Journal of Engineering Physics and Thermophysics, Vol. 81, No. 6, 2008

INFLUENCE OF CHAIN-TRANSFER REACTIONS ON THE MOLECULAR-WEIGHT-DISTRIBUTION FUNCTION OF DIENE RUBBER ON A NEODYMIUM-CONTAINING CATALYST SYSTEM

G. A. Aminova, G. V. Manuiko,
V. V. Bronskaya, T. V. Ignashina,
G. S. D'yakonov, D. V. Bashkirov,
and E. V. Demidova

UDC 66.021.3.06

The numerical solution of a system of differential equations for the concentrations of the reaction system's macromolecules, which describe the synthesis of diene rubber on a neodymium-containing catalyst system, has been obtained. The influence of the chain-transfer reactions on the number distributions of the monomer links of macromolecules with an assigned number of active sites has theoretically been investigated.

A major challenge in modern chemical engineering is to update the technology of processing of information on polymer synthesis and to establish the interrelation between the properties of the polymers and the experimental data of polymerization processes.

The most important characteristics of the molecular structure of polymers, which determine their rheological and physicomechanical properties, are molecular-weight distributions by the number of monomer links and active sites. Information on the influence of the polymerization conditions and the composition of a catalyst on the molecular-weight distribution of a polymer enables one to elucidate the mechanism of the polymerization reaction and the nature of active sites and to formulate approaches to obtaining a wide set of polymers with assigned properties. Determination of the molecular-weight distribution and search for methods of controlling it are important objectives of scientific-technological investigations in the field of catalytic polymerization.

The kinetic scheme of polymerization involves the (instantaneous) initiation of active sites, growth in the chain, chain transfer to the monomer and the polymer, and spontaneous chain transfer (or chain transfer to the solvent). No deactivation of active sites (or chain scission) is assumed in the system considered.

Differential equations for the concentration of the monomer M_k and macromolecules $R_k(i, l)$ in the kth reactor of the cascade contain terms that describe the increase in the macromolecular length as a result of the growth, change in the number of active sites belonging to these macromolecules because of the chain-transfer reactions, formation of short chains in transfer and instantaneous reinitiation, and the incoming and outgoing flows [1, 2]:

$$\frac{M_{k-1} - M_k}{\tau} - k_{\mathrm{gr}k} M_k I_0 = 0 \,, \quad k = 1, 2, 3, \ldots \,, \tag{1}$$

$$\frac{R_{k-1}(i, l) - R_k(i, l)}{\tau} - i k_{\mathrm{gr}k} M_k \frac{\partial R_k(i, l)}{\partial l} + k_{\mathrm{t.p}k} l I_0 \left[R_k(i-1, l) - R_k(i, l)\right] + (k_{\mathrm{t.p}k}(M_0 - M_k)$$
$$+ k_{\mathrm{sp}k} + k_{\mathrm{t.m}k} M_k + k_{\mathrm{t.Al}k} [\mathrm{Al}]_k) \left[(i+1) R_k(i+1, l) - i R_k(i, l)\right] + \frac{I_0}{\tau} \delta_{k1} \delta_{i1} \delta(l)$$
$$+ (k_{\mathrm{sp}k} + k_{\mathrm{t.m}k} M_k + k_{\mathrm{t.Al}k} [\mathrm{Al}]_k) I_0 \delta_{i,l} \delta(l) = 0 \,, \quad 0 \le l < \infty \,, \quad i = 0, 1, 2, \ldots \,. \tag{2}$$

Kazan' State Technological University, 68 K. Marks Str., Kazan', 420015, Russia; email: a_guzel@mail.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 81, No. 6, pp. 1203–1207, November–December, 2008. Original article submitted July 24, 2007; revision submitted May 21, 2008.

1062-0125/08/8106-1247©2008 Springer Science+Business Media, Inc.

Equations (2) are written for the steady-state process of polymerization in the long-chain approximation applied to high-molecular-weight compounds.

The condition of instantaneousness of initiation together with the absence of scission of the kinetic chain means that the total number of active sites in the polymerization system is constant. The conversion of the monomer at exit from the kth reactor is equal to $x_k = 1 - M_k/M_0$; for the arbitrary temperature distribution in the cascade reactors, it may be written that

$$x_k = \frac{\varphi_k + x_{k-1}}{\varphi_k + 1}, \tag{3}$$

where $\varphi_k = k_{\mathrm{gr}k} I_0 \tau$; the growth-rate constant is dependent on the temperature in the reactor $k_{\mathrm{gr}k} = k_{0\mathrm{gr}k} \exp(-E/RT_k)$, just as the chain-transfer constants are.

