Supporting Information

Practical Prediction of Heteropolymer Composition and Drift

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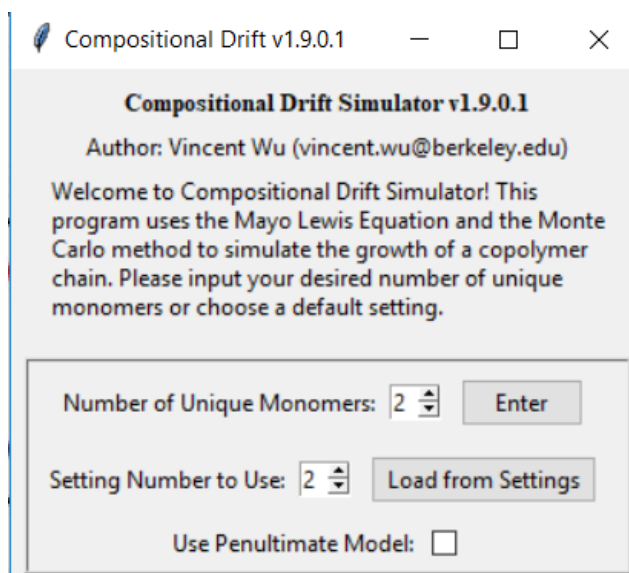
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Compositional Drift Program Tutorial

Introduction

Compositional Drift is a program which simulates RAFT polymerization through Monte Carlo simulations using the Mayo Lewis Equation. This is a guide on how to use the program.

Simulation

After launching the .exe file, you will be prompted to input some preliminary options:

Number of Unique Monomers: Input the number of different monomers you want to simulate in your polymer system. Ignore this if you are loading from a saved state.

Setting Number to Use: If you have saved a polymer system already (see **Saving Input Settings**), use this to load the saved file. Ignore this if you are using the previous setting.

Penultimate Model: Check this option if you want to use the penultimate model (only for 2-monomer systems).

Press **Enter** if you want to proceed through the Number of Unique Monomers input. Press **Load from Settings** if you want to load a saved state.

After clicking "Enter", the program will prompt for further inputs:

Here are the default inputs. To change default settings, see **Using the Configuration File**. The inputs are split into three columns. Column 1 requests information about the reaction conditions and the polymer visualization. Column 2 allows you to change the displayed graphs. Column 3 requests information about the monomer reactivities and initial monomer ratios. Below is a detailed description of each input.

Monomer Pool Size: This is the total amount of monomers in your reaction. A larger pool size means more chains will be generated, and in turn collapses the randomization into a fixed distribution. A smaller pool size results in a less accurate simulation but takes less time to simulate. You can qualitatively optimize this number by starting at a low pool size, and incrementally increase it until you see little or no change in your resulting monomer distribution. Number of chains generated is determined by dividing the Monomer Pool Size with the Number Average DP.

Number Average DP: This gives the idealized length of the polymers synthesized at 100% conversion. For RAFT, this is the monomer to RAFT agent ratio, and for ATRP and NMP it is the monomer to initiator ratio. Note that the number average DP in the output of the simulation will also be determined by the Percent Conversion

Percent Conversion: This allows you to control the conversion of the monomer pool.

Polymers to Show: This setting does not affect the simulation. It allows you to control the number of polymers shown in the visualization.

Graph 1 Type: Once the simulation has finished, the program will display two graphs which show information about the polymer composition. Graph 1 Type selects the kind of graph which will be displayed on the left-side graph. There are currently six different graph types (see **Results Analysis** for more information). If you only want to show one graph, you can select the "None" option.

Graph 2 Type: Similar to Graph 1 Type, except that it controls the type of graph displayed on the right-hand side.

Histogram 1 Monomer: See **Graph Types**

Histogram 2 Monomer: See **Graph Types**

% Monomer: Allows you to set the initial monomer fractions. Note that the sum of all fractions needs not be 1; the program will normalize the entered values to the fractions of their sum.

