

## Kinetic Studies and Monte Carlo Simulations of radical Ter- and Tetrapolymerisations

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### Abstract

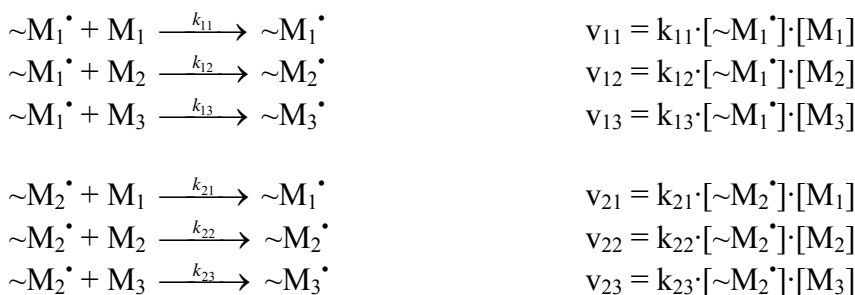
Radical polymerisation of three and more monomers with different reactivities can lead to polymers with extremely different copolymer compositions during the polymerisation process. A Monte Carlo simulation method will be presented to describe the copolymer composition dependent on the conversion, the integral and differential copolymer mixture, the comonomer conversions and sequence distributions of the comonomers. The simulations were used to develop semibatch monomer addition policies. Using the semibatch process chemically uniform polymers were obtained over a wide conversion range. The results were verified by experimental investigations of ter- and tetrapolymerisations of donor-, acceptor-, and neutral monomers in batch and semibatch experiments.

Keywords: radical polymerization, terpolymerization, tetrapolymerization, semibatch, monte carlo simulation

### 1. Theory and Computational methods

#### *Analytical Model*

In the analytical model, 9 propagation reactions are required to describe the polymerization process in case of terpolymerization (scheme 1) and 16 in case of tetrapolymerization.





Scheme 1: terpolymerization propagation reactions ( $\sim M_i^\bullet$  = macroradical,  $M_i$  = monomer,  $k_{ij}$  = propagation rate constant,  $v_{ij}$  = propagation rate ( $ij = 1, 2, 3$ ))

The  $r$ -values of the corresponding binary systems are defined as ratio of the propagation rate constants (Eq. 1).

$$r_{ij} = k_{ij} / k_{ji} \quad (ij = 1, 2, 3) \quad (1)$$

This reactivity ratios can be determined from copolymerization experiments using linearization [1] or optimization methods [2, 3, 4].

Assuming steady-state conditions ( $v_{ij} + v_{ik} = v_{ji} + v_{ki}$ ), the Alfrey-Goldfinger equation (Eq. 2) was derived [5]. The terpolymerization equation can be used for calculation of the terpolymer composition ( $m_1, m_2, m_3$ ) from the composition feed ( $M_1, M_2, M_3$ ) at low conversion. By analytical integration of this equation, the instantaneous and global composition of the terpolymer as a function of the conversion is available.

$$\begin{aligned}
 m_1 : m_2 : m_3 &= [M_1] \cdot \left( \frac{[M_1]}{r_{31} \cdot r_{21}} + \frac{[M_2]}{r_{21} \cdot r_{32}} + \frac{[M_3]}{r_{31} \cdot r_{23}} \right) \cdot \left( [M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} \right) \\
 &: [M_2] \cdot \left( \frac{[M_1]}{r_{12} \cdot r_{31}} + \frac{[M_2]}{r_{12} \cdot r_{32}} + \frac{[M_3]}{r_{32} \cdot r_{13}} \right) \cdot \left( \frac{[M_1]}{r_{21}} + [M_2] + \frac{[M_3]}{r_{23}} \right) \\
 &: [M_3] \cdot \left( \frac{[M_1]}{r_{31} \cdot r_{21}} + \frac{[M_2]}{r_{23} \cdot r_{12}} + \frac{[M_3]}{r_{13} \cdot r_{23}} \right) \cdot \left( \frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}} + [M_3] \right) \quad (2)
 \end{aligned}$$

In special cases of the terpolymerization special equations were also developed: without homopolymerization of one monomer ( $k_{33} = 0$ , HAM-equation) [6], without any homopolymerization ( $k_{11} = k_{22} = k_{33} = 0$ , Braun's equation) [7] and terpolymerization with restricted reaction possibilities ( $k_{11} = k_{13} = k_{31} = 0$ , equation from our group) [10]. The kinetic equations related to the tetrapolymerization were derived by Chen et al. [8]. All this equations describe the polymerization in a continuous and macroscopic manner.

