Initiator

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Educational software for modeling of chain polymerization processes

based on Monte Carlo algorithms

Version 0.2

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1. Introduction

The program ***Initiator*** is intended to support teaching and learning of polymer chemistry. It allows modeling of three processes of chain copolymerization and presents selected information about kinetics of the process, molecular weight distribution, microstructure of chains, and expected results of analyses by SEC and MALDI.

The Monte Carlo algorithms applied in the program give access to all details of modeled processes. However the accuracy of modeling strongly depends on the number of modeled chains. The program at its current state is a compromise between results accuracy, calculation speed, and the computer limitations. A future 64-bits version would overcome some of limitations and would offers users more flexibility. Anyway, in the author's (and his collaborators) opinion, the scale of simulation currently allowed in the program yields results which can be regarded as representative for education purposes.

Author of the program has very little experience in teaching; therefore he asks every user to send him opinions, notes, wishes, and indications helpful for improvement of the program and its documentation. The program speed and accuracy can be also improved by removing less useful functionalities. Any suggestions are welcome.

Initiator is a freeware program for private, educational, and academic use. It was written solely for the purpose of modeling polymerizations processes listed in this manual. It does not connect with Internet and does not violate user privacy.

Requirements and Installation

Actualized versions of the program and documentation can be downloaded from the program homepage: http://www.cbmm.lodz.pl/articles.php?id=93&title=Sosnowski.

Minimal requirements: Core Duo® 2 processor, 750 MB of RAM, SXGA graphic system, Windows® XP 32-bit, and only 10 MB of disk space. Larger operational memory is recommended as it facilitates modeling of larger number of chains and therefore offers better accuracy and smoother distributions.

The program does not integrate with the operating system, therefore installation is not required. Just create a folder on disk and unpack the downloaded archive to it; it can be run also from USB disk. Remove the program by deleting the folder and files "Maldix.tmp" ("x" stands for a digit) in a user temporary directory. All files in the archive were tested against viruses and malware; however the author cannot warrants the full safety.

> **Note:**
> The program needs administrator privileges when is placed on the system disk.
> **Note:**
> Any warnings appearing at the first start of the program can indicate further malfunctioning of the program. Please follow the indications bellow in this section or send description of the troubles to the author.

Known Incompatibilities and Problems

The Aero Glass theme under Vista or Windows 7 blocks displaying of balloon tips.

A non default system font size causes distortion of some program dialogs.

A multiple instances of the program cannot be run but one can make a copy of the program and run it in parallel.

On some systems the message "Error: Unable to Load Library from File" appears. This problem can be fixed by installing the Run Time Library "vcredist_x86.exe" from Microsoft® (http://www.microsoft.com/en-us/download/details.aspx?id=29). The computer has to be restarted to complete the installation process.

The message "Invalid Formula for …" can appear also when the "Maldi.dll" library cannot be accessed properly. In such case it is recommended to install the mentioned above Microsoft® library or/and to repeat installation of the program.

When other problems will appear please sent the used parameters file, MCSimulator.log file, MCSimulator.ini file and description of the accounted problem to the author: stasosno@cbmm.lodz.pl

2. Getting Started

Note: The blue and italicized texts refer to names of the program interface components.

Note: It is strongly recommended to watch the prepared Demo (by *Menu / Help / Show Demo*) and to skim the manual (by *Menu / Help / Show Manual*). They are accessible also by the *Introduction Screen* displayed at start of the program.

Note: Number of modeled chains in the provided examples was adjusted for computers with ≥ 4 GB of RAM. When the memory is lower, the *Number of Initiator Molecules* must be reduced using the *Editor of Process Parameters*. See this manual for details.

One can explore the program possibilities by executing seven simple steps, as listed below:

1. Run the program.

2. Press button. Select one of parameter files provided and press OK button.

3. Click the *Start Button* once.

4. Now the simulation will run. It can be paused temporarily and resumed by clicking the *Pause Button* .

5. You can observe the results of the simulation by switching the tabs below the buttons whenever the simulation is running, paused, or stopped.

6. Stop the simulation by clicking the *Stop Button* .

7. Close the program.

3. Available results

Instant plots

Microstructure of chains; full distribution profile of degree of polymerization (DP)

At selected time point

Molecular weight distribution (MWD); number-average molar mass (M_n); mass-average molar mass (M_w); approximate SEC chromatogram; MALDI ToF spectrum

Kinetics plots

Concentrations of initiator, monomer A, monomer B, and terminated chains (concentrations, conversions, or semi-log plots); number-average degree of polymerization (DP_n); mass-average degree of polymerization (DP_w); z-average degree of polymerization (DP_z), degree-of-polymerization dispersity $Đ_X$ (DP_w/DP_n), fractions of dyads, concentration of active centers (radicals)

Short description of available plots

Detailed characteristics of the plots, operations allowed on them, and advices for users are given in the section "Program Interface". Right clicking on a plot shows additional options.

Chains microstructure

Tab *Chains* shows the arrangement of constitutional units in a randomly selected sample of chains. Each vertical line in the box represents a single chain and each pixel corresponds to one constitutional unit. Every elementary reaction step causes immediate changes to the plot, allowing the user to follow the progress of the modeled process and changes happening to the chains lengths. Blank lines can appear in the plot as a result of chains recombination or a segmental exchange reaction. It is so, because constitutional units belonging to one chain are transferred and attached to another chain. In the case of Free Radical Polymerization (FRP) process, radicals form and deactivate very rapidly, so only a few radicals at a time are modeled. Thus, the speed of modeling is very high and it is difficult to notice the instant changes of chain lengths caused by their growth or recombination.

Distribution of DP

It can be seen in tab *DP Dist.* Each vertical line in the plot represents the number of chains with a given DP. Lengths of the lines are scaled in order to fit the box. Therefore for very narrow distributions one pixel represents a number of chains and the length can differ by one pixel from the calculated value. For broad distributions, one chain is represented by a section of some constant length.

Concentrations

Changes in concentrations over time for initiator [I], monomers [A], [B], [A]+[B] and terminated chains can be seen in tab *Conversion*. Concentrations of initiator and terminated chains are scaled relatively to the monomer concentration(s) in order to show all of them in a common scale. The data can be presented also as the conversion or in semi-log coordinates.

Average DP's and dispersity of DP

Changes of DP_n, DP_w, DP_z, and $Đ_x$ over time can be seen in the tab *DP Av.*

Active centers concentration

Changes in concentrations of active centers of polymerization (or radicals for radical processes) can be seen in tab *Act. Cent.* Active centers (radicals) located on different constitutional units (A and B) are shown separately.

Fractions of dyads

Changes in dyads fractions in the product over time can be seen in the tab *Dyads*. The dyad fractions describe quantitatively some aspects of the chains microstructure shown qualitatively in the *Chains* tab.

Average molecular weights and MWD

Full MWD (by number and by weight), M_n, and M_w can be seen in the tab *Mass Dist.* The plot is refreshed when the simulation is paused. Averaged isotopic molecular masses are assumed for macromolecules and the resolution of the plot is set to be equal to one atomic mass unit. Therefore a discrete distribution of masses can be usually observed. The slider shown above the plot allows smoothing the distribution using the running average method with different number of averaging points.

SEC chromatogram

When the simulation is paused, then the current, approximate SEC chromatogram is shown in the tab *SEC Plot*. The number-average and the weight-average molecular masses are superimposed on the SEC plot. The slider shown above the plot allows examining the appearance of SEC chromatogram for different resolutions of SEC equipment.

MALDI ToF spectrum

The tab *MALDI* allows calculating the MALDI ToF isotopic spectrum of the current modeled product when the simulation is stopped or paused. The spectrum contains signals of all allowed structures, including macromolecules with double bonds or without abstracted hydrogen atom. In order to start calculations click the *Calculation Button* ▣ . The shown sliders allow expanding and browsing the spectrum. Please refer to "Program Interface", "*MALDI*" subsection for more details.

