DYNAMIC MODELLING OF LIVING ANIONIC SOLUTION POLYMERIZATION OF STYRENE/BUTADIENE/DIVINYLBENZENE IN A CONTINUOUS STIRRED TANK REACTOR TRAIN

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ABSTRACT

Herein is reported a novel dynamic kinetic reactor model for the living anionic solution polymerization of styrene/butadiene/divinylbenzene in a continuous stirred tank reactor train. The model accounts for association of n-butyllithium the anionic initiator and the formation of tetrafunctional long chain branches via propagation with pendant carbon-carbon double bonds on divinylbenzene incorporated in the copolymer chains. The model predicts individual molecular weight distributions for polymer chains from zero to nine tetrafunctional branch points and employing Zimm-Stockmayer long chain branching equations it is possible to predict GPC (DRI/VISCOTEK) detector cell contents properties (polymer weight fraction, intrinsic viscosity and number-average molecular weight versus retention volume). This permits effective use of GPC for kinetic parameter estimation. GPC measurements on the copolymer in the effluent of a single CSTR are used to illustrate the effectiveness of parameter estimation.

INTRODUCTION AND LITERATURE REVIEW

The present investigation was motivated by the lack of a comprehensive kinetic reactor model for the living anionic solution polymerization of styrene/butadiene/divinylbenzene, which accounts for tetrafunctional long chain branching. The model extends the earlier investigations of Chang [1] who considered linear copolymer chains and used method of moments.

The data obtained with GPC measurements on polymers with long chain branching are often interpreted incorrectly. It is therefore instructive to review the mechanism by which GPC/SEC fractionates a mixture of linear and branched polymer chains. For a mixture of linear polymer chains of uniform composition having a distribution of molecular weights, there is a one to one correlation between hydrodynamic volume (radius of gyration) and molecular weight. GPC fractionates polymer chains (whether linear or branched) according to hydrodynamic volume and therefore in the absence of band broadening (peak dispersion), linear polymer chains in the detector cell will have the same hydrodynamic volume and the same molecular weight. However, with complex polymers such as those not uniform in composition or those with differing long chain branching lengths and frequencies, the interpretation of GPC data is far more complicated. In these instances, polymer solute in the GPC detector cell may differ in molecular weight and branching frequency and GPC data to be useful for kinetic parameter estimation, kinetic reactor models must be capable of predicting what the GPC is capable of measuring. A GPC (DRI/VISCOTEK) can provide a measure of polymer weight fraction and intrinsic viscosity versus retention volume or versus hydrodynamic volume, which, in the context of GPC, is defined here as the product of intrinsic viscosity times molecular weight.

The construction of the universal calibration curve (log(ηM) versus retention volume, RV) using narrow MWD polystyrene standards provides the relationship between hydrodynamic volume and retention volume for simple and complex polymers. Copolymer chains (styrene/butadiene/divinylbenzene in this example) produced in a CSTR operating at steady-state will have the same composition (except for the very short chains) and have distributions of molecular weight and long chain branching frequencies (and branch lengths). Some chains will be linear; some will have one, two and more tetrafunctional long chain branch points when synthesized by living anionic copolymerization with divinylbenzene as a co-monomer. When such a copolymer is fractionated by GPC, the polymer solute in the detector cell at retention volume, RV is made up of linear chains and chains with different long chain branching frequencies and branch lengths. All of these polymer species have the same hydrodynamic volume in the absence of significant band broadening (peak broadening or dispersion).

With modern high performance GPC column packing and equipment design, the assumption that all polymer species in the detector cell have the same hydrodynamic volume is usually valid, except perhaps for polymer samples which have a very narrow MWD. Copolymer produced in a CSTR has a broad MWD ($M_W/M_N \geq 2.0$) and hence for the present investigation, band broadening is assumed to be negligible. Hamielec et al., [2] have shown that for complex polymers, the correct molecular weight average to assign to the polymer species in the detector cell is the number-average molecular weight and that at retention volume, RV

$$\eta_{PS} M_{PS} = \eta \, M_N \tag{1}$$

where η_{PS} is the intrinsic viscosity of linear polystyrene (polystyrene standards are usually employed) of molecular weight M_{PS}. η is the intrinsic viscosity of polymer solute in the detector cell and M_N is its number-average molecular weight. In other words, GPC (DRI/VISCOTEK) can, with a measure of η versus RV, provide a measure of M_N versus RV as well. To summarize, one can say that for a copolymer with uniform composition having long chain branching, GPC (DRI/VISCOTEK) can provide measures of weight fraction of polymer, intrinsic viscosity and number-average molecular weight versus retention volume or hydrodynamic volume.

In order to be able to use such GPC data for kinetic parameter estimation, the kinetic reactor model must be capable of predicting these same quantities. The minimum requirement of the kinetic reactor model is that it be capable of predicting the full molecular weight distribution for polymeric species that are linear or have one, two, three, and more tetrafunctional branch points. In addition to this, one must employ Zimm-Stockmayer long chain branching equations, see [3], which permit one to calculate the intrinsic viscosity of a polymeric species which has one or more tetrafunctional branch points given the intrinsic viscosity of linear chains of the same molecular weight. The Mark-Houwink equation parameters for linear chains can be readily measured with GPC (DRI/VISCOTEK) using intrinsic viscosity measurements at larger retention volumes where eluting polymer chains are linear.

It should be noted, however, that very short copolymer chains synthesized in a CSTR may be non-uniform in composition and may not obey the Mark-Houwink equation and the concept of universal calibration. There is a useful range of retention volumes where the copolymer chains are uniform in composition and are linear. The appropriate Zimm-Stockmayer equation for random tetrafunctional long chain branching follows:

$$\left(\eta_b \big/ \eta_l \right)^{1/\epsilon} = \left[\left(1 + \frac{n_b}{6} \right)^{a} + \left(\frac{4n_b}{3\pi} \right) \right]^{-b} \qquad (2)$$

where η_b is the intrinsic viscosity of polymer chains of molecular weight M and having n_b tetrafunctional long chain branch points. η_l is the intrinsic viscosity of linear chains of molecular weight M. ε is the branching structure factor (sometimes called the Debye-Bueche viscosity shielding ratio).

The branching structure factor has to date not been calculated theoretically and must be used as an adjustable parameter during kinetic parameter estimation. Some researchers claim that ε can vary from 0.5 to 1.5 although the full range for ε possible is not certain. The usual procedure, see for example [3] and [4], for estimating the branching structure factor is to use a combination of GPC (DRI/VISCOTEK) and ^{13}C-NMR. A more recent and preferred method for estimating ε is to perform angular light scattering online with GPC to measure the radius of gyration versus retention volume. Angular light scattering was not employed in this investigation and as a consequence the branching structure factor ε was estimated along with kinetic rate parameters using GPC (DRI/VISCOTEK) measurements.

In equation (2), a = 0.5, b = 1.5 are constants, and n_b is the number of tetrafunctional long chain branch points per polymer chain. An appropriate kinetic reactor model, which includes the present model, should predict the molecular weight distributions for polymer chains that contains 0, 1, 2, … , 9 branch points. Given the kinetic rate constants k_p and k_p* (k_p and k_p* are pseudo kinetic rate constants which will be described later), the parameters in the Mark-Houwink equation for linear copolymer chains obtained in the present synthesis and the branching structure factor ε (in equation (2) after Zimm-Stockmayer), and parameters related to active center association, one can predict the weight fraction of copolymer and its intrinsic viscosity and number-average molecular weight versus retention volume, RV. The GPC (DRI/VISCOTEK) gives a measure directly of the weight fraction of copolymer and its intrinsic viscosity versus retention volume, RV. In addition, the use of the universal calibration curve (log(ηM_N)) versus retention volume with η measured by GPC provides a measure of M_N versus retention volume.

FOUNDATIONS OF THE KINETIC REACTOR MODEL

The present kinetic reactor model for the living anionic copolymerization of styrene/butadiene/divinylbenzene in a transient or steady-state continuous stirred tank reactor (CSTR) train is based on the method of pulses and the concepts of macromixing and micromixing (see Hamielec et al., 2000). The present model uses physical pulses while the patent covers chemical pulses. A detailed description of the polymerization process to be simulated by the present kinetic reactor model follows: Ingredients in solution in a solvent (monomers, solvent and n-butyllithium catalyst) flow into a CSTR at constant or time-varying flowrates. During reactor startup, the CSTR can be full or partially full of solution (a liquid solution of monomers, solvent and catalyst in any proportion). To simplify the process description, we assume that the CSTR is always full of solution.

Ingredients are flowing into the reactor with constant or time-varying flowrates and we describe the reactor inflows as a continuous series of pulses with each pulse formed during a constant time period, Δt. The flowrates of each ingredient into the CSTR times Δt gives the amount of each ingredient in the input pulse. When the pulse enters the CSTR, we assume that the active centers rapidly propagate at a rate which depends on the concentration of monomers in the CSTR as a whole (we assume that small molecules such as monomers and solvent experience micromixing and as a consequence, the concentration of monomers and solvent are the same for all pulses in the CSTR regardless of their age (time spent in the CSTR).

The concentration of living anionic chains and their molecular weights and long chain branching frequencies will depend on the age of the pulse. It should be noted, however, that were the input flowrate of n-butyl lithium constant, the number of living chains would be the same in pulses of different age. To maintain uniform copolymer concentration (grams per unit volume) in pulses of different age, older pulses would be of larger volume having imbedded more solvent and monomers from other pulses of younger age. However, the molar concentration of living chains would be smaller for older pulses that have expanded with time in the CSTR. In other words, we assume that polymer chains experience macromixing and do not diffuse from a pulse of one age to a pulse of another age. The polymer chains in a pulse experience the ideal residence-time distribution (or exit-age distribution function as it is often called) of a CSTR which is

$$E(t) = \frac{1}{\bar{t}} \exp\left(-\frac{t}{\bar{t}} \right) \tag{3}$$

where $\bar{t}$ is the mean residence time (reactor volume divided by the volumetric flowrate with any volume contraction with polymerization neglected) and *E(t)* is the fraction of the growing chains in a pulse which has been in the reactor for time, *t*. The kinetic reactor model therefore involves the solution of the polymerization kinetic equations for a pseudo-batch reactor where concentration of monomers and solvent and reaction volume vary with time according to inflows and outflows of monomers and solvent with time. Since the monomer and solvent concentrations are spatially uniform (these ingredients experience micromixing) their concentrations can be calculated using the usual balance equations for a CSTR operating in a transient or steady-state mode. Once these concentrations and their time dependence are known, the population balance equations can be solved using this information for a range of times from zero to perhaps 10 mean residence times where steady-state is assured. The CSTR residence time distribution, $E(t)$, is then used to mix exiting pulses of different age to provide molecular weight distributions for copolymer in the effluent of the CSTR.

The following symbols are used to describe the mechanism of living anionic polymerization of styrene/butadiene/divinylbenzene with n-butyllithium as catalyst and hexane as solvent:

$P_{r,s,t,b}$ - polymer chain with a styrene unit adjacent to at least one of the active centers with r units of styrene, s units of butadiene, t units of divinylbenzene, and b tetrafunctional branch points

$Q_{r,s,t,b}$ - butadiene benzene adjacent to at least one of the active centers, indices as above

$R_{r,s,t,b}$ - divinylbenzene adjacent to at least one of the active centers, indices as above

In the following, M_1, M_2, M_3 represent styrene, butadiene, and divinylbenzene monomers, respectively.

Initiation:

$$I + M_1 \xrightarrow{k_{i1}} P_{1,0,0,0}$$
$$I + M_2 \xrightarrow{k_{i2}} Q_{0,1,0,0}$$
$$I + M_3 \xrightarrow{k_{i3}} R_{0,0,1,0}$$

Propagation:

$$\begin{aligned}
&P_{r,s,t,b} + M_1 \xrightarrow{k_{p11}} P_{r+1,s,t,b} \\
&P_{r,s,t,b} + M_2 \xrightarrow{k_{p12}} Q_{r,s+1,t,b} \\
&P_{r,s,t,b} + M_3 \xrightarrow{k_{p13}} R_{r,s,t+1,b} \\
&Q_{r,s,t,b} + M_1 \xrightarrow{k_{p21}} P_{r+1,s,t,b} \\
&Q_{r,s,t,b} + M_2 \xrightarrow{k_{p22}} Q_{r,s+1,t,b} \\
&Q_{r,s,t,b} + M_3 \xrightarrow{k_{p23}} R_{r,s,t+1,b} \\
&R_{r,s,t,b} + M_1 \xrightarrow{k_{p31}} P_{r+1,s,t,b} \\
&R_{r,s,t,b} + M_2 \xrightarrow{k_{p32}} Q_{r,s+1,t,b} \\
&R_{r,s,t,b} + M_3 \xrightarrow{k_{p33}} R_{r,s,t+1,b}
\end{aligned}$$

The pseudo propagation rate constant, k_p is given by

$$\begin{aligned}
k_p = {}& k_{p11}\,\phi_1 f_1 + k_{p12}\,\phi_1 f_2 + k_{p13}\,\phi_1 f_3 \\
&+ k_{p21}\,\phi_2 f_1 + k_{p22}\,\phi_2 f_2 + k_{p23}\,\phi_2 f_3 \\
&+ k_{p31}\,\phi_3 f_1 + k_{p32}\,\phi_3 f_2 + k_{p33}\,\phi_3 f_3
\end{aligned} \tag{4}$$

where ϕ_1 is the fraction of active centers of type 1 (styrene is adjacent to the active center), ϕ_2 is the fraction of active centers of type 2 and ϕ_3 is the fraction of active centers of type 3. Propagation with Pendant Double Bonds (Tetrafunctional Long Chain Branching Reactions) leads to

$$\begin{aligned}
&P_{r,s,t,b} + X_{m,n,o,p} \xrightarrow{k_{p1}^{*}} Y_{r+m,s+n,t+0-1,b+p+1} \\
&Q_{r,s,t,b} + X_{m,n,o,p} \xrightarrow{k_{p2}^{*}} Y_{r+m,s+n,t+0-1,b+p+1}
\end{aligned}$$

The pseudo kinetic rate constant, k_p* is given by

$$k_p^{*} = k_{p1}^{*}\,\phi_1 + k_{p2}^{*}\,\phi_2 \tag{5}$$

It should be noted that a living anionic polymer chain with n_b tetrafunctional branch points will have n_b +l active centers. These active centers can be of type 1, type 2 or type 3 and at any instant in time the fraction of active centers on a chain of type 1 will be ϕ_l and so on. These active centers on a single polymer molecule with b tetrafunctional branch points will all be propagating with monomer simultaneously. Within a pulse, the polymer chains that have one tetrafunctional branch point will have a molecular weight (or total chain length) which is twice that of linear chains at any point in time. It is assumed, of course, that all linear chains in a pulse have the same molecular weight or total chain length.