Reactivity Ratio X: In a two-monomer system, this value is the reactivity ratio r_x of monomer x in the polymer system, as described in the paper

$$r_x = \frac{k_{xx}}{k_{xy}}$$

X-Y Reactivity: For 3- or more monomer systems, these values will show instead of Reactivity Ratio X. These values describe how likely it is for monomer Y to bind to a polymer chain ending with monomer X. All possible reactivities corresponding to the bonding combinations will be listed; for example, in a 3-monomer system, there will be 9 entries.
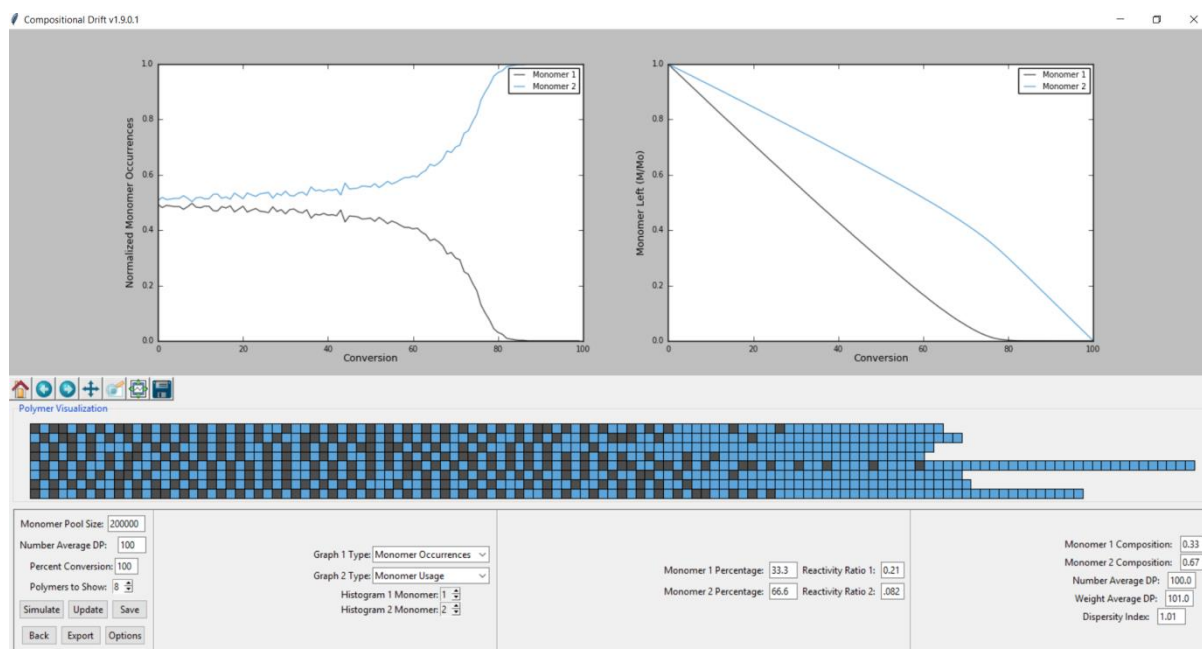
X-Y-Z Reactivity: When using the penultimate model, these values will show instead of Reactivity Ratio X. The penultimate model considers both the last (ultimate) and second to last (penultimate) monomers in a growing polymer chain when determining the probability of a monomer binding to that chain. X-Y-Z Reactivity is the probabilistic weight that monomer Z binds to a polymer chain with a penultimate monomer X and an ultimate monomer Y.

In this example, we will simulate a 2-monomer system of acrylic acid (AA) and styrene (STY). I will designate AA as Monomer 1 and STY as Monomer 2. Thus, my reactivity ratios r_1 and r_2 are 0.27 and 0.73, respectively. I also want to arbitrarily have twice as much AA (Monomer 1) as STY (Monomer 2) in my initial starting reaction. I fill out the entries accordingly:

