Influence of main chain transmitters and cross-growth reaction on characteristics of SDRC rubber

V V Bronskaya¹, G A Aminova², G V Manuyo³, T V Ignashina¹, D V Bashkirov¹, O S Kharitonova¹ and D S Balzamov⁴

¹Department of Chemical Process Engineering, Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation
²Department of Technology of Engineering Materials, Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation
³Department of Chemical Technology of Petroleum and Gas Processing, Kazan National Research Technological University, 68 Karl Marx Street, Kazan 420015, Russian Federation
⁴Department of Power Supply of Enterprises and Energy Resource Saving Technologies, Kazan State Power Engineering University, 51 Krasnoselskaya Street, Kazan 420066, Russian Federation

E-mail: olga.220499@mail.ru

Abstract. The study and modeling of the SDRC rubber synthesis process under the conditions of chain transmission and cross reactions are carried out. The influence of the main chain transmitters and the cross reaction on the characteristics of the resulting product is studied.

The analysis of literary sources showed that simultaneous cross-growth reaction of polymeric chains and chain transfer reaction to polymer is possible during the polymerization of butadiene with cobalt catalytic systems [1-4]. This suggests the existence of a mechanism of the polymerization process, which includes both the chain transfer reaction to polymer and the cross-growth reaction of macromolecules [5-10].

The most difficult is to construct and identify a mathematical model of the polymerization process, when neither the mechanism nor the constants of elementary reactions are known, but the use of mathematical methods has made it possible to speed up the solution [11-16]. In this situation the evaluation criterion is statistical because the most correct supposed mechanisms will be the one that provides minimum dispersion.

Experimental data for identification of the process mechanism are taken from a literature source, where the concept of a fractional factorial experiment of two levels was used for the study of solution polymerization of butadiene in a batch reactor using cobalt octanoate/diethylaluminy chloride/water catalyst.

According to the kinetic scheme, the system of equations, describing the change with time of concentrations of monomer and growing chains, has the form for the periodic process:

\[ \frac{dM}{dt} = -k_p MR \]  

(1)
\[
\frac{\partial R(i, \ell)}{\partial \tau} = -i k_p M \frac{\partial R(i, \ell)}{\partial \tau} + (k_{sp} + k_m M \left[i(i+1)R(i+1, \ell) - iR(i, \ell)\right] + \\
+ \frac{k_c}{2} \sum_{j=0}^{\infty} \left[j(\ell-n) + n(i-j)\right]R(j, n)R(i-j, \ell-n)dn - \\
- k_s R(i, \ell) \sum_{j=0}^{\infty} (i + j) R(j, n)dn + k_{sp} \left[R(i-1, \ell) - R(i, \ell)\right] \sum_{j=0}^{\infty} \int_{0}^{\infty} R(j, n)dn + \\
+ k_{sp} \left[(i+1)R(i+1, \ell) - iR(i, \ell)\right] \sum_{j=0}^{\infty} \int_{0}^{\infty} nR(j, n)dn + (k_{sp} + k_m M) I_0 \delta_{i,1} \delta(\ell), \\
i = 0,1,2,..., \quad (0 \leq \ell < \infty)
\]

at \(t=0\): \(M=M_0\), \(R(1,0)=I_0\), \(R(0,0)=0\), at \(i=0\) \(R(i-1, \ell)=0\).

The following assumptions were made: active centres of the same type are formed at optimal water concentration; the total concentration of active centres is constant and equal to the initiator concentration; at optimal water concentration process is considered to be “continuous” (no deactivation).

Initiation and reinitiation reactions are supposed to occur instantaneously. Since \(k_m/k_p\) and \(k_{sp}/k_p\) are always less than one, the monomer flow rate for chain transfer and reinitiation reactions in equation (1) is neglected. In equation (2), the first component on the right side describes the change of \(R(i, \ell)\) as a result of growth, the next five components are the change of \(R(i, \ell)\) as a result of chain transfer reaction and cross-growth reactions of macromolecules and the last component describes the formation of new short growing chains of macromolecules during reinitiation. The equation (2) is written in the approximation of long chains.

Since there is no deactivation in the system that means \(k_\delta=0\), then \(R = I_0\) is the number of active centers in the system and \(M\) is constant throughout the entire process.

