RIGOROUS MODELLING OF IRREVERSIBLE NON-LINEAR POLYMERIZATIONS

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This paper summarizes recent developments of a rigorous kinetic method for modelling of non-linear irreversible polymerizations with a finite number of intramolecular cyclizations. Some changes have been introduced in order to perform much more efficient computations with polyadditions. The procedure for obtaining z-averaged distributions of gyration radius for gaussian chain molecules is briefly described. Chain length distributions, gel properties (such as the concentrations of elastically active junctions and chains) and average gyration radii were computed for non-radical copolymerization of monomers with one and with two terminal double bonds. Predictions of average molecular weights before gelation for free radical copolymerization of that same kind of monomers and vinyl acetate homopolymerization are also discussed.

MODÈLE RIGOUREUX DE LA POLYMÉRISATION NON LINÉAIRE IRRÉVERSIBLE

Cet article présente une synthèse des récents progrès dans le domaine du développement d'un modèle cinétique rigoureux de la polymérisation non linéaire réversible avec un nombre fini de cyclisations intramoléculaires. Certains changements ont été introduits afin de pouvoir faire des calculs des réactions de polyaddition. La procédure pour l'obtention des distributions à moyenne de "z" des rayons de giration des molécules à chaîne gaussienne est décrite. La distribution des longueurs de chaînes, les propriétés des gels (par exemple la concentration de jonctions et de chaînes élastiques) et les rayons de giration moyenne sont calculés pour le cas de la copolymérisation non radicalaire avec des molécules disposant d'une ou deux liaisons terminales. Des prévisions des masses moléculaires moyennes de la copolymérisation radicalaire (avant le début de la gélation), ainsi que pour l'homopolymérisation de l'acétate de vinyl sont présentées.

STRENGES MODELL FÜR IRREVERSIBLE UNLINEARE POLYMERISATIONEN

Der Artikel fasst die Durchführung einer neuen strengen kinetischen Methode zum Modeling irreversibler unlinearen Polymerisationen mit einer bestimmten Zahl von intramolekularen Zyklisierungen zusammen. Einige Veränderungen erlaubten wirksamere Berechnungen mit Polyadditionen. Es gibt eine kurze Beschreibung des Vorgehens, das zur Darstellung von durchschnittlichen Distributionen des kreisenden Radius für gaussche Kettenmoleküle führt. Die Distribution der Molekülkettenlänge, die Geleigenschaften (wie zum Beispiel die Konzentrationen der elastisch wirkenden Verzweigungen und Ketten) und die durchschnittlichen kreisenden Radien wurden für die nicht-radikalartigen Monomercopolymerisation mit einer und mit zwei Enddoppelbindungen berechnet. Es wurde auch diskutiert über die Prädiktionen der durchschnittlichen Molekulargewichte vor der Gelatinierung für die nicht-radikalartige Copolymerisation der gleichen Art von Monomeren und die Homopolymerisation von Vinylacetat.

MODELO RIGUROSO DE LA POLIMERIZACIÓN NO LINEAL IRREVERSIBLE

Este artículo presenta una síntesis de los recientes progresos en el campo de desarrollo de un modelo cinético riguroso de polimerización no lineal reversible con un número terminado de ciclos intramoleculares. Se han introducido ciertos cambios con la finalidad de hacer posible la realización de los cálculos de las reacciones de poliadición. Se describe el procedimiento para la obtención de distribuciones de media " z " de los rayos de rotación de las moléculas en cadena gausiana. La distribución de la talla de las cadenas, las propiedades de geles (por ejemplo la concentración de uniones y de cadenas elásticas) y los rayos de rotación en media, se calculan en el caso de la copolimerización no radical con moléculas que disponen de uno o de dos enlaces terminales. Se presentan previsiones de masas moleculares medias de la copolimerización radical (antes del inicio de la gelación), así como para la homopolimerización del acetato de vinilo.

MODELIZAÇÃO RIGOROSA DAS POLIMERIZAÇÕES NÃO LINEARES IRREVERSÍVEIS

Este artigo resume alguns desenvolvimentos recentes de um método cinético para modelizar rigorosamente as polimerizações não lineares irreversíveis com um número finito de ciclizações intramoleculares. Algumas modificações foram introduzidas de forma a melhorar bastante o desempenho dos cálculos nas poliadições. Descreve-se brevemente o procedimento para obter as distribuições dos raios de giração moleculares médios z para moléculas de cadeia gaussiana. Distribuições de grau de polimerização, propriedades do gel (tais como as concentrações de junções e cadeias elasticamente activas) e raios de giração médios foram calculados para copolimerizações não radicalares de monómeros com uma e duas ligações duplas terminais. Também se discutem as previsões de massas moleculares médias antes da gelificação para o mesmo tipo de monómeros e para a homopolimerização do acetato de vinilo.

mots-clés ● keywords

génie des procédés • modélisation • distribution des masses moléculaires • polymérisation • irreversible
chemical engineering • modelling • molecular weight distribution • polymerization • irreversible

Polymer chain length and molecular weight distributions

A useful treatment of irreversible non-linear polymerizations with a finite number of intramolecular cyclizations results of lumping all position isomers with *same numbers* of active groups $\mathbf{A}_1$, ..., $\mathbf{A}_{N_A}$ and inactive groups (including repeating units) $\mathbf{X}_1$, ..., $\mathbf{X}_{N_X}$ into species $\mathbf{P}(\mathbf{a}, \mathbf{x})$, in which the vectors $\boldsymbol{a} = [a_1 \ldots a_{N_A}]$ and $\mathbf{x} = [x_1 \ldots x_{N_x}]$ collect those counting variables. In what follows, mole concentrations of the different species (in bold) will be denoted by the corresponding italicized variables.

