Features of Macromolecule Formation by RAFT-Polymerization of Styrene in the Presence of Trithiocarbonates

Abstract: The kinetic modelling of styrene with controlled radical polymerization, initiated by 2,2'-azobis(isobutirnitrile) and proceeded by a reversible chain transfer mechanism was carried out and accompanied by «addition-fragmentation» in the presence of dibenzyltritiocarbonate. An inverse problem of determining of the unknown temperature dependences of single elementary reaction rate constants of the kinetic scheme was solved. The adequacy of the model was revealed by comparing the theoretical and experimental values of polystyrene’s molecular-mass properties. The influence of the process controlling factors on polystyrene’s molecular-mass properties was studied.

Keywords: Controlled radical polymerization · Dibenzyltritiocarbonate · Mathematical modelling · Polystyrene · Reversible addition-fragmentation chain transfer

Introduction
Controlled radical polymerization is one of the most developed synthesis methods of narrowly dispersed polymers nowadays [1-3]. Most considerations were given to research on controlled radical polymerization, proceeded by a reversible chain transfer mechanism and accompanied by «addition-fragmentation» (RAFT – reversible addition-fragmentation chain transfer) [3]. It should be noted that for classical RAFT-polymerization (proceeding in the presence of sulphur-containing compounds, which formula is Z –C(=S)–S–R’, where Z – stabilizing group, R’ – outgoing group), valuable progress was obtained in the field of synthesis of new controlling agents (RAFT-agents), as well as in the field of research on kinetics and mathematical modelling; and for RAFT-polymerization in symmetrical RAFT-agents’ the presence, particularly, of tritiocarbonates of formula R’–S–C(=S)–S–R’, it came to naught in practice: kinetics was studied in an extremely general form [4] and mathematical modelling of the process hasn’t been carried out at all. Thus, the aim of this research is the kinetic modelling of polystyrene with controlled radical polymerization initiated by 2,2'-azobis(isobutirnitrile) (AIBN), proceeded by reversible chain transfer mechanism and accompanied by “addition-fragmentation” in the presence of dibenzyltritiocarbonate (DBTC), and also the influence of the controlling factors (temperature, initial concentrations of monomer, AIBN and DBTC) on molecular-mass properties of the polymer.

Experimental Part
Prior to using the styrene (Aldrich, 99%), it was purified of aldehydes and inhibitors at triple cleaning in a separatory funnel with a 10%-th (mass) solution of NaOH (styrene to solution ratio is 1:1), then it was scoured with distilled water to neutralize the reaction and after that it was dehumidified over CaCl₂ and rectified in a vacuum.

AIBN (Aldrich, 99%) was purified of methanol by re-crystallization.

DBTC was obtained by the method presented in the research [4]. Masses of initial substances were the same as in [4]. Emission of DBTC was 81%. NMR $^{13}$C (CCl₃D) δ, ppm: 41.37, 127.60, 128.52, 129.08, 134.75, 222.35.

Examples of polymerization were obtained by dissolution of estimated quantities of AIBN and DBTC in a monomer. Solutions were filled in tubes, 100 mm long, with an internal diameter of 3 mm, and then degassed by “freezing-defrosting” to a residual pressure of 0.01 mmHg column, the tubes were then unsoldered. Polymerization was carried out at 60°C.

Research of the polymerization’s kinetics was made with the application of the calorimetric method on a Calvet type differential automatic microcalorimeter DAK-1-1 in the mode of immediate record of heat emission rate under isothermal conditions at 60°C. Kinetic parameters of the polymerization were calculated based on the calorimetric data as
The value of polymerization enthalpy $\Delta H = -73.8 \text{ kJ}\cdot\text{mol}^{-1}$ [5] was applied in processing the data in the calculations.

Molecular-mass properties of the polymeric samples were determined by gel-penetrating chromatography in tetrahydrofuran at 35°C on chromatograph GPCV 2000 «Waters». Dissection was performed on two successive banisters PLgel MIXED-C 300×7.5 mm, filled with stir gel with 5 $\mu$m vesicles. Elution rate – 0.1 mL·min$^{-1}$. Chromatograms were processed in the program «Empower Pro» with use of calibration by polystyrene standards.

**Mathematical Modelling of the Polymerization Process**

The kinetic scheme, introduced for the description of the styrene controlled radical polymerization process in the presence of trithiocarbonates, includes the following phases.

