

Application of Monte Carlo methods for modelling of polymerization reactions

Kristina Platkowski, Karl-Heinz Reichert*

Technische Universitaet Berlin, Institut fuer Technische Chemie, Strasse des 17, Juni 135, 10623 Berlin, Germany

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Abstract

Monte Carlo methods were tested with respect to their potentials and limitations for the modelling of the kinetics of polymerization reactions and especially with regard to the various distributions of the final product. Presented here is a model concept based on a critical comparison of algorithms already published in the literature. The concept can be used generally and guarantees a high level of formalism and, therefore, a minimum developing time. It is based on the simulation of the time behaviour of molecules in small volume increments of the reaction mass and permits the calculation of kinetics as well as different product distributions. In the case of free radical polymerization reactions, computation times may be reduced if the chain length of the polymer molecules are calculated from the lifetimes of the radicals.

The model concept has been tested on the modelling of several different polymerization reactions, such as a heterogeneous polycondensation, an inverse emulsion polymerization and a thermal polymer degradation. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Monte Carlo method; Polymerization; Modelling

Nomenclature

c	concentration (mol/l)
c_M	monomer concentration (mol/l)
c_μ	stochastic rate constant (s^{-1})
DC	dichlorobenzene
d_{LT}	diameter of a latex particle (nm)
f	factor increasing the reaction rate of all reactions in which dichlorobenzene does not participate
h_μ	number of distinct molecular reactand combinations for the reaction μ
k_d	rate constant for initiator decomposition (s^{-1})
k_{des}	rate constant for desorption of radicals (s^{-1})
k_p	rate constant for propagation ($l\ mol^{-1}\ s^{-1}$)
k_{pk}	rate constant for chain propagation in the continuous phase ($l\ mol^{-1}\ s^{-1}$)
k_{td}	rate constant for bimolecular termination by disproportionation ($l\ mol^{-1}\ s^{-1}$)
k_{tk}	rate constant for bimolecular termination in the continuous phase ($l\ mol^{-1}\ s^{-1}$)
$k_{tr,M}$	rate constant for chain transfer to monomer ($l\ mol^{-1}\ s^{-1}$)
M	overall number of reactions
$n(i)$	number of radicals in the latex particle i

N/N_A	latex particle concentration in the continuous phase (mol/l)
NS	Sodium sulfide
p	entry rate coefficient (s^{-1})
$P(i)$	reaction probability for a reaction i (s^{-1})
$P_2(\mu/t)$	probability for a reaction μ at time t
P_W	weight average degree of polycondensation
P_N	number average degree of polycondensation
r_1, r_2	random numbers
r_p	reaction rate ($mol\ l^{-1}\ s^{-1}$)
t	time (s)
v	factor which considers the limited solubility of sodium sulfidehydrate
X	monomer conversion
X_E	end group conversion
ZLT	overall number of latex particles in the volume element
Δt	lifetime of a chain (s)
τ	time step between two reactions (s)

1. Introduction

The term ‘Monte Carlo method’ is commonly used for mathematical methods which simulate the behaviour of a chemical or physical system on the basis of probabilities and

* Corresponding author.

with the help of random numbers. In macromolecular chemistry, most of the methods applied are molecular-dynamic simulations which calculate the spatial movement of molecules or molecular segments [1,2]. Moreover, there are a series of publications using Monte Carlo methods for the calculation of product distributions of polymerization reactions [3,4]. These kinds of methods are based on the definition of reaction probabilities. With these probabilities and random numbers, the fate (with respect to its reaction behaviour) of a specific amount of reactant molecules is simulated. Especially in the case of very complex reaction schemes where conventional methods require a high level of sophistication and include many simplified assumptions, Monte Carlo methods seem to be a simple and flexible alternative. But, most of these methods are very different with regard to the simulation algorithm and are often tailored to the specific problem to be solved. Therefore, in the present work a model concept will be presented which is based on the result of a critical comparison of various kinds of Monte Carlo algorithms described in the literature.

2. The model concept

There are mainly two different strategies to set up a Monte Carlo method for calculating polymer product distributions. The first kind mentioned in the literature is the 'differential method' [5,6]. This is a method to calculate differential product distributions which are formed during a differential time increment in the reactor. In order to obtain the integral product distribution actually present in the reactor, the differential distributions must be integrated with respect to conversion. Therefore, it is also necessary to solve the kinetic equations by ordinary differential equation-solvers. The differential method has the disadvantage that the simulation of reactions including polymer molecules formed earlier in the polymerization (e.g. long chain branching, crosslinking, degradation reactions) is not possible [7].

The second group of Monte Carlo methods, also chosen for our general concept, is the 'integral method' which calculates integral product distributions as well as concentrations of the reactants throughout the entire course of the reaction. It is easy to correlate the number of molecules with the conversion, whereas the introduction of the time step requires much more theoretical effort. Three different methods [8–10] including the time step in a Monte Carlo method were compared [7]. The most satisfactory results were obtained using the method described by Gillespie [10]. Here, the time step is automatically adapted to the time scale of the fastest reaction so that inaccuracies in the results caused by poor choice or false computation of the time step is not possible in contrast to the other methods.