Most of the times the *vectorial discrete transform* of the distribution of polymer mole concentrations with respect to the numbers of active and inactive groups (the polymer vector chain length distribution CLD) will be easier to compute than its real-domain counterpart :

$$\overline{P}(\alpha,\xi)=\sum_{a_1=0}^{\infty}\alpha_1^{a_1}\ldots\sum_{a_{N_A}=0}^{\infty}\alpha_{N_A}^{a_{N_A}}\sum_{x_1=0}^{\infty}\xi_1^{x_1}\ldots \sum_{x_{N_x}=0}^{\infty}\xi_{N_x}^{x_{N_x}}P\left(a_1,\ldots,a_{N_A},x_1,\ldots,x_{N_x}\right) \qquad (1)$$

When the distribution relative to molecular weight is needed, the following transform is introduced:

$$\overline{P}(\mu)=\sum_{m=1}^{\infty}\mu^{M_m}P(M_m) = \overline{P}\left(\mu^{M_{A_1}},\ldots,\mu^{M_{A_{N_A}}},\mu^{M_{X_1}},\ldots,\mu^{M_{X_{N_X}}}\right) \qquad (2)$$

An efficient and accurate numerical inversion of these transforms is feasible by computing the transform in some thousands or tens of thousands of evenly spaced points in a circle or a sphere in complex plane centred at the origin and using FFT (Costa and Villermaux, 1988).

Average molecular weights

Moments relative to the numbers of groups (or chain lengths) are obtained by differentiation of (1) with respect to the natural logarithms of Laplace parameters and setting them all to unity.

Performing the same operation with (2), linear relations between moments with respect to molecular weight (or any other molecular property linearly related to the chain lengths) and moments relative to the various chain lengths can be written. Average molecular weights which are ratios of such moments are thus obtained.

Since in real problems the numbers of different groups are typically between 5 and 20 (much more if ring formation is to described, since concentrations of all ring forming groups must be explicitely followed), there are often *hundreds* or *thousands* of moments with respect to chain lengths up to order 3 to be computed.

Modelling of polyadditions improves considerably by introducing a set of *generalized monomers* , including monomers, initiators, transfer agents or by-products, which are active groups $\mathbf{A}_k$ with $k > N_A$. Not only this renders the kinetic description less confusing, but also reduces the number of active groups which appear in the distributions and therefore decreases the numbers of moments which need be computed.

Molecular structure

A key point for the usefulness of the approach proposed by the present authors is its ability to describe molecular structure and predict some average molecular properties. For that purpose, along with polymer CLD already discussed, other structural species are introduced, the bonds $\mathbf{V}_m$ and the junctions $\mathbf{J}_n$ which connect them.

Some bonds are *long* chains (i.e., amenable to length changes and therefore contributing to molecular entropy) already present in monomers, others are formed by reaction between a pair of active groups (and so have a fixed length) :

$$\mathbf{J}^-\mathbf{A}_{g_m^-} + \mathbf{J}^+\mathbf{A}_{g_m^+} \xrightarrow{k_m} \mathbf{J}^-\mathbf{V}_m\mathbf{J}^+$$

Bonds have a positive and a negative sense, unless they are formed by reactions of identical groups, as in the silanol condensation.

To each kind of bond are associated the chain length and molecular weight distributions of :

- one sided pendant chains

$$V_m^-\left(a_1,\ldots,a_{N_A},x_1,\ldots,x_{N_X}\right)$$

and $$V_m^+\left(a_1,\ldots,a_{N_A},x_1,\ldots,x_{N_X}\right) ;$$

- two sided pendant chains

$$V_m\left(a_1^-,\ldots,a_{N_A}^-,a_1^+,\ldots,a_{N_A}^+,x_1^-,\ldots,x_{N_X}^-,x_1^+,\ldots,x_{N_X}^+\right).$$

Junctions are the loci where 3 or more chains meet. They are already present in the monomers and shall be distinguished according to the numbers of groups $\mathbf{a}^J$ and $\mathbf{x}^J$ and bonds $\mathbf{v}^-$ and $\mathbf{v}^+$ to which they are connected to,

$$\mathbf{J}_n\left(a_1^J,\ldots,a_{N_A}^J,x_1^J\ldots,x_{N_X}^J,v_1^-\ldots,v_{N_V}^-,v_1^+\ldots,v_{N_V}^+\right)$$

being such a species.