The polymerization rate equations which apply in a pulse during its lifetime in a CSTR follow: We must first keep track of the chain length of linear chains and then we must keep track of chains with one, two and more tetrafunctional branch points. This then permits one to calculate number of linear chains and their molecular weight versus age of the pulse, number of chains with one tetrafunctional branch point and their molecular weight versus time and so on.

THE KINETIC REACTION EQUATIONS OF THE POLYMERIZATION PROCESS

Proceeding from the assumptions and chemical reactions outlined in the previous two sections, we are now able to state the dynamic model equations. We proceed from a reactor identified by the index i, CSTR(i), i=1,..., n_r and consider a fixed time value t within the j-th pulse, j=0,1,2,… . n_r is the total number of reactors in the train. Further model equations and details about the numerical realization are found in the subsequent section, especially also the link of the reactors in the form of pulses.

The monomer balance equations for styrene, butadiene and divinylbenzene in CSTR(i) are given by the equations

$$\frac{d\,n_1^i}{dt} = \frac{(f_{mi1}^i - \gamma^i\, f_{mo1}^i)\, s}{m_{w1}} \;-\; k_{p11}^i\, n_1^i\, q_{d01}^i \;-\; k_{p21}^i\, n_1^i\, q_{d02}^i \tag{6}$$

$$\frac{d\,n_2^i}{dt} = \frac{(f_{mi2}^i - \gamma^i\, f_{mo2}^i)\, s}{m_{w2}} \;-\; k_{p12}^i\, n_2^i\, q_{d01}^i \;-\; k_{p22}^i\, n_2^i\, q_{d02}^i \tag{7}$$

$$\frac{d\,n_3^i}{dt} = \frac{(f_{mi3}^i - \gamma^i\, f_{mo3}^i)\, s}{m_{w3}} \;-\; k_{p13}^i\, n_3^i\, q_{d01}^i \;-\; k_{p23}^i\, n_3^i\, q_{d02}^i \tag{8}$$

where s is a scaling constant, $s=1000$. Here, n_1^i, n_2^i, n_3^i denote the moles of styrene, butadiene and divinylbenzene in CSTR(i). $f_{mi1}^i, f_{mi2}^i, f_{mi3}^i$ and $f_{mo1}^i, f_{mo2}^i, f_{mo3}^i$ are input and output flowrates of the corresponding monomer to CSTR(i) measured in kg/h. m_{w1}, m_{w2}, m_{w3} are the molecular weights of styrene, butadiene, and divinylbenzene. γ^i is set to one, if CSTR(i) is operating full or at a constant level with overflow, and zero if CSTR(i) is in filling mode. The fractions of dissociated living chains with styrene adjacent to active site, ϕ_{1*}^i, and butadiene adjacent to active site ϕ_{2*}^i are given by:

$$\phi_{1*}^i = \frac{k_{p21}^i\, n_1^i}{k_{p21}^i\, n_1^i + k_{p12}^i\, n_2^i} \tag{9}$$

and

$$\phi_{2*}^{i} = 1 - \phi_{1*}^{i} \tag{10}$$

The concentration of dissociated chains $q^{i}{}_{d01}$ and $q^{i}{}_{d02}$ (see nomenclature) are determined by

$$q_{d01}^{i} = \phi_{1*}^{i}\, q_{d0}^{i} \;, \quad q_{d02}^{i} = q_{d0}^{i} - q_{d01}^{i} \tag{11}$$

The n-butyllithium balance equation is given by

$$\frac{d\, n_{*}^{i}}{dt} = \frac{f_{mi*}^{i} - \gamma^{i}\, f_{mo*}^{i}}{m_{*}} \tag{12}$$

where f_{mi*}^{i} is the input flowrate of n-butyllithium to CSTR(i) in gm/h and f_{mo*}^{i} is the output flowrate of n-butyllithium from CSTR(i) in gm/h. m_{w*} is the molecular weight of n-butyllithium.

The solvent balance equation is derived in the form

$$\frac{d\, n_{s}^{i}}{dt} = \frac{(f_{mis}^{i} - \gamma^{i}\, f_{mos}^{i})s}{m_{ws}} \tag{13}$$

As above, f_{mis}^{i} and f_{mos}^{i} denote the in- and output flow rates and m_{ws} the molecular weight of the solvent.

The polymer balance equation is given by

$$\frac{d\,w_p^i}{dt} = (f_{mip}^i - \gamma^i\, f_{mop}^i)s + (k_{p11}^i\, n_1^i\, m_{w1} + k_{p12}^i\, n_2^i\, m_{w2})\, q_{d01}^i \\ + (k_{p21}^i\, n_1^i\, m_{w1} + k_{p22}^i\, n_2^i\, m_{w2})\, q_{d02}^i \tag{14}$$

The growth of linear living chains within a pulse is given by

$$\frac{d\,r^{ij}}{dt} = \frac{\left(k_{p11}^i\, n_1^i + k_{p12}^i\, n_2^i\right) q_{d01}^i + \left(k_{p21}^i\, n_1^i + k_{p22}^i\, n_2^i\right) q_{d02}^i}{n_*^i} \tag{15}$$

Note that equation (15) as well as the subsequent population balance equations depend on an additional index for the *j*-th pulse, *j*=0,.., n_p. Here n_p is the total number of all pulses. Now we consider nine branching points, i.e., n_b =9. The corresponding differential equations are developed to determine the concentration of linear chains and chains with up to nine branch points. The general structure of the model can be expressed as:

$$\frac{d\,m_{ptl}^{ij}}{dt} = b^{ij}\,[term_1] \; - [term_2] \tag{16}$$

where *term₁* and *term₂* are defined as following:

l (number of branch points)	*term₁*
0	$-2m_{pt0}^{ij} m_*^{ij}$
1	$\left({m_{pt0}^{ij}}^2 - 4m_{pt1}^{ij} m_*^{ij}\right)$
2	$\left(4m_{pt0}^{ij} m_{pt1}^{ij} - 6m_{pt2}^{ij} m_*^{ij}\right)$
3	$\left(6m_{pt0}^{ij} m_{pt2}^{ij} + 4{m_{pt1}^{ij}}^2 - 8m_{pt3}^{ij} m_*^{ij}\right)$

4	$\left(8m^{ij}_{pt0}m^{ij}_{pt3}+12m^{ij}_{pt1}m^{ij}_{pt2}-10m^{ij}_{pt4}m^{ij}_{*}\right)$
5	$\left(10m^{ij}_{pt0}m^{ij}_{pt4}+16m^{ij}_{pt1}m^{ij}_{pt3}+9{m^{ij}_{pt2}}^{2}-12m^{ij}_{pt5}m^{ij}_{*}\right)$
6	$\left(12m^{ij}_{pt0}m^{ij}_{pt5}+20m^{ij}_{pt1}m^{ij}_{pt4}+24m^{ij}_{pt2}m^{ij}_{pt3}-14m^{ij}_{pt6}m^{ij}_{*}\right)$
7	$\left(14m^{ij}_{pt0}m^{ij}_{pt6}+24m^{ij}_{pt1}m^{ij}_{pt5}+30m^{ij}_{pt2}m^{ij}_{pt4}+16{m^{ij}_{pt3}}^{2}-16m^{ij}_{pt7}m^{ij}_{*}\right)$
8	$\left(16m^{ij}_{pt0}m^{ij}_{pt7}+28m^{ij}_{pt1}m^{ij}_{pt6}+36m^{ij}_{pt2}m^{ij}_{pt5}+40m^{ij}_{pt3}m^{ij}_{pt4}-18m^{ij}_{pt8}m^{ij}_{*}\right)$
9	$\left(9m^{ij}_{pt0}m^{ij}_{pt8}+32m^{ij}_{pt1}m^{ij}_{pt7}+42m^{ij}_{pt2}m^{ij}_{pt6}+48m^{ij}_{pt3}m^{ij}_{pt5}+25{m^{ij}_{pt4}}^{2}-20m^{ij}_{pt9}m^{ij}_{*}\right)$

$$term_2=\frac{\gamma^{i}\ m^{ij}_{pt1}V^{i}_{0}}{V^{i}}$$

where $l = 0,1,\ldots, n_b$

m^{ij}_{ptl} denotes the number of moles of polymer chains with l tetrafunctional branch points (linear chains) in the j-th pulse born at the actual time t, where l=0,1,..., n_b and where n_b denotes the total number of branching points, nine in our case. The coefficients b^{ij} depend on the fraction of divinylbenzene monomer units in the polymer chains in this pulse and are described in the subsequent section. r^{ij} is the chain length of linear chains in the pulse, m^{ij}_{*} is the number of active centers in the pulse where it is assumed that active center deactivation does not occur during the lifetime of the pulse in CSTR(i). V^{i} denotes the reactor volume in CSTR(i) in dm^3, i.e., the volume of reacting fluid in the reactor times the ratio of polymer mass in the pulse to polymer mass in the reactor. V^{i}_{0} is the volumetric output flowrate from CSTR(i) at time t in dm^3/h.

Finally, we add the temperature equation

$$\frac{dT^i}{dt} = \frac{575(f^i_{mitot}T^i_f - f^i_{motot}T^i) + 17050(1 - q^i_{rf})w^i_2}{525w^i_1} \tag{17}$$

where the reference temperature T^i_f is computed by a PID controller, see subsequent section. f^i_{motot} is the total output flow, w^i_1 and w^i_2 are kinetic parameters, and q^i_{rf} is a correction term for the temperature equation.

FURTHER SPECIFICATION OF THE DYNAMIC MODEL

In this section, we present further details of the model in a rigorous mathematical form and introduce the pulse technique in detail. To simplify the subsequent notation, we assume that there are only two reactors in the train, i.e., n_r=2. The adoption to an arbitrary number of reactors is straightforward. Moreover, we have $n_b=9$ the number of branched points, each identified by the corresponding index *l*.

The system of differential equations specified in the previous section, is repeatedly solved for n_p pulse times

$$0 = t_0 < t_0 + \Delta t = t_1 < t_1 + \Delta t = t_2 < \ldots < t_{n_p - 1} + \Delta t = t_{n_p} \tag{18}$$

We assume for simplicity that Δt remains constant. The polymerization reaction is modeled by a system of ordinary differential equations with initial values. State variables for the first reactor are

$$n_1^1, n_2^1, n_3^1, n_*^1, n_s^1, w_p^1, r^{10}, m_{pt\,l}^{10}, T^1 \tag{19}$$

where $l=0,\ldots,n_b$. At each pulse time, a certain volume fraction is passed from reactor 1 to reactor 2, which contains a mixture of all polymer chain lengths produced so far. Since the corresponding chain lengths are different, we have to add a complete set of n_b+2 equations to the existing ones. Thus, we get the state variables

$$n_1^2, n_2^2, n_3^2, n_*^2, n_s^2, w_p^2, r^{2j}, m_{ptl}^{2j}, T^2 \tag{20}$$

for the second reactor, where $j=0,\ldots,k$ and $l=0,\ldots,n_b$. k is the number of the actual pulse, i.e. $k=0,\ldots,n_p-1$. The integration is performed from $t=t_k$ to $t=t_{n_p}$. In other words, we have to solve a set of differential equations repeatedly for each pulse, i.e., n_p times, where the size increases from $2(n_b+9)$ to $n_p(n_b+2)+n_b+16$.

