Prediction of mean square radius of gyration of tree-like polymers by a general kinetic approach

Mário Rui P.F.N. Costa b,*, Rolando C.S. Dias a,1

a LSRE — Instituto Politécnico de Bragança, Quinta de S. Apolónia, 5300 Bragança, Portugal
b LSRE — Faculdade de Engenharia da Universidade do Porto, Departamento de Engenharia Química, Rua Roberto Frias, s/n, 4200-465 Porto Codex, Portugal

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Abstract

This paper describes a kinetic method to predict the z-average molecular mean square radius of gyration of tree-like polymers formed by irreversible reactions, assuming Gaussian chains. It is based on the population balance equations for the two-sided molecular distributions of pendant chains associated with every chemically distinguishable kind of bonds. An automated method for the solution of those equations is valid both before as well as after gelation for complex kinetic schemes. Examples of its use are presented with polycondensation systems leading to hyperbranched polymers, the anionic polymerization of mono- and divinyl monomers and a radical polymerization with terminal branching and transfer to polymer.

Keywords: Radius of gyration; Branching; Kinetics

1. Introduction

1.1. The statistics of the configurational structure of branched polymers

The calculation of the most relevant statistics of the counts of chemical groups and sequences in polymer molecules or fragments of them is a simpler problem which must be solved before trying to undertake a theoretical prediction of conformation dependent physical properties. Chemical groups in polymer molecules and non-polymer molecules will be named \( A_j \) with \( 1 \leq j \leq N_A \) and their counts in a polymer molecule or fragment belong to a vector \( \mathbf{a} = [a_1, \ldots, a_{N_A}] \); molar concentrations of groups and other species are named \( [A_j] \). Only a sub-set of \( N_P \) groups will be present in polymer species (such as the repeating units RUs written also as \( X_k \) with \( k = 1, \ldots, N_X \)). The other species will include monomers in chain-growth polymerizations, initiators, transfer agents and similar.

Polymer species \( P_\mu \), which differ by the counts of groups and the way they are connected, will be labelled by an integer index \( \mu \).

Polymer molecular size distribution (MSD) is considered synonymous of the distribution of numbers of molecular species with respect to counts of groups. Its probability function is the normalized concentration of polymer \( [P(\mathbf{a})]/[P] \) where \( [P] \) is the overall polymer mole concentration.

The number of position isomers increases very fast with the counts of groups and it is not possible in practice to exhaustively follow the concentrations of all of them except up to a few units, so that Monte Carlo methods have some intrinsic usability advantages on dealing with these chemical systems. Nevertheless, some of these difficulties can be overcome with suitable mathematical techniques, such as the counting method (derived from earlier G. Polya’s work) used by Stockmayer for computing the MSD for equilibrium non-linear tree-like polymers [1].
The enumeration procedure at the base of those results becomes quite difficult to use with more complex chemical systems. A significant progress has been achieved through the introduction of the theory of branching processes (TBPs) [2] by Good [3] and Gordon [4]. A key concept is the use of generating functions (GFs) of the MSD. Thus, to the MSD of the polymer molar concentrations \([P(a)]\) corresponds the GF:

\[
G(s) = \sum_{a_1=0}^{\infty} \cdots \sum_{a_{N_s}=0}^{\infty} s_1^{a_1} \cdots s_{N_s}^{a_{N_s}} [P(a_1, \ldots, a_{N_s})]
\]

(1)

and a probability generating function (PGF):

\[
G_\ast (s) = G(s)/[P]
\]

(2)

A classical example [4,13], which will be discussed along this introduction in order to illustrate the main ideas behind methods for predicting physical properties of polymers, is the step-growth polymerization of a symmetrical star-like monomer with \(f\) end groups \(A_1 X A_f\) with negligible formation of finite-sized loops (except in the network, if it exists). The repeating units in the polymer molecule are the monads \(A_0, \ldots, A_f\), where the index \(j\) in \(A_j\) represents the number of end groups \(A\) which have been converted. The overall number of RU per molecule is \(x = a_0 + \cdots + a_f\) and it is convenient to consider a scalar distribution with respect to \(x\), with a GF which can easily be related to the vector distribution with respect to all group counts:

\[
G_n(s) = G(s, \ldots, s)
\]

(3)

The related normalized weight MSD with GF \(G_n(s)\) is also often needed:

\[
\hat{G}_n(s) = \sum_{x=1}^{\infty} s^x [P(x)]/[X] = \frac{dG_n}{d \log s}/[X]
\]

(4)

where \([P(x)]\) is the molar concentration of polymer molecules with \(x\) RU and \([X]\) is the overall molar concentration of RU. Note that \(G_n(1) = 1\) when no polymer network is present. Otherwise, \(G_n(1)\) is the fraction of RU belonging to the sol.

Since the polymer molecules are trees, if chemical equilibrium holds, the “forest” may be described according to TBP through the two related probability generating functions (PGF) \(F_0(s)\) and \(F_1(s)\):

- \(F_0(s) = \sum_{m=0}^{f} p_m^0 s^m\) is the PGF of the counts of RU connected to an RU at the root of the tree (generation zero),
- \(F_1(s) = \sum_{m=0}^{f} p_m s^m\) is the PGF of the counts of RU connected to an RU not at the root of the tree (generation one and above),

where \(p_m^0\) and \(p_m\) are, respectively, the probabilities that a root or a non-root RU are connected to \(m\) of other RU. As the fractions of units connected either to root or to non-root units are related through \(p_m = (m + 1)p_{m+1}^0/\sum_{m=0}^{f} np_m^0\), the two PGFs above are related through Eq. (5):

\[
F_1(s) = \frac{dF_0}{ds} dF_0/ ds_{|s=1}
\]

(5)

These fractions can be computed knowing the equilibrium constants and the concentration of by-product [13]. The equilibrium assumption leads to the PGF of the whole population of polymer molecules in terms of weight MSD, obtained by solving the two algebraic equations (Eqs. (6) and (7)) below:

\[
u = sF_1(u)
\]

(6)

\[
\hat{G}_{\ast n}(s) = sF_0(u)
\]

(7)

No gel exists if there is no root between 0 and 1 of the above equation when \(s = 1\) besides \(u = 1\) (the trivial solution). In that case, the root lying on the same branch as the trivial solution should be chosen and next substituted in Eq. (7) (otherwise, see [32,13] for a more general relation). From the above PGF average degrees of polymerization are easily found by derivation (or contour integration) with respect to \(s\) on \(s = 1\), and numerical or even analytical expressions for the MSD are found by its inversion with appropriate methods.

Most early theoretical works have considered rather simple polymerizations at chemical equilibrium or step-growth polymerizations starting from the monomers in batch reactors, which can be well described by the TBP. However, substitution effects and the subsequent time correlations between reactive group formation, and also the use of semi-batch or continuous stirred tank reactors (CSTRs), are better dealt with using population balance equations (PBEs) which take roots in early works by Smoluchowski [5–7]; note they have also been discussed in Stockmayer’s seminal paper [1]. Its application to more complex non-linear polymerizations has been presented in several papers by Kuchanov and collaborators [8–11] (see also the review by Kuchanov et al. concerning step-growth polymerizations [12]).

Still for the same polymerization scheme of \(X A_f\) as considered above, the kinetic treatment as presented in Ref. [13] starts by defining rate constants \(k_{ij}\) for the transformations of RU according to Eq. (8):

\[
A_i + A_j \rightarrow A_{i+1} + A_{j+1} \quad 0 \leq i, j \leq f - 1
\]

(8)

For a batch reactor starting from the monomer and with negligible volume change (and so \([X]\) should remain constant), the PBE of polymer species with counts of RU \(a_0, \ldots, a_f\) in terms of the GF of the normalized distribution:

\[
\hat{G}(s_0, \ldots, s_f) = \sum_{m=0}^{\infty} \sum_{a_{i=0}}^{\infty} \sum_{a_{j=0}}^{\infty} s_0^{a_0} \cdots s_f^{a_f} [P(x_0, \ldots, x_f)]/[X]
\]

(9)
can be written as Eq. (10) below:

\[
\frac{\partial \hat{G}}{\partial t} = [X] \sum_{i=0}^{f} \sum_{j=0}^{f} \hat{k}_{ij} \left( -p_{ij} \frac{\partial \hat{G}}{\partial \log s_j} + \frac{s_{i+1} s_{j+1}}{2s_js_j} \frac{\partial \hat{G}}{\partial \log s_i} \frac{\partial \hat{G}}{\partial \log s_j} \right)
\]

\[
\hat{G}_{p=0} = s_0
\]

\[
[X]^{-1} \frac{\partial \hat{G}}{\partial t} = p_{i-1} \sum_{j=0}^{f} \hat{k}_{i-1,j} p_j - p_i \sum_{j=0}^{f} \hat{k}_{ij} p_j
\]

\[
p_{[i=0]} = \hat{\delta}_{ij}
\]