*Monte Carlo Model*

For the conversion dependent simulation of these ter- and tetrapolymerizations, the  $r$ -values of the corresponding binary systems and the initial molar compositions of the reaction mixture are required.

The applied Monte Carlo simulation executes a defined total number of monomer molecules of  $n_{\text{total}}=1 \cdot 10^8$  that are distributed among the given monomer species according to the initial molar composition of the feed (Eq. 3).

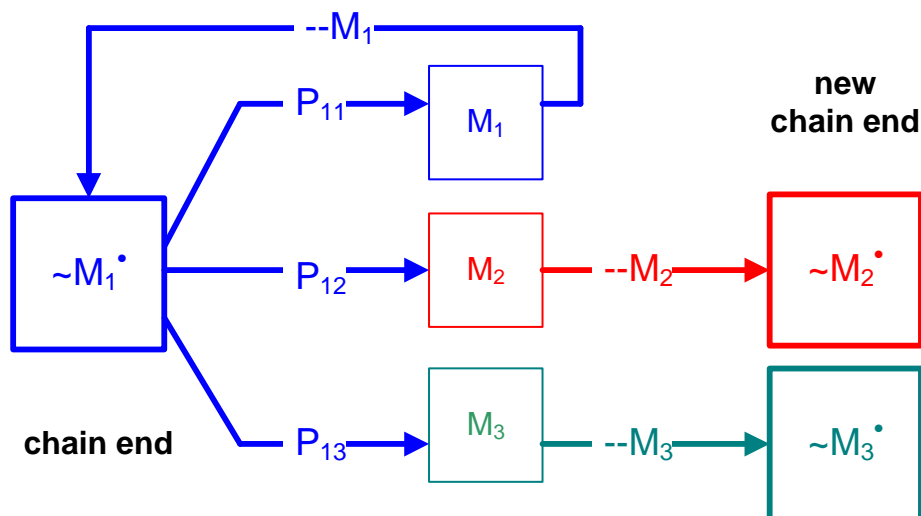
$$n_{i,0} = \frac{[M_i]_0}{n_{\text{total}}} \quad (3)$$

with:  $n_{i,0}$  = initial number of monomer molecules  
 $[M_i]_0$  = monomer concentration in the feed

The simulation is started with a randomly selected monomer at the chain end. Every single step in this Monte Carlo simulation represents the incorporation of one monomer unit into the polymer based upon the effective reaction probabilities for the given reaction conditions (Fig. 1). The reaction probabilities (Eq. 4, 5) depend only on the current number of molecules ( $n_i, n_j$ ) and the given  $r$ -values ( $r_{ij}$ ). One monomer is consumed and the chain end changes in the case of a copolymerization step.

$$P_{ij} = \frac{n_i}{n_i + \sum_{j \neq i} \frac{n_j}{r_{ij}}} \quad \text{homopolymerization step (i=j)} \quad (4)$$

$$P_{ij} = \frac{n_j}{n_i r_{ij} + r_{ij} \sum_{j \neq i} \frac{n_j}{r_{ij}}} \quad \text{copolymerization step (i \neq j)} \quad (5)$$