The initial values of the successively added equations depend on the corresponding solution values for the first reactor at $t=t_k$, when integrating the system from $t=t_{k-1}$ to $t=t_p$ for the previous pulse. For the very first integration from $t=0$ to $t=t_p$, we apply the initial conditions

$$\begin{array}{lcl}
n_1^i(0) & = & 0 \\
n_2^i(0) & = & 0 \\
n_3^i(0) & = & 0 \\
n_*^i(0) & = & 0 \\
n_s^i(0) & = & n_{s0}^i \\
w_p^i(0) & = & 0 \\
r^{ij}(0) & = & 0 \\
m_{pt0}^{ij}(0) & = & m_*^i \\
m_{ptl}^{ij}(0) & = & 0 \quad , \qquad l=1,\ldots,n_b \\
T^i(0) & = & T_0
\end{array} \tag{21}$$

with given initial temperature T_0, $n_{s0}^{i} = 1.27 \cdot 10^5$, and $m_*^i = \dfrac{f_{mi^*}\,\Delta t}{m_{w^*}}$.

For the first reactor and all subsequent pulses, the integration is repeated at initial values

$$
\begin{array}{lcl}
n_1^1(t_k) & = & \overline{n}_1^1(t_k) \\
n_2^1(t_k) & = & \overline{n}_2^1(t_k) \\
n_3^1(t_k) & = & \overline{n}_3^1(t_k) \\
n_*^1(t_k) & = & \overline{n}_*^1(t_k) \\
n_s^1(t_k) & = & \overline{n}_s^1(t_k) \\
w_p^1(t_k) & = & \overline{w}_p^1(t_k) \\
r^{10}(t_k) & = & 0 \\
m_{pt0}^{10}(t_k) & = & m_*^1 \\
m_{ptl}^{10}(t_k) & = & 0 \quad , \quad l = 1,\ldots,n_b \\
T^1(t_k) & = & \overline{T}^1(t_k)
\end{array}
\tag{22}
$$

For *k=1,...,n_p-1*, where the integration is performed from t_k to t_{n_p}. The bar indicates the solution values obtained from the previous pulse integrated from t_{k-1} to t_{n_p} at t_k.

For the second reactor, we have to pass a certain volume fraction from the previous reactor for all subsequent pulses, and define therefore the initial values by

$$
\begin{aligned}
n_1^2(t_k) &= \bar{n}_1^2(t_k) \\
n_2^2(t_k) &= \bar{n}_2^2(t_k) \\
n_3^2(t_k) &= \bar{n}_3^2(t_k) \\
n_*^2(t_k) &= \bar{n}_*^2(t_k) \\
n_s^2(t_k) &= \bar{n}_s^2(t_k) \\
w_p^2(t_k) &= \bar{w}_p^2(t_k) \\
r^{20}(t_k) &= 0 \\
m_{pt}^{20}(t_k) &= 0 \\
m_{ptl}^{20}(t_k) &= 0 \quad , \qquad\qquad l = 1,\ldots,n_b \\
r^{2j}(t_k) &= \bar{r}^{10j}(t_k) \quad , \qquad\qquad j = 1,\ldots,k \\
m_{pt0}^{2j}(t_k) &= \bar{m}_{pt}^{10j}(t_k)\, {}^{V_0^1 \Delta t}\!\big/_{V^1} \quad , \quad j = 1,\ldots,k \\
m_{ptl}^{2j}(t_k) &= \bar{m}_{ptl}^{10j}(t_k)\, {}^{V_0^1 \Delta t}\!\big/_{V^1} \quad , \quad j = 1,\ldots,k \ , \ l = 1,\ldots,n_b \\
T^2(t_k) &= \bar{T}^2(t_k)
\end{aligned}
\tag{23}
$$

For $k=1,\ldots,n_p-1$, where the integration is performed from t_k to t_{n_p}. The bar indicates the solution values obtained from the previous pulse integrated from t_{k-1} to t_{n_p} at t_k. $\bar{r}^{10j}(t_k)$, and $\bar{m}_{ptl}^{10j}(t_k)$, $l=0,\ldots,n_b$, denote the corresponding values for the first reactor at time t_k, when the integration was started at the j-th pulse, $j=1,\ldots,k$. V_0^1 is the volumetric flow defined by

$$
V_0^1 = 0.97\left(\frac{f_{mi1}^1}{m_{w1}} + \frac{f_{mi2}^1}{m_{w2}} + \frac{f_{mi3}^1}{m_{w3}} + \frac{f_{mis}^1}{m_s} + \frac{f_{mip}^1}{m_p} \right) \tag{24}
$$

with given flow rates and input densities. Here the index s stands for solvent and p for polymer.

The model accounts for an instantaneous equilibrium between associated and dissociated living chains. In the present model, the following Arrhenius equation is used to give the temperature dependence of the equilibrium constant for the association phenomenon, see [1]:

$$k_e^i = 1.572 \cdot 10^{-11} \exp\left(-\frac{26920}{1.987\, T^i} \right) \tag{25}$$

where k_e^i in (dm^3/moles)^2 is the equilibrium constant and T^i is the temperature in CSTR(i) in degree Kelvin, i=1,2..

The concentration of dissociated chains in CSTR(i), q_{d0}^i, is calculated by solving the following nonlinear equation using Newton's method,

$$q_{t0}^i = q_{d0}^i + n\, k_e^i\, {q_{d0}^i}^n \tag{26}$$

where $q_{t0}^i = n_*^i / V^i$. n is the association number for living chains, i.e., the number of chains in an associated complex. In our case, we have n=3. Note that all other parameters depend on the actual time t, and that the above nonlinear equation must be solved for each evaluation of the right-hand side of the system of differential equations.

The fractions of dissociated living chains with styrene adjacent to active site, ϕ^i_{1*}, and butadiene adjacent to active site ϕ^i_{2*}, are given by

$$\phi_{1*}^i = \frac{k_{p21}^i\, n_1^i}{k_{p21}^i\, n_1^i + k_{p12}^i\, n_2^i} \quad , \qquad \phi_{2*}^i = 1 - \phi_{1*}^i \tag{27}$$

Then q^i_{d01} and q^i_{d02} are determined from

$$q^i_{d01} = \phi^i_{1*}\, q^i_{d0}\ , \quad q^i_{d02} = q^i_{d0} - q^i_{d01} \tag{28}$$

Now let k^i_{p11} be the propagation constant of chains with styrene adjacent to the site when styrene monomer is adding to the chain, k^i_{p22} be the propagation constant of chains with butadiene adjacent to the site when butadiene monomer is adding to the chain, and k^i_{p12} be the propagation constant of chains with styrene adjacent to the site when butadiene monomer is adding to the chain. k^i_{p21} is propagation constant of chains with butadiene adjacent to the site when styrene monomer is adding to the chain. The reactivity ratios are defined as $r_{12} = k^i_{p11}/k^i_{p21}$ and $r_{21} = k^i_{p22}/k^i_{p21}$. Butylethyether (BEE) is used as a randomizing agent in the polymerization. The reactivity ratios are assumed to be independent of the temperature and are therefore the same in each of the CSTR's in series even when the train is non-isothermal. Note that temperature T^i varies from one CSTR to next and is time-dependent. The following propagation rate constants are used for styrene and butadiene, cf. [5], and are given in dm^3/ (mol.min),

$$k^i_{p11} = 2.878 \cdot 10^{11} \exp\left(-\frac{14870}{1.987\, T^i} \right) \tag{29}$$

$$k^i_{p22} = 7.024 \cdot 10^{8} \exp\left(-\frac{10332}{1.987\, T^i} \right) \tag{30}$$

and we let

$$k^i_{p13} = \frac{k^i_{p11}}{r_{13}}\ , \quad k^i_{p23} = \frac{k^i_{p22}}{r_{23}} \tag{31}$$

for given time-independent reaction rates r_{13} and r_{23}. For the subsequent model calculations, the rate constants are set to r_{12}=0.8, r_{21}=1.0, r_{13}=0.5, and r_{23}=0.7.

The input and output flow rates used in the monomer equations, are

$$f^{i}_{mo1} = n^{i}_{1} m_{w1} \frac{V^{i}_{0}}{sV^{i}} \quad , f^{i}_{mo2} = n^{i}_{2} m_{w2} \frac{V^{i}_{0}}{sV^{i}} \quad , f^{i}_{mo3} = n^{i}_{3} m_{w3} \frac{V^{i}_{0}}{sV^{i}} \tag{32}$$

and $f^{1}_{ma1} = f_{mi1}$, $f^{1}_{ma2} = f_{mi2}$, and $f^{1}_{ma3} = f_{mi3}$ for the first reactor with given flow rates, $f^{i+1}_{ma1} = f^{i}_{mo1}$, $f^{i+1}_{ma2} = f^{i}_{mo2}$, and $f^{i+1}_{ma3} = f^{i}_{mo3}$ for the next ones.

Similarly, the catalyst balance equation uses the flow rates

$$f^{1}_{mi*} = f_{mi*} \, , \quad f^{1}_{mo*} = n^{1}_{*} \, m_{w*} \frac{V^{1}_{0}}{sV^{1}} \tag{33}$$

for the first reactor and

$$f^{i+1}_{mi*} = f^{i}_{mo*} \, , \quad f^{i}_{mo*} = n^{i}_{*} \, m_{w*} \frac{V^{1}_{0}}{sV^{1}} \tag{34}$$

for the subsequent ones. Flow rates for solvent and polymer balance equation are

$$f^{1}_{mis} = f_{mis} \, , \quad f^{1}_{mos} = n^{1}_{s} \, m_{ws} \frac{V^{1}_{0}}{sV^{1}} \quad , \quad f^{1}_{mip} = f_{mip} \, , \quad f^{1}_{mop} = w^{1}_{p} \frac{V^{1}_{0}}{sV^{1}} \tag{35}$$

for the first and

$$f_{mis}^{i+1} = f_{mos}^{i} \ , \quad f_{mos}^{i} = n_s^i \, m_{ws} \, \frac{V_0^i}{sV^i} \quad , \quad f_{mip}^{i+1} = f_{mop}^{i} \ , \quad f_{mop}^{i+1} = n_s^i \, \frac{V_0^i}{sV^i} \tag{36}$$

for the subsequent reactors. In all cases, we set γ^j =1 when CSTR(i) is operating full or at a constant level with overflow, and γ^j =0 when CSTR(i) is in filling mode.

To evaluate the factor b^{ij} in the chain equations (16), we determine the volume of a pulse by

$$V_p^{ij} = \frac{75.0 \, V^i \, r^{ij} \, m_*^{ij}}{w_p^i} \tag{37}$$

V^i is the volume of reacting mixture, w_p^i is the weight of polymer in the whole reactor, i.e., for all pulses in the reactor, and m_*^{ij} is given by the following equation is the moles of active centers in the pulse,

$$m_*^{ij} = m_{pt}^{ij} + \sum_{l=1}^{n_b} (l+1) \, m_{ptl}^{ij} \tag{38}$$

By

$$i_{f3}^{i} = \frac{(k_{p13}^{i} \, \phi_{1*}^{i} + k_{p23}^{i} \, \phi_{2*}^{i}) \, m_{frac3}^{i}}{(k_{p11}^{i} \, \phi_{1*}^{i} + k_{p21}^{i} \, \phi_{2*}^{i}) \, m_{frac1}^{i} + (k_{p12}^{i} \, \phi_{1*}^{i} + k_{p22}^{i} \, \phi_{2*}^{i}) \, m_{frac2}^{i}} \tag{39}$$

with

$$m_{frac1}^{i} = \frac{n_1^i}{n_1^i + n_2^i} \quad , \quad m_{frac2}^{i} = \frac{n_2^i}{n_1^i + n_2^i} \quad , \quad m_{frac3}^{i} = \frac{n_3^i}{n_1^i + n_2^i} \tag{40}$$

we compute the instantaneous mole fraction of divinylbenzene in a differential segment of the growing chain produced in CSTR(i). Divinalbenzene used in polymerization consists of a mixture of 70.37 % meta, 29.4 % ortho and 0.39% para. It is assumed that DVB double bonds in a growing chain are free to add to active centers even when the chains are in the associated state. It is also assumed that the propagation constant for the pendant double bound to be the same as styrene.

a_{f3}^{ij} is the fraction of units in the chains that have double bonds. To explain its computation we introduce the time variable *t* again. During the integration from pulse time t_k to t_p we compute $a_{f3}^{ij}(t)$ for an actual time value *t* by

$$\begin{aligned} a_{f3}^{ij}(t) = & \frac{\sum_{\nu=1}^{\mu} (r^{ij}(\tau_\nu) - r^{ij}(\tau_{\nu-1}))(i_{f3}^i(\tau_\nu) + i_{f3}^i(\tau_{\nu-1}))}{2r^{ij}(t)} \\ & + \frac{(r^{ij}(t) - r^{ij}(\tau_\mu))(i_{f3}^i(t) + i_{f3}^i(\tau_\mu))}{2r^{ij}(t)} \end{aligned} \tag{41}$$

To outline the evaluation, we inserted again the time variable *t*, $\tau_\mu \le t < \tau_{\mu+1}$. Here $\Delta\tau$ defines a reasonably small discretization of the integration interval, to evaluate $r^{ij}(t)$ at intermediate time steps

$$t_k = \tau_0 < \tau_0 + \Delta\tau = \tau_1 < \tau_1 + \Delta\tau = \tau_2 < \ldots < \tau_{\mu-1} + \Delta\tau = \tau_\mu \le t < \tau_\mu + \Delta\tau = \tau_{\mu+1} \le t_p$$

Then we insert

$$b^{ij} = \left(k^{i}_{p1*}\ \phi^{i}_{1*} + k^{i}_{p2*}\ \phi^{i}_{2*}\right)\frac{r^{ij}\ a^{ij}_{f3}\ q^{i}_{d0}}{q^{i}_{t0}\ V^{ij}_{p}} \tag{42}$$

in the population balance equations. The reaction constants k^{i}_{p1*} and k^{i}_{p2*} are set to 1550.

