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A general kinetic method to predict sequence length distributions for non-linear irreversible multicomponent polymerizations

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Abstract

A method to predict the sequence length distribution (SLD) for homogeneous non-linear irreversible multicomponent polymerizations is described. With more than two monomers, it also predicts chain length distributions of the sub-domains containing a prescribed sub-set of the repeating units, but in all possible orderings. Its goal is the analysis of polymerization systems involving complex kinetic schemes in an automated way. The radical terpolymerization of two vinyl monomers with a divinyl monomer and a radical copolymerization including branching by transfer to polymer and by propagation on terminal double bonds are considered as case studies showing the interest of our approach. Finally, the concept of gelation of sequences is presented and discussed in comparison with the related and better known gelation of the population of polymer molecules.

Keywords: Sequence; Kinetics; Branching

1. Introduction

One of the simplest methods for improving polymer properties is the joint polymerization of different monomers. With this main goal, copolymers and terpolymers are often produced in polymer industries. Weak resistance to organic solvents, brittleness and low maximum allowed temperatures are some disadvantages of certain homopolymers that can be overcome through copolymerization. In general, multicomponent copolymerization offers the possibility to tailor-make polymers with specific desired properties [1,2]. Copolymerization of styrene with acrylonitrile and with 1,3-butadiene are two well-known examples with large industrial relevance.

Multicomponent polymerization introduces new variables with a strong influence on the polymer properties. Two examples with practical importance are the polymer composition and the length of the sequences of each kind of monomer along the polymer chains. Both of these are distributed quantities and, therefore, the presence of a polymer composition distribution and a sequence length distribution are inherent to multicomponent polymerization. It is well known that product quality is directly dependent on the composition and sequence length (often called chain microstructure) distributions: copolymers with different compositions may be immiscible and this immiscibility can be affected by the sequence length distribution [3]. Large sequences of a monomer in a polymer can also lead to microphase separation. Both of these problems are present in the styrene–acrylonitrile system.

Sequence length distributions were experimentally and theoretically studied in stepwise polymerization with particular emphasis to the system $\mathbf{UA}_2 + \mathbf{QB}_2 + \mathbf{PC}_2$ where **A** reacts with **B** and **C** but **B** and **C** do not react with themselves [4–17]. A particular chemical system of this kind with industrial importance occurs when a diisocyanate reacts with a short diol (hard diol) and a long diol (soft diol). The sequence length

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distributions of hard and soft segments are long known to determine the microphase separation of segmented polyurethanes [4]. Solutions for the sequence length distributions in batch reactors of the linear polycondensation of three monomers have also long been available from probabilistic approach [5–7], Monte Carlo simulation [8–12] and kinetic modeling [14,15]. For this kind of linear polymerizations, under homogeneous conditions and in the absence of side reactions, the sequence length follows the most probable distribution. Based on the selective acid hydrolysis [13] of polyester–polyurethanes and using size-exclusion chromatography (SEC) as a subsequent analytical technique, it is possible to measure the SLD of this family of polymers [14,15]. Sequence length distributions were also studied in the production of unsaturated polyesters formed by the reaction of maleic anhydride, phthalic anhydride and a diol [16]. Recently, the presence of microphase separation between hard microdomains and a soft segment matrix for polyurethane–urea copolymers based on ethylene–butylene soft segment was experimentally established [17]. Calculation methods for obtaining SLD and distributions of other relevant sub-structures within polymer molecules and networks in step-growth polymerizations have been recently reviewed by Kuchanov et al. [18].

Starting with the pioneering works of Mayo and Lewis [19] and Alfrey and Goldfinger [20], a considerable number of experimental and theoretical works was dedicated to the study of radical copolymerizations and namely to the influence of the reactivity ratios on the composition and sequence length distributions of the resulting polymers. Several experimental works for the quantification of sequence length distributions are based on the use of NMR [21–25]: the copolymer/co-monomer composition relationship and the sequence distributions were experimentally measured using ^{13}C NMR by Hill et al. [21] for the copolymerization of styrene and acrylonitrile. Alternative models to the terminal model (penultimate model, complex participation, complex dissociation) were also tested by the same authors [21,22]. The sequences formed in the styrene–methylmethacrylate copolymer were also experimentally investigated using proton and carbon NMR spectra [23] and for the study of the copolymerization system methacrylic acid/poly(ethylene glycol)monomethacrylate ^{1}H NMR was employed [24]. More recently [25], it was shown that the head–tail sequence length distributions of poly(3-alkylthiophenes) may be obtained from the proton NMR spectra.

Very recently [26], the copolymer poly(vinylidene chloride-*co*-vinyl acetate) was studied by using 2D NMR, allowing a deeper insight into the polymer microstructure. A different experimental technique, dynamic scanning calorimetry (DSC), was used to study the crystalline sequence lengths of ethylene/long-chain α-olefin copolymers produced by metallocenes [27]. Note that in most research works dealing with the quantification of SLD, namely in chain growth copolymerizations, a prior knowledge of reactivity ratios is needed [28,29]. A further experimental study on the acrylonitrile/methyl acrylate polymerization [30] has put into evidence the importance of the penultimate effect, as well as other chemical complexities. SLD predictions are based in models such as the Mayo–Lewis equation and, therefore, some mathematical approximations and simplifications of the kinetic scheme are inherent to these treatments. In fact, rather simple kinetic schemes are usually considered and branching is neglected. As far as it is of our knowledge, for systems where branching has an important effect on the polymer properties, the SLD was never experimentally or theoretically studied. This can be an important issue for systems where transfer to polymer (e.g. vinyl acetate), terminal branching (e.g. vinylidene fluoride) or divinyl monomers are present.

More than one decade ago, a tool for dealing with general non-linear irreversible copolymerizations avoiding the tedious and error-prone mathematical formulation of different polymerization systems was presented [31]. A general procedure for solving the resulting partial differential equations by the method of characteristics is a key point in this approach and several mathematical pitfalls of alternative approaches can be avoided. Nevertheless, severe numerical difficulties with radical polymerizations could only recently be overcome [32–36]. A comparison of the predictions of average molecular weights of this method with pseudo-kinetic method, Monte Carlo method, different versions of the method of moments and with numerical fractionation can be found in some of the aforementioned works [32,34,35]. The analysis of the calculation of the CLD before and after gelation by this method has already been presented using a non-linear radical polymerization as an example [35].

Following the same lines of thought previously used for predicting the CLD, this paper presents a general kinetic method allowing the prediction of SLD for non-linear irreversible multicomponent polymerizations. As in previous works [31–36], the present method is also valid before and after gelation (if it can occur). Based on the generality of the method, a tool for predicting SLD for irreversible non-linear multicomponent polymerizations with arbitrary complex schemes is developed. One of the most innovative concepts presented here is the sequence gelation (formation of sequences of macroscopic size), which is shown to occur later than the chain length gelation. This concept was previously introduced [37] when dealing with the kinetic analysis of the cure of tetraepoxides and diamines in the presence of etherification side reactions. The modeling concepts developed in our work allow the analysis of a more general class of polymerizations, namely radical polymerizations. Although it can, in principle, take into account a limited number of intramolecular reactions leading to the formation of loops, there is still no automated way of defining the numerous reacting fragments and pseudo-reactions which need to be defined (as discussed in the next section), and so this is a current issue.

The present method can be useful in practice in order to have a deeper insight of the microstructure of linear polymers if more complex kinetic schemes need to be considered without using some widespread mathematical approximations. Nevertheless, the most promising application of this approach is related with its ability to deal with complex non-linear polymerizations. This can be used to improve the knowledge of the formation kinetics of this kind of polymers and to understand its microstructure. It may be also interesting for the study of the sequence gelation, if it can be experimentally detected.

2. General concepts on the description of sequence structures

The analysis of irreversible polymerizations which has so far been developed does not allow position isomers to be distinguished, as the values of average degree of polymerization in copolymers are usually in the range from 10^2 to 10^4, or even more, leading to a huge number of conceivable types of isomers with different microstructures. The quantitative description of polymers comprising macromolecules with such a huge number of configurations has only been carried out by statistical methods [38].

Nevertheless, it is interesting to have a deeper understanding of the copolymer microstructure as provided by the knowledge of the detailed sequence of the repeating units in the chain. This issue has been dealt with in a recent publication [39]. As the number of position isomers grows very fast with the maximum allowed sequence length, so do the required computer resources (memory and CPU time), and in the aforementioned paper the upper value of sequence length was only about 10.

In this work, the information about position isomers is disregarded. Besides sequences with some prescribed repeating unit, we also define sub-domains 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.

Chemical groups in polymer molecules, as well as monomers, initiators, transfer agents, by-products of polymerization, and all other non-polymer molecules, are given the common name A_n, with $n = 1,\ldots, N_\mathrm{A}$. The N_Y monomers are a sub-set of these groups. For each of the monomers there is a corresponding repeating unit. At least one sub-set comprising N_YS repeating units, with $N_\mathrm{YS} < N_\mathrm{Y}$, is usually chosen at the start because it presents more interest for specifying the polymer properties.

These concepts are mostly the same as used in our previous publications [34] to describe the CLD of general irreversible polymerizations, but with a significant change: it is now necessary to distinguish chemical groups even with the same reactivity when they are attached to repeating units in different sequences or sub-domains.

Sequences or sub-domains may contain ring structures formed by intramolecular reactions, or can belong to larger-sized ring structures. A simple example is provided by the polycondensation of monomers $\mathbf{UA}_3 + \mathbf{PB}_2$ where groups $\mathbf{A}$ and $\mathbf{B}$ are supposed to react with themselves forming bonds $\mathbf{Z_{AA}}$, $\mathbf{Z_{BB}}$ and $\mathbf{Z_{AB}}$ connecting, respectively, two equal moieties $\mathbf{U}$ or $\mathbf{P}$, and two different moieties in the third case. Neglecting the formation of rings containing more than two repeating units of either kind, there will be yet five kinds of bonds in rings to consider: $\mathbf{Z^c_U}$, $\mathbf{Z^c_{UU}}$, $\mathbf{Z^c_P}$, $\mathbf{Z^c_{PP}}$ for the bonds in rings containing respectively one and two $\mathbf{U}$ and $\mathbf{P}$ moieties, and $\mathbf{Z^c_{UP}}$ for the ring containing one $\mathbf{U}$ and one $\mathbf{P}$.

Therefore, sequences of moieties $\mathbf{U}$ with sequence length one can be the monomer $\mathbf{UA}_3$, the terminal moieties $\mathbf{A}_2\mathbf{UZ_{AB}}$ or $\mathbf{AU}(\mathbf{Z_{AB}})_2$, the middle-chain moiety $\mathbf{U}(\mathbf{Z_{AB}})_3$ and the rings $\mathbf{AUZ^c_U}$, $\mathbf{Z_{AB}UZ^c_U}$, $\mathbf{AUZ^c_{UP}}$ and $\mathbf{Z_{AB}UZ^c_{UP}}$.

Sequences of length two comprise the dimer $\mathbf{A}_2\mathbf{UZ_{AA}UA}_2$ and, more generally, sequences such as $\mathbf{xyUZ_{AA}Uxy}$, where $\mathbf{x}$, $\mathbf{y} = \mathbf{Z_{AB}}$, $\mathbf{A}$ as well as $\mathbf{xU}(\mathbf{Z^c_{UU}})_2\mathbf{Uy}$, $\mathbf{xyUZ_{AA}UZ^c_{UP}}$ and $\mathbf{Z^c_{UP}UZ_{AA}UZ^c_{UP}}$.

A vector $\mathbf{q} = [q_1, q_2, \ldots, q_{N_\mathrm{YS}}]$ containing the indices of groups defining the chosen repeating units is introduced next for convenience. There are $\binom{N_\mathrm{Y}}{N_\mathrm{YS}}$ different ways of choosing that set, and so there are $\binom{N_\mathrm{Y}}{N_\mathrm{YS}}$ possible vectors $\mathbf{q}$. A sub-domain with those repeating units $\mathbf{A}_{q_1}, \mathbf{A}_{q_2}, \ldots, \mathbf{A}_{q_{N_\mathrm{YS}}}$ is named $\mathbf{S(q,a)}$, where the vector $\mathbf{a} = [a_1, a_2, \ldots, a_{N_\mathrm{A}}]$ stores the counts of groups in that sequence or sub-domain.

The mole concentration of sequences or sub-domains, $S(\mathbf{q},\mathbf{a})$, is a discrete distribution of vector $\mathbf{a}$ and determines the vector number sequence distribution. Most often it will be computed from its vectorial generating function or discrete transform, $U(\mathbf{q},\mathbf{s})$:

$$U(\mathbf{q},\mathbf{s}) = \sum_{a_1=0}^{\infty} \cdots \sum_{a_{N_\mathrm{A}}=0}^{\infty} s_1^{a_1} \ldots s_{N_\mathrm{A}}^{a_{N_\mathrm{A}}} S(\mathbf{q}, a_1, \ldots, a_{N_\mathrm{A}}) \tag{1}$$

In the simple case (see Table 3) consisting of the linear polycondensation of three monomers ($N_\mathrm{Y} = 3$), $\mathbf{UA}_2 + \mathbf{QB}_2 + \mathbf{PC}_2$ where $\mathbf{A}$ reacts with $\mathbf{B}$ and $\mathbf{C}$, but $\mathbf{B}$ and $\mathbf{C}$ do not react, two kinds of sequences (or sub-domains) can be identified:

- Sub-domains containing the moieties $\mathbf{U}$ and $\mathbf{Q}$ (…$\mathbf{UQUQ}$…), which are capped by groups $\mathbf{A}$ or $\mathbf{B}$ or by the moiety $\mathbf{P}$. In this case $N_\mathrm{YS} = 2$ with $\mathbf{q} = [4, 5]$;
- Sub-domains containing the moieties $\mathbf{U}$ and $\mathbf{P}$ (…$\mathbf{UPUP}$…), which are capped by groups $\mathbf{A}$ or $\mathbf{C}$ or by the moiety $\mathbf{Q}$. Here too $N_\mathrm{YS} = 2$ with $\mathbf{q} = [4, 6]$.

In this chemical system the sub-domains with $\mathbf{q} = [5, 6]$ cannot occur.

Within the N_A groups present in the polymerization system, the following organization (summarized in Table 1) will be defined in order to make easier its numerical implementation:

- N_AP groups, using the lowest indices, are used to identify the active groups belonging to polymer molecules.

