

Konrad-Zuse-Zentrum für Informationstechnik Berlin

Uwe Budde*

Michael Wulkow

Computation of Molecular Weight Distributions for Free Radical Polymerization Systems

* Schering AG
Müllerstraße 170-178
D-1000 Berlin 65

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Uwe Budde

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Abstract

Modeling of free radical polymerization leads to very large and usually stiff systems of ordinary differential equations which cannot be solved directly in an efficient way.

This paper presents the application of a new approach called discrete Galerkin method to a realistic example – the polymerization of methyl methacrylate (MMA). The method is characterized by a Galerkin approximation on the basis of orthogonal polynomials of a discrete variable which represents the polymer degree. It allows the efficient computation of solutions of complete kinetic schemes with time- or moment-dependent reaction coefficients by reducing the complexity to a few differential equations. The approximation error can be controlled by an error estimation. In the case of MMA polymerization a reduction of computational effort by a factor of about 25 compared to a standard method can be obtained for the quasi-steady-state approximation of the model. In addition solutions of the instationary kinetic scheme can be easily computed.

Inhalt

1	Introduction	1
2	Polymerization of Methyl Methacrylate	3
3	Discrete Galerkin Method	7
3.1	Basic Approximation Scheme	7
3.2	Schulz-Flory Distribution and Discrete Laguerre Polynomials . .	9
4	Analytical Preprocessing	11
4.1	Preprocessing of the QSSA	11
4.2	Preprocessing of the Complete Kinetic Model	14
5	Numerical Results	16
	References	22

1. Introduction

The free radical polymerization in concentrated homogeneous systems is an important industrial process to form polymers. The molecular weight distribution (MWD) respectively the chain length distribution (CLD) of the polymer and its mean values are dependent on the reaction conditions and they markedly affect the end-use mechanical properties of the polymer [20]. In the literature there are some models to describe the kinetic behavior of free radical polymerization systems and the resulting CLD ([3]–[5],[10],[11],[14],[15],[17],[19],[21]–[24]). These models - mostly used to calculate only the conversion-time history - are based on the complicated kinetic scheme of free radical polymerization which involves different numbers of basic kinetic steps. Non-conventional kinetic characteristics like the gel effect are taken into account in very different ways. The volume contraction as a further phenomenon of the polymerization reaction is often disregarded.

Since the whole kinetic system - the kinetic equations and the kinetic constants - affects the shape of the CLD it should be possible to prove the validity of model and constants by a comparison of calculated and experimental CLD data. However, the direct solution of the large stiff system of ordinary differential equations (ODE's) generated by the models of free radical polymerization cannot be obtained in a practical way, since every molecular species, especially every chain length, has to be treated by one ODE - increasing storage requirements and computing times beyond a tolerable level.

There are some methods to reduce the complexity of the kinetic system, e.g. the use of the quasi-stationary-state-approximation (QSSA) or the statistical moment treatment. Whereas the computation of the first statistical moments doesn't describe the whole CLD (a discussion is given in [9]) the modeling by the QSSA may be doubtful [13]. Even if the QSSA leads to reasonable results in some cases, its validity cannot be predicted a-priori in general and the error introduced by this approximation cannot be controlled. Especially the determination of rate constants or the verification of a model via the QSSA can introduce uncertainties.

In this paper the *discrete Galerkin method* suggested by DEUFLHARD and WULKOW in [9] and exemplified there on some model problems will be applied to a realistic example - the polymerization of methyl methacrylate (MMA) in solution. The method is based on an expansion of the CLD by polynomials of a discrete variable - the polymer degree - which are orthogonal with respect to a weight function. In the case of free radical polymerization this weight function will be the so-called Schulz-Flory distribution. By use of the orthogonality of the polynomials and some of their properties an approximation of the CLD can be obtained which is controlled by an *error estimation*. The method especially allows one to compare

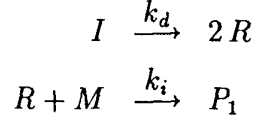
the solution of the complete kinetic scheme to the QSSA.

In Section 2 the reaction system and the effects of non-conventional kinetics taken into consideration are reviewed, Section 3 contains a short summary of the discrete Galerkin method and some needed properties. In Section 4 the method will be applied to the free radical polymerization model described in Section 2. Finally in Section 5 numerical results are given .

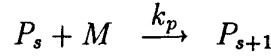
2. Polymerization of Methyl Methacrylate

Complete Model. The kinetic scheme of free radical polymerization in homogeneous systems is often described in the literature, we are following RAY ([21]) here:

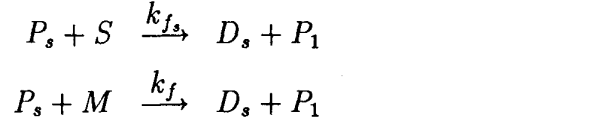
Initiation :



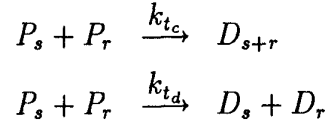
Propagation :



Chain Transfer :



Termination :



(2.1)

with I initiator, R initiated radicals, P_s radical polymer of length s , D_s dead polymer of length s , M monomer and S solvent. Not distinguishing between a chemical species and its concentration in the notation, the kinetic equations resulting from this process, including volume effects, are:

$$\begin{aligned} \text{a)} \quad I' &= -k_d I - \frac{V'}{V} I, \\ \text{b)} \quad M' &= -[2fk_d I + (k_p + k_f)MP] - \frac{V'}{V} M, \\ \text{c)} \quad S' &= -k_{fs}SP - \frac{V'}{V} S, \\ \text{d)} \quad P_1' &= 2fk_d I - k_p P_1 M + (k_{fs}S + k_f M)(P - P_1) - k_t P P_1 - \frac{V'}{V} P_1, \\ \text{e)} \quad P_s' &= k_p M(P_{s-1} - P_s) - (k_{fs}S + k_f M)P_s - k_t P P_s - \frac{V'}{V} P_s, \quad s \geq 2, \\ \text{f)} \quad P' &= 2fk_d I - k_t P^2 - \frac{V'}{V} P, \\ \text{g)} \quad D_s' &= (k_{fs}S + k_f M)P_s + k_{td} P_s P + \frac{k_{tc}}{2} \sum_{r=1}^{s-1} P_r P_{s-r} - \frac{V'}{V} D_s, \quad s \geq 1, \end{aligned} \quad (2.2)$$