The system of equations (2) with the help of the function \(f = \sum_{i=0}^{\infty} \int_{0}^{\infty} e^{-p\ell} R(i, \ell) d\ell\) can be reduced to one equation

\[
\frac{\partial f}{\partial \tau} = -\beta p f + \left(\gamma_{sp} + \gamma_m \right)(s-1)f - \gamma_s s f - \gamma_{sp} \left(1 - \frac{1}{1-x}\right) f \\
- \gamma_{sp} \left(1 + \frac{1}{\beta}\right) f + \gamma_{sp} \left(1 - \frac{1}{\beta}\right) f
\]

where \(\beta = \frac{M_0}{I_0}\) is the theoretical degree of polymerization, parameters \(\gamma_m = \frac{k_m M_0}{k_p I_0}\), \(\gamma_{sp} = \frac{k_{sp} M_0}{k_p I_0}\), \(\gamma_{c} = \frac{k_c M_0}{k_p I_0}\) characterize the intensity of transfer of the chain to the monomer and polymer, spontaneous transfer rate and cross growth rate of macromolecules, respectively.

Differentiating equation (3) the corresponding number of times by \(s\) and \(p\), the ratios for calculating the statistical moments of the distribution of macromolecules by the polymerization degree \(\ell\) and the number of active centres \(i\) are obtained.
The designations are entered: \( J_y = \left. \frac{\partial^{\nu+1} f}{\partial s^\nu \partial p} \right|_{p=0} \), by definition of moments of molecular-weight distribution (MWD) \( J_{00} = f \left|_{p=0} \right. = \mu_0 \) is the total concentration (number) of polymeric chains at time \( t; \) \( J_{10} = \left. \frac{\partial f}{\partial x} \right|_{p=0} = I_0 \) is the total concentration (number) of active centres at time \( t; \)
\( J_{01} = \left. \frac{\partial f}{\partial p} \right|_{p=0} = -\mu_1 = -M_u x \) is the concentration of polymer formed at time \( t \) (with the opposite sign);
\( J_{02} = \left. \frac{\partial^2 f}{\partial p^2} \right|_{p=0} = \mu_2, \) \( J_{03} = \left. \frac{\partial^3 f}{\partial p^3} \right|_{p=0} = -\mu_3 \) are the second and third order moments.

The system of equations for calculating the moments of the MWD is as follows
\[
\frac{dJ_{00}}{dx} = \left( \frac{\gamma_{0p}}{1-x} + \gamma_{0m} \right) I_0 - \frac{\gamma_c M_u x}{1-x} I_0
\]
\[
\frac{dJ_{02}}{dx} = -2 \beta J_{11} - \frac{2 \gamma_c}{(1-x)} J_{11} J_{02}
\]
\[
\frac{dJ_{03}}{dx} = -3 \beta J_{12} - \frac{3 \gamma_c}{(1-x)} J_{02} J_{12} - \frac{3 \gamma_c}{(1-x)} J_{11} J_{03}
\]
\[
\frac{dJ_{12}}{dx} = -2 \beta (J_{11} - J_{21}) - \left( \frac{\gamma_{0p}}{1-x} + \gamma_{0m} \right) J_{12} - \frac{\gamma_c}{(1-x)} \left( J_{12} J_{11} + 2 J_{11} J_{02} - \frac{\gamma_{0p}}{\beta} J_{02} - x J_{12} \right)
\]
\[
\frac{dJ_{11}}{dx} = -\beta J_{01} - \beta J_{20} - \left( \frac{\gamma_{0p}}{1-x} + \gamma_{0m} \right) J_{11} - \frac{\gamma_c}{(1-x)} \left( J_{11} J_{20} + J_{02} + I_0 J_{02} - \frac{\gamma_{0p}}{\beta} J_{02} + x J_{11} \right)
\]
\[
\frac{dJ_{20}}{dx} = -2 \left( \frac{\gamma_{0p}}{1-x} + \gamma_{0m} \right) J_{20} - \frac{2 \gamma_c}{(1-x)} \left[ I_0 J_{11} + J_{20} J_{11} \right] - \frac{2 \gamma_{0p}}{1-x} \left[ \frac{1}{\beta} J_{11} - x J_{20} \right]
\]
\[
\frac{dJ_{30}}{dx} = -3 \left( \frac{\gamma_{0p}}{1-x} + \gamma_{0m} \right) J_{30} - \frac{3 \gamma_c}{(1-x)} \left( 2 J_{20} J_{11} + I_0 J_{21} + J_{30} J_{11} + J_{20} J_{21} \right) - \frac{\gamma_{0p}}{1-x} \left( \frac{J_{21}}{\beta} - x J_{30} \right)
\]
\[
\frac{dJ_{21}}{dx} = -\beta J_{30} - 2 \beta J_{20} - \frac{2 \gamma_{0p}}{1-x} \left( \frac{\gamma_{0p}}{1-x} + \gamma_{0m} \right) J_{21} - \frac{\gamma_c}{(1-x)} \left( 2 J_{20} J_{02} + 2 J_{11} J_{12} + J_{30} J_{02} + 2 J_{20} J_{12} + 3 J_{21} J_{11} \right) - \frac{2 \gamma_{0p}}{1-x} \left( \frac{J_{12}}{\beta} - x J_{21} \right)
\]
Initial conditions at \( x=0 \) are \( \mu_0 = I_0 \), \( \mu_1 = \mu_2 = \mu_3 = J_{11} = J_{12} = J_{20} = J_{21} = J_{20} = 0 \),