A simple PID temperature control algorithm is integrated with the kinetic model to control the temperature of polymerisation. First, we define some auxiliary parameters

$$w^{i}_{1} = n^{i}_{1} m_{w1} + n^{i}_{2} m_{w2} + n^{i}_{s} m_{ws} + \frac{w^{i}_{p}}{s} \tag{43}$$

and

$$w^{i}_{2} = k^{i}_{p11} n^{i}_{1} q^{i}_{d01} + k^{i}_{p21} n^{i}_{1} q^{i}_{d02} + k^{i}_{p12} n^{i}_{2} q^{i}_{d01} + k^{i}_{p22} n^{i}_{2} q^{i}_{d02} \tag{44}$$

The total input flow is given by

$$f^{i}_{mitot} = f^{i}_{mi1} + f^{i}_{mi2} + f^{i}_{mis} + f^{i}_{mip} + \frac{f^{i}_{mi*}}{s} \tag{45}$$

and the total output flow by

$$f^{i}_{motot} = f^{i}_{mo1} + f^{i}_{mo2} + f^{i}_{mos} + f^{i}_{mop} + \frac{f^{i}_{mo*}}{s} \tag{46}$$

to get the temperature equation (17).

The reference temperature T_f^i is computed by a PID controller, i.e., starting from $T_f^i = T_0$, T_f^i is updated by the equation

$$T_f^i = T_f^i + f_1(e_{n0} - e_{n1}) + f_2 e_{n0} t + \frac{f_3}{t}(e_{n0} - 2e_{n1} + e_{n2}) \tag{47}$$

Before evaluating the update, we set $e_{n2} = e_{n1}, e_{n1} = e_{n0}$ and $e_{n0} = T_{sp} - T^i$, initialized by zero. The temperature correction is kept between –5 and 10, and is in addition limited by $T_f^i \leq 100$. T_{sp}, f_1, f_2, and f_3 are suitable constants that define the controller.

NUMERICAL IMPLEMENTATION

The model equations are solved by the explicit Runge-Kutta method DOPRI5 of order 4/5 with an adaptive step length, see [6].

Two integration cycles are combined. The outer one is performed over the number of pulses with increase of Δt, where the number of differential equations is increased by $n_p(n_b+2)$ in each step, to reach finally the total size $n_p(n_b+2)+n_b+16$. If, as in our situation, polymer chains with up to nine branch points are considered, i.e., $n_b=9$ and if we have for example

1,000 pulses, we get finally a set of 11,025 equations. However, the total integration interval is decreased for each pulse, reducing calculation time on the other hand.

For the interior loop, we apply the same step length, i.e., $\Delta\tau = \Delta t$. We need the generation of solution values at certain grid points for evaluating a_{f3}^{ij}, the fraction of units in the chains that have double bonds, see (41), and for storing intermediate values of r^{i0} and m_{ptl}^{i0} for l=1,...,n_b. These data are needed for initiating the differential equations by (23) when starting subsequent pulses.

As outlined in the previous section, the system of differential equations for two CSTR's is repeatedly solved for n_p pulse times given by (18). For a given pulse time t_k, i.e., the k-th pulse, we have to integrate the differential equations from t_k to the final time t_{n_p}. To indicate now the dependency of a solution from the k-th pulse, an additional index k is introduced. Thus, the state variables of our model are

$$n_1^{1k}, n_2^{1k}, n_3^{1k}, n_*^{1k}, n_s^{1k}, w_p^{1k}, r^{10k}, m_{pt0}^{10k}, m_{pt1}^{10k}, ..., m_{ptn_b}^{10k}, T^{1k} \tag{48}$$

for the first and

$$n_1^{2k}, n_2^{2k}, n_3^{2k}, n_*^{2k}, n_s^{2k}, w_p^{2k}, r^{2jk}, m_{pt}^{2jk}, m_{ptl}^{2jk}, ..., m_{pt1}^{2jk}, T^{2k} \tag{49}$$

for the second reactor.

Our goal is to calculate the molecular weights of polymers within given chain length intervals. First, a suitable grid is defined

$$0 = \bar{r}_0 < \bar{r}_0 + \Delta\bar{r} = \bar{r}_1 < \bar{r}_1 + \Delta\bar{r} = \bar{r}_2 < \ldots < \bar{r}_{n_r-1} + \Delta\bar{r} = \bar{r}_{n_r} \tag{50}$$

with a suitable increment $\Delta\bar{r}$. Then we sum up all molecular weights, for which the chain length is within two successive grid points, i.e.,

$$m_n^{1l} = \sum_{k=0}^{n_p-1} \sum_{j_r \in I_n^{10k}} m_{ptl}^{10k}(t_{j_r}) \tag{51}$$

for the first reactor, l=0,1,…,n_b, where the index set is defined by

$$I_n^{10k} = \left\{ i_r : k < i_r \leq p \ , \ \bar{r}_n < r^{10k}(t_{i_r}) \leq \bar{r}_{n+1} \ \right\} \tag{52}$$

Similarly, we get

$$m_n^{2l} = \sum_{k=0}^{n_p-1} \sum_{j=k+1}^{n_p} \sum_{j_r \in I_n^{2jk}} m_{ptl}^{2jk}(t_{j_r}) \tag{53}$$

with

$$I_n^{2jk} = \left\{ i_r : k < i_r \leq p \ , \ \bar{r}_n < r^{2jk}(t_{i_r}) \leq \bar{r}_{n+1} \ \right\} \tag{54}$$

for the second reactor, l=0,1,…,n_b. For a given small RV interval with index n, we sum up all corresponding moles over all polymer chains and all pulses, n=0, …, n_r-1.

The proposed procedure allows plotting molecular weights over retention volumes defined by the index n, $r_n = 0.5(\bar{r}_n + \bar{r}_{n+1})$, where intermediate values between adjacent values are interpolated.

Using the following intermediate calculations:

$$y_n^l = l\, r\, m_n^{1l} \quad , \quad s^l = \sum_{n=1}^{n_p} y_n^l \quad , \quad w_n^l = \frac{y_n^l}{s^l} \quad , \tag{55}$$

Number average, molecular weight and polydispersity index of individual species are respectively calculated as following:

$$x^l = \frac{l}{\displaystyle\sum_{n=0}^{n_r - 1} \frac{w_n^l}{r_n}} \quad , \quad x_w^l = l \sum_{n=1}^{n_r} r_n w_n^l \quad , \quad p^l = \frac{x_w^l}{x^l} \tag{56}$$

SIMULATION RESULTS

Styrene, butadiene and divinylbenzene (DVB) monomers copolymerize forming chains with a few DVB pendant double bonds. Three active center types are formed, including those adjacent to styrene, butadiene and DVB. DVB active center types are at a very low level and are therefore neglected when calculating copolymer production rate. In other words, the weight of copolymer equals the weight of styrene plus the weight of butadiene in the copolymer chains.

When a styrene or butadiene active center adds to a DVB pendent carbon-carbon double bonds, a tetrafunctional branch point is formed resulting in tetrafunctional long chain branching. A copolymer chain with one tetrafunctional branch point will have two active centers and a chain with n_b tetrafunctional branch points will have n_b +1 active centers. In these calculations, all active center deactivation reactions are neglected.

The growing polymer chains in a continuous stirred tank reactor experience a broad residence-time distribution. In the absence of long chain branching reactions, linear polymer chains are formed exclusively with a molecular weight distribution which is Schulz-Flory most probable distribution having a polydispersity index of 2 when the CSTR is operating at steady-state. In the presence of these tetrafunctional long chain branching reactions and because some polymer chains have a residence time which is much longer than the mean residence time of the CSTR, very high molecular weight and highly branched chains are formed. These chains have multiple active centers, grow rapidly in branching frequency and weight and this can lead to gelation (the formation of highly cross-linked network and insoluble gel).

The present calculations consider that concentrations of polymer chains having 0,1,2,3 up to 9 branch points are significant, while chains with 10 or more branch points are considered to have zero concentration. When necessary, chains with 10 or more branch points can be readily accounted for. The weight fraction of polymer chains with 9 branch points is much less than 0.01 justifying the neglect of more highly branch species. Within a pulse, it is assumed that chains with 1 branch point will have a chain length or molecular weight twice that of a linear chain and that for a chain with n_b-branch points, the molecular weight will be n_b +1 times that for a linear chain. Variations in chemical composition of the copolymer chains would complicate the calculation of molecular weight and these have been neglected so that calculations of bivariate distributions of composition and molecular weight were not done.

Based on statistical arguments one would expect that the breadth (or polydispersity index) of the molecular weight distribution for a more highly branched species to be smaller than 2, which is expected when long chain branching is negligible. However, the polydispersity index for the whole polymer (linear plus branched chains) should be ≥ 2. In other words, long chain branching broadens the molecular weight distribution of the whole polymer product.

Model calculations illustrating that effect of different pulse widths (0.07, 0.10, 0.15 hr) have been examined on molecular weight distributions and their associated number and weight-average chain lengths are shown in Figures 1, to 9 for the first reactor. We display the values of m_n^{1l}, see (51), where the dependency on the retention volume is indicated by r_n, n=0, ..., n_r.

Plots of x^l and x_w^l versus pulse width (Figures 10 and 11) shows a linear decrease with decrease in pulse width with a small slope indicating that the calculations do not depend strongly on pulse width.

Figure 12 illustrates the calculated weight fractions for chains having 0, 1, 2, 3 to 9 branch points. As expected the concentrations of highly branched chains is rather small, but at these concentrations, levels can significantly affect melt rheological responses such as zero shear viscosity, shear thinning and melt fracture.

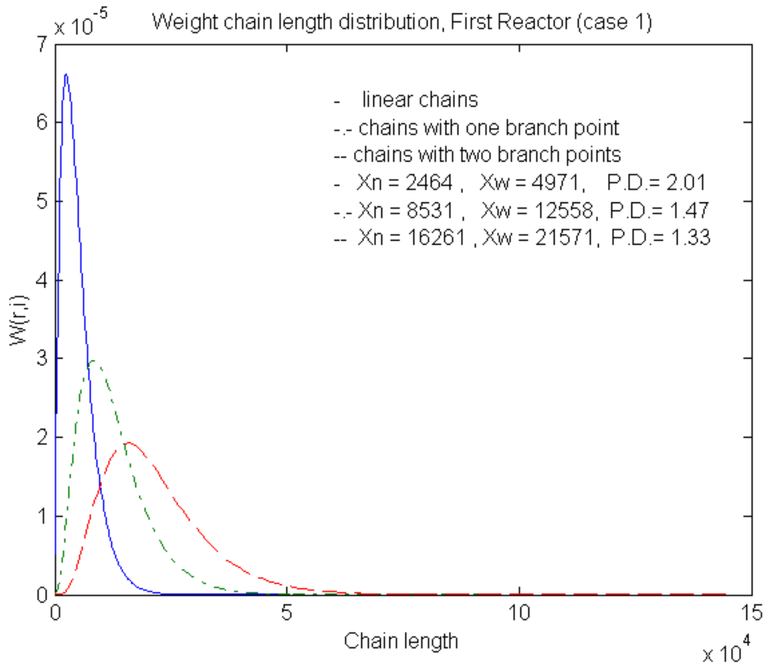


Fig.1: Weight chain length distribution for linear chains and chains with 1 and 2 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398 kg/h. Pulse width = 0.07 hrs, Mean residence time = 1 hr.

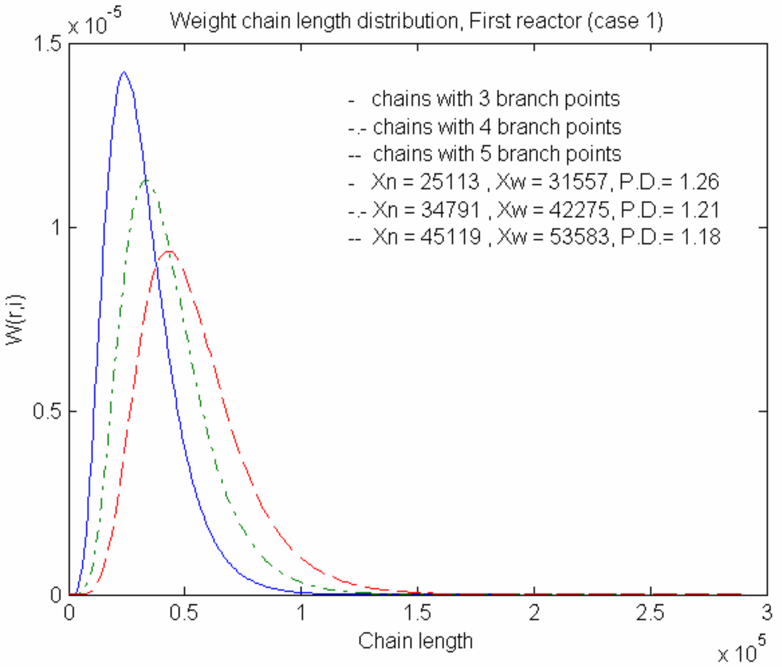


Fig.2: Weight chain length distribution for linear chains and chains with 3, 4 and 5 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398 kg/h. Pulse width = 0.07 hrs, Mean residence time = 1 hr.