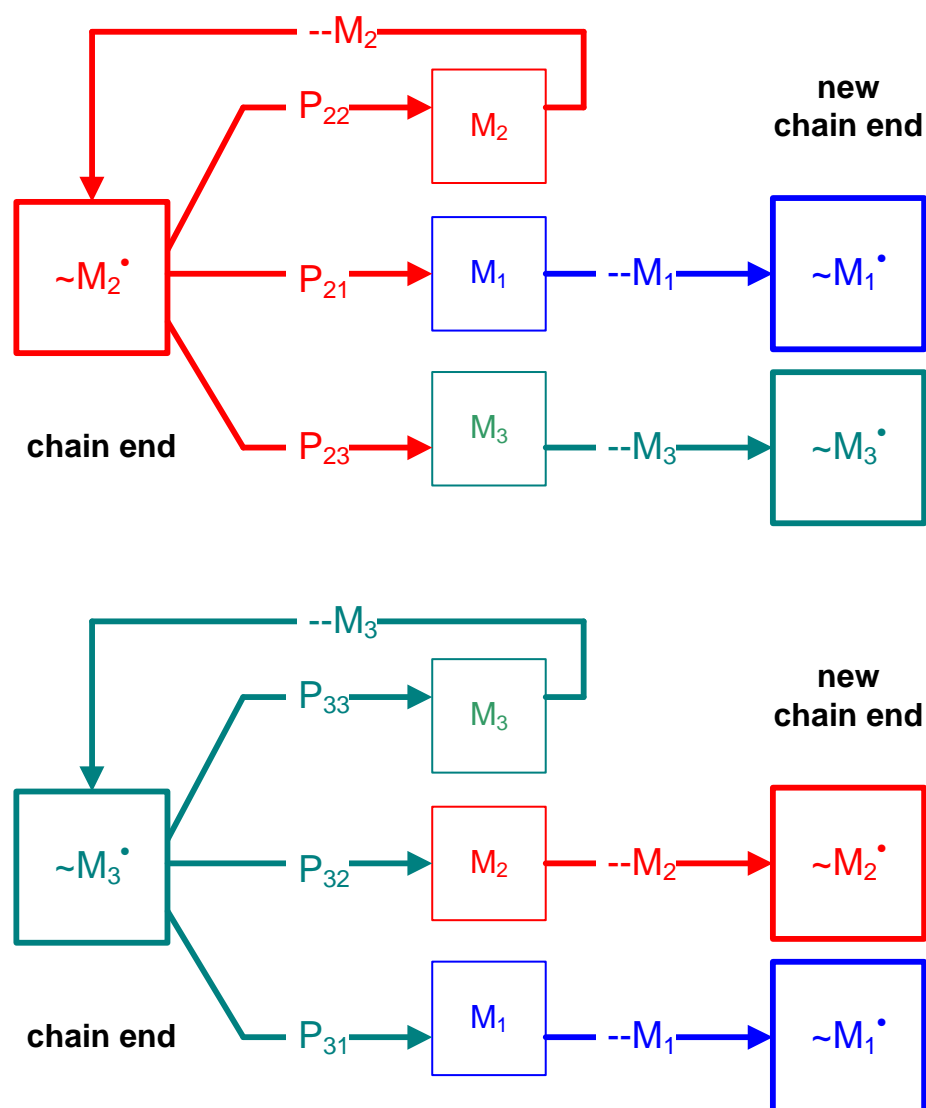


Figure 1: Monte Carlo step: reaction pathway for incorporation of one monomer unit into the polymer

The Monte Carlo simulation procedure is executed by the mcCopolymer program, programmed in C++ with a Tcl-interface, and employing the Mersenne Twister high-level 623-dimensionally equidistributed uniform pseudo-random number generator [9]. One needs approximately 15 s for the calculation of a terpolymerization up to 0.95 conversion on a AMD Opteron 8216 CPU.

The results of the simulation are tracked at steps of 0.01 of total monomer conversion and are analyzed in respect to the integral composition of the polymer, composition of the monomer feed mixture and conversion of the given monomers. By comparison with the result of the preceding analysis step, the differential polymer composition is calculated. Moreover, analysis of the sequence of monomer units provides information about the numbers for each sequence length of all involved monomers at every analysis step.

The Monte Carlo method enables the comprehensive simulation of ter- and tetrapolymerizations in an extremely straightforward manner. In our simulations monomer molecules and not the monomer concentrations are included in contrast to the analytical model. Therefore the development of semi-batch monomer addition policies is more easily to implement. The number of monomer molecules was increased at defined total monomer conversion.