where f is the initiator efficiency, $P = \sum_{r=1}^{\infty} P_r$ the total concentration of polymer radicals and V the reaction volume. The prime denotes the derivative d/dt . As a slowly disintegrating initiator is used in the present example (AIBN, $T = 65^\circ\text{C}$), so a QSSA for the initiated radicals is valid ($dR/dt = 0$) and already inserted here by setting $2fk_dI = k_iRM$. Note that the invalidity of this assumption doesn't affect the application of the discrete Galerkin method. The initial values $I(0)$, $M(0)$, $S(0)$ are given, $P_s(0) = 0$, $D_s(0) = 0$. The volume contraction is modeled as usual by

$$V = V_{X_M=0} (1 + \epsilon X_M),$$

where X_M is the monomer conversion given by

$$X_M = \frac{M(0) V_{X_M=0} - M V}{M(0) V_{X_M=0}},$$

and ϵ is the volume contraction factor, defined by

$$\epsilon = \frac{V_{X_M=1}}{V_{X_M=0}} - 1,$$

with $V_{X_M=0}$ ($V_{X_M=1}$) the reaction volume at monomer conversion $X_M = 0$ ($X_M = 1$). This leads to

$$\frac{V'}{V} = \frac{\epsilon(2fk_dI + (k_p + k_f)MP)}{M(0)}. \quad (2.3)$$

The rate coefficients are taken from [2] and listed in Table 1 at the end of this Section.

In the case of an ideal, low concentrated system a modeling with constant reaction coefficients is possible. In concentrated systems, however, an increase of viscosity arises which decreases the mobility of the polymer chains (*gel effect*). As a consequence the termination step is impeded if the polymer concentration increases. To describe this effect quantitatively, numerous attempts have been made in the literature – a survey is given in [25].

Following experimental results by BROOKS [1] the present paper will use the assumption that the termination coefficient $k_t = k_{t_c} + k_{t_d}$ can be modeled by

$$k_t \sim \eta^{-\frac{1}{2}},$$

where η is the viscosity of the polymerizing solution.

According to [18] the viscosity is described by

$$\eta = \eta_0 \left\{ 1 + P[\eta] \exp \left(\frac{K_H P[\eta]}{1 - bP} \right) \right\},$$

with η_0 the initial viscosity, $[\eta]$ the Staudinger index, K_H the Huggins constant and b an adjustable parameter.

The Staudinger index $[\eta]$ is connected with the viscosity average molecular weight M_η by the Mark-Houwink-Equation

$$[\eta] = K_{MH} M_\eta^a ,$$

with constants K_{MH} and a .

If we define the statistical moments of the dead polymer CLD D_s by

$$\mu_k := \sum_{s=1}^{\infty} s^k D_s , \quad (2.4)$$

and the number and weight average chain length (M_M the molecular weight of the monomer) by

$$M_n := \frac{\mu_1}{\mu_0} M_M , \quad M_w := \frac{\mu_2}{\mu_1} M_M ,$$

we obtain [12]:

$$M_\eta = \frac{1-a}{2} M_n + \frac{1+a}{2} M_w .$$

The computations in Section 5 are based on the assumption that the polymerizing solution can be regarded as low concentrated up to a viscosity η_{\lim} (compare [1]), whereas for higher viscosities the reaction is influenced by the gel effect:

$$\begin{aligned} k_t &= k_{t,0} & \text{if } \eta < \eta_{\lim} , \\ k_t &= k_{t,0} \left(\frac{\eta_{\lim}}{\eta} \right)^{\frac{1}{2}} & \text{if } \eta \geq \eta_{\lim} \end{aligned} \quad (2.5)$$

QSSA. Neglect of the left-hand sides of the equations (2.2.d-f) and application of the long chain hypothesis (LCH) to (2.2.b,c) lead to the QSSA of the reaction system (2.1) (compare [21]):

$$\begin{aligned} \text{a) } M' &= -k_p M P - \frac{V'}{V} M , \\ \text{b) } S' &= -\frac{V'}{V} S , \\ \text{c) } I' &= -k_d I - \frac{V'}{V} I , \\ \text{d) } D'_s &= (k_{f_s} S + k_f M + k_{t_d} P) P (1 - \alpha) \alpha^{s-1} \\ &\quad + \frac{1}{2} k_{t_c} P^2 (1 - \alpha)^2 \alpha^{s-2} (s - 1) - \frac{V'}{V} D_s , \quad s \geq 1 , \end{aligned} \quad (2.6)$$

with initial values $D_s(0) = 0$. The propagation probability α is defined by

$$\alpha = \frac{k_p M}{k_p M + k_{fs} S + k_f M + k_t P} , \quad (2.7)$$

the volume contraction now reads

$$\frac{V'}{V} = \frac{\epsilon k_p M P}{M(0)} . \quad (2.8)$$

Theoretically the systems (2.2) and (2.6) consist of infinitely many ordinary differential equations. In real applications a restriction to a maximum polymer degree s_{\max} is sufficient. In our present example a number of about 10^4 equations would remain. In the next Section we will describe how the complexity of the systems (2.2) and (2.6) can be reduced drastically.

constant	unit	value	constant	unit	value
k_d	s^{-1}	0.000015	$M(0)$	mol/l	4.32
k_p	l/mol/s	759.4	$S(0)$	mol/l	4.91
k_{fs}	l/mol/s	0.0331	$I(0)$	mol/l	0.01508
k_f	l/mol/s	0.0178	f	–	0.3
k_t	l/mol/s	34562675	ϵ	–	-0.11
k_{td}	l/mol/s	λk_t	K_H	–	0.41
k_{tc}	l/mol/s	$(1 - \lambda) k_t$	b	ml/g	0.2
λ	–	0.3	K_{MH}	ml/g	0.021
η_0	m Pa s	0.3	a	–	0.61
η_{\lim}	m Pa s	15	M_M	g/mol	100.13

Table 1: Values of the used constants ($T = 65^\circ \text{C}$) according to [2].

3. Discrete Galerkin Method

The discrete Galerkin method for the treatment of ordinary differential equations arising from polyreaction kinetics has been suggested in [9].

On the basis of a weight function, which is connected with the type of the process to be modeled, orthogonal polynomials of a discrete variable are constructed. Insertion of an expansion of the CLD by these polynomials into the kinetic equations leads to the estimation of the expansion coefficients, also called *generalized moments*. As it turns out comparatively few coefficients are needed for a good approximation of the CLD. The approximation error can be controlled by an error estimation.

We will give a short summary of the main ideas here and refer to [9] for the details.

