Prediction of Average Molecular Size of Branched Polymers by a Kinetic Method

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Summary

Correlation of melt and solution viscosity of branched polymers, as well as fundamental researches on their structure and formation mechanisms, depend on the ability to predict their average molecular size. This task is very much complicated owing to the existence of the position isomers, their number growing factorially with overall chain length. Monte Carlo simulation is possible (Tobita, 1994), but is time consuming and not very reliable even for simple kinetic schemes. Nevertheless, the Theory of Branched Processes (TBP, see Dobson and Gordon, 1964; Gordon and Malcolm, 1966) can perform an averaging among all position isomers with same numbers of repeating units for tree-like molecules present in an equilibrium mixture and thus compute average molecular sizes for gaussian chain molecules, so it can sometimes lead to useful and quick estimates.

As TBP becomes often inapplicable for irreversible, kinetic-driven polymerizations, it is important to have an alternative method for dealing with this often encountered situation.

Since the present authors have been developing a rigorous kinetic method for modeling non-linear irreversible polymerizations with a finite number of intramolecular cyclizations (Costa and Dias, 1994; Dias, 1996), with the aim of providing an automated way of dealing with complex kinetic schemes, a procedure for obtaining *z*-averaged distributions of gyration radius for gaussian chain molecules can follow using the same approach. The crux is the introduction of a general rate law allowing the prediction of the bilateral chain length distributions of pending chains associated to each bond connecting repeating units.

After a brief description of the underlying foundations of this method, some case studies concerning polycondensations and polyadditions are presented, as well as a discussion of practical numerical performance and a comparison with a few results obtainable by TBP.

Chemical groups and reactions

A set $\mathbf{X}_1, \mathbf{X}_2, \ldots, \mathbf{X}_{N_X}$ of main repeating units (MRU), which are supposed to remain unaffected by chemical reaction, are present in all polymer molecules.

To each MRU are attached end groups (EG), chosen within a set $\mathbf{A}_1, \mathbf{A}_2, \ldots, \mathbf{A}_{N_A}$.

Since only tree-like molecules are allowed, there is only one bond connecting every pair of MRU, chosen from a set $\mathbf{V}_1, \mathbf{V}_2, \ldots, \mathbf{V}_{N_V}$.

By convention, bond $\mathbf{V}_n$ is formed by reaction of end groups $\mathbf{A}_{g_n^-}$ and $\mathbf{A}_{g_n^+}$, with $g_n^- \leq g_n^+$:

$$\sum_{j=1}^{N_A} \left(\nu_{nj}^- + \nu_{nj}^+ \right) \mathbf{A}_j \xrightarrow{k_n} \mathbf{V}_n \tag{1}$$

Two sets of stoichiometric coefficients ν_{nj}, equal to the difference of numbers of moles between reagents and products when 1 mole of $\mathbf{V_n}$ is formed, have been distinguished: those which concern the EG connected to the MRU at the negative side of the bond, which contained group $\mathrm{A}_{g_n^-}$, and those related to the positive side. Because of the possibility of substitution effects, other stoichiometric coefficients besides $\nu^-_{ng_n^-}$ and $\nu^+_{ng_n^-}$ may be different from zero, and these latter are not always -1.

The rate of formation of bond $\mathrm{V_n}$ by such a reaction is written as:

$$R_{V_n} = k_n A_{g_n^-} A_{g_n^-} \tag{2}$$

The rate constant k_n in this equation is most often not a true constant but a function of the composition of the reaction media. According to Flory's Principle of Equal Reactivity, k_n does not depend on the nature of the molecule to which the end-groups are attached.

Other reactions between EG, bimolecular (such as termination by dismutation in radical polymerization) or unimolecular (termination by hydride expulsion in anionic polymerization), do not create bonds connecting MRU. Assuming there are N_R^{*} unimolecular and N_R^{**} bimolecular reactions not creating bonds between MRU, their description in terms of stoichiometric coefficients follows from the definitions below:

$$\sum_{j=1}^{N_R^{*}} \nu^{*}_{nj} \mathrm{A}_j \xrightarrow{k_n^{*}} 0 \tag{3}$$

$$\sum_{n=1}^{N_R^{**}} \left(\nu^{**-}_{nj} + \nu^{**+}_{nj} \right) \mathrm{A}_j \xrightarrow{k_n^{**}} 0 \tag{4}$$

Statistical description of polymer molecular structure and formation

The ensemble of trees with same vectors of numbers of MRU $\mathbf{x} = \left[x_1 \ldots x_{N_X} \right]$ and EG $\mathbf{a} = \left[a_1 \ldots a_{N_A} \right]$ will be named $\mathbf{P(a, x)}$. Its mole concentration is written as $P(\mathbf{a}, \mathbf{x})$, in order to simplify as much as possible the equations that follow.

