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Kinetic Modeling of Non-Linear Polymerization

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Summary: Recent developments of a method based upon population balances of generating functions of polymer chain length distributions (CLD) are presented. The calculation of the CLD and how to take into account chain length dependent reactivity are discussed. Prediction of polymer properties is also possible but only easily done for the average molecular radius of gyration; some results are presented for a radical polymerization including transfer to polymer and propagation with terminal double bonds.

Keywords: gelation; molecular weight distribution; non-linear polymers; radical polymerization; Ziegler-Natta polymerization

Introduction

Stockmayer's famous paper[1] establishing the CLD of simple non-linear polymerizations starts the subject discussed in this paper. Through a probabilistic and combinatorial reasoning, he obtained the equilibrium CLD of the polycondensation of a single monomer XA_f with f end groups **A**:

$$P_x = X \times \frac{f(fx-f)!}{x!(fx-2x+2)!} p^{x-1} (1-p)^{x(f-2)+2} \tag{1}$$

where p is the conversion of end groups A and P_x is the overall mole concentration of the set of isomers containing x units X.

In the appendix C of the same paper, a population balance equation (PBE) for the concentrations of polymer species in a batch reactor, similar to the set of equations eq 2 (a variant of Smoluchowski[2,3] coagulation equation), was written:

$$\frac{dP_x}{dt} = k\left(\frac{1}{2}\sum_{y=1}^{x-1} a_y a_{x-y} P_y P_{x-y} - A a_x P_x\right)$$
$$P_{x|t=0} = \begin{cases} X & \text{if} \quad x = 1 \\ 0 & \text{if} \quad x > 1 \end{cases} \tag{2}$$

$$\frac{dA}{dt} = -kA^2 \quad A_{t=0} = fX \tag{3}$$

The apparent rate constant k might be any function of time or of the conversion of groups A, but it should be the same for every polymer species according to Flory's Principle of Equal Reactivity.[4] $a_x = x(f-2)+2$ is the number of A end groups for isomers P_x starting from a pure species XA_f.

Stockmayer confirmed that the equilibrium CLD eq 1 is indeed a solution of eq 2 and 3.

It is difficult to generalize Stockmayer's combinatorial reasoning to more complex chemical systems, and a decisive progress was achieved through the introduction of the theory of branching processes[5] by Good[7] and Gordon.[6] A more elementary but mathematically equivalent reasoning (the "recursive approach") was later developed by Macosko and Miller.[8,9] The reader will find elsewhere detailed reviews

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covering in detail earlier works about polymerization modeling[10] as well as related state-of-art knowledge on modeling of polycondensations and hyperbranched polymer synthesis.[10,11]

Monte Carlo methods[13,14] are often used as an alternative to PBE, particularly in heterogeneous polymerizations.[15–18] Moreover, they become specially useful when the lumping of isomers as done above has to be avoided, such as for modeling reversible polymerization with random chain breakage,[19] or when the space position of groups has to be taken into account (prediction of physical properties of the polymer, cyclization reactions). PBE for individual isomers can only be used up to a fairly low upper value of the chain length, as the number of species ($\frac{f^x(fx-f)!}{(fx-2x+2)!}$ in this example[1]) rapidly goes over several millions when x is above a few tens. Therefore, the population sampling provided by Monte Carlo overcomes the huge memory and computing time expenditure needed, at the price of some accuracy loss.

The kinetic modeling of polymerizations through the use of PBE like eq 2 will not yield analytical solutions as readily as the probabilistic reasonings. But with semi-batch or continuous stirred tank reactors (CSTR) there is no alternative to it, and it became a standard practice for chemical engineers since Denbigh's pioneering work.[20] Kinetic modeling will also easily yield the correct solution in the presence of substitution effects in batch reactors, which is a tricky problem with probabilistic reasonings because of time correlations.

Generating functions or discrete transforms have long been used in polymer science and engineering as a tool for simplifying the PBE of polymer species.[21–23] Their application to non-linear irreversible polycondensations has been introduced by Kuchanov and collaborators.[24] Instead of the more current alternating polycondensation $XA_f + YB_g$ discussed in the aforementioned paper, the same treatment with a self-reacting monomer will be used for illustration purposes.