Much attention should be placed on the choice of a suitable simulation space. Such spaces can be, for instance, single particles or certain molecules. But, one possibility

applicable to most of the cases which provides most of the information is to pick out a small part of the overall reaction volume. Fig. 1 shows the general operation mode of such a method according to Gillespie's theory of the stochastic formulation of chemical kinetics [10]. Taking into account the size of the simulation volume and the initial concentrations of the reactive species the first step is to calculate the molecule numbers of all species in the simulated volume element at time $t = 0$. The second step (fully described in Refs. [7,10]) is to transform the conventional reaction rate constants into stochastic rate constants which refer to molecule numbers instead of concentrations. In the next stage, reaction probabilities were obtained with the following formula:

$$P_2(\mu/t) = \frac{c_\mu \cdot h_\mu}{\sum_{i=1}^M c_i \cdot h_i} \quad (1)$$

where $P_2(\mu/t)$ is the probability for a reaction μ at time t , c_μ is the stochastic rate constant for a reaction of kind μ , h_μ is the number of molecular reactand combinations for this single reaction at time t , and M is the overall number of reactions in the kinetic scheme. The time step between two reactions in the simulation volume is calculated according to Gillespie [10]:

$$\tau = \frac{1}{\sum_{i=1}^M c_i h_i} \ln(1/r_1) \quad (2)$$

where r_1 is a random number obtained with the help of a random number generator.

With the help of a second random number r_2 the kind of reaction is determined in the following way:

$$\frac{\sum_{i=1}^{\nu-1} c_i h_i}{\sum_{k=1}^M c_k h_k} < r_2 \leq \frac{\sum_{i=1}^{\nu} c_i h_i}{\sum_{k=1}^M c_k h_k} \quad (3)$$

That means that in the selected volume element at time $t + \tau$ the reaction ν must be simulated for whichever Eq. (3) is valid. Simulation in this context means that molecule numbers, the chain length of the molecules or other characteristic quantities of the reaction mass are changed according to reaction ν . However, also the temperature of the volume element in the case of nonisothermal reactions, the heat capacities or the volume of the reactor increment in the case of heterogeneous reactions or reactions with a large volume contraction must be changed according to the differential mass or heat balances of the reaction increment. The last step which does not have to be executed in each loop of the program is the statistical analysis of the molecule numbers, chain length, particle sizes etc. in order to calculate concentrations of the reactants, product distributions or other quantities desired. If a truncation criteria, e.g. a

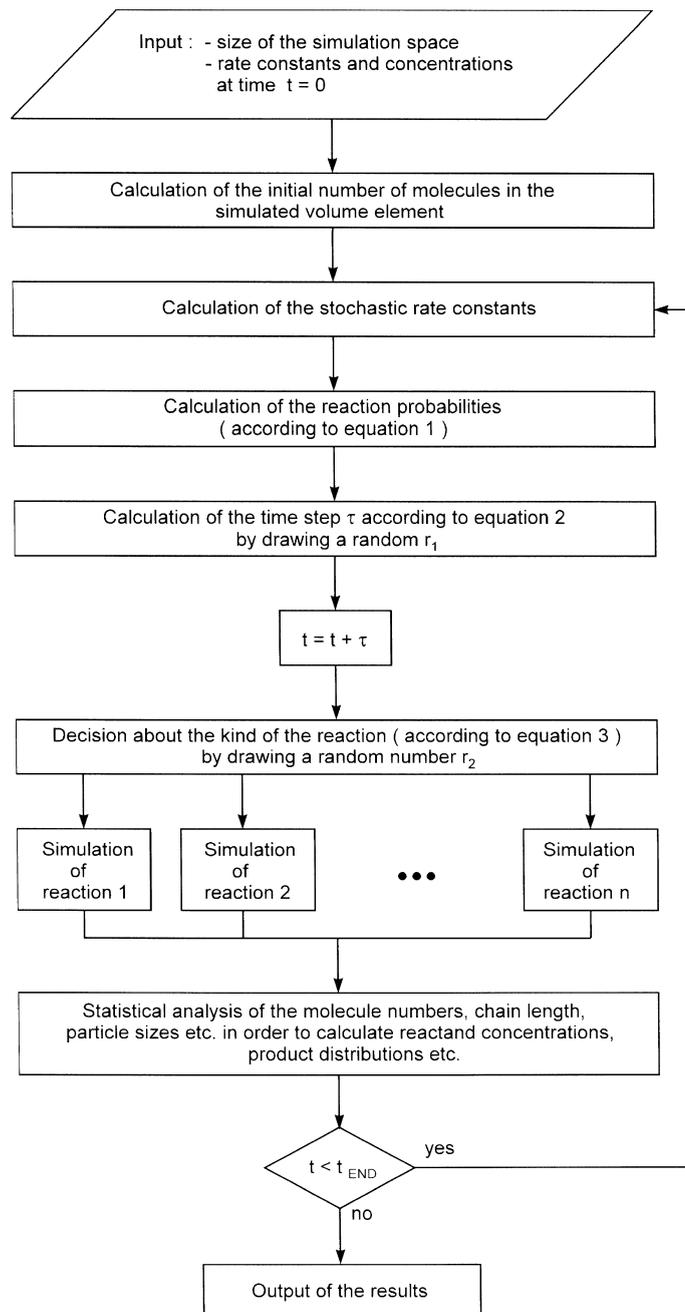


Fig. 1. General mode of the Monte Carlo method used.

specific time or conversion, is still not performed, the loop will be executed again beginning with a new calculation of the stochastic rate constants in terms of a changed temperature or volume of the reaction increment.