The system of equations (1)–(2) describes the distribution of macromolecules by the number of active sites and monomer links at exit from the kth reactor of the cascade. We will consider the set of functions $R_{0k}(l)$, $R_{1k}(l)$, ..., $R_{i,k}(l)$, ... of one variable l instead of the functions of two variables $R_k(i, l)$. Writing Eq. (2) for each concentration $R_{i,k}(l)$, we obtain a system of ordinary differential equations

$$\frac{R_{i,k-1}(l) - R_{i,k}(l)}{\varphi_k} - i\beta(1 - x_k)\frac{dR_{i,k}(1)}{dl} + \gamma_{\mathrm{t.p}k}\frac{1}{\beta}(R_{i-1,k}(l) - R_{i,k}(l))$$

$$+ \left(\gamma_{\mathrm{t.p}k} x_k + \gamma_{\mathrm{sp}k} + \gamma_{\mathrm{t.m}k} M_0 (1 - x_k) + \frac{\gamma_{\mathrm{t.Al}k}}{\left(1 + \frac{\gamma_{\mathrm{t.Al}k}\varphi_k}{\varepsilon}\right)^k}\right)[(i+1) R_{i+1,k}(l) - iR_{i,k}(l)] + \frac{I_0}{\varphi_k}\delta_{k1}\delta_{i1}\delta(l)$$

$$+ \left(\gamma_{\mathrm{sp}k} + \gamma_{\mathrm{t.m}k} M_0 (1 - x_k) + \frac{\gamma_{\mathrm{t.Al}k}}{\left(1 + \frac{\gamma_{\mathrm{t.Al}k}\varphi_k}{\varepsilon}\right)^k}\right) I_0 \delta_{i,1}\delta(l) = 0, \quad 0 \le l < N_l, \quad i = \overline{0, N_i}, \quad k = \overline{0, N_k}, \tag{4}$$

where N_l and N_i are the maximum possible numbers of links and active sites in a macromolecule respectively, N_k is the number of reactors in the cascade, $\beta = M_0/I_0$ is the theoretical degree of polymerization, $\gamma_{\mathrm{t.p}k} = \frac{k_{\mathrm{t.p}k}}{k_{\mathrm{gr}k}}\beta$, $\gamma_{\mathrm{t.m}k} = \frac{k_{\mathrm{m.p}k}}{k_{\mathrm{gr}k}}\beta$, $\gamma_{\mathrm{t.Al}k} = \frac{\varepsilon k_{\mathrm{Al.p}k}}{k_{\mathrm{gr}k}}$, and $\gamma_{\mathrm{sp}k} = \frac{k_{\mathrm{sp}k}}{k_{\mathrm{gr}k} I_0}$ are the intensities of chain transfer to the polymer, the monomer, and the organoaluminum compound, and of spontaneous chain transfer respectively.

Also, it is necessary to specify the boundary conditions for $l = 0$. No boundary conditions are required for inactive molecules $R_{0k}(l)$, since the corresponding equations of system (4) are not differential. For short active $R_{1k}(0)$ chains which are continuously fed to the first reactor (or instantaneously occur in initiation) and are formed in reinitiation in each reactor, the boundary conditions are derived from the discrete description of the evolution of the chains. For the remaining molecules, we have $R_{i,k}(0) = 0$ for $i \ge 2$.

The molecular-weight-distribution function is determined as follows:

$$f_{\mathrm{w}}(l) \equiv l\frac{\sum_i R(i, l)}{\int_0^\infty \sum_i lR(i, l)\,dl}.$$

The numerical methods of solution of the system of differential equations are known to be approximate. We carried out a check to assure ourselves that the solutions of the system of equations (3) and (4) had been obtained