A seemingly trivial change (needed for all non-linear polymerizations) consists in introducing the two-dimensional CLD $P(a, x)$ where a is the count of A end groups:

$$\frac{dP(a,x)}{dt} = k\left(\frac{1}{2}\sum_{y=1}^{x-1}\sum_{b=1}^{a+1} b(a-b+2)P(b,y)P(a-b+2,x-y) - Aa_xP(a,x)\right) \tag{4}$$

Now, on defining a vector generating function (GF):

$$G(s_A, s_X) = \sum_{a=0}^{\infty}\sum_{x=0}^{\infty} s_A^a s_X^x P(a,x) \tag{5}$$

the partial differential equation below (the "master equation") is obtained:

$$\begin{aligned}\frac{\partial G}{\partial t} &= k\frac{\partial G}{\partial \log s_A}\left(\frac{1}{2s_A^2}\frac{\partial G}{\partial \log s_A} - A\right)\\ G(s_A, s_X)_{|t=0} &= Xs_A^f s_X\end{aligned} \tag{6}$$

The method of characteristics[25] leads to a two-point boundary value problem (2PBVP) for each value of the solution vector $\mathbf{s} = (s_A, s_X)$ (Table 1), which has an analytical solution.

Table 1.
Characteristics and analytical solution of master equation eq 6.

$\frac{d\log s_A}{dt} = k\left(A - \frac{G_A}{s_A^2}\right)$	$s_{A\|t=0} = s_{A_0}$	$s_{A_0} = s_A(1-p) = ps_X s_{A_0}^{f-1}$
$\frac{dG_A}{dt} = -k\frac{G_A^2}{s_A^2}$	$G_{A\|t=0} = \frac{\partial G_A}{\partial \log s_{A\|t=0}} = fXs_{A_0}^f s_X$	$G_A/X = fs_{A_0}^f s_X - fp(s_{A_0}^{f-1}s_X)^2$
$\frac{dG}{dt} = -\frac{k}{2}\frac{G_A^2}{s_A^2}$	$G_{\|t=0} = Xs_{A_0}^f s_X$	$G/X = s_{A_0}^f s_X - fp(s_{A_0}^{f-1}s_X)^2\Big/2$

The size of the 2PBVP is twice the number of active groups in polymer species: the only one in this example is the A end group. The dummy Laplace variables associated to passive groups in polymer (the repeating units X) stay constant along the characteristics.

For more general problems, it is convenient to introduce a vector of group counts **a** of size N_P, the number of groups belonging to polymer species. In this example $N_P = 2$ and $a_1 = a$, $a_2 = x$. The moments with respect to the counts of groups will be named through a notation adapting the index convention for partial derivatives, using the abbreviation $\mathbf{1}_N$ for a vector of N components all equal to one:

$$\begin{aligned}\lambda_{n\ldots p} &= \sum_{a_1=0}^{\infty}\cdots\sum_{a_{N_P}=0}^{\infty} a_n\cdots a_p P(\mathbf{a})\\ &= \frac{\partial\ldots\partial G}{\partial\log s_n\ldots\partial\log s_p}(1_{N_P})\\ &= G_{n\ldots p}(1_{N_P})\end{aligned} \tag{7}$$

In particular, the zero order moment λ_0, the mole concentration of polymer P, is equal to $G(\mathbf{1}_{N_P})$. Number- and weight-average degrees of polymerization are the ratios of successive integer order moments with respect to the count of repeating units X $\left(\bar{x}_n = \frac{\lambda_2}{P}, \bar{x}_w = \frac{\lambda_{22}}{\lambda_2}\right)$, and in this example:

$$\begin{aligned}P &= X\left[s_{A_0}^{f} - fp(s_{A_0}^{f-1})^2\big/2\right]\\ \lambda_2 &= Xs_{A_0}^{f}\\ \lambda_{22} &= Xs_{A_0}^{f}\frac{1+ps_{A_0}^{f-2}}{1-(f-1)ps_{A_0}^{f-2}}\end{aligned} \tag{8}$$

Differentiation of the master equation eq 6 with respect to the dummy Laplace variables yields partial differential equations allowing an easy evaluation of the $G_{n\ldots p}$, since they share the same characteristics as G.

