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Modeling of Free Radical Styrene/Divinylbenzene Copolymerization with the Numerical Fractionation Technique --Manuscript Draft--

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Modeling of Free Radical Styrene/Divinylbenzene Copolymerization with the Numerical Fractionation Technique

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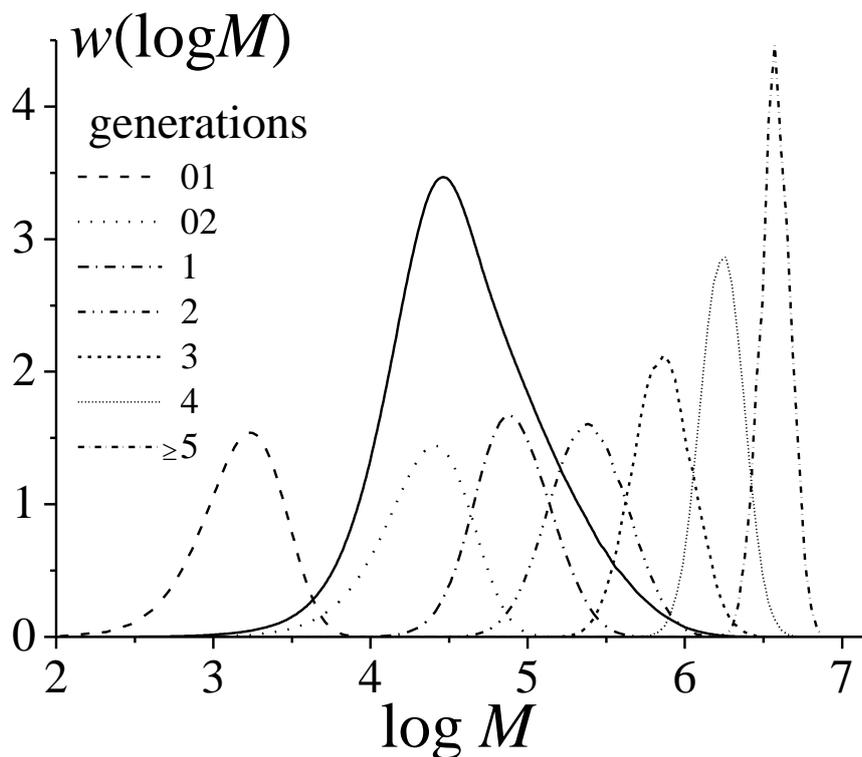
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KEYWORDS: styrene, divinylbenzene, free radical copolymerization, crosslinking, cyclization,
gelation

Summary

The modeling approach called “numerical fractionation” has been incorporated into a PREDICI model to simulate crosslinking copolymerization. To take into account inhomogeneities of the considered copolymerization, the kinetic parameters of the model are proposed to be different for each generation of the numerical fractionation. Using this approach the chain-length dependence of termination has been incorporated into the model so that even the method of moments could be applied to study crosslinking copolymerization. The styrene/m-divinylbenzene crosslinking copolymerization at low content of crosslinker has been simulated. The chain-length dependence of termination has been found to accelerate the gel point in monovinyl/divinyl copolymerization and must be taken into account for correct description of the gel points.



Introduction

1 The free radical copolymerization kinetics of monovinyl (MVM) and divinyl monomers (DVM)
2 considerably deviates from copolymerization of two MVMs. In MVM-DVM copolymerization the
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4 second double bond of a DVM, which has reacted, is easily capable to react with growing radicals,
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6 resulting in a cross-linked macromolecule. The presence of this crosslinking reaction clears the way
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9 for a quick increase of the macromolecules leading to the gelation of the system.
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14 The theoretical description of gelation started in the works by Flory, who applied the statistical
15 tree-like model of crosslinking polymerization.^[1] Stockmayer^{[2],[3]} has adopted this statistical
16 consideration to free radical MVM-DVM copolymerization. However, the predictions of the classical
17 gelation theories of Flory and Stockmayer deviate considerably from the experimental data.^[4] The
18 deviations are primary pointed out by Walling,^[5] who has investigated the crosslinking
19 copolymerization of vinyl acetate - divinyl adipate and methyl methacrylate – ethylene glycol
20 dimethacrylate and found out that the experimental gel point conversions are considerably higher (up
21 to 100 times.^[4]) than those coming from theoretical predictions. Today the following reasons are
22 reported to result in this deviation:
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36 a) The functional groups involved in crosslinking polymerization do not have equal and
37 conversion-independent reactivity;^[6]
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39 b) Statistical methods describe state functions instead of time functions of real
40 polymerization;^[7]
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42 c) The intensive intramolecular reactions in the growing chain;^[4]
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45 d) The reduction of reactivity of pendant double bonds (due to the molecular shielding effect,
46 etc.).^[4]
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50 In addition to the statistical models of network formation in crosslinking copolymerization,
51 percolation theory and kinetic models have been used.^{[4], [8]-[10]} However, these approaches allow to
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overcome the problems associated with the application of statistical models only to a certain extent.

1 The percolation theory is found to be efficient for simulation kinetics in the vicinity of the gel point; at
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3 the same time it suffers from the difficulty of introducing the realistic mobility of the functional
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5 groups. The kinetic models are based on population balances derived from a reaction scheme;
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7 therefore they result in the realistic and comprehensive description of crosslinking polymerization.
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9 However these models have significant problems with any kind of numerical simulation if the
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11 dispersity starts to increase more and more, finally leading to a singularity as the system approaches to
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13 the gel point. The simulation is particularly complicated if one tries to compute the full molecular mass
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15 distribution (MMD). Many groups have tried to overcome the difficulties inherent to the description of
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17 non-linear radical polymerization. It should be mentioned the efforts made in this direction by
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19 Hamielec, Tobita and Zhu who have developed kinetic models based on the pseudo-kinetic
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21 approach.^{[11]-[16]} Costa and Dias have used the moment generation functions;^{[17]-[22]} this approach is
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23 even applicable to calculate MMDs in the vicinity of the gel point (before and/or after gelation) using
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25 numerical inversion of probability generating functions.^{[20],[22]-[24]} Method of moments is also found to
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27 be a powerful tool for studying crosslinking polymerization,^{[9],[10]} very recently this approach has been
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29 used by Hernández-Ortiz et al.^[25] However all these kinetic approaches consider the average
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31 properties of the reaction system and therefore cannot deal correctly with the inhomogeneities of
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33 crosslinking copolymerization. It is still necessary to introduce alternative or more refined kinetic
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35 modeling ideas.
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45 In this work we want to present an exemplary model reviewing well-known “numerical
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47 fractionation”^[26] technique to overcome the numerical issues associated with the singularity induced
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49 by the gel-point. The fractionation approach allows us to define certain “generations” of polymer
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51 chains - based on the crosslink reactions - and it is straightforward to introduce generation-dependent
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53 kinetic parameters and rates.
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57 In order to illustrate this approach, we study the chain-length dependence of termination and its
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1 effect on the gelation in this paper. We will show that the resulting model can even be computed as
2 moment model, which would not be possible without fractionation due to closure problems. The model
3 has been entered into and simulated with the program package PREDICI,^[27] which makes it possible to
4 compute the full MMDs of the single fractions. Moreover, we will show that the results of the
5 fractionation approach can be used to obtain information on the range of chain-lengths related to
6 gelation.
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12 The whole examination does not aim at ultimate insights into styrene/divinylbenzene
13 copolymerization, but represents a proposal of some ways to model such systems in general.
14 Nevertheless, the acquired results have been verified by fitting the model to experimental data
15 obtained by Hild and Okasha.^[28] Since the termination, dependent on the chain-length, significantly
16 accelerates the gel point, we can show how basic model parameters of the system depend on the
17 refined modeling.
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32 **Model Development**

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35 The inhomogeneities of crosslinking copolymerization can be considered if kinetic simulation regards
36 time, conversion and chain-length dependences of the kinetic parameters of the reactions in the system.
37 However, introducing all of these dependencies complicates the integration of kinetic equations for the
38 system and increases the computation time considerably, especially if the molar-mass dispersity
39 approaches the singularity at gel-point. Therefore we propose a different approach that both considers
40 the inhomogeneities of crosslinking copolymerization and saves the computation time.
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51 For that we propose to apply the numerical fractionation technique^[26] as a model approach in
52 the simulation package PREDICI. The possibility of such kind of incorporation has been already
53 announced in ref.^[29] The main reason for using this technique is that the functional species in the
54 copolymerization system could be subdivided in different groups, named generations, depending on
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1 the chain length of these species. We propose a slight modification of the numerical fractionation
2 technique, according to which the kinetic parameters for the same reactions of species of each
3 generation are chosen to be different from the ones of species of other generations. In addition, the
4 PREDICI program package allows to easily change the kinetic parameters in time and in conversion
5 (since no quasi-steady-state approximation used by Teymour and Campbell^[26] is necessary for this
6 package). This also allows to consider the inhomogeneities of crosslinking polymerization. Then the
7 properties of the species are averaged within a generation, since the kinetic parameters for reactions of
8 the species in this generation are chosen to be the same. Therefore we propose an intermediate
9 approach between the one for which the kinetic parameters are considered to be independent of time,
10 conversion and chain-length, and the one for which these dependencies are taken into account for
11 species with each single chain length.
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26 In this work we apply the approach sketched above for the description of crosslinking
27 copolymerization at a low content of crosslinker. The styrene/m-divinylbenzene copolymerization,
28 which Hild and Okasha^[28] have carried out the experiments for, has been chosen as the subject of
29 investigation. The set of the reactions of the model with the numerical fractionation technique for this
30 copolymerization is given in Scheme 1. Note that for the copolymerization with low content of
31 crosslinker the rate coefficients for propagation, chain transfer to monomer, crosslinking and
32 cyclization are assumed to not be dependent on the generation numbers. At the same time this
33 dependence is considered for the termination rate coefficients.
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46 Scheme 1 contains all of the basic reactions – initiation, propagation and termination -
47 associated with the free radical copolymerization. The free radical initiator (I) decomposes (with rate
48 coefficient k_d) to form two primary radicals (R_0) with efficiency f (reaction (S1.1)). Chain initiation
49 occurs when the primary radical adds (reactions (S1.2) and (S1.3)) monomers S (styrene) and B
50 (divinylbenzene) forming the secondary radicals $S_{1,0}^{\bullet}$ and $B_{1,0}^{\bullet}$. The species IS and IB are so-called
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counters, allowing to take into account both the concentration of the chains produced by initiation as well as the monomer conversions due to the reactions (S1.2) and (S1.3). Chain growth continues via successive addition of monomer units to the chain-end radical centers $S_{i,j}^{\bullet}$ and $B_{i,j}^{\bullet}$ according to the terminal model of copolymerization that has been used here as the structures of monomers are close to each other (chain propagation reactions (S1.4)-(S1.7)). For $S_{i,j}^{\bullet}$ and $B_{i,j}^{\bullet}$ (and for all other species as well) the first subscript i denotes the number of monomeric units in copolymer and the second j indicates that the species belong to j -th generation. The values of CS and CB allow to count the monomer conversions in the system. The termination of $S_{i,j}^{\bullet}$ and $B_{i,j}^{\bullet}$ are assumed to take place exclusively by combination reactions: while this mode of termination for styrene-end radicals $S_{i,j}^{\bullet}$ is known to be predominant, for $B_{i,j}^{\bullet}$ this is an assumption based on the fact that the structure of divinylbenzene radicals is close to the styrene structure. The counter T allows to regard the number of combined chains through the termination events. The chain-length dependence of termination rate coefficients ($k_{t11}^{i,k,j,m}$, $k_{t12}^{i,k,j,m}$, $k_{t13}^{i,k,j,m}$, $k_{t22}^{i,k,j,m}$, $k_{t23}^{i,k,j,m}$ and $k_{t33}^{i,k,j,m}$) has been built on the basis of the composite model:^[30]

