A GENERAL MATHEMATICAL TREATMENT OF IRREVERSIBLE POLYMERIZATIONS

Mário R.N. Costa and Rolando C.S.Dias

Laboratory of Separation and Reaction Engineering, Faculdade de Engenharia da Universidade do Porto, Rua dos Bragas, 4099 Porto Codex, Portugal

SUMMARY

Irreversible non-linear polymerizations with arbitrarily great numbers of monomers are described specifying the stoichiometric coefficients of the reactions involving end-groups. Rate equations for the vectorial generating function or discrete transform of the distribution of end-groups and repeating units and its derivatives with respect to logarithms of Laplace parameters can be thus be written. Mass balance equations using them are non-linear partial differential equations solvable by the method of characteristics. Numerical methods were developed for computing molecular weight distribution and its averages before and after gelation, as well as the weight fraction of sol.

This analysis is extended in order to establish predictive methods for the distribution of chain lengths of generalized sequences (i.e. moieties with pre-established numbers of monomer units inside polymer molecules, which do not contain repeating units of certain specified kinds). Rate equations for the vectorial generating functions or discrete transforms of the distributions of sequences are established from the knowledge of stoichiometric coefficients of the reactions involving reactive groups. Mass balance equations using them are also non-linear partial differential equations solvable by the method of characteristics, using a method similar to the one previously used for determining chain length distributions of whole polymer molecules.

Introduction of the distribution of descendants of each linking group allows a matrix of extinction probabilities to be computed, leading to gel properties such as the concentration of elastically effective branch points and mass fraction of pendant chains.

The curing of a tetraepoxide with a primary diamine and the anionic copolymerization of vinyl compounds are taken as case studies. Numerical results are compared with previous approximated analysis, such as the theory of branching processes.

Introduction

Polymerization reaction engineering puts challenges without parallel to those encountered in the study of the manufacturing of smaller molecules, such as ammonia (Tirrell and al., 1987). The only design problems for a reactor to make ammonia is how to do it as efficiently as possible, since ammonia properties are uniquely determined; whereas, if a reactor to produce poly(ethylene terephtalate) (PET) is to be built and operated, one faces, to begin with, with the problem of knowing what is meant by the name PET. This is a complex mixture of several molecules with different numbers and kinds of repeating units and end-groups. Its properties vary considerably according to the distributions of chain-lengths, compositions and so on - for instance, PET may be used as a fiber or a plastic, and the average molecular weights and other chemical characteristics in either case differ considerably. So, there is a complex problem of dealing with selectivities for an infinite number of entities.

From the beginning of Polymer Science, the description of the composition of polymeric substances has been dealt with either by statistical-probabilistic approaches or by the resolution of the infinite set of mass balance equations for the polymer species (the kinetical approach). The first approach is very convenient for systems at chemical equilibrium, but it is often virtually inapplicable to kinetically controlled polymerizations. However, serious mathematical difficulties plague the use of the kinetical approach. Many problems had never been attacked by lack of suitable numerical methods, such as the evaluation of average molecular weights after gelation or the evaluation of chain-length distributions. It was even believed (Dusek, 1985) that the kinetical approach could not be used for predicting elastic properties of networks, such as the concentrations of elastically active junctions and chains (EANJ and EANC), needed for the classical rubber elasticity theory. As a consequence, approximated solutions of dubious value have been used.

This work describes briefly how previous difficulties in the use of the kinetical approach for describing polymerizing systems could be overcome. At the same time, a general framework for describing polymerizations is put forward, with the idea of developing computational means which could be flexible enough to predict the behavior of any polymerization without having to repeat the complex procedure of writing down and solving each time the mass balance equations for the polymer species. This is an idea which has become fashionable, as testify the recent papers by Jacobsen and Ray (1992) (a failed attempt of establishing a unified description of polycondensation reactions) and Achillas and Kiparissides (1992), dealing with radical copolymerizations. These works have a much lesser generality as compared to the treatment here proposed.