For $\mathbf{s} = \mathbf{1}_{N_P}$, there is always a solution $\mathbf{s}_0 = \mathbf{1}_{N_P}$ of the 2PBVP such as eq 1.

If that solution is the only valid one, the first moments with respect to the counts of groups will be equal to the overall values in the system which can be computed through PBE; thus, one should obtain $G_1(\mathbf{1}_{N_P}) = A$ and $G_2(\mathbf{1}_{N_P}) = X$.

This would mean that all molecules of polymer are finite, leading in this example to:

$$\begin{aligned}\bar{x}_n &= \frac{1}{1-fp/2}\\ \bar{x}_w &= \frac{1+p}{1-(f-1)p}\end{aligned} \tag{9}$$

Gelation occurs when the trivial solution $\mathbf{s}_0 = \mathbf{1}_{N_P}$ is a double root for some value of time (gelation time t_g). For $t > t_g$, that trivial solution is no longer valid, and the other solution branch is the one physically meaningful. In this example, this occurs when $p > \frac{1}{f-1}$.

If gelation does not occur, the moments of the CLD can be computed through the integration of an initial value problem which is obtained by differentiation of the master equation and substitution of $\mathbf{s} = \mathbf{1}_{N_P}$. This is often known as the method of moments and is well established in Polymer Reaction Engineering.[23] For instance, that method has been used for computing weight-average group counts and the critical space-time for gelation in a CSTR for this chemical system by Cozewith et al.[26]

Until recently, efficient methods for recovering the CLD from their GF were not sufficiently developed for high average chain lengths, so that consideration of the PBE in the real chain length domain and finite elements approximation[27] became the most used method, as the successful commercial package PREDICI[28] is based on it. It will compute one and two dimensional CLD while averaging the other chain-lengths, but this is not easily done in the presence of gel. So, ''numerical fractionation''[29,30] has provided a practical solution, using an approximated CLD (knowing some tens of moments) in order to make possible the treatment of such polymerization schemes. Its accuracy depends on how fast converges the underlying series used for describing the CLD (which becomes unusable close to gelation), as well as the quality of the calculation of the moments, which is affected by several underlying simplifying assumptions.[40]

Numerical Computation of Generating Functions (GF) of Polymer Chain Length Distributions (CLD) and Its Uses

It is a boring and error-prone task to write the PBE for the moments with any but the most trivial chemical systems. A number of works have therefore endeavored to establish a modeling basis and offer some means to solve the out coming equations. An implementation of the method of moments made its way into the commercial package POLYRED,[31] its polymerization modeling foundations being described in Arriola's Ph. D. thesis.[32]

A continued effort to extend the method of the moments to the calculation of other polymer properties was started by the present authors a little later, started by the need to describe average molecular weights and sequence distributions of polyurethanes. At first, a general modeling scheme usable mainly for irreversible polycondensations was established,[33] and then a thorough revision[34] made it better suited for modeling chain polymerizations.

The crux is a classification of reacting groups and non-polymer species with seven kinds of chemical reactions transforming them, which are defined through suitable stoichiometric coefficients ν. Thus, the formation of bonds $\mathrm{Z_n}$ connecting two repeating units is assumed to occur through a reaction n with apparent second order rate constant k_n such that $\sum_{j+1}^{N_A} (\nu_{nj}^{-} + \nu_{nj}^{+})\mathrm{A}_j \xrightarrow{k_n} \mathrm{Z}_n$ with $n = 1, N_R$. This formulation allows for substitution effects through the stoichiometric coefficients ν_{nj}^{-} and ν_{nj}^{+}, which are the changes in the counts of groups of the two polymer molecules which have reacted.

A general master equation for the GF of polymer CLD can be established (here omitted as it would fill one page). Its numerical solution using the method of characteristics provides $G(\mathbf{s})$ and its derivatives in the complex space of the dummy Laplace variables $\mathbf{s}$, the moments of the CLD being a particular case.

With radical polymerizations, PBE are very "stiff"[35] because of the high relative values of termination rate constants. This leads to extreme numerical sensitivity[36] of the 2PBVP needed for solution by the method of characteristics. Only rather recently a suitable method[37] could be found to solve them.

