Reynolds number, above which the self-similarity region is observed, is largely determined by flow geometry. For example, it is known that the self-similar flow regime

in which the coefficient of resistance is independent of the Reynolds number, and hence, on viscosity, is attained at Re = 500 for a flow past a sphere, whereas the corresponding value of the Reynolds number in the case of flow in cylindrical channels (invariable cross section) is a few orders of magnitude higher ($\sim 10^7$).

Because a considerably higher level of flow turbulence is achieved in the divergent–convergent channel than in the constant–cross section reaction zone at identical Reynolds numbers, it may be expected that the self-similar flow will be observed at significantly lower values of the Reynolds number in the former channel. Indeed, the self-similar flow in a divergent–convergent channel sets in at Re = $800/f(\gamma)$, where the dependency of f on the divergent angle γ can be found according to the relationship[15]

$$f(\gamma) = 0.117 + 0.0488\gamma - 0.0012\gamma^2 + 1.374 \times 10^{-5}\gamma^3$$
$$- 5.9 \times 10^{-8}\gamma^4 \quad (19)$$

Based on this consideration using dimensional analysis, simple analytical expressions have been obtained, which are suitable for engineering calculations of turbulence and reactant mixing parameters in fast processes in flow, including the case of polymer synthesis with divergent–convergent channels.

Volume-averaged flow characteristics are virtually independent of viscosity, and there are only three determining quantities: density ρ, radius R, and time-averaged velocity v. Correspondingly, the mean values of the specific turbulent kinetic energy K, its dissipation rate ε, and turbulent diffusivity D_t are as follows[6,15]:

$$K = 0.048f^2v_c^2 \quad (20)$$

$$\varepsilon = 0.0105f^3v_c^3/R_c \quad (21)$$

$$D_t = 0.024fv_cR_c \quad (22)$$

where $f = f(\gamma)$ is found from eq. (20).

Taking into account these equations and the results relevant to the ratio between mixing and chemical reaction times, relationships were proposed for estimating the characteristic mixing time in self-similar flow through a divergent–convergent channel. The turbulent mixing time τ_{turb} is determined from the equation $\tau_{turb} = l^2/D_t$ (l is the characteristic linear dimension of the region in which a uniform concentration field of reactants is supposed to be created). The micromixing time τ_{micro} that characterizes mass-transport processes, occurring in a sufficiently small volume by molecular diffusion and viscous flows, is defined as $\tau_{micro} = 17.3(\nu/\varepsilon)^{0.5}$. The mesomixing time τ_{meso}, which characterizes the medium homogenization process by exchange between large turbulent ed-

dies and small eddies occurring inside the former, is defined by $\tau_{\text{meso}} = (l^2/\varepsilon)^{1/3}$.[6] Ultimate expressions for the characteristic mixing time are as follows:

$$\tau_{\text{turb}} = 40.325 l^2/fv_c R_c \qquad (23)$$

$$\tau_{\text{micro}} = 337.711[vR_c/(f_c^3)]^{0.5} \qquad (24)$$

$$\tau_{\text{meso}} = 4.561(l^2 R_c)^{1/3}/(fv_c) \qquad (25)$$

Comparison of these times allows the limiting mechanism of leveling reactant concentration fields in the reaction zone to be determined. Of the values calculated according to eqs. (23)–(25) it is necessary to select the highest and to compare them with the characteristic time of chemical reaction τ_{ch}. If $\tau_{\text{ch}} > \tau_{\text{mx}}$ (τ_{turb}, τ_{micro}, τ_{meso}), a fast chemical process occurs in the kinetic region and diffusional constraints do not exert a negative effect on the course of the process and the quality of the product. As the viscosity of the medium increases during fast polymer synthesis reactions in solution in stirred tank reactors, the process gradually becomes controlled by micromixing. The following relation holds in this case:

$$\frac{\mu}{\rho} > 0.456 \frac{l^4 fv_c}{d_c^3} \qquad (26)$$

Thus, another undisputed advantage of the divergent–convergent reactor is revealed: the characteristics of turbulent flow and characteristic mixing times in the self-similar mode are found using simple formulas suitable for engineering computations. This allows the transport processes of substances to be controlled and a tubular reactor of optimal design to be calculated. A change in the convergent radius and linear flow velocity seems to be the only way to vary the mixing time and turbulence parameters in a reactor of the divergent–convergent design. For example, a decrease in the reactor radius R_c leads to a decrease in the numerical values of τ_{turb}, τ_{micro}, and τ_{meso}. This is a key to optimization of fast polymer synthesis processes; however, it is only up to a certain limit because the turbulent diffusivity D_t decreases and dissipation of turbulence energy ε increases with decreasing R_c. These losses can be compensated by increasing the linear velocity of streams. The upper limit for the stream velocity in a divergent–convergent reactor is determined by the pressure difference at the entrance to and the exit from the reaction zone in accordance to $\Delta p \sim v^2$, and the lower limit is determined by the value of $D_t \sim 10^{-3}$ m^2/s. It thus follows that there is an interval of R_c and v_c values in which conditions for the removal of diffusion constraints on fast polymer synthesis processes are removed, including those in viscous polymer product solutions. At technically appropriate values of R_c and v_c, the diffusion constraints

can be ruled out for reactions with a characteristic time of $\tau_{\text{ch}} > 10^{-4}$–$10^{-3}$ s.

SEPARATION OF FAST AND SLOW PROCESSES IN POLYMER SYNTHESIS ON ZIEGLER–NATTA CATALYSTS

Frequently, the major steps of a chemical process are slow as such but are preceded by steps involving the occurrence of fast chemical reactions. In particular, this is the case for polymer synthesis in the presence of Ziegler–Natta catalyst systems.

The characteristic time of chain propagation, for example, with the systems V–Al, Ti–Al, Nd–Al, and the like used to manufacture ethylene–propylene, cis-1,4-isoprene, and cis-1,4-butadiene rubbers, is about 10^2 s or longer. At the same time, the rate of initiation producing active centers occurs at a rate many orders of magnitude higher (i.e., relates to fast, component mixing-limited chemical reactions). As a result, when a catalyst and a cocatalyst are fed immediately into tank mixers, inhomogeneities in the distribution of produced active sites arise at both microscopic and macroscopic scales. This also leads to the inhomogeneity in monomer distribution throughout the reactor upon polymerization, which is naturally accompanied by the appearance of nonuniformity in the composition of macromolecules; deterioration of the molecular characteristics of the polymers formed; and, consequently, deterioration of their quality.

It was deemed appropriate to separate the fast step of generation of active sites and the slow step of (co)polymerization per se on Ziegler–Natta catalyst systems. In this case, ideal (or nearly ideal) conditions of occurrence of chemical processes can be provided for each stage. It can be achieved in a turbulent prereactor of the divergent–convergent design[11] for the first step and in a stirred tank polymerizer reactor for the second, slow step. Using the prereactor of the divergent–convergent design, the reactant micromixing time is always shorter that the residence time of the reaction mixture ($\tau_{\text{mx}} < \tau_r$). This ensures that all potential active sites of polymerization arrive in the main polymerizer reactor in the preformed state and the perfect mixing model is valid in this case.

Copolymerization of ethylene and propylene

The optimization of the composition of the V–Al catalyst system and homogenization of streams arriving in a polymerizer, as well as the separation of the fast active-site generation step and the slow step of ethylene and propylene copolymerization per se by using devices of the divergent–convergent design, led to noticeable improvement of the properties of ethylene–propylene rubbers. A decrease in the blocking ratio of ethylene units, attributed to a decrease in the amount of long blocks (by a factor of 2.5) with retaining the

TABLE II
Statistical Data on the Composition of Macromolecules of Ethylene–Propylene Terpolymer (with Ethylidenenorbornene) Before and After Inclusion of a Divergent–Convergent Prereactor into the Process Flow Chart

| Flow chart[a] | Amount of units (%) | | Amount of ethylene blocks (%) | | Ratio of propylene units in long blocks (%) | Branching ratio of macromolecules (%) |
	Ethylide norbornene	Terminal vinylidene	Long	Short		
1	28	0.29	0.17	1.1	1.9	0.29
2	29	0.19	0.06	0.9	2.6	0.17

[a] (1) Without and (2) with separation of stages.

number of short ones; an increase in the blocking ratio of the propylene units, including the growth attributed to an increase in proportion of long blocks; and a decrease in the branching ratio (by a factor of about 2) of macromolecules were observed (Table II). In this case, the amount of off-grade products and wastes dramatically decreases.[11] The copolymer (EPDM, Keltan, Dutral, Epsyn) produced in a prereactor of the divergent–convergent design is characterized by a higher uniformity (Fig. 5).