3.1 Basic Approximation Scheme

We assume that the chain length distribution $P_s(t)$ of a polymer at time t can be expanded in a series

$$P_s(t) := \Psi(s; \rho) \sum_{k=0}^{\infty} a_k(t; \rho) l_k(s; \rho), \quad s = 1, 2, \dots, \quad (3.1)$$

where $\Psi(s; \rho)$ is a positive weight function with a (possibly time-dependent) real parameter ρ and $\{l_k(s)\}_{k=0,1,\dots}$ a set of polynomials of a *discrete* variable s which represents the polymer degree.

The polynomials are associated with $\Psi(s; \rho)$ by the *orthogonality* relation

$$\sum_{s=1}^{\infty} l_j(s; \rho) l_k(s; \rho) \Psi(s; \rho) = \gamma_k \delta_{jk}, \quad \gamma_k > 0, \quad j, k = 0, 1, 2, \dots, \quad (3.2)$$

with δ_{jk} the Kronecker symbol.

By use of the orthogonality of the polynomials, for given $P_s(t)$ the coefficients $a_j(t; \rho)$ can be obtained from

$$a_j(t; \rho) = \frac{1}{\gamma_j} \langle l_j(s; \rho), P_s(t) \rangle, \quad j = 0, 1, \dots, \quad (3.3)$$

using the *inner product*

$$\langle u(s), v(s) \rangle := \sum_{s=1}^{\infty} u(s) v(s). \quad (3.4)$$

Truncation of the expansion (3.1) after $n + 1$ terms will lead to a *Galerkin approximation*

$$P_{s,\rho}^{(n)}(t) := \Psi(s; \rho) \sum_{k=0}^n a_k(t; \rho) l_k(s; \rho). \quad (3.5)$$

Obviously the approximation depends on the parameter ρ and the *truncation index* n . In order to simplify the presentation, the notation will omit these dependences in the following whenever the context is clear.

As mentioned in [9] the relative truncation error $\epsilon_n(t)$ of the approximation (3.5), defined by

$$\epsilon_n(t)^2 := \frac{\sum_{s=1}^{\infty} (P_s^{(n)}(t) - P_s(t))^2 \Psi(s; \rho)^{-1}}{\sum_{s=1}^{\infty} P_s(t)^2 \Psi(s; \rho)^{-1}}, \quad (3.6)$$

can be estimated by

$$\epsilon_n(t)^2 \doteq \frac{\frac{a_{n+1}^2(t) \gamma_{n+1}}{n+1}}{\sum_{k=0}^{\infty} a_k(t)^2 \gamma_k}. \quad (3.7)$$

It is easily seen that a good choice of the *type* of the weight function Ψ in general and of the *parameter* ρ in particular will help to keep the truncation index n small. The "closer" $\Psi(s; \rho)$ is to $P_s(t)$ the "better" the approximation will be for *small* n . Note that this is not a fitting by one parameter!

Whereas the choice of Ψ needs (for the moment) still a rough a-priori insight into the chemical process, the selection of ρ can be done adaptively on the basis of the following requirements:

$$\begin{aligned} \text{a)} \quad \nu_0(\rho) &:= \sum_{s=1}^{\infty} \Psi(s; \rho) = 1, \\ \text{b)} \quad \nu_1(\rho) &:= \sum_{s=1}^{\infty} s \Psi(s; \rho) = \frac{\mu_1(t)}{\mu_0(t)}, \end{aligned} \quad (3.8)$$

with $\mu_0(t)$, $\mu_1(t)$ the statistical moments of $P_s(t)$ at a fixed time t .

The normalization (3.8.a) ensures that $\Psi(s; \rho)$ has an interpretation as a probability distribution, condition (3.8.b) gives an implicit definition of $\rho = \rho(t)$ identifying the mean values of $\Psi(s; \rho)$ and $P_s(t)$ and aiming at certain similarities between these distributions. $\Psi(s; \rho(t))$ is then called a *moving* weight function.

Note that (3.8) implies

$$\begin{aligned} \text{a)} \quad a_0(t) &\equiv \mu_0(t) \\ \text{b)} \quad a_1(t; \rho) &\equiv 0 \end{aligned} \quad (3.9)$$

These relations are very important for numerical computations.

3.2 Schulz-Flory Distribution and Discrete Laguerre Polynomials

As it is well-known that free radical polymerization leads to molecular weight distributions which are similar (in some sense) to the *Schulz-Flory distribution*, we will specialize from now :

$$\Psi(s; \rho) := (1 - \rho)\rho^{s-1}, \quad 0 < \rho < 1, \quad s = 1, 2, \dots \quad (3.10)$$

The orthogonal polynomials associated with $\Psi(s; \rho)$ by (3.2) are the *discrete Laguerre polynomials* [16], which can be represented via their *three-term recurrence relation* ($k = 0, 1, \dots$):

$$(k+1)l_{k+1}(s; \rho) = [(k+1)\rho + k - (1-\rho)(s-1)]l_k(s; \rho) - k\rho l_{k-1}(s; \rho), \quad (3.12.a)$$

to be started with

$$l_{-1} := 0, \quad l_0 := 1. \quad (3.12.b)$$

For these polynomials (3.2) holds with

$$\gamma_k = \rho^k \quad k = 0, 1, \dots \quad (3.12)$$

For the so-called *analytical preprocessing* of a polyreaction system we need some properties of discrete Laguerre polynomials, which are listed in the following without proof (in brackets the reaction step where the relation is used).

$$l_k(s+1; \rho) - l_k(s; \rho) = (\rho - 1) \sum_{\nu=0}^{k-1} \rho^{k-1-\nu} l_\nu(s; \rho), \quad (3.13)$$

(propagation step)

$$\sum_{r=1}^{s-1} l_k(r; \rho) l_j(s-r; \rho) = \frac{1}{1-\rho} (\rho l_{k+j}(s; \rho) - l_{k+j+1}(s; \rho)), \quad (3.14)$$

(termination step)

$$\frac{\partial l_k(s; \rho)}{\partial \rho} = \frac{k}{1-\rho} (l_{k-1}(s; \rho) - l_k(s; \rho)), \quad (3.15)$$

(moving weight function control)

$$\begin{aligned}
l_k(s; \bar{\rho}) &= \sum_{\nu=0}^k d^{k,\nu}(\rho, \bar{\rho}) l_\nu(s; \rho) , \quad 0 < \bar{\rho} < 1 , \\
d^{k,\nu}(\rho, \bar{\rho}) &:= \frac{(\bar{\rho} - \rho)^{k-\nu}}{(1 - \rho)^k} (1 - \bar{\rho})^\nu \binom{k}{\nu} , \quad k \geq \nu \geq 0 ,
\end{aligned} \tag{3.16}$$