A solution of Eq. (10) can be found using the method of characteristics [11,13]. That solution can be recast in such a way that the results obtained by this rigorous kinetic treatment of irreversible polymerizations can be interpreted in terms of the TBP, provided that each monad \( A_i \) is labelled with the times \( \theta_0, \ldots, \theta_{i-1} \) of the disappearance of the end groups which were attached to it. Therefore, the polymerization model is reformulated as an age-dependent branching process. A set of \( f \) integral equations [12–15] is obtained:

\[
u_i(\theta) = s \mathcal{F}_i(\theta; \mathbf{u}) \quad i = 0, \ldots, f - 1
\]

\[
\mathcal{F}_i(\theta; \mathbf{u}) = \left( \frac{1}{\pi} \sum_{j=0}^{f} \pi_j(\theta) \frac{\delta \mathcal{F}^{(0)}(\mathbf{u})}{\delta \mathbf{u}(\theta)} \right)_{\mathbf{u}(\theta) = 1}
\]

\[
\pi_j(\theta) = \frac{\hat{k}_{0j} p_j(\theta)}{[X] \sum_{j=0}^{f} \hat{k}_{ij} p_j(\theta)}
\]

\[
\mathcal{F}^{(0)}(r; \mathbf{u}) = \sum_{i=0}^{f} \int_{\theta_i}^{\theta} \mathcal{P}_i(t; \theta_0, \ldots, \theta_{i-1}) \prod_{j=0}^{i-1} u_j(\theta_j) d\theta_j
\]

\[
\mathcal{P}_i(t; \theta_0, \ldots, \theta_{i-1}) = \exp[-I_i(t)] \prod_{j=0}^{i-1} v_j(\theta_j) \phi_j(\theta_j)
\]

\[
I_i(t) = \int_0^t \phi_i(\theta) d\theta
\]

\[
v_i(\theta) = \exp[I_{i+1}(\theta) - I_i(\theta)]
\]

\[
\phi_i(\theta) = \left[ X \sum_{j=0}^{f} \hat{k}_{ij} p_j(\theta) \right]
\]

where the introduced variational derivatives \( \delta \mathbf{u}(\theta) \) allow a more compact writing of the integrals defining the \( \mathcal{F}_i \) and show the analogy with the equilibrium branching process. The sought GF \( \mathcal{G}_w(\mathbf{s}) \) in terms of the overall number of RU \( x = \sum_{i=0}^{f} x_i \) is obtained through:

\[
\mathcal{G}_w(\mathbf{s}) = \sum_{x=1}^{\infty} x^w \mathcal{P}(\mathbf{s}) = \sum_{j=0}^{f} \frac{\partial \hat{G}}{\partial \log s_j(\theta)} = s \mathcal{F}^{(0)}(\mathbf{u})
\]

This interpretation proves to be quite useful in the prediction of elastic properties of polymer networks [14,15] and of average properties of branched molecules.

Although very powerful and theoretically appealing, this approach faces some usability problems as soon as more complex kinetic schemes have to be tackled, since it is not straightforward to obtain (and to solve) the integral equations describing the equivalent branching process as done above. Some modifications have been incorporated in the above presented kinetic method by the present authors in order to allow an easier application to complex systems, which will be discussed later, as well as an extension for computing the average radius of gyration (not valid for other physical properties), which is the main goal of this paper. So, it is worth trying some other totally different approaches for the prediction of MSD of branched polymers.

As already mentioned, the presence of a huge number of chemical isomers makes Monte Carlo simulation an attractive alternative for attacking most real problems, in which formation of loops by intramolecular reaction and molecular fragmentation by reversible reactions puts serious problems for the development of other methods. Nevertheless, in order to avoid a high computational effort when very fast and slow chemical reactions are simultaneously present, implementation of Monte Carlo simulation of these systems is not straightforward and therefore some simplifying approximations had to be done in order to obtain practical results. Hence, approximations such as considering radical polymerizations to be transfer dominated are often considered when Monte Carlo method is applied [16].

Galerkin finite-element method has been quite successful in the past decade for obtaining polymer MSD for simpler kinetic schemes, mainly with one-dimensional distributions, for which the commercial package PREDICI excels, but faces lots of difficulties close to or after gelation [17]. It has also more recently been used for two-dimensional (and even three-dimensional [18]) distributions; there is no doubt that its predictive power is comparable to Monte Carlo methods and others for this exact purpose. Still, the accurate prediction of moments is not always straightforward, since it requires a fast convergence of the underlying approximation by finite elements and expert knowledge is often needed to achieve satisfactory results.

Since more than one decade ago, the authors have been developing a tool for dealing with general non-linear irreversible copolymerizations avoiding the tedious and error-prone writing of PBE for each new polymerization system [19]. A general procedure for solving the resulting partial differential equations by the method of characteristics is a key point in this approach. More recently, its interest has considerably grown as the severe numerical difficulties found with radical systems could finally be overcome [20–24]. A comparison of the predictions of average molecular weights of this method with legacy pseudo-kinetic method for radical polymerization, Monte Carlo simulation, different versions of the method of moments and with numerical fractionation, can be found in some of the aforementioned works [20,22,23]. Successful
calculation of MSD before and after gelation by this method has already been presented using a non-linear radical polymerization as an example [23]. Recently, this approach was also extended to the calculation of sequence length distributions for non-linear irreversible multicomponent polymerizations [25].

1.2. The prediction of physical properties of branched polymers depending on their conformation

The Gaussian chain model for polymer chains describes polymer molecules as a set of beads attached to massless freely rotating rods [26] or springs. The prediction of many physical properties becomes mathematically tractable, and in spite of this huge idealization, a fairly good agreement with experimental results is observed. The effect on polymer properties of the volume effect [27, 28] can be taken into account by using a perturbation method [35], or by a simpler independent modeling not taking into account the detailed molecular structure. The direct prediction of physical properties when the excluded volume effect is very difficult; some results have been obtained using Monte Carlo simulation in cubic or planar lattices [29] for simple random branched polymers.

Graph theory provides a powerful means to describe the configuration and predict sizes of single polymer molecules [30]. But if instead of single polymer species, the goal is to carry out predictions for random mixtures as formed by polymerization, the corresponding problem turns out to be also tractable, specially when tree-like molecules (or with a limited amount of rings) are considered. The crux is the generalization of the statistical descriptions of polymer molecules as presented in the previous sub-section, which lead to predictions of physical properties of interest through averages over sets of isomers.

Using light scattering, it is possible to measure the molecular radius of gyration as a time-average for the set of the several possible molecular conformations. Therefore, an important scientific goal consists in its theoretical prediction. We will start by considering an arbitrary molecule $P_\mu$ described by the Gaussian chain model with $x = N_\mu \vec{X}$ point-like RU with position vectors $\vec{r}_k$, $k = 1, \ldots, x$, connected by $N_{\mu z} = x - 1$ freely rotating rods with equal length $b$. We will refer to these rods or elementary Gaussian chains as “links”, since they can contain several chemical bonds.

In later sections, different lengths of links and non-zero sizes of RU will be allowed. The RU $X_{\mu i}$ is supposed to have a molecular mass $M_{\mu i}$ and the overall molecular mass is $M_\mu$.

The instantaneous radius of gyration $R_{\mu i}^2$ of such an idealized molecule is the standard deviation of its space distribution of mass, which can also be written as:

$$M_\mu^2 R_{\mu i}^2 = \sum_{k=1}^{N_{\mu i}} \sum_{l=k+1}^{N_{\mu i}} M_{\mu i}^2 |\vec{r}_k - \vec{r}_l|^2$$

(13)

It will be more convenient to use an alternative relation derived from Kramers’ work [26] (Eq. (14)). Since the molecule is tree-like, if a link $Z_{\mu i}$ is severed, the molecule breaks yielding two fragments with molecular masses $M_{\mu i}^-$ and $M_{\mu i}^+$. Invoking the Gaussian chain model, the average overall conformations (denoted by the angle brackets) of the squared radius of gyration $\langle R_{\mu i}^2 \rangle$ would be:

$$M_{\mu}^2 \langle R_{\mu}^2 \rangle = b^2 \sum_{n=1}^{N_{\mu i}} M_{\mu i}^- M_{\mu i}^+$$

(14)

The MSD of the fragments obtained by cutting links will yield the average molecular radius of gyration but appropriate mathematical techniques are still needed in order to compute its averages for suitable molecular populations. Soon after Stockmayer’s calculation of the equilibrium MSD for simple step-growth polymerizations, analytical expressions for the related molecular average radius of gyration of ideal chains could be found [31] by exploiting the above relation (Eq. (14)). A much more convenient method uses TBP [32, 33] for computing the expected value of the product of the two molecular masses at either side of each arbitrary link. This leads to Eq. (15) yielding the $z$-average radius of gyration of the whole population and all conformations (denoted by an overline symbol), where the RUs have been supposed to have an equal molecular mass:

$$\overline{R}_{\mu}^2 = \sum_{\mu=1}^{N_{\mu i}} w_\mu M_\mu \langle R_{\mu}^2 \rangle / \sum_{\mu=1}^{N_{\mu i}} w_\mu M_\mu = \overline{x}_{\mu} - 1/\overline{x}_{\mu} b^2 \left( \frac{d u}{d \log s_{\mu=1}} \right)^2$$

(15)

where $w_\mu$ is the mass fraction of species $P_\mu$. The function $u(s)$ satisfies Eq. (6) and the number- and weight-average degrees of polymerization $\overline{x}_n$, $\overline{x}_w$ can be easily found by calculating the required derivatives starting from Eqs. (6) and (7):

$$\overline{x}_n = \frac{\alpha_{\mu=1}}{\alpha_{\mu=1}} G_{\mu=1}(1)$$

$$\overline{x}_w = \frac{\alpha_{\mu=1}}{\alpha_{\mu=1}} G_{\mu=1}(1)$$

(16)