Stereospecific polymerization of isoprene

The separation of the steps of generation of macromolecule growth sites and polymerization per se with the use of a tubular turbulent prereactor also has an effect on the molecular characteristics of products in the synthesis of stereoregular cis-1,4-isoprene rubbers in the presence of the Ti–Al (SKI-3, ameripol SN) and Nd–Al (SKI-5) catalyst systems.[13,14] According to the conventional technology for this process, the catalyst and monomer are added to the reaction mixture with effective mixing in the first tank polymerizer mixer of the cascade of reactors. The mixing of the reactants and the formation of the catalyst system occurs with a low efficiency in this case. The use of a prereactor of

the divergent–convergent design (installed before the first tank reactor of the chain of polymerizers) allowed the amount of cis-1,4-units in the macromolecules of stereoregular isoprene to be increased and the homogeneity of the product to be enhanced.[14] This permitted the plasticity of the product to be correlated with its Mooney viscosity for the first time in industrial-scale manufacture. As a result, it became possible to improve the quality of the product up to the level corresponding fully to theoretical predictions and to obtain the stereoregular cis-1,4-isoprene rubber SKI-5 of different brands on the same apparatus. This cannot be achieved on the basis of existing stirred tank reactors. In addition, the output of the process in the manufacture of SKI-5 increased from 34 ± 1 to 40 ± 1 t/h and the amount of the Nd–Al catalyst used and the rate of wall building on the inner surfaces of the engineering equipment decreased (by two to four times and almost an order of magnitude, respectively). The effectiveness of operation of diisobutylaluminum hydride, the chain growth regulator in isoprene polymerization, increased simultaneously.

Reasons for increasing the MMD of polymers

As a rule, polymeric products synthesized on Ziegler–Natta catalysts have a broad MMD, which is explained by several reasons. One of them is the presence of a few types of polymerization sites that differ in kinetic activity.[17,18] A method for finding the distribution function of active sites from the chain termination probability, which is based on data on the overall MMD and does not use any assumption on the type of this probability, was first proposed by Budtov et al. in their study of ethylene polymerization over titanium–magnesium catalysts. It is believed that each type of active sites produces polymer fractions whose MMD follows the law $\beta_i \exp(-\beta_i M)$ (i.e., the Flory distribution), where β, the reciprocal of M_n, characterizes the chain termination probability and is defined by $(1/m)(r_o/r_p)$ (r_p is the polymer chain propagation rate, r_o is the overall termination rate, and m is the polymer molecular mass). The final form of MMD is the superposition of distributions obtained on each polymerization site.
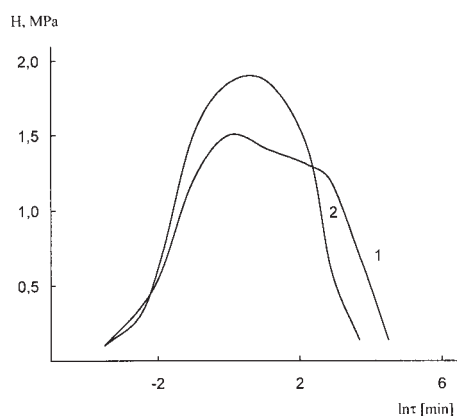

Figure 5 Pressure relaxation time spectra for ethylene–propylene–dicyclopentadiene rubber manufactured (1) by the conventional synthesis flow chart and (2) using the divergent–convergent prereactor.

The method for determining the distribution from the kinetic activity of macromolecule growth sites was developed and detailed in using, as an example, the polymerization of dienes in the presence of *cis-* and *trans-*regulating Ziegler–Natta catalyst systems. Based on experimental MMD curves of polydienes and the Tikhonov regularization procedure, kinetic activity distributions of active sites of diene polymerization were obtained for lanthanide and vanadium catalyst systems.

The broadening of MMD is determined by the presence of polymerization sites with different kinetic activities, as follows:

$$q_w(M) = \int_0^\infty \varphi(\beta) M \beta^2 \exp(-\beta M) d\beta \qquad (27)$$

where $q_w(M)$ is the experimentally determined MMD.

After passing to the new variables, $x = \ln M$ and $s = \ln \beta$, and introducing $U_\delta(x) = q_w(M)$, eq. (27) takes on the form of the Fredholm integral equation of the first kind:

$$\int_{-\infty}^\infty K(x, s)z(s)\, ds = U_\delta(x) \qquad (28)$$

where $K(x, s) = \exp[s + x - \exp(s - x)]$ is the kernel of integral eq. (28) and $z(s) = \varphi(e^s)e^{2s}$.

