# Prediction of Average Radius of Gyration of Branched Polymers by a General Kinetic Approach

M.R.P.F.N. Costa, LSRE- FEUP, Porto, P
R.C.S. Dias, LSRE- IPB, Bragança, P

**Summary**

Irreversible non-linear polymerizations leading to tree-like molecules can be described through the use of mass balance equations when only prediction of average properties concerning all isomers with same numbers of repeating units is needed. A method was found to compute distributions of average radius of gyration for molecules verifying the gaussian chain model. It is based in the introduction of the *two-sided* molecular mass distributions of pendant chains associated to every kind of bond between two neighbor repeating units.

In a last section are presented results for a "living" polymerization of Vinyl/Divinyl monomers in a batch reactor.

DECHEMA Monographs Vol. 134 – WILEY-VCH Verlag GmbH, 1998

**Zusammenfassung**

Irreversible nicht-lineare Polymerisationen, die zu baumähnlichen Molekülen führen, können mit Massenbilanz-Gleichungen beschrieben werden, wenn einzig die Voraussage gemittelter Eigenschaften betreffend Isomere mit gleicher Anzahl von Kettengliedern benötigt wird. Es wurde eine Methode gefunden, die Verteilung des mittleren Trägkeitsradius für Moleküle zu berechnen, die mit dem Gauss'schen Kettenmodell übereinstimmen. Es basiert auf der Einführung von beidseitigen Molmassenverteilungen für anhängende Ketten in Assoziation zu jeder Bindung zwischen zwei benachbarten Kettengliedern.

Im letzten Abschnitt werden Ergebnisse für eine „lebende" Polymerisation von Vinyl/Divinyl-Monomeren in einem Batch-Reaktor präsentiert.





**Introduction**

Using the theory of branching processes (TBP), Dobson and Gordon [1] and Malcolm and Gordon [2] obtained $z$-distributions of average radius of gyration for tree-like molecules verifying the gaussian chain model with some polycondensations. This has inspired the present work, which establishes a computation method based on rate equations valid for general irreversible polymerizations [3, 4], avoiding the assumption of chemical equilibrium needed for TBP to hold rigorously.

**Radius of Gyration of Single Polymer Molecules**

A generic polymer molecule $\mathbf{P_m}$, with an overall molecular mass $M_m$, is decomposed into $N_m$ repeating units, each of these with molecular mass $M_{mn}$ and time average mean square radius of gyration $\langle s^2_{mn} \rangle$. The repeating units are assumed to be freely jointed (according to the so-called "gaussian chain model", see for instance Mattice and Sutter [5]). Taking $\langle r^2_{mln} \rangle$ as the time average mean square distance between centers of mass of units $l$ and $n$, the time-average molecular radius of gyration may be obtained through:

$$M_m^2 \left\langle s_m^2 \right\rangle = \sum_{l=1}^{N_m} \sum_{n>l}^{N_m} M_{ml} M_{mn} \left\langle r_{mln}^2 \right\rangle + M_m \sum_{l=1}^{N_m} M_{ml} \left\langle s_{ml}^2 \right\rangle \qquad (1)$$

**Average Molecular Radius of Gyration of Tree-like Molecules**

Only one bond is assumed to connect neighboring repeating units. Let $M^-_{ml}$ and $M^+_{ml}$ be the molecular masses of the two fragments (*pendant chains*) formed when breaking the $l$-th bond in the molecule. Defining $b^2_{ml}$ as the time average mean square distance between centers of mass of units connected by $l$-th bond in $m$-th molecule, the relationship below (more general than the one previously deduced in [1, 2]), results:

$$M_m^2\left\langle s_m^2\right\rangle = \sum_{l=1}^{N_m-1} M_{ml}^- M_{ml}^+ b_{ml}^2 + M_m \sum_{l=1}^{N_m} M_{ml}\left\langle s_{ml}^2\right\rangle \qquad (2)$$

**Two-Sided Molecular Weight Distributions of Pendant Chains and the Average Radius of Gyration of Polydisperse Polymers**

