

A GENERAL KINETIC ANALYSIS OF NON-LINEAR IRREVERSIBLE COPOLYMERIZATIONS

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Abstract—Irreversible non-linear copolymerizations with arbitrarily great numbers of monomers are described specifying the stoichiometric coefficients of the reactions involving end-groups. Rate equations for the vectorial generating function or discrete transform of the distribution of end-groups and repeating units and its derivatives with respect to logarithms of Laplace parameters can thus be written. Similar rate equations can be written for the discrete transforms of the distributions of descendants of each linking group with respect to their numbers of end-groups. This allows the prediction of gel properties, such as the concentration of elastically active network chains and mass fraction of pendant material. Mass balance equations using these rate laws are non-linear partial differential equations solvable by the method of characteristics. Numerical methods are developed for computing molecular weight distributions and average molecular weights before and after gelation, as well as the weight fraction of sol and gel properties related to its elasticity behaviour. The curing of a tetraepoxide with a primary diamine is taken as a case study and results are compared with predictions by the theory of branching processes.

INTRODUCTION

This work stems from the kinetic approach for modelling irreversible non-linear polycondensations, developed by Kuchanov and co-workers (Pis'men and Kuchanov, 1971; Kuchanov and Pis'men, 1972a, b; Kuchanov and Povolotskaya, 1982). These earlier works have laid the foundations of a rigorous method for the prediction of average molecular weights, both before and after gelation. However, prediction of gel structure, such as computing the concentrations of elastically active network chains, has remained hitherto an unsolved problem. Moreover, numerical methods for solving the mass balance equations of the kinetic approach have not been implemented, and this has precluded its application to all but the simplest chemical systems.

In this paper, a unified treatment of essentially all irreversible non-linear polymerizations, including polycondensations and polyadditions, is carried out. This is possible because a common set of rules to describe the molecular growth can be established. In order to describe the formation of these polymers, it is necessary to identify the repeating units, which are not changed by chemical reaction, and the end-groups attached to them, which can lead to molecular growth by intermolecular reaction and linking of the units to which they are attached, or become inactivated by a termination or transfer reaction, which may be intramolecular and form a loop.

There is often a large number of those structural constituents which must be distinguished, even with as little as two or three symmetrical monomers at the start of the reaction. This happens because of the following:

(a) Substitution effects, such as the difference in reactivities of the hydroxyls of pentaerythritol after reaction with a carboxylic acid (Gordon and Leonis, 1975a, b);

(b) Intramolecular reactions between end-groups, which have a rate depending on the size of the outgoing loop, leading inevitably to the consideration of a large number of molecular fragments for their kinetic modelling, even with only the loop with the lowest possible size being allowed to form (Moschiar *et al.*, 1988).

Each time a new kinetic scheme is under study, huge systems of algebraic and differential equations must be written and solved. This is a time-consuming and error-prone task. For instance, a model of phenol-formaldehyde polycondensation (Vázquez *et al.*, 1984) requires 19 kinds of end-groups to be defined; the above-cited model of polyurethane formation with consideration of the smallest rings (Moschiar *et al.*, 1988) uses 25 molecular fragments. Still more complex models are likely to be needed.

For that reason, it is desirable that a single computer program could be able to carry out the prediction of polymer properties for any such polymerization scheme, needing only a minimum of user-supplied chemical information, and specially without the need of analytically solving mass balance equations of polymer species. So, the present treatment allows an arbitrary number of monomers and reactive groups, both in polycondensations and polyadditions, with a distribution of molecular weights in monomer classes. The problem of numerical evaluation of molecular weight averages and molecular weight distributions both before and after gelation is completely solved in this contribution, as well as the distribution of the number of cross-links in the gel, allowing therefore an estimation of the concentration of elastically active network chains and other gel properties relevant for the prediction of its elastic properties. Previous uses of the kinetic approach were limited to the prediction of gel-points and average molecular weights in the pre-gel state.

A GENERAL KINETIC MODEL OF IRREVERSIBLE NON-LINEAR COPOLYMERIZATIONS

Chemical species, their concentrations and molecular weights

Non-alternating copolymerizations, or homopolymerizations of monomers with functionality greater than two, give rise to molecules with a large number of position isomers, except, of course, when the degree of polymerization is very low. For irreversible polymerization reactions, there is no need of distinguishing polymer species according to the way their repeating units are linked, if only properties such as average molecular weights and concentration of active network chains in gel are to be computed.

Let N be the number of monomer classes. Each monomer class contains a chemically invariant moiety (the repeating unit), named U^m for the m th monomer, and a certain number f_i^m of reactive groups (most often end-groups, sometimes individual molecules), named A_i . The number of chemically distinguishable reacting groups among all monomers will be named G . Superscripts will be used in this paper whenever they refer to monomer classes, and subscripts will be introduced when they refer to reactive groups.

For instance, in a polycondensation of adipoyl chloride $\text{ClCO}(\text{CH}_2)_4\text{COCl}$ and azeloyl chloride $\text{ClCO}(\text{CH}_2)_5\text{COCl}$ with amines and/or alcohols, the acid chloride end-groups have virtually identical reactivities (provided intramolecular reactions are negligible), so that the two monomers should be considered as forming a class of difunctional monomers with two COCl end-groups. If there is caproyl chloride $\text{CH}_3(\text{CH}_2)_4\text{COCl}$ as a co-monomer, it is necessary to introduce a new class of monofunctional monomers carrying a single COCl end-group.

Monomer classes are often pre-polymers. For instance, in the formation of a polyurethane, part of the polyol component is usually a polyether or a polyester terminated by two, three or some other number of hydroxyl groups, which have a certain molecular weight distribution. Each repeating unit U^m has a certain molecular weight distribution, defined by a discrete distribution Ω^{mj} representing the mole fraction of each subspecies U^{mj} of the monomer class U^m with a molecular weight M^{mj} . The variable j is any index enumerating the repeating units and going from 0 to ∞ .

Since there is no need to distinguish among position isomers, it is enough to describe each polymer molecule through the numbers of end-groups and repeating units it contains. So, a molecule with a vector of numbers of end-groups $\mathbf{a} = [a_1 \dots a_G]$ and a vector of numbers of repeating units $\mathbf{n} = [n^1 \dots n^N]$ shall be named $P(\mathbf{a}, \mathbf{n})$. Its mole concentration will be written as $P(\mathbf{a}, \mathbf{n})$, in order to simplify as much as possible the equations that follow. This discrete distribution of vectors \mathbf{a} and \mathbf{n} is appropriately named a *vector-number-molecular-number distribution* (VNMND). It will nearly always be found from its *vectorial discrete transform*:

$$\bar{P}(\sigma, \zeta) = \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} \sum_{n^1=0}^{\infty} \dots \sum_{n^N=0}^{\infty} \sigma_1^{a_1} \dots \sigma_G^{a_G} (\zeta^1)^{n^1} \dots (\zeta^N)^{n^N} P(a_1, \dots, a_G, n^1, \dots, n^N). \quad (1)$$

In polyadditions of vinyl compounds, the monomers would be counted as polymer molecules, since there is no creation of repeating units according to this approach. However, they must be also considered as containing special reactive groups.

Each family of molecules $P(\mathbf{a}, \mathbf{n})$ is likely not to have a unique molecular weight, because of the dispersion of molecular weights of some of the monomer classes. Let P_j be a molecule with molecular weight $M(P_j)$, j being a variable used for enumerating the set of all possible molecules. The molecular weight is often not simply the sum of the molecular weights of the monomers that formed P_j , because end-groups are likely to give rise to by-products when they react with other end-groups or other molecules in the reaction medium. So, let M_i be the *decrease* of molecular weight of a polymer molecule when one of its end-groups A_i reacts. This molecular weight loss can always be supposed to be independent of the nature of this latter reaction. This is rather evident for end-groups like COCl , which loses a Cl atom when reacting with any group carrying an active hydrogen ($-\text{OH}$, $-\text{NH}_2$ and so on), so that it can safely be assumed that $M_{\text{COCl}} = M_{\text{Cl}} = 35.5$. In some special cases, like $-\text{CH}_2\text{OH}$ in phenol-formaldehyde resins, which may form either methylene $-\text{CH}_2-$ with loss of formaldehyde or oxydimethylene bridges $-\text{CH}_2\text{OCH}_2-$ with loss of water when they react, the whole molecular weight of the $-\text{CH}_2\text{OH}$ group must be considered lost when it reacts, so that $M_{\text{CH}_2\text{OH}} = 33$, and $-\text{CH}_2-$, $-\text{CH}_2\text{OCH}_2-$ must be considered end-groups with $M_{\text{CH}_2\text{OCH}_2} = 44$, $M_{\text{CH}_2} = 14$, in spite of them being unable to react further (unless their formation becomes reversible).

Mole fraction Ω^{mj} of subspecies U^{mj} is also the probability of choosing a subspecies U^{mj} when randomly picking up a unit U^m , because of the chosen normalization. Since the build-up of polymer species is independent of the nature of the subspecies, if a polymer molecule has n^m repeating units U^m , the probability of having n^{m0}, n^{m1}, \dots , numbers of subspecies U^{m0}, U^{m1}, \dots , is given by the multinomial distribution with $n^m = n^{m0} + n^{m1} + \dots$ and a set of probabilities $\Omega^{m0}, \Omega^{m1}, \dots$. It is shown in Appendix A that the discrete transform of the *number* molecular weight distribution (NMWD) is related to the discrete transform of VNMND through

$$\begin{aligned} \bar{P}(\mu) &= \sum_{j=0}^{\infty} \mu^{M(P_j)} P_j \\ &= \bar{P}[\mu^{M_1}, \dots, \mu^{M_G}, \bar{\Omega}^1(\mu), \dots, \bar{\Omega}^N(\mu)]. \quad (2) \end{aligned}$$

Expressions for the NMWD of repeating units in the important cases often encountered in practice of Schulz-Flory and Poisson distributions are given in Table 1. Also, the expressions that result for the discrete transform of the NMWD and the leading aver-

Table 1. Molecular weight distributions and average molecular weights of classes of repeating units following Schulz-Flory and Poisson's distributions

| Schulz-Flory distribution |
|---|
| $\bar{\Omega}(\mu) = \frac{(1-p)\mu^{M_E}}{1-p\mu^{M_E}}$ $(1-p)\bar{M}_n = p(M_R - M_E) + M_E$ $(1-p)^2\bar{M}_w\bar{M}_n = (M_R - M_E)^2 p^2 + (M_R^2 + 2M_R M_E - 2M_E^2)p + M_E^2$ $(1-p)^3\bar{M}_z\bar{M}_w\bar{M}_n = (M_R - M_E)^3 p^3 + (4M_R^3 - 6M_R M_E^2 + 3M_E^3)p^2 + [(M_R + M_E)^3 - 4M_E^3]p + M_E$ |
| Poisson's distribution |
| $\bar{\Omega}(\mu) = \mu^{M_E} \exp[J(\mu^{M_E} - 1)]$ $\bar{M}_n = JM_R + M_E$ $\bar{M}_w\bar{M}_n = JM_R^2 + (JM_R + M_E)^2$ $\bar{M}_z\bar{M}_w\bar{M}_n = JM_R^3 + 3JM_R^2(JM_R + M_E) + (JM_R + M_E)^3$ |

Table 2. Relations between leading moments of MWD and of VNMND

$$\begin{aligned} \lambda_{M_1} &= \sum_{m=1}^N \bar{M}_n^m \lambda^m + \sum_{i=1}^G M_i \lambda_i \\ \lambda_{M_2} &= \sum_{m=1}^N \sum_{n=1}^N \bar{M}_n^m \bar{M}_n^n \lambda^{mn} + 2 \sum_{m=1}^N \sum_{i=1}^G \bar{M}_n^m M_i \lambda_i^m + \sum_{i=1}^G \sum_{j=1}^G M_i M_j \lambda_{ij} + \sum_{m=1}^N \bar{M}_n^m (\bar{M}_w^m - \bar{M}_n^m) \lambda^m \\ \lambda_{M_3} &= \sum_{m=1}^N \sum_{n=1}^N \sum_{p=1}^N \bar{M}_n^m \bar{M}_n^n \bar{M}_n^p \lambda^{mnp} + 3 \sum_{m=1}^N \sum_{n=1}^N \sum_{i=1}^G \bar{M}_n^m \bar{M}_n^n M_i \lambda_i^{mn} + 3 \sum_{m=1}^N \sum_{i=1}^G \sum_{j=1}^G \bar{M}_n^m M_i M_j \lambda_{ij}^m \\ &\quad + \sum_{i=1}^G \sum_{j=1}^G \sum_{k=1}^G M_i M_j M_k \lambda_{ijk} + 3 \sum_{m=1}^N \bar{M}_n^m (\bar{M}_w^m - \bar{M}_n^m) \left(\sum_{n=1}^N \bar{M}_n \lambda^{mn} + \sum_{i=1}^G M_i \lambda_i^m \right) \\ &\quad + \sum_{m=1}^N [\bar{M}_z^m \bar{M}_w^m \bar{M}_n^m - 3\bar{M}_w^m (\bar{M}_n^m)^2 + 2(\bar{M}_n^m)^3] \lambda^m \end{aligned}$$

age molecular weights are given for repeating units with Schulz-Flory and Poisson's distributions of their sub-classes, assuming also that their possible molecular weights are evenly distributed according to

$$M^j = jM_R + M_E \quad (j = 0, \infty).$$

Integer-order moments of NMWD, λ_{M_i} , allow average molecular weights, such as number-, weight- and z-average molecular weights to be obtained as

$$\bar{M}_n = \lambda_{M_1} / \lambda_{M_0} \quad (3)$$

$$\bar{M}_w = \lambda_{M_2} / \lambda_{M_1} \quad (4)$$

$$\bar{M}_z = \lambda_{M_3} / \lambda_{M_2} \quad (5)$$

and these can be obtained by differentiating eq. (2) with respect to $\log \mu$ and setting $\mu = 1$. The resulting expressions are given in Table 2. Evaluation of the moments of NMWD requires the set of the moments of the VNMND, which are derivatives of \bar{P} on $\sigma = 1_G$, $\zeta = 1^N$:

$$\lambda_{ijk\dots}^{mnp\dots} = \Lambda_{ijk\dots}^{mnp\dots}(1_G, 1^N) = \frac{\partial \bar{P}}{\partial \log \sigma_i \partial \log \sigma_j \partial \log \sigma_k \dots \partial \log \zeta^m \partial \log \zeta^n \partial \log \zeta^p \dots}(1_G, 1^N). \quad (6)$$

λ_j and λ^j are, respectively, the concentrations of end-groups A_j and repeating units U^j belonging to finite molecules (the sol), and so the following equalities hold:

$$A_{js} = \lambda_j = \Lambda_j(1_G, 1^N) \quad (7)$$

$$U_s^j = \lambda^j = \Lambda^j(1_G, 1^N). \quad (8)$$

The weight fraction of sol w_s is therefore given by

$$w_s = \lambda_{M_1} = \sum_{m=1}^N \bar{M}_n^m \lambda^m + \sum_{i=1}^G M_i \lambda_i. \quad (9)$$

When dealing with polyadditions, the contributions of the smallest molecules should be subtracted from the moments, as there is always an appreciable amount of monomers along with high molecular weight polymer.

