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New developments in the kinetic modelling of complex non-linear polymerizations

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Summary

A new kinetic method for modelling and simulation of non-linear irreversible polymerizations is described. In comparison to a previous version, it is easier to use and more efficient in performing computations with polyadditions. Chain length distributions and gel properties (such as the concentrations of elasticaly active junctions and chains) were computed for anionic copolymerization of monomers with one and with two terminal double bonds. Free radical copolymerization of the same monomers could be simulated with success only before gelation because of severe numerical sensitivity.

Zusammenfassung

Ein kinetisches Verfahren für die Modellierung und Simulation von nichtlinearen irreversiblen Polymerisationen wird beschrieben. Im Vergleich zu einem vorhergehenden Verfahren ist dieses einfacher zu benutzen und effizienter bei der Berechnung von Polyadditionsreaktionen. Kettenlängenverteilungen und Eigenschaften des Gels (z. B. die Konzentrationen der elastisch-aktiven Verbindungen und Ketten) für anionische Copolymerisation von Monomern mit ein und zwei Doppelbindungen können vorausgesagt werden. Bisher ist die Simulation der Copolymerisation freier Radikale derselben Monomeren nur vor dem Stockpunkt gelungen.

General principles

A kinetic modelling of irreversible polymerizations with arbitrary stoichiometries (Costa and Dias [1]) was recently used in the description of the cure of epoxide resins, allowing the prediction of average molecular weights before and after gelation and elastic properties of gel, and will be the starting point for this analysis.

A finite number N_A of reactive groups $\mathbf{A}_1, ..., \mathbf{A}_{N_A}$ is assumed to be present in the chemical system. Their mole concentrations are named for simplicity $A_1, ..., A_{N_A}$. A set of N_B reactive compounds $\mathbf{B}_1, ..., \mathbf{B}_{N_B}$ includes monomers, initiators, transfer agents or by-products. Another set of N_X groups $\mathbf{X}_1, ..., \mathbf{X}_{N_X}$ encompasses the products of reactions between active groups, but which will not react any further. To this class belong invariant moieties named "repeating units", which may exist already in the monomers in the case of polycondensation reactions. Also, in order to describe molecular structure with enough detail so that prediction of elastic properties is possible, every group must be associated with the *junction* $\mathbf{G}_i$ to which it is attached. Some of them are already present in monomers, others are formed by reaction between a pair of groups.

Each polymer molecule is defined through the numbers of groups it contains, without taking into account its isomers. A molecule with a vector of numbers of active groups $\boldsymbol{a} = [a_1 \dots a_{N_A}]$, a vector of product groups $\mathbf{x} = [x_1 \dots x_{N_X}]$ and vectors of linking groups $\mathbf{v} = [\nu_{AA}\ \nu_{AB}\ \nu_{BB}]$ will be named $\mathbf{P}(\mathbf{a}, \mathbf{x}, \mathbf{v})$. Its mole concentration is written as $P(\mathbf{a}, \mathbf{x}, \mathbf{v})$, and it will be found most of the times through its vectorial discrete transform :

$$\overline{P}(\alpha,\xi,\phi) = \sum_{a_1=0}^{\infty} \alpha_1^{a_1} \dots \sum_{x_1=0}^{\infty} \xi_1^{x_1} \dots \sum_{\nu_1=0}^{\infty} \phi_1^{\nu_1} \dots \sum_{\nu_{N_V}=0}^{\infty} \phi_{N_V}^{\nu_{N_V}} P(a_1,\dots,a_{N_A},x_1,\dots,\nu_{N_V}) \qquad (1)$$

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

When a group $\mathbf{A}_i$ attached to some junction $\mathbf{G}$ reacts with another group $\mathbf{A}_j$ attached to a junction $\mathbf{H}$ in another molecule, creating a link $\mathbf{V}_{AA_{ij}}$ between the two junctions, the vector of numbers of active groups attached to $\mathbf{G}$ *changes* by $\nu_{AAA_{ij}} = [\nu_{AAA_{ij1}} \dots \nu_{AAA_{ijN_A}}]$ and the vector of numbers of active groups attached to $\mathbf{H}$ changes by $\nu_{AAA_{ji}} = [\nu_{AAA_{ji1}} \dots \nu_{AAA_{jiN_A}}]$:

$$\mathbf{G}\dots(\mathbf{A}_k)_m\dots+\mathbf{H}\dots(\mathbf{A}_l)_n\dots \xrightarrow{k_{AA_{ij}}} \dots(\mathbf{A}_k)_{\nu_{AAA_{ijl}}+m}\dots\mathbf{G}\mathbf{V}_{AA_{ij}}\mathbf{H}\dots(\mathbf{A}_l)_{\nu_{AAA_{jil}}+n}\dots$$