A polymerizing mixture contains $\mathbf{X}_1 \ldots \mathbf{X}_{N_X}$ kinds of repeating units, of bonds (as above defined) $\mathbf{V}_1 \ldots \mathbf{V}_{N_V}$ and active groups $\mathbf{A}_1 \ldots \mathbf{A}_{N_A}$. Classes of isomeric polymer molecules are distinguished through the numbers of active groups, repeating units and bonds they contain, given by the vectors $\mathbf{a} = [\alpha_1 \ldots \alpha_{N_A}]$, $\mathbf{x} = [\varkappa_1 \ldots \varkappa_{N_X}]$, and $\mathbf{v} = [\upsilon_1 \ldots \upsilon_{N_V}]$. Let $\mathbf{P}(\mathbf{a}, \mathbf{x}, \mathbf{v})$ be the particular molecular class grouping all molecules with those same numbers of groups, and let $P(\mathbf{a}, \mathbf{x}, \mathbf{v})$ be its mole concentration.

For each bond, a positive and a negative sense will be arbitrarily defined (in some rare situations they will be the same owing to molecular symmetry). In order to predict molecular properties, the *two sided molecular weight distributions of pendant chains* associated to each kind of bond are introduced. Let $V_l(\mathbf{a}^-, \mathbf{x}^-, \mathbf{v}^-, \mathbf{a}^+, \mathbf{x}^+, \mathbf{v}^+)$ be the mole concentration of bonds $\mathbf{V}_l$ connected to pendant chains with vectors of active groups, repeating units and bonds $\mathbf{a}^-$, $\mathbf{x}^-$, $\mathbf{v}^-$ and $\mathbf{a}^+$, $\mathbf{x}^+$, $\mathbf{v}^+$, respectively in the two above defined directions. Most often, the *discrete transforms* of these distributions $\overline{P}(\alpha, \zeta, \phi)$ and $\overline{V}_l(\alpha^-, \zeta^-, \alpha^+, \zeta^+, \phi^+)$ will be used instead of their real domain counterparts.

The transformed *mass* distribution with respect to molecular mass $\overline{P_W}(\mu)$ becomes ($\mathbf{1}_N$ and analogous expressions are vectors where all $N$ components are unity):

$$\overline{P_w}(\mu) = \sum_{m=1}^{\infty} M_m P(M_m)\mu^{M_m} = \sum_{n=1}^{N_X} M_{X_n} \frac{\partial \overline{P}}{\partial \log \xi_n}\left(\mathbf{1}_{N_A}, \mu^{M_{X_1}}, \ldots, \mu^{M_{X_{N_X}}}, \mathbf{1}_{N_V}\right) \qquad (3)$$





Now, adding the contributions of every molecule, the next relationship yields the transform of the $z$-distribution of time average radius of gyration for all polymer molecules:

$$\overline{\left\langle s^2\right\rangle}_z(\mu)\sum_{m=1}^{\infty} M_m^2 P(M_m) = \sum_{m=1}^{\infty} M_m^2 P(M_m)\mu^{M_m}\left\langle s_m^2\right\rangle = \sum_{l=1}^{N_V} b_l^2 \frac{\partial^2 \overline{V}_l}{\partial\mu^- \partial\mu^+}_{|\mu^- = \mu^+ = \mu} + \sum_{n=1}^{N_X}\sum_{p=1}^{N_X} M_{X_n} M_{X_p}\left\langle s_p^2\right\rangle \frac{\partial^2 \overline{P}}{\partial\xi_n \partial\xi_p}\left(1_{N_A}, \mu^{M_{X_1}}, \ldots, \mu^{M_{N_X}}, 1_{N_V}\right) \qquad (4)$$