General concepts

Any chemical system undergoing a polymerization reaction is defined by the nature and number of monomer classes and end-groups. Let N be the number of monomer classes. Each monomer class contains a chemically invariant moiety (the repeating unit), named $\mathbf{U}^{\mathbf{m}}$ for the m-th monomer, and a certain number f_{mi} of reactive end-groups, named $\mathbf{A}_i$, there being G of such end-groups among all monomers. Monomer classes with same number and nature of end-groups are not distinguished; there can not be two identical vectors $[f_{mi}]$ and $[f_{ni}]$ with $m \neq n$. However, monomer classes can have a molecular weight distribution, as in the case of polyetherpolyols and polyesterpolyols used in the manufacture of polyurethanes. Since there is no need to distinguish among position isomers, it is enough to describe each polymer molecule through the numbers of end-groups and repeating units it contains. So, a molecule with a vector of numbers of end-groups $\boldsymbol{a} = [a_1 \ldots a_G]$ and a vector of numbers of repeating units $\boldsymbol{n} = [n^1 \ldots n^N]$ shall be named $\mathbf{P}(\boldsymbol{a}, \boldsymbol{n})$. Its mole concentration will be written as $P(\boldsymbol{a}, \boldsymbol{n})$, in order to simplify as much as possible the writing of the equations that follow. This discrete distribution of vectors $\boldsymbol{a}$ and $\boldsymbol{n}$ is appropriately named a *vector number molecular number distribution*, abbreviated as VNMND. It will nearly always be found from its *vectorial discrete transform*

$$\bar{P}(\sigma, s) = \sum_{a_1=0}^{\infty} \cdots \sum_{a_G=0}^{\infty} \sum_{n^1=0}^{\infty} \cdots \sum_{n^N=0}^{\infty} \sigma_1^{a_1} \cdots \sigma_G^{a_G} (s^1)^{n^1} \cdots (s^N)^{n^N} P(a_1, \ldots, a_G, n^1, \ldots, n^N) \qquad (1)$$

Moments and thus molecular weight averages can be found differentiating $\bar{P}(\sigma, s)$ and setting all σ_j and s^m equal to 1. Retrieval of the distribution can be performed through a path integration, which is conveniently performed using fast Fourier transform (Costa and Villermaux, 1988).

When an end-group $\mathbf{A}_i$ attached to some repeating unit $\mathbf{X}$ reacts with another end-group $\mathbf{A}_j$ attached to some repeating unit $\mathbf{Y}$ in another molecule creating a link $\mathbf{L}_{ij}$ between the two repeating units, the vector of numbers of end-groups attached to $\mathbf{X}$ changes by $\nu_{ij} = [\nu_{ij1}, \ldots, \nu_{ijG}]$ and likewise the vector of numbers of end-groups attached to $\mathbf{Y}$ changes by $\nu_{ji} = [\nu_{ji1}, \ldots, \nu_{jiG}]$:

$$\mathbf{XA}_i + \mathbf{YA}_j \xrightarrow{k_{ij}} (\mathbf{A}_1)_{\nu_{ij1}} \ldots (\mathbf{A}_G)_{\nu_{ijG}} \quad \mathbf{XL}_{ij}\mathbf{Y}(\mathbf{A}_1)_{\nu_{ji1}} \ldots (\mathbf{A}_G)_{\nu_{jiG}}$$

An *apparent* bimolecular rate constant of the reaction between reacting groups $\mathbf{A}_i$ and $\mathbf{A}_j$, named $k_{ij} = k_{ji}$, is defined as the rate of formation of $\mathbf{L}_{ij}$ divided by the concentrations of $\mathbf{A}_i$ and $\mathbf{A}_j$. k_{ij} depends on the concentration of end-groups and catalysts.

Some other reactions do not lead to linking groups between repeating units. If a group $\mathbf{A}_i$ reacts by such a process, its apparent unimolecular rate constant is named k_i^* and the changes in number of groups $\mathbf{A}_j$ brought by that reaction are ν_{ij}^* :

$$\mathbf{XA}_i \xrightarrow{k_i^*} \mathbf{X}(\mathbf{A}_1)_{\nu_{i1}^*} \ldots (\mathbf{A}_G)_{\nu_{iG}^*}$$

The curing of tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) with 4,4'-diaminodiphenylsulfone (DADPS) and the anionic copolymerization of methylmethacrylate(MMA) with styrene (STY) were chosen in order to illustrate this approach. Their kinetic schemes are summarized in tables I and II.