It is convenient to represent the solution to eq. (28) as a plot of function $\varphi(\beta)$ in the coordinates $[z(s), \ln M]$, where $z(s) = \Psi(\ln \beta) = \beta2\varphi(\beta)$.

Using eq. (28), it is possible to find a distribution function of polymerization sites over kinetic activity from the MMD curves of polymeric products. The curves obtained are polymodal, even at small monomer conversions ($\sim$ 1%). Each distribution maximum corresponds to at least one type of active sites with a certain probability of chain growth termination, thus suggesting the existence of several types of active sites involved in polymerization of dienes on Ziegler–Natta catalysts. As the monomer conversion increases, the maximum values are shifted toward higher molecular masses, accompanied by redistribution of the relative number of active sites of different types. The use of Gaussian distribution functions makes it possible to determine the number and relative contribution of active sites of each type individually from $\Psi(\ln \beta)$–ln M plots. It turned out that the position of maximum values is shifted toward higher molecular masses in the beginning of polymerization and then remains almost unchanged as if each active site synthesizes macromolecules of a certain length independently of one another.

Inspection of the kinetic activity distribution of chain propagation sites for isoprene polymerization in
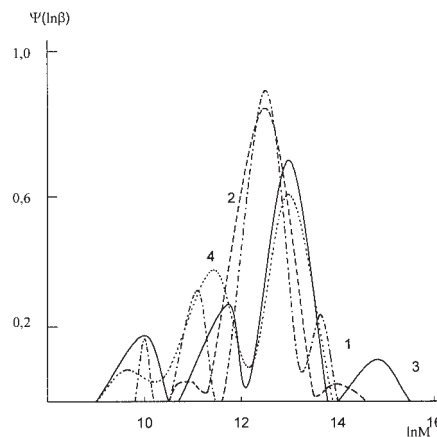

Figure 6 Activity distributions for the catalyst systems (1, 2) TiCl$_4$–(*i*-C$_4$H$_9$)$_3$Al–PiPe and (3, 4) NdCl$_3$·3IPA–(*i*-C$_4$H$_9$)$_3$Al–PiPe in isoprene polymerization in toluene: c_m = 1.5 mol/L, c_{Ti} = 7 × 10^{-3} mol/L, c_{Nd} = 2 × 10^{-3} mol/L, Ti : Al : PiPe = 1 : 1.02 : 4, Nd : Al : PiPe = 1 : 20 : 6; (1, 3) D_t ≈ 2.5 × 10^{-4} m^2/s; (2, 4) D_t ≈ 3 × 10^{-3} m^2/s.

the presence of the Ti–Al and Nd–Al catalyst systems clearly showed that, when intense turbulent mixing at the moment of generation of propagation sites and initiation is used instead of stirring in the conventional isoprene rubber manufacture technology, the disappearance of one type of active sites is observed. Disappearing in the cases of Ti–Al and Nd–Al are the sites responsible for the production of the low molecular mass polymer fraction and the fraction with a high molecular mass, respectively (Fig. 6). Given that Ti–Al and Nd–Al catalytic systems are microheterogeneous, the presence of several active sites is associated with distinction in superficial structure of the catalyst (distinction in potential energy). The different structure active sites define distinctions in rates of growth and chain termination (i.e., each active site production polymer with determined molecular weight). Apparently, the increase of turbulent mixture results in a change of structure of the surface catalyst. In this case formation of the separate active sites becomes impossible. As a consequence, the changes in the MMD curve are observed and it is possible to speak of the "disappearance" of some types active sites. Thus, a considerable increase in turbulence during the generation of polymerization sites and initiation can vary the number of types of polymerization sites or their kinetic activity, thus determining the improvement of molecular characteristics of the polymeric products formed (Table III).[13] A change in the isoprene rubber microstructure, attributed to an increase in turbulent mixing intensity during the formation of macromolecule growth sites and initiation (in particular, the increase in the proportion of *cis*-1,4 structures in the composition of macromolecules[13]), can also be associated with the change in the number of active sites with different stereospecificities.[17,18]

TABLE III
Effect of Intensity of Turbulent Mixing of Catalyst Complex Components with a Monomer Solution on the Product Characteristics in Isoprene Polymerization

Catalyst[a]	$D_i \times 10^4$ (m^2/s)	Yield (%)	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n
NdCl$_3 \cdot$ 3IPA–(i-C$_4$H$_9$)$_3$Al–PiPe	2.5	47	2.8	4.5	6.1
	30	47	2.7	7.7	3.5
	60	77	2.1	3.0	6.8
TiCl$_4$–(i-C$_4$H$_9$)$_3$Al–PiPe	2.5	46	3.5	8.3	4.2
	30	42	4.2	12.6	3.4

[a] IPA, isopropyl alcohol; PiPe, piperylene.