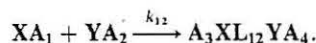
Molecular growth in polycondensation processes occurs through linking of repeating units by the reaction of the end-groups that are attached to them. Intramolecular loops are produced by reaction of two end-groups separated by a finite number of repeating units. Propagation and termination by combination play an analogous rule in polyadditions.

When an end-group A_i attached to some repeating

unit X reacts with another end-group A_j attached to some repeating unit Y in another molecule creating a link L_{ij} between the two repeating units, the vector of numbers of end-groups attached to X changes by

$v_{ij} = [v_{ij1}, \dots, v_{ijG}]$ and likewise the vector of numbers of end-groups attached to Y changes by $v_{ji} = [v_{ji1}, \dots, v_{jiG}]$. This is the key concept allowing the analysis of arbitrarily complex polymerizations.

The curing of a tetraepoxide with a diamine will be used as a case study throughout this paper. There are $N = 2$ repeating units: the one carrying the two primary amine groups (U^1) and the other repeating unit carrying the 4 epoxide groups (U^2). Each primary amine group (A_1) disappears by reaction with one epoxy group (A_2), being transformed into a secondary amine group (A_3) attached to the same U^1 repeating unit and making a secondary hydroxyl group (A_4) appear in the other repeating unit (U^2):



Therefore, $v_{121} = -1$, $v_{212} = -1$, $v_{123} = 1$, $v_{214} = 1$. The other components of v_{12} and v_{21} are nil, except the ones for the linking groups L_{12} , but it is seldom needed to keep a record of the linking groups.

It is useful to define overall stoichiometric coefficients ω_{ij} , which form a symmetrical matrix:

$$\omega_{ij} = \omega_{ji} = v_{ij} + v_{ji} \quad (10)$$

An apparent bimolecular rate constant of the reaction between end-groups A_i and A_j , named k_{ij} , will be defined as the rate of formation of L_{ij} divided by the concentrations of A_i and A_j . This set of rate constants is obviously symmetrical. k_{ij} depends most often on the concentration of end groups and catalysts. For instance, in the case of the reaction between amines and epoxy groups, there is an autocatalysis by the hydroxyl groups (Dusek, 1986) and so

$$k_{12} = k_{21} = k_{12}^0 + k'_{12}A_4. \quad (11)$$

The complete kinetic scheme of this example is presented in Table 3.

It is possible that parallel reactions exist between the same pair of end-groups A_i and A_j . A notorious example is the termination reaction between two radicals, which can go through a combination or a dismutation process. In such a case, two (or even more) apparent rate constants k_{ij}^I and k_{ij}^{II} , each one with its set of stoichiometric coefficients v_{ijk}^I and v_{ijk}^{II} , would have to be introduced.

Reactions of end-groups not leading to intermolecular links, such as intramolecular cyclization, can be modelled using a similar mathematical formalism. The numbers of end-groups of the repeating unit to which they are attached change by a vector $v_i^* = [v_{i1}^*, \dots, v_{iG}^*]$, at a rate of reaction given by $k_i^* A_i$. The apparent kinetic constants k_i^* may also be a function of the concentrations of other end-groups, such as in the example dealing with radical polymerization discussed next.

All pairs of end-groups able to react intramolecularly must be considered pseudo end-groups. The correct definition of end-groups and determination of stoichiometric coefficients is a complex task when intramolecular cyclization reactions need be considered. These reactions were neglected in the treatment of curing an epoxy resin as dealt with in this work.

Radical copolymerization of N polyvinyl compounds $X^n (=CH_2)_{f^n}$ or $U^n(A_n)_{f^n}$ ($n = 1, N$), with penultimate effects in propagation, has a great practical importance and is a good example of system with reactions involving end-groups without forming links, such as termination by dismutation and transfer reactions. Its mechanism and corresponding set of

Table 3. Kinetic scheme of the reaction between a tetraepoxide and a diamine

| Group name | Description | Formula | Index | | |
|---|---------------------|---|----------|-----------------------------|-----------------------------|
| A | Primary amine | $-\text{NH}_2$ | 1 | | |
| E | Epoxide | $\begin{array}{c} -\text{CH}-\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ | 2 | | |
| S | Secondary amine | $-\text{NH}-$ | 3 | | |
| H | Hydroxyethylamine | $-\text{N}-\text{CH}_2-\text{CH}-\text{OH}$ | 4 | | |
| HE | Hydroxyethylenether | $\begin{array}{c} \quad \\ -\text{N}-\text{CH}_2-\text{CH}-\text{O}-\text{CH}_2-\text{CH}-\text{OH} \\ \quad \end{array}$ | 5 | | |
| Reaction | i | j | k_{ij} | \bar{v}_{ij} | \bar{v}_{ji} |
| $\text{A} + \text{E} \rightarrow \text{S} + \text{H}$ | 1 | 2 | k_P | $\frac{\sigma_3}{\sigma_1}$ | $\frac{\sigma_4}{\sigma_2}$ |
| $\text{S} + \text{E} \rightarrow \text{H}$ | 3 | 2 | k_S | $\frac{1}{\sigma_3}$ | $\frac{\sigma_4}{\sigma_2}$ |
| $\text{E} + \text{H} \rightarrow \text{HE}$ | 2 | 4 | k_E | $\frac{\sigma_5}{\sigma_2}$ | $\frac{1}{\sigma_4}$ |
| $\text{E} + \text{HE} \rightarrow \text{HE}$ | 2 | 5 | k_E | $\frac{\sigma_5}{\sigma_2}$ | $\frac{1}{\sigma_5}$ |

Parameters used in simulation: $k_s/k_p = 0.2$ and $k_E/k_p = 0.055$.

Molecular weights of monomers: $M^1 = 248$ and $M^2 = 422$; for all end-groups $M_i = 0$.

stoichiometric coefficients is summarized in Appendix B. Not all reactions in radical polymerization can be analysed with this approach, because of the assumption of reaction irreversibility. For instance, depropagation and β -scission of radicals cannot be taken into account. From this point of view, Villiermaux and Blavier's tendency model (Villiermaux and Blavier, 1984) remains more general than our proposed model, although it suffers from the drawback of not being able to cope with strongly non-linear polymerizations.

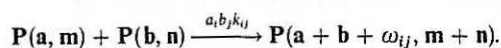
One should not overlook the possibility of a breakdown of the validity of the principle of the equal reactivity beyond gel point. Some experimental evidence (Argyropoulos *et al.*, 1987b) points to diffusional limitations having a different effect on small and large polymer molecules, these latter being entrapped in gel. No quantitative model for these effects was put forward up to now, which is not surprising, in view of the difficulty of gathering the necessary experimental data. However, the overall picture of post-gel polymerization according to classical theory (Flory, 1941a-c, 1942, 1947; Stockmayer, 1943, 1944) is fairly accurate, with the exception of the above-mentioned effect (Argyropoulos and Bolker, 1986; Argyropoulos *et al.*, 1987a, c). It seems justified to develop a mathematical treatment of non-linear polymerizations using the principle of the equal reactivity, keeping in mind its main value as a first approximation of their behaviour after gelation.

Rate equations

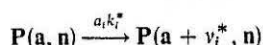
Using the principle of the equal reactivity and the above definitions of rate constants and stoichiometric coefficients, the rate equation for the end-groups can be written as follows:

$$R_{A_i} = \sum_{j=1}^G \sum_{k=1}^G k_{ijk} v_{ijk} A_i A_j + \sum_{i=1}^G k_i^* v_{ik}^* A_i \quad (12)$$

So, according to the previous definitions, each pair of end-groups A_i and A_j in molecules $P(a, m)$ and $P(b, n)$ reacts with rate $a_i b_j k_{ij} P(a, m) P(b, n)$ forming a link between repeating units and thus yields a molecule $P(a + b + \omega_{ij}, m + n)$:



A reaction of its end-groups A_i not forming inter-molecular links converts molecule $P(a, n)$ into a molecule $P(a + v_i^*, n)$:



The rate of formation of polymer species $P(a, n)$ is therefore

$$R_{P(a, n)} = \frac{1}{2} \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left[\sum_{b_1=0}^{b_1-\omega_{ij}} \dots \sum_{b_G=0}^{b_G-\omega_{ij}} \sum_{m^1=0}^{n^1} \dots \sum_{m^N=0}^{n^N} b_i P(b_1, \dots, b_G, m^1, \dots, m^N) \right. \\ \left. \times (a_j - b_j - \omega_{ij}) P(a_1 - b_1 - \omega_{ij}, \dots, a_G - b_G - \omega_{ij}, n^1 - m^1, \dots, n^N - m^N) \right. \\ \left. - a_i P(a_1, \dots, a_G, n^1, \dots, n^N) A_j \right] \\ + \sum_{i=1}^G k_i^* \sum_{m^1=0}^{n^1} \dots \sum_{m^N=0}^{n^N} [(a_i - v_i^*) \\ \times P(a_1 - v_{i1}^*, \dots, a_G - v_{iG}^*, n^1, \dots, n^N) \\ - a_i P(a_1, \dots, a_G, n^1, \dots, n^N)] \quad (13)$$

The rate of formation of species $P(a_1, \dots, a_G, n^1, \dots, n^N)$ depends only on the concentrations of species with lower numbers of end-groups and of repeating units. After insertion of eq. (13) in a mass balance equation of polymer species, a closed system of equations results, from which any set of $P(a_1, \dots, a_G, n^1, \dots, n^N)$ with $0 \leq a_i \leq a_{i, \text{MAX}}$, $0 \leq n^m \leq n_{\text{MAX}}^m$, $1 \leq i \leq G$, $1 \leq m \leq N$ can be computed. However, because of the multiple embedded sums, the evaluation of the right-hand sides of eq. (13) requires $O(a_{1, \text{MAX}} \dots a_{G, \text{MAX}} n_{\text{MAX}}^1 \dots n_{\text{MAX}}^N)^2$ operations. This is likely to be a huge number, unless the concentrations of the first oligomers are the only one to be evaluated.

Fortunately, the approach suggested by Costa and Villiermaux (1988) or Mills (1986a-c), based on the evaluation and numerical inversion of discrete transforms also works for this kind of problems and will be used next. Its first step consists in obtaining the discrete transform of rate law [eq. (13)]:

$$\bar{R}_P(\sigma, \zeta) = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_i} \left(\frac{1}{2} \bar{\omega}_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_j} - A_j \right) \\ + \sum_{i=1}^G k_i^* \frac{\partial \bar{P}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) \quad (14)$$

$$\bar{\omega}_{ij}(\sigma) = \prod_{k=1}^G \sigma_k^{\omega_{ijk}} = \bar{v}_{ij} \bar{v}_{ji} \quad (15)$$

$$\bar{v}_i^*(\sigma) = \prod_{k=1}^G \sigma_k^{v_{ik}^*} \quad (16)$$

EVALUATION OF MWD AND AVERAGE MOLECULAR WEIGHTS IN IDEAL REACTORS

Integration of mass balance equation of polymer species

Prediction of polymer properties will now be carried out for ideal reactors. A non-steady state perfectly mixed continuous stirred tank reactor (CSTR) is a convenient starting point, since batch/plug flow and semi-batch reactors can be considered as special cases.