$$k_t^{i,i} = k_t^{1,1} i^{-\alpha_1}, \quad i \leq i_c \quad (1a)$$

$$k_t^{i,i} = k_t^{1,1} (i_c)^{-\alpha_1 + \alpha_2} i^{-\alpha_2}, \quad i > i_c \quad (1b)$$

where $k_t^{i,i}$ is the rate coefficient for termination of radicals having i monomer units, $k_t^{1,1}$ is the rate coefficient for termination between monomeric radicals, α_1 is responsible for the chain-length dependence law due to center-of-mass diffusion, α_2 is responsible for the chain-length dependence law due to segmental diffusion, i_c is the boundary between the two laws.

The geometric mean

$$k_t^{i,j} = (k_t^{i,i} k_t^{j,j})^{0.5} \quad (2)$$

has been applied for estimation of cross-termination rate coefficients.

For reactions of termination of primary radicals (S1.10)-(S1.13) the laws (1)-(2) have been applied as well. To use (2) $k_t^{i,i} = k_{t0} = 3 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ is chosen for the homotermination rate coefficient, i.e. the rate of termination of primary radicals in a homopolymerization.

The values of $k_t^{1,1}$, α_1 , α_2 and i_c are chosen to be the same for all the kinetic parameters $k_{t11}^{i,k,j,m}$, $k_{t12}^{i,k,j,m}$, $k_{t13}^{i,k,j,m}$, $k_{t22}^{i,k,j,m}$, $k_{t23}^{i,k,j,m}$ and $k_{t33}^{i,k,j,m}$. In accordance with the composite model and for copolymerization with predominant content of styrene the following values of these parameters are chosen^{[31],[32]} $\alpha_1 = 0.5$, $\alpha_2 = 0.16$ and $i_c = 50$; the value of $k_t^{1,1} = 1.31 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ is found here from fitting the experimental data (Table 1). The description of how the chain-length-dependent termination is incorporated into the numerical fractionation technique is given below.

Due to the presence of double bonds of reacted divinylbenzene in the backbone of copolymer, the crosslinking reactions (S1.20) and (S1.21) take place in the system. As a result of these reactions, midchain radicals $V_{i,j}^{\bullet}$ are formed (Figure 1), the structure of which deviates from the structure of $S_{i,j}^{\bullet}$ and $B_{i,j}^{\bullet}$. However, currently it is not clear from literature how this deviation is reflected on reactivity of $V_{i,j}^{\bullet}$ compared with the ones of $S_{i,j}^{\bullet}$ and $B_{i,j}^{\bullet}$, as, for example, the propagation rate coefficients of $S_{i,j}^{\bullet}$ and $B_{i,j}^{\bullet}$ are found to be different according to previous investigations in literature; therefore the propagation rate coefficients (k_{p31} and k_{p32} in reactions (S1.8) and (S1.9)) for $V_{i,j}^{\bullet}$ are expected to be different from the one for chain-end radicals. Moreover, as the access of monomer to the midchain radicals is more restricted than to the end radicals, this steric hindrance is therefore expected to result in lower value of the propagation rate coefficients for $V_{i,j}^{\bullet}$. Therefore the

value of propagation rate coefficients for $V_{i,j}^{\bullet}$ is chosen to be a factor two lower than the one for $B_{i,j}^{\bullet}$ (Table 1). Due to the same reason the crosslinking rate coefficient (k_{cl3} in reaction (S1.22)) is chosen to be twice lower than the values for chain-end radicals (chosen to be equal to the same value: $k_{cl1}=k_{cl2}=k_{cl}$). As the termination event is controlled by diffusion the termination rate coefficients ($k_{t13}^{i,k,j,m}$, $k_{t23}^{i,k,j,m}$ and $k_{t33}^{i,k,j,m}$ in reactions (S1.16), (S1.18) and (S1.19), respectively) for $V_{i,j}^{\bullet}$ are chosen to be the same as the termination rate coefficients for chain-end radicals.

As k_{cl1} , k_{cl2} and k_{cl3} we consider the rate coefficients of crosslinking reactions of radicals $S_{i,j}^{\bullet}$, $B_{i,j}^{\bullet}$ and $V_{i,j}^{\bullet}$, respectively, with polymers having one double bond. Then for crosslinking reactions with polymer having m double bonds these rate coefficients should be multiplied on m . Therefore the crosslinking rate coefficients in reactions (S1.20) - (S1.22) are also multiplied by chain length of reacting polymer and by conversion dependent factor γ expressed as

$$\gamma = \frac{IB + CB + TB - (CL + CC)}{IS + IB + CS + CB + TB + TS} \quad (3)$$

where TS , TB , CL and CC are the counters of the chain transfer, crosslinking and cyclization reactions (note that the values of CL and CC allow for the consumption of pendant double bonds well). The γ value is the instantaneous ratio of the concentration of pendant double bonds to the concentration of reacted monomers. Multiplying this coefficient on chain length of polymer we have the number of pendant bonds in this polymer.

The event of cyclization is very difficult to simulate especially since it may take place through the primary and secondary mechanisms.^[33] Nevertheless many approaches have been developed to study the influence of this event on kinetics of crosslinking polymerization. Tobita and Hamielec^[13-16] have developed the kinetic model of crosslinking polymerization taking into account both mechanisms of cyclization. Generating functions could be effectively used for theoretical predictions including

1 cyclization before and also after gelation.^[34] Multi-dimensional method of the moments is also found
2 to be efficient for simulations with cyclization.^{[25],[35]} It should be noted that the modeling approach
3 proposed herein principally should be able to take into account a chain-length-dependent cyclization
4 rate coefficient. However, no suitable description seems to be available right now. Therefore the
5 following approach has been used. According the Stockmayer-Jacobson scaling^[36] the probability of
6 forming a ring of size x is proportional to $x^{-3/2}$ for linear macromolecule. Due to the rapid decrease in x
7 of this scaling it is expected that the cyclization takes place effectively through a restricted number of
8 monomer units in polymer. The rate coefficients of cyclization through the group of these monomer
9 units are chosen by us to be k_{c1} , k_{c2} and k_{c3} for radicals $S_{i,j}^{\bullet}$, $B_{i,j}^{\bullet}$ and $V_{i,j}^{\bullet}$, respectively, assuming
10 that each monomer unit of the group contains double bond. Then for the case of polymerization with
11 low content of crosslinker these coefficients are multiplied on factor γ (as it can be considered as a
12 portion of monomer units having double bond in the group). According to Figure 1, due to the
13 difference in the structures the cyclization probability for the midchain radical is expected to be
14 considerably less than for the chain-end radical; therefore the cyclization rate coefficient, k_{c3} , for
15 $V_{i,j}^{\bullet}$ is chosen to be one order in magnitude less than the value for chain-end radicals (chosen to be
16 equal to the same value: $k_{c1}=k_{c2}=k_c$).

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39 The coefficients of chain transfer to monomer, k_{tr11} , for reaction (S1.26) are taken from
40 literature.^[37] For other reactions (S1.27) -(S1.31) the coefficient $k_{tr,m}$ is chosen to be $k_{tr,m} = \frac{k_{p,m}}{k_{p11}} k_{tr11}$.
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46 However, calculations show that chain transfer events have only minor influence on kinetic
47 dependencies for the conditions of the copolymerization studied in this work.

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52 In addition it is necessary to indicate the simplifying assumptions of the kinetic model. As
53 indicated by Costa and Dias^{[19],[24],[38]} these assumptions might influence strongly the correctness of the
54 predictions of the model. One of the main assumptions of our approach is the negligible presence of
55 multiradicals. Kuchanov and Pis'men^[39] have pointed that accurate description of crosslinking

1 polymerization could not be done without consideration of these radicals. However Zhu and
2 Hamielec^[40] have studied the subject for MVM-DVM copolymerization by using the method of
3 moments and focusing on the pre-gel period. They have found that the effect of multiradicals is
4 expected to be not important if for studied system the ratio of propagation/termination rate coefficients
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(k_p/k_t) is smaller than 10^{-3} . It should be noted that this condition is valid for our system even for individual rate coefficients $k_t^{i,j}$. For example, even for $i=10^7$ we have $k_t^{i,i} = 2.79 \times 10^7$ so that $k_p/k_t^{i,i}$ is much smaller than 10^{-3} for any propagation rate coefficients given in Scheme 1. Therefore for our simulations of the pre-gel period the presence of multiradicals is ignored.

18 Considering only one-dimensional (chain length) species, nevertheless, the assumption - the
19 negligible presence of more than one terminal double bond per molecule – is not used in the kinetic
20 model. The fact that each species contain double bonds, which number is proportional to the chain
21 length of this species, is taken into account through the kinetic parameters; the proportionality constant
22 in these parameters is determined through the counters according to Equation (3).

31 At the same time the model has used the following assumptions: a) the negligible exit of
32 radicals from the reactor, b) chain transfer (crosslinking) only to “dead” polymer and c) closure
33 conditions for the moments.

41 **Results and Discussion**

44 *a) Numerically Averaged Chain-length Dependent Termination Mechanism.*

47 In this work the styrene/divinylbenzene copolymerization at a low content of crosslinker (below 2%)
48 has been simulated. For this case, the inhomogeneities of the copolymerization could be ignored.^[10]

53 At the same time the termination has been considered to be chain-length-dependent according to ref.^[30]

55 In the following, this dependence will be introduced into the numerical fractionation approach in a way
56 that allows the method of moments to be applied. By that the kinetic equations for the

copolymerization can easily be integrated and the simulations can considerably be accelerated by this model, in particular in view of parameter fitting. For this purpose the number-average degrees of polymerization $X_n^{S,j}$, $X_n^{B,j}$ and $X_n^{V,j}$ for each population of growing radicals $S_{i,j}^\bullet$, $B_{i,j}^\bullet$ and $V_{i,j}^\bullet$, respectively, should be estimated. Then the homotermination rate coefficient for radicals $S_{i,j}^\bullet$ is constructed on the basis of the composite model (Equation (1)) to be :

$$k_t^{S,j} = k_t^{1,1} (X_n^{S,j})^{-\alpha_1} \quad , \quad X_n^{S,j} \leq i_c \quad (4a)$$

$$k_t^{S,j} = k_t^{1,1} (i_c)^{-\alpha_1 + \alpha_2} (X_n^{S,j})^{-\alpha_2} \quad , \quad X_n^{S,j} > i_c \quad (4b)$$

The termination rate coefficient for populations of radicals $B_{i,j}^\bullet$ and $V_{i,j}^\bullet$ are determined by the same way (in Equation (4) the symbol S should be substituted by B and V, respectively). The termination rate coefficient for radicals of different populations is estimated by the geometric mean (2).