It is obvious that a variation in the number of types of macromolecule growth sites also explains the change in the polydispersity index of polymers obtainable by ethylene copolymerization with propylene over the V–Al system (Fig. 5) and upon polymerization of piperylene in the presence of Ti–Al.

To summarize, carrying out the fast step (generation of macromolecule growth sites and initiation) and slow step [olefin or diene (co)polymerization per se] in tubular turbulent jet reactors and continuously stirred tank reactors, respectively, allows the molecular characteristics of the polymeric products to be substantially improved, the number of types of polymerization sites to be varied, and the catalyst consumption in a real process to be lowered.

CONCLUSION

By the set of essentially new relationships and technical solutions revealed in this study, fast processes occurring with a chemical-reaction time of $\tau_{ch} \leq 0.1$–0.01 s during polymer synthesis [e.g., electrophilic (co)polymerization of α-olefins and dienes, chlorination of polydienes, generation of active sites in polymerization processes over Ziegler–Natta catalysts, etc.] can be assigned to a new independent class of chemical reactions that differ in their specific individuality, methodology of investigation, and industrial implementation technology. A close type is the independent class of combustion reactions having characteristic and original macroscopic features.

The most important results obtained in the field of fast processes for the manufacture of polymeric products are as follows: the possibility of formation of the macroscopic plug flow in turbulent streams in the reaction zone—in which these processes, being generally diffusion-controlled, occur in the kinetic region and under quasi-isothermal conditions; the influence of hydrodynamic conditions and geometric parameters of the reaction zone on the output of the process, the yield and quality of products, and their molecular characteristics; and new means of controlling fast chemical processes, in particular, by forced change (limitation) of geometric parameters (radius and length) of the reaction zone, its design, turbulence

scale, flow velocity, reactant concentrations, reactant feed mode, temperature and pressure in the systems, and by increasing the efficiency of heat and mass transfer.[1,3–8,11,15]

The reported salient features are common for fast chemical reactions. Moreover, the basic principles turned out to hold for many physical mass transfer processes as well. Among them, there are the processes of manufacture of fine homogeneous emulsions realized in the production of latex butadiene–α-methylstyrene rubber, extraction (in the manufacture of stereoregular cis-1,4-isoprene rubbers); mixing of liquid flows, especially with different densities and viscosities (in the manufacture of isobutylene polymers, ethylene–propylene rubbers, etc.); dissolution of gases in a liquid in the manufacture of chlorinated butyl rubber; and the like. Carrying out fast polymer synthesis processes in the plug-flow mode in turbulent streams allowed a new method for determining some reaction rate constants, in particular k_p and k_t, to be developed.

Restrictions in the choice of reaction-zone parameters for fast chemical processes predetermined the need for the development of a new type of industrial apparatus: the tubular turbulent jet reactor. The reaction zone phenomenon in the divergent–convergent design releases the diffusional constraints by substantially increasing the intensity of turbulent mixing and its stabilization throughout the volume. The possibility of realization of self-similar liquid flow in a divergent–convergent channel greatly extends the range of application of tubular reactors of this type in the conduction of mass transfer–limited processes, including operation of high-viscosity fluids. This also makes it possible to calculate the characteristics of turbulent mixing with simple formulas and, as a consequence, to control the occurrence of fast processes, as well as to build small-size tubular turbulent reactors of optimal design.

Carrying out fast processes at a high turbulence level in the divergent–convergent reaction zone, in comparison with stirred tank reactors, permits the quality of the products to be considerably improved simultaneously with the development of power- and resource-saving, environmentally friendly technolo-

gies. The savings of energy in new technologies on the basis of tubular turbulent apparatuses, in comparison with stirred tank reactors, are realized in the rate of decrease of residence time of reaction mix in reactor, absence of mechanical agitators, production of higher quality materials, and opportunities of creating high-level turbulent stirring, exclusively on the basis of geometry of the channel. Nonetheless, tubular turbulent reactors have some disadvantages: they work only continuously and are calculated for productivity of process below 1 m^3/h charge of the total amount of reaction mixture.

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