With all the necessary information inputted, I can now run the simulation by pressing the **Simulate** button. The program will run a series of simulations and then graph and visualize the results. Details on the simulation process may be found in **Algorithm Run-through**.
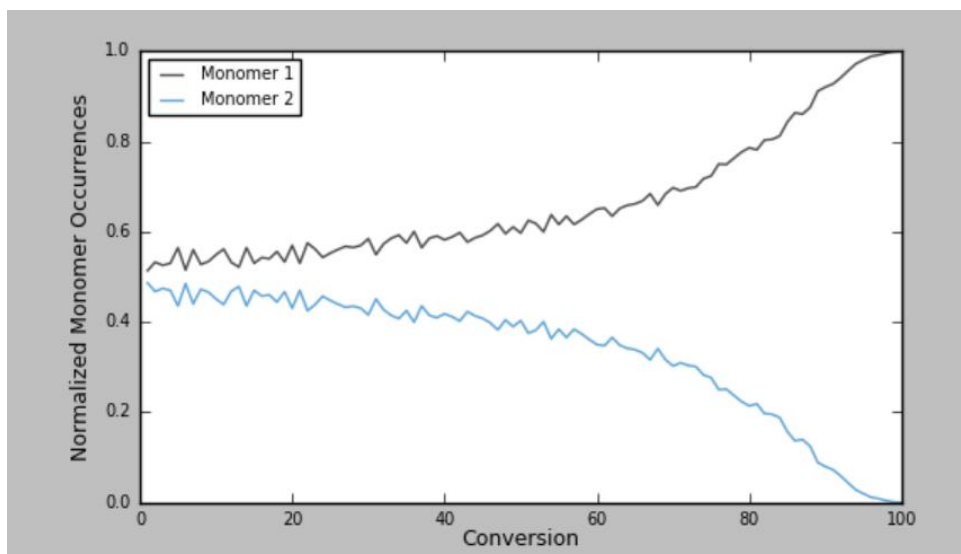
Results Analysis

Polymer Visualization: This is a qualitative output which gives the user a rough but useful visualization of what the average simulated polymer looks like. Each row of colored squares is a randomly simulated polymer. Each square is color coded with a monomer type, as described in the legend.
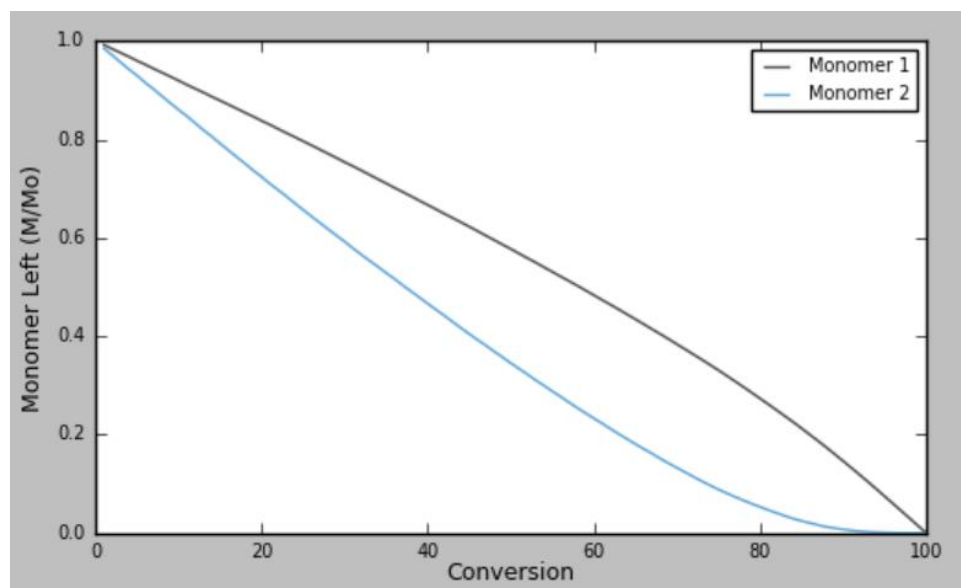
Monomer X Composition: A fourth column is added on the rightmost side detailing the average composition of all simulated polymers. When Percent Conversion is set to 100, the ratio of these values should match the ratios of the Monomer X Ratio. You can confirm this in the example above. When the conversion is less than 100, the composition will vary according to the compositional drift of the polymer.