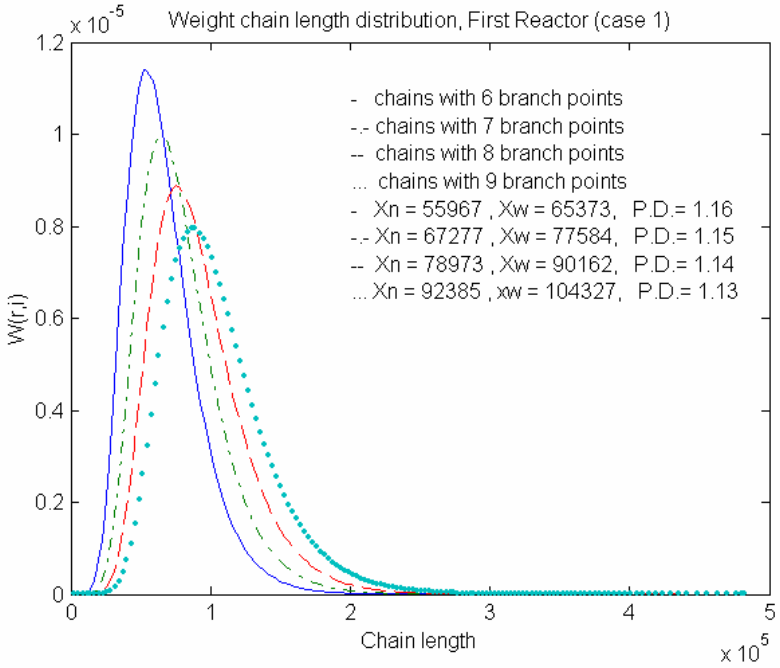


Fig.3: Weight chain length distribution for chains with 6, 7, 8 and 9 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398 kg/h. Pulse width = 0.07 hrs, Mean residence time = 1 hr.

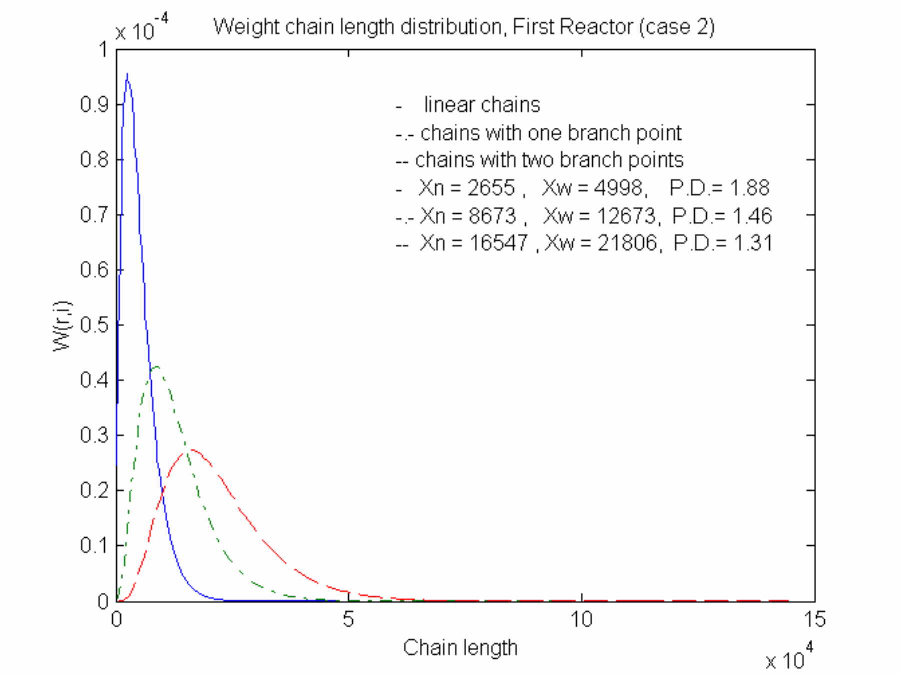


Fig.4: Weight chain length distribution for linear chains and chains with 1 and 2 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398kg/h. Pulse width = 0.10 hrs, Mean residence time = 1 hr.

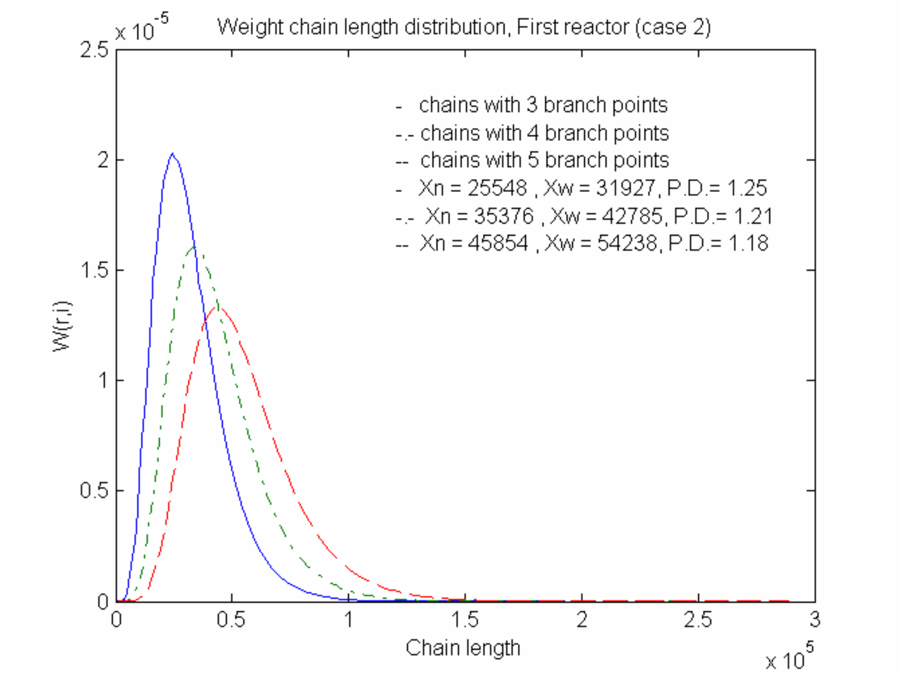


Fig.5: Weight chain length distribution for chains with 3, 4 and 5 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398 kg/h. Pulse width = 0.10 hrs, Mean residence time = 1 hr.

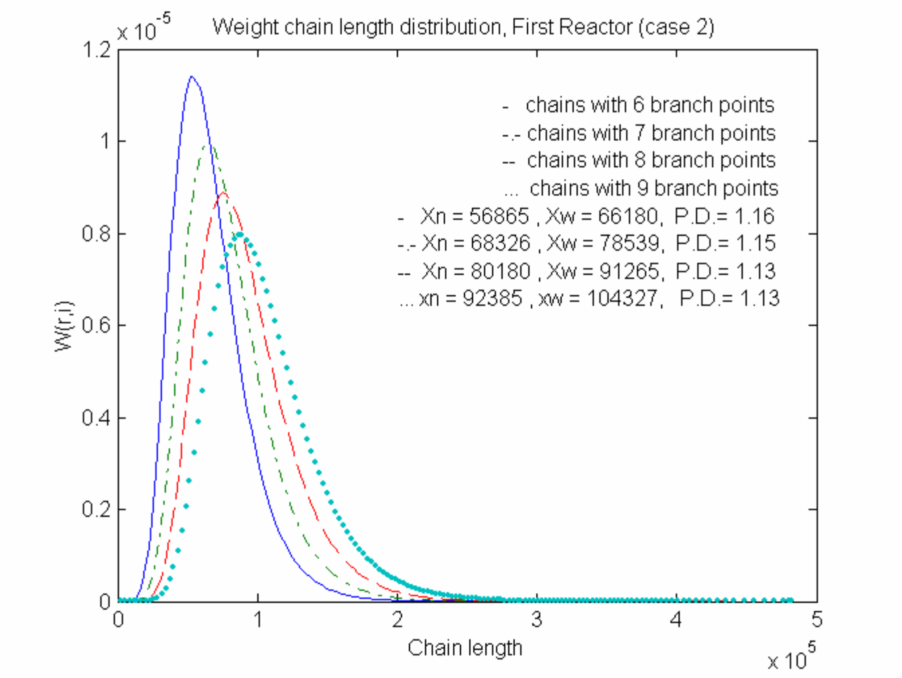


Fig.6: Weight chain length distribution for chains with 6, 7, 8 and 9 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398 kg/h. Pulse width = 0.10 hrs, Mean residence time = 1 hr.

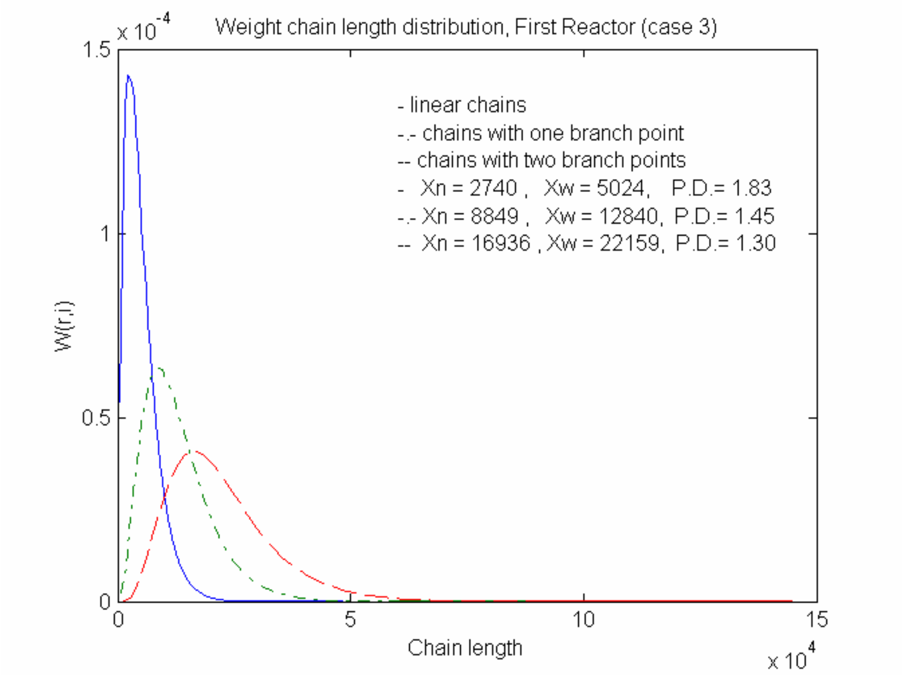


Fig.7: Weight chain length distribution for linear chains and chains with 1 and 2 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398kg/h. Pulse width = 0.15 hrs, Mean residence time = 1 hr.

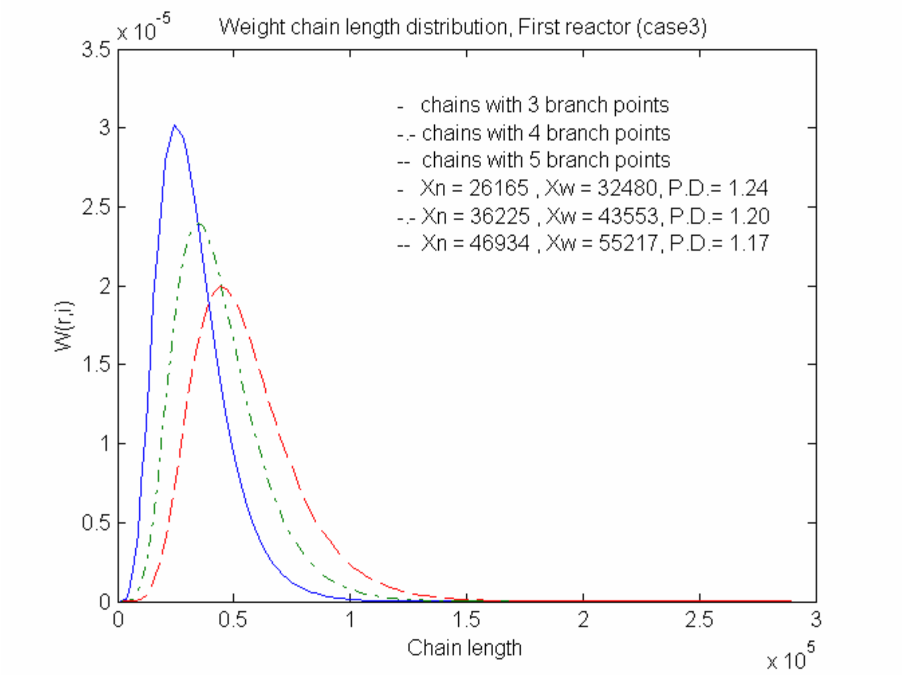


Fig.8: Weight chain length distribution for chains with 3, 4 and 5 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.675 kg/h. Pulse width = 0.15 hrs, Mean residence time = 1 hr.