Within this class, two sub-classes are distinguished: the first N_APS are attached to repeating units belonging to the sequence

Table 1
The organization of chemical groups considered in the calculation of SLD

Description of group A_j	Group attached to repeating units belonging to the sub-domain?	Index
Active groups belonging to the polymer	Yes	$j = 1,\ldots, N_\mathrm{APS}$
	No	$j = N_\mathrm{APS} + 1,\ldots, N_\mathrm{AP}$
Active groups not belonging to the polymer	Yes	$j = N_\mathrm{AP} + 1,\ldots, N_\mathrm{AP} + N_\mathrm{AMS}$
	No	$j = N_\mathrm{AP} + N_\mathrm{AMS} + 1,\ldots, N_\mathrm{AP} + N_\mathrm{AM}$
Inactive groups belonging to the polymer		$j = N_\mathrm{AP} + N_\mathrm{AM} + 1,\ldots, N_\mathrm{A}$

or sub-domain which is being considered and the remaining $N_{AP} - N_{APS}$ are attached to other kinds of repeating units.

- N_{AM} active groups not belonging to polymer molecules (such as monomers and chain transfer agents). Their indices vary between $N_{AP} + 1$ and $N_{AP} + N_{AM}$. Within this class, the first N_{AMS} of N_{AM} are attached to repeating units belonging to the sequence.
- The remaining $N_A - N_{AP} - N_{AM}$ are inactive groups belonging to the polymer.

The indicator variables $\delta^S_{G_n}$ taking values zero or one will be used to identify the groups belonging to the sequence or sub-domain: A_n belongs to the sequence or sub-domain if $\delta^S_{G_n} = 1$.

The first step for predicting sequences in a polymerization scheme should be the establishment of the table of groups according to the above-described procedure. Note that the group indices in that table will have to be changed when another **q** is chosen.

3. Kinetic description of the formation of sequences

In this section, a rate equation will be established allowing the prediction of the $S(\mathbf{q},\mathbf{a})$ through population balance equations in Laplace domain. A table of chemical reactions and stoichiometric coefficients needs to be prepared for each kinetic scheme, using the classification of chemical reactions previously used for the prediction of CLD [34]. The main development brought up by this work is the description of their effect on the concentrations of sequences.

The chemical reactions present in irreversible polymerization schemes have been classified as follows.

3.1. Intermolecular coupling reactions

Two molecules get joined through the *m*-th such reaction when group $A_{[m-]}$ in the first molecule reacts with group $A_{[m+]}$ in the second molecule, with $m = 1, \ldots, N_R$.

Examples of this kind of reactions are propagation and termination in chain growth polymerizations or end group linking as found in step-growth polymerizations. The first N_{R_P} reactions of this class are supposed to involve only groups present in the polymer molecules.

The influence of this kind of reaction in the creation or destruction of sub-domains or sequences can be further described introducing stoichiometric coefficients ν^-_m, ν^+_m as shown below:

$$\mathbf{S}\left(\mathbf{q}, \mathbf{a} - \mathbf{a}' - \nu^-_m\right) + \mathbf{S}\left(\mathbf{q}, \mathbf{a}' - \nu^+_m\right) \xrightarrow{k_m} \mathbf{S}(\mathbf{q}, \mathbf{a}) \qquad (2)$$

$$\mathbf{S}\left(\mathbf{q}, \mathbf{a} - \nu^-_m\right) + A_{[m+]} \xrightarrow{k_m} \mathbf{S}(\mathbf{q}, \mathbf{a}) \qquad (3)$$

Eq. (2) shows the effect of chemical reaction *m* in the composition of the sequence when the two groups involved in the reaction ($A_{[m-]}$ and $A_{[m+]}$) are attached to repeating units belonging to the sequence. A sequence $\mathbf{S}(\mathbf{q},\mathbf{a})$ can be created or consumed by such a reaction.

Eq. (3) describes the slightly different situation where reaction *m* occurs with only one of the reactive groups being attached to repeating units belonging to the sequence. In this kind of reaction, sub-domains or sequences are capped by repeating units not belonging to the sub-domains or sequences. Note that Eq. (3) is consistent with the convention $[m-] \leq [m+]$ and with the organization of groups presented in Table 1.

The description of sequence or sub-domain transformations by chemical reaction is done using the reaction indicator variables defined as: $\delta^{S+-}_m = 0$ if none of the groups $A_{[m-]}$ and $A_{[m+]}$ are attached to repeating units belonging to the sub-domains or sequences and $\delta^{S+-}_m = 1$ otherwise. Likewise, $\delta^{S-}_m = 1$ when the group $A_{[m-]}$ is attached to repeating units belonging to the sub-domains or sequences and $\delta^{S-}_m = 0$ otherwise. δ^{S+}_m is used in a similar way for group $A_{[m+]}$ (see Table 2). These indicator variables were not needed when just the CLD regardless of sequences or sub-domains was being computed.

For the linear polycondensation of three monomers $\mathbf{UA}_2 + \mathbf{QB}_2 + \mathbf{PC}_2$, considering the sub-domains …**UQUQ**… (see Tables 3 and 4), when the end group linking reaction $\mathbf{A} + \mathbf{B}$ occurs, the two reactive groups involved are attached to repeating units considered in the sub-domains ($\delta^{S+-}_1 = 1$) and, therefore, the size of the sub-domains increases by such a reaction, as described by Eq. (2). Likewise, in a coupling

Table 2
Reaction indicator variables for chemical reactions considered in the kinetic description of the formation of sub-domains or sequences

Description of reaction *m*	Characterization	Reaction indicator variable ($\delta^S_m = 0$ otherwise)
Polymer/polymer couplings	Two groups attached to RU belonging to sub-domains or sequences	$\delta^{S+-}_m = 1$
	Only one group attached to RU belonging to sub-domains or sequences	$\delta^{S-}_m = 1$
Polymer/non-polymer reactions	Two groups attached to RU belonging to sub-domains or sequences	$\delta^{S+-}_m = 1$
	Only one group attached to RU belonging to sub-domains or sequences and:	
	This group is in the polymer molecule	$\delta^{S-}_m = 1$
	This group is in the non-polymer molecule	$\delta^{S+}_m = 1$
Bimolecular initiations	Involving monomers containing RU belonging to sub-domains or sequences	$\delta^{SI}_m = 1$
Unimolecular reactions	Involving polymer sub-domains or sequences	$\delta^{S*}_m = 1$
Bimolecular reactions between polymers without coupling	Involving polymer sub-domains or sequences	$\delta^{S**-}_m = 1$ $\delta^{S**+}_m = 1$
Transfers to monomers	Involving polymer sub-domains or sequences	$\delta^{SM-}_m = 1$
	Involving monomers containing RU belonging to sub-domains or sequences	$\delta^{SM+}_m = 1$

Table 3
Chemical groups considered in the polycondensation of three bifunctional monomers

Description of group	Alias	Laplace parameter	Attached to the repeating units belonging to the sequence?
End group **A**	A_1	s_1	Yes ($\delta^S_{G_1} = 1$)
End group **B**	A_2	s_2	Yes ($\delta^S_{G_2} = 1$)
End group **C**	A_3	s_3	No ($\delta^S_{G_3} = 0$)
Moiety **U**	A_4	$s_4 = \xi_1$	
Moiety **Q**	A_5	$s_5 = \xi_2$	
Moiety **P**	A_6	s_6	

reaction $\mathbf{A} + \mathbf{C}$, only group **A** is attached to the repeating units belonging to the sub-domains $\delta_2^{S-} = 1$. As a result of this chemical reaction (described by Eq. (3)), sub-domains …**UQUQ**… are capped by **P**.

The other $N_R - N_{R_P}$ reactions take place between a group belonging to a polymer molecule and a non-polymeric molecule. In this case the creation or destruction of sub-domains or sequences by such a reaction can be described as follows:

$$\mathbf{S}(\mathbf{q}, \mathbf{a} - \nu_m^- - \nu_m^+) + A_{[m+]} \xrightarrow{k_m} \mathbf{S}(\mathbf{q}, \mathbf{a}) \tag{4}$$

$$\mathbf{S}(\mathbf{q}, \mathbf{a} - \nu_m^-) + A_{[m+]} \xrightarrow{k_m} \mathbf{S}(\mathbf{q}, \mathbf{a}) \tag{5}$$

$$A_{[m-]} + A_{[m+]} \xrightarrow{k_m} \mathbf{S}(\mathbf{q}, \nu_m^+) \tag{6}$$

Eq. (4) describes the reaction of a sequence with a non-polymeric molecule containing the repeating units belonging to the sub-domains or sequences and in Eq. (5), identical to Eq. (3), the reaction occurs with a non-polymeric molecule not containing these kinds of repeating units. Through this latter reaction, sub-domains or sequences are capped by repeating units not belonging to their main body, and as above, $\delta_m^{S-} = 1$, if in the reaction m the group $A_{[m-]}$ is attached to repeating units belonging to the sequence and $\delta_m^{S-} = 0$ otherwise. Eq. (6) describes the creation of new sub-domains or sequences when the group $A_{[m-]}$ is not attached to the repeating units belonging to the sub-domains or sequences, but $A_{[m+]}$ contains repeating units belonging to the sub-domains or sequences being considered.

3.2. Bimolecular initiation reactions

It is considered that N_I bimolecular initiation reactions involving a pair of groups $A_{[I_{m-}]}$ and $A_{[I_{m+}]}$, not present in the polymer, create a new polymer molecule. An example of this kind of reaction is the initiation of a monomer by primary radicals. In this case, if repeating units belonging to the sequence being considered are involved ($\delta_m^{SI} = 1$), a new sequence is created:

$$A_{[I_{m-}]} + A_{[I_{m+}]} \xrightarrow{k_{I_m}} \mathbf{S}(\mathbf{q}, \nu_{I_m}) \tag{7}$$

Table 4
Kinetic scheme considered in the polycondensation of three bifunctional monomers

Reaction name	Chemical equation	Stoichiometric functions	Binary variables
End group linking $\mathbf{A} + \mathbf{B}$	$A_1 + A_2 \xrightarrow{k_1 = k_{12}} Z_{AB}$	$\Psi_1^- = \frac{1}{s_1}$, $\Psi_1^+ = \frac{1}{s_2}$	$\delta_1^{S+-} = 1$
End group linking $\mathbf{A} + \mathbf{C}$	$A_1 + A_3 \xrightarrow{k_2 = k_{13}} Z_{AC}$	$\Psi_2^- = \frac{1}{s_1}$, $\Psi_2^+ = \frac{1}{s_3}$	$\delta_2^{S-} = 1$

3.3. Unimolecular reactions

It is assumed that there are such N_R^* unimolecular reactions, $N_{R_P}^*$ of which involving groups in polymer molecules (such as hydride expulsion in anion polymerization) and the others involving non-polymer molecules (such as initiator decomposition forming primary radicals). The first class of reactions changes the number of chemical groups in the sub-domains or sequences:

$$\mathbf{S}(\mathbf{q}, \mathbf{a} - \nu_m^*) \xrightarrow{k_m^*} \mathbf{S}(\mathbf{q}, \mathbf{a}) \tag{8}$$

Intramolecular reactions (leading or not to ring formation) can be described as unimolecular reactions in terms of the concentrations of pairs of groups which can react. This increases a lot the number of reacting groups if any, but the smallest loops are considered.

3.4. Bimolecular reactions without intermolecular coupling

N_R^{**} bimolecular reactions do not create new connections between repeating units. The first $N_{R_P}^{**}$ involve two polymer molecules (e.g. termination by dismutation), the next $N_{R_S}^{**}$ involve a polymer molecule and a small molecule (e.g. transfer to solvent) and the remaining N_S reactions concern only non-polymer molecules. The effect of these reactions over sequence formation can be described as follows:

$$\mathbf{S}(\mathbf{q}, \mathbf{a} - \nu_m^{**-}) + A_{[m+]} \xrightarrow{k_m^{**}} \mathbf{S}(\mathbf{q}, \mathbf{a}) \tag{9}$$

$$A_{[m-]} + \mathbf{S}(\mathbf{q}, \mathbf{a} - \nu_m^{**+}) \xrightarrow{k_m^{**}} \mathbf{S}(\mathbf{q}, \mathbf{a}) \tag{10}$$

When two polymer molecules are involved (first $N_{R_P}^{**}$ reactions), Eqs. (9) and (10) are possible. Otherwise, for the next $N_{R_S}^{**}$ reactions, only Eq. (9) must be considered.

3.5. Reactions of transfer to monomer

In the present analysis, N_M reactions between a group in a polymer molecule and a monomer (transfer to monomer) change the extant molecule and create a new polymer molecule. The effect of this kind of reactions on the sub-domains or sequences is described by:

$$\mathbf{S}(\mathbf{q}, \mathbf{a} - \nu_{M_m}^-) + A_{[m+]} \xrightarrow{k_{M_m}} \mathbf{S}(\mathbf{q}, \mathbf{a}) + \mathbf{S}(\mathbf{q}, \nu_{M_m}^+) \tag{11}$$

The monomer in Eq. (11) is supposed to contain a repeating unit belonging to the sequence ($\delta_m^{SM+} = 1$). Otherwise ($\delta_m^{SM+} = 0$), only the extant sequence is changed and the formation of a new sequence does not occur.