(weight function transformation)

Once a Galerkin approximation (3.5) has been computed, the first n statistical moments of the distribution $P_s^{(n)}(t)$ can be obtained from the coefficients $a_k = a_k(t; \rho)$, $0 \leq k \leq n$. Especially we have for $n \geq 2$:

$$\begin{aligned}
\text{a) } \mu_0(t) &= a_0 \\
\text{b) } \mu_1(t) &= \frac{a_0 - \rho a_1}{1 - \rho} \\
\text{c) } \mu_2(t) &= \frac{(1 + \rho)a_0 - \rho(3 + \rho)a_1 + 2\rho^2 a_2}{(1 - \rho)^2}
\end{aligned} \tag{3.17}$$

If $P_{s,\rho}^{(n)}(t)$ is known, we can transform the representation to a parameter $\bar{\rho}$ and a truncation index \bar{n} by :

$$a_j(t; \bar{\rho}) = \gamma_j(\bar{\rho})^{-1} \sum_{k=0}^j a_k(t; \rho) d^{j,k}(\rho, \bar{\rho}) \gamma_k(\rho) , \quad 0 \leq j \leq \bar{n} , \tag{3.18}$$

with $\gamma_j(\rho) := \rho^j$.

If the moving weight function property (3.9), $a_1(t; \rho) = 0$, is not valid for a given representation with parameter ρ , the condition $a_1(t; \bar{\rho}) = 0$ yields

$$\bar{\rho} = \frac{\rho(a_0(t; \rho) - a_1(t; \rho))}{a_0(t; \rho) - \rho a_1(t; \rho)} . \tag{3.19}$$

if

$$a_1(t; \rho) < a_0(t; \rho) . \tag{3.20}$$

Condition (3.20) holds whenever $P_s(t)$ has an expansion of the type (3.1).

With $\bar{\rho}$ from (3.19) we can get the new coefficients $a_j(t; \bar{\rho})$ by:

$$\begin{aligned}
\text{a) } a_0(t; \bar{\rho}) &= a_0(t; \rho) , \\
\text{b) } a_j(t; \bar{\rho}) &= \left(\frac{a_1(t; \rho)}{a_1(t; \rho) - a_0(t; \rho)} \right)^j \sum_{k=0}^j \binom{j}{k} a_k(t; \rho) \left(-\frac{a_0(t; \rho)}{a_1(t; \rho)} \right)^k .
\end{aligned} \tag{3.21}$$

On the other hand, if $a_1(t; \rho) = 0$ for some parameter ρ , a transformation to $\bar{\rho}$ is only valid if

$$\bar{\rho} > \rho^2 . \tag{3.22}$$

Note that a stable numerical implementation of (3.18) and (3.21) is possible.

4. Analytical Preprocessing

The application of the discrete Galerkin method described in Section 3.1 – the *analytical preprocessing* – is exemplified in the next two paragraphs for the QSSA of reaction (2.1) and for the complete model, including radical and dead polymer treatment, gel and volume effects.

The main concepts will be explained for the QSSA in Section 4.1, the treatment of the complete model in Section 4.2 is a more technical extension and we will not elaborate the details there.

4.1 Preprocessing of the QSSA

We consider the differential equations (2.6) for the QSSA approximation of reaction (2.1).

For the moment let us assume that the termination rate coefficient k_t and the reaction volume are constant. This implies that the differential equations for the monomer M , the solvent S and the initiator I in principle can be solved in terms of the propagation probability α and the polymer radical concentration P without knowledge of the chain length distribution $D_s(t)$ of the dead polymer.

Hence we can focus our attention on the treatment of the equations for the dead polymer

$$\begin{aligned} D'_s &= f_s^D := g_1 (1 - \alpha) \alpha^{s-1} + g_2 (s - 1)(1 - \alpha)^2 \alpha^{s-2}, \quad s \geq 1, \\ D_s(0) &= 0, \end{aligned} \quad (4.1)$$

with

$$\begin{aligned} g_1 &:= (k_{fs} S + k_f M + k_{td} P) P, \\ g_2 &:= \frac{1}{2} k_{tc} P^2. \end{aligned}$$

Starting point is the expansion

$$D_s(t) = \Psi(s; \rho) \sum_{k=0}^{\infty} b_k(t; \rho) l_k(s; \rho), \quad (4.2)$$

where $\Psi(s; \rho)$ is a Schulz-Flory distribution again. In view of (3.3) analytical preprocessing of (4.1) means the evaluation of the relations

$$\frac{1}{\gamma_j} \langle D'_s, l_j(s; \rho) \rangle = \frac{1}{\gamma_j} \langle f_s^D, l_j(s; \rho) \rangle, \quad j \geq 0, \quad (4.3)$$

using the Euclidian inner product (3.4). As we will see now this leads to a system of differential equations for the coefficients $b_j = b_j(t; \rho)$.

The still missing ODE for ρ is obtained from the condition (3.9): $b_1(t; \rho) \equiv 0$. Inserting $b_1 = 0$ in (4.7) yields

$$\rho' = \frac{\rho - 1}{b_0} \left(d^{1,0}(\alpha, \rho)(g_1 + g_2) - d^{1,1}(\alpha, \rho)g_2 \right). \quad (4.9)$$

This expression substitutes the differential equation for b_1 in (4.7) – the information contained in b_1 is shifted to the control of the moving weight function.

For the initial values (4.8) equation (4.9) is not defined at $t = 0$, since $b_0(0) = 0$. Furthermore the values $\rho(0)$, $\rho'(0)$ are missing

In order to overcome this difficulty the following *starting procedure*, which can be automated within a program, has turned out to be successful:

- (i) choice of ρ_0 , $0 < \rho_0 < 1$.
- (ii) integration of (4.7) in $[0, t_1]$, t_1 obtained from the first integration step with initial value $\rho(0) = \rho_0$, ρ constant.
- (iii) computation of ρ_1 according to (3.19) such that $b_1(t_1; \rho_1) = 0$.
computation of $b_j(t_1; \rho_1)$, $j \geq 0$, by (3.21) and continuation of the integration from t_1 , ρ time-dependent now.

Note that a careful estimation of the parameter is necessary to avoid oscillations and wrong approximations – compare the discussion in [9].

