International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.2, pp 1031-1036, 2017

Numerical study of copolymer composition and compositional heterogeneity during the synthesis of butadiene-styrene rubber

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Abstract : In the paper the algorithm of modeling of continuous free-radical butadiene-styrene emulsion-type copolymerization process based on the Monte-Carlo method is offered. The analyzed process proceeds in the battery of consistently connected polymerizers (continuous stirred tank reactors) so simulation is carried out taking into account the residence time distribution of particles in the system. The constructed model allows to research molecular-weight and viscous characteristics of the formed copolymer, to predict the weight content of butadiene and styrene in copolymer, to carry out calculation of molecular-weight distribution of the received product and predict copolymer's microheterogeneity at any moment of conducting process.
Keywords: copolymerization, butadiene, styrene, Monte-Carlo method, residence-time distribution, molecular weight distribution, microheterogeneity.

Introduction

Synthetic rubbers constitute extensive group of petrochemical products and are polymers that can be processed into the rubber during vulcanization. Styrene-butadiene synthetic rubbers are one of the most widespread large-capacity synthetic rubbers of general purpose. Process of the low-temperature emulsion-type styrene-butadiene copolymerization is the basis of the industrial production. Studying of this process becomes possible at creation of mathematical model. In turn, simulation will allow to predict properties and modify quality indicators of the received product that is an actual task today.

Experimental

Previously write out the kinetic scheme of styrene-butadiene copolymerization process. Let us assume that reactivity of the active center of the growing chain is determined by the nature of the end unit. Then the kinetic scheme of the process includes the following stages:

initiator decay

$$I \xrightarrow{k_d} 2R,$$

initiation of active centers

$$R + M^{\beta} \xrightarrow{k_{i\beta}} P^{\beta}_{A(\beta),B(\beta)},$$

chain propagation

$$P^{\alpha}_{n,m} + M^{\beta} \xrightarrow{k_{p\alpha\beta}} P^{\beta}_{n+A(\beta),m+B(\beta)},$$

chain transfer

$$P^{\alpha}_{n,m} + S \xrightarrow{k_{reg\alpha}} Q_{n,m} + R,$$

chain termination by disproportionation

$$P^{\alpha}_{n,m} + P^{\beta}_{r,q} \xrightarrow{k_{r\alpha\beta}} Q_{n+r,m+q},$$

chain termination by recombination

$$P^{\alpha}_{n,m} + P^{\beta}_{r,q} \xrightarrow{k_{d\alpha\beta}} Q_{n,m} + Q_{r,q},$$

Here $\alpha, \beta = \overline{1,2}$; M^1 and M^2 are the monomers of the first and second type; $P^{\alpha}_{n,m}$ and $Q_{n,m}$ are the active and inactive polymer chains with length $m+n$, comprising m units of the M^1 monomer and n units of the M^2 monomer; k_i, k_p, k_{reg}, k_d, k_r are the reaction rate constants of initiation, chain propagation, transfer, disproportionation and recombination elementary stages, respectively; $A(\beta) = \{1, \text{ if } \beta = 1; \text{ else } 0\}$; $B(\beta) = \{1, \text{ if } \beta = 2; \text{ else } 0\}$[1].

Earlier, in the paper[2] was considered algorithm of simulation batch process of styrene-butadiene copolymerization, based on the Monte Carlo method. But styrene-butadiene rubber is continuously produced in the several reactors, combined in the cascade.

At the modeling of periodic polymerization process all particles of system throughout the simulation time are in the same reactor. In this case, each reaction is characterized by time of modeling, which calculates according to the formula[3]:

$$\Delta t = \frac{1}{R_{sum}} \ln\left(\frac{1}{r_p}\right), \qquad (1)$$

Here R_{sum} – the sum of the rates of possible elementary reactions of the kinetic scheme of copolymerization process, r_p – random number generated in the interval [0,1]. But in the case of the continuous process worth talking about some average residence time as a random variable, which is characterized by a probability distribution function[4].

According to the issues[5,6], residence time distribution is derived from the material balance equation for the cascade of reactors with the constant volume Then the probability that a particle spends time from t to $t + dt$ in the current reactor is $p(t)dt$, but since considered polymerizers are continuous stirred tank reactors, for them value $p(t)$ calculated by the formula:

$$p(t) = \left(\frac{n}{\tau}\right)^n \frac{t^{n-1}}{(n-1)!} e^{-\frac{nt}{\tau}}, \qquad (2)$$

here n – count of reactors in the system, τ – average residence time of the reaction mixture in a single reactor (h).