This kind of consideration of chain-length-dependent termination (which will further be called the “numerically averaged chain-length dependent termination” (NACLDT)) has been applied effectively in simulations of pulse laser polymerization.^{[41],[42]} However, in that simulations the number-average degrees of polymerization have been considered for radical populations following a Poisson distributions. In the numerical fractionation approach the degree-of-polymerization dispersity of the MMDs of radical populations are considerably higher than the ones of Poisson distributions. Despite the fact that the dispersity for radical populations of higher generations become much lower^[26], the high dispersity of the radical populations of the first generations could influence the results coming from the used NACLDT strongly. Moreover, if the values of $X_n^{S,0}$, $X_n^{B,0}$ and $X_n^{V,0}$ is higher than i_c , the NACLDT mechanism will not take into account the existence of highly reactive (towards to termination) radicals having a chain length below i_c according to (1). Therefore the validity of the NACLDT mechanism, averaging the termination rate coefficient within one generation, is checked by comparing it with the model using the strict termination mechanism expressed by the

composite model with Equation (1) and geometric mean (2) for termination of radicals having different chain lengths. The results of this comparison are given in Figure 2 where the time profiles of conversion, number and weight average molecular weights are presented for simulations with the strict termination (given by points) and NACLDT (dashed lines) mechanisms. These simulations have been done for the same kinetic parameters as given in Table 1. Indeed two approaches show the considerable deviation in the results.

Nevertheless, to make the approach with NACLDT applicable for the kinetic investigations the following slight modification of the numerical fractionation technique has been used. The zero-generation has been subdivided in two generations by using the following simple population transfer mechanism



To take into better account the role of short radicals, the parameter σ has been introduced so that the termination rate coefficient of the population $S_{i,0}^{\bullet}$ is determined to be

$$k_t^{S,0} = \sigma k_t^{1,1} (X_n^{S,0})^{-\alpha_1} \quad , \quad X_n^{S,0} \leq i_c \quad (6a)$$

$$k_t^{S,0} = \sigma k_t^{1,1} (i_c)^{-\alpha_1 + \alpha_2} (X_n^{S,0})^{-\alpha_2} \quad , \quad X_n^{S,0} > i_c \quad (6b)$$

Similar expressions have been used for the populations of radicals $B_{i,0}^{\bullet}$ and $V_{i,0}^{\bullet}$ (in Equation (6) the symbol S should be substituted by B and V, respectively).

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2 The termination rate coefficients for the populations of radicals $S_{i,\tilde{0}}^*$, $B_{i,\tilde{0}}^*$ and $V_{i,\tilde{0}}^*$ are
3 expressed in (4a) through their estimated number average degrees of polymerization $X_n^{S,\tilde{0}}$, $X_n^{B,\tilde{0}}$ and
4 $X_n^{V,\tilde{0}}$. The set of reactions for the modified numerical fractionation approach is the same as given in
5 Scheme 1; the only difference is that for the zero-generation two states $j = 0$ and $j = \tilde{0}$ should be
6 considered.
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13 The values of k_{trP} and σ are varied to get a satisfactory agreement between results obtained by
14 the simulation with the NACLDT mechanism built on the basis of the modified numerical
15 fractionation technique and the simulation with the strict termination mechanism. It is found that for
16 the simulations with kinetic parameters given in Table 1 satisfactory agreements could be reached for
17 values $\sigma = 4.2$ and $k_{trP} = 100$. The results of the simulations are given in Figure 2. These results
18 confirm that the aforementioned slight modification of the numerical fractionation allows us to
19 separate high reactive short radicals (as shown in Figure 3 where the distribution of these short radicals
20 is compared to the other generations) and to regard their influence on the kinetic dependencies. It is
21 interesting that according to Figure 4 three generations are enough to take into account in simulation
22 for a satisfactory description of time dependencies for M_w . However in the following five generations
23 are chosen for simulations as the close inspection of Figure 4 shows that deviations of weight average
24 molecular weights in the vicinity of gel point for five and six generations could be completely ignored.
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43 Previously Pladis and Kiparissides^[43] have also used the fractionation of total polymer
44 population into a series of classes representing polymer chains with the same branching degree to
45 solve effectively the problems associated with the free-radical highly branched polymerizations. Here
46 we use the rule formulated by Teymour and Campbell^[26] according to which the transfer to the next
47 generation only results if a connecting occurs between two molecules in the same generation. For our
48 model this rule concerns the reactions of termination and crosslinking as shown in Scheme 1. In
49 addition we consider the subdivision of the zero-generation to separate high reactive short radicals
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(with chain lengths below i_c according to Equation (1)) and improve by this way the description of chain-length-dependent termination by the NACLDT mechanism.

Simulations by the method of moment have been carried out applying PREDICI program package. In this package the equations of all reactions steps for all species involved are combined in a modular way. The underlying equations of most of the steps are documented in ref.[29]. The closure relation used for integration of these equations is the well-known Hulburt-Katz relation.

b) Description of Experimental Data

The experimental data measured by Hild and Okasha^[28] are used for the simulation of a solution styrene/divinylbenzene copolymerization at 60 °C by using the developed model with the modified numerical fractionation technique and with the NACLDT mechanism. In these experiments benzene and 2,2'-azoisobutyronitrile (AIBN) have been used as a solvent and initiator, respectively. Furthermore, initial concentrations of styrene, m-divinylbenzene and AIBN have been chosen to be 4, 0.08 and 0.08 mol·L⁻¹, respectively.

The values of $k_t^{1,1}$, k_c and k_{cl} are varied to fit the experimental time profiles of monomer (styrene and m-divinylbenzene) concentrations, pendant double bonds content (PDBC) and the number and weight average molecular weights by the corresponding simulated dependencies. Minimizing the difference between simulated (sim_k) and experimental (exp_k) values according to the condition

$$\sum_k \frac{(exp_k - sim_k)^2}{(exp_k + sim_k)^2} \rightarrow \min \quad (6)$$

the values of $k_t^{1,1}$, k_c and k_{cl} have been estimated to be $k_t^{1,1} = 1.31 \times 10^9$ L·mol⁻¹·s⁻¹, $k_c = 940$ s⁻¹, $k_{cl} = 108.0$ L·mol⁻¹·s⁻¹. The experimental data and simulated curves obtained in the result of the fitting procedure for the time profiles of monomer concentrations, PDBC and for number and weight average molecular weights are given in Figure 5. Model predictions are in satisfactory agreement with

the experimental values for conversion dependencies (Figure 5a) and for number and weight average molecular weights (Figure 5b). However not such agreement has been observed for PDBC (Figure 5c) though an average difference between the experimental and simulated values does not exceed 15%. The experimental values show that the PDBP is expected to be approximately a constant value (≈ 2.53) up to $t = 5$ hour, then it starts to decrease strongly with time. Instead of such behavior the simulated PDBP decreases monotonically with time. There is no explanation of these different behaviors of the experimental and simulated PDBP.

Among the terms $k_{p11} \left(\sum_{i,j} [S_{i,j}^{\bullet}] \right) [S]$, $k_{p21} \left(\sum_{i,j} [B_{i,j}^{\bullet}] \right) [S]$ and $k_{p31} \left(\sum_{i,j} [V_{i,j}^{\bullet}] \right) [S]$ for the rate of monomer consumption $-\frac{d[S]}{dt}$ the first one makes the main contribution to the time profile of $[S]$ as

$\sum_{i,j} [S_{i,j}^{\bullet}]$ is much higher than $\sum_{i,j} [B_{i,j}^{\bullet}]$ and $\sum_{i,j} [V_{i,j}^{\bullet}]$. On the other hand with respect to variation $k_t^{1,1}$, k_c and k_{cl} the concentration $\sum_{i,j} [S_{i,j}^{\bullet}]$ is mainly sensitive to $k_t^{1,1}$ as this coefficient is responsible for the

consumption of radicals through termination (though cyclization and crosslinking transforms $S_{i,j}^{\bullet}$ into $V_{i,j}^{\bullet}$, this effect either is not significant or subsequent propagation of $V_{i,j}^{\bullet}$ may result again in $S_{i,j}^{\bullet}$ so

that $\sum_{i,j} [S_{i,j}^{\bullet}]$ is about two orders in magnitude higher than $\sum_{i,j} [V_{i,j}^{\bullet}]$ (according to simulations) and

slightly dependent on the variation of k_c and k_{cl}). The similar arguments are valid for $-\frac{d[B]}{dt}$. That is

why the fitting of the value of $k_t^{1,1}$ is weakly dependent on the variation of k_c and k_{cl} and the time profiles of monomer concentrations fully determine this rate coefficient for known values of copolymerization propagation rate coefficients. The obtained value $k_t^{1,1} = 1.31 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ is in accordance with the values from literature,^[31] especially with the results obtained by combining online polymerization rate measurements with living RAFT polymerizations.^[44]

1 The values of k_c and k_{cl} are correlated strongly with each other. Cyclization consumes pendant
2 double bonds strongly^[45] and therefore for the higher k_c the higher k_{cl} is necessary in the simulation to
3 fit the experimental weight average molecular weights. The content of pendant double bonds is mainly
4 dependent on the value of k_c ; this allows to easily fix this rate coefficient to be 940 s^{-1} by the fitting
5 procedure; also, $k_{cl} = 108.0 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ is estimated by fitting experimental points for time profiles of
6 M_w . This value of k_{cl} is lower than 370 and $125 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ obtained in ref [46] and [47] ; at the same
7 time, it is higher than the value $18.7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ obtained in ref. [48] through simulation of the
8 suspension styrene/divinylbenzene copolymerization without consideration of cyclization. Such kind
9 of scattering of the obtained values of the crosslinking rate coefficient indicates the complexity of the
10 styrene/divinylbenzene copolymerization even at low content of crosslinker.^[10]

26 *c) Influence of Termination Chain- Length Dependence on the Gel Point*

27 The chain-length dependence of termination in free radical polymerization is predicted theoretically
28 and proved experimentally, and very often the correct kinetic simulation could not be done without
29 consideration of this dependence.^{[31],[32],[49]} The existence and importance of chain-length dependence
30 of termination for crosslinking polymerization has been shown in ref. ^{[50]-[61]} However, a fundamental
31 understanding of the mechanism for this chain-length dependence during crosslinking polymerization
32 is still lacking. The difficulty in characterizing the chain-length dependence of termination in these
33 systems lies in the rapid development of an infinitive network or a gel at very low monomer
34 conversions. The composite model expressed with Equation (1) is only a rough approximation of the
35 chain-length dependence of termination for the crosslinking polymerization considered here. In
36 addition the system is considered only up to the gel point as no reliable chain-length-dependent
37 termination rate is known for systems after the gel point and at high conversion region.