4. Prediction of average sequence lengths and sequence length distributions in ideal reactors

Following the same methods as in previous works [31,34] to obtain the generating function of the rate equations of formation of polymer species by chemical reaction, it is possible now to write the generating function of the rate equations of formation of sub-domains or sequences by chemical reaction as Eq. (12) below:

$$\begin{aligned} U_{\mathrm{R_S}} = & \sum_{m=1}^{N_{\mathrm{R_P}}} k_m \left\{ \delta_m^{S+-} \left[\Psi_m^- \Psi_m^+ \frac{\partial U}{\partial \log s_{[m-]}} \frac{\partial U}{\partial \log s_{[m+]}} - \frac{\partial U}{\partial \log s_{[m-]}} A_{[m+]} - \frac{\partial U}{\partial \log s_{[m+]}} A_{[m-]} \right] + \delta_m^{S-} A_{[m+]} \frac{\partial U}{\partial \log s_{[m-]}} \left(\Psi_m^- - 1 \right) \right\} \\ & + \sum_{m=N_{\mathrm{R_P}}+1}^{N_{\mathrm{R}}} k_m \left[\delta_m^{S+-} \frac{\partial U}{\partial \log s_{[m-]}} A_{[m+]} \left(\Psi_m^- \Psi_m^+ - 1 \right) + \delta_m^{S-} \frac{\partial U}{\partial \log s_{[m-]}} A_{[m+]} \left(\Psi_m^- - 1 \right) + \delta_m^{S+} A_{[m-]} A_{[m+]} \Psi_m^+ \right] \\ & + \sum_{m=1}^{N_{\mathrm{I}}} \delta_m^{SI} k_{\mathrm{I}_m} A_{[\mathrm{I}_{m-}]} A_{[\mathrm{I}_{m+}]} \Psi_{\mathrm{I}_m} + \sum_{m=1}^{N_{\mathrm{R_P}}^*} k_m^* \delta_m^{S*} \frac{\partial U}{\partial \log s_{[m*]}} \left(\Psi_m^* - 1 \right) \\ & + \sum_{m=1}^{N_{\mathrm{R_P}}^{**}} k_m^{**} \left[\delta_m^{S**-} \frac{\partial U}{\partial \log s_{[m**-]}} A_{[m**+]} \left(\Psi_m^{**-} - 1 \right) + \delta_m^{S**+} \frac{\partial U}{\partial \log s_{[m**+]}} A_{[m**-]} \left(\Psi_m^{**+} - 1 \right) \right] \\ & + \sum_{m=N_{\mathrm{R_P}}^{**}+1}^{N_{\mathrm{R}}^{**}-N_{\mathrm{S}}} k_m^{**} \delta_m^{S**-} \frac{\partial U}{\partial \log s_{[m**-]}} A_{[m**+]} \left(\Psi_m^{**-} - 1 \right) \\ & + \sum_{m=1}^{N_M} k_{M_m} A_{[M_{m+}]} \left[\delta_m^{SM-} \frac{\partial U}{\partial \log s_{[M_{m-}]}} \left(\Psi_{M_m}^- - 1 \right) + \delta_m^{SM+} A_{[M_{m-}]} \Psi_{M_m}^+ \right] \end{aligned} \tag{12}$$

The stoichiometric functions [34] are defined taking into account (Table 1) that the groups either with indices up to N_{AP} or above $N_{\mathrm{AP}} + N_{\mathrm{AM}}$ belong to polymer molecules:

$$\begin{aligned} \Psi_L^U(\mathbf{s}) = & \prod_{j=1}^{N_{\mathrm{AP}}} \prod_{j=N_{\mathrm{AP}}+N_{\mathrm{AM}}+1}^{N_{\mathrm{A}}} \left(s_j \right)^{\nu_{Lj}^U} \\ & U = + \;;\; - \;;\; * \;; **+ \;;\; **- \\ & L = m \;;\; \mathrm{I}_m \;;\; M_m \end{aligned} \tag{13}$$

Integration of mass balance equations for a non-steady state perfectly mixed continuous stirred tank reactor will be done in the same way as in previous works [31,34]. Generating functions of the sequence length distributions verify mass balance equations, which are first-order partial differential equations:

$$\frac{\partial U(\mathbf{s})}{\partial t} = U_{\mathrm{R_S}} + \frac{U_{\mathrm{F}}(t) - U}{\tau} - R_v U \tag{14}$$

The initial condition is:

$$U_{|t=0} = U_0[\mathbf{s}_0(t, \mathbf{s})] \tag{15}$$

Eq. (14) must be solved simultaneously with the mass balances for chemical groups and the correspondent set of initial conditions:

$$\begin{aligned} \frac{\mathrm{d}A_n}{\mathrm{d}t} = & \sum_{m=1}^{N_{\mathrm{R}}} k_m \left(\nu_{mn}^- + \nu_{mn}^+ \right) A_{[m-]} A_{[m+]} + \sum_{m=1}^{N_{\mathrm{R}}^*} k_m^* \nu_{mn}^* A_{[m*]} \\ & + \sum_{m=1}^{N_{\mathrm{R}}^{**}} k_m^{**} \left(\nu_{mn}^{**-} + \nu_{mn}^{**+} \right) A_{[m**-]} A_{[m**+]} + \sum_{m=1}^{N_{\mathrm{I}}} k_{\mathrm{I}_m} \nu_{\mathrm{I}_{mn}} A_{[\mathrm{I}_{m-}]} A_{[\mathrm{I}_{m+}]} \\ & + \sum_{m=1}^{N_M} k_{M_m} \left(\nu_{M_{mn}}^- + \nu_{M_{mn}}^+ \right) A_{[M_{m-}]} A_{[M_{m+}]} + \frac{A_{n\mathrm{F}}(t) - A_n}{\tau} - R_v A_n \end{aligned} \tag{16}$$

$$A_{n|t=0} = A_{n_0} \tag{17}$$

In Eqs. (14) and (16), R_v represents the rate of relative change of volume caused by chemical reactions, as in previous works [34]. The general solution of Eqs. (14)–(17) using the method of characteristics and the equations for the moments of the SLD are presented in Appendix A.

A simple example is provided by the linear polycondensation of three monomers with the kinetic scheme presented in Tables 3 and 4, in a batch reactor without volume change. The SLD is obtained from the resolution of the following non-linear first-order partial differential equation:

$$\begin{aligned} \frac{\partial U}{\partial t} = & \frac{k_1}{s_1\, s_2} \frac{\partial U}{\partial \log s_1} \frac{\partial U}{\partial \log s_2} + \frac{k_2}{s_1} A_3 \frac{\partial U}{\partial \log s_1} \\ & - (k_1 A_2 + k_2 A_3) \frac{\partial U}{\partial \log s_1} - k_1 A_1 \frac{\partial U}{\partial \log s_2} \end{aligned} \tag{18}$$

with initial condition:

$$U_{|t=0} = U_0(\mathbf{s}_0) = \frac{A_{10}}{2} s_{10}^2\, s_{40} + \frac{A_{20}}{2} s_{20}^2\, s_{50} \tag{19}$$

In Eq. (18) the positive terms are due to the formation of sequences by end group linking ($\mathbf{A} + \mathbf{B}$) or by end capping ($\mathbf{A} + \mathbf{C}$). The negative terms come from the consumption of extant sequences by reaction of their end groups. For this particular chemical system it is possible to obtain an analytical solution for the SLD as presented in Appendix B.

5. Non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer

The present method is able to predict the instantaneous or the cumulative properties of the composition or the sequence distributions in an automated way. This can be done considering rather complex kinetic schemes and without assuming a set of approximation conditions generally used (namely in radical polymerizations) in order to obtain mathematical tractable problems with current methods. The quasi-steady state approximation for the concentrations of radicals and the long-chain hypothesis are two examples of often used simplifications in this context, namely with linear polymerization systems. It is known [3] that short chains may exhibit composition transients before the steady state composition is reached. This will happen when monomers are not initiated according to the quasi-steady state ratio. In these circumstances, simple probabilistic approaches are no longer valid and the appropriate derivations can be made only by kinetic equations or by Markov chain theory. The possibility to simulate other kinds of reactor operation conditions (such as continuous stirred tanks, or semi-batch reactors) in an automated way is the other distinctive key feature of the present approach.

The usefulness of the present approach even with linear radical polymerization systems was confirmed by predicting the SLD for a copolymerization with penultimate kinetic effects. Important differences between the predictions of the present method (including termination and initiation reactions) and of a probabilistic approach [3,40] were identified, namely for high monomer conversions. In order to explain these differences, the predictions of the present method without considering termination reactions and with instantaneous initiation (live polymerization) were also performed and a full agreement between the probabilistic approach and the live polymerization system was achieved. This result is consistent with the base assumptions of the probabilistic approach, since it directly takes into account only the propagation reactions and, therefore, is strictly valid only when the polymerization is dominated by these reactions.

The most innovative feature of the present approach is the possibility of calculating the sequence length distributions and/or their averages in non-linear irreversible multicomponent polymerizations. Moreover, this can be performed before and after gelation when it occurs. This issue will be introduced in the current section considering a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer. In this chemical system, sub-domains or sequences are defined as domains containing only two of the three kinds of monomeric units present in the polymer. An interesting example is the set of sub-domains or sequences formed by one kind of vinyl monomer (e.g. styrene) and the divinyl monomer (e.g. divinylbenzene). It will be shown that in this case the formation of an infinite network including only units of these two kinds (sequence gelation) is possible. The sequence gelation (when it occurs) is always delayed relatively to the CLD gelation (infinite network formation including all kinds of monomeric units). In some conditions gelation is possible for the CLD, but not for the SLD.

Note that an increase of the number of multifunctional monomers and thus of the kinds of sub-domains can introduce further gel points for the different sub-domains.

5.1. Kinetic scheme

Table 5 presents the set of chemical groups considered in this case study.

A total of $N_A = 12$ groups are used to describe the polymerization system. The first $N_{AP} = 4$ are active and present in the polymer: the related polymer radicals for each kind of monomer and the pendant double bonds from the divinyl monomer. Considering that one wishes to obtain the SLD of domains containing one kind of vinyl monomer (M_1) and the divinyl monomer (M_2), it means that in this case $\mathbf{q} = [10,11]$. Only the first $N_{APS} = 3$ of N_{AP} are attached to repeating units belonging to the sub-domains or sequences (for these groups $\delta_G^S = 1$). There are $N_{AM} = 5$ groups that are active but not present in the polymer: the three monomers, initiator and primary radicals. Their indices vary between 5 and 9, as presented in Table 5 and the first $N_{AMS} = 2$ of this set are attached to the repeating units belonging to the sub-domains or sequences (monomer M_1 and monomer M_2). The remaining $N_A - N_{AP} - N_{AM} = 3$ are inactive groups belonging to the polymer, which are here the structures coming from the polymerized monomer units.

The kinetic scheme of this case study is presented in Tables 6 and 7. Twenty nine different reactions are considered, belonging to the categories below enumerated:

- Initiator decomposition
- Monomer initiations
- Pendant double bond initiations
- Monomer propagations
- Pendant double bond propagations
- Terminations by combination
- Terminations by disproportionation

Table 5
Chemical groups considered in a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer

Description of the group	Index (m)	Alias	$\delta^S_{G_m}$
Polymer radical located at monomer M_1	1	A_1	1
Polymer radical located at monomer M_2	2	A_2	1
Pendant double bond from monomer M_2	3	A_3	1
Polymer radical located at monomer M_3	4	A_4	0
Monovinyl monomer	5	M_1	1
Divinyl monomer	6	M_2	1
Monovinyl monomer	7	M_3	0
Initiator	8	I	0
Primary radical	9	R_0	0
Polymerized unit from M_1	10	A_{10}	–
Polymerized unit from M_2	11	A_{11}	–
Polymerized unit from M_3	12	A_{12}	–

Table 6
Set of chemical reactions considered in a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer

Reaction	Chemical equation	Stoichiometric functions	Comments
Coupling reactions: polymer/polymer			
Terminations by combination			
A_1 with A_1	$A_1+A_1\xrightarrow{k_1=k_{tc11}}Z_{11}$	$\Psi_1^-=\frac{1}{s_1}$, $\Psi_1^+=\frac{1}{s_1}$	$\delta_1^{S+-}=1$
A_1 with A_2	$A_1+A_2\xrightarrow{k_2=k_{tc12}}Z_{12}$	$\Psi_2^-=\frac{1}{s_1}$, $\Psi_2^+=\frac{1}{s_2}$	$\delta_2^{S+-}=1$
A_1 with A_4	$A_1+A_4\xrightarrow{k_3=k_{tc13}}Z_{13}$	$\Psi_3^-=\frac{1}{s_1}$, $\Psi_3^+=\frac{1}{s_4}$	$\delta_3^{S-}=1$
A_2 with A_2	$A_2+A_2\xrightarrow{k_4=k_{tc22}}Z_{22}$	$\Psi_4^-=\frac{1}{s_2}$, $\Psi_4^+=\frac{1}{s_2}$	$\delta_4^{S+-}=1$
A_2 with A_4	$A_2+A_4\xrightarrow{k_5=k_{tc23}}Z_{23}$	$\Psi_5^-=\frac{1}{s_2}$, $\Psi_5^+=\frac{1}{s_4}$	$\delta_5^{S-}=1$
A_4 with A_4	$A_4+A_4\xrightarrow{k_6=k_{tc33}}Z_{33}$	$\Psi_6^-=\frac{1}{s_4}$, $\Psi_6^+=\frac{1}{s_4}$	$\delta_6^{S}=0$
Propagations of pendant double bonds			
A_1 with A_3	$A_1+A_3\xrightarrow{k_7=k_{p14}}A_2$	$\Psi_7^-=\frac{1}{s_1}$, $\Psi_7^+=\frac{s_2}{s_3}$	$\delta_7^{S+-}=1$
A_2 with A_3	$A_2+A_3\xrightarrow{k_8=k_{p24}}A_2$	$\Psi_8^-=\frac{1}{s_2}$, $\Psi_8^+=\frac{s_2}{s_3}$	$\delta_8^{S+-}=1$
A_4 with A_3	$A_3+A_4\xrightarrow{k_9=k_{p34}}A_2$	$\Psi_9^-=\frac{s_2}{s_3}$, $\Psi_9^+=\frac{1}{s_4}$	$\delta_9^{S-}=1$
Coupling reactions: polymer/non-polymer			
Propagations			
A_1 with M_1	$A_1+A_5\xrightarrow{k_{10}=k_{p11}}A_1+A_{10}$	$\Psi_{10}^-=\frac{1}{s_1}$, $\Psi_{10}^+=s_1s_{10}$	$\delta_{10}^{S+-}=1$
A_1 with M_2	$A_1+A_6\xrightarrow{k_{11}=k_{p12}}A_2+A_3+A_{11}$	$\Psi_{11}^-=\frac{1}{s_1}$, $\Psi_{11}^+=s_2s_3s_{11}$	$\delta_{11}^{S+-}=1$
A_1 with M_3	$A_1+A_7\xrightarrow{k_{12}=k_{p13}}A_4+A_{12}$	$\Psi_{12}^-=\frac{1}{s_1}$, $\Psi_{12}^+=s_4s_{12}$	$\delta_{12}^{S-}=1$
A_2 with M_1	$A_2+A_5\xrightarrow{k_{13}=k_{p21}}A_1+A_{10}$	$\Psi_{13}^-=\frac{1}{s_2}$, $\Psi_{13}^+=s_1s_{10}$	$\delta_{13}^{S+-}=1$
A_2 with M_2	$A_2+A_6\xrightarrow{k_{14}=k_{p22}}A_2+A_3+A_{11}$	$\Psi_{14}^-=\frac{1}{s_2}$, $\Psi_{14}^+=s_2s_3s_{11}$	$\delta_{14}^{S+-}=1$
A_2 with M_3	$A_2+A_7\xrightarrow{k_{15}=k_{p23}}A_4+A_{12}$	$\Psi_{15}^-=\frac{1}{s_2}$, $\Psi_{15}^+=s_4s_{12}$	$\delta_{15}^{S-}=1$
A_4 with M_1	$A_4+A_5\xrightarrow{k_{16}=k_{p31}}A_1+A_{10}$	$\Psi_{16}^-=\frac{1}{s_4}$, $\Psi_{16}^+=s_1s_{10}$	$\delta_{16}^{S+}=1$
A_4 with M_2	$A_4+A_6\xrightarrow{k_{17}=k_{p32}}A_2+A_3+A_{11}$	$\Psi_{17}^-=\frac{1}{s_4}$, $\Psi_{17}^+=s_2s_3s_{11}$	$\delta_{17}^{S+}=1$
A_4 with M_3	$A_4+A_7\xrightarrow{k_{18}=k_{p33}}A_4+A_{12}$	$\Psi_{18}^-=\frac{1}{s_4}$, $\Psi_{18}^+=s_4s_{12}$	$\delta_{18}^{S}=0$
Bimolecular initiation reactions			
Initiations of the monomers			
R_0 with M_1	$A_5+A_9\xrightarrow{k_{I_1}=k_{i1}}A_1+A_9$	$\Psi_{I_1}=s_1s_{10}$	$\delta_1^{SI}=1$
R_0 with M_2	$A_6+A_9\xrightarrow{k_{I_2}=k_{i2}}A_2+A_3+A_{11}$	$\Psi_{I_2}=s_2s_3s_{11}$	$\delta_2^{SI}=1$
R_0 with M_3	$A_7+A_9\xrightarrow{k_{I_3}=k_{i3}}A_4+A_{12}$	$\Psi_{I_3}=s_4s_{12}$	$\delta_3^{SI}=0$