$P(\mathbf{a}, \mathbf{x})$ is used to define the *number chain length distribution* (NCLD) of polymer molecules, most of the times as its *vectorial discrete transform* or generating function instead of its real counterpart:

$$\overline{P}(\alpha, \xi) = \sum_{a_1=0}^{\infty} \ldots \sum_{a_{N_A}=0}^{\infty} \sum_{x_1=0}^{\infty} \ldots \sum_{x_{N_X}=0}^{\infty} \alpha_1^{a_1} \ldots \alpha_{N_A}^{a_{N_A}} \xi_1^{x_1} \ldots \xi_{N_X}^{x_{N_X}} P(\mathrm{a}, \mathrm{x}) \tag{5}$$

The molecular mass M_m of a generic molecule $\mathbf{P(a_m, x_m)}$ is obtained from the molecular masses of its MRU and EG $M_{X_1}, \ldots, M_{X_{N_X}}$ and $M_{A_1}, \ldots, M_{A_{N_A}}$:

$$M_m = x_{1m} M_{X_1} + \ldots + x_{N_X m} M_{X_{N_X}} + a_{1m} M_{A_1} + \ldots + a_{N_A m} M_{A_{N_A}} \tag{6}$$

Number molecular mass distribution (NMMD) of polymer molecules is related to their NCLD by introducing its discrete transform or generating function $\overline{P}(\mu)$:

$$\begin{aligned}\overline{P}(\mu) &= \sum_{m=1}^{\infty} \mu^{M_m} P(M_m) = \sum_{a_1=0}^{\infty} \dots \sum_{x_{N_X}=0}^{\infty} \mu^{x_1 M_{X_1} + \dots + x_{N_X} M_{X_{N_X}} + a_1 M_{A_1} + \dots + a_{N_A} M_{A_{N_A}}} P(\mathbf{a},\mathbf{x}) \\ &= \overline{P}\left(\mu^{M_{A_1}}, \dots, \mu^{M_{N_A}}, \mu^{M_{X_1}}, \dots, \mu^{M_{N_X}}\right)\end{aligned} \tag{7}$$

Pendant chains and gel structure

For a generic polymer molecule $\mathbf{P_m}$ with vectors of numbers of MRU, EG and bonds $\mathbf{x}_m$, $\mathbf{a}_m$ and $\mathbf{v}_m$ (these latter are preferably considered a sub-set of the $\mathbf{a}_m$) with a total number of MRU $N_{X_m} = \sum_{n=1}^{N_X} x_{nm}$, EG $N_{A_m} = \sum_{n=1}^{N_A} a_{nm}$ and of bonds $N_{V_m} = \sum_{n=1}^{N_V} v_{nm}$, arbitrary labels of its MRU, EG and bonds are introduced: $\mathbf{X_{pm}}$, $\mathbf{A_{pm}}$, $\mathbf{V_{pm}}$ are respectively the p-th MRU, the p-th EG and the p-th bond in the molecule.

Since only tree-like molecules are being considered, breaking a bond $\mathbf{V_{pm}}$ connecting two MRU yields two separate fragments, which will be called *pendant chains*.

The parent molecule of molecular mass M_m has pendant chains of molecular masses M_{pm}^- and M_{pm}^+ which result from breaking bond $\mathbf{V_{pm}}$. The sum of their molecular masses is obviously the molecular mass of the parent molecule $M_m = M_{pm}^- + M_{pm}^+$.