A few other conformation dependent physical properties, denoted as $Q$ in Eq. (17) below, can also be obtained as double sums over all pairs of connected RU of some function $\Phi$ of the distance separating them, under the same simplified description of a polymer molecule as a set of $x$ connected point-like beads:

$$x^2 \langle Q \rangle_\mu = \sum_{k=1}^{x} \sum_{l=k+1}^{x} \Phi(|\vec{r}_k - \vec{r}_l|)$$

(17)

An example is the inverse of the hydrodynamic radius $1/R_\mu$, which may be found through Eq. (17) with $\Phi = 1/|\vec{r}_k - \vec{r}_l|$. The key for a convenient evaluation of those double sums was the introduction of trail generating functions [34, 35], and detailed reviews of these methods have been published by Burchard [36, 37]. A trail is defined as a linear sequence of links. If the length of the links is constant, the double sum in Eq. (17) can be evaluated knowing the numbers of distinct trails $N_{T,\mu}$ containing $n$ links for that molecule:
\[ x^2(Q)_\mu = 2 \sum_{n=1}^{x-1} N_n^{T} \phi_n \] (18)

where, assuming the Gaussian chain model:

\[ \phi_n = \Phi(nb^2) \] (19)

The recurrence below generalizing Eqs. (6) and (7) can be used for computing a trail (or path) generating function [34,36]:

\[
U_0(s) = s_0 F_0(U_1) \\
U_n(s) = s_n F_n(U_{n+1}) \quad n > 0
\] (20)

yielding the desired property as a z-average over the population of polymer molecules:

\[
x_w \bar{Q} = \sum_{\mu=1}^{\infty} x_\mu w_\mu Q_\mu = \frac{dU_0}{dx} \bigg|_{x=1}
\] (21)

More recently, a generalization of Kajiwara’s approach [38] has allowed the prediction of distributions of the radius of gyration for the classes of polymer molecules with same counts of groups and not only of its z-average for the whole population.

A different and more general approach based upon graph theory [39–41] takes into account the space coordinates of the chemical groups in polymer. Physical properties are obtained through averaging among the set of those spacial positions, so that it is convenient to describe the populations of polymer molecules with generating functionals of the space coordinates of the chemical groups they contain. An important goal is now the prediction of the two-point correlators of group densities, which describe the probability densities of the distances between pairs of chemical groups. They will lead to the prediction of conformation dependent physical properties in a more elegant way than the evaluation of the aforementioned double sums.

Still more interesting is the description of space dependent group interactions such as cyclizations and excluded volume effects, which can be carried out in a rigorous way in contrast with simpler theories which assume that polymer molecules are embedded in a fixed lattice.

However, this approach has mainly yielded complete results for chemical equilibrium, or without coupling of rates of chemical reactions with spacial position.

1.3. Experimental measurement of the mean square radius of gyration and its prediction in kinetic controlled polymerization systems

In recent years, significant research efforts have been devoted to the synthesis and characterization of branched polymers. The modification of the molecular architecture can be used as a tool to obtain tailored polymers due to its strong influence on their macroscopic properties. An important example is the introduction of controlled amounts of branching units on the polymer structure giving rise to a dramatical change in physical properties such as viscosity and solubility. Hyperbranched polymers are known to have a much lower viscosity in solution and in the molten state than their linear counterparts. The thermal properties of this kind of materials are also significantly affected by the degree of branching [42].

It has also been recently acknowledged that long-chain branching can improve the processability of polyolefins without negatively impairing their physical properties in a serious way [43–45]. Experimental studies on the branched structure of materials produced by radical polymerization, such as poly(vinyl acetate) [46] and the copolymer obtained from methyl methacrylate and ethylene glycol dimethacrylate [47], also witness the interest on the use of branched polymers in the design of new products.

A quantitative characterization of the architecture of branched polymers can be obtained from the Zimm–Stockmayer branching factor [31], which is defined as the ratio of the mean square radius of gyration of the branched polymer to that of the linear one with same molecular weight:

\[ g = \left( \frac{R_{\text{bra}}}{R_{\text{lin}}} \right)_M \] (22)

As the intrinsic viscosity [\eta] of macromolecules in solution can also be experimentally measured and the hydrodynamic volume is a major factor controlling it, the branching index defined by Eq. (23) is also widely used:

\[ g' = \left( \frac{[\eta]_{\text{bra}}}{[\eta]_{\text{lin}}} \right)_M \] (23)

The possibility to measure \( g' \) without application of a viscometer, by using size exclusion chromatography and a multi-angle laser light scattering (SEC–MALLS) is also reported in the literature [43]. It is usually accepted that \( g \) and \( g' \) are related through some power law:

\[ g' = g^\beta \] (24)

However, \( \beta \) is not a true constant and its value depends on the type of branching (regular star, regular comb, randomly branched...). Experimental measurements indicate that the parameter \( \beta \) can take values in the range 0.5–1. Therefore, it would be desirable to achieve some reliable predictive method of this latter branching factor, but this is not an easy task, as will be discussed below.

Model homopolymers with a narrow molecular weight distribution and a well-defined architecture are ideal for the experimental quantification of branching. Some recent works using size exclusion chromatography and two-angle laser light scattering measurements (SEC–TALLS) for polystyrene combs and centipedes [48,49] have confirmed the good agreement between theory and experiments for these systems. In a related work [50], computer simulations were shown to predict the SEC calibration curves for comb-branched polymers within the same accuracy (10–15% of error) of the absolute determination of molecular weights.
Randomly branched polymer mixtures are much more difficult to analyze. In SEC, polymer molecules are supposed to be fractionated by the hydrodynamic volume. It is well known that the size of branched molecules is smaller than that of linear molecules with the same molecular weight. This means that the true molecular weight distribution (MWD) cannot be measured using linear polymer standards to establish the relationship molecular weight versus elution volume. If LS intensity and concentration detectors (such as a differential refractometer) are simultaneously used, the weight-average molecular weight for each elution volume can be directly measured. Nevertheless, with branched polymer mixtures there are polymer molecules with the same hydrodynamic volume but different molar masses due to their different branched structures. This means that within the same elution volume slice there are molecules with different molecular masses and by consequence, the true MWD cannot be obtained even by using LS. This fact increases the interest of developing simulation methods allowing the prediction of the elution curve of a non-linear polymer from its formation mechanism [51].

The simulation of size exclusion chromatography of branched polymers was carried out for some polymerization systems by Tobita and coworkers using a Monte Carlo random sampling technique [16,51—54]. For the radical polymerization of vinyl acetate [16] a satisfactory agreement with the radii of gyration at a Θ state with the Zimm—Stockmayer equation for randomly branched polymers was found. This was explained through the large number of relatively small branches formed by chain transfer to polymer and terminal double bond polymerization, both contributing to the formation of a structure close to the ideal randomly branched one. But in a later work where a radical polymerization with chain transfer to polymer was investigated [52], it was shown that since the branching is less random, and the primary polymer chains do not follow the most probable distribution, the Zimm—Stockmayer equation could not be used to estimate the radii of gyration. In a related work [53] it was reported that the Zimm—Stockmayer equation clearly underestimates the radii of gyration for crosslinked polymers.

Iedema and Hoefsloot [55,56] have computed radius of gyration distributions of branched polymers in a CSTR starting with predictions of joint distributions of degree of polymerization and number of branches offered by the aforementioned kinetic method. Instead of using Monte Carlo method for the random generation of possible radii of gyration for a large sample of polymer species, they have used an approximated Kirchhoff matrix of polymer molecules (see Ref. [30]) to compute that distribution. The desired overall distribution of radii of gyration was computed by superposing the aforementioned distributions for the various molecules with different numbers of branches and degrees of polymerization. A key aspect is the found insensitivity of the distributions of the radius of gyration with respect to the detailed molecular architecture: only degree of polymerization and number of branches seem to be important. Thus, successful predictions of distributions of hydrodynamic volume using Eqs. (23) and (24), as would be measurable by SEC according to the above discussion, could be carried out.

One of the main goals of the aforementioned work on the extension of TBP of branched polymers [38] was to provide an improved prediction of polymer chromatograms through SEC. Those calculations have been carried out with rather simple chemical systems (equilibrium self-polycondensations of one monomer, but with possible substitution effects), but they are much more reliable than previous studies. Still, consideration of complex polymerization schemes for which there is no such a simple branching process puts a difficult challenge to reach similar results.

The work on the prediction of \( R_G \) for Gaussian chains by the present authors was started some years ago [57] and in the present paper a revised modeling is put forward, allowing its prediction for tree-like polymers formed by irreversible reactions in batch, semi-batch or continuous stirred tank reactors (CSTRs). This measure of molecular size can be useful as a means of improving the knowledge about the architecture of the polymer structure and possibly correlate physical properties of the polymer. The interest of this kind of simulations increases if the evolution of parameters such as molar mass and degree of branching along the polymerization is desired [47]. Experimental determination of \( R_G \) yields an important consistency check between theory and experiment (of course, the effect of chain expansion in good solvents needs to be properly accounted for). With the general method here presented there is no need to face a completely new problem when a different chemical system is analyzed. Indeed, several works dealing with the prediction of the \( z \)-average radius of gyration of different chemical systems, such as the numerous recent investigations on hyperbranched polymers [58—61,64], could have been carried out in an automated way using this approach.