The overall mass balance should be first considered. Reaction of one mole of end-groups A_i and one mole of A_j is supposed to change volume by W_{ij} and the reaction of end-group A_i without forming a linking group is supposed to change the volume by W_i^* . A relative change of reactor volume by chemical reaction R_V is found by adding all these contributions. If mixing volume is neglected, inlet and outlet volume

flow rates and reaction volume are related by

$$\begin{aligned} \frac{d \log V}{dt} &= \frac{1}{2} \sum_{i=1}^G \sum_{j=1}^G k_{ij} A_i A_j W_{ij} \\ &\quad + \sum_{i=1}^G k_i^* A_i W_i^* + \frac{Q_F(t) - Q(t)}{V} \\ &= R_V + \frac{Q_F(t) - Q(t)}{V}. \end{aligned} \quad (17)$$

This balance also holds in a batch reactor (where $Q_F = Q = 0$) and in a semi-batch reactor (where only $Q = 0$). It is natural to consider that V is constant in a CSTR and let eq. (17) be used for relating inlet and outlet flow rates. In a semi-batch reactor, it is used for computing reaction volume $V(t)$.

Therefore, a generic molecular species, such as some end-group A_k , verifies the following mass balance equation with space time τ defined as the ratio of reaction volume by inlet flow rate:

$$\frac{\partial A_k}{\partial t} = R_{A_k} + \frac{A_{kF}(t) - A_k}{\tau(t)} - R_V A_k \quad (18)$$

$$A_k|_{t=0} = A_{k0}. \quad (19)$$

Discrete transforms of number molecular number distributions or moments of these also verify this generic mass balance. So, the NMND of polymer species can be found by integrating the non-linear first-order partial differential equation

$$\begin{aligned} \frac{\partial \bar{P}}{\partial t} &= \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_i} \left(\frac{1}{2} \bar{\omega}_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_j} - A_j \right) \\ &\quad + \sum_{i=1}^G k_i^* \frac{\partial \bar{P}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) \\ &\quad + \frac{\bar{P}_F(t) - \bar{P}}{\tau} - R_V \bar{P} \end{aligned} \quad (20)$$

$$\bar{P}|_{t=0} = \bar{P}_0(\sigma, \zeta). \quad (21)$$

Because of the way the time variable t appears in eq. (20),

$$\begin{aligned} \frac{\partial \bar{P}}{\partial t} &= F\left(t, \sigma_1, \dots, \sigma_G, \bar{P}, \frac{\partial \bar{P}}{\partial \log \sigma_1}, \dots, \frac{\partial \bar{P}}{\partial \log \sigma_G}\right) \\ &= F(t, \sigma_1, \dots, \sigma_G, \bar{P}, \Lambda_1, \dots, \Lambda_G) \end{aligned} \quad (22)$$

a special adaptation of the method of characteristics (Courant and Hilbert, 1962) is worth doing, as will be shown next. Partial differentiation with respect to $\log \sigma_1, \dots, \log \sigma_G$ leads to a system now including G new partial differential equations for the $\Lambda_1, \dots, \Lambda_G$:

$$\frac{\partial \Lambda_k}{\partial t} - \sum_{i=1}^G \frac{\partial F}{\partial \Lambda_i} \frac{\partial \Lambda_k}{\partial \log \sigma_i} = \frac{\partial F}{\partial \log \sigma_k} + \frac{\partial F}{\partial \bar{P}} \Lambda_k \quad (k = 1, G) \quad (23)$$

(notice the use of the identities $\partial \Lambda_i / \partial \log \sigma_k = \partial^2 \bar{P} / \partial \log \sigma_i \partial \log \sigma_k = \partial \Lambda_k / \partial \log \sigma_i$). These new partial differential equations are semi-linear, and along the

characteristic curves defined by

$$\frac{d \log \sigma_k}{dt} = - \frac{\partial F}{\partial \Lambda_k}. \quad (24)$$

$\Lambda_1, \dots, \Lambda_G$ verify

$$\frac{d \Lambda_k}{dt} = \frac{\partial F}{\partial \log \sigma_k} + \frac{\partial F}{\partial \bar{P}} \Lambda_k. \quad (25)$$

Also, along the characteristics:

$$\begin{aligned} \frac{d \bar{P}}{dt} &= \sum_{i=1}^G \frac{\partial \bar{P}}{\partial \log \sigma_i} \frac{d \log \sigma_i}{dt} = \sum_{i=1}^G \Lambda_i \frac{d \log \sigma_i}{dt} \\ &= - \sum_{i=1}^G \Lambda_i \frac{\partial F}{\partial \Lambda_i}. \end{aligned} \quad (26)$$

Carrying out the substitution in eqs (24)–(26) of the required partial derivatives of the right-hand side of eq. (20), $\partial F / \partial \log \sigma_i$, $\partial F / \partial \Lambda_i$ and $\partial F / \partial \bar{P}$, the following system of $2G + 1$ ordinary differential equations along the characteristics $\sigma(t)$ starting at $\sigma = \sigma_0$ (ζ is constant along the characteristics) is obtained:

$$\begin{aligned} \frac{d \bar{P}}{dt} &= - \frac{1}{2} \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} \Lambda_i \Lambda_j \\ &\quad + \frac{\bar{P}_F(t) - \bar{P}}{\tau} - R_V \bar{P} \end{aligned} \quad (27)$$

$$\frac{d \log \sigma_k}{dt} = \sum_{i=1}^G k_{ki} (A_i - \bar{\omega}_{ki} \Lambda_i) + k_k^* (1 - \bar{v}_k^*) \quad (28)$$

$$\begin{aligned} \frac{d \Lambda_k}{dt} &= \frac{1}{2} \sum_{i=1}^G \sum_{j=1}^G k_{ij} \omega_{ijk} \bar{\omega}_{ij} \Lambda_i \Lambda_j + \sum_{i=1}^G k_i^* \bar{v}_{ik}^* \bar{v}_i^* \Lambda_i \\ &\quad + \frac{\Lambda_{kF}(t) - \Lambda_k}{\tau} - R_V \Lambda_k \end{aligned} \quad (29)$$

$$\bar{P}|_{t=0} = \bar{P}_0(\sigma_0, \zeta) \quad (30)$$

$$\sigma_k|_{t=0} = \sigma_{k0} \quad (31)$$

$$\Lambda_k|_{t=0} = \Lambda_{k0}(\sigma_0, \zeta) = \frac{\partial \bar{P}_0}{\partial \log \sigma_{k0}}(\sigma_0, \zeta). \quad (32)$$

In order that a certain characteristic passes through a previously specified value of σ at a time t , a system of G algebraic equations must be solved to find the starting vector σ_0 at time $t = 0$:

$$\log \sigma_k(\log \sigma_0, \zeta) - \log \sigma_k = 0. \quad (33)$$

The Newton–Raphson method can be used to solve this system of algebraic equations, with some care in the choice of the starting values of σ_0 . The Jacobian of system (33),

$$S_{ki} = \frac{\partial \log \sigma_k}{\partial \log \sigma_{i0}} \quad (34)$$

can be found after introducing the auxiliary sensitivities

$$S_i^k = \frac{\partial \log \Lambda_k}{\partial \log \sigma_{i0}} \quad (35)$$

and solving eqs (28)–(29) and eqs (31)–(32) simultaneously with the additional $2G^2$ ordinary differential

equations:

$$\frac{dS_{kl}}{dt} = - \sum_{i=1}^G k_{ki} \bar{\omega}_{kl} \left(S_i^l + \Lambda_i \sum_{j=1}^G \omega_{kij} S_{jl} \right) - k_k^* \bar{v}_k^* \sum_{j=1}^G v_{kj}^* S_{jl} \quad (36)$$

$$\frac{dS_i^k}{dt} = \sum_{j=1}^G \sum_{h=1}^G k_{ij} \omega_{ijk} \bar{\omega}_{ij} \Lambda_i \left(S_j^h + \frac{1}{2} \Lambda_j \sum_{h=1}^G \omega_{ijh} S_{hl} \right) + \sum_{i=1}^G k_i^* v_{ik}^* \bar{v}_i^* \left(S_i^l + \Lambda_i \sum_{j=1}^G v_{ij}^* S_{jl} \right) + \frac{\Lambda_{klF}(t) - S_i^k}{\tau} - R_V S_i^k \quad (37)$$

$$S_{kl}|_{t=0} = \begin{cases} 1 & \text{if } k=l \\ 0 & \text{otherwise} \end{cases} \quad (38)$$

$$S_i^k|_{t=0} = \Lambda_{k10} = \frac{\partial^2 \bar{P}_0}{\partial \log \sigma_{k0} \partial \log \sigma_{10}} (\sigma_0, \zeta). \quad (39)$$

Most often, the marginal distribution with respect to the number of repeating units $\bar{P}(1_G, \zeta)$ is sought and so $\sigma = 1_G$. If also $\zeta = 1^N$, the starting point σ_0 should be a vector of numbers as close to zero as necessary, so that $\sigma = 1_G$ is approached only by values of $\sigma_i < 1$. Now, a possible solution of eqs (27)–(32) for $\sigma = 1_G$ and $\zeta = 1^N$ leads to $\Lambda_i = A_i$ and $\sigma_0 = 1_G$. If Newton-Raphson's method converges towards this solution, it means that the gelation time has not yet been attained, because all reactive groups belong to finite molecules. If $\sigma = 1_G$ can be attained with some or all $\sigma_{i0} < 1$, it will result in $\Lambda_i < A_i$ for some i and gelation has occurred.

In order to estimate any marginal distribution according to the number of repeating units U^m by numerical inversion of \bar{P} , n_{MAX}^m values of this discrete transform must be evaluated along a circle in complex plane with $|\zeta^m| = \text{constant} \leq 1$, with all other values of ζ^n or σ_i equal to 1. The starting value of vector σ_0 for the computation of each of these points should be the one found in the previous computation. The first of all should be a vector of small positive real numbers for the evaluation along the real positive axis.

Evaluation of average molecular weights and weight fraction of gel

In order to compute the moments of the VNMND, rate equations for the derivatives of \bar{P} are obtained by differentiation of eq. (14) with respect to $\log \sigma_k$ and/or $\log \zeta^m$:

$$R_{\Lambda_k} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left[\frac{\partial \Lambda_k}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \frac{1}{2} \omega_{ijk} \bar{v}_{ij} \Lambda_i \Lambda_j \right] + \sum_{i=1}^G k_i^* \left[\frac{\partial \Lambda_k}{\partial \log \sigma_i} (\bar{v}_i^* - 1) + v_{ik}^* \bar{v}_i^* \Lambda_i \right] \quad (40)$$

$$R_{\Lambda_i^k} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \Lambda_i^k}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j)$$

$$+ \sum_{i=1}^G k_i^* \frac{\partial \Lambda_i^k}{\partial \log \sigma_i} (\bar{v}_i^* - 1) \quad (41)$$

$$R_{\Lambda_{ij}} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left\{ \frac{\partial \Lambda_{ij}}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \bar{\omega}_{ij} \left[\frac{1}{2} \omega_{ijk} \omega_{ijl} \Lambda_i \Lambda_j + \Lambda_{ik} \Lambda_{jl} + \Lambda_j (\omega_{ijk} \Lambda_{il} + \omega_{ijl} \Lambda_{ik}) \right] \right\} + \sum_{i=1}^G k_i^* \left[\frac{\partial \Lambda_{ij}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) + \bar{v}_i^* (v_{ik}^* \Lambda_{il} + v_{il}^* \Lambda_{ik} + v_{ik}^* v_{il}^* \Lambda_i) \right] \quad (42)$$

$$R_{\Lambda_i^k} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left[\frac{\partial \Lambda_i^k}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \bar{\omega}_{ij} (\Lambda_i^k \Lambda_{jl} + \omega_{ijl} \Lambda_j \Lambda_i^k) \right] + \sum_{i=1}^G k_i^* \left[\frac{\partial \Lambda_i^k}{\partial \log \sigma_i} (\bar{v}_i^* - 1) + v_{il}^* v_i^* \Lambda_i^k \right] \quad (43)$$

$$R_{\Lambda^{kl}} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left[\frac{\partial \Lambda^{kl}}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \bar{\omega}_{ij} \Lambda_i^k \Lambda_j^l \right] + \sum_{i=1}^G k_i^* \frac{\partial \Lambda^{kl}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) \quad (44)$$

$$R_{\Lambda_{ilm}} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left\{ \frac{\partial \Lambda_{ilm}}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \bar{\omega}_{ij} [\Lambda_{ikl} \Lambda_{jlm} + \Lambda_{ikm} \Lambda_{jl} + \Lambda_{ilm} \Lambda_{jk} + \omega_{ijk} \Lambda_{il} \Lambda_{jm} + \omega_{ijl} \Lambda_{ik} \Lambda_{jm} + \omega_{ijm} \Lambda_{ik} \Lambda_{jl} + \Lambda_j (\frac{1}{2} \omega_{ijk} \omega_{ijl} \omega_{ijm} \Lambda_i + \omega_{ijk} \Lambda_{ilm} + \omega_{ijl} \Lambda_{ikm} + \omega_{ijm} \Lambda_{ikl} + \omega_{ijk} \omega_{ijl} \Lambda_{im} + \omega_{ijk} \omega_{ijm} \Lambda_{il} + \omega_{ijl} \omega_{ijm} \Lambda_{ik})] \right\} + \sum_{i=1}^G k_i^* \left[\frac{\partial \Lambda_{ilm}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) + \bar{v}_i^* (v_{ik}^* \Lambda_{ilm} + v_{il}^* \Lambda_{ikm} + v_{im}^* \Lambda_{ikl} + v_{ik}^* v_{il}^* \Lambda_{im} + v_{ik}^* v_{im}^* \Lambda_{il} + v_{il}^* v_{im}^* \Lambda_{ik} + v_{ik}^* v_{il}^* v_{im}^* \Lambda_i) \right] \quad (45)$$