The extension of the preprocessing to the realistic model is very simple now:

The termination rate coefficient k_t from (2.5) is defined by use of the statistical moments μ_0, μ_1, μ_2 of the dead polymer CLD which are totally determined by b_0, b_1, b_2 (3.17). Thus the preprocessing remains the same.

The effect of volume contraction leads to the extended system

$$D'_s = f_s^D - \frac{V'}{V} D_s, \quad s \geq 1,$$

with $\frac{V'}{V}$ according to (2.8). Since

$$\rho^{-j} \left\langle -\frac{V'}{V} D_s, l_j(s; \rho) \right\rangle = -\frac{V'}{V} b_j, \quad (4.10)$$

we have only to add the module $-\frac{V'}{V} b_j$ to the right-hand side of (4.7).

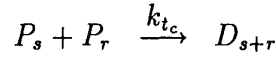
Summarizing (4.7), (4.9), (4.10) we end up with

$$\begin{aligned} b'_0 &= g_1 + g_2 - \frac{V'}{V} b_0, \\ b'_j + \frac{j\rho'}{(1-\rho)\rho} (b_j - b_{j-1}) &= \rho^{-j} (d^{j,0}(\alpha, \rho)(g_1 + g_2) - d^{j,1}(\alpha, \rho)g_2) - \frac{V'}{V} b_j, \\ \rho' &= \frac{\rho - 1}{b_0} (d^{1,0}(\alpha, \rho)(g_1 + g_2) - d^{1,1}(\alpha, \rho)g_2), \end{aligned} \quad (4.11)$$

$j \geq 2, t > t_1 > 0, \rho' = 0$ if $t \in [0, t_1]$, α, P from Section 2. The differential equations (2.6.a-c) have to be added. For a given truncation index n this system can be solved by a standard integration routine. It will be shown in Section 5 that only a few coefficients b_j are needed to obtain a good approximation of the dead polymer CLD.

4.2 Preprocessing of the Complete Kinetic Model

To exemplify the possibility of a stepwise preprocessing in view of an automatic preprocessor we consider in this Section only one reaction step in detail. The termination by combination



is modeled for a given radical distribution $P_s(t)$ by

$$P'_s = g_s^P := -k_{tc} P_s P, \quad s \geq 1, \quad P = \sum_{r=1}^{\infty} P_r, \quad (4.12)$$

for the polymer radicals and by

$$D'_s = g_s^D := \frac{k_{tc}}{2} \sum_{r=1}^{s-1} P_r P_{s-r}, \quad s \geq 1, \quad (4.13)$$

for dead polymer. We begin with two expansions now:

$$\begin{aligned} \text{a)} \quad P_s(t) &= \Psi(s; \rho_1) \sum_{k=0}^{\infty} a_k(t; \rho_1) l_k(s; \rho_1), \\ \text{b)} \quad D_s(t) &= \Psi(s; \rho_2) \sum_{k=0}^{\infty} b_k(t; \rho_2) l_k(s; \rho_2), \end{aligned} \quad (4.14)$$

with the possibly different parameters ρ_1 and ρ_2 .

In analogy with (4.3) we have to evaluate the relations

$$\begin{aligned} \text{a)} \quad \rho_1^{-j} \langle P'_s, l_j(s; \rho_1) \rangle &= \rho_1^{-j} \langle g_s^P, l_j(s; \rho_1) \rangle, \\ \text{b)} \quad \rho_2^{-j} \langle D'_s, l_j(s; \rho_2) \rangle &= \rho_2^{-j} \langle g_s^D, l_j(s; \rho_2) \rangle. \end{aligned} \quad (4.15)$$

(4.15.a) is easily reduced to

$$a'_j + \frac{\rho'_1}{(1 - \rho_1)\rho_1} (a_j - a_{j-1}) = -k_{tc} a_j a_0, \quad j \geq 1, \quad (4.16)$$

and $a_0 = P$.

The treatment of (4.15.b) will be done by using transformation (3.16) again. With a result from [9] we have

$$\langle g_s^D, l_\nu(s; \rho_1) \rangle = \rho_1^\nu \frac{k_{tc}}{2} \left[\sum_{\mu=0}^{\nu} a_\mu a_{\nu-\mu} - \rho_1^{-1} \sum_{\mu=0}^{\nu-1} a_\mu a_{\nu-1-\mu} \right]. \quad (4.17)$$

In analogy to (4.6) the preprocessing of the single reaction step (4.13) yields:

$$\rho_2^{-j} \langle g_s^D, l_j(s; \rho_2) \rangle = \rho_2^{-j} \sum_{\nu=0}^j d^{j,\nu}(\rho_1, \rho_2) \langle g_s^D, l_\nu(s; \rho_1) \rangle. \quad (4.18)$$

Summing up all right-hand sides of such preprocessed modules and including the volume contraction we finish:

$$\begin{aligned} a'_0 &= h_2 - k_t a_0^2 - a_0 \frac{V'}{V}, \\ a'_j + \frac{\rho'_1}{(1-\rho_1)\rho_1} (a_j - a_{j-1}) &= -k_p M \frac{1-\rho_1}{\rho_1} \sum_{\nu=0}^{j-1} a_\nu - h_1 (a_j - a_0) - \\ &\quad - k_t a_j a_0 + h_2 - a_j \frac{V'}{V}, \\ b'_j + \frac{\rho'_2}{(1-\rho_2)\rho_2} (b_j - b_{j-1}) &= \rho_2^{-j} \sum_{\nu=0}^j d^{j,\nu}(\rho_1, \rho_2) \left[\rho_1^\nu (h_1 + k_{td} a_j) a_0 + \right. \\ &\quad \left. + \langle g_s^D, l_\nu(s; \rho_1) \rangle \right] - b_j \frac{V'}{V}, \end{aligned} \quad (4.19)$$

where $h_1 := k_{fs}S + k_fM$, $h_2 := 2fk_dI$. The equations for M, S, I have to be added from (2.2), $a_j(0) = b_j(0) = 0$, $j \geq 0$.

In Section 3.2 we have listed the properties of discrete Laguerre polynomials which are used to derive this system, in [9] a more detailed computation for initiation and termination step can be found.

For both species the moving weight function condition

$$a_1(t; \rho_1) = b_1(t; \rho_2) = 0, \quad t > 0,$$

has to be inserted (cf. Section 4.1) – in practice by a program.