4. Program Interface

a) Introduction Screen
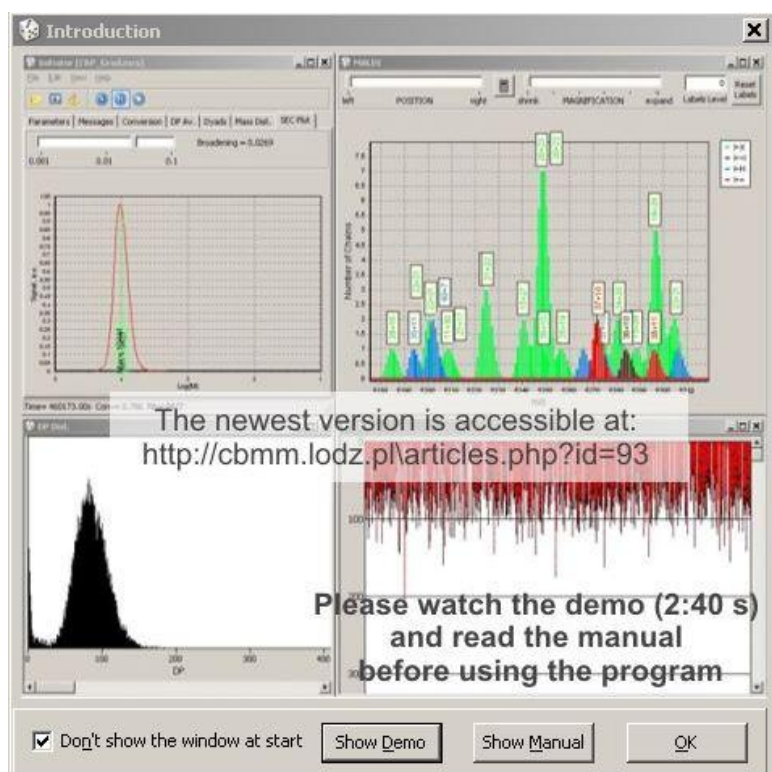
The *Introduction Screen* displayed at start of the program facilitates access to information important for new users. User can prevent displaying the screen at start by checking option *Don't display the window at start*. At any time the screen is accessible by *Menu / View / Intro* Screen. The new users are encouraged to see the short demo (2 min 40 s) and skim the manual before starting of using the program.

b) Interface Components

The program interface consists of four components: *Main Menu*, *Button Bar*, *Switchable Tabs*, and *Status Bar*. These elements work as in other Windows program, except for the *Switchable Tabs* which can be undocked into floating windows and placed everywhere on the Windows desktop. The tab *Messages* is non-dockable.
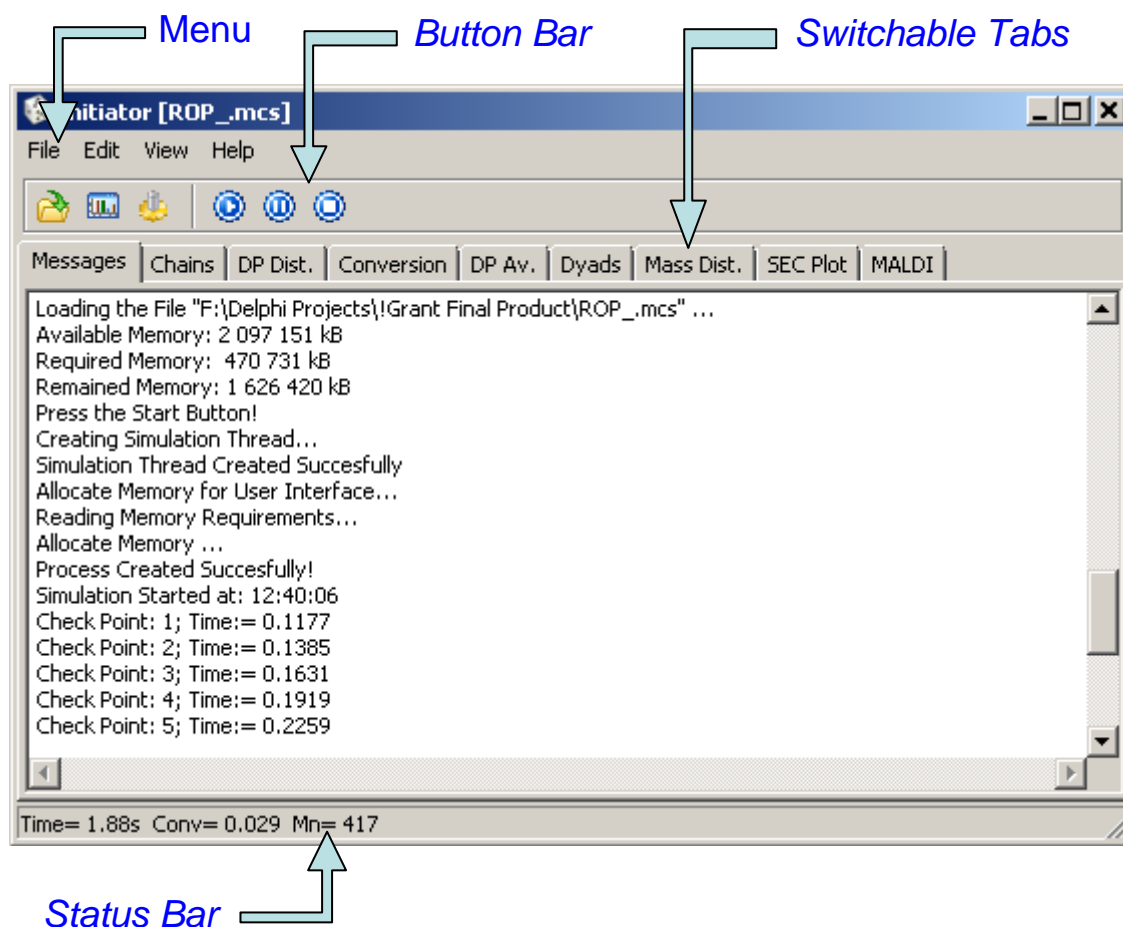
c) Docking