Graphs: The program plots six different graphs. Although only two graphs may be shown at a time, you can switch which graphs are displayed by selecting them from the dropdown menus in "Graph X Type" and pressing the **Update** button. This updates the graphs without rerunning the simulations. Additionally, pressing the **Export** button will export all the data tables used in each of the six graphs into an excel file named graphData.xlsx, located in the same directory as the program. Below is a detailed description of each graph type.
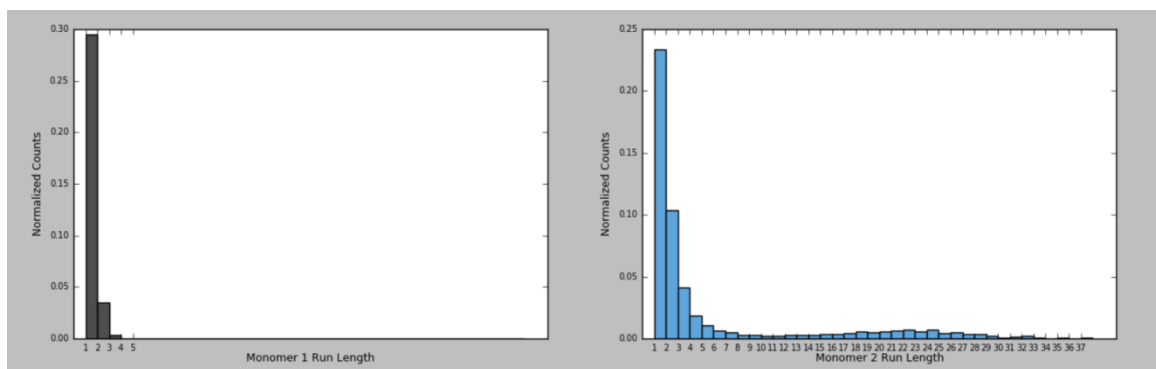
Monomer Occurrences: For each unique monomer X, this plots the relative incorporation of monomers, as a function of conversion.

Percentage Monomer: For each unique monomer X, this plots the relative amount of unreacted monomer X remaining in the pool as a function of conversion. The amount of monomer X remaining is expressed as a ratio, M/M_0, where M is the instantaneous amount of X remaining and M_0 is the starting amount of X.

Monomer Separation: For a given monomer X, this plots the normalized average separation contributed by each block size. For example, 10 isolated blocks of monomer X in a polymer would give 10*1 = 10 units of separation, but 10 homodyads of monomer X would give 10*2 = 20 units of separation. The "Histogram X Monomer" scrollbox allows you to select which monomer to graph.

Hydrophilic/ Hydrophobic Blocks: Monomers may be assigned as hydrophobic or hydrophilic in the "Options" button. This plots the separation of hydrophobic and hydrophilic run lengths using the same method as "Monomer Separation".

Algorithm Run-Through

This section gives a run through on how the program simulates RAFT polymerization.

The algorithm cycles through the three phases of polymerization: initiation, propagation, and termination. Ideal RAFT polymerization is assumed: all polymer chains initiate simultaneously and do not die until either the reaction is stopped (Conversion <100) or all monomers in the pool are used up (Conversion = 100). . The Mayo Lewis Equation/ Penultimate Model is used to determine the probabilities of each unique monomer bonding to a propagating polymer chain.

Initiation

The algorithm first calculates the total number of polymers to simulate

The total number of polymers simulated N is determined by dividing the Monomer Pool Size S by R, the Number Average DP:

$$N = \frac{S}{R}$$

The algorithm then initiates N polymers through the following method:

2-Monomer System (including Penultimate Model): The instantaneous Mayo Lewis Equation is used to determine the probability that monomer x will initiate the chain:

$$F_1 = 1 - F_2 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

F_1 and F_2 are the respective fraction of chains that start with monomers 1 and 2, r_1 and r_2 are the respective reactivity ratios, and f_1 and f_2 are the respective initial pool monomer fractions. A weighted random selector then chooses whether monomer 1 or 2 initiates the polymer chain using F_1 and F_2 as the corresponding weights w_1 and w_2. The chosen monomer is then taken out of the monomer pool, changing the values of f_1 and f_2.