TABLE I: Kinetic scheme of the anionic copolymerization of MMA and STY

Group name	**Description**	**Formula**	**Index**
I	Initiator	Li C_4H_9 (for instance)	1
MMA	Unreacted MMA	$CH_2{=}C(CH_3)COOCH_3$	2
STY	Unreacted STY	$CH_2{=}CHC_6H_5$	3
M	Anion from MMA	$-CH_2CH^-(CH_3)COOCH_3$	4
S	Anion from STY	$-CH_2CH^-C_6H_5$	5

Reaction	i	j	k_{ij}	$\bar{\nu}_{ij}$	$\bar{\nu}_{ji}$
I + MMA $\longrightarrow$ M	1	2	k_{iM}	$1/\sigma_1$	σ_4/σ_2
I + STY $\longrightarrow$ S	1	3	k_{iS}	$1/\sigma_1$	σ_5/σ_3
M + MMA $\longrightarrow$ M	4	2	k_{pMM}	$1/\sigma_4$	σ_4/σ_2
M + STY $\longrightarrow$ S	4	3	k_{pMS}	$1/\sigma_4$	σ_5/σ_3
S + MMA $\longrightarrow$ M	5	2	k_{pSM}	$1/\sigma_5$	σ_4/σ_2
S + STY $\longrightarrow$ S	5	3	k_{pSS}	$1/\sigma_5$	σ_5/σ_3

Parameters used in simulations: $k_{pMM} / k_{pMS} = 6.4$; $k_{pSS} / k_{pSM} = 0.12$ (Elias, 1977).
In the absence of experimental data, initiation reactions were assumed to occur at same rate as homopropagations : $k_{iM} / k_{pMM} = k_{iS} / k_{pSS} = 1$.

Prediction of chain-length distributions and average molecular weights

Using these general definitions, the following kinetic rate laws can be written for the concentrations of reacting groups and for the discrete transform of VNMND:

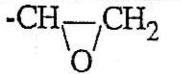
$$R_{A_k} = \frac{1}{2} \sum_{i=1}^{G} \sum_{j=1}^{G} k_{ij} \nu_{ijk} A_i A_j + \sum_{i=1}^{G} k_i^* \nu_{ik}^* A_i \tag{2}$$

$$\bar{R}_P(\sigma, s) = \sum_{i=1}^{G} \sum_{j=1}^{G} k_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_i} \left(\frac{1}{2} \bar{\omega}_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_j} - A_j \right) + \sum_{i=1}^{G} k_i^* \frac{\partial \bar{P}}{\partial \log \sigma_i} \left(\bar{\nu}_i^* - 1 \right) \tag{3}$$

$$\bar{\omega}_{ij}(\sigma) = \prod_{k=1}^{G} \sigma_k^{\omega_{ijk}} = \bar{\nu}_{ij} \bar{\nu}_{ji} \quad (4) \qquad \bar{\nu}_i^*(\sigma) = \prod_{k=1}^{G} \sigma_k^{\nu_{ik}^*} \tag{5}$$

Insertion of these rate expressions in mass balance equations leads to a system of partial differential equations for $\bar{P}$. It can be numerically solved using the method of characteristics, yielding the chain length distributions through numerical inversion.

TABLE II: Kinetic scheme of the curing of an epoxide resin with a primary amine

Group name	**Description**	**Formula**	**Index**
A	Primary amine	$-NH_2$	1
E	Epoxyde		2
S	Secondary amine	-NH-	3
H	Hydroxyethylamine	$-\underset{\mid}{N}-CH_2-\underset{\mid}{C}H-OH$	4
HE	Hydroxyethylenether	$-\underset{\mid}{N}-CH_2-\underset{\mid}{C}H-O-CH_2-\underset{\mid}{C}H-OH$	5