1. **Real initiation**

   \[ I \xrightarrow{k_1} 2R(0) \, . \]

2. **Thermal initiation [6].** It should be noted that polymer participation in thermal initiation reactions must reduce the influence thereof on molecular-mass distribution (MMD). However, since the final mechanism of these reactions has not been ascertained in recording of differential balance equations for polymeric products so far, we will ignore this fact.

   \[ 3M \xrightarrow{k_{i1}} 2R(1) \, , \]

   \[ 2M+P \xrightarrow{k_{i2}} R(1)+R(i) \, , \]

   \[ 2P \xrightarrow{k_{i3}} 2R(i) \, . \]

   In these three reactions the summary concentration of the polymer is recorded as $P$.

3. **Chain growth**

   \[ R(0)+M \xrightarrow{k_p} R(1) \, , \]

   \[ R^++M \xrightarrow{k_p} R(1) \, , \]

   \[ R(i)+M \xrightarrow{k_p} R(i+1) \, . \]

4. **Chain transfer to monomer**

   \[ R(i)+M \xrightarrow{k_{tr}} P(i, 0, 0, 0) + R(1) \, . \]

5. **Reversible chain transfer [4].** As a broadly used assumption lately, we shall assume that intermediates fragmentation rate constant doesn’t depend on leaving of the radical’s length [7].

   \[ R(i)+RAFT(0, 0) \xleftarrow{k_{f1}} \text{Int}(i, 0, 0) \xrightarrow{k_{f2}} RAFT(i, 0)+R' \quad (I) \]

   \[ R(j)+RAFT(i, 0) \xleftarrow{k_{f2}} \text{Int}(i, j, 0) \xrightarrow{k_{f1}} RAFT(i, j)+R' \quad (II) \]

   \[ R(k)+RAFT(i, j) \xleftarrow{k_{f2}} \text{Int}(i, j, k) \xrightarrow{k_{f1}} RAFT(i, j, k) \quad (III) \]

6. **Chain termination [4].** For styrene’s RAFT-polymerization in the presence of trithiocarbonates, besides the reactions of radical quadratic termination

   \[ R(0)+R(0) \xrightarrow{k_{i1}} R(0)-R(0) \, , \]

   \[ R(0)+R^+ \xrightarrow{k_{i1}} R(0)-R^+ \, , \]

   \[ R^++R^+ \xrightarrow{k_{i1}} R^+-R^+ \, , \]

   \[ R(0)+R(i) \xrightarrow{k_{i1}} P(i, 0, 0, 0) \, , \]

   \[ R^++R(i) \xrightarrow{k_{i1}} P(i, 0, 0, 0) \, , \]

   \[ R(j)+R(i-j) \xrightarrow{k_{i1}} P(i, 0, 0, 0) \]

are character reactions of radicals and intermediates cross termination.

\[ R(0)+\text{Int}(i, 0, 0) \xrightarrow{k_{i2}} P(i, 0, 0, 0) \, , \]

\[ R(0)+\text{Int}(i, j, 0) \xrightarrow{k_{i2}} P(i, j, 0, 0) \, . \]
\[ R(0) + \text{Int}(i, j, k) \xrightarrow{k_{d2}} P(i, j, k, 0), \]
\[ R^1 + \text{Int}(i, 0, 0) \xrightarrow{k_{d2}} P(i, 0, 0, 0), \]
\[ R^2 + \text{Int}(i, j, 0) \xrightarrow{k_{d2}} P(i, j, 0, 0), \]
\[ R^3 + \text{Int}(i, j, k) \xrightarrow{k_{d2}} P(i, j, k, 0), \]
\[ R(j) + \text{Int}(i, 0, 0) \xrightarrow{k_{d2}} P(i, j, 0, 0), \]
\[ R(k) + \text{Int}(i, j, 0) \xrightarrow{k_{d2}} P(i, j, k, 0), \]
\[ R(m) + \text{Int}(i, j, k) \xrightarrow{k_{d2}} P(i, j, k, m). \]

In the introduced kinetic scheme: I, R(0), R(i), R', M, RAFT(i, j), Int(i, j, k), P(i, j, k, m) – reaction system’s components (refer to Table 1); i, j, k, m – a number of monomer links in the chain; kd – a real rate constant of the initiation reaction; k1, k12, k13, – thermal rate constants of the initiation reaction’s; kp, ktr, ka1, ka2, kf, kt1, kt2 are the values of chain growth, chain transfer to monomer, radicals addition to low-molecular RAFT-agent, radicals addition to macromolecular RAFT-agent, intermediates fragmentation, radicals quadratic termination and radicals and intermediates cross termination reaction rate constants, respectively.