Thus, for modeling a continuous polymerization process, which takes place in the cascade of continuous stirred tank reactors, each particle of the system (molecule or macromolecule) must be characterized by the residence time in the reactor, which is determined using the distribution (2). It is necessary to choose the subinterval *dt*, to the sum of the probabilities for each variant of the residence time for the time interval from *0* to t_{max} was equal to one.

After that necessary to generate random number $r_p \in [0,1]$ and choose the value of the serial number f, to the inequality:

$$\sum_{i=1}^{f-1} p((f-1)\cdot dt) < r_p < \sum_{i=1}^{f} p(f\cdot dt). \qquad (3)$$

Consequently, as a result of the simulation to the selected particle corresponds the residence time $f \cdot dt$. Then the process for which corresponds average residence time of the reaction mixture 1.125 hours, such time interval is the interval from 0 to 5 hours in 0.1 hours.

The detailed simulation algorithm is described in the paper[7]. The developed model makes it possible to study the characteristics and composition of styrene-butadiene copolymer. The information on the state of the resulting product may be obtained as the output from each reactor and in achieving the required conversion values.

Results and Discussion

On the basis of the developed model the software package was created in the integrated development programming environment Visual Studio in the C# and Visual C++ languages. It allow to carry out computing experiments of simulation of styrene-butadiene copolymerization process in the cascade of continuous stirred tank reactor. The software package makes it possible to solve the direct problem of determining the molecular weight and viscosity characteristics of the resulting product and investigate compositional heterogeneity of formed copolymer.

During the computational experiment was investigated styrene-butadiene copolymerization process with the following parameters of the process and the production's recipe of portion of the reaction mixture[8]:

- the load on the cascade by monomers: 3.5 t/h (butadiene – 70 w.p., styrene – 30 w.p.);
- dosage of initiator (pinane hydroperoxide): 0.054 w.p.;
- dosage of chain-transfer agent (tertiary dodecyl mercaptan): 0.125 w.p. – 1st point (1 polymerizer), 0.027 w.p. – 2nd and 3rd point (3 and 6 polymerizers);
- ratio water / monomers = 204.7 / 100;
- working volume of polymerizer V = 10.8 m^3;
- count of polymerizers: 11;
- volumetric flow rate C_f = 9.5982 m^3/h.
- residence time of the reaction mixture in polymerizer $\theta = V / C_f$ = 1.125 h.

Figure 1-2 shows the behavior of conversion's curve and dependence of the intrinsic viscosity on reactor's serial number and conversion of monomers. The results were obtained on the basis of the simulation 15 and 30 hours of the process (dotted and solid lines) and are consistent with the experimental data (points).

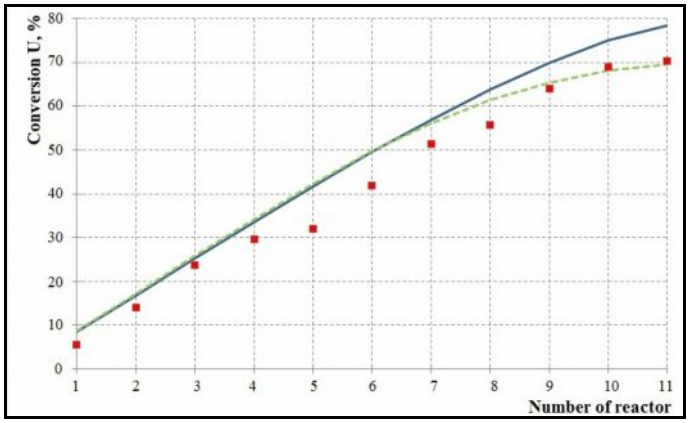

Figure 1: The dependence of the calculated (lines) and experimental (points) conversion's values from reactor's number in the cascade