38 In the following, the influence of chain-length dependence of termination on the gel point in
39 crosslinking copolymerization will be studied. This subject has been partially considered by Zhu.^[62]

The chain-length dependence of termination is found to lead to a considerable change in MMDs compared with the case of copolymerization without this dependence. In addition, it is claimed that the chain-length dependence of termination should always delay the gel point, as in the presence of this dependence “the favoured short-short chain combination does not make a sufficient contribution to the molecular weight buildup”.^[62] However, Zhu considered the specific system of polyolefin/peroxide polymerisation. In this system the creation of backbone radicals takes place after an abstraction of hydrogen from polymer by primary radicals formed in the result of decomposition of peroxides molecules. No propagation of these radicals takes place in such a system as no monomer exists in it. Therefore, it is reasonable to consider a crosslinking copolymerization system including all the basic reactions for free radical copolymerization – initiation, propagation and termination - to study the influence of chain-length-dependent termination on kinetics of this system and compare the results of this study with the ones obtained by Zhu. Here the styrene/divinylbenzene copolymerization system is considered as an example of such a system.

In Figure 6a the conversion dependences of weight average molecular weight, M_w , have been presented for the cases of chain-length-dependent termination (solid line) and without this dependence (dashed line). For the case of chain-length-dependent termination the curves from Figure 5 have been recalculated to obtain the dependence of M_w on the overall conversion $\eta = ([S]_0 + [B]_0 - [S] - [B]) / ([S]_0 + [B]_0)$. To plot the curve for the case of chain-length-independent termination, the same kinetic parameters as given in Table 1 are used but the ones for termination. For this event an average termination rate coefficient $\langle k_t \rangle$ is found by fitting the same experimental conversion dependencies given in Figure 5a to be $\langle k_t \rangle = 2.09 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. This fitting, providing approximately the performance of Equation (7)

$$\langle k_t \rangle = \frac{\sum_{i,k,j,m} k_t^{i,k,j,m} ([S_{i,j}^\bullet] + [B_{i,j}^\bullet] + [V_{i,j}^\bullet]) ([S_{k,m}^\bullet] + [B_{k,m}^\bullet] + [V_{k,m}^\bullet])}{\left[\sum_{i,k,j,m} ([S_{i,j}^\bullet] + [B_{i,j}^\bullet] + [V_{i,j}^\bullet]) \right]^2}, \quad (7)$$

is the condition for the comparison of two cases - with and without chain-length-dependent termination.

Zhu has considered the influence of chain-length-dependent termination on the gel point showing the dependences of M_w on crosslink density (CD).^[62] For our system such dependences are given in Figure 6b. To plot the dependence $M_w = M_w(\text{CD})$ the crosslink density has been determined through the counters according to expression (8)

$$\text{CD} = \frac{CL}{IS + IB + TS + TB - T - CL} \quad (8)$$

In Figure 6 the gel points for dependencies $M_w = M_w(\eta)$ and $M_w = M_w(\text{CD})$ have been also shown by the dotted vertical lines. To find these gel points here we use the fact that for the ideal Flory approach, which does not pay attention to cyclization and chain length dependence of termination, the crosslink density at the gel point is known to be equal to $\text{CD}_g = 0.5$.^{[11-13],[62]} Therefore, to characterize the location of the gel point with respect to the curve $M_w = M_w(\text{CD})$ for the Flory approach, the parameter δCD has been introduced, which has been chosen to $\delta\text{CD} = 0.5 - \text{CD}_f$, where CD_f is crosslink density at $M_w = 10^8 \text{ g}\cdot\text{mol}^{-1}$. Thereby, using our model with $k_c = k_{c3} = 0$, $\langle k_t \rangle = 2.09 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (no chain-length dependence of termination) and $k_{cl} = k_{clv} = 66 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ (other kinetic parameters are the same as in Table 1; this choice gives satisfactory description of experimental weight average molecular weights shown in Figure 5b) the ideal Flory approach is simulated and the value of δCD has been estimated to be 0.0055. Assuming that the value of δCD is approximately the same if cyclization and chain-length dependence of termination are taken into consideration, the gel points for the curves $M_w = M_w(\text{CD})$ in Figure 6b has been found to be located at $\text{CD}_f + \delta\text{CD}$

In order to find the gel points for Figure 6a the numerical dependence $\eta = \eta(\text{CD})$ has been considered for the simulation by the Flory approach. From this dependence the parameter $\delta\eta$ that characterizes the location of the gel point with respect to the curve $M_w = M_w(\eta)$ for the Flory approach has been estimated according to $\delta\eta = \frac{\partial\eta}{\partial\text{CD}} \delta\text{CD}$ (the value of partial derivative $\frac{\partial\eta}{\partial\text{CD}}$ is estimated

numerically). The obtained value of $\delta\eta$ ($= 0.0036$) has been used to find the gel points for dependencies $M_w = M_w(\eta)$ in Figure 6a to be located at $\eta_f + \delta\eta$, where η_f is the overall conversion at $M_w = 10^8 \text{ g}\cdot\text{mol}^{-1}$.

Two important conclusions could be made on the basis of the results presented in Figure 6. Firstly, to estimate the correct crosslinking rate coefficient by fitting the experimental weight to the average molecular weights, one needs to know the mechanism of chain-length dependence of termination near the gel point. The model for the chain-length-dependent termination used in this paper results in $k_{cl} = 108.0 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ from fitting the experimental weight average molecular weights; this value is more than 20 % less than the value obtained by the model without the chain-length dependence of termination (for which the value of $k_{cl} = 131 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ has been obtained by fitting the same experimental data).

Secondly, the chain-length dependence of termination results in an acceleration of the gel point. This result contradicts the one obtained by Zhu for polyolefin/peroxide polymerisation for which the delay of the gel point has been observed by simulation. This means that the influence of chain-length dependence of termination on the gel point is found to be dependent on the actual crosslinking system and for the present vinyl/divinyl copolymerization an acceleration of the gel point is observed. This behaviour could be explained by considering the time profiles of concentrations radicals and dead macromolecules of all the generations above the fourth one ($R_5 = \sum_{i=1, j=5} ([S_{i,j}^\bullet] + [B_{i,j}^\bullet] + [V_{i,j}^\bullet])$ and

$D_5 = \sum_{i=1, j=5} [D_{i,j}]$). These profiles, shown in Figure 7, have been obtained by simulation with chain-length dependent termination (solid lines) and without this dependence (dashed lines). The simulation shows that at times before gelation the contents of both radicals and dead macromolecules for the case of chain-length-dependent termination are much higher than the ones for the case of without this dependence. Compared with the case of chain-length-independent termination in the presence of the chain-length dependence of termination more and more long radicals survive with time; furthermore,

1 for the radicals with higher polymer degree the probability of termination is less. The growing and
2 crosslinking of these large radicals is mainly responsible for the rapid increase of M_w with time and for
3 the acceleration of the gel point.
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6 Having such strong difference in the gel points shown in Figure 6 for the chain-length-
7 dependent and λ -independent termination cases further investigation has been undertaken to compare
8 these cases. In this comparison for the case with the chain-length-independent termination the kinetic
9 parameters are chosen to be the same as in Scheme 1 except the termination and crosslinking rate
10 coefficients for which the following values are used: $\langle k_t \rangle = 2.09 \times 10^8 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $k_{cl} = 131$
11 $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. Such choice of the kinetic parameters firstly ensures the performance of Equation (7)
12 (which is the basis for comparison of the two cases) and secondly both the cases are expected to give a
13 satisfactory description of time dependence of M_w given in Figure 5b. In Figure 8 for the two cases the
14 simulated time dependences of M_w for different concentrations of crosslinker (a), initiator (b) and
15 styrene (c) have been presented. Not to complicate the presentation of these dependencies the gel
16 points are not shown by vertical lines; the location of these gel points are very close to the abscissa at
17 $M_w = 10^8 \text{ g}\cdot\text{mol}^{-1}$ for each dependence.
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35 The dependencies shown in Figure 8 are in accord qualitatively with the results obtained by
36 Okay^[63] by simulation of styrene/divinylbenzene copolymerization at higher concentrations of
37 crosslinker for the chain-length-independent termination case. The results in Figure 8a confirm well
38 known feature that the increase of crosslinker content results in acceleration of the gel point; this has
39 been confirmed both experimentally and theoretically many times (for example, in^[30]). Also in context
40 of our comparison of the two cases we observe that both of them result in the identical gel points with
41 respect to time for simulations at different crosslinker contents.
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52 For the both chain-length-dependent and λ -independent termination cases the decrease of
53 concentration of initiator results in acceleration of the gel points as shown in Figure 8b. This feature
54 has a clear explanation: for the lower concentration of initiator the longer dead macromolecules are
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1 formed; crosslinking of the longer macromolecules results in faster reaching of a global
2 macromolecule or the gel point. However the gel points for the different termination cases start to
3 deviate more considerably for lower concentrations of initiator (Figure 8b). The reason of such
4 behavior of the gel points with concentration of initiator is that in the presence of chain-length
5 dependence of termination longer radicals (for the lower concentration of initiator number-average
6 degree of polymerization of radicals are longer) have high probability to survive compared with
7 shorter radicals; as described above this results in acceleration of the gel points. Besides for the chain-
8 length-independent termination case the gel points with respect to time become insensitive to the
9 amount of initiator in the system for lower concentrations of the initiator in accordance with simulation
10 results obtained by Okay.^[63] For this case the difference in the gel points for curves 1 and 2 is about
11 3.5% while for the chain-length-dependent termination case this difference is more than 10%.
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25 Additional important consequence of the results presented in Figure 8b is the following: if the
26 termination in the system is chain-length-dependent then the gel points (with respect to time) measured
27 at different initiator concentrations cannot be described by the single crosslinking rate coefficient by
28 using the model with chain-length-independent termination. Generally it could be assumed that if the
29 gel points are measured at conditions for which number-average degree of polymerization changes
30 significantly then these gel points could not be described by single value of k_{crl} without consideration
31 of chain-length dependence of termination. This assumption is confirmed by simulation of time
32 dependencies of M_w at different concentrations of styrene keeping the concentration of initiator and
33 crosslinker to be constant (and to be equal to 0.08 and 0.08 mol·L⁻¹). This simulation (with the results
34 shown in Figure 8c) is equivalent to the one at different concentrations of solvent (5.33, 2.69 and 0
35 mol·L⁻¹ for curves 1, 2 and 3, respectively). The increase of the concentration of styrene results
36 definitely in corresponding increase of number-average degree of polymerization. And the gel points
37 for the different termination cases again deviate considerably for the higher concentrations of styrene
38 as shown in Figure 8c. This confirms simultaneously that the gel points measured at different
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1 concentrations of styrene could not be described by single value of k_{cl} using the model with chain-
2 length-independent termination.