Regrouping the contributions of all polymer molecules for the same kind of bonds V_l, a NMMD $V_l(M_m^-, M_m^+)$ of the mole concentrations of pendant chains (*two-sided molecular mass distribution of the pendant chains*, MMDPC), can be defined, with discrete transform:

$$\overline{V}_l(\mu^-, \mu^+) = \sum_{i=1}^{\infty} V_l(M_i^-, M_i^+)(\mu^-)^{M_i^-}(\mu^+)^{M_i^+} \tag{8}$$

In the same way as the NMMD of polymer molecules, the NMMDPC can be related to the corresponding transformed NCLD:

$$\begin{aligned}\overline{V}_l(\mu^-, \mu^+) &= \sum_{m=1}^{\infty} (\mu^-)^{M_m^-} (\mu^+)^{M_m^+} V_l(M_m^-, M_m^+) \\ &= \overline{V}_l\left[(\mu^-)^{M_{A_1}}, \dots, (\mu^-)^{M_{A_{N_A}}}, (\mu^-)^{M_{X_1}}, \dots, (\mu^-)^{M_{X_{N_X}}}, (\mu^+)^{M_{A_1}}, \dots, (\mu^+)^{M_{A_{N_A}}}, (\mu^+)^{M_{X_1}}, \dots, (\mu^+)^{M_{X_{N_X}}}\right]\end{aligned} \tag{9}$$

Radius of gyration of single polymer molecules

The MRU and EG are assumed to be freely jointed, according to the so-called "gaussian chain model" (Mattice and Sutter, 1994).

Bond length $\langle b_n^2 \rangle$ is taken as the time average mean square distance between the centers of mass of the MRU linked by $\mathbf{V_n}$. The time average mean square distance between the centers of mass of the EG $\mathbf{A_n}$ and the MRU to which it is attached will be called $\langle b_{A_r}^2 \rangle$. Time average gyration radii of MRU and EG, $\langle s_{X_n}^2 \rangle$ and $\langle s_{A_n}^2 \rangle$, also have a (mostly minor) contribution to average molecular radius of gyration.

The following generalization of a previous result by Gordon and Malcolm (1966) (who had only considered the first term, and even this one with some unnecessary simplifications) yields the time-averaged molecular radius of gyration $\langle s_m^2 \rangle$:

$$M_m^2\langle s_m^2\rangle = \sum_{p=1}^{N_{V_m}} M_{pm}^{-} M_{pm}^{+}\langle b_{pm}^2\rangle + \sum_{l=1}^{N_X} x_{lm} M_{X_l} \sum_{n=1}^{N_A} a_{nm} M_{A_n}\langle b_{A_n}^2\rangle + M_m \sum_{n=1}^{N_X} x_{nm} M_{X_n}\langle s_{X_n}^2\rangle + M_m \sum_{n=1}^{N_A} a_{nm} M_{A_n}\langle s_{A_n}^2\rangle \tag{10}$$

An overall distribution of gyration radius is obtained by superposing the contributions of each molecule in the mixture to $M_m^2\langle s_m^2\rangle$, so a z-molecular mass distribution will be obtained.

Defining the discrete transform with respect to molecular mass of that z distribution of time average squared gyration radii $\overline{\langle s^2\rangle}_z(\mu)$ (z-DTASGR) as:

$$\overline{\langle s^2\rangle}_z(\mu) = \sum_{m=1}^{\infty} M_m^2 P_m \mu^{M_m}\langle s^2\rangle_m \Big/ \sum_{m=1}^{\infty} M_m^2 P_m \tag{11}$$

Considering (10), it is thus related to the NMMDPC through:

$$\overline{\langle s^2\rangle}_z(\mu)\sum_{m=1}^{\infty} M_m^2 P_m = \sum_{l=1}^{N_V}\langle b_l^2\rangle \frac{\partial^2 \overline{V}_l}{\partial\log\mu^-\partial\log\mu^+}\bigg|_{\mu^-=\mu^-=\mu} + \left[\sum_{l=1}^{N_X}\sum_{n=1}^{N_X} M_{X_n} M_{X_l}\langle s_{X_n}^2\rangle \frac{\partial^2\overline{P}}{\partial\xi_l\partial\xi_n} + \sum_{l=1}^{N_A}\sum_{n=1}^{N_X}\left(\langle b_{A_l}^2\rangle + \langle s_{A_l}^2\rangle + \langle s_{X_n}^2\rangle\right) M_{A_l} M_{X_n}\frac{\partial^2\overline{P}}{\partial\alpha_l\partial\xi_n} + \sum_{l=1}^{N_A}\sum_{n=1}^{N_A}\langle s_{A_l}^2\rangle M_{A_l} M_{A_n}\frac{\partial^2\overline{P}}{\partial\alpha_l\partial\alpha_n}\right]_{\substack{\alpha_1=\mu^{M_{A1}}\\ \dots \\ \xi_{N_X}=\mu^{M_{X_{N_X}}}}} \tag{12}$$