The Polymerization process is described as a function of the polymerization rate and not as a function of time.

## 2. Experimental section

### *Materials*

Methyl methacrylate/MMA (Fluka) and styrene/S (BASF) were distilled under reduced pressure. Acrylonitrile/AN was distilled at ambient pressure. N-phenylmaleimide was recrystallized from methanol. All other chemicals were used without further purification.

### *Polymerization*

All reactions were carried out under N<sub>2</sub>-atmosphere under a nitrogen atmosphere at 60 °C with AIBN (0.04 mol/L) as initiator in 1,4-dioxane. The overall monomer concentration was 6.6 mol/L. To stop the reaction, the samples were cooled rapidly. The polymer was obtained by precipitation in a tenfold volume excess of methanol. After drying the product in a vacuum oven at 50 °C, the conversion was determined gravimetrically. For elemental analysis the product was dissolved in THF, reprecipitated in methanol and dried again.

### *Elemental Analysis*

The determination of copolymer composition was carried out by means of an elemental analysis system vario-EL from Elementar Analysensysteme. This instrument works in the independent operation modes CHN and O. For determination of the elemental composition three measurements were carried out for each sample.

## 3. Results and Discussion

### *Terpolymerization*

According to the polarity of their double bonds, given by their  $e$ -value, monomers can be divided into donor (D), acceptor (A) and neutral (N) monomers. The terpolymer MMA/S/NPI is an N/D/A-system, containing styrene as a strong donor and NPI as a strong acceptor monomer. Different monomer compositions were polymerized for 6 hours. The time dependent terpolymer composition has been determined from the elemental analysis data.

For the conversion dependent simulation of this polymerization experiments the  $r$ -values of the corresponding binary systems are required. All values are published from our group [10] and are summarized in table 1.

monomers	MMA	S	NPI	AN
MMA	---	0.42	1.41	1.13
S	0.52	---	0.03	0.41
NPI	0.19	0.10	---	3.43
AN	0.15	0.04	2.05	---

Table 1: copolymerization ratios

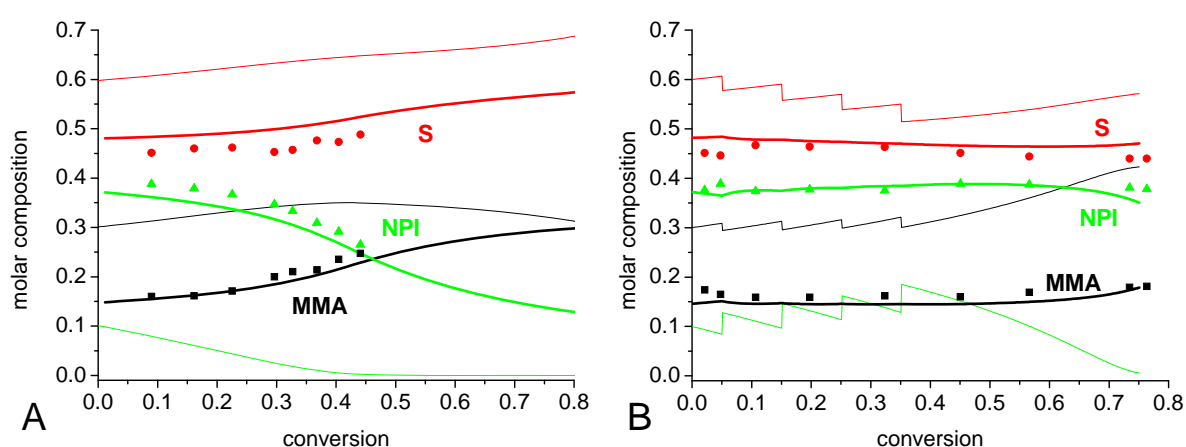


Figure 2: Terpolymerization of MMA/S/NPI (0.3/0.6/0.1),  
 symbols: experimental polymer composition from elemental analysis  
 broad lines: simulated polymer composition  
 thin lines: residual monomer composition  
 A: batch experiment  
 B: semibatch experiment

Figure 2-A presents the comparison of conversion dependent experimental and simulated polymer compositions. The agreement between the experimental polymer compositions and the results from the Monte Carlo simulation is very good. The calculated residual NPI content shows, that the used NPI is consumed completely at 45 % overall monomer conversion. At higher conversions, only a copolymerization of styrene and MMA occurs.