5. Numerical Results

In this Section the efficiency of the discrete Galerkin method applied to the kinetic equations (2.2) and (2.6) is illustrated. A discussion of the model (2.1) under the aspects conversion-time history, rate constants and viscosity has been done in [2], we will focus our attention on the approximation of chain length distributions here. In preparation of the numerical computations some remarks have to be made:

- (a) The solution of the preprocessed equations (4.11) for the QSSA and (4.19) for the complete model have been obtained by the extrapolation codes DIFEX1 (nonstiff case) and EULSIM (stiff case) described by DEUFLHARD in [7]. In order to obtain reliable results, an appropriate scaling turned out to be crucial – see [8], Chapter C.1, for details.
- (b) The evaluation of the Galerkin approximation (3.5) for given coefficients a_k has to be done carefully because instabilities can arise. The use of a fast algorithm as described in [6] is essential.

QSSA. As shown in Section 4, the analytical preprocessing of the system (2.6) yields (4.11). For a given truncation index n this system has been solved with the non-stiff integrator DIFEX1 with an integration tolerance $TOL = 10^{-4}$. The initial value $\rho(0) = 0.9993$ has been chosen in view of $\alpha(0) = 0.9992 \dots$. The correctness of the starting process can be checked by computing the analytical value ρ_0 which removes the singularity at $t = 0$ in (4.9). A short calculation yields

$$\rho_0 = \frac{\alpha(0)g_1 + (1 + \alpha(0))g_2}{g_1 + 2g_2} < 1.$$

This value could be obtained for a sufficient small starting step ($t_1 = 10^{-4}$) up to 8 decimals.

The integrator needed about 50 right-hand side evaluations of system (4.11), which has only $n + 4$ components for truncation index n . For a comparison note that a computation of selected fractions [2] would lead to at least 100 equations. A discretization in the monomer conversion has been performed there with 100 steps, so that 10000 evaluations of right-hand side components are needed. By the discrete Galerkin method this number could be reduced to 350 for a comparable solution with controlled error. Moreover the representation of the solution by the Galerkin method is *global*, i.e. the concentration of every single species is available – no a-priori selection of fractions and of a maximum polymer degree has to be done. The obtained approximations $D_s^{(n)}(t)$ of the dead polymer CLD are shown for $n = 0, 2, 3, 5, 10$ in Figure 1. Final time of integration is $t = 4.5h$, comparable to the experiments described in [2]. Figure 1 reflects the fast convergence of the method on the basis of a Schulz-Flory distribution ($n = 0$). On the other hand we

can see that a pure Schulz-Flory distribution is not sufficient to describe the CLD.

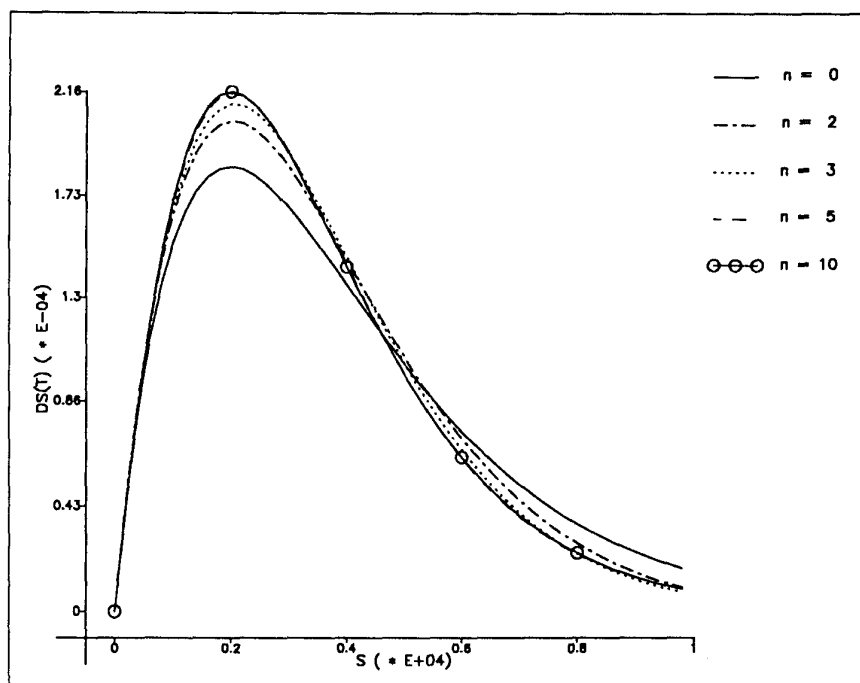


Figure 1: Discrete Galerkin approximations of the CLD of dead polymer for $n = 0, 2, 3, 5, 10$, $t = 4.5h$, $s_{max} = 10000$.

Table 2 shows the (cheap) estimated relative error $\epsilon_n(t)$ due to (3.7) compared to a true error $\bar{\epsilon}_n(t)$, computed by a highly accurate reference solution, for $n = 2, 3, 5, 10, 15$. As we can see the error estimation turns out to be very satisfactory.

truncation index n	estimated error ϵ_n	true error $\bar{\epsilon}_n$
2	$5.1 \cdot 10^{-2}$	$6.0 \cdot 10^{-2}$
3	$2.6 \cdot 10^{-2}$	$3.0 \cdot 10^{-2}$
5	$5.7 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$
10	$0.9 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$
15	$1.6 \cdot 10^{-6}$	$1.7 \cdot 10^{-6}$

Table 2: Comparison of estimated and true approximation error for dead polymer CLD, $t = 4.5h$, $n = 2, 3, 5, 10, 15$.

Complete Model In the following we will show that by the discrete Galerkin method it is possible to calculate approximations of the total CLD (MWD) for both the polymer radicals and the dead polymer with an acceptable amount of work. (Note that all computations have been done on a SUN 3/60 workstation, requiring only a few seconds CPU time.) This permits a more detailed study of reactions and the verification of the validity of models and approximations. In the case of the complete model the system of preprocessed equations is stiff, therefore the integrator EULSIM has been used with tolerance $TOL=10^{-4}$. In order to illustrate the starting phase of the process, Figure 2 shows the development of the parameter ρ_1 belonging to the polymer radicals in the time interval $[0, 0.1]$. The initial forming of the polymer radicals at the beginning of the reaction, neglected by the QSSA, is reflected. The dense integration points, marked by stars, show the high complexity of the reaction in this phase. An approximately stationary state of ρ_1 is reached after about 10 seconds.