Docking and undocking works as in other Windows programs by dragging a tab (or a window) into a destination place. Positions, sizes, and docking status of the windows are stored in the configuration file when the program is closed.
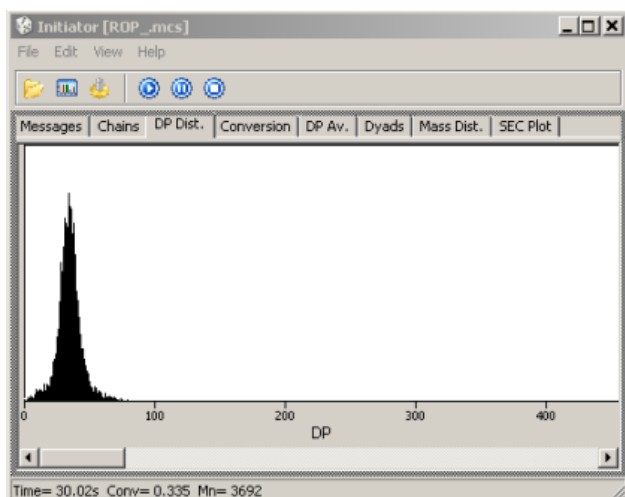
Docked and undocked charts
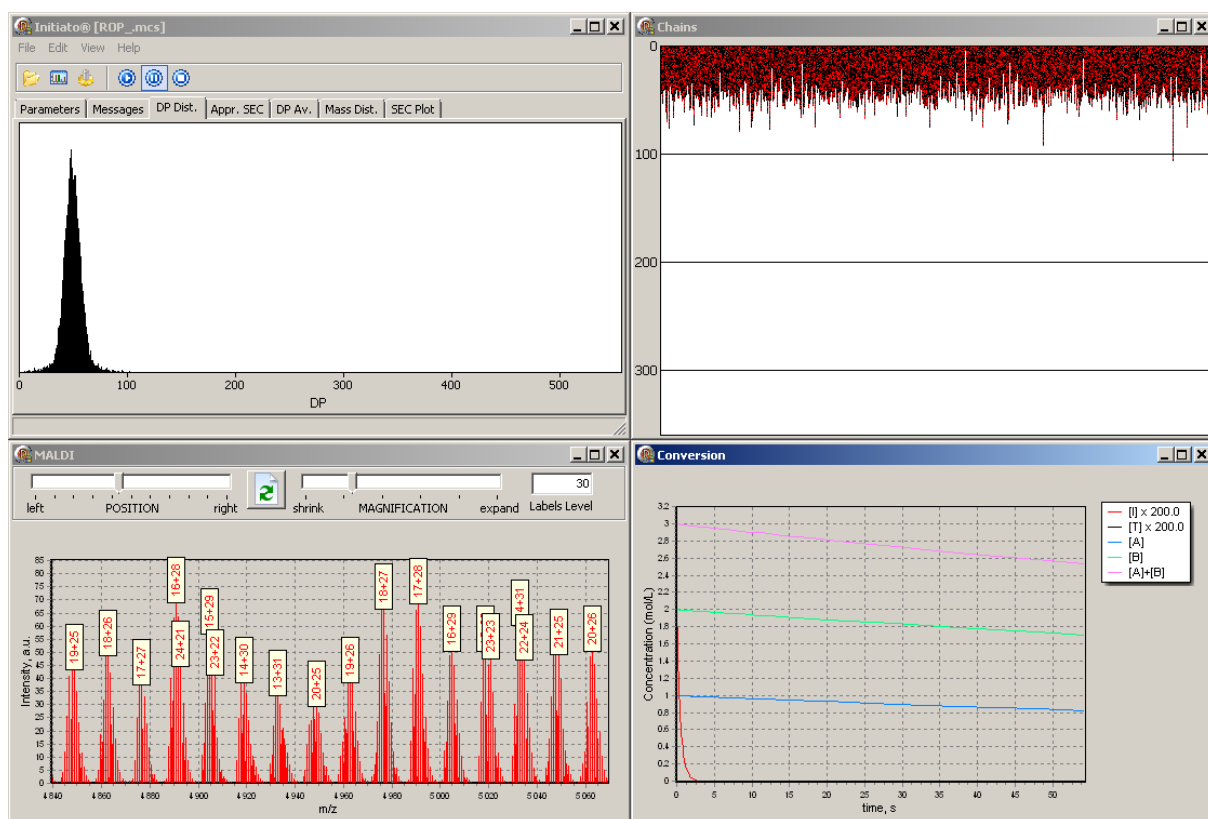
d) Main Menu

The Main Menu also offers access to functionalities used less often. Some items of the Main Menu can be disabled when a simulation is running.

File/Open Parameters: opens a file containing the set of parameters defining the modeled process; accessible also by *Button Bar* or key shortcut (Ctrl+O). The name of an existing parameter file can be used as the first parameter in command line or in the desktop shortcut.

File/Clear: clears memory used by simulation thread and plots before the start of a next simulation. In case of malfunction of the program, it is recommended to exit and start the program again instead of using this function.

File/MALDI ToF DLL: it is enabled when the DLL cannot be located by the program. Although the DLL can be stored anywhere on the disk, it is recommended to place it in the same directory as the program.

Edit/Parameter Settings: displays an editor form for defining a modeled process; accessible also by *Button Bar* ⚙.

View/Show All Plots: allows showing all created charts which were closed by the user in current session.

View/Create Plots: opens *Plots Selection Form* allowing the user to define plots being created; accessible also by *Button Bar* 📊. See paragraph "Plot Selection Form" below for details.

View/Show Intro: opens *Introduction Screen.*

Help/About: shows information about the program and address of the author.

Help/Show Demo: opens animation showing selected features of the program.

Help/Show Manual: opens PDF document containing this manual.

e) Button Bar

The *Button Bar* contains several buttons that provide quick access to frequently used functions.
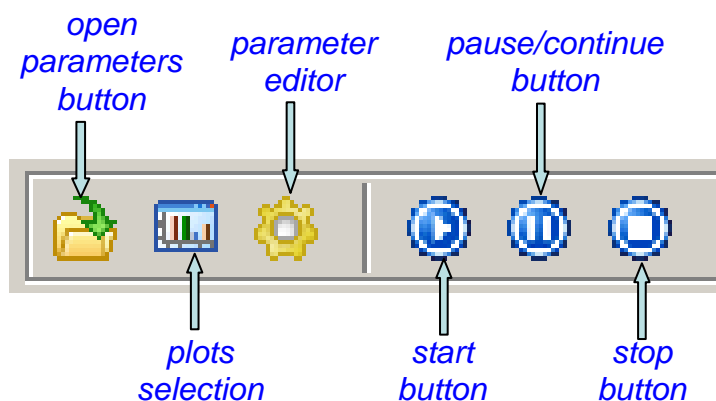
f) Plots Selection Form

This form allows the user to decide which plots will be prepared and displayed during simulations. A large number of selected plots would slow down calculations and consumes memory which otherwise can be utilized for increasing the number of modeled chains.
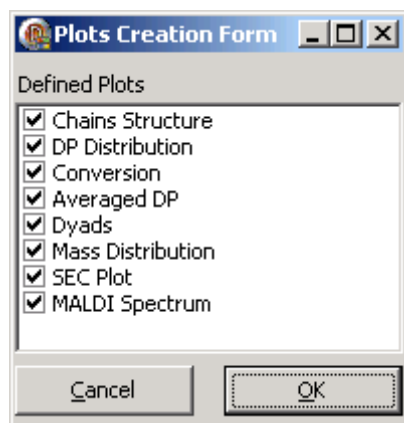
It is recommended to select the required plots before starting the simulation and leave them opened during all process. Theoretically all these plots can be created, closed, or opened at any time, but in such case stability of the program is not yet warranted.

g) Switchable Tabs

The *Switchable Tabs* allows switching charts containing different kinds of information about the simulated process. Some charts allow zooming, scrolling, and editing the details. Zooming in can be done by dragging the mouse from the left to the right side of area of interest. For zooming out, drag the mouse in the opposite direction. For scrolling, drag the mouse with the mouse right button pressed. Some charts permit editing all details using a chart editor, which can be accessed by double-clicking on the chart. Modifications made in the editor are immediately updated in the chart, thus it is easy to explore all possibilities offered to the user. Unfortunately, a help for the editor is not provided. Many options in the editor are self-explanatory. On the other hand some helpful information can be found in the Internet. Look up for "Steema TeeChart Software".
More information about the data displayed on different tabs is given in the following paragraphs.

Messages

This tab shows important messages about the preparation and progress of the simulation which can be useful for debugging when abnormal program behavior is noticed. When the program is closed, the content of the window is saved in a file "filename.log" where filename is the name of the executable file (default name of the log file is MCSimulator.log).