$$R_{\Lambda_{im}^k} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left\{ \frac{\partial \Lambda_{im}^k}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \bar{\omega}_{ij} [\Lambda_i^k \Lambda_{jlm} + \Lambda_{il}^k \Lambda_{jm} + \Lambda_{im}^k \Lambda_{jl} + \omega_{ijl} (\Lambda_{jm} \Lambda_i^k + \Lambda_j \Lambda_{im}^k) + \omega_{ijm} (\Lambda_{jl} \Lambda_i^k + \Lambda_j \Lambda_{il}^k) + \omega_{ijl} \omega_{ijm} \Lambda_j \Lambda_i^k] \right\} + \sum_{i=1}^G k_i^* \left[\frac{\partial \Lambda_{im}^k}{\partial \log \sigma_i} (\bar{v}_i^* - 1) + \bar{v}_i^* (v_{il}^* \Lambda_{im}^k + v_{im}^* \Lambda_{il}^k + v_{il}^* v_{im}^* \Lambda_i^k) \right] \quad (46)$$

$$R_{\Lambda_i^k} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left\{ \frac{\partial \Lambda_m^{kl}}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \bar{\omega}_{ij} [\Lambda_i^{kl} \Lambda_{jm} + \Lambda_{im}^k \Lambda_j^l + \Lambda_i^k \Lambda_{jm}^l] + \omega_{ijm} (\Lambda_j \Lambda_i^{kl} + \Lambda_i^k \Lambda_j^l) \right\} + \sum_{i=1}^G k_i^* \left[\frac{\partial \Lambda_m^{kl}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) + v_{im}^* \bar{v}_i^* \Lambda_i^{kl} \right] \quad (47)$$

$$R_{\Lambda_i^{km}} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \left[\frac{\partial \Lambda^{klm}}{\partial \log \sigma_i} (\bar{\omega}_{ij} \Lambda_j - A_j) + \bar{\omega}_{ij} (\Lambda_i^{kl} \Lambda_j^m + \Lambda_i^{km} \Lambda_j^l + \Lambda_i^k \Lambda_{jm}^l) \right] + \sum_{i=1}^G k_i^* \frac{\partial \Lambda^{klm}}{\partial \log \sigma_i} (\bar{v}_i^* - 1). \quad (48)$$

Inserting these expressions in mass balance equations, such as the one in a CSTR, a system of non-linear first-order partial differential equations results. Its characteristics are the same as the ones used for computing \bar{P} , eqs (27)–(32). Along with them, the derivatives of \bar{P} verify

$$\frac{d\Lambda^k}{dt} = \frac{\Lambda_F^k(t) - \Lambda^k}{\tau} - R_V \Lambda^k \quad (49)$$

$$\frac{d\Lambda_{kl}}{dt} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} [\Lambda_{ik} \Lambda_{jl} + \Lambda_j (\omega_{ijk} \Lambda_{il} + \omega_{ijl} \Lambda_{ik}) + \frac{1}{2} \omega_{ijk} \omega_{ijl} \Lambda_i \Lambda_j] + \sum_{i=1}^G k_i^* [\bar{v}_i^* (v_{ik}^* \Lambda_{il} + v_{il}^* \Lambda_{ik} + v_{ik}^* v_{il}^* \Lambda_i)] + \frac{\Lambda_{klF}(t) - \Lambda_{kl}}{\tau} - R_V \Lambda_{kl} \quad (50)$$

$$\frac{d\Lambda_i^k}{dt} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} (\Lambda_i^k \Lambda_{jl} + v_{ijl} \Lambda_j \Lambda_i^k) + \sum_{i=1}^G k_i^* v_{il}^* \bar{v}_i^* \Lambda_i^k + \frac{\Lambda_{iF}^k(t) - \Lambda_i^k}{\tau} - R_V \Lambda_i^k \quad (51)$$

$$\frac{d\Lambda^{kl}}{dt} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} \Lambda_i^k \Lambda_j^l + \frac{\Lambda_F^{kl}(t) - \Lambda^{kl}}{\tau} - R_V \Lambda^{kl} \quad (52)$$

$$\begin{aligned} \frac{d\Lambda_{klm}}{dt} = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} [\Lambda_{ikl} \Lambda_{jm} + \Lambda_{ikm} \Lambda_{jl} + \Lambda_{ilm} \Lambda_{jk} \\ & + \omega_{ijk} \Lambda_{il} \Lambda_{jm} + \omega_{ijl} \Lambda_{ik} \Lambda_{jm} + \omega_{ijm} \Lambda_{ik} \Lambda_{jl} \\ & + \Lambda_j (\omega_{ijk} \Lambda_{ilm} + \omega_{ijl} \Lambda_{ikm} + \omega_{ijm} \Lambda_{ikl} \\ & + \omega_{ijk} \omega_{ijl} \Lambda_{im} + \omega_{ijk} \omega_{ijm} \Lambda_{il} + \omega_{ijl} \omega_{ijm} \Lambda_{ik} \\ & + \frac{1}{2} \omega_{ijk} \omega_{ijl} \omega_{ijm} \Lambda_i)] + \sum_{i=1}^G k_i^* \bar{v}_i^* (v_{ik}^* \Lambda_{ilm} \\ & + v_{il}^* \Lambda_{ikm} + v_{im}^* \Lambda_{ikl} + v_{ik}^* v_{il}^* \Lambda_{im} \\ & + v_{ik}^* v_{im}^* \Lambda_{il} + v_{il}^* v_{im}^* \Lambda_{ik} + v_{ik}^* v_{il}^* v_{im}^* \Lambda_i) \\ & + \frac{\Lambda_{klmF}(t) - \Lambda_{klm}}{\tau} - R_V \Lambda_{klm} \end{aligned} \quad (53)$$

$$\begin{aligned} \frac{d\Lambda_{lm}^k}{dt} = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} [\Lambda_i^k \Lambda_{jlm} + \Lambda_{il}^k \Lambda_{jm} + \Lambda_{im}^k \Lambda_{jl} \\ & + \omega_{ijl} (\Lambda_{jm} \Lambda_i^k + \Lambda_j \Lambda_{im}^k) \\ & + \omega_{ijm} (\Lambda_{jl} \Lambda_i^k + \Lambda_j \Lambda_{il}^k) + \omega_{ijl} \omega_{ijm} \Lambda_j \Lambda_i^k] \\ & + \sum_{i=1}^G k_i^* \bar{v}_i^* (v_{il}^* \Lambda_{im}^k + v_{im}^* \Lambda_{il}^k + v_{il}^* v_{im}^* \Lambda_i^k) \\ & + \frac{\Lambda_{lmF}^k(t) - \Lambda_{lm}^k}{\tau} - R_V \Lambda_{lm}^k \end{aligned} \quad (54)$$

$$\begin{aligned} \frac{d\Lambda_m^{kl}}{dt} = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} [\Lambda_i^{kl} \Lambda_{jm} + \Lambda_{im}^k \Lambda_j^l + \Lambda_i^k \Lambda_{jm}^l] \\ & + \omega_{ijm} (\Lambda_j \Lambda_i^{kl} + \Lambda_i^k \Lambda_j^l) + \sum_{i=1}^G k_i^* v_{im}^* \bar{v}_i^* \Lambda_i^{kl} \\ & + \frac{\Lambda_{mF}^{kl}(t) - \Lambda_m^{kl}}{\tau} - R_V \Lambda_m^{kl} \end{aligned} \quad (55)$$

$$\begin{aligned} \frac{d\Lambda^{klm}}{dt} = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \bar{\omega}_{ij} (\Lambda_i^{kl} \Lambda_j^m + \Lambda_i^{km} \Lambda_j^l + \Lambda_i^k \Lambda_{jm}^l) \\ & + \frac{\Lambda_F^{klm}(t) - \Lambda^{klm}}{\tau} - R_V \Lambda^{klm}. \end{aligned} \quad (56)$$

A simpler and computationally more efficient method should be used before gelation. Rate equations for the moments λ_{ijk}^{mnp} are obtained replacing $\sigma = 1_G$, $\zeta = 1^N$ in eqs (40)–(48). As there is no gel, all end-groups belong to finite molecules, and so the following equalities hold:

$$A_k = \lambda_k = \Lambda_k(1_G, 1^N) \quad (57)$$

$$U_k = \lambda^k = \Lambda^k(1_G, 1^N) \quad (58)$$

and the moments verify a set of ordinary differential equations given in Table 4.

GEL STRUCTURE AND ELASTIC PROPERTIES

Several pioneers of polymer science, such as Kuhn, Guth, James, Mark, Flory, Gee and Treloar, have contributed to the theory of rubber elasticity [see Flory (1953) and Treloar (1975)]. However, many essential problems remain incompletely understood in spite of 50 years of research. Even the simpler problem of the prediction or correlation of the small-strain equilibrium shear modulus, G_e , has no clear-cut solution. Two extreme models are available for describing the network, the affine and the phantom models. In addition, it was once believed that an appreciable contribution to G_e came from the so called "trapped entanglements" (Langley, 1968). In the early eighties, it was generally accepted that the following relation held for G_e :

$$G_e = (v_e - h\mu_e)RT + G_{Ne}^0 T_e. \quad (59)$$

In this equation, v_e and μ_e are, respectively, the mole concentrations of elastically active chains (EANC) and junctions (EANJ) (they will be rigorously defined below). The empirical parameter h , between 0 and 1, allows for intermediate behaviour between affine

Table 4. Mass balance equations for the moments of VNMND in a CSTR before gelation

$$\begin{aligned}
\frac{d\lambda_{kl}}{dt} &= \sum_{i=1}^G \sum_{j=1}^G k_{ij} [\lambda_{ik} \lambda_{jl} + A_j (\omega_{ijk} \lambda_{il} + \omega_{ijl} \lambda_{ik}) + \frac{1}{2} \omega_{ijk} \omega_{ijl} A_i A_j] + \sum_{i=1}^G k_i^* (v_{ik}^* \lambda_{il} + v_{il}^* \lambda_{ik} + v_{ik}^* v_{il}^* A_i) \\
&\quad + \frac{\lambda_{klF} - \lambda_{kl}}{\tau} - R_V \lambda_{kl} \\
\frac{d\lambda_i^k}{dt} &= \sum_{j=1}^G \sum_{l=1}^G k_{ij} (\lambda_i^k \lambda_{jl} + \omega_{ijl} A_j \lambda_i^k) + \sum_{i=1}^G k_i^* v_{il}^* \lambda_i^k + \frac{\lambda_{iF}^k - \lambda_i^k}{\tau} - R_V \lambda_i^k \\
\frac{d\lambda^{kl}}{dt} &= \sum_{i=1}^G \sum_{j=1}^G k_{ij} \lambda_i^k \lambda_j^l + \frac{\lambda_F^{kl} - \lambda^{kl}}{\tau} - R_V \lambda^{kl} \\
\frac{d\lambda_{klm}}{dt} &= \sum_{i=1}^G \sum_{j=1}^G k_{ij} [\lambda_{ikl} \lambda_{jm} + \lambda_{ikm} \lambda_{jl} + \lambda_{ilm} \lambda_{jk} + \omega_{ijk} \lambda_{il} \lambda_{jm} + \omega_{ijl} \lambda_{ik} \lambda_{jm} + \omega_{ijm} \lambda_{ik} \lambda_{jl} + A_j (\omega_{ijk} \lambda_{ilm} + \omega_{ijl} \lambda_{ikm} \\
&\quad + \omega_{ijm} \lambda_{ikl} + \omega_{ijk} \omega_{ijl} \lambda_{im} + \omega_{ijk} \omega_{ijm} \lambda_{il} + \omega_{ijl} \omega_{ijm} \lambda_{ik} + \frac{1}{2} \omega_{ijk} \omega_{ijl} \omega_{ijm} A_i)] \\
&\quad + \sum_{i=1}^G k_i^* (v_{ikl}^* \lambda_{ilm} + v_{il}^* \lambda_{ikm} + v_{im}^* \lambda_{ikl} + v_{ik}^* v_{il}^* \lambda_{im} + v_{ik}^* v_{im}^* \lambda_{il} + v_{il}^* v_{im}^* \lambda_{ik} + v_{ik}^* v_{il}^* v_{im}^* A_i) \\
&\quad + \frac{\lambda_{klmF} - \lambda_{klm}}{\tau} - R_V \lambda_{klm} \\
\frac{d\lambda_{lm}^k}{dt} &= \sum_{i=1}^G \sum_{j=1}^G k_{ij} [\lambda_i^k \lambda_{jl} + \lambda_{im}^k \lambda_{jl} + \lambda_{ilm}^k \lambda_{jl} + \omega_{ijl} (\lambda_{jm}^k + A_j \lambda_{im}^k) + \omega_{ijm} (\lambda_{jl} + A_j \lambda_{il}^k) + \omega_{ijl} \omega_{ijm} A_j \lambda_i^k] \\
&\quad + \sum_{i=1}^G k_i^* (v_{il}^* \lambda_{im}^k + v_{im}^* \lambda_{il}^k + v_{il}^* v_{im}^* \lambda_i^k) + \frac{\lambda_{lmF}^k - \lambda_{lm}^k}{\tau} - R_V \lambda_{lm}^k \\
\frac{d\lambda_{jm}^{kl}}{dt} &= \sum_{i=1}^G \sum_{l=1}^G k_{ij} [\lambda_i^{kl} \lambda_{jm} + \lambda_{im}^{kl} \lambda_j^l + \lambda_i^{kl} \lambda_{jm}^l + \omega_{ijm} (A_j \lambda_i^{kl} + \lambda_i^{kl} \lambda_j^l)] + \sum_{i=1}^G k_i^* v_{im}^* \lambda_i^{kl} + \frac{\lambda_{jmF}^{kl} - \lambda_{jm}^{kl}}{\tau} - R_V \lambda_{jm}^{kl} \\
\frac{d\lambda^{klm}}{dt} &= \sum_{i=1}^G \sum_{j=1}^G k_{ij} (\lambda_i^{kl} \lambda_j^m + \lambda_i^{km} \lambda_j^l + \lambda_i^{lm} \lambda_j^k) + \frac{\lambda_F^{klm} - \lambda^{klm}}{\tau} - R_V \lambda^{klm}
\end{aligned}$$

($h = 0$) and phantom networks ($h = 1$) (Dossin and Graessley, 1979). The term $G_{Ne}^0 T_e$ was introduced in order to take into account entanglements between chains. It is the product of a modulus G_{Ne}^0 , in principle depending only on the chemical nature of polymer, and of a factor T_e , representing the fraction of the maximum concentration of topological interactions.