The inversion of numerically computed GF of polymer CLD has been successfully carried out for polycondensations[44–46] using the discrete Poisson summation formula DPSF, requiring the knowledge of *G(s)* for a set N of complex values $\{s_n\}$ which are equally spaced on a circle centered in the origin $s = 0$:

$$\begin{aligned} P_x &= \frac{1}{2\pi i}\oint_C s^{-n-1} G(s)\,ds \\ &= \frac{1}{N|s|^n}\sum_{n=0}^{N-1} e^{-\frac{2\pi i n x}{N}} G\left[|s|\exp\left(\frac{2\pi i n}{N}\right)\right] \\ &\quad - \sum_{l=1}^{\infty} P_{x+Nl}|s|^{Nl} \end{aligned} \tag{10}$$

All mole concentrations P_x up to $x = N-1$ can be evaluated with the same set of *G(s)* values with this formula, but this is not feasible if x goes above a few thousands. An adaptation of methods used for inversion of Laplace transforms[50–53] alleviates that problem.[47] More recent works by Asteasuain, Sarmoria et al.[48,49] have been using this approach. Successful modeling of the polyolefin random scission and radical polymerizations, either linear or including transfer to polymer (with at most with one radical site per molecule) has been reported.

The number N of the required values of *G(s)* can be drastically reduced, while keeping a very high and controlled accuracy. The authors have tested numerical recovery methods with several CLD and put forward some improvements.[54] In most cases, only some tens of values of *G(s)* are needed for an accurate inversion, even with broad CLD.

A more challenging problem occurs when trying to use generating functions of the CLD for the analysis of polymerization schemes where at least some rate constants depend on polymer chain length. This is not a rare situation, as it is well known[55] that rates of intramolecular ring forming reactions depend on the size of the ring. Likewise, a lot of experimental evidence shows that termination rate constants in radical polymerization depend on the chain length of the radicals.[56] The most likely explanation of the mild chain length dependence observed at low polymer concentration is an excluded volume effect[57] and so it is expected also to be found important with other chemical systems, such as step growth polymerizations in a dilute solution.

By consequence, some new terms with complex contour integrals arise in the PBE in Laplace domain, and thorough modifications of the numerical methods for solving them are needed. Some preliminary results[54] lead to believe that these kind of problems are tractable using the same expansions in discrete Laguerre functions[58] which have been successfully used for CLD recovery from the generating functions.

Application Examples: Metallocene and Radical Polymerizations

In the metallocene catalyzed olefin polymerization, long chain branching is introduced through the polymerization of terminal double bonds generated by β-hydride elimination. The copolymerization with a non-conjugated diene also produces long chain branching and the polymer contains pendant double bonds from the diene monomer in addition to those resulting from β-hydride elimination. Gelation becomes possible, and this must be avoided in industrial production.

An olefin/diene polymerization system was recently simulated in the pre-gel region by using a finite element procedure,[42] with a kinetic scheme considering initiations, propagations, chain transfers (to hydrogen), β-hydride elimination and deactivation of polymer chains.

An application of the approach here described[43,54] considers $N_A = 13$ chemical groups, $N_P = 9$ of them being present in the polymer molecules (olefin-terminated active chain OTAC A_1, diene-terminated active chain DTAC A_2, pendant double bond-terminated active chain A_3, terminal double bond-terminated active chain TTAC A_4, pendant double bond PDB A_5, terminal double bond TDB A_6, polymerized olefin unit A_{11}, polymerized diene unit A_{12} and branching point A_{13}), from which the former $N_{A_P} = 6$ are active. The remaining four active reagents are the olefin and diene monomers A_7 and A_8, the initiator A_9 and the chain transfer agent A_{10}.

Taking into account the different initiations, propagations, chain transfer, β-hydride elimination and deactivation reactions, a total number of 32 chemical reactions are obtained. Transfer to monomers, deactivation of the catalysts or ring formation have been neglected; they could be easily included if needed so, as shown with other polymerization systems.[34,36,39–41]

The numerical values of the parameters of this kinetic scheme used in simulations reported in Table 2 are similar to those used before in related works.[42] Other values have been postulated taking into account the decreased reactivity of pendant and terminal double bonds.