Rate equations for polymer species and pendant chains

Transformed rate equations for the polymer species and the pendant chains concentrations can be written, using a method previously described by Costa and Dias (1994 and 1995):

$$\overline{R}_P(\alpha,\xi) = \sum_{l=1}^{N_V} k_l\left(\overline{\nu}_l^-\overline{\nu}_l^+\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}}\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}} - \frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}}A_{g_l^-} - \frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}}A_{g_l^-}\right) + \sum_{l=1}^{N_R^{*}} k_l^{*}\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^{*}}}\left(\overline{\nu}_l^{*}-1\right) + \sum_{l=1}^{N_R^{**}} k_l^{**}\left[\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^{**-}}}A_{g_l^{**-}}\left(\overline{\nu}_l^{**-}-1\right) + \frac{\partial\overline{P}}{\partial\log\alpha_{g_l^{**-}}}A_{g_l^{**-}}\left(\overline{\nu}_l^{**+}-1\right)\right] \tag{13}$$

$$\overline{\nu}_n^{Z}(\alpha) = \prod_{j=1}^{N_A}(\alpha_{nj})^{\nu_{nj}^{Z}} \qquad Z = {}^{+};{}^{-};{}^{*};{}^{**-};{}^{**+} \tag{14}$$

$$\overline{R}_{V_m}(\alpha^-,\alpha^{\pm}) = k_l\overline{\nu}_l^-(\alpha^-)\overline{\nu}_l^+(\alpha^+)\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}^-}\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}^+} + \sum_{l=1}^{N_V} k_l\left\{\frac{\partial\overline{V}_m}{\partial\log\alpha_{g_l^-}^-}\left[\overline{\nu}_l^-(\alpha^-)\overline{\nu}_l^+(\alpha^-)\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}^-} - A_{g_l^-}\right] + \frac{\partial\overline{V}_m}{\partial\log\alpha_{g_l^-}^-}\left[\overline{\nu}_l^-(\alpha^-)\overline{\nu}_l^+(\alpha^-)\frac{\partial\overline{P}}{\partial\log\alpha_{g_l^-}^-} - A_{g_l^-}\right]\right.$$

$$\left. + \sum_{l=1}^{N_R^{*}} k_l^{*}\left\{\frac{\partial\overline{V}_m}{\partial\log\alpha_{g_l^{*}}^-}\left[\overline{\nu}_l^{*}(\alpha^-)-1\right] + \frac{\partial\overline{V}_m}{\partial\log\alpha_{g_l^{*}}^+}\left[\overline{\nu}_l^{*}(\alpha^+)-1\right]\right\}\right.$$

$$+\frac{\partial \overline{V}_m}{\partial \log \alpha^+_{g_l^-}}\left[\overline{\nu}_l^-(\alpha^+)\overline{\nu}_l^+(\alpha^+)\frac{\partial \overline{P}}{\partial \log \alpha^+_{g_l^-}} - A_{g_l^-}\right] + \frac{\partial \overline{V}_m}{\partial \log \alpha^-_{g_l^-}}\left[\overline{\nu}_l^-(\alpha^+)\overline{\nu}_l^+(\alpha^+)\frac{\partial \overline{P}}{\partial \log \alpha^+_{g_l^-}} - A_{g_l^-}\right]\Bigg\}$$

$$+\sum_{l=1}^{N_R^{**}} k_l^{**}\Bigg\{A_{g_l^{**-}}\frac{\partial \overline{V}_m}{\partial \log \alpha^-_{g_l^{**-}}}\left[\overline{\nu}_l^{**-}(\alpha^-)-1\right] + A_{g_l^{**-}}\frac{\partial \overline{V}_m}{\partial \log \alpha^+_{g_l^{**-}}}\left[\overline{\nu}_l^{**-}(\alpha^+)-1\right] +$$

$$A_{g_l^{**-}}\frac{\partial \overline{V}_m}{\partial \log \alpha^-_{g_l^{**-}}}\left[\overline{\nu}_l^{**+}(\alpha^-)-1\right] + A_{g_l^{**-}}\frac{\partial \overline{V}_m}{\partial \log \alpha^+_{g_l^{**-}}}\left[\overline{\nu}_l^{**+}(\alpha^+)-1\right]\Bigg\} \qquad (15)$$