Although at one time it seemed that eq. (59) had a sound experimental basis [see e.g. Pearson and Graessley (1980), Valles and Macosko (1979), Gottlieb *et al.* (1981) and also Dusek (1986)], Flory and co-workers have criticized the concept of trapped entanglements between chains contributing to network elasticity (Flory and Erman, 1984) and have refined the elasticity theory based on different assumptions (Flory, 1977; Erman and Flory, 1978). Recent experimental and theoretical studies (Lee and Eichinger, 1990) do not support the need of Langley's contribution. Nevertheless, we will discuss briefly how T_e can be predicted, after dealing with the much more important problem of predicting the EANJ and EANC concentrations.

Theory of branching processes (TBP) has been used for computing concentrations of EANC and EANJ soon after its introduction (Dobson and Gordon, 1964). The mathematically equivalent "recursive approach" by Macosko and Miller (Miller and Macosko, 1976, 1980) has later been used with more complex chemical systems. This could not render TBP obsolete, and application of TBP to prediction of

polymer structure has lately been extended and perfected (Dusek, 1985).

However, TBP describes exactly only systems at chemical equilibrium. Some irreversible batch polycondensations (specially when strict equal reactivity of end-groups holds) lead to the same polymer structure as if a chemical equilibrium prevailed, but this assumption usually breaks down in the presence of substitution effects. No kinetically based treatment was available to cope with this situation. In fact, it was even believed that such a treatment could not be found (Dusek, 1985).

In this paper, the problem of mathematically predicting the concentration of network structures relevant to the prediction of elastic properties is solved for a general irreversible non-linear polymerization, provided that repeating units combine to form tree-like molecules. As before, the key information is the set of stoichiometric coefficients of the reactions between reactive groups, which are used for establishing the needed mass balance equations.

INTERNAL JUNCTIONS IN REPEATING UNITS, DISTRIBUTIONS OF JUNCTIONS AND EXTINCTION PROBABILITIES

Elastic properties of gel are determined by its *elastically active junctions* (EANJ) which are defined (Scanlan, 1960; Case, 1960; Flory, 1982) as molecular fragments linked to three or more independent network chains (chains going to infinity). Elastically ac-

tive chains (EANC) are all independent chains connecting EANJ.

Repeating units can sometimes be considered to contain a single junction, such as pentaerythritol units $C(CH_2OH)_4$ reacting with an isocyanate. Most often, they have multiple internal junctions connected by relatively long flexible chains. This is illustrated by polyamines used for curing epoxide resins with more than one primary amine group linked by relatively long flexible chains, which must be counted as EANCs if the two amine end-groups react with three or more epoxide groups.

So, let J^M be the number of distinguishable junction classes G^{MJ} in repeating unit M ($M = 1, N$; $J = J^M$). The number of junctions G^{MJ} in repeating unit M will be named ρ^{MJ} . Each junction is initially attached to f_i^{MJ} A_i end-groups and to g^{MJK} other junctions G^{MK} (see Fig. 5). A chain linking junctions G^{MJ} and G^{MK} is named L^{MJK} . Because of the assumption that all junctions in each class are indistinguishable, there will be at most $J^M(J^M + 1)/2$ kinds of distinguishable links between junctions in each repeating unit.

As chemical reactions progress, in addition to the fixed number of links to other junctions a variable number of linking groups are added to each junction, sometimes new end-groups too, which are formed by reaction of previously existent end-groups. Let $G^{MJ}(a, l)$ be a junction G^{MJ} attached to a end-groups and l linking groups, respectively, and let $G^{MJ}(a, l)$ be its mole concentration, according to our usual convention, $\bar{G}^{MJ}(\alpha, \zeta)$ be its vectorial discrete transform,

$$\bar{G}^{MJ}(\alpha, \zeta) = \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} \sum_{l_{11}=0}^{\infty} \dots \sum_{l_{GG}=0}^{\infty} \alpha_1^{a_1} \dots \alpha_G^{a_G} \zeta_{11}^{l_{11}} \dots \zeta_{GG}^{l_{GG}} G^{MJ}(a_1, \dots, a_G, l_{11}, \dots, l_{GG}). \quad (60)$$

The elastic properties of the gel are related to the distributions of junctions. Each junction G^{MJ} is said to have a rank $x = 0, 1, 2$, and so on, according to the number x of network chains which start from it. So, the key quantities for the characterization of gel will be the distributions of numbers of network chains $T^{MJ}(a, x)$ or their generating functions $\bar{T}^{MJ}(\alpha, \zeta)$.

In what follows, a tree-like structure of the repeating units and of the polymer will be assumed. The extension of this approach to structures containing loops should be possible, but we could as yet find no simple procedure for systematically excluding dangling loops.

For each linking group L_{ij} or L^{MJK} , the fractions of chains which stem from it, in both directions, and do not go to infinity, are the extinction probabilities v_{ij} and v_{ji} (most of the times they are different when $i \neq j$), or v^{MJK} and v^{MKJ} . So, the following relation is the base of the present kinetic treatment:

$$\bar{T}^{MJ}(\alpha, \zeta) = \prod_{K=1}^{J^M} [v^{MJK} + \zeta(1 - v^{MJK})] g^{MJK} \times \bar{G}^{MJ}[\alpha, v + \zeta(1_{GG} - v)]. \quad (61)$$

CONCENTRATIONS OF EANJ, EANC, WEIGHT FRACTION OF PENDANT MATERIAL AND TRAPPING FACTOR

An elastically active network junction (EANJ) is defined as a junction linked to three or more network chains. Their overall concentration, μ_e , is therefore

$$\begin{aligned} \mu_e &= \sum_{M=1}^N \sum_{J=1}^{J^M} \sum_{x=3}^{\infty} \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} T^{MJ}(a, x) \\ &= \sum_{M=1}^N \sum_{J=1}^{J^M} \left[\bar{T}^{MJ}(1_G, 1) - \bar{T}^{MJ}(1_G, 0) \right. \\ &\quad \left. - \frac{\partial \bar{T}^{MJ}}{\partial \xi}(1_G, 0) - \frac{1}{2} \frac{\partial^2 \bar{T}^{MJ}}{\partial \xi^2}(1_G, 0) \right]. \quad (62) \end{aligned}$$

The concentration of elastically active network chains (EANC) v_e is one-half the concentration of network chains carried by all elastically active junctions:

$$\begin{aligned} v_e &= \frac{1}{2} \sum_{M=1}^N \sum_{J=1}^{J^M} \sum_{x=3}^{\infty} \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} x T^{MJ}(a, x) \\ &= \frac{1}{2} \sum_{M=1}^N \sum_{J=1}^{J^M} \left[\frac{\partial \bar{T}^{MJ}}{\partial \xi}(1_G, 1) - \frac{\partial \bar{T}^{MJ}}{\partial \xi}(1_G, 0) \right. \\ &\quad \left. - \frac{\partial^2 \bar{T}^{MJ}}{\partial \xi^2}(1_G, 0) \right]. \quad (63) \end{aligned}$$

The weight fraction of pendant material in gel, w_p , is the weight fraction of material linked to the gel by no more than two active network chains. The sum of w_p with weight fraction of sol w_s is then

$$\begin{aligned} w_p + w_s &= \sum_{M=1}^N \sum_{J=1}^{J^M} \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} (\bar{M}_n^{MJ} + a_1 M_1 \\ &\quad + \dots + a_G M_G) [T^{MJ}(a_1, \dots, a_G, 0) \\ &\quad + T^{MJ}(a_1, \dots, a_G, 1) \\ &\quad + T^{MJ}(a_1, \dots, a_G, 2)] \\ &= \sum_{M=1}^N \sum_{J=1}^{J^M} \left\{ \bar{M}_n^{MJ} \left[\bar{T}^{MJ}(1_G, 0) \right. \right. \\ &\quad \left. \left. + \frac{\partial \bar{T}^{MJ}}{\partial \xi}(1_G, 0) + \frac{1}{2} \frac{\partial^2 \bar{T}^{MJ}}{\partial \xi^2}(1_G, 0) \right] \right. \\ &\quad \left. + M_1 \left[\frac{\partial \bar{T}^{MJ}}{\partial \alpha_1}(1_G, 0) + \frac{\partial^2 \bar{T}^{MJ}}{\partial \alpha_1 \partial \xi}(1_G, 0) \right. \right. \\ &\quad \left. \left. + \frac{1}{2} \frac{\partial^3 \bar{T}^{MJ}}{\partial \alpha_1 \partial \xi^2}(1_G, 0) \right] + \dots \right. \\ &\quad \left. + M_G \left[\frac{\partial \bar{T}^{MJ}}{\partial \alpha_G}(1_G, 0) + \frac{\partial^2 \bar{T}^{MJ}}{\partial \alpha_G \partial \xi}(1_G, 0) \right. \right. \\ &\quad \left. \left. + \frac{1}{2} \frac{\partial^3 \bar{T}^{MJ}}{\partial \alpha_G \partial \xi^2}(1_G, 0) \right] \right\}. \quad (64) \end{aligned}$$

In writing eq. (64), the molecular weight of each repeating unit was assumed to be shared by its junctions. \bar{M}_n^{MJ} is the number-average molecular weight allocated to junction G^{MJ} . No molecular weight was allocated to links between junctions.

The original definition of Langley's trapping factor T_e must be generalized, so as to encompass any network. T_e is proportional to the product of probabili-

ties of contacts between repeating units linked to the network by two or more network chains. We will define a non-normalized T_e^* as the square of weight fractions of material linked to the gel to two or more network chains (volume fractions could also be introduced). Consequently, T_e is T_e^* divided by its maximum possible value, T_{eMAX}^* , which can often be taken as the value for exact stoichiometric balance. Therefore, we write

$$\begin{aligned}\sqrt{T_e^*} &= \sqrt{T_e T_{eMAX}^*} = 1 - \sum_{M=1}^N \sum_{J=1}^{J^M} \sum_{a_1=0}^{\infty} \cdots \sum_{a_G=0}^{\infty} \\ &\quad \times (\bar{M}_n^{MJ} + a_1 M_1 + \cdots + a_G M_G) \\ &\quad \times [T^{MJ}(a, 0) + T^{MJ}(a, 1)] \\ &= 1 - \sum_{M=1}^N \sum_{J=1}^{J^M} \left\{ \bar{M}_n^{MJ} \left[\bar{T}^{MJ}(1_G, 0) \right. \right. \\ &\quad \left. \left. + \frac{\partial \bar{T}^{MJ}}{\partial \xi}(1_G, 0) \right] + M_1 \left[\frac{\partial \bar{T}^{MJ}}{\partial \alpha_1}(1_G, 0) \right. \right. \\ &\quad \left. \left. + \frac{\partial^2 \bar{T}^{MJ}}{\partial \alpha_1 \partial \xi}(1_G, 0) \right] + \cdots + M_G \left[\frac{\partial \bar{T}^{MJ}}{\partial \alpha_G}(1_G, 0) \right. \right. \\ &\quad \left. \left. + \frac{\partial^2 \bar{T}^{MJ}}{\partial \alpha_G \partial \xi}(1_G, 0) \right] \right\}. \quad (65)\end{aligned}$$