Extinction probabilities are the fractions of finite pendant chains, normalized 0-th order moments of chain length distributions of one sided pendant chains (1_N is a vector with N one's):

$$u_m^{\pm}=\frac{\overline{V}_m^{\pm}\left(1_{N_A},1_{N_X}\right)}{V_m} \qquad (3)$$

They allow the evaluation of the transform of distribution of mole concentrations of junctions $\mathbf{T}_n$ connected to z infinite chains :

$$\overline{T}_n\left(\alpha^J,\xi^J,\zeta\right)=\overline{J}_n\left[\alpha^J,\xi^J,\mathbf{u}^-+\zeta\left(1_{N_V}-\mathbf{u}^-\right),\mathbf{u}^++\zeta\left(1_{N_V}-\mathbf{u}^+\right)\right] \qquad (4)$$

Network properties

Elastically active network junctions EANJ are connected to 3 or more independent infinite chains, so that overall EANJ concentration μ_e becomes :

$$\mu_e = \sum_{n=1}^{N_J} \left[\overline{T}_n\left(1_{N_A}, 1_{N_X}, 1\right) - \overline{T}_n\left(1_{N_A}, 1_{N_X}, 0\right) \left. \frac{\partial \overline{T}_n\left(1_{N_A}, 1_{N_X}, \zeta\right)}{\partial \zeta} \right|_{\zeta=0} - \frac{1}{2} \left. \frac{\partial^2 \overline{T}_n\left(1_{N_A}, 1_{N_X}, \zeta\right)}{\partial \zeta^2} \right|_{\zeta=0} \right] \quad (5)$$

Elastically effective network chains EANC connect two EANJ, and total EANC concentration ν_e is therefore :

$$\nu_e = \frac{1}{2} \sum_{n=1}^{N_J} \left[\left. \frac{\partial \overline{T}_n\left(1_{N_A}, 1_{N_X}, \zeta\right)}{\partial \zeta} \right|_{\zeta=1} - \left. \frac{\partial \overline{T}_n\left(1_{N_A}, 1_{N_X}, \zeta\right)}{\partial \zeta} \right|_{\zeta=0} - \left. \frac{\partial^2 \overline{T}_n\left(1_{N_A}, 1_{N_X}, \zeta\right)}{\partial \zeta^2} \right|_{\zeta=0} \right] \quad (6)$$

These variables can be computed knowing the first moments of the T_n and the extinction probabilities.

Average molecular radius of gyration of polymers with gaussian chains

The average radius of gyration $\langle s^2 \rangle_m$ of a tree-like molecule m with gaussian chains is related to the molecular masses of the two fragments which result from breaking each bond (its average squared length being b_{ml}^2) :

$$\langle s^2 \rangle_m = \frac{\sum_{l=1}^{N_{V_m}} M_{ml}^- M_{ml}^+ b_{ml}^2}{M_m^2} \quad (7)$$

When the contributions of all isomers with all possible chain lengths are added, the following expression results for the transformed z-MWD of average gyration radius of all molecules:

$$\overline{\langle s^2 \rangle}_z(\mu) = \frac{\sum_{m=1}^{\infty} M_m^2 P_m \mu^{M_m} \langle s^2 \rangle_m}{\sum_{m=1}^{\infty} M_m^2 P_m} = \frac{\sum_{l=1}^{N_V} b_l^2 \left. \frac{\partial^2 \overline{V}_l}{\partial \log \mu^- \partial \log \mu^+} \right|_{\mu^- = \mu^+ = \mu}}{\sum_{m=1}^{\infty} M_m^2 P_m} \quad (8)$$

Kinetic modelling

The crux of this description is the introduction of the *stoichiometric coefficients* for the reactions among active species.

The reaction which forms a bond $\mathbf{V}_l$ (examples being propagation, termination by combination, and so on), with a rate $k_l A_{g_l}^- A_{g_l}^+$, is the process :

$$\left\langle \begin{matrix} \sum_{i=1}^{N_A} a_i^- \mathbf{A}_i \\ \sum_{i=1}^{N_X} x_i^- \mathbf{X}_i \end{matrix} \right\rangle \mathbf{J}^- + \mathbf{J}^+ \left\langle \begin{matrix} \sum_{i=1}^{N_A} a_i^+ \mathbf{A}_i \\ \sum_{i=1}^{N_X} x_i^+ \mathbf{X}_i \end{matrix} \right. \xrightarrow{k_l} \left. \begin{matrix} \sum_{i=1}^{N_A} \left(a_i^- + \nu_{li}^-\right) \mathbf{A}_i \\ \sum_{i=1}^{N_X} \left(x_i^- + \nu_{X_{li}}^-\right) \mathbf{X}_i \end{matrix} \right\rangle$$

$$\mathbf{J}^- \mathbf{V}_l \mathbf{J}^+ \left\langle \begin{matrix} \sum_{i=1}^{N_A} \left(a_i^+ + \nu_{li}^+\right) \mathbf{A}_i \\ \sum_{i=1}^{N_X} \left(x_i^+ + \nu_{X_{li}}^+\right) \mathbf{X}_i \end{matrix} \right.$$

The first N_R bonds are supposed to come from reactions between active groups belonging to polymers, while the next N_R' are formed by reactions between such a group and a generalized monomer and, finally, the last N_R'' bonds result from reactions involving generalized monomers.