With regard to the product distributions, a discretization into fractions with different molecular weights, particle sizes etc. is recommended. This seems to be reasonable considering that most methods for the measurement of product distributions, e.g. gel permeation chromatography, provide such fractions. Using more than 50 fractions, discretization error can be neglected in comparison to the error of the measurement. Numerical parameters of such

calculations are the number of fractions and the class width of a single fraction. Especially in the case of time-dependent simulation species formed in the beginning and at the end of the reaction can vary largely in their properties. Therefore, it may be necessary to vary the class width in the course of the simulation.

A significant disadvantage of the Monte Carlo methods, especially in the case of polymerization reactions, is the length of time needed for the computation owing to the tremendous amount of propagational events during the lifetime of a growing polymer chain. This disadvantage may be overcome if the propagation step is considered only

indirectly by calculating the polymer chain length via its lifetime Δt and the local monomer concentration c_M according to Lichti et al. [11]:

$$\text{chain length} = k_p \cdot c_M \cdot \Delta t \quad (4)$$

In doing so, the calculation time can be reduced to a few minutes. Numerical parameters of these kinds of Monte Carlo methods are:

- the size of the chosen reaction increment (the greater the size the greater the precision of the results, however, the longer the simulation time);
- the quality of the random numbers (tests for uniformity and serial correlation are described in Refs. [7,12,13]);
- number of fractions of the discrete product distributions as well as class width of these fractions.

As far as the main logic of simulation algorithm is concerned, further details are fully examined in Ref. [7]. Time for programming was reduced by using a modular concept in such a way that recurrent algorithms were programmed in subroutines and can then be used for every problem. The programs are written in Visual Basic 4.0 and run under Windows on a standard PC.

3. Application of the model concept

In order to test the general validity of this concept it was applied to the modelling of various kinds of polyreactions. A detailed description of these modelling approaches is given in Refs. [7,14,15]. In this paper, only the potentials revealed by such methods are to be shown. The correspondence of results obtained by this model concept with conventional methods was checked in different cases. Results obtained by application of the Monte Carlo method for modelling the solution polymerization of methyl methacrylate fully agree with those obtained by using the method of moments [7]. The results of modelling the thermal degradation of poly-*l*-lactide in the melt were proofed using a Galerkin-h-p-method. Also, in this case, an excellent agreement could be obtained [7,14,22].

3.1. Modelling the polycondensation of sodium sulfidehydrate and 1,4-dichlorobenzene to poly(thio-1,4-phenylen)

First the results of modelling the heterogeneous polycondensation reaction of sodium sulfidehydrate and 1,4-dichlorobenzene to poly(thio-1,4-phenylen) in the organic solvent *n*-methylpyrrolidone are discussed:

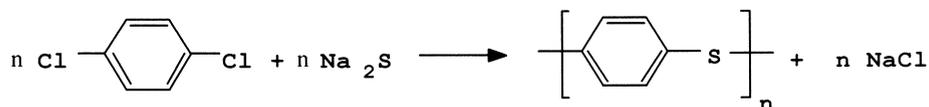
Studies of this reaction applying differential scanning calorimetry in the temperature range from 220°C to 250°C led to the conclusion that the kinetics of this reaction obey an autocatalytic reaction rate law of the first order [15]. Carrying out the reaction in glass ampoules, it was observed that the reaction mixture at all times is a multiphase system. Whereas 1,4-dichlorobenzene dissolves completely in the organic solvent even at room temperature, the technical sodium sulfidehydrate did not show any significant sign of solubility in the organic phase. It may be expected that the first order in the formal reaction rate law is attributed to the very low solubility of sodium sulfidehydrate in *n*-methylpyrrolidone. The autocatalytic effect also reported by other authors is mostly traced back to an increasing end group activity of the oligomeric intermediate products during the first condensation steps.

Owing to the heterogeneous nature of the reaction system the measurements of the nonstirred system in a differential scanning calorimeter should be considered critically. The absence of mixing may lead to a false interpretation of the heat flow measured.

It is well known that the molecular weight distribution and its mean values indicates the mechanism of a polyreaction. Therefore, testing the conclusions by modelling molecular weights seems to be a valuable supplement to d.s.c. measurements. Polymer samples taken from experiments in a stirred laboratory autoclave and analysed by means of high temperature gel permeations chromatography or end group analysis by chloro analysis [16] has shown that, in contrast to the theory of an ideal polycondensation, macromolecular species were formed already at end group conversions below 25% (see Fig. 2). The Monte Carlo method is be used to clarify whether or not the following suggestions taken from d.s.c. experiments are in agreement with the abnormal courses of the average degree of polycondensation:

1. the autocatalytic reaction rate time course is caused by an increasing end group reactivity of the oligomeric intermediates;
2. the formal first order of the reaction has its cause in the limited solubility of the sodium sulfidehydrate in the organic solvent.