Reaction	i	j	k_{ij}	$\bar{\nu}_{ij}$	$\bar{\nu}_{ji}$
$A + E \longrightarrow S + H$	1	2	k_P	σ_3 / σ_1	σ_4 / σ_2
$S + E \longrightarrow H$	3	2	k_S	$1 / \sigma_3$	σ_4 / σ_2
$E + H \longrightarrow HE$	2	4	k_E	σ_5 / σ_2	$1 / \sigma_4$
$E + HE \longrightarrow HE$	2	5	k_E	σ_5 / σ_2	$1 / \sigma_5$

Parameters used in simulations: $k_S / k_P = 0.2$ and $k_E / k_P = 0.055$; molecular weights of monomers DADPS and TGDDM: $M^1 = 248$ and $M^2 = 422$ (Tsou and Peppas, 1988).

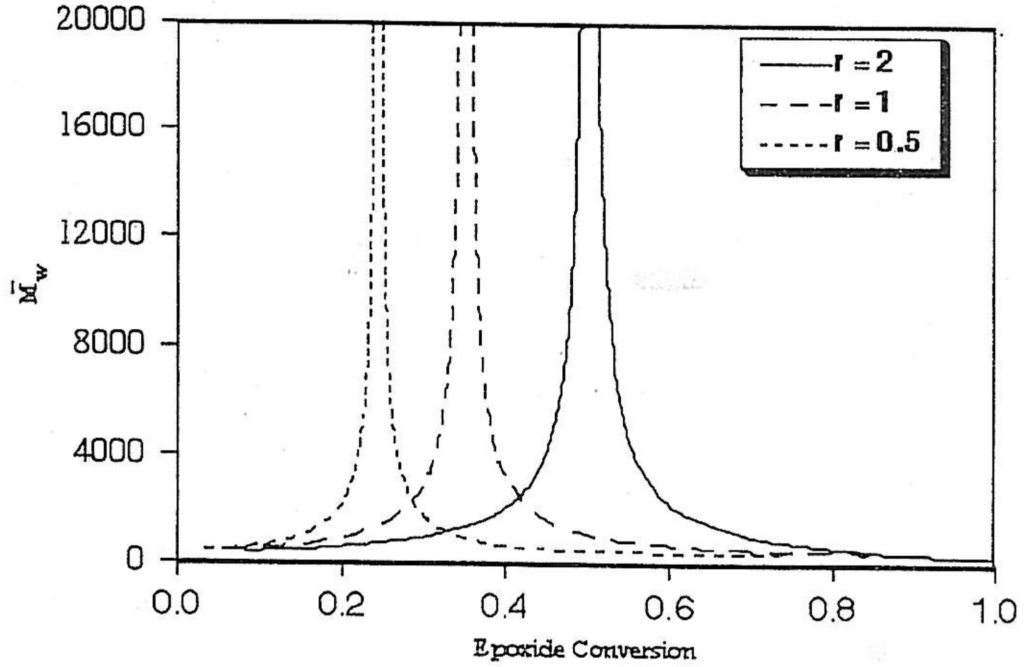


Figure 1: Weight average molecular weight of sol $\bar{M}_w$ versus epoxide conversion, for three different values of initial molar ratio of active hydrogens in amines to epoxide group r, in batch reaction of TGDDM and DADPS.

A similar procedure can be used to compute the derivatives of $\bar{P}$ for all s and σ equal to 1, as their mass balance equations have the same characteristics as the 0-th order derivative $\bar{P}$, leading to the moments of the distribution. Those moments are used for computing average molecular weights of the sol fraction, as well as the mass fraction of gel (Costa and Dias, 1993a).

Gelation occurs when two characteristics meet at all s and σ equal to 1. In that case, if the reaction is allowed to go beyond gelation, an infinite network grows at the expense of lower molecular weight material. In figure 1, an example of the evolution of the weight average molecular weights of the soluble fraction for the reaction between TGDDM and DADPS is shown.

Elastic properties of gel

A major extension of this procedure is the prediction of gel properties, such as the concentration of elastically effective junctions and chains and the weight fraction of dangling chains (see figure 2).