Taking into account eq. (61), the selected gel properties are related to the \bar{G}^{MJ} and their derivatives by

$$\begin{aligned}\mu_e &= \sum_{M=1}^N \sum_{J=1}^{J^M} \left[\bar{G}^{MJ}(1_G, 1_{GG}) \right. \\ &\quad - (H^{MJ} + H^{MJ'} + \frac{1}{2} H^{MJ''}) \bar{G}^{MJ}(1_G, v) \\ &\quad - (H^{MJ} + H^{MJ'}) \sum_{i=1}^G \sum_{j=1}^G (1 - v_{ij}) \Gamma^{MJij}(1_G, v) \\ &\quad - \frac{1}{2} H^{MJ} \sum_{i=1}^G \sum_{j=1}^G \sum_{k=1}^G \sum_{l=1}^G (1 - v_{ij}) \\ &\quad \left. \times (1 - v_{kl}) \Gamma^{MJijkl}(1_G, v) \right] \quad (66)\end{aligned}$$

$$\begin{aligned}v_e &= \frac{1}{2} \sum_{M=1}^N \sum_{J=1}^{J^M} \left\{ I^{MJ} \bar{G}^{MJ}(1_G, 1_{GG}) \right. \\ &\quad - (H^{MJ'} + H^{MJ''}) \bar{G}^{MJ}(1_G, v) \\ &\quad + \sum_{i=1}^G \sum_{j=1}^G (1 - v_{ij}) [\Gamma^{MJij}(1_G, 1_{GG}) \\ &\quad - (H^{MJ} + 2H^{MJ'}) \Gamma^{MJij}(1_G, v)] \\ &\quad - H^{MJ} \sum_{i=1}^G \sum_{j=1}^G \sum_{k=1}^G \sum_{l=1}^G (1 - v_{ij}) \\ &\quad \left. \times (1 - v_{kl}) \Gamma^{MJijkl}(1_G, v) \right\} \quad (67)\end{aligned}$$

$$\begin{aligned}w_p + w_s &= \sum_{M=1}^N \sum_{J=1}^{J^M} \left\{ \bar{M}_n^{MJ} \left[(H^{MJ} + H^{MJ'}) \right. \right. \\ &\quad \left. \left. + \frac{1}{2} H^{MJ''} \right] \bar{G}^{MJ}(1_G, v) + (H^{MJ} + H^{MJ'}) \right. \\ &\quad \left. \times \sum_{i=1}^G \sum_{j=1}^G (1 - v_{ij}) \Gamma^{MJij}(1_G, v) \right\}\end{aligned}$$

$$\begin{aligned}&+ \frac{1}{2} H^{MJ''} \sum_{i=1}^G \sum_{j=1}^G \sum_{k=1}^G \sum_{l=1}^G (1 - v_{ij}) \\ &\quad \times (1 - v_{kl}) \Gamma^{MJijkl}(1_G, v) \Big] \\ &+ \sum_{m=1}^G M_m \left[\Gamma_m^{MJ}(1_G, v) \right. \\ &+ \sum_{i=1}^G \sum_{j=1}^G (1 - v_{ij}) \Gamma_m^{MJij}(1_G, v) \\ &+ \frac{1}{2} \sum_{i=1}^G \sum_{j=1}^G \sum_{k=1}^G \sum_{l=1}^G (1 - v_{ij}) \\ &\quad \left. \times (1 - v_{kl}) \Gamma_m^{MJijkl}(1_G, v) \right] \Big\} \quad (68)\end{aligned}$$

$$\begin{aligned}\sqrt{T_e^*} &= 1 - \sum_{M=1}^N \sum_{J=1}^{J^M} \\ &\quad \times \left\{ \bar{M}_n^{MJ} \left[(H^{MJ} + H^{MJ'}) \bar{G}^M(1_G, v) \right. \right. \\ &\quad \left. \left. + H^{MJ} \sum_{i=1}^G \sum_{j=1}^G (1 - v_{ij}) \Gamma^{MJij}(1_G, v) \right] \right. \\ &\quad \left. + \sum_{m=1}^G M_m \left[\Gamma_m^{MJ}(1_G, v) \right. \right. \\ &\quad \left. \left. + \sum_{i=1}^G \sum_{j=1}^G (1 - v_{ij}) \Gamma_m^{MJij}(1_G, v) \right] \right\} \quad (69)\end{aligned}$$

where

$$\Gamma_{mn \dots}^{MJijkl \dots} = \frac{\partial \bar{G}^{MJ}}{\partial \alpha_m \partial \alpha_n \dots} (\alpha, \zeta) \quad (70)$$

$$H^{MJ} = \prod_{K=1}^{J^M} (v^{MJK})^{g^{MJK}} \quad (71)$$

$$H^{MJ'} = H^{MJ} \sum_{K=1}^{J^M} g^{MJK} \frac{1 - v^{MJK}}{v^{MJK}} \quad (72)$$

$$\begin{aligned}H^{MJ''} &= H^{MJ} \left[\left(\sum_{K=1}^{J^M} g^{MJK} \frac{1 - v^{MJK}}{v^{MJK}} \right)^2 \right. \\ &\quad \left. - \sum_{K=1}^{J^M} g^{MJK} \frac{(1 - v^{MJK})^2}{(v^{MJK})^2} \right] \quad (73)\end{aligned}$$

$$I^{MJ} = \sum_{K=1}^{J^M} g^{MJK} (1 - v^{MJK}). \quad (74)$$

RATE EQUATIONS FOR PREDICTING GEL PROPERTIES

The concentrations of linking groups L_{ij} need to be predicted. Regardless of whether they belong to the gel or not, their rate of formation is simply

$$R_{L_{ij}} = k_{ij} A_i A_j. \quad (75)$$

The extinction probabilities can be computed, without the need of invoking TBP, by following the concentrations of dangling chains $X_{ij}(a)$ which start at an L_{ij} , go towards the repeating unit previously carrying the end-group A_j and lead finally to a end-groups of different kinds. Each extinction probability v_{ij} is simply the fraction of those fragments which are finite,

regardless of the numbers of their end-groups:

$$v_{ij} = \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} X_{ij}(a_1, \dots, a_G) / L_{ij}. \quad (76)$$

Introducing the vectorial discrete transform

$$\bar{X}_{ij}(\sigma) = \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} \sigma_1^{a_1} \dots \sigma_G^{a_G} X_{ij}(a_1, \dots, a_G) \quad (77)$$

eq. (76) becomes

$$v_{ij} = \bar{X}_{ij}(1_G) / L_{ij}. \quad (78)$$

A rate equation for $X_{kl}(\mathbf{a})$ can easily be written, realizing that an existent $X_{kl}(\mathbf{a})$ grows by reaction of its end-groups with $P(\mathbf{a}, \mathbf{n})$ or by non-intermolecular reaction of a larger fragment, is destroyed by reaction of its end-groups and is created whenever an end-group A_k reacts intermolecularly with an end-group A_l belonging to a polymer molecule $P(\mathbf{a}, \mathbf{n})$:

$$\begin{aligned} \bar{R}_{X_{kl}}(\sigma) = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \bar{X}_{kl}}{\partial \log \sigma_i} \left(\bar{\omega}_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_j} - A_j \right) \\ & + \sum_{i=1}^G k_i^* \frac{\partial \bar{X}_{kl}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) \\ & + k_{kl} A_k \bar{v}_{lk} \frac{\partial \bar{P}}{\partial \log \sigma_l}. \end{aligned} \quad (79)$$

Coming now to the links between junctions, their rate of formation is obviously nil and so their concentration is easily determined by knowing the concentrations of repeating units:

$$L^{MIJ} = \rho^{MI} g^{MIJ} U^M. \quad (80)$$

Similarly, it is necessary to introduce the concentrations of dangling chains $X^{MIJ}(\mathbf{a})$ which start at a G^{MI} junction and go towards a junction G^{MJ} , leading to end-groups of different kinds. Extinction probability v^{MIJ} is the fraction of those fragments which are finite, regardless of the numbers of their end-groups:

$$v^{MIJ} = \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} X^{MIJ}(a_1, \dots, a_G) / L^{MIJ}. \quad (81)$$

The rate law for $X^{MIJ}(\mathbf{a})$ is identical to eq. (79), except for the absence of the term coming from the creation of new links:

$$\begin{aligned} \bar{R}_{X^{MIJ}}(\sigma) = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \bar{X}^{MIJ}}{\partial \log \sigma_i} \left(\bar{\omega}_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_j} - A_j \right) \\ & + \sum_{i=1}^G k_i^* \frac{\partial \bar{X}^{MIJ}}{\partial \log \sigma_i} (\bar{v}_i^* - 1). \end{aligned} \quad (82)$$

Inserting rate laws (79) or (82) in the relevant mass balance equations of the reactor, partial differential equations are obtained. They must be solved simultaneously with the mass balance equation for the discrete transform of VNMND, $\bar{P}(\sigma, \zeta)$, for $\zeta = 1^N$ [eqs (27)–(32)]. In the case of the CSTR, those equations are first-order and semi-linear:

$$\frac{\partial \bar{X}_{kl}}{\partial t} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \bar{X}_{kl}}{\partial \log \sigma_i} \left(\bar{\omega}_{ij} \frac{\partial \bar{P}}{\partial \log \sigma_j} - A_j \right)$$

$$\begin{aligned} & + \sum_{i=1}^G k_i^* \frac{\partial \bar{X}_{kl}}{\partial \log \sigma_i} (\bar{v}_i^* - 1) + k_{kl} A_k \bar{v}_{lk} \frac{\partial \bar{P}}{\partial \log \sigma_l} \\ & + \frac{\bar{X}_{klF}(t) - \bar{X}_{kl}}{\tau} - R_V \bar{X}_{kl} \end{aligned} \quad (83)$$

$$\bar{X}_{kl}|_{t=0} = \bar{X}_{kl0}(\sigma). \quad (84)$$

Adding the G^2 equations (83) to eq. (20) does not change the characteristics $\sigma(t)$, which are computed using eqs (27)–(35) as before. Along the characteristics, \bar{X}_{kl} and \bar{X}^{MKL} are determined by integrating

$$\frac{d\bar{X}_{kl}}{dt} = k_{kl} A_k \bar{v}_{lk} A_l + \frac{\bar{X}_{klF}(t) - \bar{X}_{kl}}{\tau} - R_V \bar{X}_{kl} \quad (85)$$

$$\frac{d\bar{X}^{MKL}}{dt} = \frac{\bar{X}^{MKL}(t) - \bar{X}^{MKL}}{\tau} - R_V \bar{X}^{MKL}. \quad (86)$$

Before the gel point, $\bar{X}_{kl}(1_G) = L_{kl}$, since $\sigma(t) = 1_G$ along the characteristic that ends at 1_G , and (82) degenerates into the rate law for L_{kl} , equation (75).

It remains now to establish rate laws for the G^{MI} and their derivatives $\Gamma_{mn\dots}^{MIjkl\dots}$ in order to compute the right-hand sides of eqs (66)–(69). This is also easily done, since

$$G^{MI}(\mathbf{a}, \mathbf{l}) + A_j$$

$$\xrightarrow{a_{kij}} G^{MI}(\mathbf{a} + v_{ij}, l_{11}, \dots, l_{ij} + 1, \dots, l_{GG})$$

and therefore

$$\begin{aligned} \bar{R}_{G^{MI}}(\alpha, \zeta) = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \bar{G}^{MI}}{\partial \log \alpha_i} A_j [\zeta_{ij} \bar{v}_{ij}(\alpha) - 1] \\ & + \sum_{i=1}^G k_i^* \frac{\partial \bar{G}^{MI}}{\partial \log \alpha_i} [\bar{v}_i^*(\alpha) - 1]. \end{aligned} \quad (87)$$

Differentiation of eq. (87) leads to the rate laws of the $\Gamma_{mn\dots}^{MIjkl\dots}$:

$$\begin{aligned} R_{\Gamma_i^{MI}} = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} A_j \left[\frac{\partial \Gamma_i^{MI}}{\partial \log \alpha_i} (\zeta_{ij} \bar{v}_{ij} - 1) \right. \\ & \left. + \zeta_{ij} \bar{v}_{ij} v_{ijk} \Gamma_i^{MI} \right] \\ & + \sum_{i=1}^G k_i^* \left[\frac{\partial \Gamma_i^{MI}}{\partial \log \alpha_i} (\bar{v}_i^* - 1) + \bar{v}_i^* v_{ik}^* \Gamma_i^{MI} \right] \end{aligned} \quad (88)$$

$$\begin{aligned} R_{\Gamma^{MI}} = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} \frac{\partial \Gamma^{MI}}{\partial \log \alpha_i} A_j (\zeta_{ij} \bar{v}_{ij} - 1) \\ & + \sum_{i=1}^G k_i^* \frac{\partial \Gamma^{MI}}{\partial \log \alpha_i} (\bar{v}_i^* - 1) + k_{kl} \bar{v}_{kl} \Gamma_k^{MI} A_l \end{aligned} \quad (89)$$

$$\begin{aligned} R_{\Gamma_{kl}^{MI}} = & \sum_{i=1}^G \sum_{j=1}^G k_{ij} A_j \left[\frac{\partial \Gamma_{kl}^{MI}}{\partial \log \alpha_i} (\zeta_{ij} \bar{v}_{ij} - 1) \right. \\ & \left. + \zeta_{ij} \bar{v}_{ij} (v_{ijl} \Gamma_{kl}^{MI} + v_{ijk} \Gamma_{li}^{MI} + v_{ijk} v_{ijl} \Gamma_{li}^{MI}) \right] \\ & + \sum_{i=1}^G k_i^* \left[\frac{\partial \Gamma_{kl}^{MI}}{\partial \log \alpha_i} (\bar{v}_i^* - 1) \right. \\ & \left. + \bar{v}_i^* v_{ik}^* (\Gamma_{il}^{MI} + v_{il}^* \Gamma_i^{MI}) \right] \end{aligned} \quad (90)$$

$$R_{\Gamma^{MI}} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} A_j \left[\frac{\partial \Gamma^{MI}}{\partial \log \alpha_i} (\zeta_{ij} \bar{v}_{ij} - 1) + \zeta_{ij} \bar{v}_{ij} v_{ijm} \Gamma_i^{MI} \right] + \sum_{i=1}^G k_i^* \left[\frac{\partial \Gamma^{MI}}{\partial \log \alpha_i} (\bar{v}_i^* - 1) + \bar{v}_i^* v_{im}^* \Gamma_i^{MI} \right] + k_{kl} A_l \bar{v}_{kl} (\Gamma_{mk}^{MI} + v_{klm} \Gamma_k^{MI}) \quad (91)$$

$$R_{\Gamma^{MIklmn}} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} A_j \frac{\partial \Gamma^{MIklmn}}{\partial \log \alpha_i} (\zeta_{ij} \bar{v}_{ij} - 1) + \sum_{i=1}^G k_i^* \frac{\partial \Gamma^{MIklmn}}{\partial \log \alpha_i} (\bar{v}_i^* - 1) + k_{kl} A_l \bar{v}_{kl} \Gamma_k^{MI} + k_{mn} A_n \bar{v}_{mn} \Gamma_m^{MI} \quad (92)$$