The main goal of the present work is therefore to show that with similar concepts already used in the prediction of the MSD it is also possible to calculate the mean square radius of gyration of tree-like polymers. The general equations needed for the development of a kind of interpreter of irreversible polymerizations are presented and three different case studies are discussed. Step-growth polymerizations leading to hyperbranched polymers, the anionic copolymerization of mono- and divinyl monomers and a radical polymerization with terminal branching and transfer to polymer are chosen as case studies. The reliability of the predictions is confirmed throughout the comparison with analytical solutions for simple systems or with alternative methods. The usefulness of the present approach is further shown when a complex scheme for radical polymerization with terminal branching and transfer to polymer is considered. In all situations, it is shown that the calculations can be extended beyond the gel point.

2. Description of polymer structure related to the average molecular radius of gyration

For each of the \( N_X \) monomers, \( Y_1, \ldots, Y_{N_X} \), a root group (RG) of the repeating unit (RU) is identified and their set is supposed to be \( X_1, \ldots, X_{N_X} \). The RUs are assumed to be
star-like, with all other groups being directly attached to it. Chemical reactions do not change root groups after their creation through incorporation of a monomer into a polymer chain. From the total number \( N_A \) of kinds of chemical moieties \( A_j \), the number of those belonging to polymer molecules will be defined as \( N_{AP} \). Polymer groups with indices above \( N_{AP} \) are not consumed by chemical reaction.

Since only tree-like molecules are considered, there is only one link connecting every pair of RG. A set of \( N_Z \) links \( Z_1, \ldots, Z_{N_Z} \) is defined, according to the nature of the two groups which have reacted and produced them by chemical reaction. To each link corresponds a pair of reacted chemical groups which have reacted and produced them by chemical reaction. To each link is attached to each of the respective RU. The link \( Z_n \) is formed by the reaction of groups \( A_{k_n} \) and \( A_{s_n} \), and it will be assumed that \( g_n \leq g^+ \). A positive sense and a negative sense are associated with each link. By convention, the group with lower index was attached to the RU originally at the negative side of the link. In order to avoid multiple levels of indexing, a notation inspired in the way computer assembly languages describe indirect addressing will be used, as vectors \( g^+ \) and \( g^- \) are just collections of indices. Thus, the two groups directly involved in the \( n \)-th reaction sticking together two polymer molecules will rather be designated as \( A_{[n-1]} \) and \( A_{[n+1]} \).

A limited number of intramolecular reactions forming loops might be considered, but the details are not straightforward and we will rather not discuss the matter for brevity.

As we are interested in predicting molecular dimensions using the Gaussian chain model, a length \( b_n \) will be defined as the mean-squared distance between the centers of mass of the root groups connected to that link. So, \( b_n \) does not change when other groups attached to the root groups react. However, the center of mass of the RU does not always lie at the position of the root group, and so for a more exact modeling the variable contributions of all groups in the RU have to be taken into account.

These concepts will be illustrated using the hypothetical polymerization of benzene to poly(1,4-phenylene); in more usual chemical systems, the effective bond lengths to be used in the Gaussian chain model would have to be increased, and the effective bond lengths to be used in the Gaussian chain model would have to be increased, with respect to the true ones in order to take into account the effect of atomic repulsions in real molecular conformations. The root groups will be conveniently placed at the geometrical centers of the aromatic rings, since this is also their center of mass (see Fig. 1). Therefore, the length of the link connecting two consecutive RUs is \( b = 3b_{C-C} \) where \( b_{C-C} \) is the length of a carbon−carbon aromatic chemical bond.

It is also necessary to know the molecular mass \( M^A \) and the contribution of each group to the radius of gyration of the RU where it is inserted, such that the average squared radius of gyration \( \left\langle R_g^2 \right\rangle \) of an RU carrying \( a_1^+, \ldots, a_{N_A}^+ \) groups \( A_1, \ldots, A_{N_A} \) would be computed through Eq. (25):

\[
\left\langle R_g^2 \right\rangle = \sum_{j=1}^{N_A} a_j^+ M_j^A R_j^2
\]

(25)

In the above example, the average gyration radius of the RU may be found using

\[
(6M_C + 4M_H) \left\langle R_g^2 \right\rangle = 6M_C b_{C-C}^2 + 4M_H(b_{C-C} + b_{C-H})^2
\]

(26)

In general, the group contributions to the radius of gyration \( R_j^2 \) will take into account the distribution of their masses and distances to the center of mass of the RU.

The molar mass \( M_{\mu} \) of a generic molecule \( P_\mu \) is the sum of the molar masses of the groups it contains:

\[
M_{\mu} = \sum_{j=1}^{N_A} a_j M_j^A = a_\mu M^A
\]

(27)

Moments with respect to molecular mass, needed for computing average molecular masses, can be obtained by repeated application of the operator \( D_M \) as shown below:

\[
\lambda^M = \sum_{\mu=1}^{\infty} M_{\mu} [P_\mu] = D_M G_{[\mu=1]} = \sum_{j=1}^{N_A} M_j^A \frac{\partial G}{\partial \log s_{j[\mu=1]}}
\]

(28)

\[
\lambda^{MM} = \sum_{\mu=1}^{\infty} M_{\mu}^2 [P_\mu] = D_M^2 G_{[\mu=1]}
\]

Since a generic polymer molecule \( P_\mu \) is a tree, breaking its \( j \)-th link of kind \( Z_n, Z_{n_{\mu j}} \) (where the index \( j \) is some number not greater than the count of links in the parent molecule \( a_{\mu m}^n \)) yields two separate fragments, which will be called pendant chains. The group counts of the two fragments pendant chains will be named \( a_{\mu_{\mu j}} \) and \( a_{\mu_{\mu j}} \). Their sum is the vector of group counts of the parent molecule, \( a_\mu = a_{\mu_{\mu j}} + a_{\mu_{\mu j}} \).

Regrouping the contributions of all polymer molecules for the same kind of links \( Z_n, Z_{n_{\mu j}} \) their overall molar concentrations \( [H_\mu(a_1^+, \ldots, a_{N_A}^+, \alpha_1^+, \ldots, \alpha_{N_A}^+)] \) will be used for describing the size distribution of double-sided pendant chains (abbreviated as PCSDs) with GF \( G_h(s^-, s^+) \) as below defined:

\[
G_h(s^-, s^+) = \sum_{a_1^+ = 0}^{\infty} \cdots \sum_{a_{N_A}^+ = 0}^{\infty} \sum_{a_{\mu_{\mu j}} = 0}^{\infty} \sum_{a_{\mu_{\mu j}} = 0}^{\infty} (s_1^+)^{a_1^+} \cdots (s_{N_A}^+)^{a_{N_A}^+} \times \left[ H_\mu(a_1^+, \ldots, a_{N_A}^+, \alpha_1^+, \ldots, \alpha_{N_A}^+) \right]
\]

(29)

The expected value of the product of pendant molecular masses at the two sides of the severed links may be obtained through:

\[
\langle M \rangle = \sum_{a_1^+ = 0}^{\infty} \cdots \sum_{a_{N_A}^+ = 0}^{\infty} \sum_{a_{\mu_{\mu j}} = 0}^{\infty} \sum_{a_{\mu_{\mu j}} = 0}^{\infty} (s_1^+)^{a_1^+} \cdots (s_{N_A}^+)^{a_{N_A}^+} \times \left[ H_\mu(a_1^+, \ldots, a_{N_A}^+, \alpha_1^+, \ldots, \alpha_{N_A}^+) \right]
\]

(29)
\[ \lambda^{M-M^+n} = \sum_{i=1}^{N_2} \sum_{j=1}^{N_3} M_i^4 M_n^4 \frac{\partial^2 G_n^H}{\partial \log s_j \partial \log s_m}(1,1) \]

\[ = \sum_{i=1}^{N_2} \sum_{j=1}^{N_3} M_i^4 M_n^4 s_j^\mu \] (30)

The symbol 1 has been used above to denote a vector of \( N_A \) ones.

Only finite molecules have been included in the above sums. So, if there is an infinite network, \( G_n^H(1, 1) < [Z_n] \).