This process is repeated *N* times until all polymers to be simulated have been initiated with one monomer.

n-Monomer System, n > 3: n-monomer systems use a simpler choosing method; the weight w_x given to each monomer x is equal to its pool monomer fraction f_x. A weighted random selector then uses these weights to choose the initiating monomer, which is taken out of the monomer pool.

This process is repeated *N* times until all polymers to be simulated have been initiated with one monomer.

Propagation

To model RAFT polymerization, the algorithm randomly adds monomers to polymers. The specificmonomer to be added is determined in the following ways.

Mayo Lewis Model: The weights w_x of each monomer is determined through the following equation,

$$w_x = f_x r_{xy}$$

where r_{xy} is the relative probability of monomer x adding onto a polymer chain ending in monomer y. In the case of a 2-monomer system, r_{xy} is simplified to the reactivity ratio r_x, and hetero-polymerization constants are assumed to be 1. A weighted random selector then uses these weights to choose which monomer will be added to the chain, and removes that monomer from the pool..

Penultimate Model: This model is almost identical to the Mayo Lewis Model; it only differs in that the reactivity ratio used is r_{xyz}, which gives the relative probability of monomer x reacting to a polymer with an ultimate monomer y and a penultimate monomer z.

Termination

As the algorithm models a living polymerization, termination is completely dependent on the inputted "Percent Conversion" value. At 100% conversion, the maximum number of monomers are used by the reaction and the chains stop growing. If a conversion less than 100% is added, it stops at that specific monomer conversion.

Using the Configuration File

A config file, called config.txt, is generated when you first run the program and is located in the same directory as the .exe file. Subsequent uses of the program read this file to generate default input values. The file can be edited to change default settings. Deleting this file will cause the program to generate and read a new default config file. The following table lists which default values can be changed in the file.

Name	Description	Default
Number of Unique Monomers	Value of Number of Unique Monomers input	2
Number of Simulations	The number of times the entire pool is simulated;	1

	deprecated	
Number of Polymers to Show	The number of rows shown in polymer visualization	8
Graph 1 Type	Value of Graph1 Type input	0
Graph 2 Type	Value of Graph 2 Type input	1
Histogram 1 Monomer	Value of Histogram 1 Monomer input	1
Histogram 2 Monomer	Value of Histogram 2 Monomer input	2
Percentage to Analyze for Histogram	Ratio from 0 to 1 of amount of polymer to analyze for histograms; deprecated	1
Monomer Pool Size	Value of Monomer Pool Size input	200000
Number average DP	Value of number average DP	100
Hydrophobicity	0: Sets all monomers to hydrophillic 1: Sets all monomers to hydrophobic	1
Default Setting	Deprecated	1
Monomer Cap	Limit to how large the monomer pool size can be; used to prevent overly long simulation times	5000000
Dyad	0: Will not visualize homodyads 1: Will visualize homodyads with different colors	0
Style	Style of plots; see Options for complete list	Classic
Legend	0: Turns legend off 1: Displays legend	1
Percent Conversion	Value of Percent Conversion input	100
Maintain	0: Removes monomers from pool during simulation 1: Maintains the same initial pool composition; monomers are not removed from pool	0
Color1	Graph color 1	#4D4D4D
Color2	Graph color 2	#5DA5DA
Color3	Graph color 3	#F15854
Color4	Graph color 4	#DECF3F
Color5	Graph color 5	#60BD68
Color6	Graph color 6	#F17CB0
Color7	Graph color 7	#B276B2
Color8	Graph color 8	#FAA43A

Saving Input Settings

The "Save" button on the interface will generate a save file which saves the polymer system. The values in the third column (Monomer X Ratio and Reactivity Ratio X/ X-Y/ X-Y-Z) will be stored in a file called stateN.txt, with N being the state identifier. To load a saved state, enter your desired state in the initial screen and pressed "Load from Settings". You can view and edit the .txt state files, which are located in the same directory as the .exe file.

Program File Outputs

In addition to the graphData excel file created when the "Export" button is pressed, the program will also automatically generate several more files.

polymerArray.txt - This file contains a list of all polymers generated by the simulation.

polymerImage.txt – This is a .jpg file of the polymer visualization.