Some other reactions do not create bonds :

- Bimolecular group exchange (transfers, termination by dismutation), with rates $k_n^{**} A_{g_l^{\cdots}} A_{g_l^{\cdots +}}$; the first $N_R'^{**}$ concern reactions between active groups belonging to polymers, as before the next $N_R'^{**}$ are reactions between such a group and a generalized monomer, the next $N_R''^{**}$ reactions involve generalized monomers and the last N_T are reactions between an active group in polymer with a generalized monomer creating a new polymer molecule at the side of the previously extant generalized monomer (an example is transfer to a vinyl monomer) ;
- Unimolecular reactions (spontaneous termination, initiations), with rates $k_n^* A_{g_n}$; as above, the first N_R^* concern reactions of active groups belonging to polymer and the last $N_R'^*$ reactions are unimolecular reactions of generalized monomers.

Transformed rate equations

Using the principle of equal reactivity, rate equations for the various chemical species, such as polymer molecules, pendant chains and junctions can be written :

$$\begin{aligned} \overline{R}_P(\alpha, \xi) = & \sum_{l=1}^{N_R} k_l \left(\overline{\nu}_l^- \overline{\nu}_l^+ \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}} \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}} - \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}} A_{g_l^+} - \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}} A_{g_l^-} \right) + \sum_{l=1}^{N_R'} k_l^* \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^*}} \left(\overline{\nu}_l^* - 1\right) \\ & + \sum_{l=N_R+1}^{N_R+N_R'} k_l \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}} A_{g_l^+} \left(\overline{\nu}_l^- \overline{\nu}_l^+ - 1\right) + \sum_{l=N_R+N_R'+1}^{N_R+N_R'+N_R''} k_l A_{g_l^-} A_{g_l^+} \overline{\nu}_l^- \overline{\nu}_l^+ \\ & + \sum_{l=N_R+N_R'+1}^{N_R+N_R'+N_R''} k_l A_{g_l^-} A_{g_l^+} \overline{\nu}_l^- \overline{\nu}_l^+ + \sum_{l=1}^{N_R''} k_l^{**} \left[\frac{\partial \overline{P}}{\partial \log \alpha_{g_l^{\cdots -}}} A_{g_l^{\cdots +}} \left(\overline{\nu}_l^{**-} - 1\right) + \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^{\cdots +}}} A_{g_l^{\cdots -}} \left(\overline{\nu}_l^{**+} - 1\right) \right] \\ & + \sum_{l=N_R''+1}^{N_R''+N_R'''} k_l^{**} \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^{\cdots -}}} A_{g_l^{\cdots +}} \left(\overline{\nu}_l^{**} - 1\right) + \sum_{l=N_R''+1}^{N_R''+N_T} k_l^{**} A_{g_l^{\cdots -}} A_{g_l^{\cdots +}} \overline{\nu}_l^{***+} \end{aligned} \quad (9)$$

$$\overline{v}_l^{\pm} = \prod_{k=1}^{N_A} \alpha_k^{v_{lk}^{\pm}} \prod_{j=1}^{N_X} \xi_j^{v_{xlj}^{\pm}} \qquad (10a) \qquad \overline{v}_l^{*} = \prod_{k=1}^{N_A} \alpha_k^{v_{lk}^{*}} \prod_{j=1}^{N_X} \xi_j^{v_{xlj}^{*}} \qquad (10b) \qquad \overline{v}_l^{**\pm} = \prod_{k=1}^{N_A} \alpha_k^{v_{lk}^{**\pm}} \prod_{j=1}^{N_X} \xi_j^{v_{xlj}^{**\pm}} \qquad (10c)$$

$$\begin{aligned}
\overline{R}_{V_m}\left(\alpha^-,\xi^-,\alpha^+,\xi^+\right) &= \overline{R}_{BV_m}\left(\alpha^-,\xi^-,\alpha^+,\xi^+\right) + \sum_{l=1}^{N_R} k_l \left\{ \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^-}^-} \left[\overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}^+} - A_{g_l^+} \right] \right. \\
&+ \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^+}^-} \left[\overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) \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{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}^+} - A_{g_l^+} \right] \\
&\left. + \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^+}^+} \left[\overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) \frac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}^+} - A_{g_l^-} \right] \right\} + \sum_{l=N_R+1}^{N_R+N_R'} k_l A_{g_l^+} \left\{ \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^-}^-} \left[\overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) - 1 \right] \right. \\
&\left. + \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^-}^+} \left[\overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) - 1 \right] \right\} + \sum_{l=1}^{N_R^*} k_l^* \left\{ \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^*}^-} \left[\overline{v}_l^-\left(\alpha^-,\xi^-\right) - 1 \right] + \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^*}^+} \left[\overline{v}_l^+\left(\alpha^+,\xi^+\right) - 1 \right] \right\} \\
&\sum_{l=1}^{N_R^{**}} k_l^{**} \left\{ A_{g_l^{**+}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{**-}}^-} \left[\overline{v}_l^{**-}\left(\alpha^-,\xi^-\right) - 1 \right] + A_{g_l^{**-}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{**+}}^+} \left[\overline{v}_l^{**+}\left(\alpha^+,\xi^+\right) - 1 \right] \right. \\
&\left. + A_{g_l^{**-}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{**+}}^-} \left[\overline{v}_l^{**+}\left(\alpha^-,\xi^-\right) - 1 \right] + A_{g_l^{**-}} \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{**+}}^+} \left[\overline{v}_l^{**+}\left(\alpha^+,\xi^+\right) - 1 \right] \right\} \\
&+ \sum_{l=N_R^{**}+1}^{N_R^{**}+N_R^{***}} k_l^{**} A_{g_l^{**+}} \left\{ \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{**-}}^-} \left[\overline{v}_l^{**-}\left(\alpha^-,\xi^-\right) - 1 \right] + \frac{\partial \overline{V}_m}{\partial \log \alpha_{g_l^{**-}}^+} \left[\overline{v}_l^{**-}\left(\alpha^+,\xi^+\right) - 1 \right] \right\}
\end{aligned} \qquad (11a)$$