A generalization of Eq. (14) taking into account the contribution of all repeating groups to the radius of gyration is:

\[ M_\mu^2 \left\langle R_\mu^2 \right\rangle = \sum_{n=1}^{N_2} b_n^2 M_n^4 M_\mu^4 + M_\mu \sum_{i=1}^{N_3} a_i M_i^4 R_i^2 \]

\[ = \sum_{n=1}^{N_2} b_n^2 \sum_{j=1}^{N_3} M_n^4 M_j^2 \alpha_{nj} \alpha_{mj} \]

\[ + \sum_{k=1}^{N_3} \sum_{l=1}^{N_4} M_k^4 M_l^2 \alpha_{kl} \alpha_{ml} \] (31)

where, for that polymer molecule with counts of links \( a_{\mu}^1 \cdots a_{\mu}^{N_2} \), \( \alpha_{nj} \) and \( \alpha_{mj} \) are the vector counts of the chemical groups in the two fragments resulting from severing the \( j \)-th link of kind \( Z_m \). Summing the contributions for all polymer species \( P_\mu \) as provided by the above relation, multiplied by their molar concentrations and the dummy Laplace variables raised to their counts of groups, it results:

\[ \sum_{\mu=1}^{\infty} s_{1\mu}^{a_{\mu}} \cdots s_{N_2\mu}^{a_{\mu}^{N_2}} M_\mu^2 \left\langle R_\mu^2 \right\rangle [P_\mu] = \sum_{n=1}^{N_2} b_n^2 \sum_{k=1}^{N_3} M_k^4 M_l^2 \]

\[ \sum_{\mu=1}^{\infty} s_{1\mu}^{a_{\mu}} \cdots s_{N_2\mu}^{a_{\mu}^{N_2}} a_{\mu}^1 \cdots a_{\mu}^{N_2} \alpha_{nj} \alpha_{mj} [P_\mu] \]

\[ + \sum_{k=1}^{N_3} \sum_{l=1}^{N_4} M_k^4 M_l^2 \alpha_{kl} \sum_{\mu=1}^{\infty} s_{1\mu}^{a_{\mu}} \cdots s_{N_2\mu}^{a_{\mu}^{N_2}} [P_\mu] \] (32)

The left hand side of Eq. (32) will be used for defining a GF of the \( z \)-distribution of the radius of gyration with respect to group counts of the molecule \( G_{R_\mu}(s) \) as

\[ G_{R_\mu}(s) \sum_{\mu=1}^{\infty} M_\mu^2 [P_\mu] = \sum_{\mu=1}^{\infty} s_{1\mu}^{a_{\mu}} \cdots s_{N_2\mu}^{a_{\mu}^{N_2}} M_\mu^2 [P_\mu] \left\langle R_\mu^2 \right\rangle [P_\mu] \] (33)

We will now rewrite the first sum in the right hand side of Eq. (32) in terms of the PCSD, since the molar concentration of the double-sided pendant chain of kind \( n \) in molecule \( P_\mu \) is simply the number of links of that kind times the molar concentration of the molecule, \( [H_{\mu}] = a_{\mu}^n [P_\mu] \), yielding thus:

\[ \lambda^{M-M^+n} = \sum_{\mu=1}^{\infty} \sum_{j=1}^{N_3} s_j^\mu \frac{\partial^2 G_n^H}{\partial \log s_j \partial \log s_m}(1,1) \]

\[ = \sum_{\mu=1}^{\infty} b_\mu^2 \sum_{j=1}^{N_3} M_\mu^4 M_n^4 \frac{\partial^2 G_n^H}{\partial \log s_j \partial \log s_m}(1,1) \]

\[ + \sum_{\mu=1}^{\infty} \sum_{j=1}^{N_3} M_\mu^4 M_n^4 \frac{\partial^2 G}{\partial \log s_j \partial \log s_m}(s_i \rightarrow s_j \rightarrow s_k) \] (34)

The distribution of the number average mean-squared gyration radius of the isomers with the same counts of groups (lumped distribution) can be obtained from Eq. (34) as discussed in Appendix A for a simple chemical system.

In most situations only the averages of this distribution are desired. These averages can also be calculated from Eq. (34) by differentiation or integration with respect to the parameters \( s_j \) and evaluated at \( s = 1 \). The example with more practical importance is the \( z \)-average obtained simply by setting \( s = 1 \) in Eq. (34):

\[ \lambda^{MM} R_\mu^2 = \lambda^{M^+} G_{R_\mu}(1) = \sum_{\mu=1}^{\infty} b_\mu^2 \lambda^{M-M^+n} + \sum_{\mu=1}^{\infty} M_\mu^4 M_n^4 \]

\[ \lambda^{M^+} G_{R_\mu}(1) \] (35)

Expressions previously found by Gordon and collaborators [32,33] such as Eq. (14) (leading to Eq. (15)) are particular cases of Eq. (35), with constant molecular masses of the RU and lengths of the links \( (b_\mu = b) \), and also negligible contributions from the radii of gyration of the groups \( (R_i^2 = 0) \). Now, instead of using TBP, an alternative kinetic approach can be developed starting from this formulation, with some advantages (such as the easiness to take into account substitution effects) which will become apparent in the remaining of this paper.

3. Population balance equations for polymer molecules and pendant chains

A convenient general classification of the chemical reactions interverting on a generic polymerization system was previously presented [22]. Here, the same notation is used and only the effects of chemical reactions on the pendant chains need still to be discussed.

In Table 1 are some examples of the effects of the polymerization reactions on the pendant chains. Note that the polymer species with a single RU resulting from the \( N_M \) reactions of transfer to monomer or from one of the \( N_I \) reactions of a monomer with an initiating species (radical, ion or catalyst site), eventually coming from transfer to solvent, are devoided of pendant chains, which are assumed to exist only when the polymer molecule contains at least two RUs.

The \( N_R \) chemical reactions creating connections between RU will create new links \( Z_n \) labelled with the same index as the reaction, either when two polymer molecules are fused (the \( N_R \) reactions with lower indices, e.g. termination by combination) or when a non-polymeric molecule adds to the polymer (the remaining \( N_R - N_R \) reactions, e.g. propagation with
monomers). Pendant chains will also modify their group counts owing to these reactions on either side.

There is no creation of new links for the $N_R^*$ unimolecular reactions, the $N_R^+$ bimolecular reactions, the $N_1$ bimolecular initiations reactions and the $N_M$ reactions of transfer to monomer, although they modify the group counts in the pendant chains. Other reactions, either unimolecular or bimolecular, do not involve groups in polymers and they are not involved in the PBE of polymers or pendant chains.

In the case of irreversible polymerizations, a general master equation describing the time change of the generating functions of polymer MSD for a non-steady state perfectly mixed CSTR (other ideal reactors being particular cases) can be established [22,19]:

\[
\frac{\partial G}{\partial t} = \sum_{n=1}^{N_{RP}} k_n \left( \psi_m^+ \frac{\partial G}{\partial \log s_{[m-1]}} \psi_m^+ - \psi_m^- \frac{\partial G}{\partial \log s_{[m-1]}} \right) [A_{[m-1]}] + \sum_{m=2}^{N_{MP}+1} k_m \frac{\partial G}{\partial \log s_{[m-1]}} [A_{[m-1]}] (\psi_m^- - 1)
\]

with initial condition:

\[
G_{t=0} = G_0 [s_0(t,s)]
\]  

(37)

An analogous PBE for the pendant chains (in Laplace domain) can also be written:

\[
\frac{\partial G^H}{\partial t} = \mathbf{R}_{BZ_n} + \sum_{n=1}^{N_{RP}} k_n \left( \psi_m^+ \frac{\partial G^H}{\partial \log s_{[m-1]}} \psi_m^+ - \psi_m^- \frac{\partial G^H}{\partial \log s_{[m-1]}} \right) [A_{[m-1]}] + \sum_{m=2}^{N_{MP}+1} k_m \frac{\partial G^H}{\partial \log s_{[m-1]}} [A_{[m-1]}] (\psi_m^- - 1)
\]

(38)

The population balance (Eq. (38)) of the PCSD in Laplace domain is a semi-linear first-order partial differential equation which must be solved together with the PBE determining MSD. The generating function of the MSD, $G(s)$, is obtained by solving Eq. (36) with the initial condition (Eq. (37)).
Table 1
Polymerization reactions and some examples of their direct effect on pendant chains

<table>
<thead>
<tr>
<th>Reaction description</th>
<th>Number</th>
<th>Direct effect on pendant chains (examples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimolecular/new links</td>
<td>$N_R$</td>
<td>$\alpha \cdot R^- + R^+ a^{-\lambda} (a^- + v_{\alpha}) X \cdot Z \cdot X^+(a^+ + v_{\alpha}^-)$</td>
</tr>
<tr>
<td>Polymer/polymer</td>
<td>$N_{R_P}$</td>
<td>$\alpha \cdot X^- + X^+ a^{-\lambda} (a^- + v_{\alpha}) X \cdot Z \cdot X^+(a^+ + v_{\alpha}^-)$</td>
</tr>
<tr>
<td>Polymer/monomer</td>
<td>$N_{R_P} - N_{R_{P0}}$</td>
<td>$\alpha \cdot X^- + X^+ a^{-\lambda} (a^- + v_{\alpha}) X \cdot Z \cdot X^+(a^+ + v_{\alpha}^-)$</td>
</tr>
<tr>
<td>Unimolecular</td>
<td>$N^*_R$</td>
<td>None</td>
</tr>
<tr>
<td>Involving polymer</td>
<td>$N^*_R$</td>
<td>$\alpha \cdot Z a^{-\lambda} (a^- + v_{\alpha}) Z_a^+$</td>
</tr>
<tr>
<td>Not involving polymer</td>
<td>$N^*<em>R - N</em>{R_{P0}}$</td>
<td>None</td>
</tr>
<tr>
<td>Bimolecular/not connecting RU</td>
<td>$N^*_R$</td>
<td>$\alpha \cdot Z a^{-\lambda} a^+ + A_{0m+1} \alpha^{-\lambda} a^+ Z_a(a^+ + v_{\alpha}^{+++}) + \cdots$</td>
</tr>
<tr>
<td>Polymer/polymer</td>
<td>$N^*_R$</td>
<td>$\alpha \cdot Z a^{-\lambda} a^+ + S \rightarrow a^{-\lambda} Z a(a^+ + v_{\alpha}^{+++}) + \cdots$</td>
</tr>
<tr>
<td>Polymer/non-polymer</td>
<td>$N^<em>_R^</em>$</td>
<td>None</td>
</tr>
<tr>
<td>Only small molecules</td>
<td>$N_S$</td>
<td>None</td>
</tr>
<tr>
<td>Initiations</td>
<td>$N_I$</td>
<td>$a^{-\lambda} Z a^+ + M \rightarrow a^{-\lambda} Z a(a^+ + v_{\alpha}) + \cdots$</td>
</tr>
<tr>
<td>Transfers to monomers</td>
<td>$N_M$</td>
<td>$a^{-\lambda} Z a^+ + M \rightarrow a^{-\lambda} Z a(a^+ + v_{\alpha}) + \cdots$</td>
</tr>
</tbody>
</table>

Note that Eq. (36) is a first-order non-linear partial differential equation, with an independent solution yielding $G(s^-)$, $G(s^+)$ and the derivatives of $G(s)$ evaluated at $s^-$ or $s^+$. These quantities must be inserted in Eq. (38), which becomes then a semi-linear partial differential equation. This means that, following similar principles as in previous works [19,22], the solution of Eq. (38) + Eq. (36) can also be obtained by the method of characteristics [66]. The characteristics of this problem are obtained by solving the system of ordinary differential equations presented in the Supporting information of this paper.