Corresponding to the general operation scheme in Fig. 1, a Monte Carlo method was developed. The limited solubility of the sodium sulfidehydrate in the organic solvent was considered with the factor ν . For simplification, the assumption was made that the concentration of sodium sulfidehydrate in the solvent is constant for as long as a



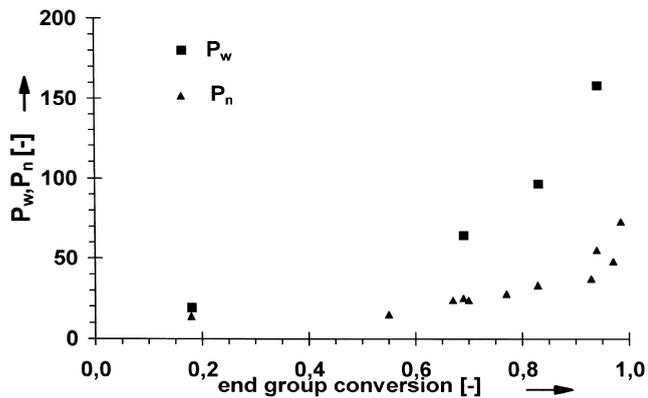


Fig. 2. Experimental values (from Koschinski [16]) of the weight and number average degree of polycondensation of sodium sulfidehydrate and 1,4-dichlorobenzene. $T = 200\text{--}265^\circ\text{C}$, $c_{\text{NS}} = 1.47 \text{ mol kg}^{-1}$, $c_{\text{DC}} = 1.48 \text{ mol kg}^{-1}$.

sufficient amount of this substance is available in the overall system. Therefore, the factor ν is defined as the ratio of the concentration of sodium sulfidehydrate in the organic solvent to the initial concentration of dichlorobenzene in this phase. For the simulation, different kinds of species must be taken into account. These species get the following notation:

Dichlorobenzene	$AA(1)$
Polymeric or oligomeric species possessing two chloro groups	$AA(n > 1)$
Sodium sulfidehydrate	$BB(1)$
Polymeric or oligomeric species with two sulfide groups	$BB(n > 1)$
Species with one chloro group and one sulfide group	$AB(n)$

As a first approximation the autocatalytic reaction rate is

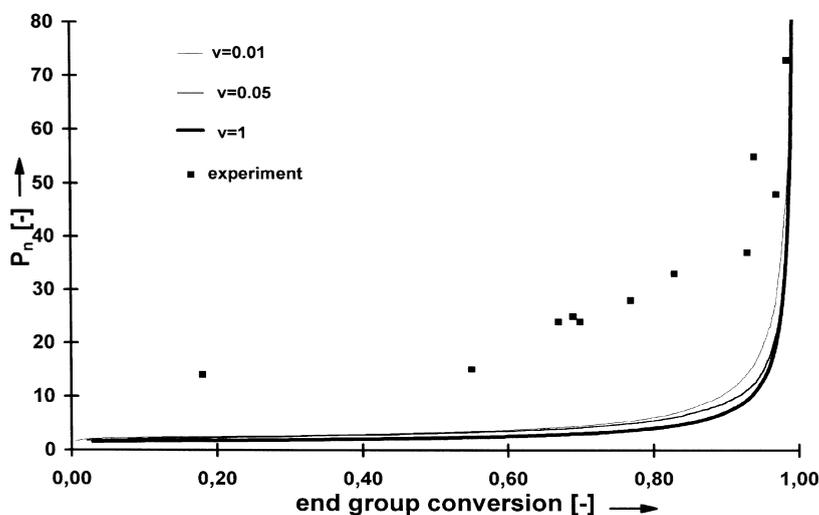


Fig. 3. Simulated course of the number average degree of polycondensation with consideration of the limited solubility ν . Reaction conditions correspond to Fig. 2.

considered by factor f which does increase the reaction rate of all reactions in which dichlorobenzene does not participate. The definition of the various reaction rate constants for the different reactions can be seen from Table 1.

This distinction is reasonable according to Fahey and Ash [17]. Calculating the reaction probabilities, attention must be paid to the number of distinct reactant combinations. This number refers to the number of combinations of the endgroups which may react together. Reaction probabilities were defined in the following way:

$$P(1) = 4k_1 AA(1) \sum_{i=1}^{\infty} BB(i)$$

$$P(2) = 2k_1 AA(1) \sum_{i=1}^{\infty} AB(i)$$

$$P(3) = 4fk_1 \sum_{i=2}^{\infty} AA(i) \sum_{j=1}^{\infty} BB(j)$$

$$P(4) = 2fk_1 \sum_{i=2}^{\infty} AA(i) \sum_{j=1}^{\infty} AB(j)$$

$$P(5) = 2fk_1 \sum_{i=1}^{\infty} AB(i) \sum_{j=1}^{\infty} BB(j)$$

$$P(6) = 2f(0.5k_1) \sum_{i=1}^{\infty} AB(i) \sum_{j=1}^{\infty} (AB(j) - 1)$$

After each simulation loop, the number of active species and the mass of the simulated increment must be changed according to the mass balance of the heterogenous system. In other words, NaCl-species formed by the condensation reaction leave the proper reaction volume because they are not soluble in the organic solvent. In contrast,

Table 1

Definition of the rate constants for modelling the polycondensation of sodium sulfidehydrate and dichlorobenzene

	AA(1)	AA($n > 1$)	BB(n)	AB(n)
AA(1)	—	—	k_1	k_1
AA($n > 1$)	—	—	$f \cdot k_1$	$f \cdot k_1$
BB(n)	k_1	$f \cdot k_1$	—	$f \cdot k_1$
AB(n)	k_1	$f \cdot k_1$	$f \cdot k_1$	$f \cdot k_1$

sodium sulfidehydrate molecules are added to the proper reaction volume according to their solubility in the organic solvent.