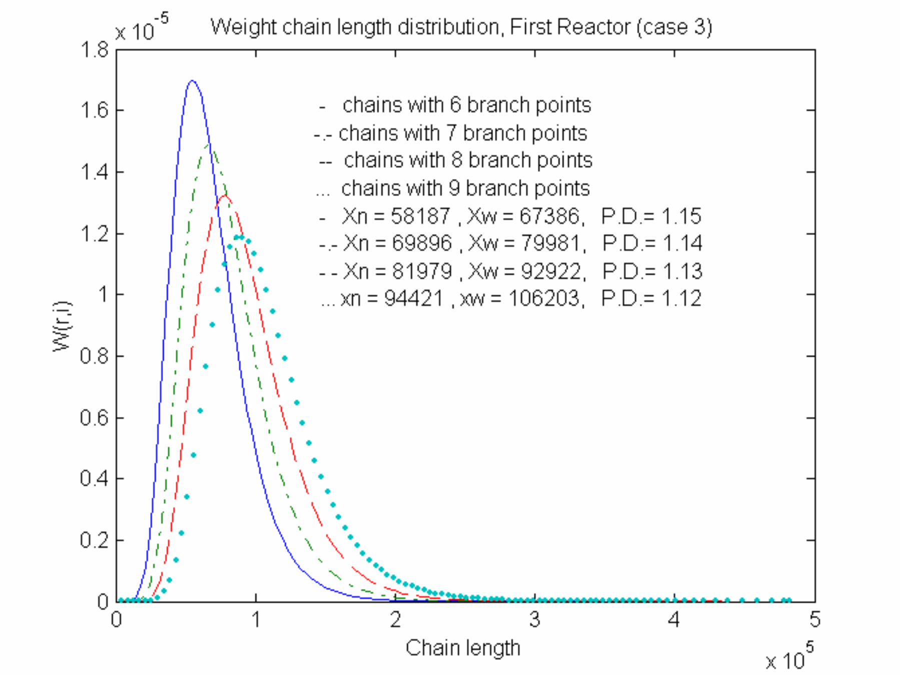


Fig.9: Weight chain length distribution for chains with 6, 7, 8 and 9 branch points. BuLi flow: 0.675 kg/h, Hexane flow: 973 kg/h, Styrene flow: 64 kg/h, Butadiene flow: 194 kg/h, Divinylbenzene flow: 0.0398 kg/h. Pulse width = 0.15 hrs, Mean residence time = 1 hr.

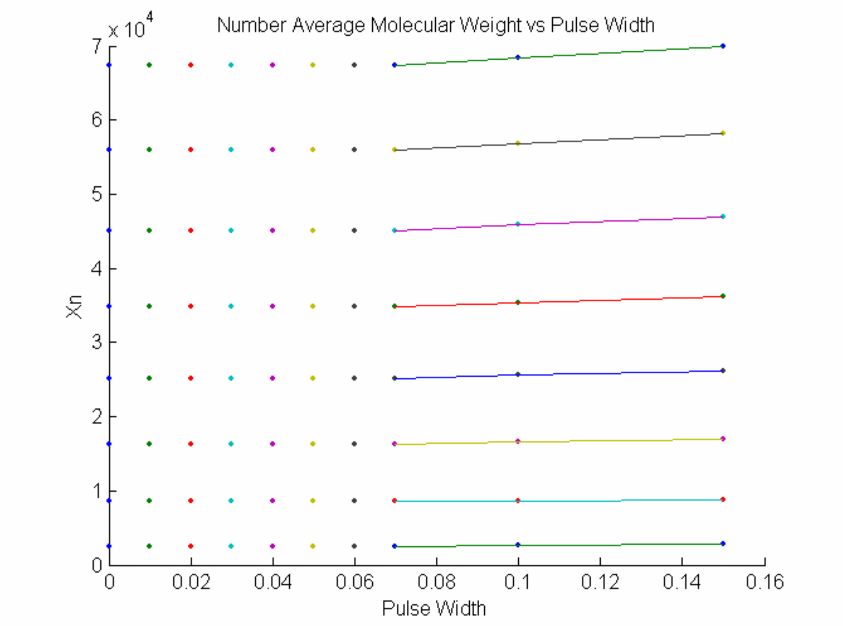


Fig.10: Number-average molecular weight for linear chains and chains with 1 to 7 branch points versus pulse width. x_n^l increases as the number of branch points *l* increases.

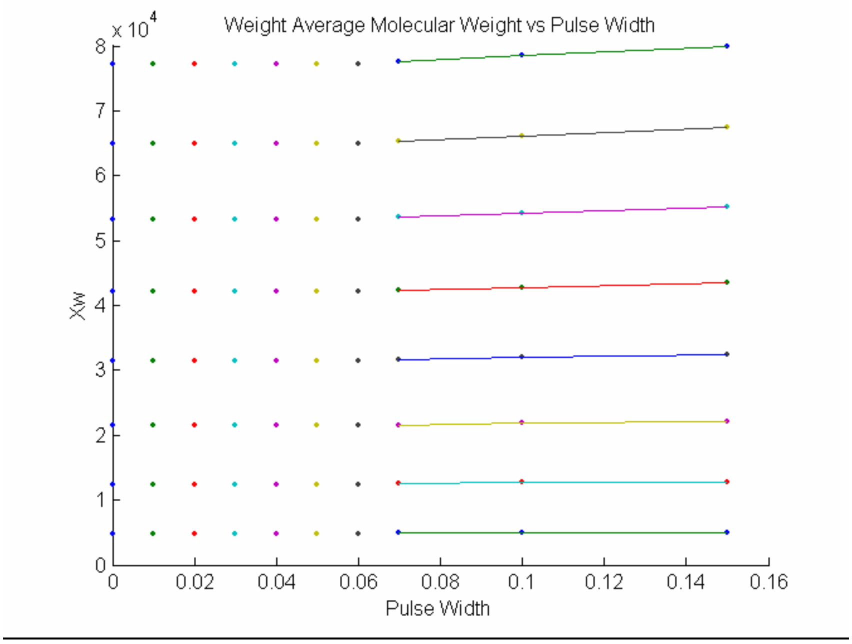


Fig.11: Weight-average molecular weight for linear chains and chains with 1 to 7 branch points versus pulse width. x_w^l increases as number of branch l points increases.

Data	*Dimension/Comment*
$r_{12} = 0.8$	Experiments were done in the presence of randomiser.
$r_{21} = 1.0$	Experiments were done in the presence of randomiser.
$r_{13} = 0.5$	
$r_{23} = 0.7$	
$n = 3$	
$kp^{*} = 1550$	l/(mol min) at 80 °C
$k_e = 1.572_{10}\text{-}11\exp(26920/RT)$	$(l/mol)^2$
$k_{11} = 2.878_{10}\text{-}10\ \exp(-14870/RT)$	l/(mol min)
$k_{22} = 7.024_{10}\text{-}8\ \exp(-10323/RT)$	l/(mol min)

Tab. 1: Kinetic data for butadiene-styrene-divinylbenzene polymerization

EXPERIMENTAL SETUP

Polymerization runs were conducted on a $2m^3$ reactor operating at 80 ^oC. The typical feed operating conditions are n-hexane at 973 kg/h, styrene at 64 kg/h, butadiene at 194 kg/h, n-butyllithium at 0.675 kg/h and divinylbenzene at 0.0398 kg/h. The production rate is 192 kg/h with a total monomer conversion of 74%.

Three samples of polymer, at intervals of about one hour, are taken from the exit stream for GPC analysis. The GPC contains three linear columns of μ-styragel and the mobile phase is THF at 1.0 ml/min. The injection volume is 100 micro liters and a dual detector system DRI/VICOTEC is employed. GPC analysis of the 3 samples provided Mark-Houwink constants for the linear copolymer chains and measurements for intrinsic viscosity versus retention volume, number-average molecular weight versus retention volume, and the distribution of polymer weight fraction versus hydrodynamic volume. In addition, it is necessary to confirm that the reactor residence-time distribution (RTD) is close enough to the ideal residence-time distribution,

$$E(t) = \frac{1}{\bar{t}} \exp\left(-\frac{t}{\bar{t}} \right) \tag{57}$$

where E(t)dt is the fraction of fluid in the exit stream with a residence time, t, and $\bar{t}$ is the mean residence time. The RTD is measured using heptane as a tracer. Heptane is chosen since it essentially acts as an inert solvent for all of the reaction occurring during the polymerization. The sampling frequency varies between 2 to 30 minutes depending on the point in the RTD response curve. The samples are analyzed immediately by GC and the results are used as a guideline to determine the changing sampling interval as the trial is proceeding. The exit-age distribution function *E(t)* is calculated using the equation

$$E(t) = \frac{c(t)}{\int_0^{\infty} c(\tau)\,d\tau} \tag{58}$$

Where *c(t)* is the concentration of heptane in the reactor exit stream at time *t*. The time *t* is measured from the point of heptane injection into the reactor as a pulse. The measured *E(t)* is fitted with a model response involving two CSTR's of unequal volume in series. The relationship is

$$E(t) = \frac{1}{\bar{t}_2 - \bar{t}_1}\left(\exp(-\frac{t}{\bar{t}_2}) - \exp(-\frac{t}{\bar{t}_1}) \right) \tag{59}$$

where $\bar{t}_1$ and $\bar{t}_2$ are the mean residence times for the two CSTR's in series. We thus use a 2-parameter search to find the best values of $\bar{t}_1$ and $\bar{t}_2$ to fit the experimental *E(t)* data. The estimates are $\bar{t}_1$ = 59 minutes and $\bar{t}_2$= 5 minutes. Since $\bar{t}_1$ is considerably larger than $\bar{t}_2$, one can approximate the RTD using the ideal RTD or that for a single CSTR with $\bar{t}_1$= 60 minutes.

ESTIMATING PARAMETERS OF THE ZIMM-STOCKMAYER EQUATION

The polymerization model predicts the weight, molecular weight and hydrodynamic volume of linear chains, the same for chains with one up to nine branch points. The use of GPC universal molecular weight calibration curve permits one to assign a retention volume to each hydrodynamic volume. We then choose a particular retention volume and consider all of the linear and branched chains, which would elute at this retention volume. We calculate intrinsic viscosity of the mixture of linear and branched chains, which are in the detector cell at this retention.

Our goal is to predict the intrinsic viscosity of branched species which is based on the Zimm-Stockmayer equation. Assuming that a=0.5 and b=1.5, see (2), we want to estimate the branching structure factors ε_l, l=1, ..., n_b. By defining intrinsic viscosity ratio:

$$i^l = \eta_b / \eta_l \tag{60}$$

see (2), the data fitting procedure is to be applied to the equation

$$\left(i^l\right)^{\varepsilon_l} = \left[\left(1+\frac{l}{6}\right)^a + \left(\frac{4l}{3\pi}\right)\right]^{-b} \tag{61}$$

given for all branching points, l=1, ..., n_b.

We proceed from the molecular weights as computed in the last step of the post-processing analysis, and mean chain lengths

$$r_n^l = \frac{1}{2}(l+1)(\bar{r}_n + \bar{r}_{n+1}) \tag{62}$$

for $l=0,\ldots,n_b$ and for $n=0,\ldots,n_r-1$. Since the regression is performed with either reactor one or two, we omit the reactor index to simplify the notation, and set $m_n^l = m_n^{1l}$ or $m_n^l = m_n^{2l}$, respectively.

A data fitting or nonlinear regression problem, respectively, is formulated proceeding from given measurements

$$r_v^\sigma \ , \ \eta^\sigma \ , \ m_{nv}^\sigma \ , \ w_{rv}^\sigma \tag{63}$$

for $\sigma=1,\ldots,n_{exp}$, either for reactor one or two, and where n_{exp} is the total number of experimental data. η^σ , m_{nv}^σ , w_{rv}^σ are taken for given equidistant retention volumes r_v^σ with increment Δr_v. Therefore, a mathematical model is derived to compute

$$\eta(r_v)\ , \ m_{nv}(r_v)\ , \ w_{rv}(r_v) \tag{64}$$

for any given retention volume r_v. Starting from given intrinsic viscosity ratios, we try to improve these given values by minimizing the deviations of the predicted model values from the experimental data in the least squares norm, i.e.,

$$\min_{\varepsilon_1,\ldots,\varepsilon_{n_b} \in \Re} \quad \sum_{\sigma=1}^{n_{\exp}} (\eta(r_v^\sigma) - \eta^\sigma)^2 + \sum_{i=1}^{n_{\exp}} (m_{nv}(r_v^\sigma) - m_{nv}^\sigma)^2 + \sum_{i=1}^{n_{\exp}} (w_{rv}(r_v^\sigma) - w_{nv}^\sigma)^2 \tag{65}$$

Fitting parameters to be estimated, are the exponents ε_l, l=1, ..., n_b of equation (2). To evaluate the model function values, the integral of molecular weight distribution over chain length is approximated by

$$m^l = \frac{1}{2}\sum_{n=0}^{n_r-1}\left(m_n^l + m_{n+1}^l\right)\left|r_n^l - r_{n+1}^l\right| \tag{66}$$

Then we define the quantities

$$f_n^l = \frac{m_n^l}{m^l} \quad , \quad \overline{f}_n^l = f_n^l r_n^l \quad , \quad \overline{f}^l = \frac{1}{2}\sum_{n=0}^{n_r-1}(\overline{f}_n^l + \overline{f}_{n+1}^l)\left|r_n^l - r_{n+1}^l\right| \tag{67}$$

and the intrinsic volumes (Mark-Houwink equation)

$$i_n^l = 0.0001515\, i^l\, (\overline{m}_n^l)^{0.76} \tag{68}$$

that depend on the parameters to be estimated through the Zimm-Stockmayer equation (61), and

$$\overline{m}_n^l = 61.4\, r_n^l \tag{69}$$

Approximate retention volumes are computed by

$$\overline{r}_n^l = \frac{35.2 - \log(\overline{m}_n^l\, i_n^l)}{1.344} \tag{70}$$

The constants in equation (70) are from GPC universal calibration and 61.4 is the average molecular weight of styrene and butadiene.