$$\overline{R}_{BV_l}\left(\alpha^-,\xi^-,\alpha^+,\xi^+\right) = \begin{cases} k_l \overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) \dfrac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}^-} \dfrac{\partial \overline{P}}{\partial \log \alpha_{g_l^+}^+}, & \text{if} \quad 1 \le l \le N_R \\ k_l \overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) \dfrac{\partial \overline{P}}{\partial \log \alpha_{g_l^-}^-} A_{g_l^+}, & \text{if} \quad N_R + 1 \le l \le N_R + N_R' \\ k_l \overline{v}_l^-\left(\alpha^-,\xi^-\right)\overline{v}_l^+\left(\alpha^+,\xi^+\right) A_{g_l^-} A_{g_l^+}, & \text{if} \quad N_R + N_R' + 1 \le l \le N_R + N_R' + N_R'' \\ 0, & \text{if} \quad N_R + N_R' + N_R'' \prec l \end{cases} \qquad (11b)$$

$$\begin{aligned}
\overline{R}_{V_m^{\pm}}(\alpha,\xi) &= \overline{R}_{V_m^{\pm}}(\alpha,\xi) + \sum_{l=1}^{N_R} k_l \left[\frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^-}} \left(\overline{v}_l^- \overline{v}_l^+ \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^+}} - A_{g_l^+} \right) + \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^+}} \left(\overline{v}_l^- \overline{v}_l^+ \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^-}} - A_{g_l^-} \right) \right] \\
&+ \sum_{l=N_R+1}^{N_R+N_R'} k_l A_{g_l^+} \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^-}} \left(\overline{v}_l^- \overline{v}_l^+ - 1 \right) + \sum_{l=1}^{N_R^*} k_l^* \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^*}} \left(\overline{v}_l^* - 1 \right) \\
&+ \sum_{l=1}^{N_R^{**}} k_l^{**} \left[A_{g_l^{**+}} \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^-}} \left(\overline{v}_l^{**-} - 1 \right) + A_{g_l^{**-}} \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^+}} \left(\overline{v}_l^{**+} - 1 \right) \right] + \sum_{l=N_R^{**}+1}^{N_R^{**}+N_R^{***}} k_l^{**} A_{g_l^{**+}} \frac{\partial \overline{V}_m^{\pm}}{\partial \log \alpha_{g_l^-}} \left(\overline{v}_l^{**-} - 1 \right)
\end{aligned} \qquad (12a)$$

$$\overline{R}_{BV_l^{\pm}}(\alpha,\xi) = \begin{cases} k_l \overline{v}_l^{\pm} \dfrac{\partial \overline{P}}{\partial \log \alpha_{g_l^{\pm}}} A_{g_l^{\pm}}, & \text{if} \quad 1 \le l \le N_R \\ k_l \overline{v}_l^{\pm} A_{g_l^-} A_{g_l^+}, & \text{if} \quad N_R + 1 \le l \le N_R + N_R' + N_R'' \\ 0, & \text{if} \quad N_R + N_R' + N_R'' \prec l \end{cases} \qquad (12b)$$

$$\bar{R}_{J_n}\left(\alpha^J,\xi^J,\varphi^-,\varphi^+\right)=\sum_{l=1}^{N_R}k_l\left\{\frac{\partial\bar{J}_n}{\partial\log\alpha^J_{g_l^-}}A_{g_l^+}\left[\bar{v}_l^-\left(\alpha^J,\xi^J\right)\varphi^+-1\right]+\frac{\partial\bar{J}_n}{\partial\log\alpha^J_{g_l^+}}A_{g_l^-}\left[\bar{v}_l^+\left(\alpha^J,\xi^J\right)\varphi^--1\right]\right\}$$
$$+\sum_{l=N_R+1}^{N_R+N'_R}k_lA_{g_l^+}\frac{\partial\bar{J}_n}{\partial\log\alpha^J_{g_l^-}}\left[\bar{v}_l^-\left(\alpha^J,\xi^J\right)\varphi^+-1\right]+\sum_{l=1}^{N^*_R}k^*_l\frac{\partial\bar{J}_n}{\partial\log\alpha^J_{g_l^*}}\left[\bar{v}_l^*\left(\alpha^J,\xi^J\right)-1\right]$$
$$+\sum_{l=1}^{N^{**}_R}k^{**}_l\left[A_{g_l^{**+}}\frac{\partial\bar{J}_n}{\partial\log\alpha^J_{g_l^{**-}}}\left[\bar{v}_l^{**-}\left(\alpha^J,\xi^J\right)-1\right]+A_{g_l^{**-}}\frac{\partial\bar{J}_n}{\partial\log\alpha^J_{g_l^{**+}}}\left[\bar{v}_l^{**+}\left(\alpha^J,\xi^J\right)-1\right]\right]$$
$$+\sum_{l=N^{**}_R+1}^{N^{**}_R+N^{***}_R}k^{**}_lA_{g_l^{***}}\frac{\partial\bar{J}_n}{\partial\log\alpha^J_{g_l^{***-}}}\left[\bar{v}_l^{***-}\left(\alpha^J,\xi^J\right)-1\right] \qquad (13)$$

Insertion of these rate expressions in mass balance equations in ideal reactors lead to 1st order non-linear partial differential equations, which can be solved by the method of characteristics (Costa and Dias, 1994).