Results of the simulation are presented in Figs 3–5. The data of the mass averaged degree of polycondensation show, in principal, the same tendencies. Presented in Fig. 3 are the results obtained by considering only the low solubility of sodium sulfidehydrate in the organic solvent. It can be seen that the consideration of the low solubility alone is not sufficient for the explanation of the abnormal courses of the average degree of polycondensation.

Fig. 4 shows, in contrast, the results obtained by exclusively considering the increasing rate of all condensation reactions including no dichlorobenzol. However, this assumption alone can also not explain the unusual courses of the average degree of polycondensation.

Results from Fig. 5 were derived by combining the effects of low solubility of sodium sulfidehydrate and the increasing rate of all condensation reactions in which dichlorobenzol is not involved. When considering both assumptions together, a better agreement between experiment and simulation is found. Differences at the beginning may have other explanations.

Therefore, it can be summarized that the results of the Monte Carlo simulations confirm the hypothesis framed by the interpretation of d.s.c. measurements of this polycondensation, namely:

- the formal reaction order of one is caused by a low

solubility of sodium sulfidehydrate in the organic solvent; and

- that the reason for the autocatalytical reaction rate is caused by an increasing end group activity with regard to chain length.

3.2. Modelling the inverse emulsion polymerization of acrylamide

As a second example, the results of modelling of the inverse emulsion polymerization of acrylamide will be presented. Experimental studies of this system were carried out by Proß [18] using adiabatic calorimetry, viscosimetry and scanning electron microscopy. A detailed description of the model is given in Ref. [7].

Especially, such complex systems like an inverse emulsion polymerization require the consideration of many physical and chemical processes. For most of these processes, many model conceptions are found in the literature.

Each of these models contain some parameters of unknown quantity, where mostly the total number of parameters exceeds the number of parameters experimentally available. For that reason, the interpretation of the results requires in most cases a series of assumptions which can hardly be proofed. Therefore, in the following model approach, less mechanistical details stand in the centre of the reflections, but the aim is preferably to get a good simulation quality with a minimum of freely adjustable parameters. Fig. 6 shows a figurative representation of the mechanism involved in the model:

- The initiator decomposes in the continuous oil phase. Radicals arising from this reaction add monomer solubilized in the oil phase and grow to oligoradicals. These oligoradicals can terminate mutually or with primary radicals arising from the initiator decomposition.
- If growing oligoradicals reach a critical chain length z_{crit} they become insoluble in the continuous phase and enter

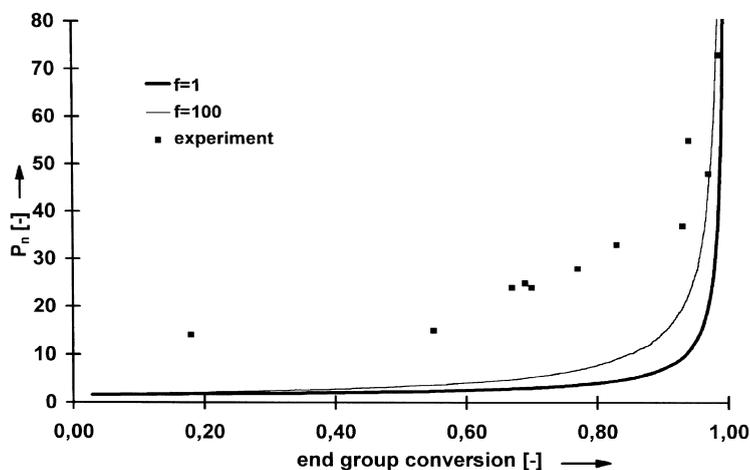


Fig. 4. Simulated course of the number average degree of polycondensation with consideration of the reactivity factor f . Reaction conditions correspond to Fig. 2.

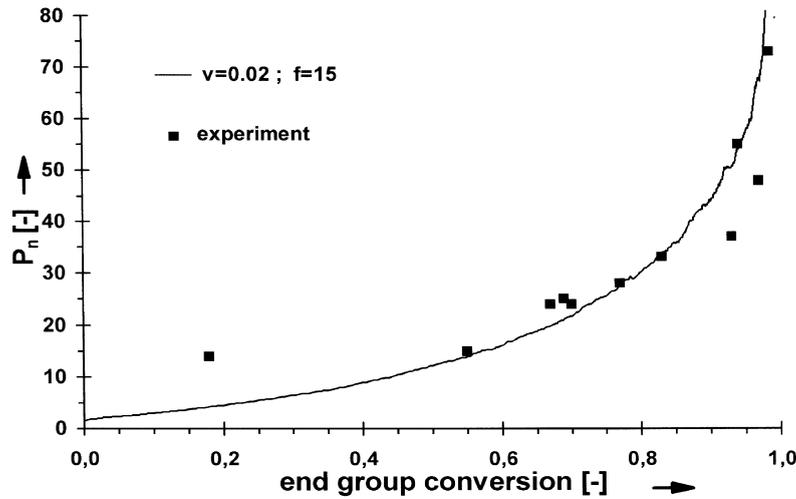


Fig. 5. Simulated course of the number average degree of polycondensation with consideration of the limited solubility v and the reactivity factor f . Reaction conditions correspond to Fig. 2.

the latex particles already formed or the micelles which in that case become latex particles. The parameter γ takes into consideration that entry of radicals in latex particles has a greater probability [19] than entry in micelles.