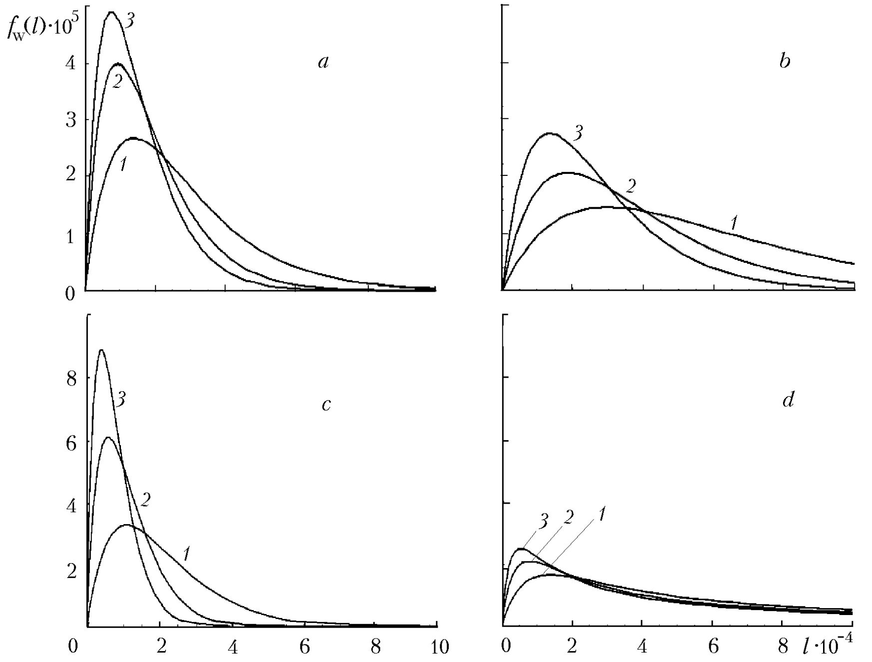

Fig. 1. Influence of the intensity of chain transfer to the organoaluminum compound (a) (1) $\gamma_{t.Al}$ = 2, 2) 4, and 3) 6) and the monomer (b) (1) $\gamma_{t.m}$ = 2, 2) 4, and 3) 6) and of spontaneous chain transfer (c) (1) γ_{sp} = 2, 2) 4, and 3) 6) and chain transfer to the polymer (d) (1) $\gamma_{t.p}$ = 6, 2) 4, and 3) 2 on the molecular-weight distribution in the absence of all the remaining chain transfers. M_0 = 1.5 mole/liter, $I_0 = 15\cdot10^{-6}$ mole/liter, and x = 0.73.

with an acceptable degree of accuracy. The check implied that the first moment of the molecular-weight distribution from the determination of μ_{1k} is equal to the concentration of the polymer formed: $\mu_{1k} = M_0 x_k$. In comparing the first moment of the molecular-weight distribution, calculated from the determination and from the model, the error was no higher than 5%. The character of the molecular-weight distribution, just as the microstructure of a polymer chain, is among the most important molecular parameters; therefore, we have made a theoretical analysis of the relationship between the conditions of the process and the molecular-weight distribution of polymerization products in rubber synthesis in a cascade of continuous reactors.

A fairly large part of theoretical investigations of the process of polymerization of butadiene is carried out under the conditions of a periodic process [3]. Industrial processes of polymerization are studied mainly on the basis of experimental observations and empirical dependences. A number of results on the average degrees of polymerization and molecular-weight distribution of a polymer has currently been obtained, but these results are incomplete. Furthermore, the influence of chain transfer has been determined only for polymerization with one active site on the polymer chain, although polymers with different numbers of active sites are frequent in the polymerization system. Therefore, to bring the technological processes closer to a commercial level it is expedient to investigate the distinctive features of the continuous process of coordinated anionic polymerization and to calculate the molecular-weight characteristics of the polymers formed in the system in question in a more general case.

Investigations of the influence of the basic chain transfers have been carried out under the conditions of an isothermal process with increase in the number of reactors. In the initial period of polymerization, we have only "living" chains whose molecular-weight distributions are described by the Poisson distribution $M_w/M_n = 1$, where M_n and M_w are the number-average and weight-average molecular weights. As the polymerization time increases, "dead" chains formed by the chain transfers to the monomer and the organoaluminum compound are accumulated and the molecular-weight distribution of the polymer is close to a Flory distribution with $M_w/M_n = 2$. In the first reactor, the chain transfer to the monomer, unlike the chain transfer to the aluminum-organic compound, influences the broadening of the molecular-weight distribution to a greater extent (Fig. 1). Furthermore, the calculations have shown that the influence