Practical issues of computations

The problems which can be treated using this approach can be classified in two very different levels of difficulty :

1) *Average MW and average gyration radii before gelation*

Leads to initial value ODE system, with hundreds or thousands of equations, according to the number of required moments.

2) *CLD prediction and prediction of average properties after gelation*

Non-linear two-point boundary value problems with N_A equations 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).

Case study I : living polyaddition of a mono- and a difunctional monomer in a batch reactor

A theoretical reanalysis of these kind of systems has been recently performed by Tobita (1994) using analytical and Monte Carlo methods. The approach here described is an efficient alternative method of computing CLD (see fig. 1) even with complex kinetic schemes. Moreover, prediction of elastic properties is readily performed (fig. 2) as well as z-average radius of gyration (fig. 3).

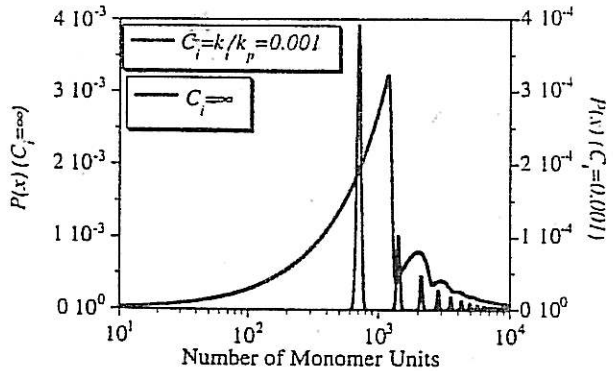

Fig. 1 CLD in the polyaddition without termination of a mono- and a difunctional monomer in a batch reactor at gel time, showing the effect of slow relative initiation rate constant C_i.

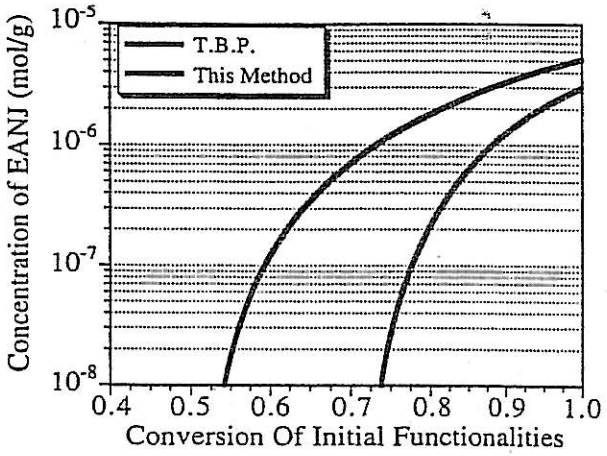

Fig. 2 Comparison between predictions of EANJ concentration vs. conversion of initial functionalities in the polyaddition without termination of a mono- and a difunctional monomer in a batch reactor, showing the huge error incurred by straightforward application of the Theory of branching Processes TBP.

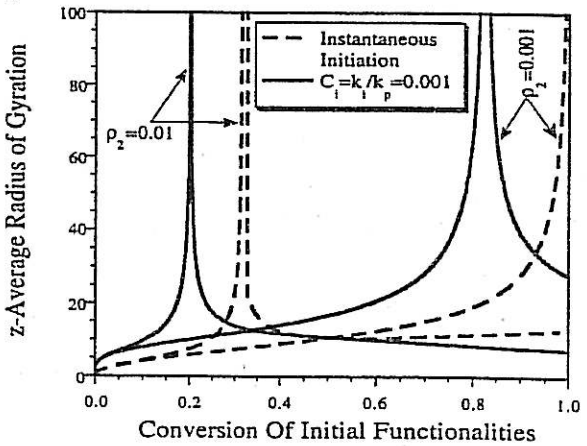

Fig. 3 Predicted normalized z-average radius of gyration vs. conversion of initial functionalities in the polyaddition without termination of a mono- and a difunctional monomer in a batch reactor, showing the effect of initial mole fraction of functionalities in difunctional monomer ρ_2 and relative initiation rate constant C_i.