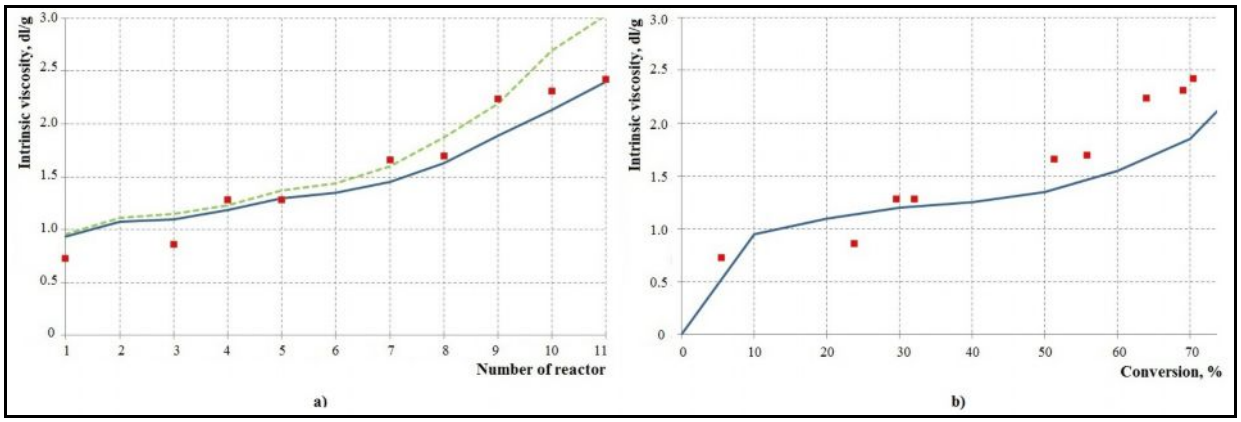

Figure 2: The dependence of the calculated (lines) and experimental (points) intrinsic viscosity's values from reactor's number in the cascade (a) and conversion of monomers (b)

The behavior of the curve of intrinsic viscosity is associated with the consumption of chain transfer agent. The nature of changes of the molecular weight of formed styrene-butadiene copolymer displays the dependence the polydispersity index from polymerizer's serial number in the cascade (Fig. 3). Following the results of modeling of 30 hours of conducting process the value of polydispersity index changes from 2 units in the first reactor to 4.2 units in the last reactor of the cascade that corresponds to standard measures of styrene-butadiene rubber. The point of inflection of the curve characterizing dependence of polydispersity index from serial number of reactor are associate with the fractional addition of the chain transfer agent.

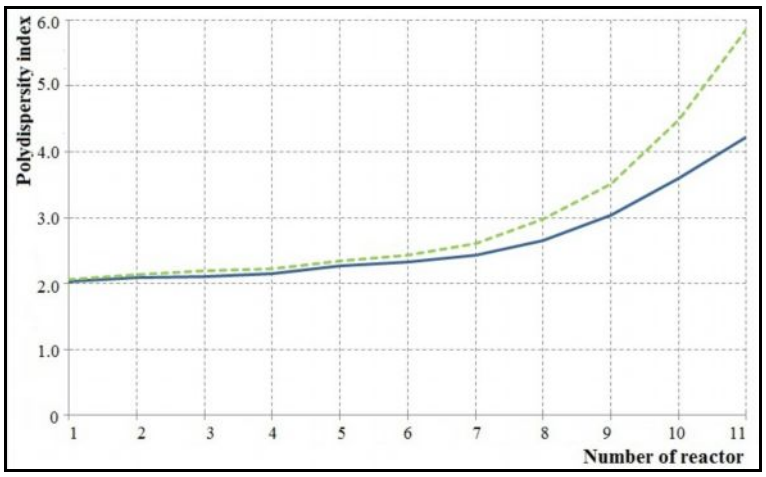

Figure 3: Changing polydispersity index of the formed copolymer depending on the number of reactor

There are the following changing the weight composition of the formed styrene-butadiene copolymer: butadiene content varies from 80% in the first reactor to 72% to the last reactor of the cascade, styrene - from 20% to 28%, respectively.

Fig. 4 displays a differential curve of the molecular weight distribution (MWD), which shows the ratio of macromolecules of different molecular weights in a sample of the copolymer. MWD of styrene-butadiene copolymer with an increase of volume of the reaction mixture reproduces the behavior of the Schulz-Flory model distribution, that takes into account chain termination a result of the interaction with chain transfer agent.