Considering both batch and CSTR operation, Figure 1a shows examples of the predicted average molecular weights, whereas the time evolution of the CLD for the olefin + diene metallocene-catalyzed polymerization system is presented in Figure 1b. The calculations have been checked by comparing the results obtained with Papoulis, Weeks and Durbin's inversion methods.

The modeling of radical polymerization is one of the most important problems in

Table 2.
Reaction scheme in the metallocene catalyzed polymerization of an olefin O with a non-conjugated diene D.

Initiations	
Olefin O $A_7 + A_9 \xrightarrow{k_{i1}=1000} A_1 + A_{11}$	Diene D $A_8 + A_9 \xrightarrow{k_{i2}=140} A_2 + A_5 + A_{12}$
PDB $A_5 + A_9 \xrightarrow{k_{i3}=70} A_3 + A_{13}$	TDB $A_6 + A_9 \xrightarrow{k_{i4}=35} A_4$
Propagations	
OTAC + O $A_1 + A_7 \xrightarrow{k_{p11}=1000} A_1 + A_{11}$	OTAC + D $A_1 + A_8 \xrightarrow{k_{p12}=140} A_2 + A_5 + A_{12}$
OTAC + PDB $A_1 + A_5 \xrightarrow{k_{p13}=70} A_3 + A_{13}$	OTAC + TDB $A_1 + A_6 \xrightarrow{k_{p14}=35} A_4 + A_{13}$
DTAC + O $A_2 + A_7 \xrightarrow{k_{p21}=40} A_1 + A_{11}$	DTAC + D $A_2 + A_8 \xrightarrow{k_{p22}=4} A_2 + A_5 + A_{11}$
DTAC + PDB $A_1 + A_5 \xrightarrow{k_{p23}=2} A_3 + A_{13}$	DTAC + TDB $A_2 + A_6 \xrightarrow{k_{p24}=1} A_4 + A_{13}$
PTAC + O $A_3 + A_7 \xrightarrow{k_{p31}=20} A_1 + A_{11}$	PTAC + D $A_3 + A_8 \xrightarrow{k_{p32}=2.9} A_2 + A_5 + A_{11}$
PTAC + PDB $A_3 + A_6 \xrightarrow{k_{p33}=1.45} A_3 + A_{13}$	PTAC + TDB $A_3 + A_7 \xrightarrow{k_{p34}=0.725} A_4 + A_{13}$
TTAC + O $A_4 + A_5 \xrightarrow{k_{p41}=10} A_1 + A_{11}$	TTAC + D $A_4 + A_6 \xrightarrow{k_{p42}=1.43} A_2 + A_5 + A_{11}$
TTAC + PDB$A_4 + A_5 \xrightarrow{k_{p43}=0.715} A_3 + A_{13}$	TTAC + TDB $A_4 + A_6 \xrightarrow{k_{p44}=0.3575} A_4 + A_{13}$
β-hydride eliminations	
$A_j \xrightarrow{k_{\beta j}=0.01} A_6 + A_9$	$j = 1 \ldots 4$: OTAC, DTAC, PTAC, TTAC
Deactivation of catalyst sites	
$A_j \xrightarrow{k_{dj}=0.001}$ Inactive products	$j = 1 \ldots 4$: OTAC, DTAC, PTAC, TTAC
Chain transfers	
$A_j + A_{10} \xrightarrow{k_{trj}=10} A_9$	$j = 1 \ldots 4$: OTAC, DTAC, PTAC, TTAC

Rate constants $k_{\beta j}$ and k_{dj} have units s^{-1} and the others are expressed in $dm^3\ mol^{-1}\ s^{-1}$.

Polymer Reaction Engineering. In order to obtain tractable models before the availability of sufficiently powerful mathematical methods such as the above described (or POLYRED software in the absence of gel), it was inevitable to use simplifying assumptions such as:

1. Quasi-steady state for radical concentrations;
2. Negligible rates of initiation and termination reactions relatively to propagation and transfer;
3. Negligible presence of multiple radical centers;
4. Negligible presence of more than one terminal double bond per molecule;
5. Negligible exit of radicals from the reactor:
6. Chain transfer only to ''dead'' polymer:
7. Closure conditions for the moments.