Chains

This tab contains a box which shows the microstructure of chains. Each pixel of the box represents one constitutional unit. It allows getting the highest program speed and the highest density of information displayed. The box is updated after each reaction event therefore the user can observe changes of chain length caused by all elementary reactions: initiation, propagation, and termination. When two chains terminate by recombination, the content of one of them is attached to the other and a blank line appears.
The box shows randomly selected sample of chains, however in case of FRP it shows every *n*-th chain, where *n* is the ratio of the number of chains expected at the last *Checking Point* divided by the box width (expressed in screen pixels).
User can change colors assigned to both monomers.
When, due to a high resolution display, the displayed data are unreadable then size of pixel can be enlarged using the loop button appearing on the *Button Bar*. Pressing the button freezes temporarily the simulation and shows enlarged chains. The magnification degree can be set by using the context menu. Pressing the button restores the small pixels and restarts the simulation.

> ***Note*:**
> A dedicated software for screen magnification can be more convenient. Many of them can be found at:
> http://www.magnifiers.org/links/Download_Software/Screen_Magnifiers/Windows_Freeware_and_shareware/. The relatively new and powerful is the freeware „Virtual

Magnifying Glass" v. 3.5
(<u>http://sourceforge.net/projects/magnifier/files/magnifier%20for%20Windows/3.5/Vmg3.5_install.exe/download</u>).

DP Dist.

This tab contains a box which the DP distribution of chains. The box is updated after every reaction event. Each line represents the number of chains of a given value of DP. Lengths of the lines are scaled at each *Checking Point* in order to fit in the box. Therefore for very narrow distributions one pixel represents a number of chains and the length can differ by one pixel from the proper value. For broad distributions one chain is represented by a section of some constant length.

Act. Cent.

This tab shows concentration of active centers of polymerization. Active centers (radicals) located on different constitutional units (A and B) and the total concentration are represented by separate curves.

Determination of the active centers concentration for living processes is a trivial task, because the concentration of active centers is high. However in case of modeling of the radical processes a very large number of chains (more than millions) is required for obtaining a reliable result. Fortunately, it is possible to find a good approximation of the concentrations for small scale of simulation using the method of calculation described in the paper: R. Szymanski, S. Sosnowski, "Modeling of Low Concentrations of Reactive Species in Kinetic Monte Carlo Simulations" *Macromol. Theory Simul.* **2012**, *21*, 510–515. The method allows calculating concentrations of compounds which appears in the modeled system only sporadically.
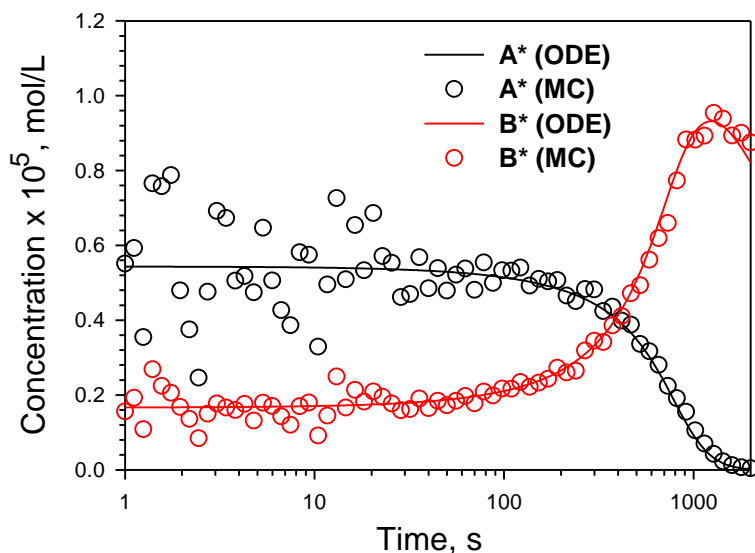
The figure presents results obtained from modeling of FRP process by integration of differential equations (lines) and from simulation by Monte Carlo method (points). The parameters used in this simulation are collected in the delivered file "FRP_Rand.mcs".

Note:
The original method requires fitting by polynomial and numerical differentiation. Here the simplest method of differentiation was used – calculation of the slope of point-to-point line segments, which gives something noisy results, but is very fast.

Conversion

This tab shows a chart displaying changes of concentrations over time. The concentrations of initiator and terminated chains are scaled relatively to monomer concentrations in order to show all of them in a common coordinate system. Alternatively, the conversion or the semi-logarithm coordinates can be applied.

DP Av.

It displays changes in the number-average, the mass-average, and the z-average DP and also in the dispersity index over time.

Dyads

The chart in this tab shows the changes of the content of various dyads in the modeled chains over time. It is actualized at each *Checking Point*. The dyads contents describe quantitatively the microstructure of the modeled chains.

Mass Dist.

Here the current molecular mass distributions of modeled chains (by number and by mass) are shown at each *Checking Point* or when the simulation is paused. Resolution of the plot is set to one atomic mass unit, therefore a discrete distribution of masses is usually observed. It is possible to smooth the distribution using the running average method with the number of averaged points from range 1-99 using the shown slider.
The number-averaged and the weight-averaged masses are superimposed on the distribution plots.

SEC Plot

The current, approximate SEC plot is shown when the simulation is paused or stopped. Resolution of the plot depends on mass range of simulated chains. One thousand of points were assigned for the full range shown on chart. The number-averaged and the weight-averaged masses are superimposed on the SEC plot.
The user can explore how the SEC equipment optimization can affect the quality of the obtained SEC plot. Under some assumptions, the broadening of SEC signal can be modeled by a simple equation (M. Buback, M. Bush, L.A. Lämmel, "Modeling of molecular weight distribution in pulsed laser free-radical homopolymerizations" *Macromol. Theory Simul.* **1996**, *5*, 845-861).

MALDI
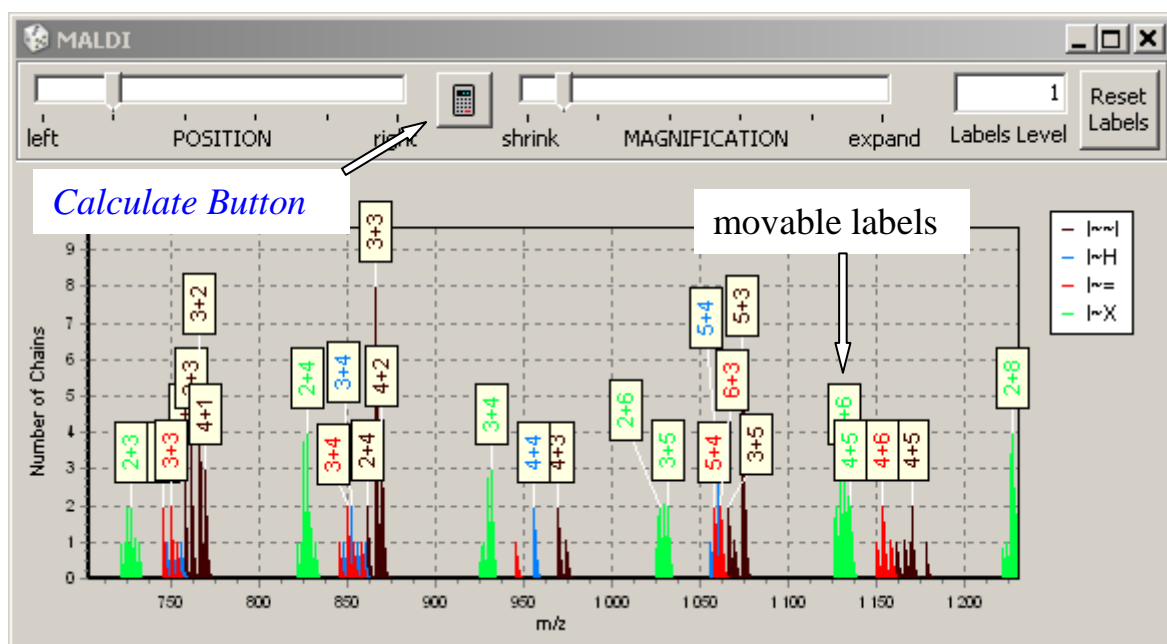
MALDI isotopic spectrum can be calculated when the simulation is paused or stopped.
In order to start calculations click the *Calculation Button.* A dialog window *MALDI Settings*
will appear, allowing selection of a cation and defining an upper mass limit of the calculated
spectrum.
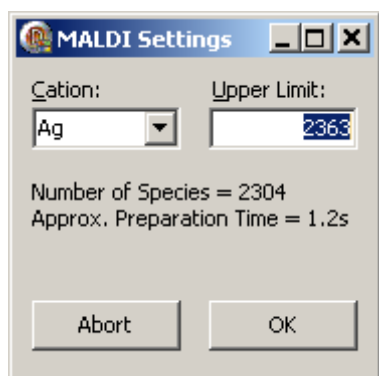
A new cation can be added to the selection list by typing its chemical symbol and pressing
enter. Calculations are time-consuming and require a lot of memory; therefore they should be
limited to a reasonable mass limit. For the given *Upper Limit* number of expected species and
approximate calculation time are calculated and displayed in the window. The message is
yellow when the estimated calculation time exceeds 10 s and red when the time exceeds 60 s.
The calculation starts after clicking the OK button.
Resolution of the spectrum (the m/z ratio) is equal 0.1 of atomic mass unit. The intensity is
expressed as a number of macromolecules in the modeled population appearing at given m/z
ratio. Spectra of all products are shown (they may overlap) including different products of
chains termination. It is possible to switch on/off each plot by double clicking the chart and
checking/unchecking the plot in the appeared chart editor.
The most intensive isotopic peak of a signal of molecules with a given composition can be
labeled. The label shows the number of units of both comonomers incorporated in the chains
ascribed to given m/z ratio. Number of displayed labels can be controlled by setting the value