Inserting these rate laws in the mass balance in a CSTR, a system of first-order semi-linear partial differential equations is obtained. Its characteristics verify

$$\frac{d \log \alpha_k}{dt} = \sum_{i=1}^G k_{ki} A_i (1 - \zeta_{ki} \bar{v}_{ki}) + k_k^* (1 - \bar{v}_k^*) \quad (93)$$

$$\alpha_k|_{t=0} = \alpha_{k0} \quad (94)$$

In order to pass through a previously specified value of α at a time t for a certain matrix ζ , a system of G algebraic equations must be solved to find the starting vector α_0 :

$$\log \alpha_k (\log \alpha_0, \zeta) - \log \alpha_k = 0 \quad (95)$$

Just as before, Newton-Raphson's method can be used to solve this system of algebraic equations, choosing small enough starting values for α_0 . The Jacobian of system (95),

$$Z_{ki} = \frac{\partial \log \alpha_k}{\partial \log \alpha_{i0}} \quad (96)$$

can be found by solving eq. (93) simultaneously with the additional G^2 ordinary differential equations:

$$\frac{dZ_{ki}}{dt} = - \sum_{i=1}^G k_{ki} A_i \zeta_{ki} \bar{v}_{ki} \sum_{j=1}^G v_{kij} Z_{ji} - k_k^* \bar{v}_k^* \sum_{j=1}^G v_{kj}^* Z_{kj} \quad (97)$$

$$Z_{ki}|_{t=0} = \begin{cases} 1 & \text{if } k = i \\ 0 & \text{otherwise} \end{cases} \quad (98)$$

After computing the starting vector α_0 , the remaining differential equations for computing \bar{G}^{MI} and its derivatives along the characteristics can be simultaneously integrated until the final value of α :

$$\frac{d\bar{G}^{MI}}{dt} = \frac{\bar{G}_F^{MI}(t) - \bar{G}^{MI}}{\tau} - R_V \bar{G}^{MI} \quad (99)$$

$$\frac{d\Gamma_k^{MI}}{dt} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} \zeta_{ij} \bar{v}_{ij} v_{ijk} A_j \Gamma_i^{MI} + \sum_{i=1}^G k_i^* \bar{v}_i^* v_{ik}^* \Gamma_i^{MI} + \frac{\Gamma_{kF}^{MI}(t) - \Gamma_k^{MI}}{\tau} - R_V \Gamma_k^{MI} \quad (100)$$

$$\frac{d\Gamma^{MI}}{dt} = k_{kl} \bar{v}_{kl} \Gamma_k^{MI} A_l + \frac{\Gamma_F^{MI}(t) - \Gamma^{MI}}{\tau} - R_V \Gamma^{MI} \quad (101)$$

$$\frac{d\Gamma_{kl}^{MI}}{dt} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} A_j \zeta_{ij} \bar{v}_{ij} \times (v_{ijl} \Gamma_{ki}^{MI} + v_{ijk} \Gamma_{il}^{MI} + v_{ijk} v_{ijl} \Gamma_i^{MI}) + \sum_{i=1}^G k_i^* \bar{v}_i^* v_{ik}^* (\Gamma_{il}^{MI} + v_{il}^* \Gamma_i^{MI}) + \frac{\Gamma_{klF}^{MI}(t) - \Gamma_{kl}^{MI}}{\tau} - R_V \Gamma_{kl}^{MI} \quad (102)$$

$$\frac{d\Gamma_m^{MI}}{dt} = \sum_{i=1}^G \sum_{j=1}^G k_{ij} A_j \zeta_{ij} \bar{v}_{ij} v_{ijm} \Gamma_i^{MI} + \sum_{i=1}^G k_i^* \bar{v}_i^* v_{im}^* \Gamma_i^{MI} + k_{kl} A_l \bar{v}_{kl} (\Gamma_{mk}^{MI} + v_{klm} \Gamma_k^{MI}) + \frac{\Gamma_{mF}^{MI}(t) - \Gamma_m^{MI}}{\tau} - R_V \Gamma_m^{MI} \quad (103)$$

$$\frac{d\Gamma^{MIklmn}}{dt} = k_{kl} A_l \bar{v}_{kl} \Gamma_k^{MI} + k_{mn} A_n \bar{v}_{mn} \Gamma_m^{MI} + \frac{\Gamma_F^{MIklmn} - \Gamma^{MIklmn}}{\tau} - R_V \Gamma^{MIklmn} \quad (104)$$

THE ALTERNATING POLYCONDENSATION OF TWO POINT-LIKE MONOMERS

Since this kinetic treatment is entirely new, we illustrate it with the analysis of the irreversible alternating polycondensation of two point-like monomers $U^1(A_1)_f$ and $U^2(A_2)_f$ in a batch reactor, for which an analytical solution can be found.

There are no reactions consuming end-groups without forming links ($v_{ij}^* = 0$ for all i, j). The discrete transform of the matrix of the stoichiometric coefficients of reactions forming links is

$$[\bar{v}_{ij}] = \begin{bmatrix} 0 & 1/\sigma_1 \\ 1/\sigma_2 & 0 \end{bmatrix} \quad (105)$$

Mass balance equations for end-groups, linking groups, polymer molecules and dangling chains in a batch reactor without volume changes can be written as

$$\frac{dA_1}{dt} = \frac{dA_2}{dt} = - \frac{dL_{12}}{dt} = -k_{12} A_1 A_2 \quad (106)$$

$$k_{12}^{-1} \frac{\partial \bar{P}}{\partial t} = \frac{1}{\sigma_1 \sigma_2} \frac{\partial \bar{P}}{\partial \log \sigma_1} \frac{\partial \bar{P}}{\partial \log \sigma_2} - A_1 \frac{\partial \bar{P}}{\partial \log \sigma_2} - A_2 \frac{\partial \bar{P}}{\partial \log \sigma_1} \quad (107)$$

$$k_{12}^{-1} \frac{\partial \bar{X}_{12}}{\partial t} = \frac{\partial \bar{X}_{12}}{\partial \log \sigma_1} \left(\frac{1}{\sigma_1 \sigma_2} \frac{\partial \bar{P}}{\partial \log \sigma_2} - A_2 \right) + \frac{\partial \bar{X}_{12}}{\partial \log \sigma_2} \left(\frac{1}{\sigma_1 \sigma_2} \frac{\partial \bar{P}}{\partial \log \sigma_1} - A_1 \right)$$

$$+ \frac{A_1}{\sigma_2} \frac{\partial \bar{P}}{\partial \log \sigma_2} \quad (108)$$

$$k_{12}^{-1} \frac{\partial \bar{X}_{21}}{\partial t} = \frac{\partial \bar{X}_{21}}{\partial \log \sigma_1} \left(\frac{1}{\sigma_1 \sigma_2} \frac{\partial \bar{P}}{\partial \log \sigma_2} - A_2 \right) + \frac{\partial \bar{X}_{21}}{\partial \log \sigma_2} \left(\frac{1}{\sigma_1 \sigma_2} \frac{\partial \bar{P}}{\partial \log \sigma_1} - A_1 \right) + \frac{A_2}{\sigma_1} \frac{\partial \bar{P}}{\partial \log \sigma_1} \quad (109)$$

If the polycondensation starts from monomers only, the initial conditions are:

$$A_1|_{t=0} = f_1 U^1 \quad (110)$$

$$A_2|_{t=0} = f_2 U^2 \quad (111)$$

$$\bar{P}|_{t=0} = U^1 \zeta^1 \sigma_1^{f_1} + U^2 \zeta^2 \sigma_2^{f_2} \quad (112)$$

$$\bar{X}_{12}|_{t=0} = \bar{X}_{21}|_{t=0} = 0. \quad (113)$$

The equations of characteristics become:

$$k_{12}^{-1} \frac{d \log \sigma_1}{dt} = A_2 - \frac{\Lambda_2}{\sigma_1 \sigma_2} \quad (114)$$

$$k_{12}^{-1} \frac{d \log \sigma_2}{dt} = A_1 - \frac{\Lambda_1}{\sigma_1 \sigma_2} \quad (115)$$

$$\frac{d \Lambda_1}{dt} = \frac{d \Lambda_2}{dt} = \frac{d \bar{P}}{dt} = - \frac{k_{12} \Lambda_1 \Lambda_2}{\sigma_1 \sigma_2} \quad (116)$$

$$k_{12}^{-1} \frac{d \bar{X}_{12}}{dt} = \frac{A_1 \Lambda_2}{\sigma_2} \quad (117)$$

$$k_{12}^{-1} \frac{d \bar{X}_{21}}{dt} = \frac{A_2 \Lambda_1}{\sigma_1} \quad (118)$$

$$\sigma_1|_{t=0} = \sigma_{10} \quad (119)$$

$$\sigma_2|_{t=0} = \sigma_{20} \quad (120)$$

$$\Lambda_1|_{t=0} = f_1 U^1 \zeta^1 \sigma_{10}^{f_1} \quad (121)$$

$$\Lambda_2|_{t=0} = f_2 U^2 \zeta^2 \sigma_{20}^{f_2} \quad (122)$$

$$\bar{P}|_{t=0} = U^1 \zeta^1 \sigma_{10}^{f_1} + U^2 \zeta^2 \sigma_{20}^{f_2}. \quad (123)$$

Conversions of end-groups p_1 and p_2 are convenient variables for writing the solution of eqs (114)–(123) in a way which is independent from changes of volume and of apparent rate constant k_{12} with end-group concentrations, and thus with time. The following relations are independent of volume changes:

$$A_1 = f_1 U^1 (1 - p_1) \quad (124)$$

$$A_2 = f_2 U^2 (1 - p_2) \quad (125)$$

$$L_{12} = L_{21} = f_1 U^1 p_1 = f_2 U^2 p_2. \quad (126)$$

Both conversions are related through the initial stoichiometric ratio r :

$$p_2 = \frac{p_1}{r} = \frac{f_1 U^1}{f_2 U^2} p_1. \quad (127)$$

Solution of eqs (114)–(127) leads to:

$$\frac{\Lambda_1}{\sigma_1 A_1} = \frac{\Lambda_{10}}{\sigma_{10} A_{10}} = \zeta^1 \sigma_{10}^{f_1 - 1} \quad (128)$$

$$\frac{\Lambda_2}{\sigma_2 A_2} = \frac{\Lambda_{20}}{\sigma_{20} A_{20}} = \zeta^2 \sigma_{20}^{f_2 - 1} \quad (129)$$

$$\bar{P} = \bar{P}|_{t=0} - \frac{\Lambda_{10} \Lambda_{20}}{\sigma_{10} \sigma_{20} A_{10} A_{20}} (A_{10} - A_1) = U^1 \zeta^1 \sigma_{10}^{f_1} + U^2 \zeta^2 \sigma_{20}^{f_2} - p_1 f_1 U^1 \zeta^1 \zeta^2 \sigma_{10}^{f_1 - 1} \sigma_{20}^{f_2 - 1} \quad (130)$$

$$\bar{X}_{12} = \frac{\Lambda_{20}}{\sigma_{20} A_{20}} (A_{20} - A_2) = p_2 A_{20} \sigma_{20}^{f_2 - 1} \quad (131)$$

$$\bar{X}_{21} = \frac{\Lambda_{10}}{\sigma_{10} A_{10}} (A_{10} - A_1) = p_1 A_{10} \sigma_{10}^{f_1 - 1}. \quad (132)$$

The starting point of a characteristic passing through prescribed values of $\sigma_1, \sigma_2, \zeta^1$ and ζ^2 , defined by σ_{10} and σ_{20} , must be obtained by solving the two coupled algebraic equations

$$\sigma_{10} = \sigma_1 (1 - p_1) + p_1 \frac{\Lambda_{20}}{\sigma_{20} A_{20}} = \sigma_1 (1 - p_1) + p_1 \zeta^2 \sigma_{20}^{f_2 - 1} \quad (133)$$

$$\sigma_{20} = \sigma_2 (1 - p_2) + p_2 \frac{\Lambda_{10}}{\sigma_{10} A_{10}} = \sigma_2 (1 - p_2) + p_2 \zeta^1 \sigma_{10}^{f_1 - 1}. \quad (134)$$

A double root $\sigma_{10} = \sigma_{20} = 1$, when $\sigma_1 = \sigma_2 = \zeta^1 = \zeta^2 = 1$, defines the gel point, which occurs when

$$p_1 p_2 = \frac{1}{(f_1 - 1)(f_2 - 1)}. \quad (135)$$

The physically meaningful roots of eqs (123) and (124) when $\sigma_1 = \sigma_2 = \zeta^1 = \zeta^2 = 1$ are the lowest real positive roots not greater than 1. When at least one of the final values of variables $\sigma_1, \sigma_2, \zeta^1$ or ζ^2 is not 1, the roots must be found by a continuation procedure.