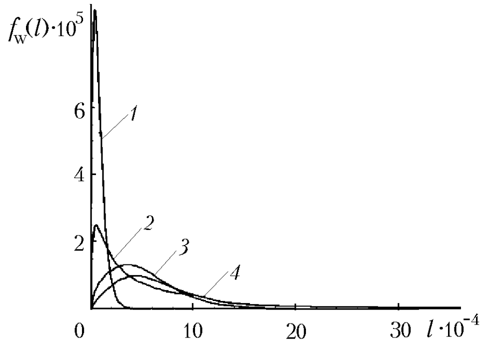

Fig. 2. Molecular-weight distributions at exit from the first reactor of the cascade (1, 3) and at exit from the fourth reactor of the cascade (2, 4) in the absence of all the remaining chain transfers: 1 and 2) $\gamma_{sp} = 6$; 3 and 4) $\gamma_{t.p} = 6$. $M_0 = 1.5$ mole/liter and $I_0 = 15\cdot 10^{-6}$ mole/liter.

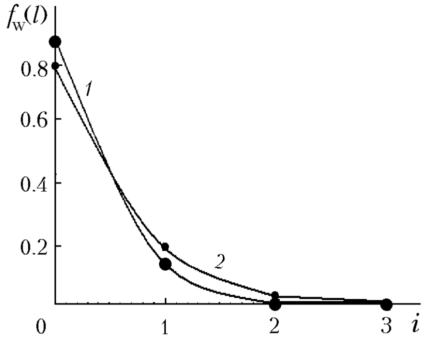

Fig. 3. Distribution of the weight fraction of macromolecules at exit from the third reactor of the cascade by the number of active sites i: 1) $\gamma_{t.p} = 0.1$ and 2) 1.4. $M_0 = 1.5$ mole/liter, $I_0 = 15\cdot 10^{-6}$ mole/liter, $\gamma_{sp} = 0.5$, $\gamma_{t.m} = 5$, and $x_3 = 0.9$.

TABLE 1. Maxima of the Molecular-Weight-Distribution Function and of the Polydispersity Coefficient as Functions of the Chain-Transfer Intensity

Parameters	$\gamma_{t.p}$			γ_{sp}			$\gamma_{t.Al}$			$\gamma_{t.m}$		
	2	4	6	2	4	6	2	4	6	2	4	6
$f_{w,max}(l)\cdot 10^5$	1.8	2.1	2.6	3.4	6.1	8.9	2.6	3.7	4.7	1.1	2.1	2.6
M_w/M_n	2.40	2.88	3.27	1.98	1.99	2.00	1.97	1.98	1.99	1.74	1.90	1.97

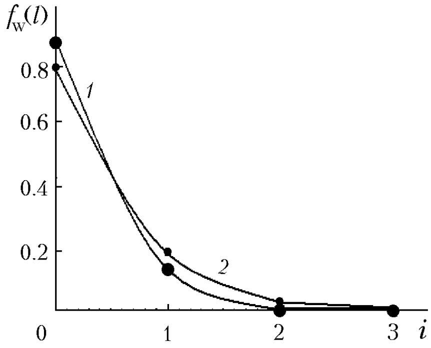

Fig. 4. Weight molecular-weight distributions of the polymers formed at exit from the third reactor of the cascade with a final conversion of the monomer of 50% (1), 75% (2), and 95% (3). $M_0 = 1.5$ mole/liter and $I_0 = 15\cdot 10^{-6}$ mole/liter.

of these transfers become comparable as the number of reactors in the cascade increases. Spontaneous chain transfer leads to a narrowing of the molecular-weight distribution (Fig. 1d); the appearance of the "tail" of the molecular-weight distribution in the high-molecular-weight region points to the formation of molecules with a more branched structure. The calculation results are given in Table 1. As the number of the reactors grows, we observe a shift of the peak of the molecular-weight distribution to the high-molecular-weight region and an increase in the polydispersity of macromolecules (Fig. 2).

The calculations show that growth in the intensity of chain transfer to the polymer increases the weight fraction of long chains. From Fig. 3, it is clear that the weight fraction of inactive macromolecules decreases with growth in $\gamma_{\mathrm{t.p}}$ and the weight fractions of macromolecules with one, two, and three active sites increase, which may be of importance for subsequent operations with the polymer. The fraction of inactive molecules increases with monomer conversion at exit from the reactor cascade, which is natural, since the influence of chain-transfer reactions becomes stronger (Fig. 4).