3 As practically all the free radical polymerization systems are expected to possess the chain-
4 length-dependent termination,^{[30],[31]} according to the results presented in Figure 8b and Figure 8c this
5 dependence must be taken into account for correct prediction of the gel points in non-linear radical
6 polymerization.
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12 **Conclusion**

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18 In order to take into account inhomogeneities in the modelling of crosslinking copolymerization, the
19 numerical fractionation technique with different kinetic parameters for each generation has been
20 proposed. Using this approach, a chain-length dependence of termination has been used so that the
21 method of moments could be applied in numerical simulations. This has been exemplified on a
22 styrene/m-divinylbenzene crosslinking copolymerization model applied to describe experiments
23 carried out at low content of crosslinker and at 60 °C. The values of $k_t^{1,1}$, k_c and k_{cl} have been estimated
24 to be $k_t^{1,1} = 1.31 \times 10^9 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k_c = 940 \text{ s}^{-1}$, $k_{cl} = 108.0 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ by fitting experimental time
25 profiles of monomer concentrations, pendant double bonds content, number and weight average
26 molecular weights. The chain-length dependence of termination is found to influence distinctly the gel
27 point, so that the correct estimation of the crosslinking rate coefficient by fitting the experimental
28 weight average molecular weights could not be done if the model used for the fitting did not pay
29 attention to this dependence. The influence of chain-length dependence of termination on the gel point
30 is found to be dependent on the actual crosslinking system, resulting in an acceleration of the gel point
31 for the considered monovinyl/divinyl copolymerization. For simulations of gel points measured at
32 polymerization conditions resulting in a significant change of number-average degree of
33 polymerization the chain-length dependence of termination must be taken into account.
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Nomenclature

1 I - initiator

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3 S - styrene

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5 B - divinylbenzene

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7 [S]₀ – initial concentration of initiator

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9 [B]₀ – initial concentration of divinylbenzene

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11 R₀ - primary radical

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13 S[•]_{i,j} - secondary styrene-end radical of *j*-th generation with *i* monomeric units

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15 B[•]_{i,j} - secondary divinylbenzene-end radical of *j*-th generation with *i* monomeric units

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17 V[•]_{i,j} - midchain radical of *j*-th generation with *i* monomeric units

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19 M_n - number average molecular weight

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21 M_w - weight average molecular weight

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23 X_n^{S,j} - number-average degree of polymerization for styrene-end radicals of *j*-th generation

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25 X_n^{B,j} - number-average degree of polymerization for divinylbenzene-end radicals of *j*-th generation

26
27 X_n^{V,j} - number-average degree of polymerization for midchain radicals of *j*-th generation

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29 *k*_d – decomposition rate coefficient

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31 *f* - initiation efficiency

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33 *k*_{t11}^{i,k,j,m} - cross-termination rate coefficient for styrene-end radicals of *k*-th and *m*-th generations having

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35 *i* and *j* monomer units

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37 *k*_{t12}^{i,k,j,m} - cross-termination rate coefficient for styrene-end and divinylbenzene-end radicals of *k*-th and

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39 *m*-th generations having *i* and *j* monomer units

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41 *k*_{t13}^{i,k,j,m} - cross-termination rate coefficient for styrene-end and midchain radicals of *k*-th and *m*-th

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43 generations having *i* and *j* monomer units

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45 *k*_{t22}^{i,k,j,m} - cross-termination rate coefficient for divinylbenzene-end radicals of *k*-th and *m*-th

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47 generations having *i* and *j* monomer units

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49 *k*_{t23}^{i,k,j,m} - cross-termination rate coefficient for divinylbenzene-end and midchain radicals of *k*-th and

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51 *m*-th generations having *i* and *j* monomer units

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1 $k_{t33}^{i,k,j,m}$ - cross-termination rate coefficient for midchain radicals of k-th and m-th generations having i
2 and j monomer units
3 $k_t^{i,i}$ - rate coefficient for termination of radicals having i monomer units
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5 $k_t^{1,1}$ - rate coefficient for termination between monomeric radicals
6
7
8 $k_t^{i,j}$ - cross-termination rate coefficient of radicals having i and j monomer units
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11 k_{t0} - homotermination rate coefficient for primary radicals
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13 i_c - boundary between the two chain-length dependence laws for termination in the composite model
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16 k_{cl1} - crosslinking rate coefficient for styrene-end radicals
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18 k_{cl2} - crosslinking rate coefficient for divinylbenzene-end radicals
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21 k_{cl3} - crosslinking rate coefficient for midchain radicals
22
23 k_{cl} - crosslinking rate coefficient for styrene-end and divinylbenzene-end radicals
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25
26 k_{c1} - cyclization rate coefficient for styrene-end radicals
27
28 k_{c2} - cyclization rate coefficient for divinylbenzene-end radicals
29
30 k_{c3} - cyclization rate coefficient for midchain radicals
31
32 k_c - crosslinking rate coefficient for styrene-end and divinylbenzene-end radicals
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35 k_{p11} - homopropagation rate coefficient for styrene-end radicals
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37 k_{p22} - homopropagation rate coefficient divinylbenzene-end radicals
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39 k_{p12} - rate coefficient of addition of divinylbenzene to styrene-end radical
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41 k_{p21} - rate coefficient of addition of styrene to divinylbenzene-end radical
42
43 k_{p31} - rate coefficient of addition of styrene to midchain radical
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45 k_{p32} - rate coefficient of addition of divinylbenzene to midchain radical
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48 k_{tr11} - rate coefficient of chain transfer to styrene for styrene-end radical
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51 k_{tr12} - rate coefficient of chain transfer to divinylbenzene for styrene-end radical
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54 k_{tr21} - rate coefficient of chain transfer to styrene for divinylbenzene-end radical
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57 k_{tr22} - rate coefficient of chain transfer to divinylbenzene for divinylbenzene-end radical
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1 k_{tr31} -rate coefficient of chain transfer to styrene for midchain radical

2 k_{tr32} -rate coefficient of chain transfer to styrene for midchain radical

3
4 $k_t^{S,j}$ - homotermination rate coefficient for styrene-end radicals of j-th generation

5
6 $k_t^{B,j}$ - homotermination rate coefficient for divinylbenzene-end radicals of j-th generation

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8
9 $k_t^{V,j}$ - homotermination rate coefficient for midchain radicals of j-th generation

10
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12 $\langle k_t \rangle$ - average termination rate coefficient

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14 k_{trP} - population transfer rate coefficient for zero generation

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16 CD – crosslinking density

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18 CDg - crosslink density at gel point

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21 CDf - crosslink density at $M_w = 10^8 \text{ g}\cdot\text{mol}^{-1}$

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23 IS - counter for addition of styrene to primary radical

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25 IB – counter for addition of divinylbenzene to primary radical

26
27 CS - counter for addition of styrene to radicals

28
29 CB- counter for addition of divinylbenzene to radicals

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31 T – counter for termination events

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33 TS – counter for chain transfer to styrene

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35 TB - counter for chain transfer to divinylbenzene

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37 CL – counter for crosslinking events

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39 CC – counter for cyclization events

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46 *Abbreviations*

47
48 AIBN - 2,2'-azoisobutyronitrile

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50 DVM – divinyl monomer

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52 MMD - molecular mass distribution

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54 MVM – monovinyl monomer

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57 NACLDT - tnumerically averaged chain-length-dependent termination

PDBC - pendant double bonds content

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3 **Greek Characters**
4

5 α_1 - exponent for the chain-length dependence law due to center-of-mass diffusion
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8 α_2 exponent for the chain-length dependence law due to segmental diffusion
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10 σ – constant for correction of termination of short radicals
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12 η – overall monomer conversion
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4 **Captions to Figures/Schemes**
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7 **Figure 1.** The structures of styrene-end (S•), m-divinylbenzene-end (B•) and midchain (V•) radicals.
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10 **Figure 2.** The time profiles of the styrene concentration [S] (a) and number and weight average
11 molecular weights (b) calculated for the strict termination mechanism (points) and for the NACLDT
12 mechanisms built on the basis of the original (dashed line) and modified (solid line) numerical
13 fractionation technique.
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21 **Figure 3.** Simulated distributions (normalized) for different generations and total distribution (solid
22 curve) at 3.8 hour from the beginning of styrene/divinylbenzene copolymerization.
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27 **Figure 4.** The time profiles of the weight average molecular weight calculated by simulation, taking
28 into account different number of generations.
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32 **Figure 5.** The experimental (points) and simulated (curves) time profiles of (a) the relative monomer
33 concentrations $[M]/[M]$ for styrene (triangles and solid line) and divinylbenzene (squares and dashed
34 line), of (b) number (squares and dashed line) and weight (triangles and solid line) average molecular
35 weights and of (c) pendant double bonds content (PDBC)
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43 **Figure 6.** The dependences of weight average molecular weight (M_w) on (a) overall conversion (η)
44 and (b) crosslinking density (CD) in the cases of chain-length dependent termination (solid line) and
45 without this dependence (dashed) line. In vertical lines the gel points are shown.
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52 **Figure 7.** The time profiles of the concentrations of radicals (a) and dead (b) macromolecules of all
53 generations above the fourth one $R_5 = \sum_{i=1, j=5} ([S_{i,j}^{\bullet}] + [B_{i,j}^{\bullet}] + [V_{i,j}^{\bullet}])$ and $D_4 = \sum_{i=1, j=5} [D_{i,j}]$ for the cases of
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simulation with chain-length-dependent termination (solid line) and without this dependence (dashed line).

Figure 8. The time dependences of weight average molecular weight (M_w) simulated for different concentrations of crosslinker (a), initiator (b) and styrene (c) by using the models with the chain-length-dependent (solid curves) and chain-length -independent (dashed curves) termination.

Scheme 1. Styrene/m-divinylbenzene copolymerization mechanisms

Table 1. Kinetic parameters for simulation of styrene/divinylbenzene copolymerization at 60 °C.