of *Labels Level*, e.g. a minimal number of molecules under a signal required for peak labeling. Labels can be dragged by the mouse.

> *Note:*
> Some operations can distort the placements of labels in the plots. The default label positions can be restored by clicking the *Reset Labels* Button.
> *Note:*
> Calculation of the MALDI spectra is based on the procedure described by Rockwood, A.L., Haimi, P.: "Efficient calculation of Accurate Masses of Isotopic Peaks", *J. Am. Soc. Mass Spectrometry*, **2006**, *17*, 415–419. The source code in C++ was published by P. Haimi (http://www.helsinki.fi/science/lipids/software.html).

h) Status Bar

It displays a summary of simulation status at the last checking point: time, conversion, and number-average degree of polymerization (DP).

i) Popup menus

Some charts possess a context sensitive popup menu (accessible by right-clicking on the plot) which facilitates copying, printing, or saving the plots or the plotted data. Some of them offer provisions for changing the coordinates or editing other properties. An image of the popup menu is shown below.
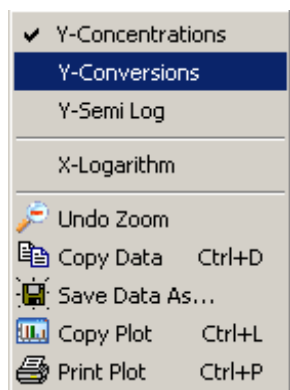
5. Process Parameters Editor

All parameters required for the simulation of a given process are stored in a file organized as a typical Windows .ini file. It can be edited directly, but it is recommended to use the Editor because it is more convenient to use, and additionally it allows the user to check the correctness and completeness of parameters. Moreover, it temporarily evaluates the amount of required memory and checks its availability. Unfortunately, the memory checking can be only provisional because the total required memory depends on user's activity and demands (for example on range of the generated MALDI spectrum). The editor allows opening and modifying of an existing parameter file.

All necessary parameters are divided into four categories as discussed below.

a) General Parameters Page
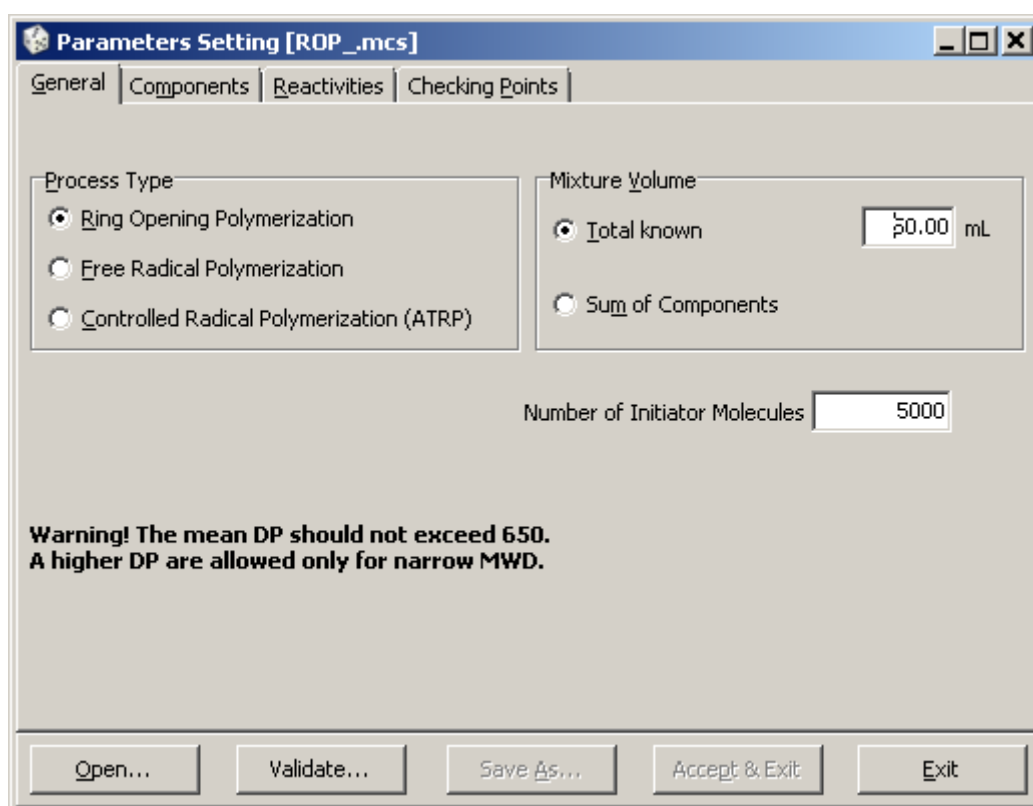
On this tab the user can define the type of the modeled process, the number of modeled chains, and the volume of polymerizing mixture. Currently there are three predefined processes (Living Polymerization (LP), CRP, and FRP) described in detail in the section "Modeled Processes".

The *Mixture Volume* option allows specifying the volume of the polymerization mixture which is used for the calculation of the reagent concentrations (monomers, initiator, activator, etc.) and of other parameters used by the simulation thread. The mixture volume can be entered directly or calculated as the sum of monomer- and solvent- volumes entered on page *Components* (the volume contraction is neglected).

The *Number of Initiator Molecules* defines the scale for the simulation; the scale is limited by ca. 2GB of memory available for 32-bit programs. Because of this limit, the modeled number of chains should not exceed 50,000. The highest allowed number can be tested by using the

Validate button. It must be noted that in the case of FRP, the value of *Number of Initiator Molecules* should be twice less than for the other systems because in this case each initiator molecule generates two chains.

The *Number of Initiator Molecules* parameter and the real volume of the modeled system V_m (being of order 10^{-18} L) are mutually proportional. The modeled volume can be calculated using the following equation:

$$V_m = \frac{Number\ of\ Initiator\ Molecules}{[I]_0 \cdot N_A}$$

Where N_A is the Avogadro number and $[I]_0$ is initial concentration of initiator.