Finally, the formulation of the problem becomes complete with the consideration of the PBE of the chemical groups (A) and (if needed) of the rate of change of reaction volume. These equations have been previously presented [22] and so are not here reproduced by conciseness.

Owing to the symmetry of the equations for the variables corresponding to the two senses of the links, there is no need to recompute the characteristics if the final vectors verify $s^- = s^+ = s$. In this case the characteristics are the same which are needed for the evaluation of $G(s)$.

The equations of change along the characteristics for the derivatives of $G^H$ needed for computing the $z$-average radius of gyration are to be evaluated at $s^- = s^+ = 1$, as follows from Eq. (35). This means that the aforementioned simpler situation for the computation of the characteristics holds for the prediction of the $z$-average radius of gyration. From Eq. (35) it is clear that the computation of $\overline{R}_g$ is possible if the second order moments ($\lambda_{ij}$) can be obtained and if the second order moments of PCSD ($\lambda^n_{i,j}$) can also be calculated. The equations for $\lambda_{ij}$ have already been presented [22] and also are not here reproduced by conciseness. The general equation needed for the computation of the third order moments ($\lambda_{ijk}$) of the MSD is available in the Supporting information of this work.

Population balance equations for $\lambda^n_{i,j,p}$ are obtained by differentiation of Eq. (38), yielding a system of first-order partial differential equations. Its solution can be found in a similar way as for $G^H$. Indeed, that system of PDE becomes also semi-linear and its characteristics are also shared by the moments of the PCSD.

With the application of these principles, the moments of the PCSD needed for the calculation of $\overline{R}_g$ are obtained from the solution along the characteristics of the set of ordinary differential equations shown in the Supporting information.

4. Case studies

4.1. Case study I: hyperbranched polymers formed by step-growth polymerization

The simplest polymerization system is the ideal irreversible step-growth polymerization of a single monomer with structure $AB$. The two end groups $A$ and $B$ react irreversibly creating a link $Z$. It is well known that the MSD of the resulting polymer is the Schulz–Flory distribution and the $z$-average radius of gyration for Gaussian chains is given by $\overline{R}_g = b^2 p/(1 - p^2)$, where $p$ represents the conversion of end groups.

This simple system was used as a first test of the reliability of the general method here presented and of its computational implementation. Three different chemical species are present: the end group $A$ ($A_1$), the end group $B$ ($A_2$) and the link $Z$ ($A_3$). The single chemical reaction is the reaction between $A$ and $B$ with the following associated vectors of stoichiometric coefficients: $\nu_1 = [-1, 0, 1]$ and $\nu_2 = [0, -1, 0]$. The expected results were reproduced by simulating this system with the present approach, as can be observed in Figs. 2 and 3. The slope of the linear relation represented in Fig. 3 is 1/6, as expected for $z$-average characteristic ratio $\overline{R}_g/(b^2 \overline{\pi}_z)$ of linear polymers.

In the last two decades, a lot of research activity in polymer science has been focused on the synthesis and modeling of the formation of highly branched macromolecules such as dendrimers and hyperbranched polymers [62]. Dendrimers are associated with the birth of a new macromolecular architecture with several applications in the emerging field of synthetic nanochemistry [63]. These polymers have unique physical and chemical properties: relatively low viscosity, high solubility, non-entanglement and numerous terminal groups. Randomly branched hyperbranched polymers are easily obtained by one-step step-growth polymerization of several kinds of
monomers [64]. On the contrary, the synthesis of dendrimers usually involves several iterative stages. For this reason, hyperbranched polymers are more convenient for commercial applications. Molecular weight, degree of branching and mean square radius of gyration are key parameters used in the description of hyperbranched polymers.

The general kinetic approach presented here will now be used to predict the mean square radius of gyration of this class of hyperbranched polymers. One of the advantages of this method is the possibility to analyze different chemical systems by changing only the input to the developed computer program. Indeed, several highly branched polymers resulting from the step-growth polymerization of monomers like $AB_2 + AB$, $A_1 + B_2$, $AB_3$, $AB_4$ can be easily simulated simply by changing the initial conditions of the polymerization if the same kinetics of the reaction between $A$ and $B$ is considered. Another advantage of the present method is the possibility of describing the reaction beyond gel point if needed. A comparison with previous results [64] obtained with alternative approaches in the $AB_2 + AB$ polymerization will be used as another reliability test of the present method.

For a simple analysis of the $AB_2 + AB$ polymerization system, the same stoichiometric coefficients written above for the $AB$ system can be used. One needs only to change the initial condition of the population balance of polymer in terms of generating functions, which becomes now:

$$G_{t=0} = G_0 \left[ s_0(t, s) \right] = \left[ X_1 \right] s_{10} s_{20}^2 + \left[ X_2 \right] s_{10} s_{20}^2$$

In this equation, $[X_1]$ represents the initial mole concentration of the monomer $AB_2$, $[X_2]$ is the initial mole concentration of the monomer $AB$, $s_{10}$ and $s_{20}$ are the initial values of the dummy Laplace variables associated with groups $A$ and $B$, respectively.

In Figs. 2 and 3 are also presented the computed $\overline{R_g}$ for this kind of hyperbranched polymers. The initial composition of the system is represented by the mole fraction of the $AB_2$ monomer, which is $y_2 = [X_1]/([X_1] + [X_2])$. As expected, for the same $t_\ast$, the $z$-average radius of gyration of the hyperbranched $AB_2 + AB$ polymer is smaller than with the $AB$ linear system. It is also important to note that the results here obtained for the $AB_2 + AB$ step-growth polymerization fully agree with the simulations of the same system by alternative methods [64]. This constitutes a supplementary test of the reliability of the present approach.

Another randomly branched hyperbranched system with growing industrial interest [67] is obtained through the step-growth polymerization $A_2 + B_3$. This polymerization can also be simulated with the same principles used for the other two step-growth polymerization systems. Again, the initial condition below needs to be changed:

$$G_{t=0} = G_0 \left[ s_0(t, s) \right] = \left[ X_1 \right] s_{10}^2 + \left[ X_2 \right] s_{10}^2$$

The behavior of this system is also presented in Figs. 2 and 3. An important feature is its possibility of gelation. The initial composition ($y_2 = 0.5$) was chosen in order to observe the same concentration of both end groups considered in the $AB_2 + AB$ step-growth polymerization. With this initial composition, gelation occurs when the conversion of end groups $A$ is 0.866 (and 0.577 for $B$) but the present method can be used to calculate the $z$-average radius of gyration of the soluble fraction of the polymer after gelation, as can be observed in Fig. 2. For the same $t_\ast$, $\overline{R_g}$ for the $A_2 + B_3$ polymer is larger than with the $AB_2 + AB$ system (see Fig. 3). Note also that for the $A_2 + B_3$ system, the relation between $t_\ast$ and $\overline{R_g}$ is the same before and after gelation, which is a consequence of the randomness of this polymerization system. This situation does not hold for non-random branching systems, as will be shown in the next case study.
4.2. Case study II: anionic polymerization of mono- and divinyl monomers

In order to verify the ability of the general method proposed to predict \( R_g \) and to test its computational implementation, yet another simple case study, the linear anionic polymerization of a monovinyl monomer will be discussed. At least four different chemical species need to be considered: the carbanion in the polymer chain end \((A_1)\), the monovinyl monomer \((A_2)\), the initiator \((A_3)\) and the polymerized monomer unit \((A_4)\). If an ideal polymerization is assumed, only the elementary reactions monomer initiation (rate coefficient \( k_i \)) and monomer propagation (rate coefficient \( k_p \)) are present. The vectors of stoichiometric coefficients associated with these reactions are: initiation, \( \nu_i = [1, -1, -1, 1] \); propagation, \( \nu_p = [-1, 0, 0, 0] \) and \( \nu_i^* = [1, -1, 0, 1] \).

If the initiation is much faster than propagation (e.g. \( C_i = (k_i/k_p) > 10 \)), it is well known that the CLD of the polymer is a Poisson distribution. In these circumstances, the evolution of z-average radius of gyration can be analytically obtained: 

\[
R_g^2 = b^2 \phi (\phi^2 + 6 \phi + 6) / [6(\phi^2 + 3 \phi + 1)],
\]

where \( \phi = r \rho - 1 \), \( r = \left[ M_0 \right] / \left[ I_0 \right] \) and \( p \) represents the monomer conversion. A single kind of links connecting RU in the polymer (with length \( b \)) is considered. These known results were fully reproduced using the computational implementation of the general method presented here as can be observed in Figs. 4 and 5.