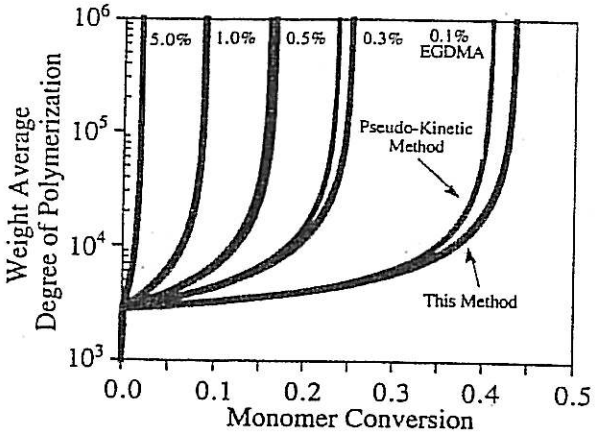

Fig. 4 Predicted weight-average degree of polymerization vs. monomer conversion in batch bulk radical polymerization of methyl methacrylate and ethylene glycol dimethacrylate for different initial weight fractions of difunctional monomer, according to pseudo-kinetic method (Li et al., 1989) and present approach.

Case study II : bulk radical copolymerization of methyl methacrylate/ ethylene glycol dimethacrylate

A reanalysis of experimental results and modelling by Li, Hamielec and Crowe (1989) was performed. If the same parameters as that reference are used, a slight shift of the approximate pseudo-kinetic method predicted curves of average molecular weight vs. time is observed relative to our more exact calculations (fig. 4), specially with low amounts of difunctional monomer. Thus, lower deviations between predicted and experimental gel conversions can be achieved (fig. 5), even without a new fit of parameters.

It was not yet possible to obtain predictions after gel point for this system because of severe numerical problems: parallel shooting was not yet implemented with "stiff" systems of ordinary differential equations.

Case study III : homogeneous radical polymerization of vinyl acetate in batch and continuous stirred tank reactors

In spite of the fairly large experimental and theoretical researches on this system, many inconsistencies have subsisted concerning values of kinetic parameters in different situations such as different solvent concentrations, different initiators and even between batch and continuous stirred tank reactors.

Several simplifications have been used in the past [Nagasubramanian and Graessley (1970), Chatterjee (1977), Verlaine (1982), Tobita (1994b)] which have a deleterious effect in the predictions of the reaction behaviour, such as the neglect of existence of poly-radicals, neglect of kinetic terms due to initiation, neglect of inhibition reactions and primary radical termination, use of a closure condition for the rates of moments. A detailed discussion is for the moment available only in Dias (1996), along with a brief report in Dias and Costa (1996). Present approach is specially convenient, because it eliminates the need of that kind of simplifications, leading always to a (closed) system of ordinary differential equations for the moments,

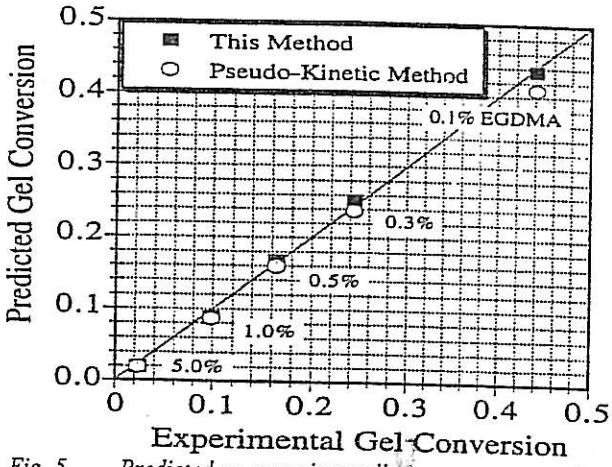

Fig. 5 Predicted vs. experimentally monomer conversion at gel point in batch bulk radical polymerization of a methyl methacrylate and ethylene glycol dimethacrylate using pseudo-kinetic method (Li et al., 1989) and present approach.

verifying initial conditions. A new fit of kinetic parameters has been performed, and agreement with experiment is excellent in all available data (figs. 6, 7 and 8).

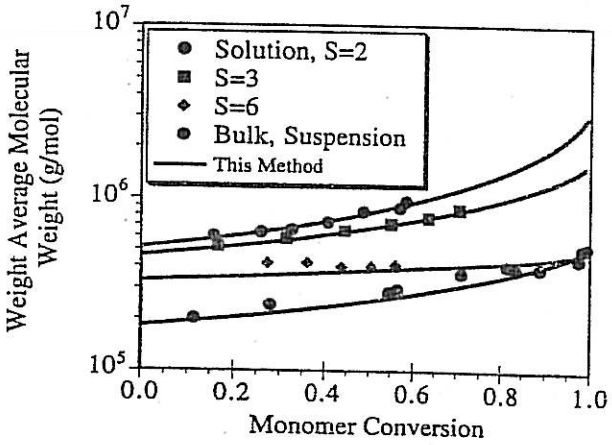

Fig. 6 Predicted vs. experimentally measured weight average molecular weight as a function of monomer conversion in batch bulk, solution (several initial mole ratios of t-butanol S) and suspension radical polymerization of vinyl acetate using present approach and newly fit kinetic parameters.