**Table 1.** Signs of components in a kinetic scheme

<table>
<thead>
<tr>
<th>Component</th>
<th>Sign</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CH₃ NC CH₃</td>
</tr>
<tr>
<td>R(0)</td>
<td>NC CH₃</td>
</tr>
<tr>
<td>R'</td>
<td>CH₃</td>
</tr>
<tr>
<td>M</td>
<td>CH₃ NC CH₃</td>
</tr>
<tr>
<td>RAFT(0,0)</td>
<td>CH₃</td>
</tr>
</tbody>
</table>

**Diagram:**

- I (top left)
- R(0) (top right)
- R' (bottom left)
- M (bottom right)
- RAFT(0,0) (bottom center)
The differential equations system describing this kinetic scheme is as follows:

\[
\frac{d[R]}{dt} = -k_1[R(0)\sum_{i=1}^{l} (\sum_{j=1}^{i} (\sum_{k=1}^{j} \text{Int}(i, j, k)))];
\]

\[
\frac{d[M]}{dt} = -k_2[R(0)\sum_{i=1}^{l} (\sum_{j=1}^{i} (\sum_{k=1}^{j} \text{Int}(i, j, k)))];
\]

\[
\frac{d[R']}{dt} = -k_3[R'(0)\sum_{i=1}^{l} (\sum_{j=1}^{i} (\sum_{k=1}^{j} \text{Int}(i, j, k)))];
\]

\[
\frac{d[R(1)]}{dt} = 3k_1[R(0)\sum_{i=1}^{l} (\sum_{j=1}^{i} (\sum_{k=1}^{j} \text{Int}(i, j, k)))];
\]

\[
\frac{d[R(i)]}{dt} = k_1[R(0)\sum_{i=1}^{l} (\sum_{j=1}^{i} (\sum_{k=1}^{j} \text{Int}(i, j, k)))];
\]

\[
\frac{d[R(1,i)]}{dt} = k_2[R(0)\sum_{i=1}^{l} (\sum_{j=1}^{i} (\sum_{k=1}^{j} \text{Int}(i, j, k)))];
\]

\[
\frac{d[R(i)]}{dt} = k_3[R(0)\sum_{i=1}^{l} (\sum_{j=1}^{i} (\sum_{k=1}^{j} \text{Int}(i, j, k)))];
\]
\[
d[\text{Int}(i, j, 0)]/dt = k_2 [\text{RAFT}(i, 0)][\text{RAFT}(j)]-3k_2 [\text{Int}(i, j, 0)][\text{RAFT}(i, j)]-
-k_2 [\text{Int}(i, j, 0)][\text{RAFT}(0)][\text{RAFT}(0)]+\text{[RAFT}(i, 0)]+3k_2 [\text{Int}(i, j, 0)];
\]

\[
d[\text{RAFT}(i, j)]/dt = k_1 [\text{Int}(i, j, 0)]-3k_2 [\text{Int}(i, j, k)]-k_2 [\text{RAFT}(i, j)][\text{RAFT}(i, j)]+k_2 [\text{RAFT}(i, j)][\text{RAFT}(0)]+3k_2 [\text{Int}(i, j, k)];
\]

\[
d[\text{P}(i, 0, 0, 0)]/dt = k_1 [\text{RAFT}(i, 0)][\text{RAFT}(0)]+\text{[RAFT}(i, 0)]+2k_2 [\text{Int}(i, 0, 0)]-k_2 [\text{RAFT}(0)];
\]

\[
d[\text{P}(i, j, 0, 0)]/dt = k_1 [\text{RAFT}(i, j)][\text{RAFT}(0)]+\text{[RAFT}(i, j)]+2k_2 [\text{Int}(i, j, 0)]-k_2 [\text{RAFT}(0)];
\]

\[
d[\text{P}(i, j, k, 0)]/dt = k_1 [\text{RAFT}(i, j, k)][\text{RAFT}(0)]+\text{[RAFT}(i, j, k)]+2k_2 [\text{Int}(i, j, k, 0)]-k_2 [\text{RAFT}(0)];
\]