\[
\bar{P}_n = \mu_1 / \mu_0 , \quad \bar{P}_m = \mu_2 / \mu_1 , \quad \bar{P}_z = \mu_3 / \mu_2 .
\]

The influence of different chain transfer reactions and the cross-growth reaction of macromolecules on molecular-weight characteristics of the polymer is compared.

Unlike monomer transmission, spontaneous transfer leads to a decrease in the average polymerization degree in monomer conversions which are close to 1. At low intensities the average mass degree of polymerization monotonously increases with the conversion, but at higher intensities it decreases after reaching some maximum value. Polydispersity coefficient can be more 2 at high conversions.

Decreasing medium degrees of polymerization at high conversions is the most significant difference between spontaneous the chain transfer and to the monomer. In addition, since the ratio of the rate of growth and the rate of transmission to monomer does not change with conversion, the average polymerization degrees does not depend on the monomer concentration under the transfer to monomer, while this dependence is under the spontaneous transfer.

The influence of chain transfer reactions on polymer and cross growth was not separately researched, because these reactions have already led to gel formation with insignificant monomer conversions. Therefore, the influence of these reactions and spontaneous chain transfer reactions on the polymerization process was considered.

**Figure 1.** Change of average polymerization degree with monomer conversion at different intensity of spontaneous chain transfer.

**Figure 2.** Change of the medium-weight degree of polymerization with monomer conversion at different intensity of spontaneous chain transfer.

**Figure 3.** Change of the medium-weight degree with the conversion when transferring the chain to the polymer (\( \gamma_{tp} = 0; 0.5; 1; 2; 5 \)) and during the spontaneous transfer (\( \gamma_{sp}=1 \)).

**Figure 4.** Change of polydispersity coefficient during chain transfer to polymer (\( \gamma_{tp} = 0; 0.5; 1; 2 \)) and spontaneous transfer (\( \gamma_{sp}=1 \)).
Transfer to polymer does not affect the average polymerization degree, since the number of chains does not change in this reaction. However, transmission to polymer leads to the formation of a branched polymer, thus expanding the MWD. The main molecular-weight characteristics are given in figures 3, 4. The results of the numerical experiment showed that the transfer to polymer causes an additional increase in the polydispersion coefficient \( \overline{P_n}/\overline{P_w} \), but it is significant only at \( \gamma_p \gg 1 \). In any case, the contribution of transmission to polymer to increasing polydispersion is much less than the contribution of spontaneous transfer. This is because the main effect that causes the expansion of the MWD is a sharp decrease \( \overline{P}_n \) under the spontaneous transfer, while the transfer to the polymer does not change \( \overline{P}_n \).

\[\gamma_p = 5, \ldots \text{ - without taking into account the cross-growth reaction of macromolecules } \gamma_r = 1 \text{; } \overline{P}_n/\beta\text{,}\]
\[\overline{P}_w/\beta\text{,}\]
\[\gamma_p = 1, \gamma_w = 5 \text{.}\]

Figures 5 and 6 show that, unlike the chain transmission to the polymer, the cross-growth reaction of macromolecules increases the average polymerization degree and has a greater effect on the average mass and medium sedimetrical degree of polymerization than on the average one. The difference between chain transfer reactions to polymer and cross-growth reaction is especially noticeable in high monomer conversion, so the greatest effect on process has the cross-growth reaction with regard to gel formation in the reactor.