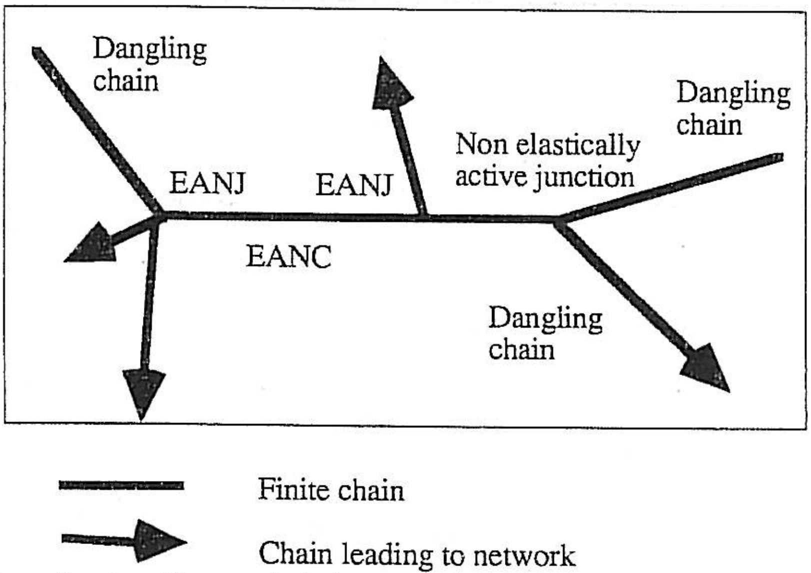


Figure 2: Elastically active junctions and chains.

This was formerly thought to be impossible by a non-probabilistic approach (and so no exact results could be computed for non equilibrium systems). The key point is the evaluation of the *extinction probabilities* v_{ij}, which are the fractions of chains starting at a link L_{ij} which do not go to infinity in the direction of the repeating unit previously carrying A_i towards the repeating unit previously carrying A_j. Defining the functions $X_{ij}(a_1,\ldots, a_G)$ as the concentrations of links L_{ij} leading to $a_1,\ldots, a_G$ end-groups of the different kinds in the direction of the repeating unit previously carrying A_j, extinction probability v_{ij} is simply the fraction of those fragments which are finite, regardless of the numbers of their end-groups:

$$v_{ij} = \sum_{a_1=0}^{\infty} \cdots \sum_{a_G=0}^{\infty} X_{ij}(a_1,\ldots, a_G) / L_{ij} = \bar{X}_{ij}(1, \ldots, 1) / L_{ij} \tag{6}$$

where use was made of the vectorial discrete transform

$$\bar{X}_{ij}(\sigma) = \sum_{a_1=0}^{\infty} \cdots \sum_{a_G=0}^{\infty} \sigma_1^{a_1} \cdots \sigma_G^{a_G} X_{ij}(a_1,\ldots, a_G) \tag{7}$$

A rate equation for $\bar{X}_{ij}(\sigma)$ can be written:

$$\bar{R}_{\mathrm{X_{kl}}}(\sigma) = \sum_{i=1}^{G} \sum_{j=1}^{G} k_{ij} \frac{\partial \bar{X}_{kl}}{\partial \log \sigma_i} (\bar{\omega}_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_j} - A_j) + \sum_{i=1}^{G} k_i^* \frac{\partial \bar{X}_{kl}}{\partial \log \sigma_i} (\bar{\nu}_i^* - 1) + k_{kl} A_k \bar{\nu}_{lk} \frac{\partial \bar{P}}{\partial \log \sigma_l} \quad (8)$$

The balance equations for the $\bar{X}_{ij}(\sigma)$ are integrated at the same time as that for $\bar{P}$, since their characteristics are the same. Knowing the extinction probabilities, the concentrations of elastically effective junctions and chains can be obtained, by writing and solving mass balance equations for the repeating units linked to the different possible numbers and kinds of links (Costa and Dias, 1993b). A sample of the results of such computations for the batch reaction of different relative amounts of TGDDM and DADPS are shown in figure 3.