\[
d[\text{P}(i, j, k, m)]/dt = k_1 [\text{RAFT}(i, j, k, m)][\text{RAFT}(0)]+\text{[RAFT}(i, j, k, m)]+2k_2 [\text{Int}(i, j, k, m, 0)]-k_2 [\text{RAFT}(0)];
\]

\[
\text{Here } f – \text{initiator’s efficiency; } [R] = \sum_{i=1}^{\infty} \text{[RAFT}(i)] – \text{summary concentration of macroradicals; } t – \text{time.}
\]

A method of generating functions was used for transition from this equation system to the equation system related to the unknown MMD moments [8].

Number-average molecular mass (Mn), polydispersity index (PD) and weight-average molecular mass (Mw) are linked to MMD moments by the following expressions:

\[
M_n = \frac{\Sigma \mu_1}{\Sigma \mu_0}, \quad PD = \frac{\Sigma \mu_2}{\Sigma \mu_1^2}, \quad M_w = \text{PD} \cdot M_n,
\]

where \(\Sigma \mu_0, \Sigma \mu_1, \Sigma \mu_2\) – sums of all zero, first and second MMD moments; \(M_{ST} = 104 \text{ g/mol} – \text{styrene’s molecular mass.}

\section*{Rate Constants}

\subsection*{Real and Thermal Initiation}

The efficiency of initiation and temperature dependence of polymerization with the real initiation reaction rate constant by AIBN initiator are determined based on the data in this research, which have established a good reputation for mathematical modelling of leaving in mass styrene radical polymerization [6]:

\[
f = 0.5, \quad k_d = 1.58 \times 10^{13} e^{15500/T} \text{ s}^{-1},
\]

where T – temperature, K.

As it was established in the research, thermal initiation reaction rate constants depend on the reaction rate constants of chain growth, the radicals quadratic termination and the monomer’s initial concentration:

\[
k_{11} = 1.95 \times 10^{13} \frac{k_{11}}{k_p^0 M_0^3} e^{20923/T} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1};
\]

\[
k_{12} = 4.30 \times 10^{17} \frac{k_{12}}{k_p^0 M_0^3} e^{23978/T} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1};
\]

\[
k_{13} = 1.02 \times 10^8 \frac{k_{13}}{k_p^0 M_0^3} e^{14807/T} \text{ L} \text{ mol}^{-1} \text{ s}^{-1} \text{ [6].}
\]

\subsection*{Chain Transfer to Monomer Reaction’s Rate Constant}

On the basis of the data in research [6]:

\[
k_{\text{tr}} = 2.31 \times 10^{6} e^{6376/T} \text{ L} \text{ mol}^{-1} \text{ s}^{-1}.
\]

\section*{Rate Constants for the Addition of Radicals to Low-Molecular and Macromolecular RAFT-Agents}

In the research [9], it was shown by the example of dithiobenzoates, at first, that the chain transfer to low- and macromolecular RAFT-agents of rate constants are functions of respective elementary constants. Let us demonstrate this for our process. For this record, the change of concentrations \[\text{[Int}(i, 0, 0)]], \[\text{[Int}(i, j, 0)]], \[\text{RAFT}(0, 0)]\) and \[\text{RAFT}(i, 0)] in quasistationary approximation for the initial phase of polymerization is as follows:
The equation (1) expresses the following concentration $[\text{Int}(i, 0, 0)]$:

$$[\text{Int}(i, 0, 0)] = \frac{k_{a_1}}{3k_f} [\text{RAFT}(0,0)][R].$$

Substituting the expansion gives the following $[\text{Int}(i, 0, 0)]$ expression to equation (3):

$$[\text{RAFT}(i, 0)]/dt = -k_{a_1}[\text{RAFT}(i, 0)][R] + k_f \frac{k_{a_1}}{3k_f} [\text{RAFT}(i, 0)][R].$$

After transformation of the last equation, we have:

$$[\text{RAFT}(0,0)]/dt = \frac{2}{3}k_{a_1}[R]dt.$$

Solving this equation (initial conditions: $t = 0$, $[R] = [R]_0 = 0$, $[\text{RAFT}(0,0)] = [\text{RAFT}(0,0)]_0$), we obtain:

$$\ln \frac{[\text{RAFT}(0,0)]}{[\text{RAFT}(0,0)]_0} = -\frac{2}{3}k_{a_1}[R]t.$$