Kinetic parameter	Value	Reference
k_d	$9.55 \times 10^{-6} \text{ s}^{-1}$	[64]
f	0.6	[65]
k_{p11}	$341.0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	[66]
k_{p22}	$608.0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	[67],[47]
k_{p12}	$791.0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	[46]
k_{p21}	$262.0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	This work
k_{p31}	$131.0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	This work
k_{p32}	$304.0 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	This work
k_{t0}	$3.0 \times 10^8 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	This work
$k_t^{1,1}$	$1.31 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	This work

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α_1	0.5	[31], [32]
α_2	0.16	[31], [32]
i_c	50	[31], [32]
k_{cl}	108 L·mol ⁻¹ ·s ⁻¹	This work
k_{cl3}	54 L·mol ⁻¹ ·s ⁻¹	This work
k_c	940 s ⁻¹	This work
k_{c3}	94 s ⁻¹	This work
k_{tr11}	1.12×10 ⁻² L·mol ⁻¹ ·s ⁻¹	[37]

Figure 1

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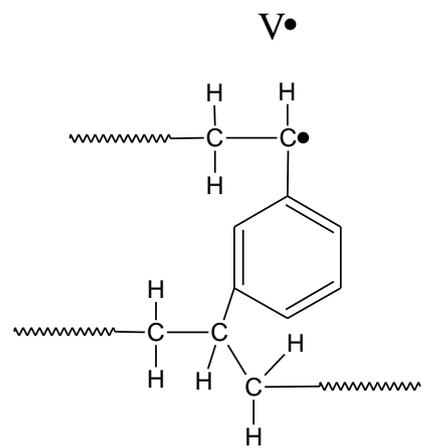
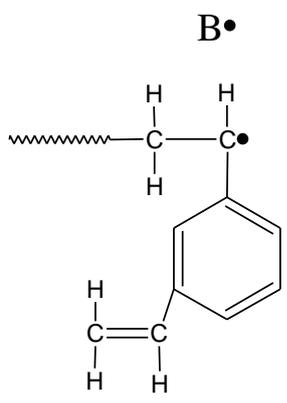
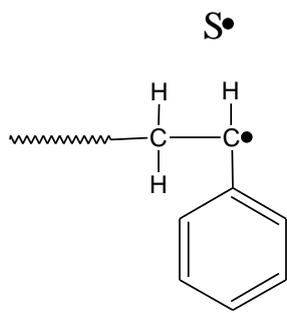


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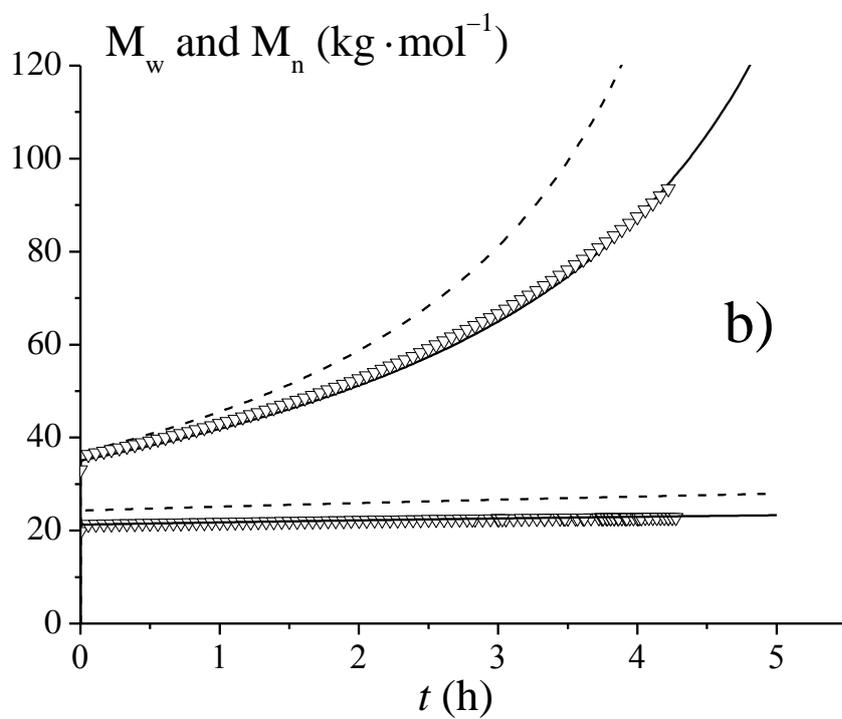
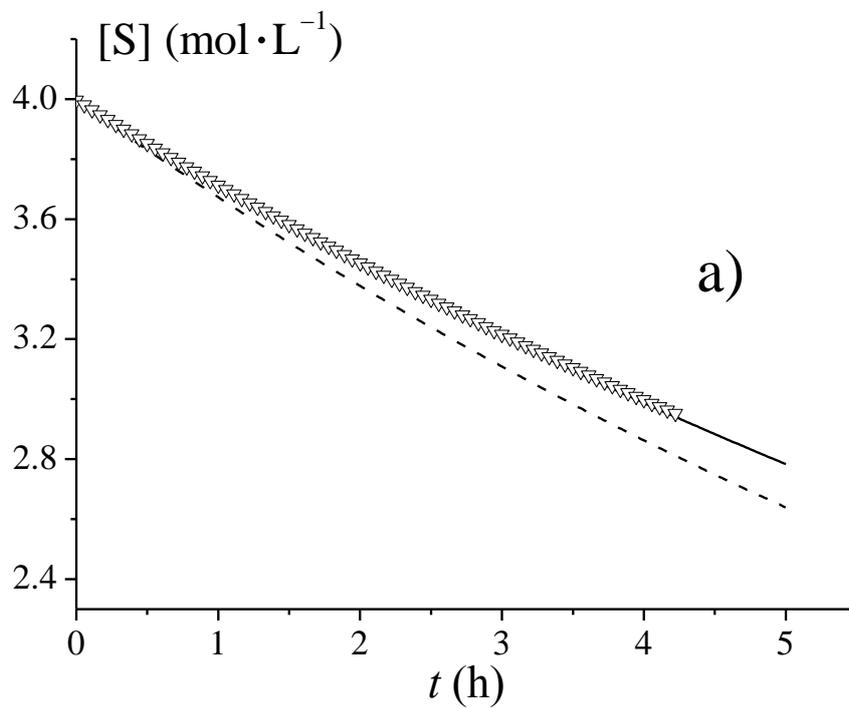
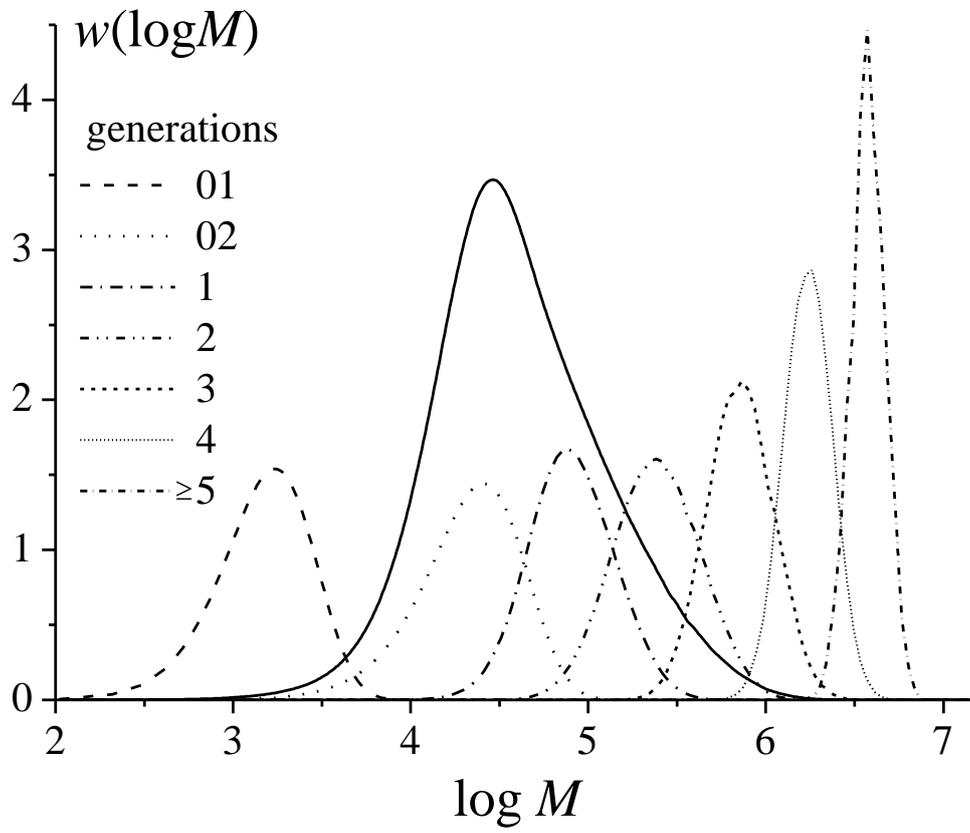
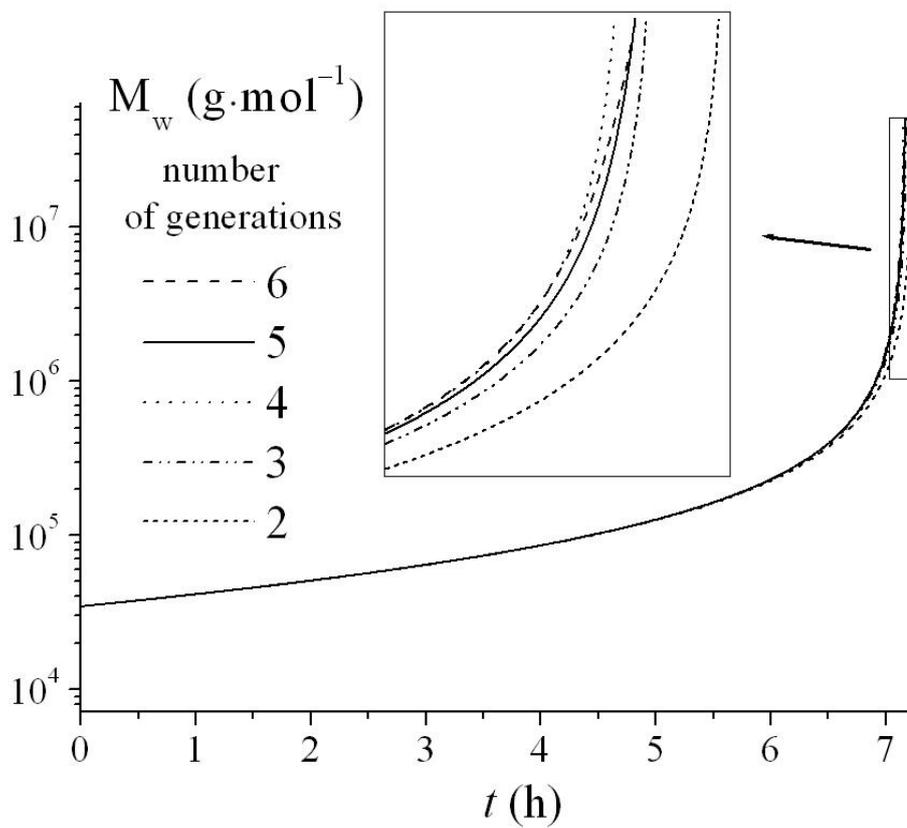