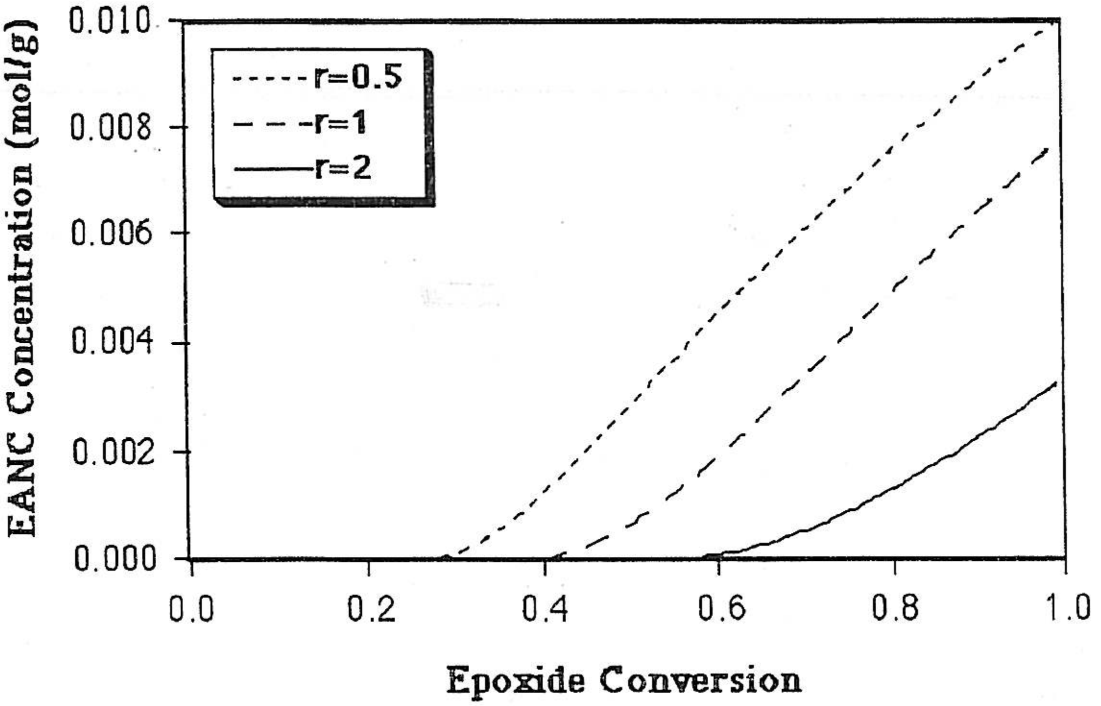


Figure 3: Concentration of elastically active network chains (EANC) versus epoxide conversion for three different values of initial mole ratio of active hydrogens in amines to epoxide group r, in a batch reaction between TGDDM and DADPS.

Sequence length distributions

The analysis of irreversible polymerizations which has so far been developed does not allow position isomers to be distinguished. Therefore, a sequence must be defined as the ensemble of sets of certain fixed numbers of repeating units linked in all possible ways inside polymer molecules, which are bounded by end-groups and by certain kinds of repeating units.

A certain sub-set of N_S repeating units, with $N_S < N$, must be first chosen. Let us define $\boldsymbol{q} = [q^1 \dots q^{N_S}]$ as the vector containing the look-up table of the indexes of the chosen repeating units. There are $\binom{N}{N_S}$ different ways of choosing that set, and so there are $\binom{N}{N_S}$ possible vectors $\boldsymbol{q}$.

A sequence of those monomers U^{q_1}, U^{q_2}, ..., $\mathrm{U}^{q_{N_S}}$, capped by end-groups so that their number is a vector $\boldsymbol{a} = [a_1 \dots a_G]$ and containing $\boldsymbol{n} = [n^1 \dots n^N]$ repeating units (where obviously $n^m = 0$ if there is no $j \leq N_S$ such that $q^j = m$) will be named $\mathrm{S}(\boldsymbol{q}, \boldsymbol{a}, \boldsymbol{n})$. . For instance, in a vinyl copolymerization of two monomers U^1 and U^2, there are only two kinds of sequences, those containing only repeating units of type $\mathbf{U}^1$ with $\boldsymbol{q} = \boldsymbol{q}_1 = [1]$ and those containing only repeating units of type $\mathbf{U}^2$, with $\boldsymbol{q} = \boldsymbol{q}_2 = [2]$.