Some other reactions do not produce linking groups between repeating units. If a group $\mathbf{A}_i$ reacts in that way by an unimolecular reaction, the apparent constant is named $k^*_{A_i}$, and if the reaction is bimolecular and involves $\mathbf{A}_j$, its apparent constant is $k^*_{AA_{ij}}$. The changes in numbers of groups $\mathbf{A}_k$, $\mathbf{B}_k$, $\mathbf{X}_k$ brought up by those reactions are $\nu^*_{AA_{ik}}, \nu^*_{AB_{ik}}, \nu^*_{AX_{ik}}$ and $\nu^*_{AAA_{ijk}}, \nu^*_{AAB_{ijk}}, \nu^*_{AAX_{ijk}}$. Other reactions among groups and isolated compounds are described by a similar notation.

Using the principle of equal reactivity, rate laws can be written for the various chemical species, yielding in the case of the polymer molecules:

$$\overline{R}_P = \sum_{i=1}^{N_A}\sum_{j=1}^{N_A} k_{AA_{ij}} \frac{\partial \overline{P}}{\partial \log \alpha_i}\left(\frac{\overline{\omega}_{AA_{ij}}}{2}\phi_{AA_{ij}}\frac{\partial \overline{P}}{\partial \log \alpha_j} - A_j\right) + \sum_{i=1}^{N_A} k^*_{A_i}\frac{\partial \overline{P}}{\partial \log \alpha_i}\left(\overline{\nu}^*_{Ai} - 1\right) +$$
$$\sum_{i=1}^{N_A}\sum_{j=1}^{N_A} k^*_{AA_{ij}}\frac{\partial \overline{P}}{\partial \log \alpha_i}A_j\left(\frac{\overline{\omega}^*_{AA_{ij}}}{2} - 1\right) + \sum_{i=1}^{N_B}\sum_{j=1}^{N_B} k_{BB_{ij}}\frac{\overline{\omega}_{BB_{ij}}}{2}\phi_{BB_{ij}}B_iB_j \qquad (2)$$
$$+\sum_{i=1}^{N_A}\sum_{j=1}^{N_B}\frac{\partial \overline{P}}{\partial \log \alpha_i}B_j\left[k_{AB_{ij}}\left(\overline{\omega}_{AB_{ij}}\phi_{AB_{ij}} - 1\right) + k^*_{AB_{ij}}\left(\overline{\omega}^*_{ABij} - 1\right)\right]$$

$$\overline{\nu}_{MN_{ij}} = \prod_{k=1}^{N_A}\alpha_k^{\nu_{MNA_{ijk}}}\prod_{x=1}^{N_X}\xi_x^{\nu_{MNX_{ijx}}} \qquad (3)$$

$M, N \in \{A, B\}$

$$\omega_{MN_{ij}} = \nu_{MN_{ij}} + \nu_{MN_{ji}} \qquad (4)$$
$$\overline{\omega}_{MN_{ij}} = \overline{\nu}_{MN_{ij}}\,\overline{\nu}_{MN_{ji}}$$
$M, N \in \{A, B\}$

$$\overline{\nu}^*_{AM_{ij}} = \prod_{k=1}^{N_A}\alpha_k^{\nu^*_{AMA_{ijk}}}\prod_{x=1}^{N_X}\xi_x^{\nu^*_{AMX_{ijx}}} \qquad (5)$$

$M = A$ or B

$$\omega^*_{AM_{ij}} = \nu^*_{AM_{ij}} + \nu^*_{AM_{ji}} \qquad (6)$$
$$\overline{\omega}^*_{AM_{ij}} = \overline{\nu}^*_{AM_{ij}}\,\overline{\nu}^*_{AM_{ji}}$$
$M = A$ or B

$$\bar{\nu}^{\bullet}_{A_i} = \prod_{k=1}^{N_A} \alpha_k^{\nu^{\bullet}_{AA_{ik}}} \prod_{x=1}^{N_X} \xi_x^{\nu^{\bullet}_{AX_{ix}}} \qquad (7)$$

Insertion of these rate expressions in mass balance equation of polymer species leads to a partial differential equation for $\bar{P}$, which can be solved by the method of characteristics.