Figure 3



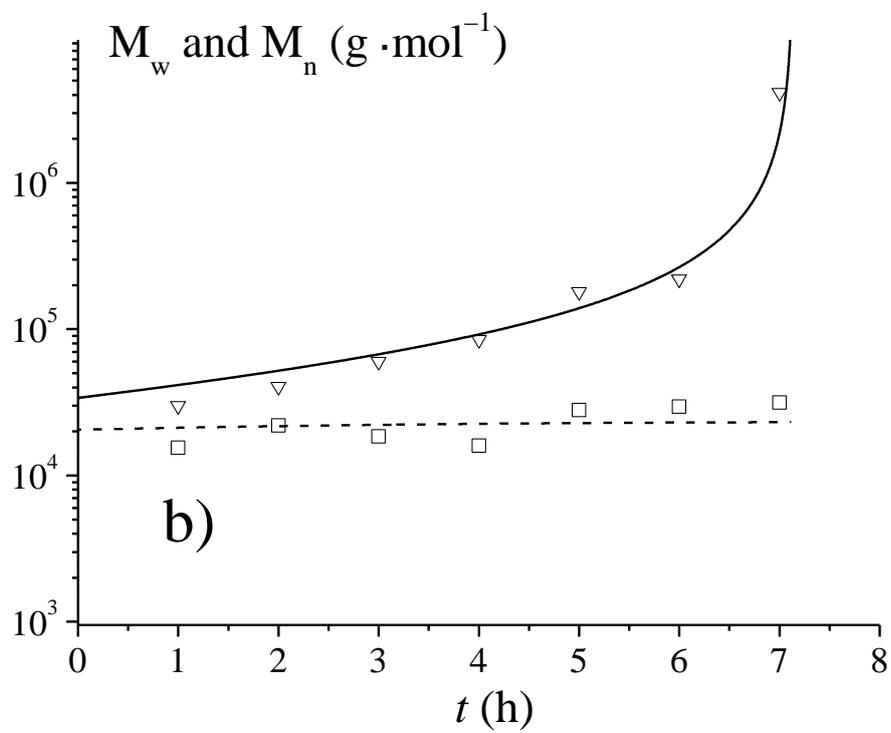
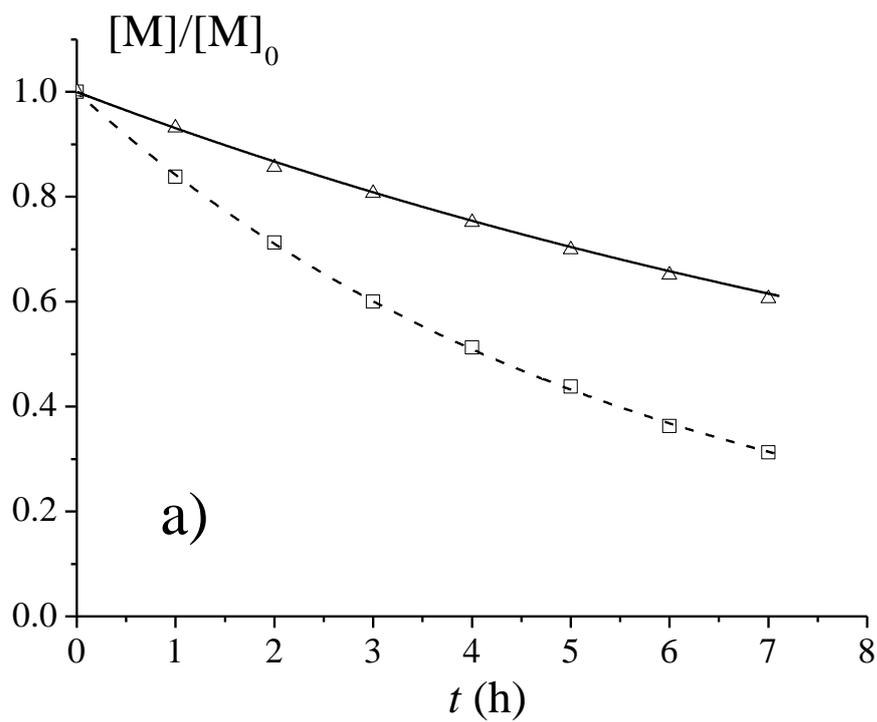
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Figure 4

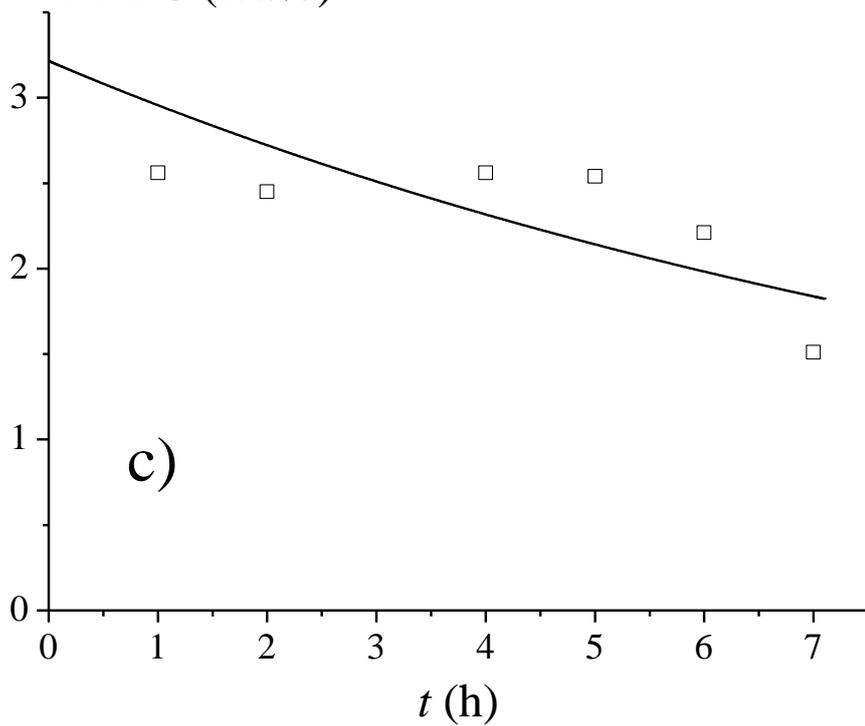


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Figure 5



PDBC (wt.%)



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Figure 6

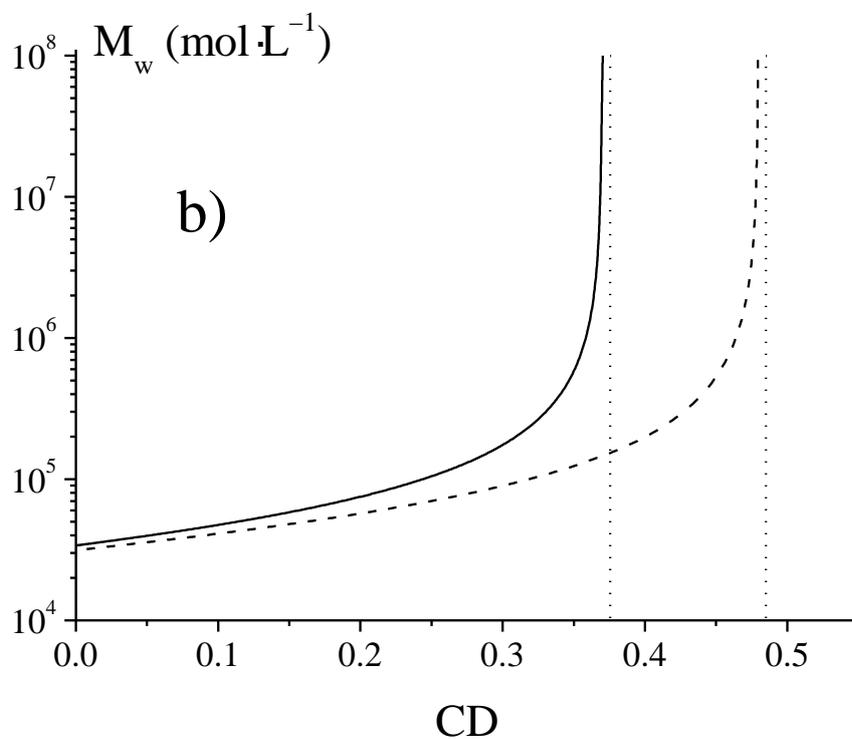
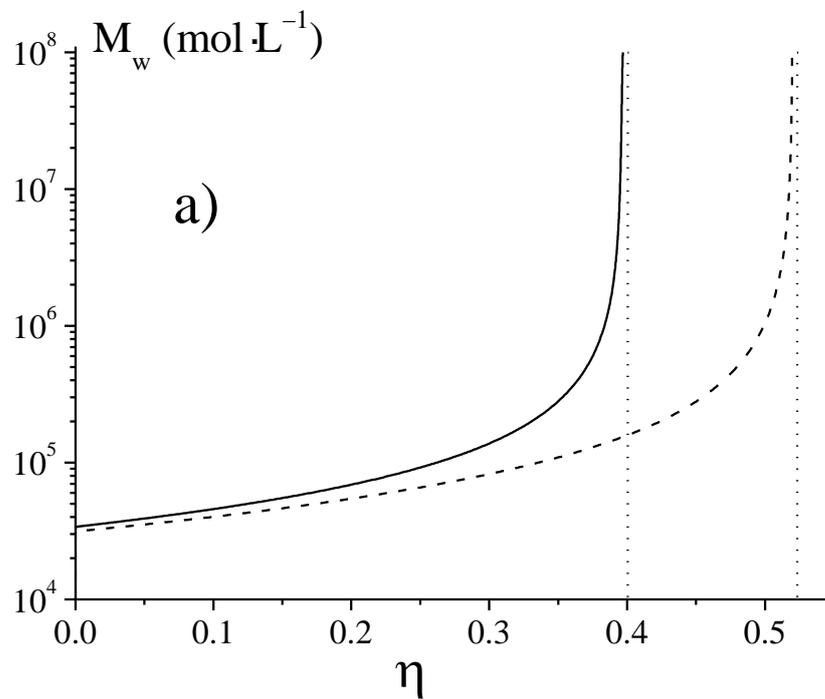