> *Note:*
> In the case of the FRP process, the small modeled volume can be a reason of the confined volume effect. See paragraph **7.c** for details.

b) Components Page

Amount of *Solvent* can be specified as volume or weight if the option *Sum of Components* was selected earlier on the page *General*.

Amounts of other components can be given using different qualities (*Volume, Weight, Moles*, or *Concentration*). When the total volume have to be calculated from amounts of components the necessary edit fields will appear in the form and they have to be filled with appropriate data.

In any case the molecular formulas have to be given in order to calculate components concentration and generate the MALDI spectrum.

Length means a number of chemical bonds which will be built into the main backbones of macromolecules formed; not used in current version.

In case of the CRP process, the *Activator* panel will be active and allows to specify an amount of the used activator and its oxidized form (present as an impurity or added intentionally). The amount of the *Oxidized* form has to be expressed in relation to the mole amount (or concentration) of the non-oxidized form.

c) Reactivities Page

This page allows editing the rate constants of all kinetics steps of the selected process. I, A, and B describe the initiator, monomer A, and monomer B, respectively. Ac and Bc stand for constitutional units A and B, respectively. The asterisk indicates active centers located on initiator molecule or on respective monomeric unit. X is a halogen radical and L is an activator molecule.

The user has to fill all edit fields, with the rate constants expressed in $mol \cdot L^{-1} \cdot s^{-1}$. The zero value is allowed, and it means that appropriate reaction is excluded from the modeled process.

The *Reactivities* page for LP processes (left) and FRP processes (right).

Note:

For FRP process some combinations of values of initiation and termination rate constants and small number of modeled initiator molecules give the effect of confined volume, e.g. acceleration of termination reaction. Such conditions are detected and the program warns the user. See also the paragraph **7.c**.

The *Reactivities* page for CRP processes.

The *Reactivities* page for RLP processes

d) Checking Points Page

Checking Points are the preselected time points at which simulation results are calculated, e.g. reagent concentrations, averaged DPs', molecular mass distribution, SEC plot etc. Up to one hundred points can be defined using the provided generator. The points can be distributed by equal distance in linear or logarithmic scale. The *Checking Points* can be also edited and/or corrected manually.
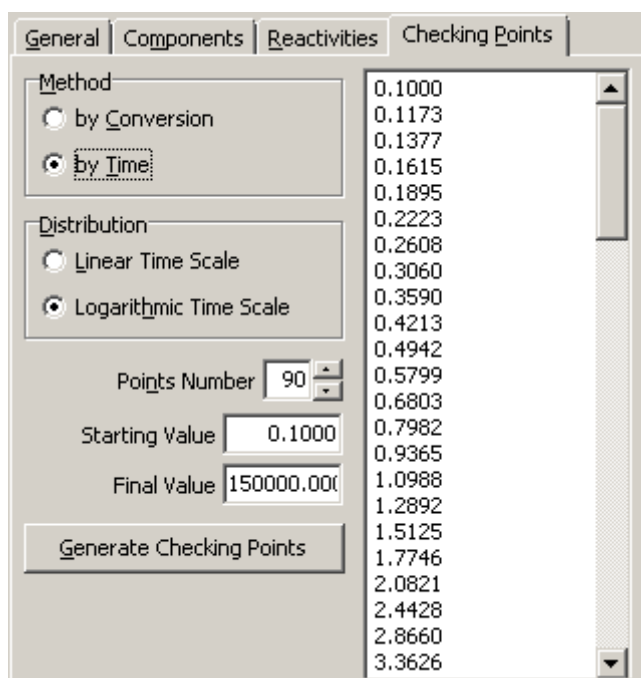
Note:
Defining the *Checking Points* by conversion was not yet implemented in the current version.

Note:
Pressing the *Accept & Exit* button causes immediate overwriting the actually used parameter file and leaves the editor. So that the loaded parameter set can be lost if not saved before by pressing *Save As...* button.

6. Simulation algorithms

The program uses three different Monte Carlo algorithms for modeling the polymerization processes: Gillespie's (D.T. Gillespie, *J. Phys. Chem.* **1977**, *81*, 2340), Szymanski (R. Szymanski, *e-Polymers* **2009**, 044; R. Szymanski, S. Sosnowski, *Macromol. Theory Simul.* **2012**, *21*, 411), and Sosnowski (S. Sosnowski, *Macromol. Theory Simul.* **2010**, *19*, 483; S. Sosnowski, *Polimery* **2011**, *56*, 549).

The validity of the Monte Carlo algorithms in these simulations was tested by comparing the results with the data obtained from the numerical integration of appropriate sets of differential equations. It should be noticed that not all parameters attainable by Monte Carlo modeling can be validated by numerical integration. In such cases, the validity was examined by comparing the results obtained by using all the three Monte Carlo algorithms mentioned. The fastest algorithms for each class of processes were implemented in the program.

The upper limit for the DP of simulated chains is equal 2^{15} (32767). Thus growth of the chains above the limit is forbidden, and they can terminate by disproportionation only. It can lead to incorrect results. Therefore the reasonable planned number-average DP should be limited to about 600. A higher DP can be applied when the expected dispersity index is low.

Note:

All not executed events involved the long chains are logged into the log file. Occurrence of a few such events during a simulation practically does not affect accuracy of the obtained results.

7. Modeled processes

Processes schemes shown can be simplified, for example to homopolymerization processes, by setting some rate constants or the monomer B quantity to zero. Also reactions can be excluded from the simulation by setting of their rate constants to zero.

Note:
Constant volume of polymerizing mixture was assumed.
Note:
Termination rate constants in FRP and CRP processes are used against the rules recommended by IUPAC. Please refer to paper R. Szymanski "On the Incorrectness of the Factor 2 in the Radical Termination Equation", *Macromol. Theory Simul*. **2011**, *20*, 8–12.

a) Living Polymerization

The Living Polymerization process consists of kinetics steps shown below. Example parameter sets are given in files "LP.msc" and "ROP.mcs".

$$
\begin{array}{ll}
\text{initiation} \left\{ \begin{array}{l}
I^* + A \xrightarrow{k(I^*,A)} IA^* \\
I^* + B \xrightarrow{k(I^*,B)} IB^*
\end{array}\right. \\[2em]
\text{propagation} \left\{ \begin{array}{l}
{\sim}A^* + A \xrightarrow{k(A^*,A)} {\sim}AcA^* \\
{\sim}A^* + B \xrightarrow{k(A^*,B)} {\sim}AcB^* \\
{\sim}B^* + A \xrightarrow{k(B^*,A)} {\sim}BcA^* \\
{\sim}B^* + B \xrightarrow{k(B^*,B)} {\sim}BcB^*
\end{array}\right. \\[3em]
\text{segmental exchange} \left\{ \begin{array}{l}
I^* + XAcM_m^* \xrightarrow{k(I^*,A_c)} IAcM_m^* + X^* \\
I^* + XBcM_m^* \xrightarrow{k(I^*,B_c)} IBcM_m^* + X^* \\
{\sim}M_nA^* + XAcM_m^* \xrightarrow{k(A^*,A_c)} {\sim}M_nAcAcM_m^* + X^* \\
{\sim}M_nA^* + XBcM_m^* \xrightarrow{k(B^*,B_c)} {\sim}M_nAcBcM_m^* + X^* \\
{\sim}M_nB^* + XAcM_m^* \xrightarrow{k(B^*,A_c)} {\sim}M_nBcAcM_m^* + X^* \\
{\sim}M_nB^* + XBcM_m^* \xrightarrow{k(B^*,B_c)} {\sim}M_nBcBcM_m^* + X^*
\end{array}\right.
\end{array}
$$
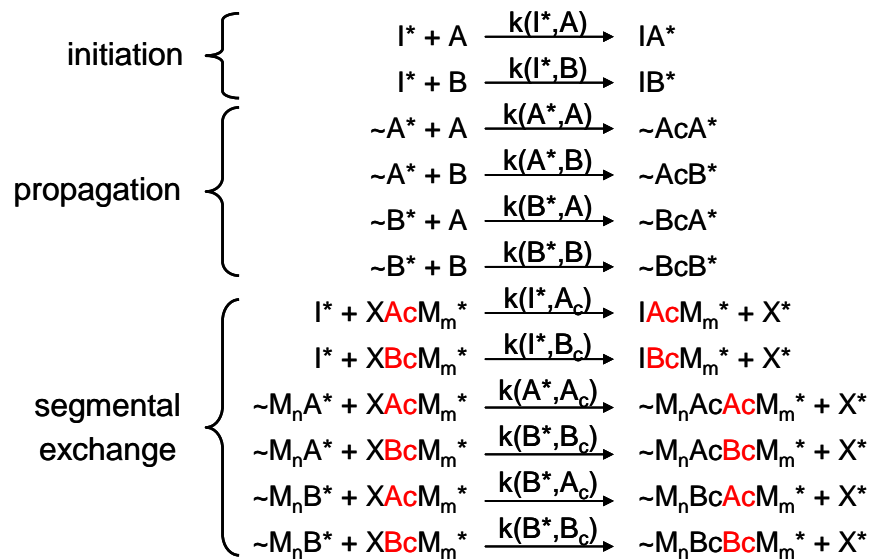
Where: M = Ac, Bc means a constitutional unit formed from monomer A or B, respectively; X = I, ~A, ~B where I stands for an initiator; ~A and ~B describe chains beginning with the initiator moiety and the end being the constitutional unit A or B, respectively. The asterisk indicates an active center. The red color was used for labeling of the constitutional units being attacked by an active center.