- Monomer and water from the droplets are transported to the growing latex particles. This process is considered in the model by the swelling parameter χ . The main part of polymerization occurs in the latex particles.

A detailed description of the simulation is given in Ref. [7]. The following reactions were considered using the definition of reaction probabilities:

1. initiator decomposition

$$P(1) = k_d \cdot INI$$

2. bimolecular termination of radicals in the latex particles by disproportionation

$$P(2) = 0.5 \cdot k_{td} \sum_{i=1}^{ZLT} [n(i) \cdot (n(i) - 1)]$$

3. desorption of radicals from the latex particles

$$P(3) = k_{des} \cdot \sum_{i=1}^{ZLT} n(i)$$

4. transfer to monomer in the latex particles

$$P(4) = (k_{tr,M} \cdot C_M^{LT} - k_{des}) \cdot \sum_{i=1}^{ZLT} n(i)$$

where $n(i)$ is the number of radicals in the latex particle i , ZLT is the total number of latex particles in the simulated reaction increment, INI is the number of initiator molecules in the continuous phase of the simulated reaction increment. k_d , k_{td} and k_{des} are the stochastic reaction rate constants for initiator decomposition, termination by disproportionation and desorption, respectively (which refer to molecule numbers and, therefore, have the unit s^{-1}). $k_{tr,M}$ is the rate

constant for chain transfer to monomer and C_M^{LT} is the monomer concentration in the latex particle. In the case of chain transfer to monomer, the deterministic rate constant is used owing to the fact that monomer concentration in the latex

Continuous Phase (isooctane, emulsifier, initiator)

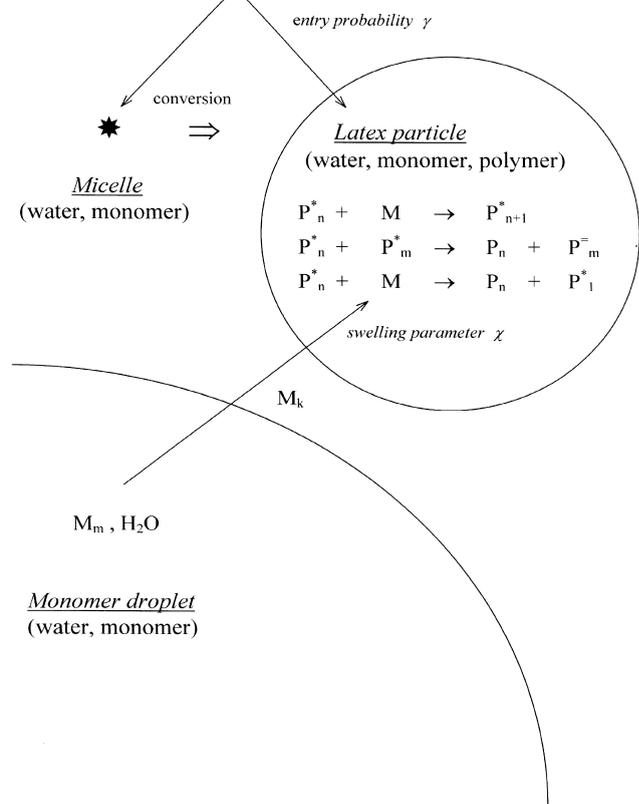


Fig. 6. Mechanistic scheme of the inverse emulsion polymerization.

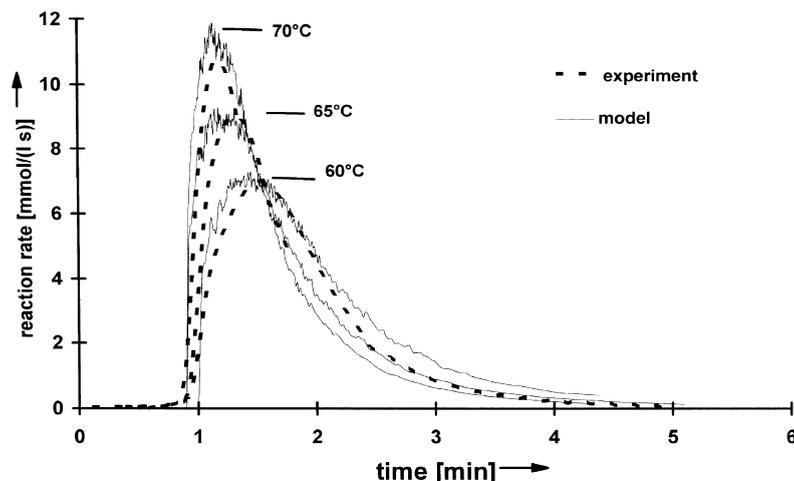


Fig. 7. Adiabatic inverse emulsion polymerization of acrylamide. Variation of the starting temperature. $\phi = 0.19$, $c_{\text{AAm}} = 2.8 \text{ mol/l}$, $c_{\text{PEM}} = 38 \text{ mmol/l}$, $c_{\text{ADVN}} = 0.94 \text{ mmol/l}$, $n = 300 \text{ min}^{-1}$.

particles is used instead of the number of monomer molecules in the latex particles.