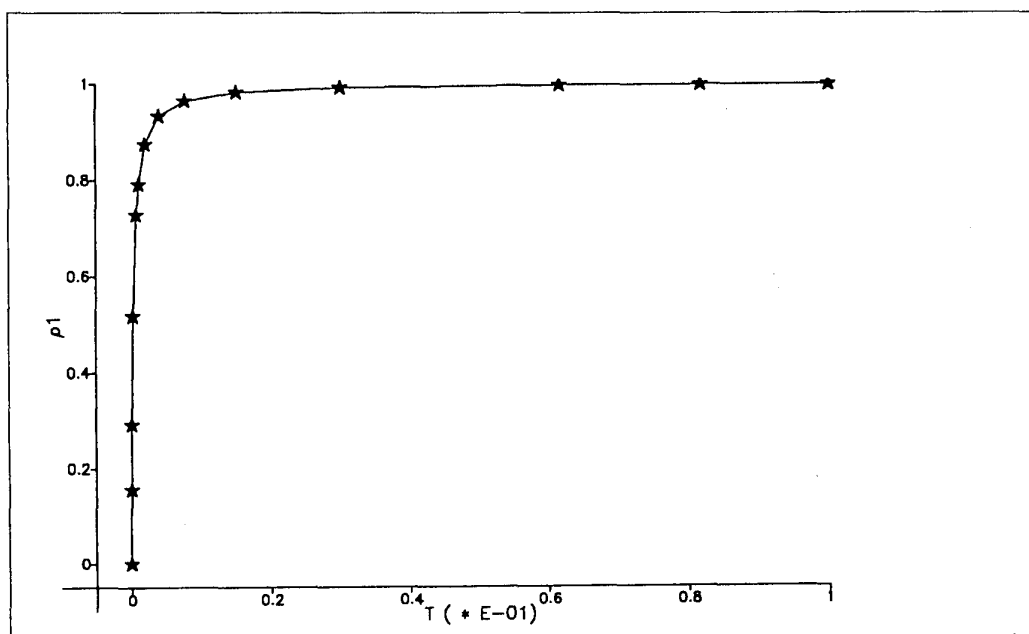


Figure 2: Initial phase of the parameter ρ_1 .

A consequence can be seen in Figure 3, where QSSA and CLD of the dead polymer is plotted for $t = 0.5s, 1s, 5s, 20s$. The stationary state is reached after 20 seconds reaction time. The truncation indices have been $n_P = n_D = 5$ for all computations.

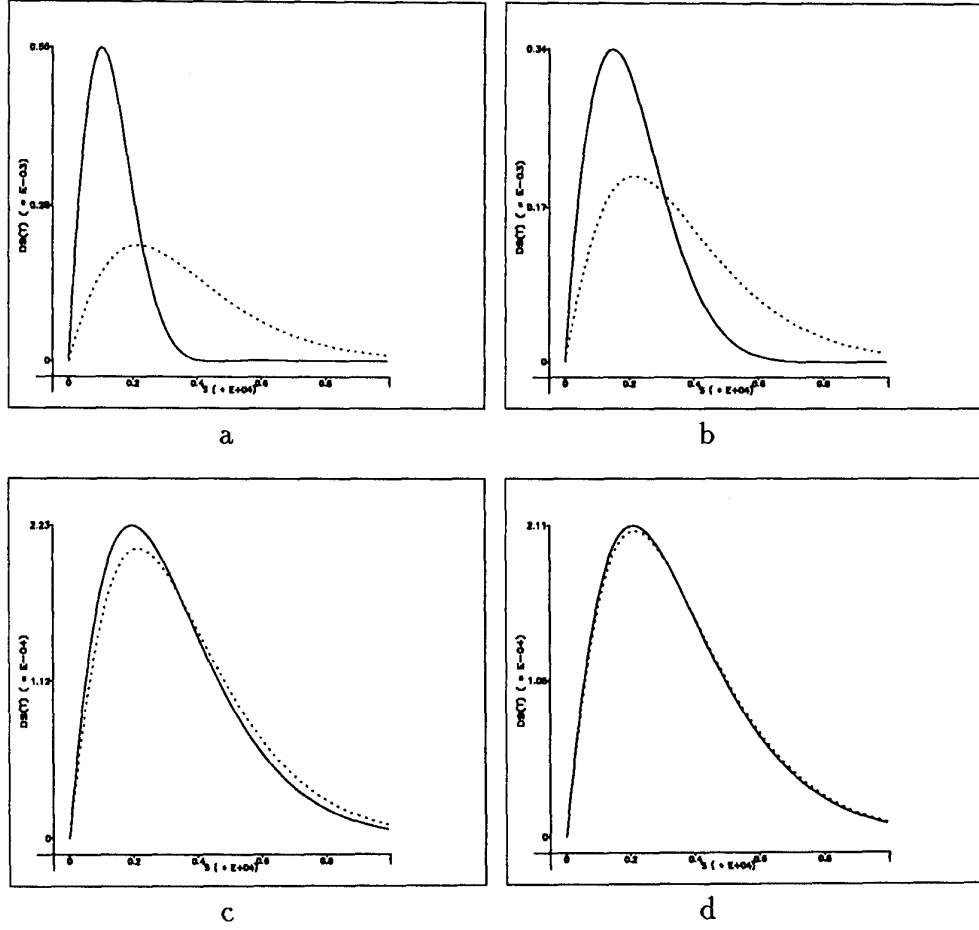


Figure 3: Comparison between QSSA and full scheme solution of dead polymer CLD for (a) $t = 0.5s$, (b) $t = 1s$, (c) $t = 5s$, (d) $t = 20s$. The dotted line denotes the QSSA solution.

After reaching the stationary state, the reaction remains there for hours. The CLD's for dead polymers are not significantly different from the QSSA for the rest of the process, whereas it can be seen that the radical distributions for QSSA and complete model diverge from $t = 3h$ to the end of the process. This fact is presented in Figure 5 for $t = 3h, 4.5h, 6h$. Again the truncation indices $n_P = n_D = 5$ were chosen for the presentation. The estimated errors at $t = 6h$ are

$$\epsilon_5^P = 10^{-6}, \quad \epsilon_5^D = 3 \cdot 10^{-3}.$$

It is not surprising that the differences between the QSSA solution and the complete solution are relatively small, because the system remains nearly ideal. A

more reactive initial mixture of monomer, solvent and initiator could increase the auto-catalytic behavior of the system. The differences between QSSA and complete solution would increase for higher concentrated systems (bulk polymerization), but for this case the model used herein is unsatisfactory since the so-called *glass effect* is neglected.