The closure condition for the PBE of moments would be avoided if the presence of multiple radical centers could be neglected,[38] but the definitive solution is to abolish the division between ''dead'' and ''living'' polymer molecules for modeling purposes.

An analysis of the influence of these assumptions for vinyl/divinyl radical polymerizations[36] shows that appreciable errors can occur with the legacy ''pseudo-kinetic method'' when the reactivity of pendant double bonds is much different of the one observed with primary bonds. Similar issues are present when dealing with transfer to polymer and terminal double bond propagation.[39,40]

Figure 2a shows average molecular weights and sol fraction during the start-up of a CSTR with a radical polymerization. The kinetic scheme for this case study[40] and the values for its parameters are presented in Table 3.

It includes $N_A = 12$ groups, $N_P = 7$ of them being present in the polymer molecules: polymer radicals A_1, terminal double bonds originated by transfer to monomer A_2, terminal double bonds originated by

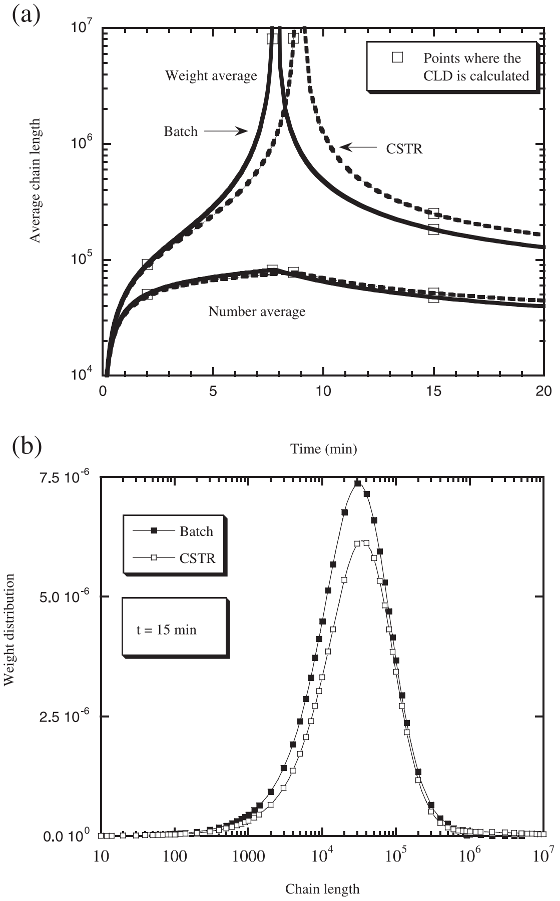

Figure 1.
Metallocene catalyzed copolymerization of an olefin with a non-conjugated diene in a batch and a transient CSTR ($\tau = 5$ min): (a) Average molecular weights (b) Predicted chain length distributions at $t = 15$ min.

termination by disproportionation A_3, sites of transfer to polymer A_4, the polymerized monomer units A_{10}, the fragments from initiator A_{11} and from the solvent A_{12}. From this set, the former $N_{A_P} = 4$ are active. The remaining five active reagents are the monomer A_5, the solvent A_6, primary radicals from the initiator A_7, primary radicals from the solvent A_8 and the initiator A_9.

Prediction of Average Molecular Radius of Gyration and Other Physical Properties of Polymers

The prediction of the structure of branched polymers in the approximation of the Gaussian chain model has been carried out using the theory of branching processes[59,60] in order to compute the needed concentrations of polymer molecules or sequences.[61,62]

The time dependent spatial correlations of polymer groups can be described through an elegant statistical mathematical formalism involving generating functionals of time and space coordinates.[64] Practical results are mostly limited to polycondensations[63] and its extension to general polymerization schemes is not an easy problem.