In the case of initiator decomposition it is decided by using a random number whether radicals terminate in the continuous phase or grow up to the critical chain length and then enter latex particles or micelles. In this context, the theory of radical entry according to Maxwell [20] was used:

$$p = \left(\frac{2k_d c_I N_A}{N} \right) \left(\frac{2k_{tK}^{0.5} k_d^{0.5} c_I^{0.5}}{k_{pK} c_{M,K}} + 1 \right)^{1 - z_{kr}} \quad (6)$$

where N/N_A is the latex particle concentration in the continuous phase, k_{pK} and k_{tK} are rate constants for chain propagation and bimolecular termination in the continuous phase, the values are set equal to those used in the disperse phase in the preliminary approach, and $c_{M,K}$ is the monomer concentration in the continuous phase. The second term of Eq. (5) was used in the kind of a radical efficiency. A random number was compared with this efficiency factor in order to decide which radicals terminate in the continuous phase and which enter a micelle or latex particle.

Unknown parameters of the model are the entry probability γ , the swelling parameter χ and the critical chain length z_{crit} . These parameters were estimated by adjustment to the experimental reaction rate time curves, mean molecular weights and mean particle sizes. By eliminating the propagation step via the lifetime of the chains, the simulation procedure was accelerated in such a manner that the inclusion in a parameter adjusting algorithm became possible. Kinetic parameters of the acrylamid polymerization were taken from Hunkeler et al. [21] and then fine-tuned. With the help of the Monte Carlo method, including the established model, it is possible to predict reaction rate time curves, mean particle sizes and the mass averaged molecular weights in the range of the emulsifier concentration from 28 to 47 mmol/l, of the initiator concentrations from 0.04 to 5 mmol/l and of the starting temperature from 60°C to 70°C. As an example, Fig. 7 shows simulated and experimental reaction rate time curves for different starting temperatures. Also, the mean values of the particle sizes and the mass averaged molecular weight are in good agreement with the experiment. Because measuring of the entire

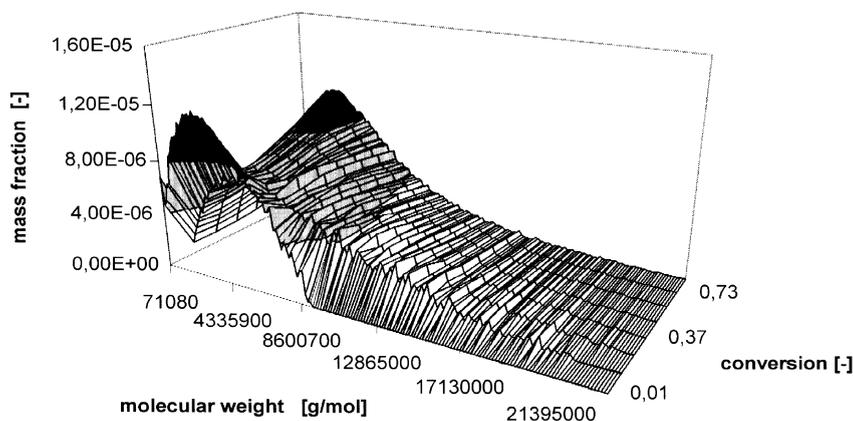


Fig. 8. Calculated molecular weight distribution of PAAm of the adiabatic inverse emulsion polymerization of acrylamide. $\phi = 0.19$, $c_{\text{AAm}} = 2.8 \text{ mol/l}$, $c_{\text{PEM}} = 38 \text{ mmol/l}$, $c_{\text{ADVN}} = 0.94 \text{ mmol/l}$, $T_{R,0} = 60^\circ\text{C}$, $n = 300 \text{ min}^{-1}$.

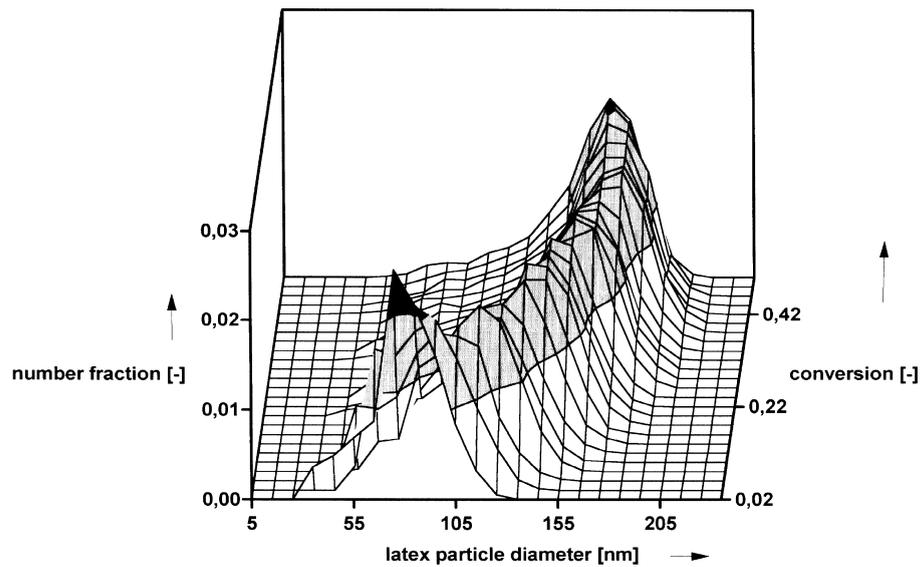


Fig. 9. Calculated particle size distribution of the latex adiabatic inverse emulsion polymerization of acrylamide. $\phi = 0.19$, $c_{\text{AAm}} = 2.8 \text{ mol/l}$, $c_{\text{PEM}} = 38 \text{ mmol/l}$.

particle size distribution of the gel like latices and of the entire molecular weight distribution of the very shear sensitive polyacrylamide was not possible, Figs 8 and 9 show only the simulated molecular weight distribution and particle size distribution for standard conditions.