Gel properties, such as the concentration of elasticaly active junctions and chains and the weight fraction of dangling chains, as well as distributions of average mean square molecular radius, assuming valid the Gaussian chain model for describing the polymer molecules, can also be computed, but space limitations prevent us from presenting the details.

Simulation of copolymerizations of mono + divinyl monomers

A copolymerization of a monovinyl compound **RCH=CH$_2$ (B_1)** with a divinyl compound **R'(CH=CH$_2$)$_2$ (B_2)**is initiated by an organolithium **R"Li (B_3)**. We took as example styrene + 1,4-divinylbenzene + **LiC$_6$H$_5$**. Each monomer was considered a single junction. This is essentially a "living" polymerization at temperatures below ambient, but a slow spontaneous anion deactivation (Bywater [2]) occurs at higher temperatures, preventing full conversion of double bonds and even gelation. Rate of propagation was considered to depend only on the nature of the monomer which reacts and not on the kind of anion. However, reactivity of pendant double bonds was distinguished from the prevailing before initiation or propagation and initiation was supposed to have a finite rate. Chemical species and reactions are described in table I.

TABLE I: Reaction stoichiometry of the anionic copolymerization of a monovinyl monomer **RCH=CH$_2$** with a divinyl monomer **R'(CH=CH$_2$)$_2$**

Reaction name	Chemical equation	Transformed stoich. coefficients
Monovinyl initiation	$B_1 + B_3 \xrightarrow{k_{BB_{13}}=k_{I_1}} A_1 + X_4 + X_3 + V_{BB_{13}}$	$\bar{\nu}_{BB_{13}} = \alpha_1\xi_4$ $\bar{\nu}_{BB_{31}} = \xi_3$
Divinyl initiation	$B_2 + B_3 \xrightarrow{k_{BB_{23}}=k_{I_2}} A_1 + A_2 + X_3 + V_{BB_{23}}$	$\bar{\nu}_{BB_{23}} = \alpha_1$ $\bar{\nu}_{BB_{32}} = \xi_3$
Internal vinyl initiation	$A_2 + B_3 \xrightarrow{k_{AB_{23}}=k_{I_3}} A_1 + X_3 + V_{AB_{23}}$	$\bar{\nu}_{AB_{23}} = \alpha_1/\alpha_2$ $\bar{\nu}_{BA_{32}} = \xi_3$
Monovinyl propagation	$A_1 + B_1 \xrightarrow{k_{AB_{11}}=k_{p_1}} X_4 + A_1 + V_{AB_{11}}$	$\bar{\nu}_{AB_{11}} = \xi_4/\alpha_1$ $\bar{\nu}_{BA_{11}} = \alpha_1$
Divinyl propagation	$A_1 + B_2 \xrightarrow{k_{AB_{12}}=k_{p_2}} A_1 + A_2 + V_{AB_{12}}$	$\bar{\nu}_{AB_{12}} = \dfrac{1}{\alpha_1}$ $\bar{\nu}_{BA_{21}} = \alpha_1\alpha_2$
Internal vinyl propagation	$A_1 + A_2 \xrightarrow{k_{AA_{12}}=k_{p_3}} A_1 + X_5 + V_{AA_{12}}$	$\bar{\nu}_{AA_{12}} = 1/\alpha_1$ $\bar{\nu}_{AA_{21}} = \dfrac{\alpha_1\xi_5}{\alpha_2}$
Hydride elimination	$A_1 \xrightarrow{k^{\bullet}_{A_1}=k_t} A_3 + B_4$	$\bar{\nu}^{\bullet}_{A_1} = \alpha_3/\alpha_1$
Hydride exchange	$A_1 + A_3 \xrightarrow{k^{\bullet}_{AA_{13}}=k_e} X_2 + X_1$	$\bar{\nu}^{\bullet}_{AA_{13}} = \xi_2/\alpha_1$ $\bar{\nu}^{\bullet}_{AA_{31}} = \xi_1/\alpha_3$

We present in figure 1 an example of the computed chain length distribution of sol molecules and in figure 2 the predicted values of elasticaly active network junctions and chains. In both cases, they are very different from the predictions of the theory of branching processes.