There are a total number of $N_R=18$ different reactions creating connections between repeating units, with the first $N_{R_P}=9$ (6 terminations by combination and 3 propagations of pendant double bonds) involving two active groups belonging to the polymer. The remaining $N_R-N_{R_P}=9$ involve the reaction between groups in the polymer and a non-polymer group and correspond to the different propagation reactions of polymer radicals with the three monomers. The characterization of the influence of these reactions in the sub-domains or sequences is defined through the associated reaction indicator variable δ_m^S.

Another $N_I=3$ reactions are the bimolecular initiations of the three monomers by the primary radicals. There are $N_R^{**}=7$ bimolecular reactions without the creation of connection between repeating units. The first $N_{R_P}^{**}=6$ are the terminations by disproportionation and they involve only polymer groups. The single remaining reaction (hence, $N_{R_S}^{**}=1$) involves a polymer molecule and a small molecule and consists in the initiation of the pendant double bonds.

Finally, the kinetic scheme includes one unimolecular reaction, the initiator decomposition into primary radicals ($N_R^*=1$).

5.2. Kinetic parameters and operation conditions

In order to carry out the numerical simulations of the present case study, the values of the 30 kinetic parameters

Table 7
Set of chemical reactions considered in a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer (continuation from Table 6)

Reaction	Chemical equation	Stoichiometric functions	Comments
Bimolecular reactions without coupling			
Terminations by disproportionation			
A_1 with A_1	$A_1 + A_1 \xrightarrow{k_1^{**}=k_{\mathrm{td}11}} \mathrm{SG} + \mathrm{UG}$	$\Psi_1^{**-} = \frac{1}{s_1},\ \Psi_1^{**+} = \frac{1}{s_1}$	$\delta_1^{S**-} = 1,\ \delta_1^{S**+} = 1$
A_1 with A_2	$A_1 + A_2 \xrightarrow{k_2^{**}=k_{\mathrm{td}12}} \mathrm{SG} + \mathrm{UG}$	$\Psi_2^{**-} = \frac{1}{s_1},\ \Psi_2^{**+} = \frac{1}{s_2}$	$\delta_2^{S**-} = 1,\ \delta_2^{S**+} = 1$
A_1 with A_4	$A_1 + A_4 \xrightarrow{k_3^{**}=k_{\mathrm{td}13}} \mathrm{SG} + \mathrm{UG}$	$\Psi_3^{**-} = \frac{1}{s_1},\ \Psi_3^{**+} = \frac{1}{s_4}$	$\delta_3^{S**-} = 1,\ \delta_3^{S**+} = 0$
A_2 with A_2	$A_2 + A_2 \xrightarrow{k_4^{**}=k_{\mathrm{td}22}} \mathrm{SG} + \mathrm{UG}$	$\Psi_4^{**-} = \frac{1}{s_2},\ \Psi_4^{**+} = \frac{1}{s_2}$	$\delta_4^{S**-} = 1,\ \delta_4^{S**+} = 1$
A_2 with A_4	$A_2 + A_4 \xrightarrow{k_5^{**}=k_{\mathrm{td}23}} \mathrm{SG} + \mathrm{UG}$	$\Psi_5^{**-} = \frac{1}{s_2},\ \Psi_5^{**+} = \frac{1}{s_4}$	$\delta_5^{S**-} = 1,\ \delta_5^{S**+} = 0$
A_4 with A_4	$A_4 + A_4 \xrightarrow{k_6^{**}=k_{\mathrm{td}33}} \mathrm{SG} + \mathrm{UG}$	$\Psi_6^{**-} = \frac{1}{s_4},\ \Psi_6^{**+} = \frac{1}{s_4}$	$\delta_6^{S**-} = 0,\ \delta_6^{S**+} = 0$
Initiation of pendant double bonds			
R_0 with A_3	$A_3 + A_9 \xrightarrow{k_7^{**}=k_{i4}} A_2$	$\Psi_7^{**-} = \frac{s_2}{s_3},\ \Psi_7^{**+} = 1$	$\delta_7^{S**-} = 1,\ \delta_7^{S**+} = 0$
Unimolecular reactions			
Initiator decomposition			
I decomposition	$A_8 \xrightarrow{k_1^{*}=k_{\mathrm{d}}} 2fA_9$	$\Psi_1^{*} = 1$	$\delta_1^{S*} = 0$

involved must be specified. As stated before, the priority of the present work has been the development of a method capable of taking into account the complexities of these kinds of polymerization systems and hopefully flexible enough to incorporate further reactions. Therefore, in this work, once again no particular chemical system has been selected and the simulations were carried out using a typical set of kinetic parameters. This information is presented in Table 8. The reactivity ratio r_{12} is the same as that of styrene in the copolymerization styrene/*m*-divinylbenzene [41], r_{31} and r_{13} are the same than in the system styrene/methylmethacrylate [2]. The homopropagation rate coefficients k_{p11} and k_{p33} are also the same as in the polymerization of styrene and methylmethacrylate at 60 °C [2,41] and the global termination rate constant k_t was chosen to be the same as in the styrene homopolymerization. The initiator decomposition kinetics (f and k_d) is typical of AIBN.

Table 8
Set of kinetic parameters considered for a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer

Parameter	Relative value	Absolute value ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$)
Reference set [2,41]		
k_{p11}		145
k_{p12}	$r_{12} = k_{p11}/k_{p12} = 0.44$	329.5
k_{p33}		515
k_{p31}	$r_{31} = k_{p33}/k_{p31} = 0.46$	1119.6
k_{p13}	$r_{13} = k_{p11}/k_{p13} = 0.52$	278.8
k_t		2.9×10^7
k_d		$9 \times 10^{-6}\ \mathrm{s^{-1}}$
f		0.5 (adimensional)
Assumptions in this and related works [34]		
k_{p21}	$C_{p21} = k_{p21}/k_{p11} = 1$	145
k_{p22}	$r_{21} = k_{p22}/k_{p21} = 1/r_{12} = 1/0.44$	329.5
k_{p23}	$C_{p23} = k_{p23}/k_{p33} = 1$	515
k_{p32}	$r_{32} = k_{p33}/k_{p32} = 1/r_{23} = 515/329.5$	329.5
k_{p14}	$C_{p14} = k_{p14}/k_{p11} = 0.138$	20.01
k_{p24}	$C_{p24} = k_{p24}/k_{p22} = 0.138$	45.471
k_{p34}	$C_{p34} = k_{p34}/k_{p33} = 0.138$	71.07
k_{i1}	$k_{i1}/k_{p11} = 1$	145
k_{i2}	$k_{i2}/k_{p22} = 1$	329.5
k_{i3}	$k_{i3}/k_{p33} = 1$	515
k_{i4}	$k_{i4}/k_{p24} = 1$	45.471
$k_{\mathrm{ct}ij}$	$k_{\mathrm{tc}ij} = 0.5 \times k_t/\sqrt{ij}$	
$k_{\mathrm{dt}ij}$	$k_{\mathrm{td}ij} = 0.5 \times k_t/\sqrt{ij}$	

To obtain the numerical values of the remaining kinetic parameters some assumptions must be also used due to the difficulty in measuring kinetic parameters when a small fraction of divinyl monomer is present in a copolymerization [41]. The reactivity of the pendant double bonds and of the radical from divinyl monomer was quantified using similar rules to the one before considered in the study of the system styrene/*m*-divinylbenzene [34]. Termination is supposed to occur with the same frequency by combination and by disproportionation and the dependence relatively to the nature of the radicals involved is described in Table 8.

Simulations were performed considering constant rate coefficients in an isothermal batch reactor with a global initial monomer concentration $M_0 = M_{10} + M_{20} + M_{30} = 4\ \mathrm{mol\ dm^{-3}}$ and an initiator concentration $I_0 = 0.08\ \mathrm{mol\ dm^{-3}}$. The initial mole fraction of the monomer M_1 was always set equal to $f_{10} = 0.9$. Different values of the mole fraction of divinyl monomer (f_{20}) were considered and the mole fraction of the third monomer is obtained from $f_{30} = 1 - f_{10} - f_{20}$.

5.3. Predictions of average sequence lengths

The prediction of average sequence lengths can be split into two sub-problems. Before gelation, the population balance equations of the moments are integrated along the trivial solution of the characteristics, $\mathbf{s} = 1$, leading to an initial value problem. If the goal is the prediction of number- and weight-average sequence lengths, moments up to the second order must be obtained. In this particular chemical system, one must integrate a system of $N_{eq} = N_{AP} + N_{AM} + N_P + N_P(N_P + 1)/2 + 1 = 45$ ordinary differential equations. Writing explicitly the differential equations for the moments is a time-consuming and error-prone task. It is, therefore, preferable to use a generic computer program where these equations are generated automatically. This is a rather general program, independent of the chemical system, and for this reason the general model developed by the authors can be thought as a kind of interpreter of irreversible polymerization schemes, now applied to the prediction of sequence lengths.

The whole computation of average sequence lengths before gelation is done with a single integration in which the SLD gelation is identified by the divergence of the second order moments. For the current chemical system, required CPU times are about 5 s. Computations were carried out in a workstation with a double Xeon 2.8 GHz processor with 4 Gb memory, running Red Hat Linux 9.0 (kernel version 2.4.20-8). Fortran sources were compiled using GNU compiler g77 based on gcc 3.2.2.

If predictions past gel point must be obtained, a non-trivial solution for the characteristics has to be found and this can be a very difficult problem, especially in radical polymerizations. Nevertheless, for the SLD prediction, the same technique successfully applied to the calculation of the CLD past gelation [32–36] can be used. For the present chemical system, the numerical integration of the characteristics consists in the resolution of a two-point boundary value problem with $N_{eq} = 3N_{AP} + N_{AM} = 17$ ordinary differential equations. The CPU time spent for solving each problem of characteristics is about 389 s. The solution for the characteristics thus obtained is used to integrate the moments along the non-trivial solution, and therefore to compute the number and weight-average sequence lengths after gelation. This two-step procedure must be repeated for each different value of the chosen final time $t = t_f$. Typically, a single point in the post-gel region needs 392 s of CPU time, which clearly demonstrates that the solution of the characteristics is the controlling step in terms of CPU time in the post-gel region.

In Fig. 1 are presented the number- and weight-average sequence lengths of the domains containing only M_1 and M_2 units as a function of the global monomer conversion. With this initial composition, $f_{10} = 0.9$, $f_{20} = 0.06$ and $f_{30} = 0.04$, sequence gelation is predicted when the global monomer conversion is around 0.847 (23.6 h). Sequence gelation is identified by the divergence of the second order moments of the SLD (weight-average in the figure) and corresponds to the formation of domains of macroscopic size. Note that with the present method, predictions are also possible in the post-gelation region, as presented in Fig. 1.

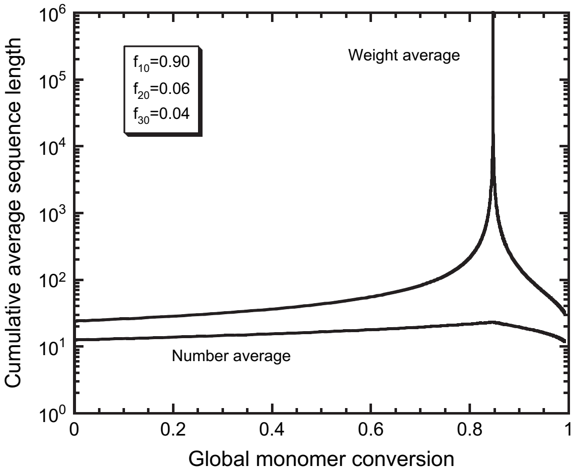

Fig. 1. Cumulative number- and weight-average overall sequence lengths of M_1 and M_2 units in a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer. Initial composition: $f_{10} = 0.9$, $f_{20} = 0.06$ and $f_{30} = 0.04$.