Calculations on the proposed mathematical model showed that at monomer conversion values, that is more than 0.8, spontaneous transmission of the chain leads to a more significant decrease in the average polymerization degree than the transfer of the chain to the monomer. At the same time the average mass polymerization degree decreases less intensively, so the polydispersion coefficient reaches values 3-4.

Calculations show that, unlike the chain transfer reaction to polymer, the cross-growth reaction of macromolecules increases all medium polymerization degrees \( \overline{P}_n, \overline{P}_w, \overline{P}_z \) and the influence on the average mass degree of polymerization is stronger than on average polymerization degree. The difference between cross-growth and chain transfer reactions to polymer is particularly noticeable with monomer conversion that is more than 0.4. Therefore, the process of gel formation in the reactor is more influenced by the cross-growth reaction of macromolecules.

References
[1] Arest-Jakubovich A A and Litvinenko G 1996 Chain transfer reactions in anionic polymerization
of nonpolar monomers Prog. Polym. Sci. 21 335

[2] Roovers J 1985 Encyclopedia of Polymer Science and Engineering New York: Wiley&Sons 2 210

[3] Litvinenko G I and Arest-Yakubovich A A 1992 Proc. European Polymer Federation Workshop on Anionic Polymerization 71

[4] Halasa F and Hsu W L 2002 Polymer 43 7111-8

[5] Aminova G A, Manuiko G V, Bronskaya V V, Ignashina T V, Litvinenko G I, D’yakonov G S, Bashkirov D V and Demidova E V 2008 Effect of the operating conditions of synthesizing diene rubber with a neodymium-based catalytic system on its branching characteristics Theoretical Foundations of Chemical Engineering 42 60-6

[6] Aminova G A, Manuiko G V, Litvinenko G I, D’yakonov G S, Zolotarev V L, Filipova A G, Ignashina T V, Davydova V V and Antonova O V 2002 Mechanism of butadiene polymerization on cobalt-containing catalyst A Russian Journal of Applied Chemistry 75 1146-50

[7] Aminova G A, Bronshtein M D, Manuiko G V, Ignashina T V, Davydova V V, Antonova O V, D’yakonov G S, Reshetova I G and Kharitonova N E 2002 Method of solution of a system of equations describing the continuous process of polymerization under conditions of a polyaddition reaction Inzhenerno-Fizicheski Zhurnal 75 165-9

[8] Aminova G A, Manuiko G V, Bronskaya V V, Ignashina T V, D’yakonov G S, Bashkirov D and Demidova É V 2008 Influence of chain-transfer reactions on the molecular-weight-distribution function of diene rubber on a neodimium-containing catalyst system Journal of Engineering Physics and Thermophysics 81 1247-51

[9] Tapia J J B, Lopez J A T, Herrera R and Guerrero L R 2020 J. Appl. Polym. Sci. 116 3103-10

[10] McIntosh W C, Hamann E, Oertel R and Bartke M 2007 Macromol. Symp. 259 102-9

[11] Iovu M C, Buzdugan E, Teodorescu M, Britchi A G, Hubca G and Iovu H 1999 Die Angewandte Makromolekulare Chemie 271 18-23

[12] Chang C C, Halasa A F, Miller J W and Hsu W L 1994 Polymer International 33 151-9

[13] Lopez J A T, Tapia J J B and Diaz M C C 2009 Macromol. React. Eng. 3 473–85

[14] Lopez J A T, Tapia J J B, Hernandez N E C and Diaz M C C 2011 J. Polym Res. 18 927–38

[15] Tanaka Y, Sato H, Ogawa M, Hatada K and Yoshio T 1974 Polym. Lett. Ed. 12 369-73

[16] Iovu H, Hubca G, Racoti D and Hurst J S 1999 Modelling of the butadiene and isoprene polymerization processes with a binary neodimium-based catalyst European Polymer Journal 35 335

[17] Pros A, Marquardt P, Reichert K-H et al 1993 Modelling the polymerization of 1,3-butadiene in solution with a neodimium catalyst Die Angewandte makromolekuleare Chemie 211 89