When the relative rate of initiation is very slow (e.g. \( C_i = 10^{-4} \)), the MSD of the polymer becomes the Gold [69] distribution. In this case, it is not possible to obtain a simple analytical solution for \( R_g^2 \) but a numerical solution can be readily calculated using the present method. These results are also shown in Fig. 4. As expected, with a slow initiation, for the same monomer conversion a higher value of \( R_g \) is predicted relatively to the instantaneous initiation system. Nevertheless, either for slow or for instantaneous initiation, the same linear relation between z-average radius of gyration and z-average degree of polymerization is predicted (see Fig. 5). Since the polymer chains are linear, the z-average characteristic ratio for these systems is also 1/6.

A more complex system results from the consideration of the anionic polymerization of vinyl monomers in the presence of divinyl monomers. An important feature of this kind of systems is their possible gelation. A discussion about the kinetics and its influence on the evolution of the average molecular weights (before and after gelation) for this kind of polymerizations was already published by the present authors [22]. For conciseness, only essential details needed for the calculation of \( R_g \) for this system will be presented here.

The kinetic scheme comprises the following kinds of reactions:

- Initiations (6),
- Propagations (6),
- Hydride eliminations (2),
- Transfers to solvent (2),
- Terminations (4).

So, a total number of 20 chemical reactions are considered. The simplest set of chemical groups contains 12 different species: initiator, monovinyl monomer (MVM), divinyl monomer (DVM), solvent (S), MVM anion, DVM anion, S anion, pendant vinyl group in the polymer, terminal vinylene from MVM, terminal vinylene from DVM, polymerized MVM unit and polymerized DVM unit.

The initial composition of the system considered in the simulations was: \( \text{MVM}_0 = 3.996, \text{DVM}_0 = 0.004, I_0 = 0.004 \) and \( S_0 = 4 \text{ mol dm}^{-3} \). The kinetic parameters here considered were the same as used in Ref. [22]. For these conditions, gelation is predicted when the global monomer conversion is around 0.48, as can be observed in Fig. 4. In the same figure, it is shown that the prediction of the evolution of \( R_g \) can be predicted more accurately with the relative rate of initiation much faster than propagation, the same linear...
carried out before and after gelation also for this more complex polymerization system. From Fig. 5 it is clear that the dimension of the non-linear polymer chains is much smaller than their linear counterparts with same degree of polymerization.

For this non-linear system, the relations between $\kappa_z$ and $R_g$ before and after gelation do not collapse to a single curve. This is a consequence of the non-random character of this polymerization system, in contrast with the polycondensation systems analyzed in the previous section.

4.3. Case study III: radical polymerization with terminal branching and transfer to polymer

In several radical polymerization systems, long-chain branching can occur due to propagation into terminal double bonds and transfer to polymer. As a result of these mechanisms of branching, trifunctional units are present in the structure of the polymer [68,70,71]. Polymerizations of vinyl acetate, ethylene, methyl acrylate, vinylidene fluoride and vinylidene chloride are examples of chemical systems involving long-chain branching.

The analysis of this kind of systems has already been carried out by using the present approach for the calculation of average degree of polymerization or the MSD itself, before and after gelation, in batch and CSTR reactors [21,23]. The main objective of the present section is to show that the method here presented for the prediction of $z$-average radius of gyration can also be used with those complex chemical systems. Calculations before and after gelation are possible and as previously discussed [21,23] significant gains in accuracy in comparison to alternative simplified methods can be achieved.

Another advantage of the present approach is the possibility of analyzing polymerization systems in an automated way, keeping error-prone human intervention to a minimum.

Table 2 Description of groups in a radical polymerization with terminal double bonds branching and transfer to polymer

<table>
<thead>
<tr>
<th>Group description</th>
<th>$j$</th>
<th>$\delta_{Pj}$</th>
<th>$\delta_{Aj}$</th>
<th>Chemical formula (example)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radical from monomer (FR1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$\text{--CH}_2\text{-HYC}$</td>
</tr>
<tr>
<td>Radical from MS (FR2)</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>$\text{CH}_2\text{=CHY}$</td>
</tr>
<tr>
<td>Radical from TDBM (FR3)</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>$\text{--CH}_2\text{-CHY}$</td>
</tr>
<tr>
<td>Radical from TDBD (FR4)</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>$\text{CH=CH}$</td>
</tr>
<tr>
<td>Radical from STP (FR5)</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>$\text{CH=CH}_2$</td>
</tr>
<tr>
<td>Terminal double bond TDBM</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>$\text{CH}=\text{CH}$</td>
</tr>
<tr>
<td>Terminal double bond TDBD</td>
<td>7</td>
<td>1</td>
<td>1</td>
<td>$\text{CH}_2\text{=CH}$</td>
</tr>
<tr>
<td>Site of transfer to polymer STP</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>$\text{CH}_2\text{=CH}_2$</td>
</tr>
<tr>
<td>Monomer</td>
<td>9</td>
<td>0</td>
<td>1</td>
<td>$\text{CH}_2\text{=CHY}$</td>
</tr>
<tr>
<td>Primary radical</td>
<td>10</td>
<td>0</td>
<td>1</td>
<td>$(\text{CH}_3)_2\text{CNCN}$</td>
</tr>
<tr>
<td>Initiator</td>
<td>11</td>
<td>0</td>
<td>1</td>
<td>$(\text{CH}_3)_2\text{CNNC}=(\text{NC})\text{(CN)(CH}_2)_2$</td>
</tr>
<tr>
<td>Polymerized monomer unit</td>
<td>12</td>
<td>1</td>
<td>0</td>
<td>$\text{--CH}_2\text{-CHY}$</td>
</tr>
</tbody>
</table>
For generality, no particular chemical system has been selected for this case study. However, the chosen kinetic parameters should allow a simulation as far as possible close to the real behavior of free-radical long-chain branching polymerizations. With this purpose, a basic set of kinetic parameters will be established as presented in Table 3. Rate coefficients for the reference monomer propagation, transfer to monomer, transfer to polymer and propagation of TDBM are the same as currently accepted for vinyl acetate polymerization. Nevertheless, termination is considered to occur by both mechanisms (combination and disproportionation) and TDBDs are considered to be active (in the present case with lower activity than TDBM). With the exception of these few kinetic parameters, most of the information needed for the model is missing. Therefore, several of the 59 kinetic parameters will be guessed based on qualitative considerations. It is not our purpose to discuss in depth the complex problem of kinetic modeling and parameter estimation for these chemical systems but to show that the present method is capable of taking into account their complexity and hopefully stay flexible enough to incorporate further reactions.

Going along the sequence of radicals FR1 to FR5, a decrease in reactivity is plausible. The kinetic parameters for the propagations of monomer, TDBM and TDBD with the different radicals have been established using the following simple rules: \( k_{p1} = k_p / i \), \( k_{p2} = k_p^* / i \), \( k_{p3} = k_p^{**} / i \) with \( i = 1, \ldots, 5 \). Owing to the decrease of reactivity of the double bonds in the sequence monomer: TDBM: TDBD with the different radicals have been established using the following simple rules: \( k_{p1} = k_p / i \), \( k_{p2} = k_p^* / i \), \( k_{p3} = k_p^{**} / i \) with \( i = 1, \ldots, 5 \). As terminations are bimolecular reactions involving the different kinds of radicals, their rate coefficients were considered to obey the following rules: \( k_{tcij} = k_{tc} / ij \) and \( k_{adj} = k_{adj} / ij \) with \( i = 1, \ldots, j \) and \( j = 1, \ldots, 5 \).

The simulations performed with this case study are presented in Figs. 6 and 7. A batch reactor starting with \([M]_0 = 10.83 \text{ mol dm}^{-3}\) was always considered. Again, a first important check was done by considering a linear radical polymerization. This system can be simulated by deleting from the general kinetic scheme all mechanisms of branching (\( K_1 = K_2 = C_p = 0 \)) or by considering another simplified kinetic scheme. With the last option a lower CPU time is needed but the results obtained are obviously the same. It is important to note that the expected result for z-average characteristic ratio \( \left( \frac{R_z^2}{\langle b^2 \rangle_z} \right) = 1/6 \) was again obtained.

Three different non-linear systems were considered in this case study. In the first one, all above discussed mechanisms of branching are present and both mechanisms of termination are supposed to occur with equal probability (\( C_{tc} = C_{td} = 0.5 \)).