In Fig. 2 the evolution of the weight-average sequence length is presented for systems with different initial compositions. As expected, the monomer conversion (or time) needed for sequence gelation increases as the initial mole fraction of the divinyl monomer is decreased: 0.572 (9.2 h) for $f_{20} = 0.08$, 0.847 (23.6 h) for $f_{20} = 0.06$ and 0.973 (59.4 h) for $f_{20} = 0.04$. Note that with $f_{20} = 0.02$ no sequence gelation is predicted and the final weight-average sequence length is around 40. In Fig. 3 the evolutions of the weight-average lengths of the CLD and SLD distributions for the system with initial composition $f_{20} = 0.06$ are compared. It is interesting to note that for the CLD, gelation is predicted when the monomer conversion is about 0.157 (1.6 h) which is lower than the conversion needed for sequence gelation. CLD gelation corresponds to the formation of an infinite network including all kinds of monomer units and in SLD gelation only the domains containing M_1 and M_2 are accounted. This means that in the gel (correspondent to CLD) one can only find sub-domains or sequences that are of finite size, as it can be observed in Fig. 3. Similar conclusions on the relation between CLD and SLD gelation can be obtained for the systems with $f_{20} = 0.08$ and $f_{20} = 0.04$. With $f_{20} = 0.02$ CLD gelation is predicted when the monomer conversion is around

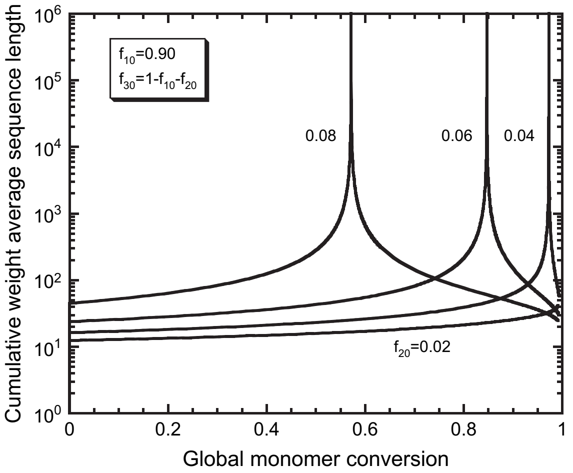

Fig. 2. Cumulative weight-average overall sequence length of M_1 and M_2 units in a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer. Different initial compositions with fixed $f_{10} = 0.9$.

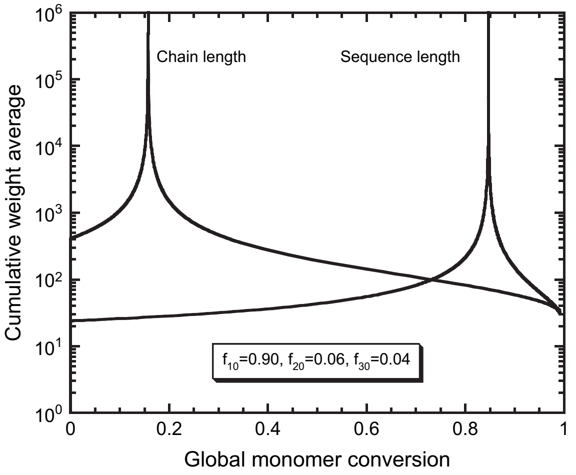

Fig. 3. Weight-averages of chain and sequence lengths in a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer. Initial composition: $f_{10} = 0.9$, $f_{20} = 0.06$ and $f_{30} = 0.04$.

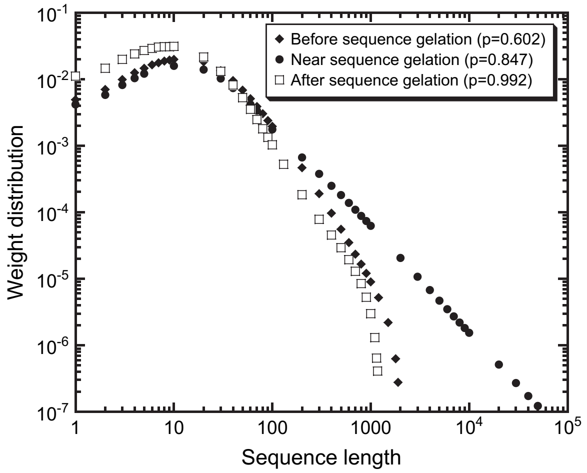

Fig. 4. The evolution of the sequence length distribution in a non-linear radical terpolymerization of two vinyl monomers with a divinyl monomer. Initial composition: $f_{10} = 0.9$, $f_{20} = 0.06$ and $f_{30} = 0.04$.

0.538 (8.1 h) but the formation of macroscopic sub-domains or sequences is absent.

5.4. Predictions of sequence length distributions

The prediction of sequence length distributions can be numerically performed using the same methods applied before for the calculation of chain length distributions [35]. Indeed, in both cases, a probability generating function (Eq. (1) for SLD) must be inverted. In general, $U(\mathbf{s})$ can only be numerically computed solving the problem Eqs. (A1)–(A6) and therefore numerical methods to invert probability generating functions must be used.

Fig. 4 illustrates the evolution of the SLD for the present polymerization system. In this case the sequence length corresponds to the length of domains containing only units with one kind of vinyl monomer and the divinyl monomer and, therefore, to the overall count of units M_1 with M_2: $n = n_{10} + n_{11}$. The weight SLD presented in Fig. 4 has the usual definition: $S_w(n) = nS(n)/\sum_{n=0}^{\infty} nS(n)$.

Three different monomer conversions (times of polymerization) were chosen to predict the SLD: before sequence gelation ($p = 0.602$), near the sequence gelation ($p = 0.847$) and after sequence gelation ($p = 0.992$). For this system the evolution of the average sequence lengths is presented in Fig. 1. For all values of conversion, the number average sequence length is very similar: 17.8 for $p = 0.602$, 23.2 for $p = 0.847$ and 11.9 for $p = 0.992$. Nevertheless, the correspondent weight-average sequence lengths present a huge variation, due to the gelation phenomena: 55.5, 10^9 and 31.8, respectively. The variation of the dispersion of the SLD along the polymerization becomes clear if a log–log plot of this distribution is compared, as done in Fig. 4. The main difference between the distributions occurs in the end tail corresponding to high sequence lengths. For the conversions $p = 0.602$ and $p = 0.992$ the distributions vanish around $n = 1100$ and $n = 1000$, respectively. However, in the sequence gel point, as expected, sub-domains or sequences with a huge size are predicted to exist. Note that at this conversion the first moment of $S_w(n)$, $\sum_{n=0}^{\infty} nS_w(n)$, is infinite.

6. Non-linear radical copolymerization including transfer to polymer and terminal double bonds branching

In many radical polymerizations, long-chain branching can occur due to propagation on terminal double bonds and transfer to polymer [1]. Ethylene, methyl acrylate, vinyl chloride and vinyl acetate are some examples where branching is present as a consequence of these mechanisms. The influence of these kinds of branching on the CLD of the resulting homopolymers has already been studied using the present kinetic approach [33,35]. In this section, the modeling is extended to the SLD predictions and for this purpose, a non-linear radical copolymerization including transfer to polymer and terminal double bonds branching is considered. It will be shown that in some circumstances the formation of an infinite network including only units of one kind of monomer (sequence gelation) is possible. The sequence gelation (when it occurs) is always delayed relatively to the CLD gelation (infinite network formation including all kinds of monomeric units). Also in this case, in some conditions, gelation is possible for the CLD, but not for the SLD.

6.1. Kinetic scheme

Table 9 presents the set of chemical groups considered in this case study. A total of $N_A = 12$ groups are used to describe this polymerization system. The first $N_{AP} = 6$ are active and present in the polymer: for each kind of monomer the related polymer radicals, terminal double bonds originated by transfer to monomer and transfer to polymer centers are distinguished. Considering that one wants to compute the SLD of one kind of monomer unit, let us say M_1 and therefore $\mathbf{q} = [11]$, only the first $N_{APS} = 3$ of N_{AP} are attached to the repeating units

Table 9
Chemical groups considered in a non-linear radical copolymerization including branching by transfer to polymer and propagation on terminal double bonds

Description of the group	Index (m)	Alias	$\delta^S_{G_m}$
Polymer radical located at monomer M_1	1	A_1	1
Terminal double bond originated by transfer to monomer M_1	2	A_2	1
Transfer to polymer center located at monomer M_1	3	A_3	1
Polymer radical located at monomer M_2	4	A_4	0
Terminal double bond originated by transfer to monomer M_2	5	A_5	0
Transfer to polymer center located at monomer M_2	6	A_6	0
Monomer 1	7	M_1	1
Monomer 2	8	M_2	0
Initiator	9	I	0
Primary radical	10	R_0	0
Polymerized unit from M_1	11	A_{11}	–
Polymerized unit from M_2	12	A_{12}	–

belonging to the sub-domains or sequences (for these groups $\delta^S_G = 1$).

There are $N_{\mathrm{AM}} = 4$ groups that are active, but not present in the polymer: the two monomers, initiator and primary radicals. Their indices vary between 7 and 10, as presented in Table 9 and the first $N_{\mathrm{AMS}} = 1$ of this set is attached to repeating units belonging to the sequences (monomer M_1). The remaining $N_{\mathrm{A}} - N_{\mathrm{AP}} - N_{\mathrm{AM}} = 2$ are inactive groups belonging to the polymer that in this case study are the structures correspondent to the polymerized monomer units.

The kinetic scheme considered for this case study is presented in Tables 10 and 11. Twenty-seven different reactions are considered, belonging to the categories described below:

- Initiator decomposition
- Monomer initiations
- Terminal double bond initiations
- Monomer propagations
- Transfers to monomers
- Transfers to polymer
- Terminations by combination
- Terminations by disproportionation

$N_{\mathrm{R}} = 11$ different reactions create connections between repeating units, with the first $N_{\mathrm{R_P}} = 7$ (3 terminations by combination and 4 propagations of terminal double bonds originated from transfers to monomers) involving two active groups belonging to the polymer. The remaining $N_{\mathrm{R}} - N_{\mathrm{R_P}} = 4$ involve the reaction between group in the polymer and a non-polymer

Table 10
Set of chemical reactions considered in a non-linear radical copolymerization including branching by transfer to polymer and propagation on terminal double bonds

Reaction name	Chemical equation	Stoichiometric functions	Observations
Coupling reactions: polymer/polymer			
Terminations by combination			
A_1 with A_1	$A_1 + A_1 \xrightarrow{k_1 = k_{tc11}} Z_{11} + A_3 + A_3$	$\Psi_1^- = \frac{s_3}{s_1}$, $\Psi_1^+ = \frac{s_3}{s_1}$	$\delta_1^{S+-} = 1$
A_1 with A_4	$A_1 + A_4 \xrightarrow{k_2 = k_{tc12}} Z_{12} + A_3 + A_6$	$\Psi_2^- = \frac{s_3}{s_1}$, $\Psi_2^+ = \frac{s_6}{s_4}$	$\delta_2^{S-} = 1$
A_4 with A_4	$A_4 + A_4 \xrightarrow{k_3 = k_{tc22}} Z_{22} + A_6 + A_6$	$\Psi_3^- = \frac{s_6}{s_4}$, $\Psi_3^+ = \frac{s_6}{s_4}$	$\delta_3^{S} = 0$
Propagations of terminal double bonds originated from transfers to monomers			
A_1 with A_2	$A_1 + A_2 \xrightarrow{k_4 = k^*_{p11}} A_3 + A_1$	$\Psi_4^- = \frac{s_3}{s_1}$, $\Psi_4^+ = \frac{s_1}{s_2}$	$\delta_4^{S+-} = 1$
A_1 with A_5	$A_1 + A_5 \xrightarrow{k_5 = k^*_{p12}} A_3 + A_4$	$\Psi_5^- = \frac{s_3}{s_1}$, $\Psi_5^+ = \frac{s_4}{s_5}$	$\delta_5^{S-} = 1$
A_4 with A_2	$A_2 + A_4 \xrightarrow{k_6 = k^*_{p21}} A_1 + A_6$	$\Psi_6^- = \frac{s_1}{s_2}$, $\Psi_6^+ = \frac{s_6}{s_4}$	$\delta_6^{S-} = 1$
A_4 with A_5	$A_4 + A_5 \xrightarrow{k_7 = k^*_{p22}} A_6 + A_4$	$\Psi_7^- = \frac{s_6}{s_4}$, $\Psi_7^+ = \frac{s_4}{s_5}$	$\delta_7^{S} = 0$
Coupling reactions: polymer/non-polymer			
Monomer propagations			
A_1 with M_1	$A_1 + A_7 \xrightarrow{k_8 = k_{p11}} A_3 + A_1 + A_{11}$	$\Psi_8^- = \frac{s_3}{s_1}$, $\Psi_8^+ = s_1 s_{11}$	$\delta_8^{S+-} = 1$
A_1 with M_2	$A_1 + A_8 \xrightarrow{k_9 = k_{p12}} A_3 + A_4 + A_{12}$	$\Psi_9^- = \frac{s_3}{s_1}$, $\Psi_9^+ = s_4 s_{12}$	$\delta_9^{S-} = 1$
A_4 with M_1	$A_4 + A_7 \xrightarrow{k_{10} = k_{p21}} A_6 + A_1 + A_{11}$	$\Psi_{10}^- = \frac{s_6}{s_4}$, $\Psi_{10}^+ = s_1 s_{11}$	$\delta_{10}^{S+} = 1$
A_4 with M_2	$A_4 + A_8 \xrightarrow{k_{11} = k_{p22}} A_6 + A_4 + A_{12}$	$\Psi_{11}^- = \frac{s_6}{s_4}$, $\Psi_{11}^+ = s_4 s_{12}$	$\delta_{11}^{S} = 0$
Bimolecular initiation reactions			
Initiations of the monomers			
R_0 with M_1	$A_7 + A_{10} \xrightarrow{k_{I_1} = k_{i1}} A_1 + A_{11}$	$\Psi_{I_1} = s_1 s_{11}$	$\delta_1^{SI} = 1$
R_0 with M_2	$A_8 + A_{10} \xrightarrow{k_{I_2} = k_{i2}} A_4 + A_{12}$	$\Psi_{I_2} = s_4 s_{12}$	$\delta_2^{SI} = 0$

Table 11
Set of chemical reactions considered in a non-linear radical copolymerization including branching by transfer to polymer and propagation on terminal double bonds (continued from Table 10)