Insertion of the above rate expressions in mass balances of ideal reactors, such as a CSTR in a transient state, leads to first order non-linear partial differential equations ($Z = P.V_n$: R_V is the rate of volume change by chemical reaction) of the generic aspect below shown:

$$\frac{\partial \overline{Z}}{\partial t} = \overline{R}_Z + \frac{\overline{Z}_F - \overline{Z}}{\tau} - R_V \overline{Z} \qquad (16)$$

$$\overline{Z}_{|t=0} = \overline{Z}_0(\alpha, \xi) \qquad (17)$$

They can be solved by the method of characteristics in order to get the distributions in Fourier domain or their moments as shown by Costa and Dias (1994).

Case studies and discussion

a) Polycondensation in a batch reactor of two multifunctional monomers

An alternating irreversible polycondensation of $\mathbf{X}_1(\mathbf{A}_1)_{f_1}$ with $\mathbf{X}_2(\mathbf{A}_2)_{f_2}$ with no substitution effects, in a batch reactor, starting from the pure monomers, will be first considered. Only one bond $\mathbf{V}_1$ exists. It might be considered equivalent to a group $\mathbf{A}_3$, which would be arbitrarily associated to MRU $\mathbf{X}_1$. but this will not be considered. So, $N_A = 2$ and the index variables associated to the polycondensation reaction are $g_1^- = 1$ and $g_1^+ = 2$.

Initial mole ratio between groups is called r, and from this variable the ratio between MRU concentrations for this chemical system can also be found:

$$r = \frac{A_{2_0}}{A_{1_0}} = \frac{f_2 X_2}{f_1 X_1} \qquad (18)$$

Conversions of EG p_1 and p_2 are also related through that initial mole ratio:

$$\begin{aligned} A_1 &= f_1 X_1 (1 - p_1) \\ A_2 &= f_2 X_2 (1 - p_2) = f_1 X_1 (r - p_1) \\ V_1 &= f_1 X_1 p_1 \end{aligned} \qquad (19)$$

The vectors of stoichiometric coefficients associated to the reaction between EG are $\nu_1^- = \begin{bmatrix} -1 \\ 0 \end{bmatrix}$ and $\nu_1^+ = \begin{bmatrix} -1 \\ 0 \end{bmatrix}$. Their discrete transforms are $\overline{\nu}_1^- = \frac{1}{\alpha_1}$ and $\overline{\nu}_1^+ = \frac{1}{\alpha_2}$.

The solution of the mass balance equation (16) for $\tau = \infty$ (batch reactor) yields:

$$\overline{P} = X_1\xi_1\alpha_{1_0}^{f_1} + X_2\xi_2\alpha_{2_0}^{f_2} - V_1\xi_1\xi_2\alpha_{1_0}^{f_1-1}\alpha_{2_0}^{f_2-1} \tag{20}$$

The starting point of the characteristics of $\overline{P}$, at t=0, is obtained through the solution of the two algebraic equations:

$$\alpha_{1_0} = \alpha_1(1-p_1) + p_1\xi_2\alpha_{2_0}^{f_2-1} \tag{21}$$

$$\alpha_{2_0} = \alpha_2(1-p_2) + p_2\xi_1\alpha_{1_0}^{f_1-1} \tag{22}$$

If $\alpha_1 = \alpha_2 = \xi_1 = \xi_2 = 1$, the root $\alpha_{1_0} = \alpha_{2_0} = 1$ becomes double at the gel point conversion $p_{1_g} = rp_{2_g}$ which verifies:

$$p_{1_g}p_{2_g} = \frac{1}{(f_1-1)(f_2-1)} \tag{23}$$

For conversions beyond gel point, there is one root with α_{1_0} and α_{2_0} less than 1 when $\alpha_1 = \alpha_2 = \xi_1 = \xi_2 = 1$, which is the one with physical meaning, and it marks the start of the branch containing the true solution for all other values of α_1, α_2, ξ_1 and ξ_2 not all equal to 1.