The Living Polymerization process proceeds with constant concentrations of active centers (called also "immortal" or "living" active centers). When only initiation and propagation reactions are considered then the scheme describes the ionic polymerization of vinyl monomers. The full scheme above applies to the Ring Opening Copolymerization (ROP) with segmental exchange reactions.

b) Reversible Living Polymerization (RLP)

All reactions considered in modeling of the RLP type copolymerization process are shown in the scheme below. An example parameter set is given in file "RLP.msc".

$$
\begin{array}{ll}
\text{initiation} \left\{
\begin{array}{l}
I^* + A \xrightarrow{k_p(I^*,A)} IA^* \\
I^* + B \xrightarrow{k_p(I^*,B)} IB^*
\end{array}
\right.
\end{array}
$$

$$
\text{propagation} \left\{
\begin{array}{l}
{\sim}A^* + A \xrightarrow{k_p(A^*,A)} {\sim}AA^* \\
{\sim}A^* + B \xrightarrow{k_p(A^*,B)} {\sim}AB^* \\
{\sim}B^* + A \xrightarrow{k_p(B^*,A)} {\sim}BA^* \\
{\sim}B^* + B \xrightarrow{k_p(B^*,B)} {\sim}BB^*
\end{array}
\right.
$$

$$
\text{depropagation} \left\{
\begin{array}{l}
IA^* \xrightarrow{k_d(IA^*)} I^* + A \\
IB^* \xrightarrow{k_d(IB^*)} I^* + B \\
{\sim}AA^* \xrightarrow{k_d(AA^*)} {\sim}A^* + A \\
{\sim}AB^* \xrightarrow{k_d(BB^*)} {\sim}A^* + B \\
{\sim}BA^* \xrightarrow{k_d(AA^*)} {\sim}B^* + A \\
{\sim}BB^* \xrightarrow{k_d(BB^*)} {\sim}B^* + B
\end{array}
\right.
$$
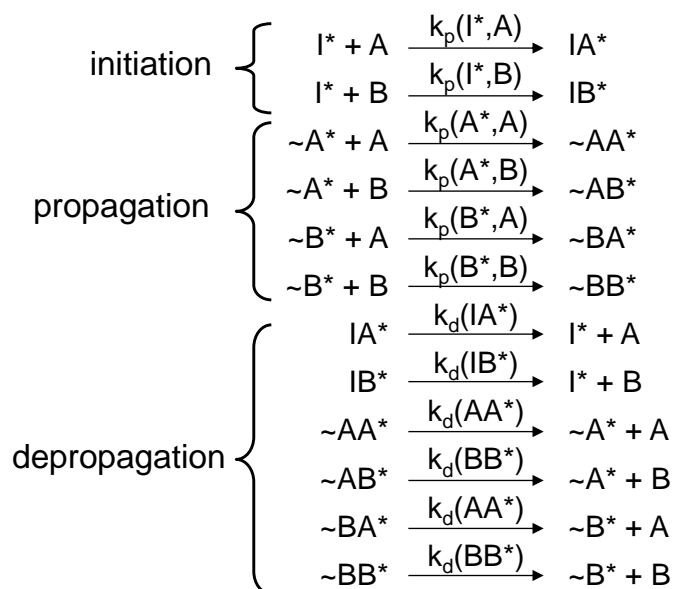
Where: A, B means a monomer molecules or constitutional unit, I stands for an initiator; ~A, ~B, ~AA, ~AB, ~BA, ~BB describe chains beginning with the initiator moiety and the end composed of appropriate constitutional units. The asterisk indicates an active center.
Above scheme apply to polymerization of several classes of cyclic monomers, especially trendy case is polymerization of L-dilactide, biodegradable and renewable cyclic ester.

Note:
Attaining the true equilibrium for the RLP needs very long time. Therefore it is recommended reducing the number of modeled chains below 5 000 or closing the *DP Distr.* window. Closing the *Chains* tab and low value of the monomer/initiator ratio will also increase the speed. Future releases would probably reduce the speed problem of the simulation.

c) Controlled Radical Polymerization (CRP)

The scheme below shows the kinetics steps in modeling the copolymerization of the CRP type. An example parameter set is given in file "CRP.msc".

activation - deactivation

$$I^\bullet + LX \underset{k_a(I^\bullet)}{\overset{k_{da}(I^\bullet)}{\rightleftarrows}} IX + L$$

$$\sim A^\bullet + LX \underset{k_a(A^\bullet)}{\overset{k_{da}(A^\bullet)}{\rightleftarrows}} \sim AX + L$$

$$\sim B^\bullet + LX \underset{k_a(B^\bullet)}{\overset{k_{da}(B^\bullet)}{\rightleftarrows}} \sim BX + L$$

initiation

$$I^\bullet + A \xrightarrow{k_i(I^*,A)} IA^\bullet$$

$$I^\bullet + B \xrightarrow{k_i(I^*,B)} IB^\bullet$$

propagation

$$\sim A^\bullet + A \xrightarrow{k_p(A^*,A)} \sim AA^\bullet$$

$$\sim A^\bullet + B \xrightarrow{k_p(A^*,B)} \sim AB^\bullet$$

$$\sim B^\bullet + A \xrightarrow{k_p(B^*,A)} \sim BA^\bullet$$

$$\sim B^\bullet + B \xrightarrow{k_p(B^*,B)} \sim BB^\bullet$$

recombination

$$\sim A^\bullet + \sim A^\bullet \xrightarrow{k_r(A^*,A^*)} \sim AA\sim$$

$$\sim A^\bullet + \sim B^\bullet \xrightarrow{k_r(A^*,B^*)} \sim AB\sim$$

$$\sim B^\bullet + \sim B^\bullet \xrightarrow{k_r(B^*,B^*)} \sim BB\sim$$

disproportionation

$$\sim A^\bullet + \sim A^\bullet \xrightarrow{k_d(A^*,A^*)} \sim A' + \sim A''$$

$$\sim A^\bullet + \sim B^\bullet \xrightarrow{k_d(A^*,B^*)} \sim A' + \sim B'' \ (\sim A'' + \sim B')$$