Monte Carlo simulation has been used by Tobita and collaborators,[65–67] and also by Iedema and Hoefsloot,[68] for predicting the average molecular radius of gyration for

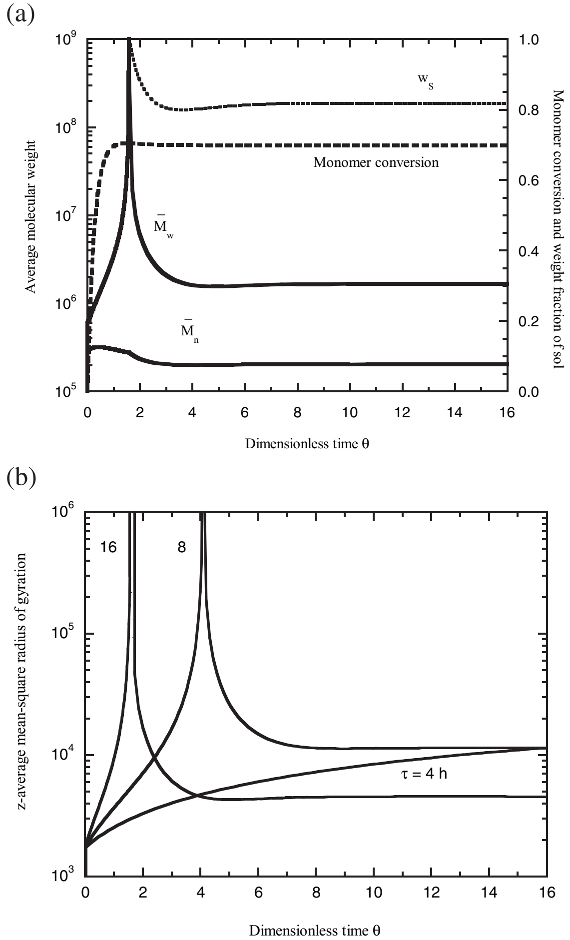

Figure 2.
Radical polymerization with terminal branching and transfer to polymer in a transient CSTR ($\tau = 16$ h): (a) $\overline{M}_n$, $\overline{M}_w$ and sol fraction (b) Normalized z-average mean square radius of gyration $\overline{\langle s^2\rangle}_z \big/ b^2$.

branched polymers as well as the trace of the size-exclusion chromatogram.

The molecular z-average radius of gyration $\overline{\langle s^2\rangle}_z$ for tree-like polymers can be predicted[69] using the PBE of the two-sided pendant chains $Z_n(\mathbf{a}^-, \mathbf{a}^+)$ associated to the bonds of chemical class Z_n (see Figure 3). For instance, when there is only one kind of bond with length b, such as in the XA_f step-growth polymerization above discussed, and the mass of polymer belonging to end groups can be neglected:

$$\overline{\langle s^2\rangle}_z \Big/ b^2 = \frac{\partial^2 G_Z}{\partial s_X^- \partial s_X^+}\bigg|_{\mathbf{s}^- = \mathbf{s}^+ = \mathbf{1}} \Bigg/ \lambda_{22} \qquad (11)$$

A PBE for the GF G_Z in a batch reactor starting from the monomer leads to the 1st order PDE below:

$$\begin{aligned} k^{-1}\frac{\partial G_Z}{\partial t} &= \frac{G_A(s_A^-)G_A(s_A^+)}{2s_A^- s_A^+} \\ &+ \frac{\partial G_Z}{\partial \log s_A^-}\left[\frac{G_A(s_A^-)}{(s_A^-)^2} - A\right] \\ &+ \frac{\partial G_Z}{\partial \log s_A^+}\left[\frac{G_A(s_A^+)}{(s_A^+)^2} - A\right] G_{Z|t=0} = 0 \end{aligned} \qquad (12)$$

The three terms in the right hand side represent, respectively, the birth of a

Table 3.
Reaction scheme in a radical polymerization with terminal double bonds branching and transfer to polymer.