![Fig. 6. Evolution of the z-average mean square radius of gyration \( (R_z^2/b^2) \) in a radical polymerization with terminal branching and transfer to polymer.](image1)

![Fig. 7. The z-average mean square radius of gyration vs. z-average degree of polymerization in a radical polymerization with terminal branching and transfer to polymer.](image2)

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Relative value</th>
<th>Absolute value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_p )</td>
<td></td>
<td>( 1.17 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_i )</td>
<td></td>
<td>( 2.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( f )</td>
<td></td>
<td>( 9 \times 10^{-6} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>( k^* )</td>
<td></td>
<td>( 0.5 )</td>
</tr>
<tr>
<td>( K_1 = \frac{k_i}{k_p} )</td>
<td>( 0.8 )</td>
<td>( 9.36 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( K_2 = \frac{k_i}{k_p} )</td>
<td>( 0.6 )</td>
<td>( 7.02 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_t )</td>
<td></td>
<td>( 1.17 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_{mi} )</td>
<td></td>
<td>( 1.9 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_{pi} )</td>
<td></td>
<td>( 2.223 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_{tp} )</td>
<td></td>
<td>( 1.2 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_{am} )</td>
<td></td>
<td>( 1.25 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
<tr>
<td>( k_{ad} )</td>
<td></td>
<td>( 1.25 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} )</td>
</tr>
</tbody>
</table>
In this case, gelation occurs when the monomer conversion is 0.83. A different system was simulated by supposing that only termination by disproportionation is possible and that TDBDs are inactive \((C_{id} = 1 - C_{ic} = 1, K_2 = 0)\). In this case no gelation is predicted. A third system results when termination occurs exclusively by combination \((C_{ic} = 1)\) with a predicted monomer conversion of 0.81 at the gel point (see Fig. 6). It is very interesting to observe the effect of these mechanisms of branching in the dimension of polymer chains as illustrated in Fig. 7. The relation between \(\pi_c\) and \(R_g\) is again not the same before and after gelation as a consequence of the non-randomness of these polymerization systems. These kinds of differences can be used in practice to investigate the architecture and the formation kinetics of this kind of polymers. Notice that \(M_w\) (or \(\pi_c\)) is also available from the predictions of the present method and therefore, a full experimental study of the formation kinetics of these networks should be possible by using light scattering [36].

5. Conclusions

In this work, a general kinetic method was presented for the prediction of mean square radius of gyration of tree-like polymers with Gaussian chains. The major distinctive features of this analysis are:

- The generality of the method here presented allows the prediction of the mean square radius of gyration for different irreversible polymerization systems with a common tool (a kind of interpreter for irreversible polymerization systems);
- This simulation method avoids a set of approximating conditions with widespread use in modeling of non-linear polymerizations, namely in radical polymerizations, such as the absence of multiple radical sites per molecule and the pseudo-steady state for radical concentrations;
- The present method allows the extension of the prediction of mean square radius of gyration past gel point;
- The consideration of detailed kinetic schemes with distinction of several active species (e.g. macro-radicals) and chemical reactions is possible and therefore more realistic polymerization systems can be simulated.

The generality of the present method was shown by carrying out the simulation of three completely different polymerization systems: step-growth polymerizations with the formation of hyperbranched polymers, ionic polymerization of mono- and divinyl monomers and a radical polymerization with terminal branching and transfer to polymer.

With the step-growth systems considered, it was possible to confirm the reliability of the simulations of the present method throughout its comparison with analytical solutions or alternative methods for the prediction of the mean square radius of gyration for hyperbranched polymers. With these simple chemical systems it was possible to easily extend the prediction of \(R_g\) beyond the gel point.

Supplementary tests on the reliability of the present predictions were carried out with the ionic polymerization of a monovinyl monomer with different relative initiation rates. The more complex system consisting in the anionic polymerization of mono- and divinyl monomers with gel formation was also analyzed. In this case the influence of some side reactions such as hydride elimination and transfers to vinylene groups was considered.

The usefulness of this approach becomes undeniable when complex systems such as a radical polymerization with terminal branching and transfer to polymer are tackled. In this case, a detailed kinetic scheme with the distinction of five macro-radicals, two kinds of terminal double bonds and a site of transfer to polymer was considered. In spite of the large number of chemical species and reactions, it was shown that it is possible to obtain the predictions of \(R_g\) before and after gelation. The influence of the kinetic scheme on the mean square radius of gyration of the resulting polymers has been discussed. Due to the large number of ordinary differential equations involved and their stiffness, the CPU time needed for these computations is much higher than with the other polymerization systems considered in this work. The ability of the present method to predict the variation of \(R_g\) with the reaction time for complex polymerization systems may be used in practice to make comparisons with experimental values of \(R_g\) obtained by light scattering. In this way, it is possible to improve the knowledge about the architecture and the kinetics of formation of non-linear polymers.

Another possible use of this method is to carry out confirmation checks of more elaborate predictions of polymer structure (such as the results of Monte Carlo simulations).

Acknowledgments

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Appendix A

Molecular size distribution for a restricted polymer population in the \(A_3\) self-polycondensation

The molecular size distribution in the \(A_3\) self-polycondensation in a batch reactor will be determined by considering the restricted polymer population formed by the monomer, dimer, trimer and the two isomeric tetramers. The rates of formation and consumption of these small species can be readily found by taking into account all the possibilities of reaction between molecules. In this way the following set of ordinary differential equations results for a batch reactor:

\[
\frac{d[A]}{dt} = -k[A]^2
\]

(A-1)
The concentrations of the two isomers of the tetramer are represented by \([P_4]\) and \([P_3]\), respectively. The concentrations of the two isomers of the tetramer are represented by \([P_4]\) (linear) and \([P_{4b}]\) (branched) (their structure is depicted in Fig. 8).

The initial conditions for the system of differential equations Eqs. (A-1)–(A-6) are: \([A]_0 = [A]/[A]_0\), \([P_1]_0 = [P_1]/[A]_0\), \([P_2]_0 = [P_2]/[A]_0/3\), \([P_3]_0 = [P_3]/[A]_0/10\), \([P_{4l}]_0 = [P_{4l}]/[A]_0/60\), \([P_{4b}]_0 = [P_{4b}]/[A]_0/60\). It is possible to obtain an analytical solution for the problem Eqs. (A-1)–(A-6) by introducing the change of variable:

\[
\frac{d\theta}{dt} = k[A]dt
\] (A-7)

followed by the sequential resolution of the system of differential equations, using the method of the integrating factor:

\[
[A] = [A]_0 e^{-\theta}
\] (A-8)

\[
[P_1] = \frac{[A]_0}{3} e^{-3\theta}
\] (A-9)

\[
[P_2] = \frac{[A]_0}{2} (1 - e^{-\theta}) e^{-4\theta}
\] (A-10)

\[
[P_3] = \frac{[A]_0}{2} (1 - e^{-3\theta} - 2e^{-\theta}) e^{-5\theta}
\] (A-11)

\[
[P_{4l}] = 2[A]_0 (1 - 3e^{-\theta} - e^{-3\theta} + 3e^{-2\theta}) e^{-6\theta}
\] (A-12)

\[
[P_{4b}] = [A]_0 \left( \frac{1}{3} - e^{-\theta} - \frac{e^{-3\theta}}{3} + e^{-2\theta} \right) e^{-6\theta}
\] (A-13)

Note that from Eq. (A-8), the end-group conversion, \(\alpha = 1 - [A]/[A]_0\), is related to the variable \(\theta\) by \(\theta = -\ln(1 - \alpha)\) and therefore, the concentrations of the considered polymer species can be analytically evaluated along the reaction.

Considering that mass points with \(M = 1\) are located at the repeating units and that the length of the link is constant \((b = 1\) for simplicity), using the definition (see Eq. (A-14) for instance), the mean square radius of gyration of each kind of polymer molecule is: \(\langle R^2_g \rangle_1 = 0, \langle R^2_g \rangle_2 = 1/4, \langle R^2_g \rangle_3 = 4/9, \langle R^2_g \rangle_{4l} = 10/16\) and \(\langle R^2_g \rangle_{4b} = 9/16\). It is therefore possible to calculate the real molecular size distribution of this population. This result is presented in Fig. 9, where the \(z\)-distribution means \(\langle z^2 \rangle/[P_i]/\sum \langle z^2 \rangle\) and can obviously be obtained from the previous equations for each value of end group conversion considered. Note that in the real distribution of radius of gyration, the two isomers of the tetramer are distinguished.

In Eq. (33), all isomers with same molecular masses are lumped into a single species with global concentration equal to the sum of the individual concentrations. Its mean square radius of gyration is the number average of the mean square radius of gyration of these population of isomers, as can be easily shown from Eqs. (14) and (33) [32]. In this particular example, the effect can be observed in Fig. 9 where the lumping does not affect the distribution of the dimer and trimer (there are no isomers in those classes) but the tetramer obviously includes the two isomers. For the particular case presented the average square radius of gyration of \([P_{4l}]\), the sum of \([P_4]\) and \([P_{4b}]\), is the number average of the mean square radius of the two isomers with a numerical value of about 0.6161.

For general polymerization systems, the lumped distribution of radius of gyration can be obtained using the present method through inversion of Eq. (33). The real distribution is not available because the method intrinsically lumps all isomers with the same counts of groups into a single species. Nevertheless, it should be mentioned that the \(z\)-average radius

![Fig. 8. The structures of monomer \((P_1)\), dimer \((P_2)\), trimer \((P_3)\) and the two isomers of the tetramer \((P_{4l} \text{ and } P_{4b})\) considered in the self-reaction of \(A_3\).](image)

![Fig. 9. Real molecular size distribution, lumped molecular size distribution and \(z\)-average mean square radius of gyration for the reduced polymer population considered in the self-reaction of \(A_3\) \((\alpha = 0.4)\).](image)
of gyration predicted by this method is the correct $z$-average of the real molecular size distribution. In fact from Eqs. (14) and (33) it is easily proved that the $z$-average radius of gyration can be calculated from the real or the lumped molecular size distributions. This is also illustrated in Fig. 9 for the simple chemical system considered in this example.

Appendix B. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2007.01.033.

References