**Kinetic Modeling**

Introducing the *stoichiometric coefficients* $\nu$ for the reactions among active species, the reaction which forms a bond $\mathbf{V}_l$ (examples being propagation, termination by combination), with a rate $k_l A_{g^-} A_{g^+}$, *is the process:*

$$\left\langle \sum_{i=1}^{N_A} a_i^- \mathbf{A}_i \right\rangle \mathbf{X}_{g_{X_l}^-} + \mathbf{X}_{g_{X_l}^+} \left\langle \sum_{i=1}^{N_A} a_i^+ \mathbf{A}_i \right\rangle \xrightarrow{k_l} \left\langle \sum_{i=1}^{N_A} (a_i^- + \nu_{li}^-)\mathbf{A}_i \right\rangle \mathbf{X}_{g_{X_l}^-} \mathbf{V}_l \mathbf{X}_{g_{X_l}^+} \left\langle \sum_{i=1}^{N_A} (a_i^+ + \nu_{li}^+)\mathbf{A}_i \right\rangle$$

In a similar way, $N_R^{**}$ bimolecular reactions, with rates $k_n^{**} A_{g_n^{**-}} A_{g_n^{**+}}$ (such as transfer reactions, termination by dismutation) and $N_R^*$ unimolecular reactions (spontaneous termination, initiations), with rates $k_n^* A_{g_n^*}$, neither of which create bonds, are also considered in the kinetic schemes.

Using the principle of equal reactivity, transformed rate equations for the polymer species and the pendant chains concentrations can be written, as described in [3, 4]:

$$\overline{R}_P = \sum_{l=1}^{N_V} k_l \left( \overline{\nu}_l^- \overline{\nu}_l^+ \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}} \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}} - \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}} A_{g_l^+} - \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}} A_{g_l^-} \right) +$$

$$\sum_{l=1}^{N_R^{**}} k_l^{**} \left[ \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^{\cdots -}}} A_{g_l^{\cdots +}} \left( \overline{\nu}_l^{**-} - 1 \right) + \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^{\cdots +}}} A_{g_l^{\cdots -}} \left( \overline{\nu}_l^{**+} - 1 \right) \right] + \tag{5}$$

$$\sum_{l=1}^{N_R^*} k_l^* A_{g_l^*} \left( \overline{\nu}_l^* - 1 \right)$$

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

$$\frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}^-} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^-}^-} + \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}^+} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^+}^+} + \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}^+} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^-}^+}$$

$$\left. - A_{g_l^-} \left( \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^+}^-} + \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^+}^+} \right) - A_{g_l^+} \left( \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^-}^-} + \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^-}^+} \right) \right] + \tag{6}$$

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

$$\left\{ A_{g_l^{\cdots +}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{\cdots -}}^-} \left[ \overline{\nu}_l^{**-} \left( \alpha^-, \xi^- \right) - 1 \right] + A_{g_l^{\cdots +}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{\cdots -}}^+} \left[ \overline{\nu}_l^{**-} \left( \alpha^+, \xi^+ \right) - 1 \right] \right.$$

$$\left. + A_{g_l^{\cdots -}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{\cdots +}}^-} \left[ \overline{\nu}_l^{**+} \left( \alpha^-, \xi^- \right) - 1 \right] + A_{g_l^{\cdots -}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{\cdots +}}^+} \left[ \overline{\nu}_l^{**+} \left( \alpha^+, \xi^+ \right) - 1 \right] \right.$$

$$\overline{\nu}_l^{\pm} = \varphi_l \prod_{k=1}^{N_A} \alpha_k^{\nu_{lk}^{\pm}} \prod_{j=1}^{N_X} \xi_j^{\nu_{X_{lj}}^{\pm}} \tag{7}$$

$$\overline{\nu}_l^Z = \prod_{k=1}^{N_A} \alpha_k^{\nu_{lk}^Z} \prod_{j=1}^{N_X} \xi_j^{\nu_{X_{lj}}^Z} \qquad Z = *, **^+, **^- \tag{8}$$





Insertion of the above rate expressions in mass balances of ideal reactors leads to first order non-linear partial differential equations, which can be solved in order to get the distributions in Fourier domain or their moments as shown by Costa and Dias [3, 4].