Reaction name	Chemical equation
Initiator decomposition	$A_9 \xrightarrow{k_d=9*10^{-6}} A_7$
Monomer initiation by primary radicals from initiator	$A_5 + A_7 \xrightarrow{k_{i1}=1.17*10^4} A_1 + A_{10} + A_{11}$
Monomer initiation by primary radicals from solvent	$A_5 + A_8 \xrightarrow{k_{i2}=1.17*10^4} A_1 + A_{10} + A_{12}$
Propagation of TDBM	$A_1 + A_2 \xrightarrow{k_{pTM}=9360} A_4 + A_1$
Propagation of TDBD	$A_1 + A_3 \xrightarrow{k_{pTD}=9360} A_4 + A_1$
Termination by combination	$A_1 + A_1 \xrightarrow{k_{tc}=1.25*10^8} A_4 + A_4$
Propagation of monomer	$A_1 + A_5 \xrightarrow{k_p=1.17*10^4} A_4 + A_1 + A_{10}$
Transfer to polymer	$A_1 + A_4 \xrightarrow{k_{fP}=1.404} A_1$
Termination by disproportionation	$A_1 + A_1 \xrightarrow{k_{td}=1.25*10^8} A_3$
Initiation of TDBM by primary radical from initiator	$A_2 + A_7 \xrightarrow{k_{iTM}=9360} A_1 + A_{11}$
Initiation of TDBM by primary radical from solvent	$A_2 + A_8 \xrightarrow{k_{iSTD}=9360} A_1 + A_{12}$
Initiation of TDBD by primary radical from initiator	$A_3 + A_7 \xrightarrow{k_{iTD}=9360} A_1 + A_{11}$
Initiation of TDBD by primary radical from solvent	$A_3 + A_8 \xrightarrow{k_{iSTD}=9360} A_1 + A_{12}$
Transfer to solvent	$A_1 + A_6 \xrightarrow{k_{fS}=0.351} A_8$
Transfer to monomer	$A_1 + A_5 \xrightarrow{k_M=2.223} A_1 + A_2 + A_{10}$

k_d units are s^{-1} and the remaining kinetic parameters are in $dm^3\ mol^{-1}\ s^{-1}$.

moiety $Z(a^-, a^+)$ and the modification of the number of its pendant groups by chemical reaction in either side. The solution is found in the same way as for the expressions in Table 1:

$$G_Z = \frac{1}{2} f X p s_X^- s_X^+ (s_{A_0}^- s_{A_0}^+)^{f-1}$$
$$s_{A_0}^J = s_A^J (1-p) + p s_X^J (s_{A_0}^J)^{f-1} \quad J = +,- \tag{13}$$

leading to:

$$\overline{\langle s^2 \rangle}_z = \frac{f p s_{A_0}^{f-2}}{2(1 + p s_{A_0}^{f-2})[1 - (f-1) p s_{A_0}^{f-2}]} \tag{14}$$

Before gelation the well-known result[70] is obtained:

$$\overline{\langle s^2 \rangle}_z = \frac{fp}{2(1+p)[1-(f-1)p]} \tag{15}$$

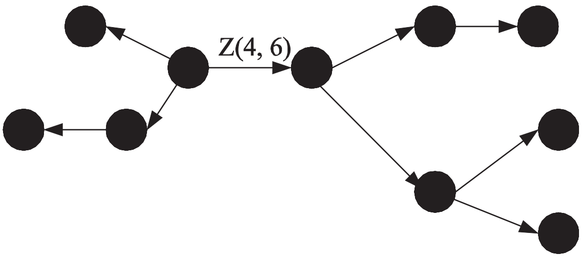

Figure 3.
Example of a two-sided pendant chain Z(4, 6) for an oligomer species with 10 repeating units formed by step-growth polymerization of a monomer XA_3.

Note that the above described approach will also work for a semibatch reactor or a CSTR, in contrast with the classical probabilistic reasonings. But these calculations rapidly become very cumbersome with even slightly more complex kinetic schemes, requiring in practice an automated procedure.[71] Figure 2b shows an example of the results thus obtained with a non-linear radical polymerization.

The distribution of the radius of gyration can also be obtained, but as the isomers with same molecular masses are inevitably lumped, the prediction of the size-exclusion chromatogram can not carried out without some simplifying assumptions. Even so, the availability of this alternative method, which is computationally fast and as accurate as its base physical assumptions allow, should be useful to check the results obtained by other approaches, in particular using Monte Carlo calculations.

Conclusion

It has been shown that a general population balance of polymer species combined with suitable numerical methods can be used for predicting not only average molecular weights but also CLD and physical properties of branched polymers formed by homogeneous irreversible polymerizations. Gel properties can also be computed. Some preliminary calculations lead to believe that it can be modified in order to take into account the chain-length dependence of rate constants.

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