To transfer from time $t$, being a part of equation (5), to conversion of monomer $C_M$, we put down a balance differential equation for monomer concentration, assuming that at the initial phase of polymerization, thermal initiation and chain transfer to monomer are not of importance:

$$\frac{d[M]}{dt} = -k_p[R][M].$$

Transforming the equation (6) with its consequent solution at initial conditions $t = 0$, $[R] = [R]_0 = 0$, $[M] = [M]_0$:

$$\ln \frac{[M]}{[M]_0} = -k_p[R]t.$$

Link rate $[M]/[M]_0$ with monomer conversion ($C_M$) in an obvious form like this:

$$C_M = \frac{[M]-[M]}{[M]_0} = 1 - \frac{[M]}{[M]_0},$$

$$[M]_0 = 1 - C_M.$$

We substitute the last ratio to equation (7) and express time $t$:

$$t = \frac{\ln(1 - C_M)}{k_p[R]}.$$

After substitution of the expression (8) by the equation (5), we obtain the next equation:

$$\ln \frac{[\text{RAFT}(0,0)]}{[\text{RAFT}(0,0)]_0} = \frac{2}{3}k_{a_1}\ln(1 - C_M).$$

By analogy with introduced $[M]/[M]_0$ to monomer conversion, reduce ratio $[\text{RAFT}(0,0)]/[\text{RAFT}(0,0)]_0$ to conversion of low-molecular RAFT-agent $-C_{\text{RAFT}(0,0)}$. As a result, we obtain:

$$[\text{RAFT}(0,0)]/[\text{RAFT}(0,0)]_0 = 1 - C_{\text{RAFT}(0,0)}.$$

Substitute the derived expression for $[\text{RAFT}(0,0)]/[\text{RAFT}(0,0)]_0$ from equation (10) to equation (9):

$$\ln(1 - C_{\text{RAFT}(0,0)}) = \frac{2}{3}k_{a_1}\ln(1 - C_M).$$

In the research [9], the next dependence of chain transfer to low-molecular RAFT-agent constant $C_{\text{tr1}}$ is obtained on the monomer and low-molecular RAFT-agent conversions.
Comparing equations (12) and (11), we obtain dependence of chain transfer to low-molecular RAFT-agent constant $C_{tr1}$ on the constant of radicals in addition to macromolecular RAFT-agent and the chain growth reaction rate constant:

$$C_{tr1} = \frac{2k_{a1}}{3k_p}.$$  \hspace{1cm} (13)

From equation (13), we derive an expression for constant $k_{a1}$, which will be based on the following calculation:

$$k_{a1} = \frac{1.5C_{tr1}k_p}{k} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$  \hspace{1cm} (14)

As a numerical value for $C_{tr1}$, we assume the value of 53, derived from research [4] on the base of equation (12), at immediate experimental measurement of monomer and low-molecular RAFT-agent conversions. Since chain transfer reactions in RAFT-polymerization is usually characterized by a low value of activation energy, compared to the activation energy of chain growth, it is supposed that constant $C_{tr1}$ doesn’t depend or slightly depends on temperature. We will propose as an assumption that $C_{tr1}$ doesn’t depend on temperature [10].

By analogy with $k_{a1}$, we deduce the equation for constant $k_{a2}$. From equation (2) we express such a concentration $[\text{Int}(i, j, 0)]$:

$$[\text{Int}(i, j, 0)] = \frac{k_{a2}}{3k_p}[\text{RAFT}(i, 0)][\text{R}].$$

Substitute expressions, derived for $[\text{Int}(i, 0, 0)]$ and $[\text{Int}(i, j, 0)]$ in equation (4):

$$d[\text{RAFT}(i, 0)]=\frac{-2}{3}k_{a1}[\text{RAFT}(0,0)][\text{R}]-\frac{1}{3}k_{a2}[\text{RAFT}(i, 0)][\text{R}].$$  \hspace{1cm} (14)

Since in the end it was found that constant of chain transfer to low-molecular RAFT-agent $C_{tr1}$ is equal to the division to constant $k_p$ coefficient before expression $[\text{RAFT}(0,0)][\text{R}]$ in the balance differential equation for $[\text{RAFT}(0,0)]$, from equation (14) for constant of chain transfer to macromolecular RAFT-agent, we obtain the next expression:

$$C_{tr2} = \frac{1}{3k_p}.$$  \hspace{1cm} (15)