**Results and Discussion**

A check of this method was first done with a simple polycondensation in a batch reactor, which leads to an analytical solution, and the classical results obtained by Zimm and Stockmayer [6] were again obtained.

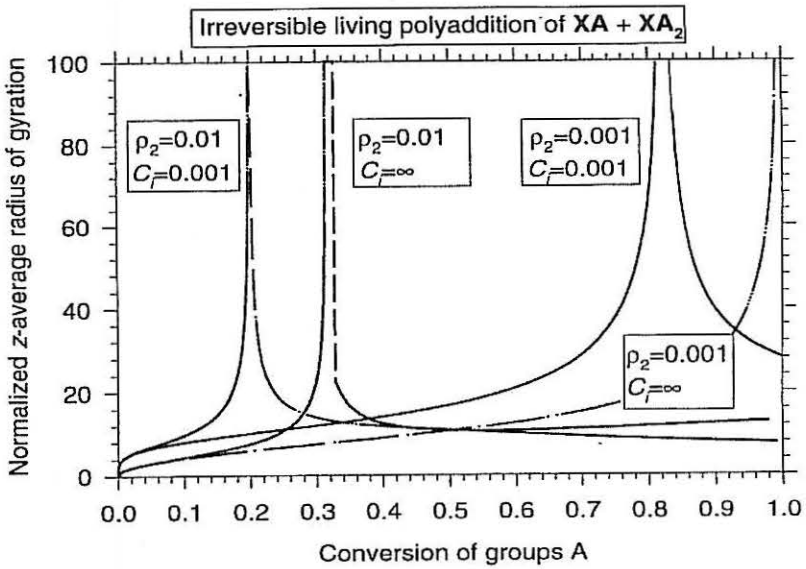


Figure 1: Predicted $z$-average radius of gyration, normalized by the value for dimer, vs. conversion of **A** groups in the polyaddition without termination of **XA** + **XA$_2$** in a batch reactor, for different values of initial mole fraction of **A** groups in difunctional monomer $\varrho_2$ and of relative initiation rate constant $C_i = k_i/k_p$ (see Costa and Dias [4]).

No complete analytical solution exists for the polyaddition of a mixture of mono- + difunctional monomers $\mathbf{XA} + \mathbf{XA_2}$ in a batch reactor (analyzed by Tobita [7] by Monte Carlo simulation and by Costa and Dias [3] using the present approach, without results concerning molecular sizes). This kind of chemical systems can not be described by TBP in a straightforward way (for the linear case, classical TBP will predict a Schulz-Flory chain length distribution instead of a Poisson distribution). Despite severe numerical difficulties after gelation, a complete study, summarized in fig. 1, could be undertaken for this and similar systems. Without loss of generality, the radii of gyration of repeating units was in this case study considered negligible, all bonds were assumed to have same length and results have been normalized by the value for dimer.

Still more complex systems (radical polymerizations, polycondensations with ring formation) have also been simulated using this approach.

**Acknowledgements**

Financial support by Fundação de Ciência e Tecnologia through program PRAXIS XXI (contract 3/3.1/CEG/2525/95) and by Instituto Politécnico de Bragança is gratefully acknowledged.





**Literature References**

[1] G. R. Dobson and M. Gordon, J. Chem. Phys. 41 (1964), 2389.

[2] M. Gordon and G. N. Malcolm, Proc. Roy. Soc. London A 295 (1966), 29.

[3] M. R. N. Costa and R. S. Dias, Chem. Eng. Sci. 49 (1994), 491.

[4] M. R. N. Costa and R. S. Dias, 5-th International Workshop on Polymer Reaction Engineering, DECHEMA Monographs 131 (1995), 523.

[5] W. L. Mattice and U. W. Sutter, Conformational Theory of Large Molecules, Wiley (1994), 5.

[6] B. H. Zimm and W. H. Stockmayer, J. Chem. Phys. 17 (1949), 1301

[7] H. Tobita, J. Polym. Sci. 32(B) (1994), 911.