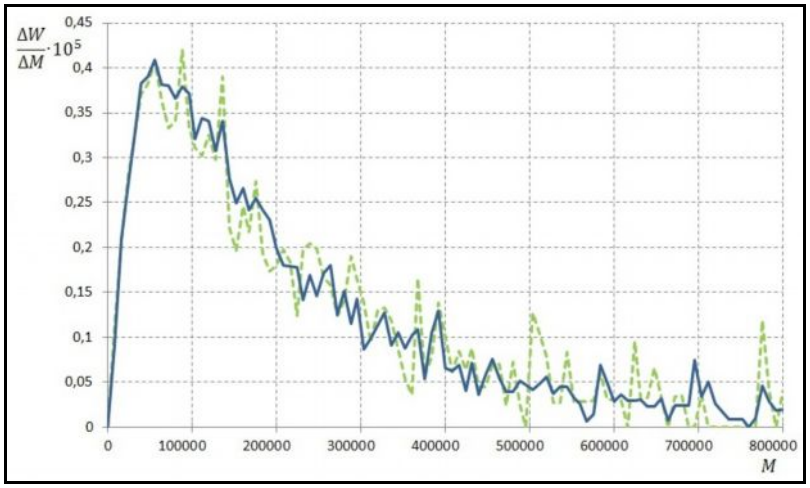

Figure 4: Differential curve of the molecular weight distribution of the styrene-butadiene copolymer

Study the change of the characteristics of styrene-butadiene copolymer with different control flow modes, corresponding process parameters and production's recipe: chain transfer agent in three points (1, 3 and 6 polymerizers) and two points (1 and 6 polymerizers) cascade. Three-point chain transfer agent reduces weight average molecular weight of the formed product with MWD characterized by increasing the part of low molecular weight fractions and a slight decrease in the part of high molecular weight fractions.

Flow chain transfer agent additionally in the third polymerizer of the cascade promotes an insignificant change of microheterogeneity index in contrast to the two-point chain transfer agent flow (Fig. 5). In addition, in comparison with two-point feeding an increase in the part of butadiene diad in the formed copolymer and thus decrease the part of styrene dyads. Significant change part od dyads in the last reactor of the cascade is associated with a full consumption of the chain transfer agent.

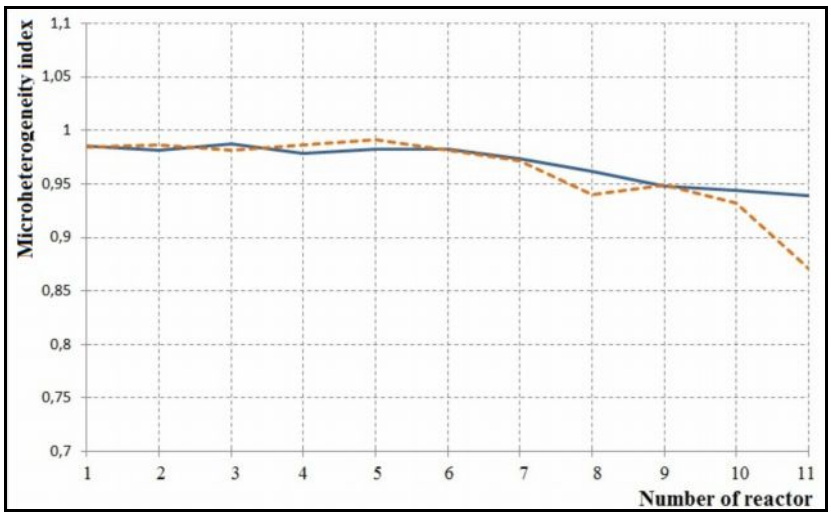

Figure 5: Changing microheterogeneity index of the formed copolymer depending on the number of reactor: the dotted line – two-point mode, the solid line – three-point mode of chain transfer agent flow

Conclusions

Thus, the proposed simulation algorithm based on Monte Carlo method, adequately describes the continuous process of styrene-butadiene copolymerization, which takes place in the cascade of continuous stirred tank reactors. Obtained information as a result of simulation provides an opportunity to explore molecular weight and viscosity characteristics, as well as compositional heterogeneity of the formed copolymerization product in the dynamics at continuous loading of reaction mixture.

Acknowledgements

Research work was supported by the grant of Russian Foundation for Basic Research №16-31-00162_mol_a «Development of mathematical methods for studying the structure and properties of free-radical copolymerization products in order to increase the efficiency of innovation production» and by the project №2629 «Development of the theory and methods of mathematical modeling of processes in the conditions of partial uncertainty of the original physical-chemical and technological information» implemented as a part of the base portion of the state task of Ministry of Education and Science of the Russian Federation.

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