The characteristics of $\overline{V_1}$ verify relationships analogous to (21) and (22) with:

$$\overline{V_1} = V_1\xi_1^-\left(\alpha_{1_0}^-\right)^{f_1-1}\xi_2^+\left(\alpha_{2_0}^+\right)^{f_2-1} \tag{24}$$

In order to simplify the equations and save some space, molecular mass and radii of gyration of the EG will be neglected. Through differentiation of (20) and (24) and substitution in (12), the discrete transform of z-DTASGR is obtained:

$$\beta_{1_0} = 1 - p_1 + p_1\mu^{M_{X_2}}\beta_{2_0}^{f_2-1} \tag{25}$$

$$\beta_{2_0} = 1 - p_2 + p_2\mu^{M_{X_1}}\beta_{1_0}^{f_1-1} \tag{26}$$

$$\overline{\langle s^2\rangle}_z(\mu)\left\{\begin{matrix} X_1M_{X_1}\beta_{1_0}^{f_1-1}\left[M_{X_1}\beta_{1_0} + M_{X_2}f_1p_1\beta_{2_0}^{f_2-1} + M_{X_1}p_1p_2(f_2-1)\beta_{1_0}^{f_1-1}\beta_{2_0}^{f_2-2}\right] + \\ X_2M_{X_2}\beta_{2_0}^{f_2-1}\left[M_{X_2}\beta_{2_0} + M_{X_1}f_2p_2\beta_{1_0}^{f_1-1} + M_{X_2}p_1p_2(f_1-1)\beta_{1_0}^{f_1-2}\beta_{2_0}^{f_2-1}\right]\end{matrix}\right\} =$$
$$\langle b_1^2\rangle V_1\frac{\left[M_{X_1}\beta_{1_0}^{f_1-1} + M_{X_2}p_1(f_1-1)\beta_{1_0}^{f_1-2}\beta_{2_0}^{f_2-1}\right]\left[M_{X_2}\beta_{2_0}^{f_2-1} + M_{X_1}p_2(f_2-1)\beta_{1_0}^{f_1-1}\beta_{2_0}^{f_2-2}\right]}{1 - p_1p_2(f_1-1)(f_2-1)\beta_{1_0}^{f_1-2}\beta_{2_0}^{f_2-2}} \tag{27}$$

The classical result obtained by Zimm and Stockmayer (1949) for the z-average radius of gyration is obtained setting μ=1 in the above relationships.

b) Living polyaddition of mono- + difunctional monomers in a batch reactor

The functional group in both monomers (unsaturated bond, easily open ring) is A_1 and the activated group formed by reaction with the initiator is A_2. Propagation reaction creates the only bond in this system (k_1=k_p in our notation).

Initiation is considered as a pseudo-unimolecular reaction converting A_1 into A_2, with a rate k_i I A_1, I being the concentration of free initiator, and so in our notation $k_1^* = k_iI$. Vectors of stoichiometric coefficients are $\nu_1^- = \begin{bmatrix}-1\\1\end{bmatrix}$, $\nu_1^+ = \begin{bmatrix}0\\-1\end{bmatrix}$ and $\nu_1^* = \begin{bmatrix}-1\\1\end{bmatrix}$. The discrete transform of the initial NCLD is given by:

$$\overline{P}_{t=0} = X_{10}\xi_1\alpha_{1_0} + X_{20}\xi_2\alpha_{1_0}^2 \tag{28}$$

If the initiation is instantaneous, there is no need to take it into account, only the initial conditions must be modified. Defining p_i as the initial fraction of the A_1 converted into A_2, the discrete transform of the initial NCLD becomes now:

$$\overline{P}_{t=0} = X_{10}\xi_1\left[\alpha_{1_0}(1-p_i)+\alpha_{2_0}p_i\right] + X_{20}\xi_2\left[\alpha_{1_0}(1-p_i)+\alpha_{2_0}p_i\right]^2 \tag{29}$$

No complete analytical solution exists for this system, studied by Tobita (1994) using Monte Carlo simulation and by Costa and Dias (1995) using the present approach (without computing molecular sizes). Some numerical results are shown in fig. 1 (gyration radius of MRU and EG was neglected, constant bond length).