From the last equation we obtain an expression for constant $k_{a2}$, which is based on the following calculation:

$$k_{a2} = 3C_{tr2}k_p \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}. \hspace{1cm} (15)$$

In research [4] on the base of styrene and DBTK, a macromolecular RAFT-agent was synthesized, thereafter with a view to experimentally determine constant $C_{a2}$, polymerization of styrene was performed with the use of the latter. In the course of the experiment, it may be supposed that constant $C_{a2}$ depends on monomer and macromolecular RAFT-agent conversions by analogy with equation (12). As a result directly from the experimentally measured monomer and macromolecular RAFT-agent conversions, value $C_{a2}$ was derived, equal to 1000. On the ground of the same considerations as for that of $C_{tr1}$, we assume independence of constant $C_{a2}$ on temperature.

**Rate Constants of Intermediates Fragmentation, Termination between Radicals and Termination between Radicals and Intermediates**

In the research [4] it was shown, that RAFT-polymerization rate is determined by this equation:

$$(W_0 / W)^2 = 1 + \frac{k_{12}}{k_{11}}K[\text{RAFT}(0,0)]_0 + \frac{k_{13}}{k_{11}}K^2[\text{RAFT}(0,0)]^2_0,$$

where $W_0$ and $W$ – polymerization rate in the absence and presence of RAFT-agent, respectively, s$^{-1}$; $K$ – constant of equilibrium (III), L·mol$^{-1}$; $k_{13}$ – constant of termination between two intermediates reaction rate, L·mol$^{-1}$·s$^{-1}$ [11].

For initiated AIBN styrene polymerization in DBTC’s presence at 80°C, it was shown that intermediatesquadratic termination wouldn’t be implemented and RAFT-polymerization rate was determined by equation [4]:

$$(W_0 / W)^2 = 1 + 8[\text{RAFT}(0,0)]_0.$$  \hspace{1cm} (14)

Since $\frac{k_{12}}{k_{11}} = 1$, then at 80°C $K = 8$ L·mol$^{-1}$ [4]. In order to find dependence of constant $K$ on temperature, we did research on polymerization kinetics at 60°C. It was found, (Figure 1), that the results of the kinetic measurements well rectify in
coordinates \((W_0/W)^2 = f([RAFT(0,0)]_0)\). At 60°C, \(K = 345\ \text{L} \cdot \text{mol}^{-1}\). Finally, the dependence of the equilibrium constant on temperature was determined in the form of Vant-Goff’s equation:

\[ K = 4.85 \cdot 10^{-27} \cdot e^{22123/T} \cdot \text{L} \cdot \text{mol}^{-1}. \]  

(16)

**Figure 1.** Dependence \((W_0/W)^2\) on DBTC concentration at 60°C

In compliance with the equilibrium (III), the constant is equal to

\[ K = \frac{k_{2f}}{3k_f}, \ \text{L} \cdot \text{mol}^{-1}. \]

Hence, the reactions of the intermediates fragmentation rate constant will be as such:

\[ k_f = \frac{k_{2f}}{3K}, \ \text{s}^{-1}. \]

(17)

The reactions of the intermediates fragmentation rate constant was built into the model in the form of dependence (17) considering equations (15) and (16).

As it has been noted above, ratio \(k_{12}/k_{11}\) equals approximately one, therefore it will taken, that \(k_{12} \approx k_{11}\) [4]. For the description of the gel-effect, the dependence as a function of monomer conversion \(C_M\) and temperature \(T\) (K) [12] was applied:

\[ k_{12} \approx k_{11} \approx 1.255 \cdot 10^9 \cdot e^{-844/T} \cdot e^{-2(A_1C_M + A_2C^2_M + A_3C^3_M)} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}, \]

where \(A_1 = 2.57 - 5.05 \cdot 10^{-3} \cdot T\); \(A_2 = 9.56 - 1.76 \cdot 10^{-2} \cdot T\); \(A_3 = -3.03 + 7.85 \cdot 10^{-3} \cdot T\).