Chemically uniform products formed by radical multicomponent polymerization can only be obtained under semi-batch conditions. The Monte Carlo method can be used to develop semi-batch monomer addition policies for the synthesis of chemically uniform polymers.

The stepwise monomer addition (4 steps, monomer NPI) was calculated and experimentally verified for the terpolymerization of MMA/S/NPI. Chemically uniform polymers were obtained over a wide conversion range.

*Tetrapolymerization*

For the examination of the tetrapolymerization we extended the terpolymer system of MMA/S/NPI by acrylonitrile (AN) that acts as additional acceptor monomer. Using the reactivity ratios from table 1, the conversion dependent residual monomer and copolymer composition of this system were calculated with the Monte Carlo simulation. The results of the simulation and the experimentally determined tetrapolymer composition are shown in Fig. 3-A. The semibatch experiment (Fig. 3-B) also leads to chemically uniform polymers. The good agreement of experiment and simulation shows the universal applicability of our simulation method.

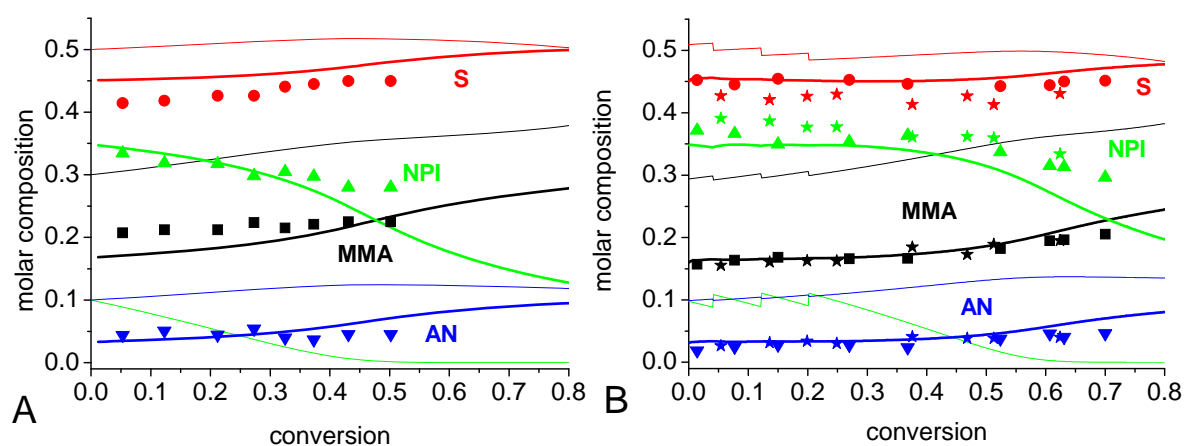


Figure 3: Tetrapolymerization of MMA/S/NPI/AN (0.3/0.5/0.1/10),  
 symbols: experimental polymer composition from elemental analysis  
 broad lines: simulated polymer composition  
 thin lines: residual monomer composition  
 A: batch experiment  
 B: semibatch experiment (2 experiments, test of the reproducibility)

**4. Conclusion**

Comparison between the experimental results and the Monte Carlo simulation for radical polymerisations of donor, acceptor and neutral monomers with highly different reactivities, demonstrates the precision of the presented Monte Carlo model for terpolymerizations and tetrapolymerizations. If the  $r$ -values of the binary subsystems are correctly known, copolymer compositions, comonomer compositions and monomer conversions can be described in good agreement with experimental data up to high conversions. The calculated, differential copolymer compositions and sequence distributions lead to a better understanding of the correlations between polymer structure and feed composition for multicomponent polymerizations. Furthermore, these Monte Carlo simulations are a powerful tool for the development of semi-batch monomer addition policies for the synthesis of chemically uniform polymers.

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