$$\sim B^\bullet + \sim B^\bullet \xrightarrow{k_d(B^*,B^*)} \sim B' + \sim B''$$
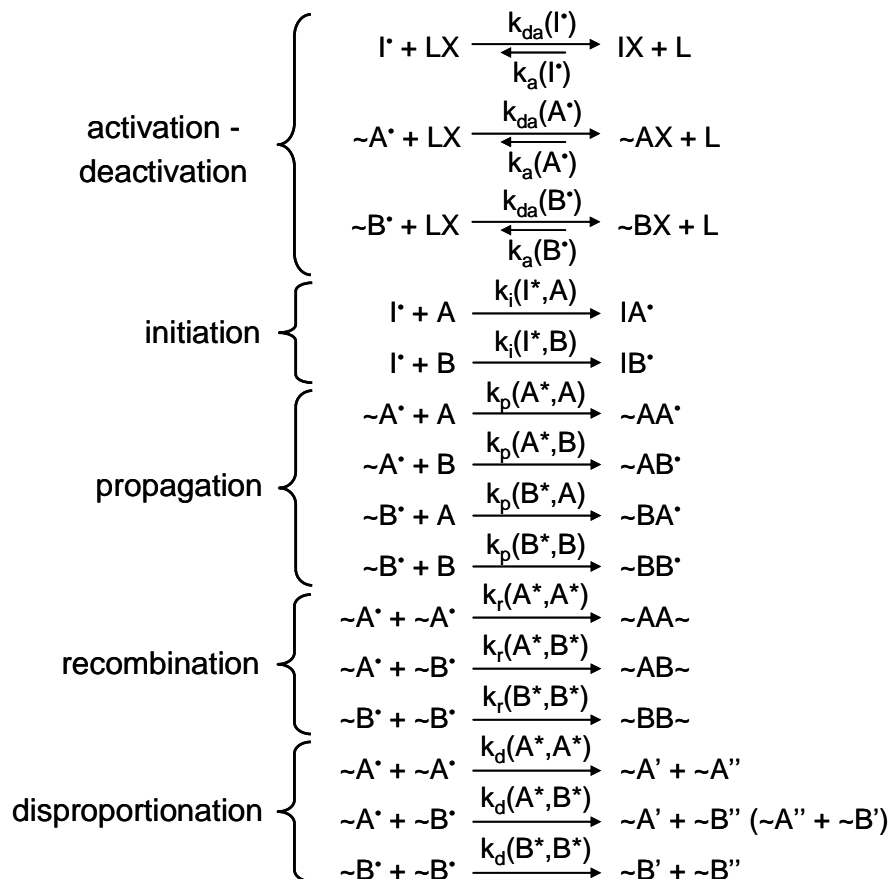
Where $L = MtX_n$ is an activator; $Mt = Cu$, Fe, Ru, etc...; $X = Cl$, Br; I, A, and B mean initiator, monomer A, and monomer B molecules, respectively. ~A and ~B design a chain fragment beginning with the initiator moiety and constitutional unit A or B at the end. Dots indicate the radical functionality. A' and B' describe terminated chains with a double bond formed by hydrogen abstraction, A" and B" describe chains with attached a hydrogen atom.

d) Radical Polymerization (FRP)

All reactions considered in modeling of the FRP type copolymerization process are shown in the scheme below. An example parameter set is given in file "FRP.msc".

decomposition $\{$	$I_2 \xrightarrow{k_{dec}}$	$2f\ I^{\bullet}$
initiation $\{$	$I^{\bullet} + A \xrightarrow{k_i(I^*,A)}$	$IA^{\bullet}$
	$I^{\bullet} + B \xrightarrow{k_i(I^*,B)}$	$IB^{\bullet}$
propagation $\{$	$\sim A^{\bullet} + A \xrightarrow{k_p(A^*,A)}$	$\sim AA^{\bullet}$
	$\sim A^{\bullet} + B \xrightarrow{k_p(A^*,B)}$	$\sim AB^{\bullet}$
	$\sim B^{\bullet} + A \xrightarrow{k_p(B^*,A)}$	$\sim BA^{\bullet}$
	$\sim B^{\bullet} + B \xrightarrow{k_p(B^*,B)}$	$\sim BB^{\bullet}$
recombination $\{$	$\sim A^{\bullet} + \sim A^{\bullet} \xrightarrow{k_r(A^*,A^*)}$	$\sim AA\sim$
	$\sim A^{\bullet} + \sim B^{\bullet} \xrightarrow{k_r(A^*,B^*)}$	$\sim AB\sim$
	$\sim B^{\bullet} + \sim B^{\bullet} \xrightarrow{k_r(B^*,B^*)}$	$\sim BB\sim$
disproportionation $\{$	$\sim A^{\bullet} + \sim A^{\bullet} \xrightarrow{k_d(A^*,A^*)}$	$\sim A' + \sim A''$
	$\sim A^{\bullet} + \sim B^{\bullet} \xrightarrow{k_d(A^*,B^*)}$	$\sim A' + \sim B''\ (\sim A'' + \sim B')$
	$\sim B^{\bullet} + \sim B^{\bullet} \xrightarrow{k_d(B^*,B^*)}$	$\sim B' + \sim B''$
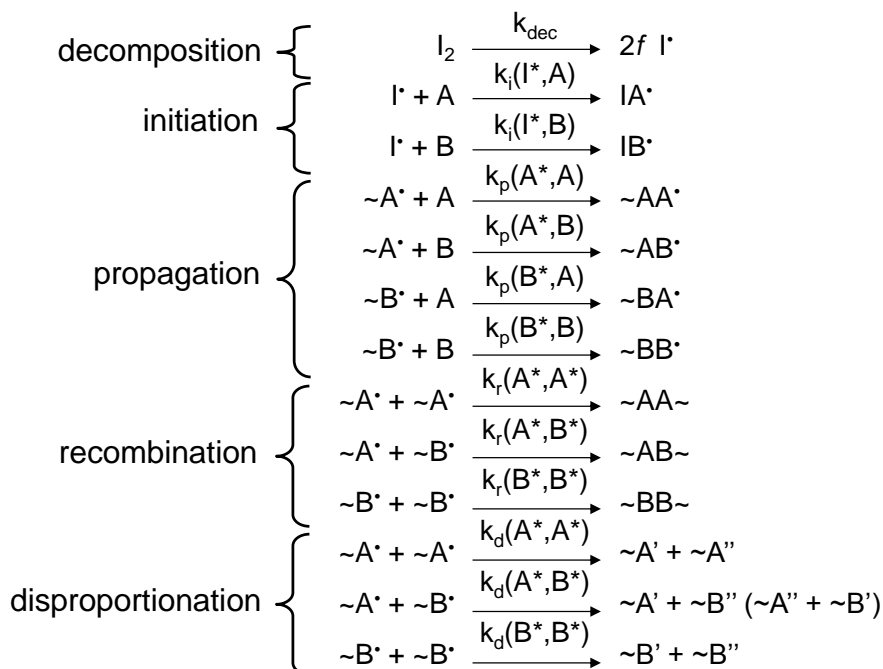
Where: f – initiator efficiency coefficient, all other used symbols are the same as in CRP scheme.

Note:
For the FRP process, some combinations of values for initiation and termination rate constants and small number of modeled initiator molecules, give the effect of the confined volume. Simply speaking, the concentration of instantly generated radicals is higher than in bulk and therefore termination reactions are accelerated. In result, propagation rate is lower in comparison to processes carried in large scale. Such conditions are detected by the program and it warns the user. The effect can be avoided using different strategies:
- by increase of number of modeled chains
- by increase of initiation rate constants and/or initiation efficiency coefficient
- by decrease termination rate constant
- by dilution of polymerizing mixture components