The total weight after *l*-1 branching steps is given by

$$w_{tot}^{l} = \sum_{n=0}^{n_r - 1} m_n^{l} \, r_n^{l} \tag{71}$$

and weight distributions are calculated by

$$w_n^{l} = \frac{\overline{m}_n^{l} \, \overline{f}_n^{l}}{61.4 \cdot 1.30946 \, \overline{f}_n^{l}} \tag{72}$$

and

$$w_{tf}^{l} = \frac{w_{tot}^{l}}{w_p} \quad , \quad \overline{w}_n^{l} = w_{tf}^{l} \, w_n^{l} \Delta r_v \tag{73}$$

with given pulse weight w_p. Weight fractions and total weight are given by

$$w_e^{\sigma l} = \sum_{n \in I_\sigma^{l}} \overline{w}_n^{l} \tag{74}$$

with

$$I_\sigma^{l} = \left\{ n : 0 < n < n_r \ , \ r_v^{\sigma} - \frac{\Delta r_v}{2} < \overline{r}_n^{l} \le r_v^{\sigma} + \frac{\Delta r_v}{2} \right\} \tag{75}$$

and

$$w_{tot}^{\sigma} = \sum_{l=1}^{n_b} w_e^{\sigma l} \tag{76}$$

Intrinsic viscosity and molecular weights of mixture are obtained linear interpolation. First, we determine an index σ^l for each branch l for which the distance of $\overline{r}_n^{\,l}$ from r_v^{σ} is minimal. Let i_{σ}^{l} , w_{σ}^{l} , $\overline{m}_{\sigma}^{\,l}$ be the interpolated values of $i_{\sigma^l}^{l}$, $w_{\sigma^l}^{l}$, $\overline{m}_{\sigma^l}^{\,l}$ subject to the closest neighbour $r_v^{l(n-1)}$ or $r_v^{l(n+1)}$, respectively. Then we define

$$\eta(r_v^{\sigma}) = \frac{1}{w_{tot}^{\sigma}} \sum_{l=0}^{n_b} w_e^{\sigma l}\, i_{\sigma}^{l} \quad , \quad w_{rv}(r_v^{\sigma}) = \sum_{l=0}^{n_b} w_{tf}^{l}\, w_{\sigma}^{l} \quad , \quad m_{nv}(r_v^{\sigma}) = \frac{w_{tot}^{\sigma}}{\sum_{l=0}^{n_b} \frac{w_e^{\sigma l}}{\overline{m}_{\sigma}^{\,l}}} \ . \tag{77}$$

This finalized the computation of the model values for which experimental data are available at given retention volumes.

However, the model functions $\eta(r_v)$, $m_{nv}(r_v)$, $w_{rv}(r_v)$ are not differentiable subject to the parameters ε_l, l=1, ..., n_b. Thus, standard Gauss-Newton-type algorithms cannot be applied and must be adapted. The least squares problem is solved numerically by a combination of a direct search method and a Gauss-Newton-type method. Successive line searches are performed along the unit vectors by comparing function values only. The one-dimensional minimization is based on a quadratic interpolation. After the search cycle the Gauss-Newton-type method DFNLP is executed with a given number of iterations. If a solution is not obtained with sufficient accuracy, the search cycle is repeated, see [7], [8], [9] for details. The least squares solver is started at parameter values ε_l=1, l=1, ..., n_b and a termination tolerance 10^{-6}. A maximum number of 50 function evaluations are set for the successive line searches and initial steplength is 0.1.

RESULTS

Samples were taken from the exit stream of a single CSTR and analyzed by GPC with a dual detector system (DRI/VISCOTEK). GPC measurements of intrinsic viscosity versus retention volume, number-average molecular weight versus retention volume and polymer weight fraction versus retention volume were used to estimate in the first instance, the Mark-Houwink parameters for linear copolymer chains, at larger retention volumes, polymer chains in the detector cells are essentially linear. It was assumed that GPC axial dispersion was negligible and therefore that all of the polymer chains in the detector cells have the same molecular weight. The GPC measurements thus provide a measure of intrinsic viscosity versus molecular weight for linear chains and thus providing data for the estimation of Mark-Houwink constants which were α=0.64 and k=0.000891 for linear chains of styrene/butadiene copolymer chains. These parameters for linear chains can now be used along with the Zimm-Stockmayer equations to calculate the intrinsic viscosity of chains with 1, 2, 3,…,9 long chain branch points and therefore the hydrodynamic volume of these same branched chains. The polymerization kinetic model is now capable of predicting the GPC measurements given the kinetic model parameters and thus permitting kinetic model parameter estimation to proceed. The GPC repeat measurements show good reproducibility over a wide range of retention volumes (r_v: 13.5 to 19.0 ml) and molecular weights (20,000 to 8.5 million). The signal-to-noise ratio for the GPC detectors were too low when r_v > 19.0 and r_v < 13.5. It should be noted, however that the useful range of retention volumes 13.5 to 19.0 covered more than 98 wt% for the polymer injected.

A data fitting run is performed proceeding from available experimental data and the model outlined in the previous section. Fitting criterion $m_{nv}(r_v^{\sigma})$ and the corresponding measurements are logarithmically scaled to have all data approximately in the same range. The scaled sum of residuals is reduced from 0.062 to 0.0096 after 200 cycles of the iterative process. The model parameters are shown in Table 1. The kinetic parameter kp* is a pseudo-kinetic rate constant which is defined by equation (5). The estimated parameters are listed in Table 2. The corresponding intrinsic viscosity i^l are obtained from (61) for the final parameters and these are plotted in Figure 12.

It is of interest to note that intrinsic viscosity in equation (2), the Zimm-Stockmayer equation, vary linearly with number of tetrafunctional branch points from 1 to 5 branch points per chain and then is constant independent of number of branch points per chain in the range, 5 to 9 branch points per chain. Branching structure factors that are published for polymers other than styrene-butadiene-divinylbenzene seem to vary in the range 0.5 to 1.5 for whole polymer samples.

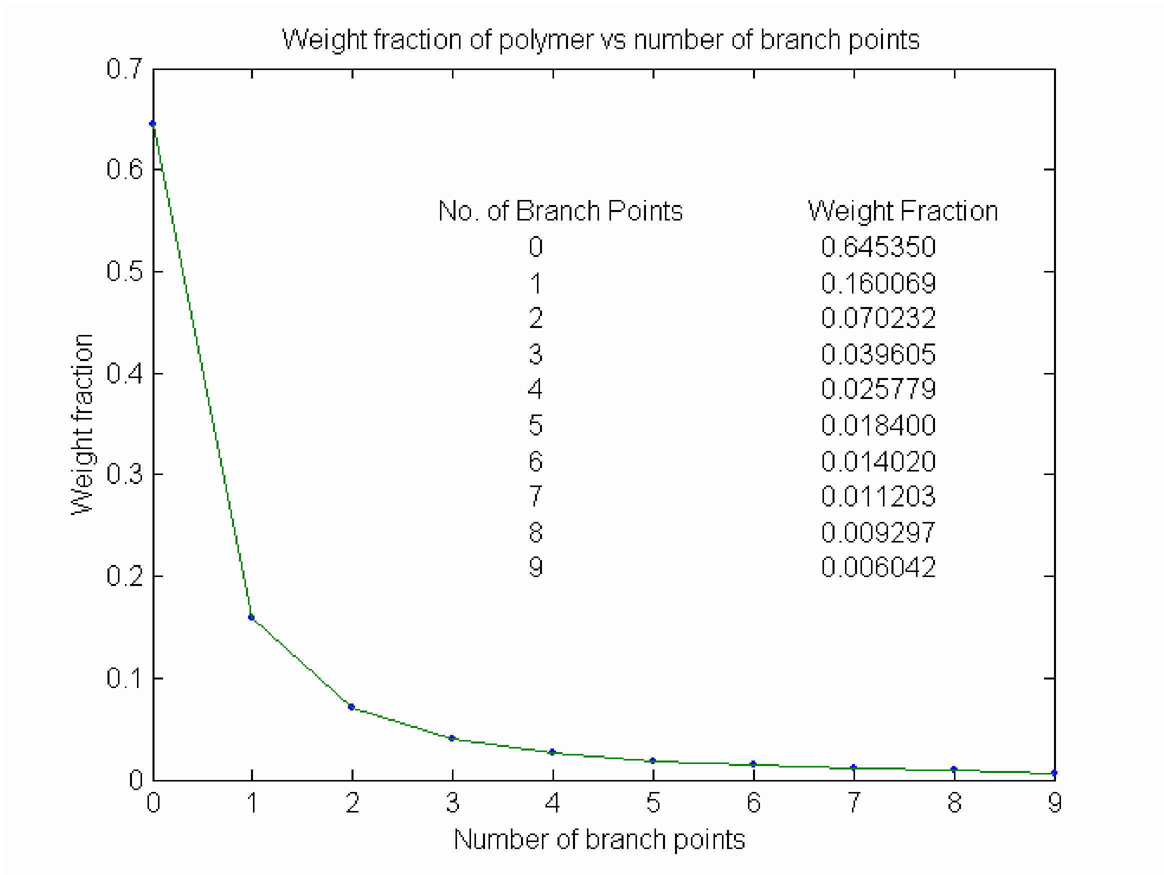
Intrinsic viscosity versus retention volume measured by GPC and calculated by the present model is compared in Figure 13. The agreement between measured and predicted intrinsic viscosities is satisfactory in the retention volume range 15.0 to 18.0. The retention volume range 17.0 to 19.0 involves mainly linear chains, while the range, 13.5 to 15.0 involves highly branched chains. The poor agreement at high retention volumes cannot be explained. The scatter observed for the model calculations suggests some inadequacy in the model, which might be related to pulse width used.

Figure 14 shows a comparison of the number-average molecular weight for polymer chains in the GPC detector cell versus retention volume measured and calculated by the present model. The agreement is excellent for the retention volume range 13.5 to 18 ml. However, again model calculations are highly scattered in the retention volume range 18.0 to 19.0 ml. The reasons for this scatter are unclear.

Figure 15 shows a comparison of measured (by GPC) and model predicted weight fraction of polymer in the GPC detector cell versus retention volume. The agreement is fair with a shift in model calculations to higher retention volumes required to improve the fit. GPC gives a valid measure of the number-average molecular weight of the whole polymer and a comparison of measured and model calculated values are shown in Figure 15. There are several possible reasons for the disagreement between GPC measured data and that model calculated. These include the fact that GPC with a DRI/VISCOTEK dual detector system cannot provide a valid measurement of the weight-average molecular weight of the contents of the detector cell for a mixture of linear and branched chains. This information would be invaluable in evaluating the effectiveness of the Zimm-Stockmayer long chain branching equations and also assessing that validity of the assumption that living polymer chains behave as a macro fluid. A further and more complete evaluation of the present method of physical pulses on which model calculations are based is called for and this awaits a future investigation involving a GPC with DRI/VISCOTEK/LALLA detector system. The use of variable angle light scattering to measure radius of gyration of polymer chains in the detector cell would be even better.

l	ε_l	i^l
1	1.4950	0.3998
2	1.3718	0.2354
3	1.1967	0.1910
4	1.1476	0.1486
5	1.1520	0.1147
6	1.0919	0.1047
7	1.1138	0.0830
8	1.1281	0.0645
9	1.1896	0.0515

Tab. 2: Estimated branching structure factors and intrinsic viscosity of branched species.



No. of Branch Points	Weight Fraction
0	0.645350
1	0.160069
2	0.070232
3	0.039605
4	0.025779
5	0.018400
6	0.014020
7	0.011203
8	0.009297
9	0.006042

Fig.12: Weight fraction of polymer versus number of branch points.