Mole concentration of sequences will be written as $S(\boldsymbol{q}, \boldsymbol{a}, \boldsymbol{n})$. This discrete distribution of vectors $\boldsymbol{a}$ and $\boldsymbol{n}$ determines the *vector number sequence distribution.* Most often it will be computed from its *vectorial discrete transform*

$$\bar{S}(\boldsymbol{q}, \sigma, s) = \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} \sum_{n^1=0}^{\infty} \dots \sum_{n^N=0}^{\infty} \sigma_1^{a_1} \dots \sigma_G^{a_G} s_1^{n^1} \dots s_N^{n^N} S(\boldsymbol{q}, a_1 \dots a_G, n^1 \dots n^N) \tag{9}$$

With these definitions, monomers belong always to some sequences, since a key assumption of this approach is to consider repeating units are neither created nor destroyed. This does not cause any problem in polycondensations, but in polyadditions it is necessary to subtract the concentrations of unreacted monomers of the overall concentrations of sequences in which they appear.

Rate equations for the sequences are the same as those of polymer molecules with a supplemental term, which is due to the effect of the capping of the sequences by reaction with end-groups attached to units not belonging to the sequences, with the concentration $A_j - B_j(\boldsymbol{q})$:

$$\begin{aligned} R_{\mathbf{S}}(\boldsymbol{q}, \sigma, s) = & \sum_{i=1}^{G} k_i^* \frac{\partial \bar{S}}{\partial \log \sigma_i} (\bar{\nu}_i^* - 1) + \\ & \sum_{i=1}^{G} \sum_{j=1}^{G} k_{ij} \frac{\partial \bar{S}}{\partial \log \sigma_i} \left\{ \frac{1}{2} \bar{\omega}_{ij} \frac{\partial \bar{S}}{\partial \log \sigma_j} - A_j + \bar{\nu}_{ij} \; [A_j - B_j(\boldsymbol{q})] \right\} \end{aligned} \tag{10}$$

The concentration of end-groups $\mathbf{A}_\mathbf{j}$ attached to repeating units belonging to the sequences was above introduced as $B_j(\boldsymbol{q})$. It can be predicted knowing the concentrations of the end-groups $\mathbf{A}_\mathbf{i}$ attached to units $\mathbf{U}^\mathbf{n}$, $\mathbf{A}_\mathbf{i}^\mathbf{n}$. Their rate of formation can be written as follows :

$$R_{\mathbf{A}_\mathbf{k}^\mathbf{n}} = \sum_{i=1}^{G} \sum_{j=1}^{G} k_{ij} \nu_{ijk} A_i^n A_j + \sum_{i=1}^{G} k_i^* \nu_{ik}^* A_i^n \tag{11}$$

$B_j(\boldsymbol{q})$ for any vector $\boldsymbol{q}$ is obtained by adding up the contributions of all repeating units included in the sequences which are being considered :

$$B_j(\boldsymbol{q}) = \sum_{m=1}^{N_S} A_j^{qm} \tag{12}$$

Average sequence lengths for the blocks of each monomer in the case of the anionic copolymerization in a batch reactor starting from an equimolecular mixture of styrene (STY) and methylmethacrylate (MMA) are shown in figure 4. Notice the consequences of the slower consumption of styrene, leading to a much broader distribution of sequences.

Discussion and conclusions

The analysis of irreversible polymerizations that has been briefly summarized here allows in principle arbitrarily complex chemical systems to be described. Notice, however, that its practical performance with systems of several tens of groups, or with radical polymerizations, is not yet known.

The scope of this approach goes much beyond the evaluation of average molecular weights in the pre-gel state, as virtually in all the previous works. Its capacity to compute sequence length distributions and elastic properties of gel is noteworthy. A mathematically correct way of computing those properties out of chemical equilibrium is now available. Comparison with results of the previously used methods (based on the theory of branching processes) show sometimes very significant numerical differences between the two approaches, mainly in the case of polyadditions.