Reaction name	Chemical equation	Stoichiometric functions	Observations
Bimolecular reactions without coupling			
Terminations by disproportionation			
A_1 with A_1	$A_1 + A_1 \xrightarrow{k_1^{**}=k_{\mathrm{td}11}} \mathrm{SG} + \mathrm{UG}$	$\Psi_1^{**-} = \frac{1}{s_1},\ \Psi_1^{**+} = \frac{1}{s_1}$	$\delta_1^{S**-} = 1,\ \delta_1^{S**+} = 1$
A_1 with A_4	$A_1 + A_4 \xrightarrow{k_2^{**}=k_{\mathrm{td}12}} \mathrm{SG} + \mathrm{UG}$	$\Psi_2^{**-} = \frac{1}{s_1},\ \Psi_2^{**+} = \frac{1}{s_4}$	$\delta_2^{S**-} = 1,\ \delta_2^{S**+} = 0$
A_4 with A_4	$A_4 + A_4 \xrightarrow{k_3^{**}=k_{\mathrm{td}22}} \mathrm{SG} + \mathrm{UG}$	$\Psi_3^{**-} = \frac{1}{s_4},\ \Psi_3^{**+} = \frac{1}{s_4}$	$\delta_3^{S**-} = 0,\ \delta_3^{S**+} = 0$
Transfers to polymer			
A_1 with A_3	$A_1 + A_3 \xrightarrow{k_4^{**}=k_{\mathrm{f}p11}} A_1$	$\Psi_4^{**-} = \frac{1}{s_1},\ \Psi_4^{**+} = \frac{s_1}{s_3}$	$\delta_4^{S**-} = 1,\ \delta_4^{S**+} = 1$
A_1 with A_6	$A_1 + A_6 \xrightarrow{k_5^{**}=k_{\mathrm{f}p12}} A_4$	$\Psi_5^{**-} = \frac{1}{s_1},\ \Psi_5^{**+} = \frac{s_4}{s_6}$	$\delta_5^{S**-} = 1,\ \delta_5^{S**+} = 0$
A_4 with A_3	$A_3 + A_4 \xrightarrow{k_6^{**}=k_{\mathrm{f}p21}} A_1$	$\Psi_6^{**-} = \frac{s_1}{s_3},\ \Psi_6^{**+} = \frac{1}{s_4}$	$\delta_6^{S**-} = 1,\ \delta_6^{S**+} = 0$
A_4 with A_6	$A_4 + A_6 \xrightarrow{k_7^{**}=k_{\mathrm{f}p22}} A_4$	$\Psi_7^{**-} = \frac{1}{s_4},\ \Psi_7^{**+} = \frac{s_4}{s_6}$	$\delta_7^{S**-} = 0,\ \delta_7^{S**+} = 0$
Initiation of terminal double bonds originated from transfers to monomers			
R_0 with A_2	$A_2 + A_{10} \xrightarrow{k_8^{**}=k_{i1}^{*}} A_1$	$\Psi_8^{**-} = \frac{s_1}{s_2},\ \Psi_8^{**+} = 1$	$\delta_8^{S**-} = 1,\ \delta_8^{S**+} = 0$
R_0 with A_5	$A_5 + A_{10} \xrightarrow{k_9^{**}=k_{i2}^{*}} A_4$	$\Psi_9^{**-} = \frac{s_4}{s_5},\ \Psi_9^{**+} = 1$	$\delta_9^{S**-} = 0,\ \delta_9^{S**+} = 0$
Transfers to monomers			
A_1 with M_1	$A_1 + A_7 \xrightarrow{k_{M_1}=k_{\mathrm{f}m11}} A_1 + A_2 + A_{11}$	$\Psi_{M_1}^{-} = \frac{1}{s_1},\ \Psi_{M_1}^{+} = s_1 s_2 s_{11}$	$\delta_1^{SM-} = 1,\ \delta_1^{SM+} = 0$
A_1 with M_2	$A_1 + A_8 \xrightarrow{k_{M_2}=k_{\mathrm{f}m12}} A_4 + A_5 + A_{12}$	$\Psi_{M_2}^{-} = \frac{1}{s_1},\ \Psi_{M_2}^{+} = s_4 s_5 s_{12}$	$\delta_2^{SM-} = 1,\ \delta_2^{SM+} = 0$
A_4 with M_1	$A_4 + A_7 \xrightarrow{k_{M_3}=k_{\mathrm{f}m21}} A_1 + A_2 + A_{11}$	$\Psi_{M_3}^{-} = \frac{1}{s_4},\ \Psi_{M_3}^{+} = s_1 s_2 s_{11}$	$\delta_3^{SM-} = 0,\ \delta_3^{SM+} = 1$
A_4 with M_2	$A_4 + A_8 \xrightarrow{k_{M_4}=k_{\mathrm{f}m22}} A_4 + A_5 + A_{12}$	$\Psi_{M_4}^{-} = \frac{1}{s_4},\ \Psi_{M_4}^{+} = s_4 s_5 s_{12}$	$\delta_4^{SM-} = 0,\ \delta_4^{SM+} = 0$
Unimolecular reactions			
Initiator decomposition			
I decomposition	$A_9 \xrightarrow{k_1^{*}=k_{\mathrm{d}}} 2fA_{10}$	$\Psi_1^{*} = 1$	$\delta_1^{S*} = 0$

group and are correspondent to the different propagation reactions of polymer radicals with the two monomers. $N_{\mathrm{I}} = 2$ other reactions are the bimolecular initiations of the two monomers by the primary radicals. There are $N_{\mathrm{R}}^{**} = 9$ bimolecular reactions without creation of connections between repeating units. The first $N_{\mathrm{R_P}}^{**} = 7$ are the terminations by disproportionation (three reactions) and transfers to polymer (four reactions), and they involve only polymer groups. The remaining $N_{\mathrm{R_S}}^{**} = 2$ reactions involve a polymer molecule and a small molecule and consist in the initiation of the terminal double bonds. Another class of reactions is the set of the $N_{\mathrm{M}} = 4$ transfers to monomer with the creation of terminal double bonds. The kinetic scheme considered here becomes complete with the $N_{\mathrm{R}}^{*} = 1$ unimolecular reaction associated to the initiator decomposition with the formation of primary radicals.

6.2. Kinetic parameters and operation conditions

In order to simulate the present case study, the value of the 28 kinetic parameters involved must be specified. As in the previous sections, no particular chemical system has been selected and only a typical set of kinetic parameters (System I) was used as a basis in the calculations. This information is presented in Table 12: the reactivity ratios (r_1 and r_2) and the homopropagation rate coefficients (k_{p11} and k_{p22}) are the same as in the copolymerization of vinyl acetate and vinyl chloride at 60 °C [2,42]. The global termination rate constant k_{t} is estimated as the geometric mean of the homotermination rate constants of the same monomers. The normalized constant of chain transfer to monomer C_{M_1} is the same as for vinyl acetate and the initiator decomposition kinetics (f and k_{d}) is valid for AIBN.

The remaining kinetic parameters were fixed using the vinyl acetate polymerization as reference, namely, the reactivity of terminal double bonds originated from transfer to monomer (K_1) and the chain transfer to polymer constant (C_{P_1}) [33]. For the co-monomer the following simple relations were considered: $K_2 = K_1/2$, $C_{\mathrm{P}_2} = C_{\mathrm{P}_1}/2$ and $C_{M_2} = C_{M_1}/2$. For these mechanisms, the kinetic parameters of the cross-reactions were obtained using the same reactivity ratios as in the propagation reactions. The termination is supposed to occur with the same frequency by combination and disproportionation and the dependence relatively to the nature of the radicals involved is expressed in Table 12. System II is obtained from System I by replacing $r_1 = 0.24$ for $r_1 = 10^4$ and,

Table 12
Sets of kinetic parameters considered in a non-linear radical copolymerization including branching by transfer to polymer and propagation on terminal double bonds

Parameter	Relative value	Absolute value ($dm^3\ mol^{-1}\ s^{-1}$)	
		System I ($r_1 = 0.24$)	System II ($r_1 = 10^4$)
Reference set [2,42]			
k_{p11}		1.17×10^4	1.17×10^4
k_{p22}		1.02×10^4	1.02×10^4
k_{p12}	$r_1 = k_{p11}/k_{p12} = 0.24$	4.875×10^4	1.17
k_{p21}	$r_2 = k_{p22}/k_{p21} = 1.8$	5.682×10^3	5.682×10^3
k_t	$k_t = \sqrt{2.5 \times 10^8 \times 1.04 \times 10^9}$	5.1×10^8	5.1×10^8
k_{fm11}	$C_{M_1} = k_{fm11}/k_{p11} = 1.9 \times 10^{-4}$	2.223	2.223
k_d		$9 \times 10^{-6}\ s^{-1}$	$9 \times 10^{-6}\ s^{-1}$
f		0.5 (adimensional)	0.5 (adimensional)
Assumptions in this and related works [33]			
k_{i1}	$k_{i1}/k_{p11} = 1$	1.17×10^4	1.17×10^4
k_{i2}	$k_{i2}/k_{p22} = 1$	1.02×10^4	1.02×10^4
k_{tij}	$k_{tcij} = k_{tdij} = 0.5 \times k_t/\sqrt{ij}$		
k_{fm22}	$C_{M_2} = C_{M_1}/2 = k_{fm22}/k_{p22}$	0.969	0.969
k_{fm12}	$k_{fm11}/k_{fm12} = r_1$	9.263	2.223×10^{-4}
k_{fm21}	$k_{fm22}/k_{fm21} = r_2$	0.538	0.538
k^*_{p11}	$K_1 = k^*_{p11}/k_{p11} = 0.8$	9.36×10^3	9.36×10^3
k^*_{p22}	$K_2 = K_1/2 = k^*_{p22}/k_{p22} = 0.4$	4.08×10^3	4.08×10^3
k^*_{p12}	$k^*_{p11}/k^*_{p12} = r_1$	3.9×10^4	0.936
k^*_{p21}	$k^*_{p22}/k^*_{p21} = r_2$	2.27×10^3	2.27×10^3
k^*_{i1}	$k^*_{i1}/k^*_{p11} = 1$	9.36×10^3	9.36×10^3
k^*_{i2}	$k^*_{i2}/k^*_{p22} = 1$	4.08×10^3	4.08×10^3
k_{fp11}	$C_{P_1} = k_{fp11}/k_{p11} = 1.2 \times 10^{-4}$	1.404	1.404
k_{fp22}	$C_{P_2} = C_{P_1}/2 = k_{fp22}/k_{p22}$	0.612	0.612
k_{fp12}	$k_{fp11}/k_{fp12} = r_1$	5.85	1.404×10^{-4}
k_{fp21}	$k_{fp22}/k_{p21} = r_2$	0.34	0.34

System III is obtained from System I as System II, but with $r_1 = 500$.

therefore, decreasing the cross-reactions of radical from monomer M_1 with species 2 (k_{p12}, k_{fm12}, k^*_{p12} and k_{fp12}). In this way, the end capping of sequences of monomer M_1 by monomer M_2 is decreased, as it will be discussed later in this section. In a similar way, System III is obtained from System I by replacing $r_1 = 0.24$ for $r_1 = 500$.

The simulations were carried out considering constant rate coefficients in an isothermal batch reactor with a global initial monomer concentration $M_0 = M_{10} + M_{20} = 4\ mol\ dm^{-3}$ and an Initiator concentration $I_0 = 10^{-3}\ mol\ dm^{-3}$. The initial composition of the system was fixed considering that the mole fraction of the monomer M_1 in the mixture was $f_{10} = 0.8$.

6.3. Predictions of average sequence lengths

For this particular chemical system, one must integrate a system of $N_{eq} = N_{AP} + N_{AM} + N_P + N_P(N_P + 1)/2 + 1 = 55$ ordinary differential equations if moments up to second order are needed. The required CPU times for pre-gel calculations are about 14 s when gelation is present (System II) and 5 s when gelation is absent (System I). In the post-gel region, the numerical integration of the characteristics consists in the resolution of a two-point boundary value problem with $N_{eq} = 3N_{AP} + N_{AM} = 22$ ordinary differential equations. The CPU time spent for solving each problem of characteristics is of the order of 1007 s. The solution for the characteristics thus obtained is used to integrate the moments along the non-trivial solution and, typically, a single point in the post-gel region needs 1011 s of CPU time. As before, this clearly demonstrates that the solution of the characteristics is the controlling step in terms of CPU time in the post-gel region.

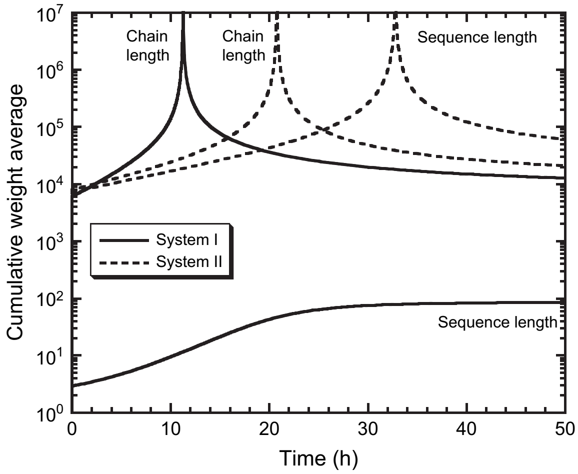

Fig. 5. Weight-averages of chain and sequence lengths in a non-linear radical copolymerization including branching by transfer to polymer and propagation on terminal double bonds. Initial composition: $f_{10} = 0.8$, $f_{20} = 0.2$.

Fig. 5 presents the time evolution of the weight-average sequence lengths of System I and System II. In the same figure are also presented the predictions for the weight-average chain lengths of these systems. The CLD gelation is predicted for both systems: System I at around 11.2 h and System II at 20.8 h. Nevertheless, for System I no gelation of the sequences is predicted and this is explained through the high frequency of end capping of sequences of M_1 by M_2 units, preventing the formation of an infinite network containing only M_1 units. On the contrary, for System II SLD gelation is predicted at $t = 32.8$ h and this should result from the low value of k_{p12}, which makes possible the formation of sequences of macroscopic size. Note that, as expected, the gelation time for the SLD is higher than for the CLD. In Fig. 5, predictions for these average properties are presented before and after CLD and/or SLD gelation. With System III, CLD gelation is predicted at around the same time of System I (20.8 h) but this phenomenon is not present in the SLD of System III. At $t_f = 50$ h the number- and weight-average SLD are about 430 and 2210, respectively for System III.