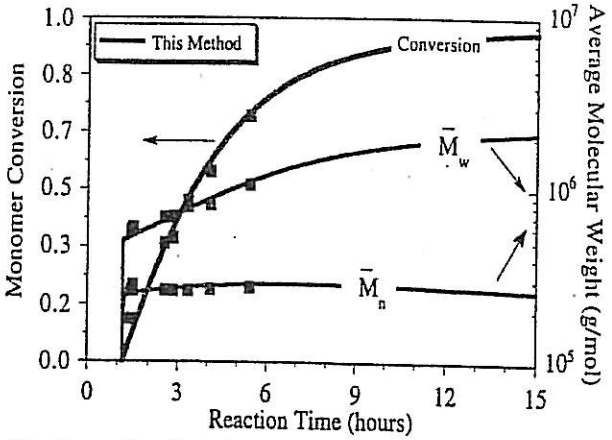

Fig. 7 Predicted vs. experimentally measured (Nagasubramanian and Graessley, 1970) monomer conversion and weight average molecular weight as functions of time in batch solution (initial mole ratio of t-butanol S = 2) radical polymerization of vinyl acetate using present approach and newly fit kinetic parameters.

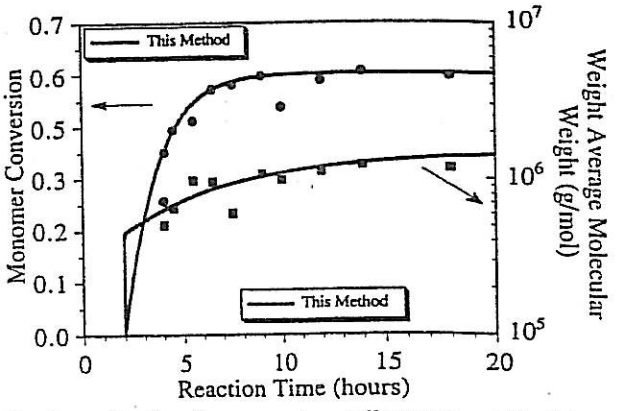

Fig. 8 Predicted vs. experimentally measured (Verlaine, 1982) monomer conversion and weight average molecular weight as functions of time for solution (initial mole ratio of t-butanol S = 2) radical polymerization of vinyl acetate in a transient CSTR using present approach and newly fit kinetic parameters.

Current problems under study

1) *Ring formation*

A systematic procedure is being prepared in order to define in an automated way the fragments and their stoichiometric coefficients when intramolecular reactions are present.

2) *Post-gel reaction and CLD prediction in non-linear radical polymerization*

A parallel shooting routine for two point boundary value problems with stiff ODE is being implemented.

CONCLUSIONS

For the simulations which could be successfully performed up now (free radical polymerizations before gel point, polycondensations, non-radical polyadditions), the proposed method of polymerization modelling has required only reasonable computation resources. Kinetic modelling of complex irreversible polymerizations can be done with less severe simplifying assumptions than current approaches, and leads to better predictions of average polymer and network properties.

More exact results concerning radical polymerization (presence of multiple radicals, no need of pseudo-steady state hypothesis) could thus be obtained.

This method has been developped with the aim of providing an automated way of dealing with complex kinetic schemes. It can be accepted that such goal is now close to be achieved.

Further improvements in basic numerical methods are still needed to cope with some aspects of radical polymerization.

Acknowledgements

Financial support by JNICT through project 3/3.1/CEG/2525/95 and by Instituto Politécnico de Bragança (grant to R. Dias) is gratefully acknowledged.

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La régression PLS
Théorie et pratique

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De nombreux problèmes industriels ou de management peuvent être décrits sous la forme d'un système à entrées-sorties : les variables de sortie Y du système dépendent de variables d'entrée X plus ou moins contrôlables. Il s'agit de comprendre et de décrire les relations souvent très complexes entre X et Y, en l'absence d'un modèle théorique.

La régression PLS (Partial Least Squares) est une méthode d'analyse des données spécifiquement construite pour l'étude de ce type de problème. Elle a été proposée en 1983 par Svante Wold et ses collaborateurs et connaît depuis de grands développements, principalement dans le domaine des industries chimiques, pétrolières et agro-alimentaires.

La régression PLS doit pouvoir s'appliquer à de nombreux domaines avec le même succès qu'en chimie. C'est ce que nous voulons démontrer dans ce livre dont l'objet est de faire le point sur cette méthode, à la fois sur les plans théorique et pratique.

Sur le plan théorique, nous avons eu trois objectifs :

- Situer la régression PLS parmi les méthodes d'association et de prédiction en analyse des données : analyse canonique, analyse factorielle inter-batteries, analyse des redondances, algorithme NIPALS, algorithme SIMPLS et approche PLS.
- Décrire l'algorithme de régression PLS dans sa forme originale telle qu'elle est programmée dans des logiciels comme SIMCA ou The Unscrambler.
- Présenter en détail les principales propriétés mathématiques de la régression PLS car leur connaissance est essentielle pour une bonne utilisation de la méthode.

Sur le plan pratique, nous illustrons l'apport de la régression PLS en l'utilisant sur de nombreux exemples tirés de la littérature. Nous décrivons avec un maximum de détails les sorties du logiciel de référence (SIMCA) à partir de ces exemples. Ainsi, un utilisateur de la régression PLS de vrait trouver dans ce livre toute l'aide nécessaire pour une exploitation optimale des résultats.

Table des matières

1998. Relié, 16 x 24, 264 p., 94 fig., 35 tabl., 320 F
ISBN 2-7108-0735-1

Editions TECHNIP
27 rue Ginoux, 75737 Paris cedex 15