Information on the influence of the chain transfer on the number of the monomer links of macromolecular fractions with an assigned number of active sites present us with new possibilities for selection of the conditions of synthesis of polymers with optimum properties. Construction of the molecular-weight distribution of a polymer followed by determination of molecular-weight characteristics makes it possible to establish an intimate relationship between the mathematical model and the experimental database. Furthermore, a comparison of the calculated and experimental molecular-weight distribution functions will give additional information on the correctness of selection of the mechanism of the polymerization process and will make it possible to refine the values of kinetic constants.

Thus, we have proposed the mathematical model of the process of synthesis of SKDN rubber in the cascade of k continuous reactors and the procedure of calculation of the molecular-weight distribution function and have analyzed the influence of the basic chain-transfer reactions on the kinetics of change in the molecular-weight distribution. The results obtained are a scientific base for development of recommendations on carrying out the industrial process of synthesis of butadiene rubber on a neodymium-containing catalyst system.

This work was carried out with financial support from the Foundation of the President of the Russian Federation, grant MK 554.2006.8, the Ministry of Education and Science of the Russian Federation, grant RNP 2.1.2.15, and the Russian Foundation for Basic Research, grant 06-08-00167a.

NOTATION

$[\mathrm{Al}]_0$, initial concentration of the aluminum-organic compound (AOC); $[\mathrm{Al}]_k$, running concentration of the AOC; E, total activation energy for the kth reactor; f_{w}, molecular-weight distribution function; I_0, initial concentration of the initiator; k, cascade reactor number.; k_{gr}, $k_{\mathrm{t.Al}}$, $k_{\mathrm{t.m}}$, k_{sp}, and $k_{\mathrm{t.p}}$, rate constants of growth, chain transfer to the AOC, chain transfer to the monomer, spontaneous chain transfer, and chain transfer to the polymer; M_0, initial concentration of the monomer; M_k, running concentration of the monomer; M_{n} and M_{w}, number-average and weight-average molecular weights; $M_{\mathrm{w}}/M_{\mathrm{n}}$, polydispersity coefficient; N_l and N_i, maximum possible number of links and active sites in a macromolecule respectively; $R(i, l)$, concentration of macromolecules (i, number of active sites, l, chain length); R, universal gas constant; T, temperature in the reactor; V, reactor volume; V_{mix}, volumetric flow rate of the mixture; x_k, conversion of the monomer in the kth reactor; β, M_0/I_0, degree of polymerization of the living polymer in complete conversion; $\delta(l) = \begin{cases} \infty, & l=0 \\ 0, & l \neq 0 \end{cases}$, Dirac function; $\delta_{i,j}$, Kronecker symbol; $\varepsilon = [\mathrm{Al}]_0/I_0$, molar ratio of the concentration of the AOC to the concentration of neodymium; $\varphi_k = k_{\mathrm{gr}k} I_0 \tau$, effective parameter characterizing an ideally stirred reactor; $\gamma_{\mathrm{t.m}}$, $\gamma_{\mathrm{t.p}}$, $\gamma_{\mathrm{t.Al}}$, and γ_{sp}, intensities of chain transfer to the monomer, the polymer, and the AOC, and of spontaneous chain transfer respectively; $\tau = V/V_{\mathrm{mix}}$, average time of residence of the reaction mixture in the reactor. Subscripts: n, number; sp, spontaneous chain transfer; t.m, chain transfer to the monomer; t.p, chain transfer to the polymer; t.Al, chain transfer to aluminum; w, weight; gr, chain-growth reaction; 0, initial instant of time; mix, mixture; max, maximum.

REFERENCES

1. G. A. Aminova, G. V. Manuiko, V. V. Bronskaya, T. V. Ignashina, A. I. Ismagilova, G. I. Litvinenko, G. S. D'yakonov, and D. V. Bashkirov, Determination of the optimum conditions for synthesis of diene rubber based on a neodymium-containing catalyst system with the aim of producing a polymer with definite branching characteristics, *Inzh.-Fiz. Zh.*, **80**, No. 2, 153–160 (2007).
2. A. A. Arest-Jakubovich and G. I. Litvinenko, Chain transfer reactions in anionic polymerization of nonpolar monomers, *Prog. Polym. Sci.*, **21**, 335–398 (1996).
3. T. S. Usmanov, E. R. Maksyutova, I. K. Gataullin, et al., Inverse kinetic problem of coordinated ionic polymerization of dienes, *Vysokomol. Soed. A*, **45**, No. 2, 181–187 (2003).