Figure 7

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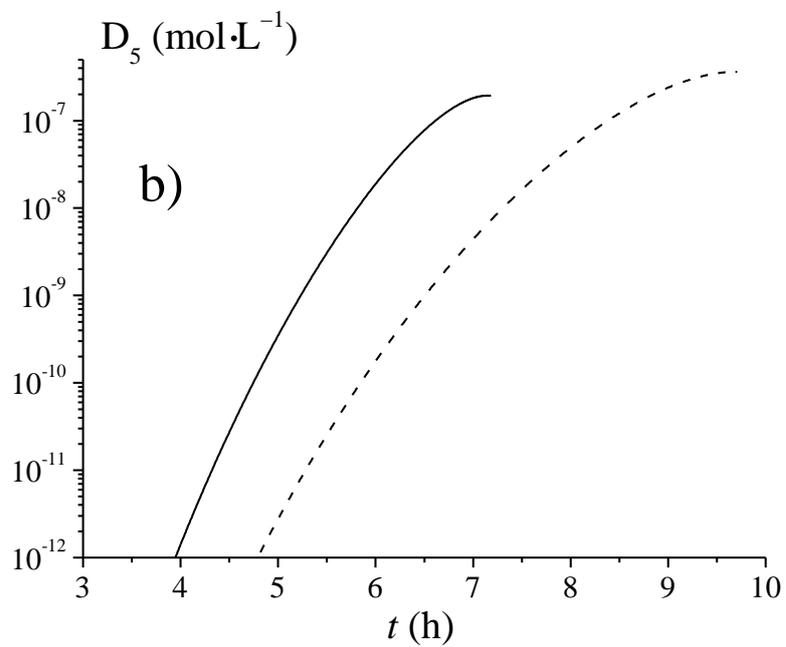
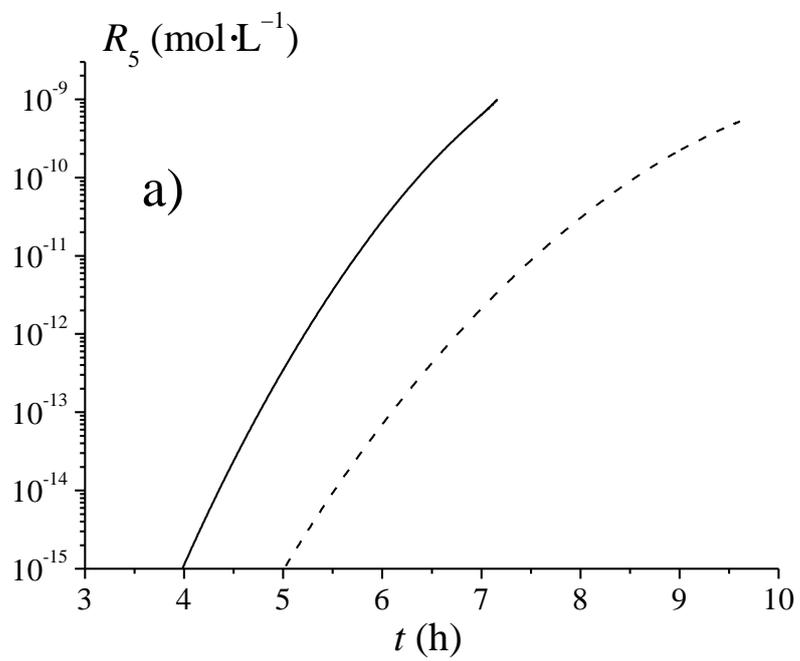
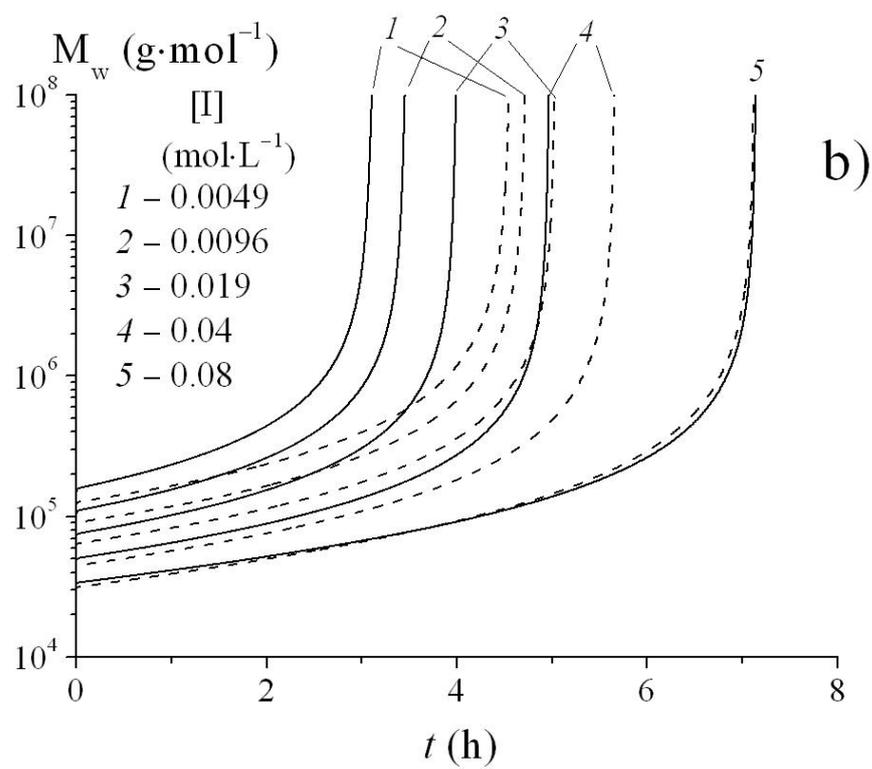
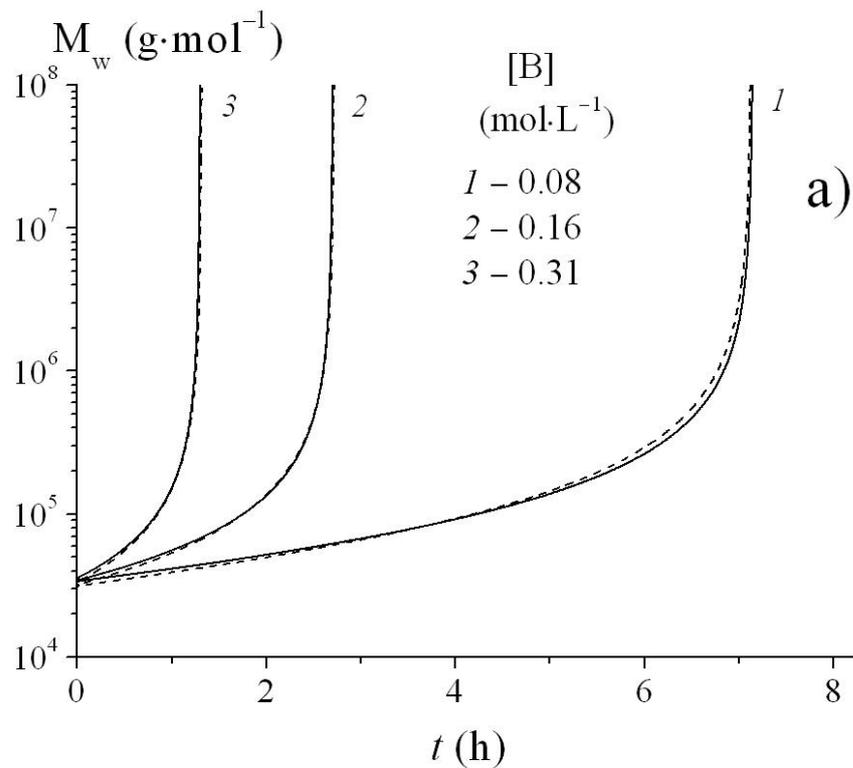
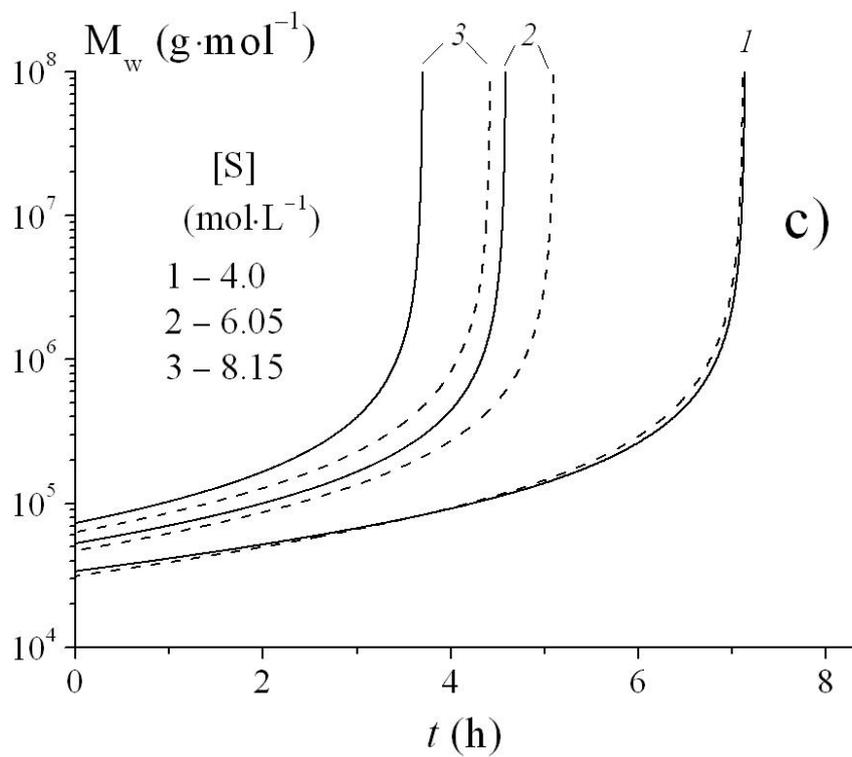


Figure 8





Scheme 1

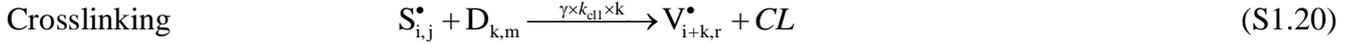


Termination of primary radicals

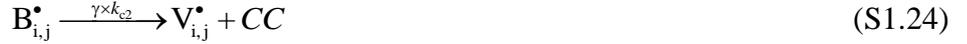




(for all the termination reactions: $r = j+1$ if $j=m$ and $j \neq 0$; $r = \max(j,m)$ if $j > m$ or $j < m$; $r=0$ if $j=m=0$)



(for all the crosslinking reactions: $r = j+1$ if $j=m$; $r = \max(j,m)$ if $j > m$ or $j < m$)



Chain transfer

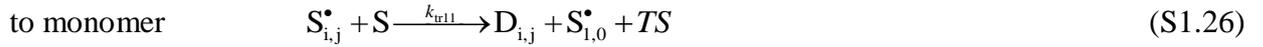


Table of Contents

The modeling approach called “numerical fractionation” has been incorporated into a PREDICI model to simulate crosslinking copolymerization. The kinetic parameters of the model are proposed to be different for each generation of the numerical fractionation. The styrene/m-divinylbenzene copolymerization at low content of crosslinker has been simulated. The chain-length dependence of termination has been found to accelerate the gel point in monovinyl/divinyl copolymerization.