**Rate Constant for Chain Growth**

The method of polymerization, being initiated by pulse laser radiation [13] is used for determination of rate constant for chain growth \(k_p\). It is anticipated that such an estimation method is more correct, than the traditionally used revolving sector method [12]. We made our choice on temperature dependence of the rate constant for chain growth that was derived on the ground of the method of polymerization, being initiated by pulse laser radiation:

\[ k_p = 4.27 \cdot 10^7 \cdot e^{3910/T} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}, \]

(18)

since this dependence is more adequately describes the change of polymerization reduced rate with monomer conversion in the network of the developed mathematical model (Figure 2), than temperature dependence, which is derived by the revolving sector method [12]:

\[ k_p = 1.057 \cdot 10^7 \cdot e^{3667/T} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}. \]

(19)
Figure 2. Dependence of initiated AIBN ([I]₀=0.01 mol·L⁻¹) styrene polymerization reduced rate on monomer conversion at 60°C (1 – experiment; 2 – estimation by introduced in this research mathematical model with temperature dependence of k_p (18); 3 – estimation by introduced in this research mathematical model with temperature dependence of k_p (19): [RAFT(0,0)]₀ = 0 mol·L⁻¹ (a), 0.007 (b).

The adequacy of the Model

The results of polystyrene’s molecular-mass properties calculations by the introduced mathematical model are presented in Figures 3 and 4. The mathematical model of styrene’s RAFT-polymerization in the presence of trithio carbonates, taking into account the radicals and intermediates cross termination, adequately describes the experimental data that prove the process mechanism, built in the model. The essential proof of the mechanism’s correctness is that in case of conceding the absence of radicals and intermediates cross termination – the experimental data wouldn’t substantiate theoretical calculation by the mathematical model, introduced in this assumption (Figure 5).

Figure 3. Dependence of number-average molecular mass (a) and polydispersity index (b)-(d) on monomer conversion for being initiated by AIBN ([I]₀=0.01 mol·L⁻¹) styrene bulk RAFT-polymerization at 60°C in the presence of DBTC (lines – estimation by model; points – experiment): [RAFT(0,0)]₀ = 0.005 mol·L⁻¹ (1), 0.007 (2), 0.0087 (3), 0.0174 (4), 0.087 (5)
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Figure 4. Dependence of number-average molecular mass (a) and polydispersity index (b) on monomer conversion for being initiated by AIBN ([I]_0=0.01 mol·L⁻¹) styrene bulk RAFT-polymerization at 80°C in DBTC presence (lines – estimation by model; points – experiment): [RAFT(0,0)]_0 = 0.01 mol·L⁻¹ (1), 0.02 (2), 0.1 (3) [4]

Figure 5. Dependence of number-average molecular mass on monomer conversion for initiated AIBN ([I]_0=0.01 mol·L⁻¹) styrene bulk RAFT-polymerization at 60 °C in DBTC presence [RAFT(0,0)]_0 = 0.005 mol·L⁻¹ (lines – estimation by model assuming that radicals and intermediates cross termination are absent; points – experiment)

Due to adequacy of the model realization at numerical experiment it became possible to determine the influence of process controlling factors on polystyrene molecular-mass properties.

Numerical Experiment

The research on the influence of the process controlling factors on the molecular-mass properties of polystyrene, synthesized by RAFT-polymerization method in the presence of AIBN and DBTC, was done in the range of initial concentrations of: initiator – 0-0.1 mol·L⁻¹; monomer – 4.35-8.7 mol·L⁻¹, DBTC – 0.001-0.1 mol·L⁻¹; and at temperatures – 60-120°C.