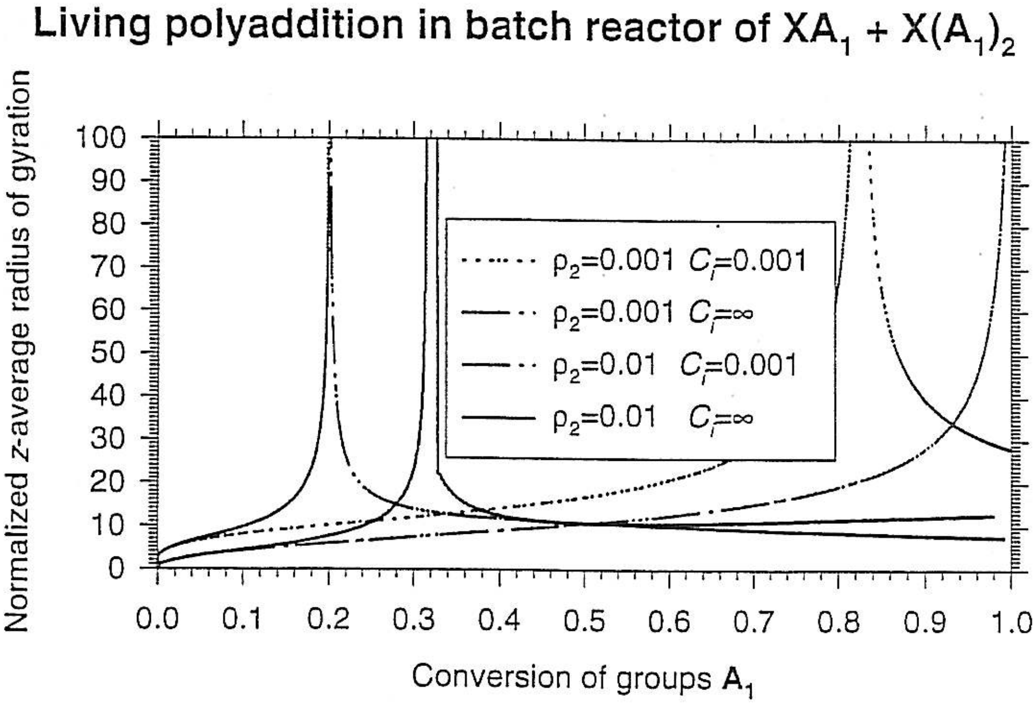

Fig. 1: Predicted z-average radius of gyration, normalized by the value for dimer, vs. conversion of A_1 groups in the living polyaddition without termination $XA_1 + X(A_1)_2$ in batch reactor, p_i =0.001, for different values of initial mole fraction of A_1 groups in difunctional monomer ρ_2 and of relative initiation rate constant $C_i = k_i/k_p$.

This kind of chemical systems can not be described by TBP in a straightforward way. For the linear case, classical TBP predicts a geometrical (Schulz-Flory) chain length distribution instead of a Poisson distribution. Gelation prediction by TBP also fails badly (Costa and Dias, 1995).

Despite severe numerical difficulties after gelation, which could be solved using parallel shooting, a complete study could be undertaken for this and similar systems.

Discussion

Even for very simple kinetic schemes, numerical resolution is mandatory and the general method of solution here presented renders possible to tackle a vast number of polymerization systems.

There are two well distinct levels of difficulty according to the goals of the simulation:

- Average MW and average gyration radii before gelation

  This leads to an initial value ODE system, with hundreds or thousands of equations, according to the number of required moments. This is a relatively simple problem for nowadays' computers if the number of chemical groups is not too large.

- CLD prediction
- Average properties after gelation

  Both aims lead to non-linear two-point boundary value problems with N_A equations, which are repeatedly solved for each value of final time.

  Integration along the characteristics of the same initial value problem as before gelation is performed after convergence of 2-point BVP is achieved.

  Convergence difficulties are overcome by a continuation procedure.

  Parallel shooting is generally needed (except for some polycondensations).

Development of predictions for more complex systems (radical polymerizations, polycondensations with ring formation) using this approach is under way.

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