Initial mole ratios of initiator and double bonds and of divinyl and the monovinyl monomers were 0.001.

Free-radical copolymerization of the same monomers was also analysed. Transfer reactions have been neglected. Rate of propagation was considered to depend on the nature of the unit carrying the radical and of the monomer with which it reacts, but the reactivity of the two double

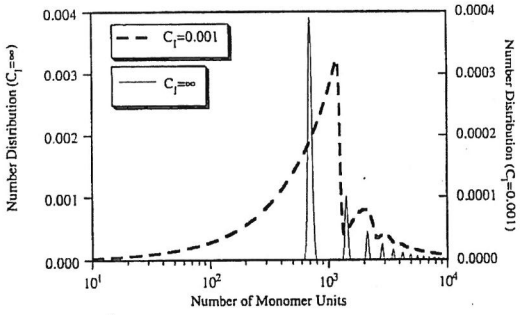

Figure 1: Chain length distribution of sol at gel point in anionic polymerization of styrene + p-divinylbenzene for instantaneous ($C_l = \infty$) and slow($C_l = 0.001$) initiation.

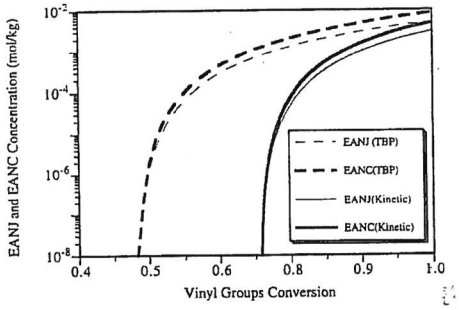

Figure 2: Concentration of elasticaly active network junctions (EANJ) and chains (EANC) in anionic polymerization of styrene + p-divinylbenzene according to kinetic modelling, for instantaneous initiation, and TBP.

bonds in the same monomer was considered to change after reacting one of them. The reported parameter values were taken from a previous study on the system methyl methacrylate (MMA) / ethylene glycol dimethacrylate (EGDMA) at 70 C, initiated by AIBN (Li et. al. [3]), for different initial weight fractions of EGDMA. Initial concentration of AIBN was 0.0516 mol dm^{-3}.

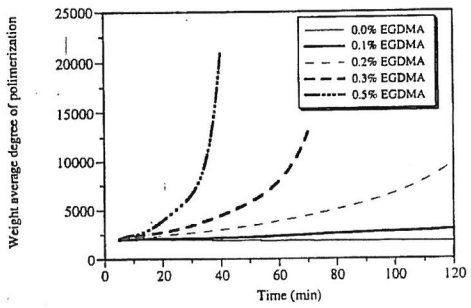

Figure 3: Predicted weight average degree of polymerization vs. time in a batch radical polymerization of MMA + EGDMA at 70 C, before gelation, for different initial weight fractions of EGDMA.

It has not yet been possible to obtain numerical results beyond gel point for this chemical system. The integration along the characteristics usually breaks down after a very short time interval, and it is very difficult to find out an initial estimate of the initial α_k. The solution is likely to come from the combination of the continuation principle with a multiple-shooting method adapted to "stiff" systems of ordinary differential equations.

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 (not greater than for the Monte Carlo method described by Tobita [4], which has a more limited scope and relies on quasi-steady state hypothesis and a number of other approximations). Therefore, it is likely to remain a useful tool in the future, specially when the present numerical problems will be overcome.

Acknowledgements

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A kinetic study of the polymerization of MMA

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Summary

Kinetic studies on the bulk polymerisation of methyl methacrylate (MMA) have been carried out using differential scanning calorimetry (DSC), both in the absence and the presence of 2,2' - azo-bis-isobutyronitrile (AIBN). A long induction period was found when AIBN was not used. Nevertheless, the reaction started and reached high conversion. A more severe test was carried out by inducing the polymerisation without having removed the inhibitor present in commercial MMA. Again, the reaction started, but after a longer induction period, and it did not reach a high conversion. The tests carried out without AIBN were characterised by the appearance of an exothermic peak before the onset of the auto acceleration, probably due to the formation of radicals by the monomer itself. A more detailed study of the reaction has been performed when the initiator was used. All the thermokinetic parameters have been measured or calculated and show good agreement with those in the literature.

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