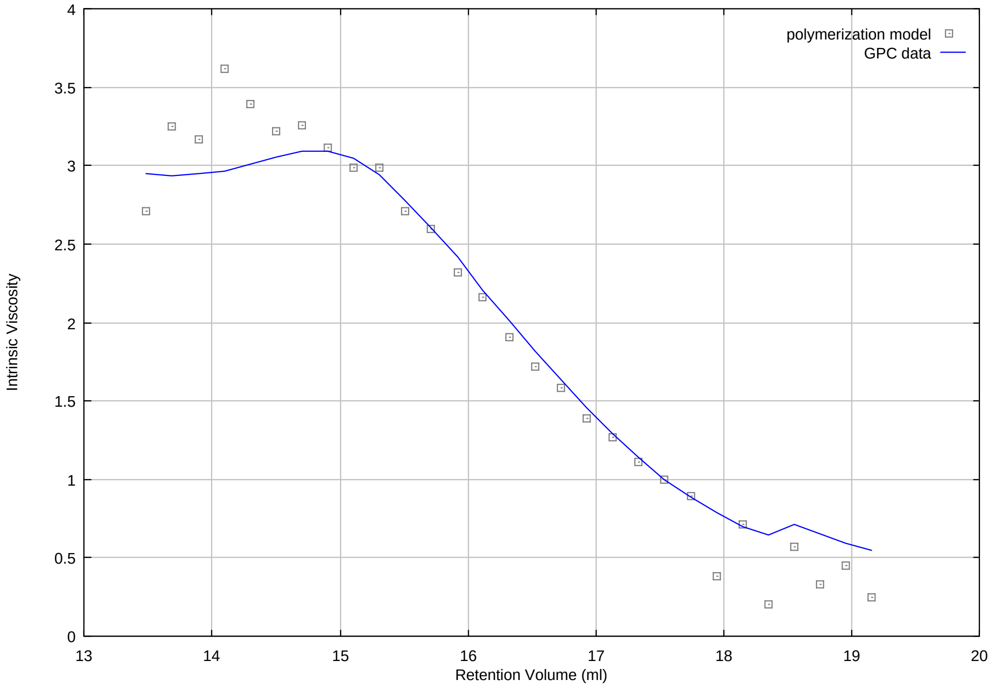


Fig. 13: A comparison of measured intrinsic viscosity with model prediction.

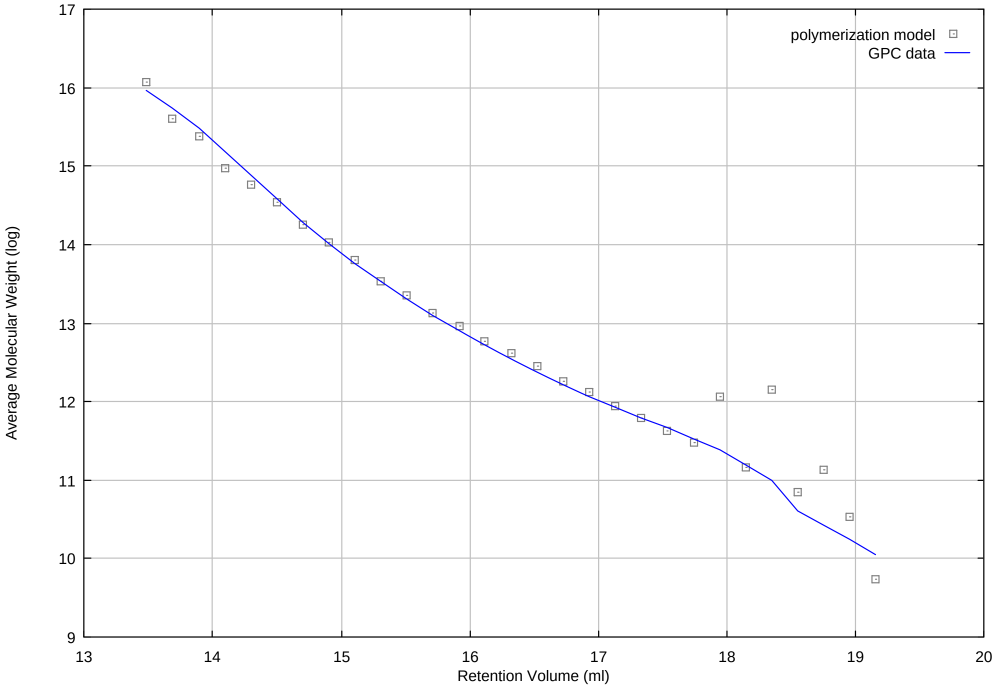


Fig. 14: A comparison of measured number-average molecular weight with model prediction

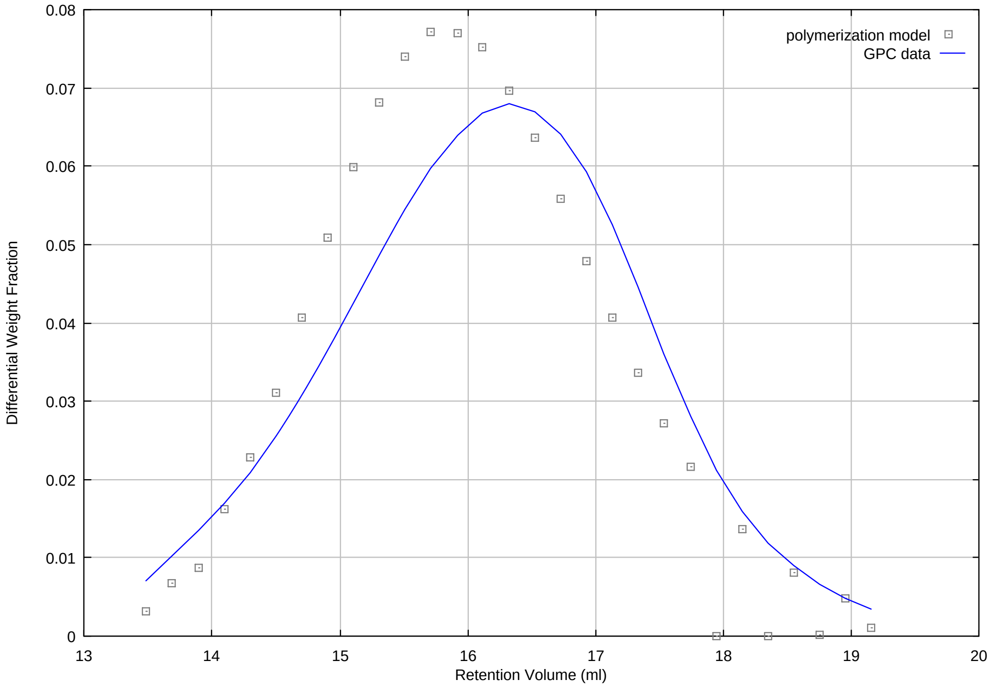


Fig. 15: A comparison of measured weight fraction distribution with model prediction

Mn (GPC) = 163,400. Mn(Model) = 172,480

SUMMARY AND REMARKS

A general dynamic model for continuous anionic polymerization of styrene-butadiene in the presence of divinylbenzene using active centers based on n-butyllithium in hexane has been developed. The model accounts for the association of living chains and tetrafunctional long chain branching. A new and efficient method of calculating the weight chain length distribution is described which does not require the solution of a large set of algebraic or ordinary differential equations (population balance equations).

We believe that the Zimm-Stockmayer equation, which relates the intrinsic viscosity of branched species to that of the linear counterpart having the same molecular weight, may predict ratios η_i/η_L which are too large for highly branched species. We do not have the theoretical background to pinpoint the precise reasons for this discrepancy in the Zimm-Stockmayer theory. For our practical purposes of modeling we suggest the use a modified empirical form of the Zimm-Stockmayer equation to give smaller intrinsic viscosity ratios for η_6/η_L , η_7/η_L , η_8/η_L, η_9/η_L . This will certainly permit the polymerization model to more accurately predict the η versus retention volume in the range 13.5 to 15.0, and give also a more accurate prediction of the differential weight fraction versus retention volume distribution.

NOMENCLATURE

af^i_3	Fraction of the units in the chain that have a double bond.
ak^ip_{12}	Apparent propagation constant for chains with styrene at site when butadiene adding to the chain.
ak^ip_{22}	Apparent propagation constant for chains with butadiene at site when butadiene adding to chain.
ak^ip_{22}	Apparent propagation constant for chains with butadiene at site when butadiene adding to the chain.

ak^ip_{21}	Apparent propagation constant for chains with butadiene at site when styrene adding to the chain.
ε_l	Branching structure factor.
$\eta(r_v)$	Intrinsic volume subject to retention volume.
f^i_{mi1}	Styrene input flow to CSTR(i) in kg/h.
f^i_{mo1}	Styrene output flow from CSTR(i) in kg/h.
f^i_{mi2}	Butadiene input flow to CSTR(i) in kg/h.
f^i_{mo2}	Butadiene output flow from CSTR(i) in kg/h.
f^i_{mi*}	Butyllithium input flow to CSTR(i) in gm/h.
f^i_{mis}	Input flow of the solvent.
f^i_{mos}	Output flow rate of the solvent.
f^ij	Frequency distribution of chain length r for chains with j branch points in CSTR(i) for a pulse.
γ	Reactor mode: γ = 1 if running full or at constant level with overflow, γ = 0 if reactor is in filling mode.
if^i_3	Instantaneous mole fraction of divinylbenzene in a chain.
i	Number of CSTR in CSTR train.
i^l_n	Intrinsic volumes.
I^{10k}_n	Index set.
I^{2jk}_n	Index set.
k_p	Kinetic rate constant.
k_p*	Kinetic rate constant.
k^ip_{1*}	Branching rate constant with styrene at site.

$k^i p_{2*}$	Branching constant with butadiene at site.
kp^i_{11}	Propagation constant for chains with styrene at site when styrene is adding to the chain in CSTR(i).
$k^i p_{12}$	Propagation constant for chains with styrene at site when butadiene adding to the chain.
$k^i p_{22}$	Propagation constant for chains with butadiene at site when butadiene adding to the chain.
$k^i p_{21}$	Propagation constant for chains with butadiene at site when styrene adding to the chain.
$ak^i p_{11}$	Apparent propagation constant for chains with styrene at site when styrene is adding to the chain in CSTR(i).
k^i_e	Equilibrium constant for association of active sites in CSTR(i) in $(dm^3/mol)^2$.
m^l	Molecular weight distribution over chain length.
m^i_{ptj}	Total moles of polymer chains with j branch points per chain in a pulse in CSTR(i).
m_{ws}	Molecular weight of the solvent.
m^i_*	The moles of butyllithium in a pulse in CSTR(i).
m^i_{fracj}	Mole fraction of monomer j (j =1,3) in CSTR(i).
mw_1, mw_2, mw_3	Molecular weight of styrene, butadiene and DVB.
$m_{nv}(r_v)$	Average molecular weight subjet to retention volume.
n_p	Number of pulse times.
n_b	number of tetrafunctional long chain branch points.
η_l	Intrinsic viscosity of linear chains.
n	Aggregation number of associated complex.

n^i_1	Moles of styrene in CSTR(i).
n^i_2	Moles of butadiene in CSTR(i).
n^i_3	Moles of divinylbenzene in CSTR(i).
n^i_*	Moles of butyllithium in CSTR(i).
n^i_s	Moles of solvent in CSTR(i).
p^l	Polydispersity index of individual species.
ϕ_1	Fraction of active centers of type 1.
ϕ_2	Fraction of active centers of type 2.
ϕ_3	Fraction of active centers of type 3.
ϕ^i_{1*}	Ratio of $q^i_{d01}(t)/q^i_{d0}(t)$.
ϕ^i_{2*}	Ratio of $q^i_{d02}(t)/q^i_{d0}(t)$.
q^i_{t0}	Total concentration of living chains in CSTR(i), in mol/dm^3.
q^i_{d0}	Concentration of dissociated chains in CSTR(i), in mol/dm^3
q^i_{d01}	Concentration of dissociated chains with styrene at the site in CSTR(i), in mol/dm^3.
q^i_{d02}	Concentration of dissociated chains with butadiene at the site in CSTR(i), in mol/dm^3 in a pulse.
r	Chain length.
r^l_n	Mean chain lengths.
r_{12}	Reactivity ratio for chains with styrene at active center (styrene/butadiene).
r_{21}	Reactivity ratio for chains with butadiene at active center (styrene/butadiene).
r_{13}	Reactivity ratio for chains with styrene at active center (styrene/DVB).

r_{23}	Reactivity ratio for chains with butadiene at active center (butadiene/DVB).
r_v	Retention volume.
t	Time, hours.
T_0	Initial temperature.
T_f^i	Reference temperature.
t_k	Pulse time
$\bar{t}_1$	Mean residence time in CSTR(1) in minute.
$\bar{t}_2$	Mean residence time in CSTR(2) in minute.
$C(t)$	Concentration of tracer in ppm.
$E(t)$	Normalized residence time distribution.
V^i	Volume of reaction mixture in dm^3 in CSTR(i).
V^i_o	Total volumetric flowrate in dm^3/h out of CSTR(i).
V^i_p	Volume of a pulse in CSTR(i).
w_p^i	Pulse weight.
w^i_j	Weight chain length distribution of chains with j branch points in CSTR(i).
w_j	Weight chain length distribution of the whole polymer (linear chains + branched chains).
w_{tot}^l	Total weight of polymer after *l*-1 branching steps.
$w_{rv}(r_v)$	Weight fraction at every retention volume.
x_w^l	Molecular weight of individual species.
x^l	Number average of individual species.

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