3.3. Application of the model concept to other polyreactions

The simulation concept was also verified by modelling the thermal degradation of poly-*l*-lactide in the melt [7,14,22]. Various chain length increasing and decreasing reactions were summarized in a simple reaction scheme including a polyaddition step and a statistical degradation step. Fig. 10 shows experimental and simulated data of the number and mass averaged molecular weight. In Fig. 11, a

molecular weight distribution obtained experimentally by gel permeations chromatography is compared with the simulated distribution.

Further applications of the model concept are the simulation of the macrogelation of poly(acrylic acid) dispersions [7,23,24] and the simulation of the adiabatic solution and suspension polymerization of methyl methacrylate [7].

4. Conclusions

A model concept was derived by a comparison of Monte Carlo methods presented in literature which permits the calculation of kinetics as well as different product

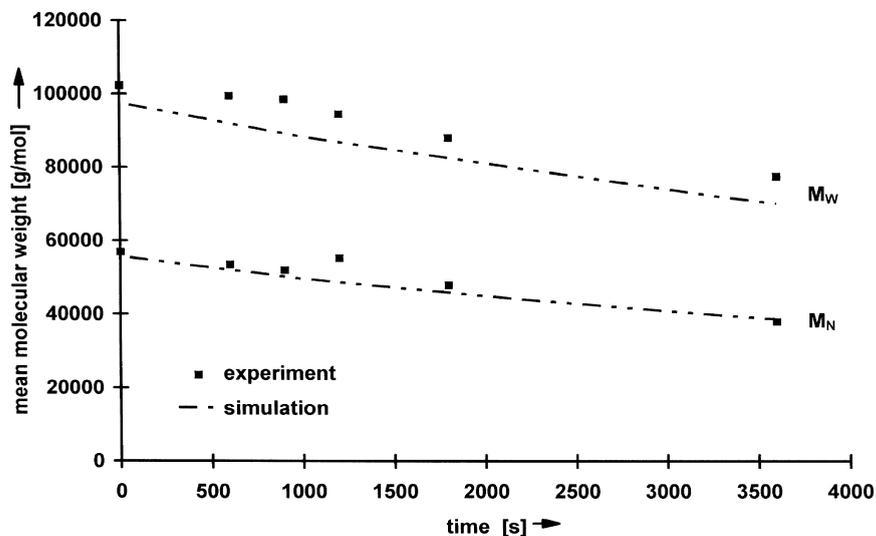


Fig. 10. Thermal degradation of poly-*l*-lactide in the melt. Experimental and simulated courses of the number and weight average molecular weight. $T = 200^\circ\text{C}$.

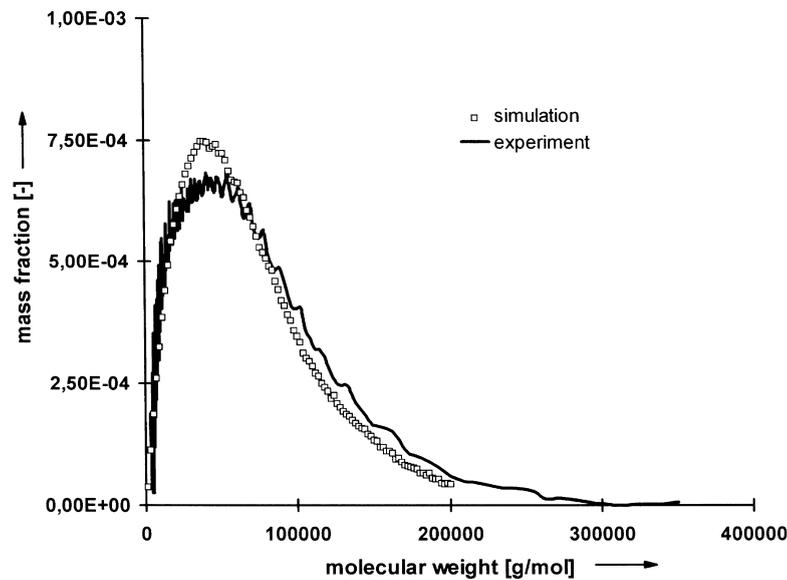


Fig. 11. Thermal degradation of poly-*L*-lactide in the melt. Experimental and simulated molecular weight distribution. $T = 200^{\circ}\text{C}$, $t = 60$ min.

distributions of polyreactions. The application of the model concept to different kinds of polyreactions leads to the conclusion that it may be applied successfully to most reactions in polymer science. The method is not restricted to the steady state assumption, and chain length depending reactions such as crosslinking and long chain branching can be easily included. The method is numerically stable and the precision of the results may be controlled by the size of the simulated volume element. Unfortunately, the computation time increases overproportionally to the desired precision. Therefore, a compromise is necessary between computation time and desired accuracy of the results. However, precision in the order of the experimental error, i.e. $\pm 5\%$, can be obtained in most cases in the range of a few minutes using a Pentium 90 Mhz.

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