In order to compare experimental data with numerical computations Figure 4 presents the measured and computed CLD of the dead polymer after 3h45min reaction time. The data are selected from [2] and linearly interpolated. It can be seen that the modeling by *BUDDE* in [2] summarized in Section 2 leads to a good description of the system treated in this paper.

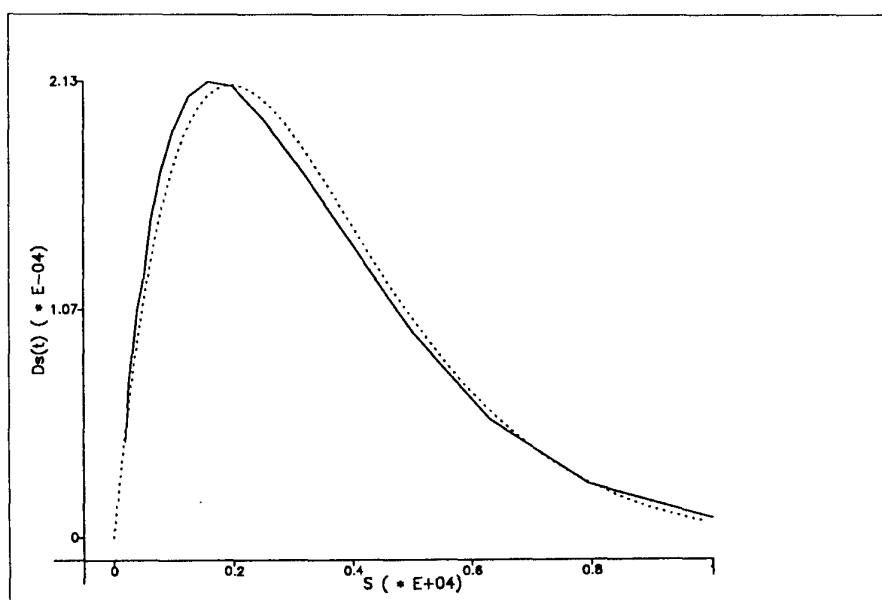


Figure 4: Comparison between experimental data according to [2] and computed (dotted line) dead polymer CLD.

Finally we note that extensions to other rate coefficients which are time- or moment-dependent can be done without changing the preprocessing. Additional reaction steps e.g. transfer to dead polymer or reactions involving polymer species with a double bond (Vinylacetat reactions) can be treated for itself and added then to the system. The treatment of chain length dependent termination coefficients (compare [23]) will be the subject of further work.

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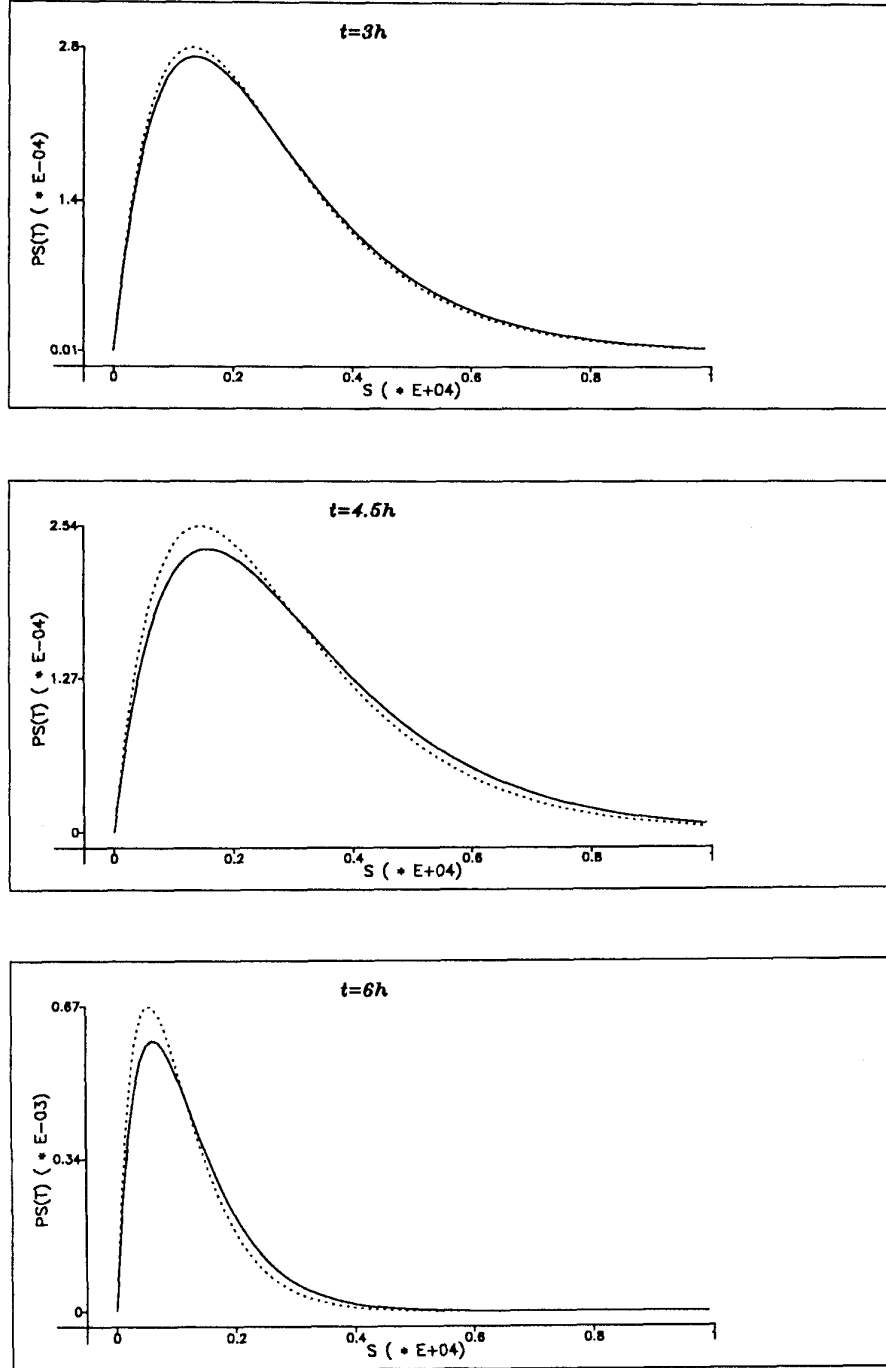


Figure 5: Comparison between CLD of polymer radicals obtained by QSSA (dotted line) and by Galerkin approximation of complete model ($n_P = n_D = 5$).

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