6.4. Predictions of sequence length distributions

The influence of the kinetic scheme on the sequence length distribution for this polymerization system is presented in Fig. 6. The predicted weight SLD for Systems I, II and III are compared at the same time of polymerization ($t_f = 30$ h)

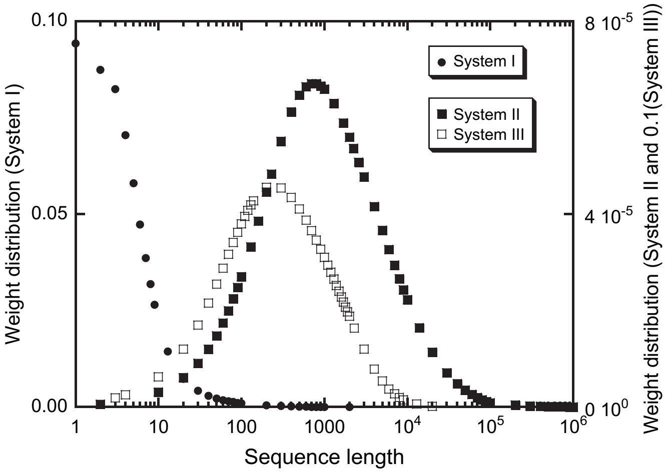

Fig. 6. The influence of the kinetic scheme on the sequence length distribution in a non-linear radical copolymerization including branching by transfer to polymer and propagation on terminal double bonds. Initial composition: $f_{10} = 0.8$, $f_{20} = 0.2$. In both cases the time of polymerization is $t_f = 30$ h.

and considering the same initial composition ($f_{10} = 0.8, f_{20} = 0.2$). Sequence length corresponds to the length (n) of domains containing only M_1 polymerized monomer units and the weight SLD as presented is defined through: $S_w(n) = nS(n)/\sum_{n=0}^{\infty} nS(n)$.

At $t_f = 30$ h the number- and weight-average SLD are about 4.6 and 74.9, respectively for System I, 3659 and 2.6×10^5, respectively for System II and 574 and 2237, respectively for System III. These differences are reflected in the SLD presented in Fig. 6. For System I, the fraction of sequences with length above 100 units becomes very small. On the contrary, for System II the weight SLD has a maximum around $n = 800$ and the distribution presents a long end tail for very high ($n > 10^5$) values of sequence length. The weight SLD of System III has also a maximum around $n = 200$, but the tail of the distribution is vanishing for $n > 20{,}000$. This kind of simulations can be very useful in practice to get a deeper understanding of the kinetics of the formation of these polymers.

7. Conclusions

In this paper, a kinetic method was presented to predict the sequence length distributions, or, more generally, chain length distributions of sub-domains, for non-linear irreversible multicomponent polymerizations. Taking advantage of the generality of this method, it is possible to compute the SLD for polymerization systems involving complex kinetic schemes in an automated way. The interpreter of polymerization systems developed by the present authors predicting chain length distributions is now extended to chain length distributions of sequences or sub-domains.

The application of the method was illustrated with the prediction of the SLD for the linear system consisting in the polycondensation of three monomers. An analytical solution for the SLD in agreement with classical probabilistic approaches is obtained.

The most innovative feature of this method is the ability to deal with the SLD prediction for non-linear polymerization systems. The radical terpolymerization of two vinyl monomers with a divinyl monomer was considered in order to illustrate the formation of non-linear sub-domains or sequences. The influence of the initial feed composition on the length of domains including only one kind of vinyl monomer and the divinyl monomer was investigated. The formation of domains of macroscopic size (gelation of sequences) was shown to be possible. The gelation of sequences was compared with the gelation of molecules in the same systems and, as expected, it was predicted that it can only occur after the gelation of molecules. Predictions for SLD (and obviously for CLD) are possible before and after both gelation points. A similar study was carried out for a copolymerization including branching by transfer to polymer and propagation on terminal double bonds. It was shown that in certain circumstances gelation of sequences is also possible for this kind of polymerization systems.

The present method can be useful in practice to get a deeper insight of the microstructure of linear polymers if more complex kinetic schemes need to be considered without using some widespread mathematical approximations. Nevertheless, the most promising application of this approach is related to its ability to deal with complex non-linear polymerizations. This can be used to improve the knowledge of the kinetics of formation of this kind of polymers and to understand their microstructure, and this knowledge could be exploited in the future to predict the onset of microphase separation. For the first time, the concept of sequence gelation could be exploited in depth, and it might become interesting for the study of the properties of polymer networks if it can be experimentally measured. It can be speculated that some electrical or optical property typical of some subdomains or sequences would present a percolation threshold due to sequence gelation.

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Appendix A

A.1. Prediction of SLD and its moments in ideal reactors using the method of characteristics in a CSTR

The solution of equations similar to Eqs. (14)–(17) can be found using the method of characteristics as already been presented in detail elsewhere [31]. Following these lines of thought, the solution of the present problem is:

$$\begin{aligned}\frac{\mathrm{d}\log s_j}{\mathrm{d}t} ={}& \sum_{m=1}^{N_{\mathrm{R_P}}} k_m\Big\{\delta_m^{S+-}\Big[\delta_{[m-]}^{j}\big(A_{[m+]}-\Psi_m^{-}\Psi_m^{+}U_{[m+]}\big)+\delta_{[m+]}^{j}\big(A_{[m-]}-\Psi_m^{-}\Psi_m^{+}U_{[m-]}\big)\Big]+\delta_m^{S-}A_{[m+]}\delta_{[m-]}^{j}\big(1-\Psi_m^{-}\big)\Big\}\\ &+\sum_{m=N_{\mathrm{R_P}}+1}^{N_{\mathrm{R}}} k_m\Big[\delta_m^{S+-}\delta_{[m-]}^{j}A_{[m+]}\big(1-\Psi_m^{-}\Psi_m^{+}\big)+\delta_m^{S-}\delta_{[m-]}^{j}A_{[m+]}\big(1-\Psi_m^{-}\big)\Big]+\sum_{m=1}^{N_{\mathrm{R_P}}^{*}} k_m^{*}\delta_m^{S*}\delta_{[m*]}^{j}\big(1-\Psi_m^{*}\big)\\ &+\sum_{m=1}^{N_{\mathrm{R_P}}^{**}} k_m^{**}\Big[\delta_m^{S**+}\delta_{[m**+]}^{j}A_{[m**-]}\big(1-\Psi_m^{**+}\big)+\delta_m^{S**-}\delta_{[m**-]}^{j}A_{[m**+]}\big(1-\Psi_m^{**-}\big)\Big]\\ &+\sum_{m=N_{\mathrm{R_P}}^{**}+1}^{N_{\mathrm{R}}^{**}-N_{\mathrm{S}}} k_m^{**}\delta_m^{S**-}\delta_{[m**-]}^{j}A_{[m**+]}\big(1-\Psi_m^{**-}\big)+\sum_{m=1}^{N_M} k_{M_m}A_{[M_{m+}]}\delta_m^{SM-}\delta_{[M_{m-}]}^{j}\big(1-\Psi_{M_m}^{-}\big)\end{aligned} \tag{A1}$$

Here, as usual, Krönecker's symbol $\delta_{[k]}^{j}=1$, if $j=[k]$ and $\delta_{[k]}^{j}=0$ otherwise.

$$\begin{aligned}\frac{\mathrm{d}U_j}{\mathrm{d}t} ={}& \sum_{m=1}^{N_{\mathrm{R_P}}} k_m\Big[\delta_m^{S+-}\Big(\nu_{mj}^{-}+\nu_{mj}^{+}\Big)\Psi_m^{-}\Psi_m^{+}U_{[m-]}U_{[m+]}+\delta_m^{S-}\nu_{mj}^{-}\Psi_m^{-}A_{[m+]}U_{[m-]}\Big]\\ &+\sum_{m=N_{\mathrm{R_P}}+1}^{N_{\mathrm{R}}} k_m\Big[\delta_m^{S+-}\Big(\nu_{mj}^{-}+\nu_{mj}^{+}\Big)\Psi_m^{-}\Psi_m^{+}U_{[m-]}A_{[m+]}+\delta_m^{S-}\nu_{mj}^{-}\Psi_m^{-}U_{[m-]}A_{[m+]}+\delta_m^{S+}\nu_{mj}^{+}\Psi_m^{+}A_{[m-]}A_{[m+]}\Big]\\ &+\sum_{m=1}^{N_{\mathrm{I}}}\delta_m^{SI}k_{\mathrm{I}_m}\nu_{\mathrm{I}_{mj}}\Psi_{\mathrm{I}_m}A_{[\mathrm{I}_{m-}]}A_{[\mathrm{I}_{m+}]}+\sum_{m=1}^{N_{\mathrm{R_P}}^{*}} k_m^{*}\delta_m^{S*}\nu_{mj}^{*}\Psi_m^{*}U_{[m*]}\\ &+\sum_{m=1}^{N_{\mathrm{R_P}}^{**}} k_m^{**}\Big(\delta_m^{S**-}\nu_{mj}^{**-}\Psi_m^{**-}U_{[m**-]}A_{[m**+]}+\delta_m^{S**+}\nu_{mj}^{**+}\Psi_m^{**+}U_{[m**+]}A_{[m**-]}\Big)+\sum_{m=N_{\mathrm{R_P}}^{**}+1}^{N_{\mathrm{R}}^{**}-N_{\mathrm{S}}} k_m^{**}\delta_m^{S**-}\nu_{mj}^{**-}\Psi_m^{**-}U_{[m**-]}A_{[m**+]}\\ &+\sum_{m=1}^{N_M} k_{M_m}A_{[M_{m+}]}\Big(\delta_m^{SM-}\nu_{M_mj}^{-}\Psi_{M_m}^{-}U_{[M_{m-}]}+\delta_m^{SM+}A_{[M_{m-}]}\nu_{M_mj}^{+}\Psi_{M_m}^{+}\Big)+\frac{U_{j\mathrm{F}}(t)-U_j}{\tau}-R_vU_j\end{aligned} \tag{A2}$$

with $U_j=\partial U/\partial\log s_j$.

$$\begin{aligned}\frac{\mathrm{d}U}{\mathrm{d}t} ={}& -\sum_{m=1}^{N_{\mathrm{R_P}}}\delta_m^{S+-}k_m\Psi_m^{-}\Psi_m^{+}U_{[m-]}U_{[m+]}\\ &+\sum_{m=N_{\mathrm{R_P}}+1}^{N_{\mathrm{R}}}\delta_m^{S+}k_m\Psi_m^{+}A_{[m-]}A_{[m+]}+\sum_{m=1}^{N_{\mathrm{I}}}\delta_m^{SI}k_{\mathrm{I}_m}\Psi_{\mathrm{I}_m}A_{[\mathrm{I}_{m-}]}A_{[\mathrm{I}_{m+}]}\\ &+\sum_{m=1}^{N_M}\delta_m^{SM+}k_{M_m}\Psi_{M_m}^{+}A_{[M_{m+}]}A_{[M_{m-}]}+\frac{U_{\mathrm{F}}(t)-U}{\tau}-R_vU\end{aligned} \tag{A3}$$

The initial conditions for Eqs. (A1)–(A3) are:

$$s_{j|t=0}=s_{j0} \tag{A4}$$

$$U_{j|t=0}=\frac{\partial U_0}{\partial\log s_j}(\mathbf{s}_0) \tag{A5}$$

$$U_{|t=0}=U_0(\mathbf{s}_0) \tag{A6}$$

Vector $\mathbf{s_0}$ defining the starting point of the characteristic at time $t=0$ must be computed in order that the characteristic curve passes through the prescribed values of $\mathbf{s}$ at time t. Therefore, a two-point boundary value problem for the above system of ordinary differential equations must be solved. In the prediction of average sequence lengths, only the solution at $\mathbf{s}=\mathbf{1}_{N_\mathrm{A}}$ is wanted and the problem becomes much simpler if there is no gelation, because the solution is then $\mathbf{s}_0=\mathbf{1}_{N_\mathrm{A}}$ and there is no need to solve the above-mentioned two-point boundary value problem. After computing vector $\mathbf{s}_0$ (in case there is gel) or, alternatively, by setting it equal to $\mathbf{1}_{N_\mathrm{A}}$, it becomes possible to obtain $U(\mathbf{s})$ and any of its derivatives at $\mathbf{s}=\mathbf{1}_{N_\mathrm{A}}$, yielding thus the moments of the SLD and leading to the fraction of finite sub-domains or sequences and to the average sequence lengths. In the general case, if the SLD (and not only its moments) is to be computed, $U(\mathbf{s})$ must be evaluated in the complex domain for $|s|\le 1_{N_\mathrm{A}}$. The number of evaluations and the location of $\mathbf{s}$ in the complex plane depend on the method used to invert $U(\mathbf{s})$. The problem of the integration of the characteristics and the numerical inversion of PGF have already been addressed by the present authors when dealing with CLD [32–36]. The same techniques will now be used in the prediction of SLD.