The Influence of AIBN Initial Concentration by Numerical Experimentation

It was set forth that in generally the same conditions, with an increase of AIBN initial concentration number-average, the molecular mass of polystyrene decreases (Figure 6). In all used initial RAFT-agent concentrations, there is a linear or close to linear growth of the number-average molecular mass of polystyrene with monomer conversion. This means that even the lowest initial RAFT-agent concentrations affect the process of radical polymerization. It should be noted that at high initial RAFT-agent concentrations (Figure 7) the change of AIBN initial concentration practically doesn’t have any influence on the number-average molecular mass of polystyrene. But at increased temperatures (Figure 8), in case of high initial AIBN concentration, it is comparable to high initial RAFT-agent concentration; polystyrene molecular mass would be slightly decreased due to thermal initiation.
Since the main product of styrene RAFT-polymerization process, proceeded in the presence of trithiocarbonates, is a narrow-dispersed high-molecular RAFT-agent (marked in the kinetic scheme as RAFT(i, j)), which is formed as a result of reversible chain transfer, and widely-dispersed (minimal polydispersity – 1.5) polymer, formed by the radicals quadratic termination, so the common polydispersity index of the synthesized product is their ratio. In a broad sense, with an increase of initial AIBN concentration, the part of the widely-dispersed polymer, which is formed as a result of the radicals quadratic termination, increase in mixture, thereafter general polydispersity index of the synthesized product increases. However, at high temperatures this regularity can be discontinued – at low initial RAFT-agent concentrations the increase of initial AIBN concentration leads to a decrease of the polydispersity index (Figure 9, curves 3 and 4). This can be related only thereto that at high temperatures thermal initiation and elementary reactions rate constants play an important role, depending on temperature, chain growth and radicals quadratic termination reaction rate constants, monomer initial concentration in a complicated way [6]. Such complicated dependence makes it difficult to analyze the influence of thermal initiation role in the process kinetics, therefore the expected width of MMD of the polymer, which is expected to be synthesized at high temperatures, can be estimated in every specific case in the frame of the developed theoretical regularities.
Features of macromolecule formation by RAFT-polymerization of styrene in the presence of trithiocarbonates

Figure 9. Dependence of polydispersity index PD on monomer conversion $C_M$ (120°C) $[M]_0 = 8.7$ mol·L$^{-1}$, $[RAFT(0, 0)]_0 = 0.001$ mol·L$^{-1}$, $[I]_0 = 0$ mol·L$^{-1}$ (1), 0.001 (2), 0.01 (3), 0.1 (4)

Special attention shall be drawn to the fact that for practical objectives, realization of RAFT-polymerization process without an initiator is of great concern. In all cases at high temperatures as the result of styrene RAFT-polymerization implementation in the presence of RAFT-agent without AIBN, a more highly-molecular (Figure 10) and more narrowly-dispersed polymer (Figure 9, curve 1) is built-up than in the presence of AIBN (Figure 9, curves 2-4).

Figure 10. Dependence of number-average molecular mass $M_n$ on monomer conversion $C_M$ (120°C) $[M]_0 = 8.7$ mol·L$^{-1}$, $[RAFT(0, 0)]_0 = 0.001$ mol·L$^{-1}$, $[I]_0 = 0$ mol·L$^{-1}$ (1), 0.001 (2), 0.01 (3), 0.1 (4)

The Influence of Monomer Initial Concentration by Numerical Experiment

In other identical conditions, the decrease of the initial monomer concentration reduces the number-average molecular mass of polymer. The polydispersity index doesn’t practically depend on the initial monomer concentration.

Influence of initial RAFT-agent concentration by numerical experimentation

In other identical conditions, increase of initial RAFT-agent concentration reduces the number-average molecular mass and polydispersity index of the polymer (Figure 11).

Figure 11. Dependence of number-average molecular mass $M_n$ (a) and polydispersity index PD (b) on monomer conversion $C_M$ (90°C) $[I]_0 = 0.01$ mol·L$^{-1}$, $[M]_0 = 6.1$ mol·L$^{-1}$, $[RAFT(0, 0)]_0 = 0.001$ mol·L$^{-1}$ (1), 0.01 (2), 0.1 (3)
The Influence of Temperature by Numerical Experiment

Generally, in other identical conditions, the increase of temperature leads to a decrease of number-average molecular mass of polystyrene (Figure 12 (a)). Thus, polydispersity index increases (Figure 12 (b)). If initial RAFT-agent concentration greatly exceeds initial AIBN concentration, then the temperature practically doesn’t influence the molecular-mass properties of polystyrene.

![Figure 12. Dependence of number-average molecular mass M_n (a) and polydispersity index PD (b) on monomer conversion C_M.][7]

Conclusions

The kinetic model developed in this research allows an adequate description of molecular-mass properties of polystyrene, obtained by controlled radical polymerization, which is proceeded by reversible chain transfer mechanism and accompanied by “addition-fragmentation”. This means, that the model can be used for development of technological applications of styrene RAFT-polymerization in the presence of trithiocarbonates.

Researches were supported by Russian Foundation for Basic Research (project. no. 12–03–97050-r_povolzh’e_a).

References