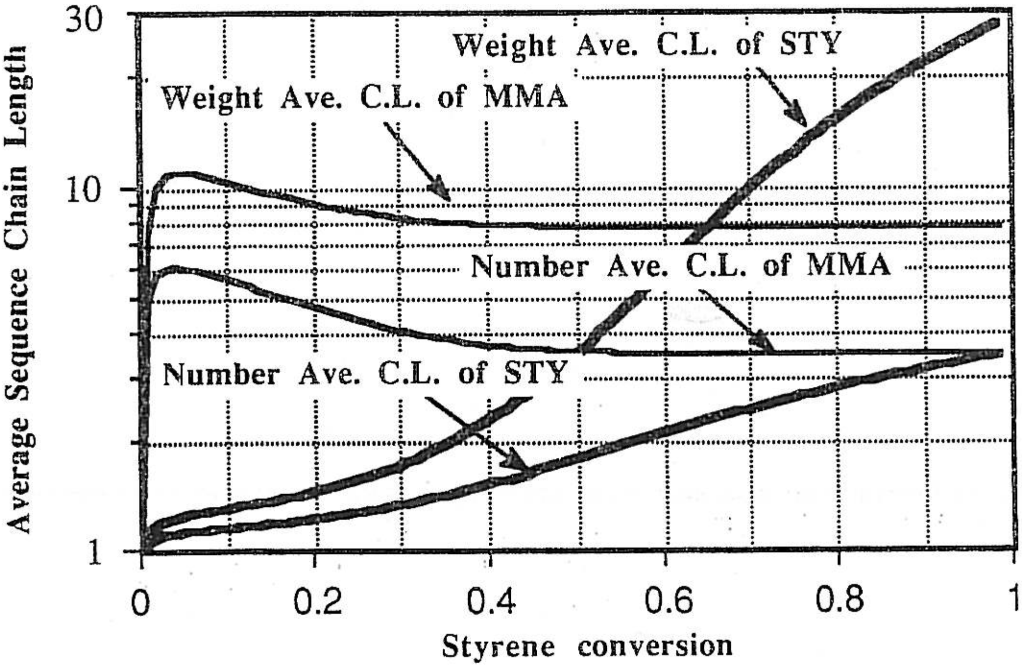


Figure 4: Predicted average sequence lengths in the anionic copolymerization of styrene (STY) and methylmethacrylate (MMA) in a batch reactor starting from an equimolar mixture.

Prediction of certain molecular parameters, such as the average radius of gyration, as well as the description of reversible polymerizations, can only be done if the distributions of position isomers are taken into account, at least in an implicit way. This is not possible without major changes in the analysis here presented, and it remains a currently unsolved problem.

Acknowledgments

Financial support by JNICT (project 502/90/MPF) is gratefully acknowledged.

References

D. S. Achillas and C. Kiparissides, 1992, *J. Macromol. Sci. Revs. Macromol. Chem. Phys.*, **C32**, 183-234.

M. R. N. Costa and J. Villermaux, 1988, *Ind. Eng. Chem. Res.*, **27**, 421-429.

M. R. N. Costa and R. S. Dias, 1993a, A general kinetic analysis of non-linear irreversible copolymerizations. 1. Prediction of molecular weights and molecular weight distribution of the soluble fraction. Submitted to *Chemical Engineering Science* in Nov. 1992.

M. R. N. Costa and R. S. Dias, 1993b, A general kinetic analysis of non-linear irreversible copolymerizations. 2. Prediction of gel structures related to elastic properties. Submitted to *Chemical Engineering Science* in Nov. 1992.

K. Dusek, 1985, *Brit. Polym. J.*, **17**, 185-189.

H. G. Elias, 1977 *Macromolecules . 2. Synthesis and Materials*, Plenum, New York, p. 791.

L. L. Jacobsen and W. H. Ray, 1992, *J. Macromol. Sci. Revs. Macromol. Chem. Phys.*, **C32**, 407-519.

M. Tirrell, R. Galvan and R. L. Laurence, 1987, in *Chemical Reaction and Reactor Engineering*, J. J. Carberry and A. Varma (Eds.), Marcel Dekker, New York, pp. 735-778.

A. H. Tsou and N. Peppas, 1988, *J. Polym. Sci. Polym. Phys. Ed.*, **26**, 2043-2060.