Differentiation of Eq. (14) leads to additional ordinary differential equations analogous to Eq. (A3), which are used to compute higher positive integer order derivatives of U, such as:

$$\begin{aligned}
\frac{\mathrm{d}U_{jk}}{\mathrm{d}t} = {} & \sum_{m=1}^{N_{\mathrm{R_P}}} k_m \Big\{ \delta_m^{S+-} \Psi_m^- \Psi_m^+ \Big[\left(\nu_{mj}^- + \nu_{mj}^+\right)\left(\nu_{mk}^- + \nu_{mk}^+\right) U_{[m-]} U_{[m+]} + \left(\nu_{mj}^- + \nu_{mj}^+\right)\left(U_{[m-]k} U_{[m+]} + U_{[m+]k} U_{[m+]}\right) \\
& + \left(\nu_{mk}^- + \nu_{mk}^+\right)\left(U_{[m-]j} U_{[m+]} + U_{[m+]j} U_{[m-]}\right) + U_{[m-]j} U_{[m+]k} + U_{[m+]j} U_{[m-]k} \Big] \\
& + \delta_m^{S-} A_{[m+]} \Psi_m^- \left(\nu_{mk}^- U_{[m-]j} + \nu_{mj}^- U_{[m-]k} + \nu_{mj}^- \nu_{mk}^- U_{[m-]}\right) \Big\} \\
& + \sum_{m=N_{\mathrm{R_P}}+1}^{N_{\mathrm{R}}} k_m \Big\{ \delta_m^{S+-} \Psi_m^- \Psi_m^+ A_{[m+]} \Big[\left(\nu_{mj}^- + \nu_{mj}^+\right)\left(\nu_{mk}^- + \nu_{mk}^+\right) U_{[m-]} + \left(\nu_{mj}^- + \nu_{mj}^+\right) U_{[m-]k} + \left(\nu_{mk}^- + \nu_{mk}^+\right) U_{[m-]j} \Big] \\
& + \delta_m^{S-} A_{[m+]} \Psi_m^- \left(\nu_{mk}^- U_{[m-]j} + \nu_{mj}^- U_{[m-]k} + \nu_{mj}^- \nu_{mk}^- U_{[m-]}\right) + \delta_m^{S+} A_{[m-]} A_{[m+]} \Psi_m^+ \nu_{mj}^+ \nu_{mk}^+ \Big\} \\
& + \sum_{m=1}^{N^*_{\mathrm{R_P}}} k_m^* \delta_m^{S*} \Psi_m^* \left(\nu_{mk}^* U_{[m*]j} + \nu_{mj}^* U_{[m*]k} + \nu_{mj}^* \nu_{mk}^* U_{[m*]}\right) \\
& + \sum_{m=1}^{N^{**}_{\mathrm{R_P}}} k_m^{**} \Big[\delta_m^{S**-} A_{[m**+]} \Psi_m^{**-} \left(\nu_{mk}^{**-} U_{[m**-]j} + \nu_{mj}^{**-} U_{[m**-]k} + \nu_{mj}^{**-} \nu_{mk}^{**-} U_{[m**+]}\right) \\
& + \delta_m^{S**+} A_{[m**-]} \Psi_m^{**+} \left(\nu_{mk}^{**+} U_{[m**+]j} + \nu_{mj}^{**+} U_{[m**+]k} + \nu_{mj}^{**+} \nu_{mk}^{**+} U_{[m**+]}\right) \Big] \\
& + \sum_{m=N^*_{\mathrm{R_P}}+1}^{N^{**}_{\mathrm{R}}-N_{\mathrm{S}}} k_m^{**} \delta_m^{S**-} A_{[m**+]} \Psi_m^{**-} \left(\nu_{mk}^{**-} U_{[m**-]j} + \nu_{mj}^{**-} U_{[m**-]k} + \nu_{mj}^{**-} \nu_{mk}^{**-} U_{[m**-]}\right) \\
& + \sum_{m=1}^{N_M} k_{M_m} A_{[M_{m+}]} \Big[\delta_m^{SM+} A_{[M_{m-}]} \nu_{M_{mj}}^+ \nu_{M_{mk}}^+ \Psi_{M_m}^+ + \delta_m^{SM-} \Psi_{M_m}^- \left(\nu_{M_{mj}}^- U_{[M_{m-}]k} + \nu_{M_{mk}}^- U_{[M_{m-}]j} + \nu_{M_{mj}}^- \nu_{M_{mk}}^- U_{[M_{m-}]}\right) \Big] \\
& + \sum_{m=1}^{N_{\mathrm{I}}} \delta_m^{SI} k_{\mathrm{I}_m} A_{[\mathrm{I}_{m-}]} A_{[\mathrm{I}_{m+}]} \nu_{\mathrm{I}_{mj}} \nu_{\mathrm{I}_{mk}} \Psi_{\mathrm{I}_m} + \frac{U_{jk_{\mathrm{F}}}(t) - U_{jk}}{\tau} - R_v U_{jk}
\end{aligned} \tag{A7}$$

Appendix B

B.1. Analytical SLD for the linear polycondensation of three monomers

In order to illustrate the application of the present method to the prediction of SLD, the simple case consisting in the step-growth polymerization of three monomers will be considered. It is supposed that the polymerization starts with a mixture of $\mathbf{UA}_2 + \mathbf{QB}_2 + \mathbf{PC}_2$ where **A** reacts with **B** and **C** but **B** and **C** do not react with each other, and none of these groups reacts with itself. For the operation in a batch reactor with equal reactivity of the chemical groups there is an analytical solution [4–6].

The goal will be to compute the distribution of the sub-domains or sequences involving only the moieties **U** and **Q**. These sub-domains or sequences are thus capped by end groups **A**, **B** or by the moiety **P**. In Table 3, the set of chemical groups considered in this polymerization system is described and in Table 4 the correspondent kinetic scheme is shown. These chemical groups comprise the three different kinds of end groups (**A**, **B** and **C**) and the moieties coming from each monomer. The three latter species are present in the polymer, but they are inactive. The kinetic scheme comprises only the reactions of end group linking. These reactions create connections between repeating units and involve the reaction between active groups present in the polymer. It is supposed that the only product of these reactions is a link, either $\mathbf{Z_{AB}}$ or $\mathbf{Z_{AC}}$. The reactivity of the end groups often changes because of substitution effects, but in the present case study this effect will be disregarded for simplicity.

B.2. Model equations

Applying the general method presented above, the SLD for this system is obtained through the resolution of the following boundary value problem:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = -\frac{k_{12}}{s_1 s_2} U_1 U_2 \tag{B1}$$

$$\frac{\mathrm{d}U_1}{\mathrm{d}t} = -\frac{k_{12}}{s_1 s_2} U_1 U_2 - \frac{k_{13}}{s_1} A_3 U_1 \tag{B2}$$

$$\frac{\mathrm{d}U_2}{\mathrm{d}t} = -\frac{k_{12}}{s_1 s_2} U_1 U_2 \tag{B3}$$

$$\frac{\mathrm{d}U_3}{\mathrm{d}t} = 0 \tag{B4}$$

$$\frac{\mathrm{d}\log s_1}{\mathrm{d}t} = k_{12}\left(A_2 - \frac{U_2}{s_1 s_2}\right) + k_{13} A_3 \left(1 - \frac{1}{s_1}\right) \tag{B5}$$

$$\frac{\mathrm{d}\log s_2}{\mathrm{d}t} = k_{12}\left(A_1 - \frac{U_1}{s_1 s_2}\right) \tag{B6}$$

$$\frac{\mathrm{d}\log s_3}{\mathrm{d}t} = 0 \tag{B7}$$

$$U_{|t=0} = U_0(\mathbf{s}_0) = \frac{A_{10}}{2}s_{10}^2\xi_1 + \frac{A_{20}}{2}s_{20}^2\xi_2 \tag{B8}$$

$$U_{1|t=0} = \frac{\partial U_0}{\partial \log s_1}(\mathbf{s}_0) = A_{10}s_{10}^2\xi_1 \tag{B9}$$

$$U_{2|t=0} = \frac{\partial U_0}{\partial \log s_2}(\mathbf{s}_0) = A_{20}s_{20}^2\xi_2 \tag{B10}$$

$$U_{3|t=0} = \frac{\partial U_0}{\partial \log s_3}(\mathbf{s}_0) = 0 \tag{B11}$$

$$s_{1|t=0} = s_{10},\ s_{2|t=0} = s_{20},\ s_{3|t=0} = s_{30} \quad s_{1|t=t_\mathrm{f}} = s_{2|t=t_\mathrm{f}} = s_{3|t=t_\mathrm{f}} = 1 \tag{B12}$$

From Eqs. (B4), (B7), (B11) and (B12) it is easily determined that $U_3 = 0$ and $s_3 = s_{30} = 1$. This was expected, as there are no A_3 groups in the sub-domains or sequences. The remaining system of ordinary differential equations is solved taking also into account the mass balances of active groups:

$$\frac{\mathrm{d}A_1}{\mathrm{d}t} = -k_{12}A_1A_2 - k_{13}A_1A_3 \tag{B13}$$

$$\frac{\mathrm{d}A_2}{\mathrm{d}t} = -k_{12}A_1A_2 \tag{B14}$$

$$\frac{\mathrm{d}A_3}{\mathrm{d}t} = -k_{13}A_1A_3 \tag{B15}$$

with:

$$A_{1|t=0} = A_{10},\ A_{2|t=0} = A_{20},\ A_{3|t=0} = A_{30} \tag{B16}$$

B.3. Analytical solution for the SLD

From Eqs. (B2), (B5), (B13) and Eqs. (B3), (B6), (B14) it can be shown that:

$$\frac{\mathrm{d}\log\left(\dfrac{U_1}{A_1 s_1}\right)}{\mathrm{d}t} = 0 \tag{B17}$$

$$\frac{\mathrm{d}\log\left(\dfrac{U_2}{A_2 s_2}\right)}{\mathrm{d}t} = 0 \tag{B18}$$

and therefore:

$$\frac{U_1}{A_1 s_1} = \frac{U_{10}}{A_{10}s_{10}} = s_{10}\xi_1 \tag{B19}$$

$$\frac{U_2}{A_2 s_2} = \frac{U_{20}}{A_{20}s_{20}} = s_{20}\xi_2 \tag{B20}$$

If these results are inserted in Eqs. (B5) and (B6) the following simplified equations are obtained:

$$\begin{aligned}\frac{\mathrm{d}\log s_1}{\mathrm{d}t} &= k_{12}\left(A_2 - A_2\frac{s_{20}\xi_2}{s_1}\right) + k_{13}A_3\left(1 - \frac{1}{s_1}\right)\\ &= k_{12}A_2 + k_{13}A_3 - \frac{1}{s_1}(k_{12}A_2s_{20}\xi_2 + k_{13}A_3)\\ &= -\frac{\mathrm{d}\log A_1}{\mathrm{d}t} + \frac{1}{A_1 s_1}\left(s_{20}\xi_2\frac{\mathrm{d}A_2}{\mathrm{d}t} + \frac{\mathrm{d}A_3}{\mathrm{d}t}\right)\end{aligned} \tag{B21}$$

$$\frac{\mathrm{d}\log s_2}{\mathrm{d}t} = k_{12}\left(A_1 - \frac{s_{10}\xi_1}{s_2}A_1\right) = -\left(1 - \frac{s_{10}\xi_1}{s_2}\right)\frac{\mathrm{d}\log A_2}{\mathrm{d}t} \tag{B22}$$

The integration of Eqs. (B21) and (B22) results in the following system of algebraic equations:

$$(1-p_1)s_1 = s_{10} - s_{20}\xi_2 r_2 p_2 - r_3 p_3 \tag{B23}$$

$$(1-p_2)s_2 = s_{20} - s_{10}\xi_1 p_2 \tag{B24}$$

where p_1, p_2 and p_3 represent the conversions of groups **A**, **B** and **C**, respectively. The parameters $r_2 = A_{20}/A_{10}$ and $r_3 = A_{30}/A_{10}$ are the initial molar ratios of groups **B** and **C** relative to **A**. The relations in Eqs. (B19) and (B20) can also be used to integrate Eq. (B1) and, therefore, to obtain the PGF of the SLD:

$$\frac{\mathrm{d}U}{\mathrm{d}t} = -\frac{k_{12}}{s_1 s_2}U_1U_2 = -k_{12}A_1A_2s_{10}s_{20}\xi_1\xi_2 = \frac{\mathrm{d}A_2}{\mathrm{d}t}s_{10}s_{20}\xi_1\xi_2 \tag{B25}$$

and therefore:

$$\begin{aligned}U &= U_0 + (A_2 - A_{20})s_{10}s_{20}\xi_1\xi_2\\ &= \frac{A_{10}}{2}s_{10}^2\xi_1 + \frac{A_{20}}{2}s_{20}^2\xi_2 - A_{20}p_2s_{10}s_{20}\xi_1\xi_2\end{aligned} \tag{B26}$$

The values of s_{10} and s_{20} are obtained from the system of algebraic equations (Eqs. (B23) and (B24)). From the substitution of this solution in Eq. (B26) it results:

$$\begin{aligned}\frac{U(\mathbf{s})}{M_{10}} &= \frac{(1-p_1)^2\xi_1}{1 - r_2p_2^2\xi_1\xi_2}s_1^2 + \frac{r_2(1-p_2)^2\xi_2}{1 - r_2p_2^2\xi_1\xi_2}s_2^2\\ &\quad + \frac{2r_2p_2(1-p_1)(1-p_2)\xi_1\xi_2}{1 - r_2p_2^2\xi_1\xi_2}s_1s_2 + \frac{2r_3p_3(1-p_1)\xi_1}{1 - r_2p_2^2\xi_1\xi_2}s_1\\ &\quad + \frac{2r_2p_2r_3p_3(1-p_2)\xi_1\xi_2}{1 - r_2p_2^2\xi_1\xi_2}s_2 + \frac{(r_3p_3)^2\xi_1}{1 - r_2p_2^2\xi_1\xi_2}\end{aligned} \tag{B27}$$

Each one of the six terms in this equation represents the SLD for the different possible combinations of end groups of the sub-domains or sequences, namely: **AA**, **BB**, **AB**, **AP**, **BP** and **PP**. In the last three cases, the sub-domains or sequences are end-capped by units **P** of the monomer **PC**$_2$. Note that for all kinds of sub-domains or sequences, the SLD is a geometric distribution of the parameter $r_2p_2^2$ as can be concluded from the inspection of the denominators in Eq. (B27).

If the goal is to obtain the SLD with respect to the number of units **Q**, regardless of the kind of end groups or number of units **U** (e.g. SLD of hard segments in segmented polyurethanes), the correspondent PGF is obtained from Eq. (B27) with $s_1 = s_2 = \xi_1 = 1$:

$$\frac{U(\xi_2)}{M_{20}} = \frac{\left(1 - r_2 p_2^2\right)^2 \xi_2}{1 - r_2 p_2^2 \xi_2} \tag{B28}$$

Note that in Eq. (B28) the zero-sized sub-domains or sequences with respect to the number of units **Q**, with a concentration $M_{10}(1 - r_2 p_2)^2$, were excluded. It should also be noticed that $M_{20} = r_2 M_{10}$. From the analytical inversion of the previous equation, the well-known geometric distribution is obtained:

$$S(n_2) = M_{20}\left(1 - r_2 p_2^2\right)^2 \left(r_2 p_2^2\right)^{n_2 - 1} \tag{B29}$$

where n_2 represents the number of units **Q** in the sequence. The number- or weight-average sequence lengths are obtained from Eq. (B29) or directly by derivation of Eq. (B28) with respect to $\log \xi_2$.

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