Extinction probabilities can be computed as follows:

$$v_{12} = \frac{\bar{X}_{12}(1, 1)}{L_{12}} = \frac{\Lambda_{20}}{\sigma_{20} A_{20}} \Big|_{\sigma_1 = \sigma_2 = 1} = \sigma_{20}^{f_2 - 1} \Big|_{\sigma_1 = \sigma_2 = 1} \quad (136)$$

$$v_{21} = \frac{\bar{X}_{21}(1, 1)}{L_{21}} = \frac{\Lambda_{10}}{\sigma_{10} A_{10}} \Big|_{\sigma_1 = \sigma_2 = 1} = \sigma_{10}^{f_1 - 1} \Big|_{\sigma_1 = \sigma_2 = 1}. \quad (137)$$

The concentrations of EANJ, EANC and other gel properties related to elastic properties are obtained by computing the distributions \bar{G}^1 and \bar{G}^2 of numbers of end-groups and linking groups around each repeating unit, leading to mass balances

$$k_{12}^{-1} \frac{\partial \bar{G}^1}{\partial t} = \frac{\partial \bar{G}^1}{\partial \log \alpha_1} A_2 \left(\frac{\zeta_{12}}{\alpha_1} - 1 \right) + \frac{\partial \bar{G}^1}{\partial \log \alpha_2} A_1 \left(\frac{\zeta_{21}}{\alpha_2} - 1 \right) \quad (138)$$

$$k_{12}^{-1} \frac{\partial \bar{G}^2}{\partial t} = \frac{\partial \bar{G}^2}{\partial \log \alpha_1} A_2 \left(\frac{\zeta_{12}}{\alpha_1} - 1 \right)$$

$$+ \frac{\partial \bar{G}^2}{\partial \log \alpha_2} A_1 \left(\frac{\zeta_{21}}{\alpha_2} - 1 \right) \quad (139)$$

$$\bar{G}^1|_{t=0} = U^1 \alpha_{10}^{f_1} \quad (140)$$

$$\bar{G}^2|_{t=0} = U^2 \alpha_{20}^{f_2} \quad (141)$$

The characteristics of eqs (138) and (139) are the same, being determined by the system of ordinary differential equations

$$\frac{d \log \alpha_1}{dt} \bigg/ k_{12} = A_2 \left(\frac{\zeta_{12}}{\alpha_1} - 1 \right) \quad (142)$$

$$\frac{d \log \alpha_2}{dt} \bigg/ k_{12} = A_1 \left(\frac{\zeta_{21}}{\alpha_2} - 1 \right) \quad (143)$$

which are easily solved, leading to

$$\alpha_{10} = \zeta_{12} + (1 - p_1)(\alpha_1 - \zeta_{12}) \quad (144)$$

$$\alpha_{20} = \zeta_{21} + (1 - p_2)(\alpha_2 - \zeta_{21}) \quad (145)$$

$$\bar{G}^1(\alpha, \zeta) = U^1 [p_1 \zeta_{12} + (1 - p_1) \alpha_1]^{f_1} \quad (146)$$

$$\bar{G}^2(\alpha, \zeta) = U^2 [p_2 \zeta_{21} + (1 - p_2) \alpha_2]^{f_2} \quad (147)$$

These solutions were not unexpected. They mean that repeating units U^1 are surrounded by A_1 end-groups or L_{12} linking groups, their numbers following a binomial distribution, their total number being f_1 . An analogous result is valid for the units U^2 :

$$G^1 = U^1 p_1^{f_1 - a_1} (1 - p_1)^{a_1} \quad (148)$$

$$G^2 = U^2 p_2^{f_2 - a_2} (1 - p_2)^{a_2} \quad (149)$$

The transforms of concentrations of repeating units linked to prescribed numbers of end-groups and x network chains can be computed according to eq. (61) from the knowledge of \bar{G}^1 , \bar{G}^2 and the extinction probabilities:

$$\bar{T}^1(\alpha, \zeta) = U^1 \{ p_1 [v_{12} + \zeta(1 - v_{12})] + (1 - p_1) \alpha_1 \}^{f_1} \quad (150)$$

$$\bar{T}^2(\alpha, \zeta) = U^2 \{ p_2 [v_{21} + \zeta(1 - v_{21})] + (1 - p_2) \alpha_2 \}^{f_2} \quad (151)$$

Inversion of these transforms leads to the distributions according to the numbers of end-groups and network chains, which are multinomial distributions.

The concentrations of EANJ and EANC are easily computed using eqs (64) and (65) after obtaining the moments $\Gamma_{mn}^{ijkl} \dots$ by differentiating eqs (146) and (147), or, preferably, by using directly definitions (62) and (63):

$$\begin{aligned} \mu_e &= U^1 [1 - \phi_1^{f_1} - p_1 f_1 (1 - v_{12}) \phi_1^{f_1 - 1} \\ &\quad - \frac{1}{2} p_1^2 f_1 (f_1 - 1) (1 - v_{12})^2 \phi_1^{f_1 - 2}] \\ &\quad + U^2 [1 - \phi_2^{f_2} - p_2 f_2 (1 - v_{21}) \phi_2^{f_2 - 1} \\ &\quad - \frac{1}{2} p_2^2 f_2 (f_2 - 1) (1 - v_{21})^2 \phi_2^{f_2 - 2}] \quad (152) \end{aligned}$$

$$\begin{aligned} v_e &= \frac{1}{2} U^1 [p_1 f_1 (1 - v_{12}) (1 - \phi_1^{f_1 - 1}) \\ &\quad - p_1^2 f_1 (f_1 - 1) (1 - v_{12})^2 \phi_1^{f_1 - 2}] \\ &\quad + \frac{1}{2} U^2 [p_2 f_2 (1 - v_{21}) (1 - \phi_2^{f_2 - 1}) \end{aligned}$$

$$- p_2^2 f_2 (f_2 - 1) (1 - v_{21})^2 \phi_2^{f_2 - 2}]. \quad (153)$$

ϕ_1 and ϕ_2 are the fractions of initial end-groups not leading to network chains:

$$\phi_1 = 1 - p_1 + p_1 v_{12} \quad (154)$$

$$\phi_2 = 1 - p_2 + p_2 v_{21}. \quad (155)$$

Prediction of the weight fraction of pendant material w_p requires the simultaneous knowledge of the weight fraction of sol, w_s . This can be done using eq. (9) and evaluating, by integration along the characteristics, the moments with respect to numbers of repeating units λ^1 and λ^2 and with respect to numbers of end-groups λ_1 and λ_2 :

$$\begin{aligned} w_s &= \bar{M}_n^1 \lambda^1 + M_1 \lambda_1 + \bar{M}_n^2 \lambda^2 + M_2 \lambda_2 \\ &= \bar{M}_n^1 U^1 \sigma_{10}^{f_1} |_{\sigma_1 = \sigma_2 = 1} + M_1 A_1 \sigma_{10}^{f_1 - 1} |_{\sigma_1 = \sigma_2 = 1} \\ &\quad + \bar{M}_n^2 U^2 \sigma_{10}^{f_2} |_{\sigma_1 = \sigma_2 = 1} + M_2 A_2 \sigma_{20}^{f_2 - 1} |_{\sigma_1 = \sigma_2 = 1} \\ &= U^1 v_{21} [\bar{M}_n^1 \phi_1 + M_1 f_1 (1 - p_1)] \\ &\quad + U^2 v_{12} [\bar{M}_n^2 \phi_2 + M_2 f_2 (1 - p_2)]. \quad (156) \end{aligned}$$

Use of eq. (64) yields the following expression, allowing w_p to be computed:

$$\begin{aligned} w_s + w_p &= U^1 \{ \bar{M}_n^1 [\phi_1^{f_1} + p_1 f_1 (1 - v_{12}) \phi_1^{f_1 - 1} \\ &\quad + \frac{1}{2} p_1^2 f_1 (f_1 - 1) (1 - v_{12})^2 \phi_1^{f_1 - 2}] \\ &\quad + M_1 f_1 (1 - p_1) [\phi_1^{f_1 - 1} + p_1 (1 - v_{12}) \\ &\quad \times (f_1 - 1) \phi_1^{f_1 - 2} + \frac{1}{2} p_1^2 (f_1 - 1) \\ &\quad \times (f_1 - 2) (1 - v_{12})^2 \phi_1^{f_1 - 3}] \} \\ &\quad + U^2 \{ \bar{M}_n^2 [\phi_2^{f_2} + p_2 f_2 (1 - v_{21}) \phi_2^{f_2 - 1} \\ &\quad + \frac{1}{2} p_2^2 f_2 (f_2 - 1) (1 - v_{21})^2 \phi_2^{f_2 - 2}] \\ &\quad + M_2 f_2 (1 - p_2) [\phi_2^{f_2 - 1} + p_2 (1 - v_{21}) \\ &\quad \times (f_2 - 1) \phi_2^{f_2 - 2} + \frac{1}{2} p_2^2 (f_2 - 1) \\ &\quad \times (f_2 - 2) (1 - v_{21})^2 \phi_2^{f_2 - 3}] \}. \quad (157) \end{aligned}$$

Langley's trapping factor is computed similarly, starting from eq. (65) and taking into account that $T_{eMAX}^* = 1$, which occurs at full conversion of both end-groups, possible only at stoichiometric balance $r = 1$:

$$\begin{aligned} \sqrt{T_e} &= 1 - U^1 \{ \bar{M}_n^1 [\phi_1^{f_1} + p_1 f_1 (1 - v_{12}) \phi_1^{f_1 - 1}] \\ &\quad + M_1 f_1 (1 - p_1) [\phi_1^{f_1 - 1} + p_1 (1 - v_{12}) \\ &\quad \times (f_1 - 1) \phi_1^{f_1 - 2}] \} \\ &\quad - U^2 \{ \bar{M}_n^2 [\phi_2^{f_2} + p_2 f_2 (1 - v_{21}) \phi_2^{f_2 - 1}] \\ &\quad + M_2 f_2 (1 - p_2) [\phi_2^{f_2 - 1} + p_2 (1 - v_{21}) \\ &\quad \times (f_2 - 1) \phi_2^{f_2 - 2}] \}. \quad (158) \end{aligned}$$

These results are identical to earlier predictions using TBP, as it will be shown next. They were quite useful to check the results of the computer program later used for analysing the curing of epoxy resins.

COMPARISON WITH PREDICTIONS OF THEORY OF BRANCHING PROCESSES

Theory of branching processes (TBP), as introduced by Good and Gordon in polymer science (Good, 1962; Gordon, 1962; Gordon and Scantlebury, 1964), defines two probability generating functions for each repeating unit U^M , named $F_0^M(\zeta)$ and $F_1^M(\zeta)$. The former is the vectorial discrete transform of the normalized distribution of numbers of repeating units $U^1 \dots U^N$ linked to a repeating unit U^M in the root of a tree. If the repeating unit U^M is not at the root of a tree, then $F_1^M(\zeta)$ is taken as the vectorial transform of the normalized distribution of the numbers of repeating units $U^1 \dots U^N$ linked to that unit, independently of its position in the tree (this independence is not guaranteed outside the chemical equilibrium, and may invalidate TBP in that case). These two distributions are related through

$$F_1^M(\zeta) = \frac{\sum_{n=1}^N \frac{\partial F_0^M}{\partial \zeta^n}}{\sum_{n=1}^N \frac{\partial F_0^M}{\partial \zeta^n} (1^N)} \quad (159)$$

For instance, in the polycondensation of $U^1(A_1)_1$ and $U^2(A_2)_2$,

$$F_0^1 = (1 - p_1 + p_1 \zeta^2)^{f_1} \quad (160)$$

$$F_1^1 = (1 - p_1 + p_1 \zeta^2)^{f_1 - 1} \quad (161)$$

$$F_0^2 = (1 - p_2 + p_2 \zeta^1)^{f_2} \quad (162)$$

$$F_1^2 = (1 - p_2 + p_2 \zeta^1)^{f_2 - 1} \quad (163)$$

According to TBP, the discrete transform $\bar{W}^M(\zeta)$ of the distribution with respect to numbers of repeating units of trees with a repeating unit U^M in their root is given by

$$\bar{W}^M(\zeta) = \zeta^M F_0^M(v) \quad (164)$$

in which vector v verifies the system of algebraic equations

$$v_i = \zeta^i F_1^i(v) \quad (i = 1, N). \quad (165)$$

These results can be compared with the kinetic approach taking into account the relation between \bar{P} and \bar{W}^M :

$$\bar{W}^M(\zeta) = \frac{\partial \bar{P}}{\partial \log \zeta^M} (1_G, \zeta) / U^M = \Lambda^M(1_G, \zeta) / U^M. \quad (166)$$

In the example of the alternating polycondensation of two monomers,

$$v_1 = \zeta^1 (1 - p_1 + p_1 v_2)^{f_1 - 1} \quad (167)$$

$$v_2 = \zeta^2 (1 - p_2 + p_2 v_1)^{f_2 - 1} \quad (168)$$

$$\bar{W}^1 = \zeta^1 (1 - p_1 + p_1 v_2)^{f_1} \quad (169)$$

$$\bar{W}^2 = \zeta^2 (1 - p_2 + p_2 v_1)^{f_2}. \quad (170)$$

The mathematical equivalence with results of kinetic approach is readily proved, since

$$\sigma_{10}|_{\sigma_i = \sigma_j = 1} = 1 - p_1 + p_1 v_2 \quad (171)$$

$$\sigma_{20}|_{\sigma_i = \sigma_j = 1} = 1 - p_2 + p_2 v_1. \quad (172)$$

Prediction of concentrations of EANJ and EANC or other gel properties through TBP is based on the calculation of extinction probabilities u^M of each repeating unit (not of each linking group). They are defined as the probabilities of a root starting by a certain repeating unit U^M being finite, and so they verify the algebraic equations

$$u^M = F_1^M(u). \quad (173)$$

So, in the case of the alternating polycondensation of two monomers,

$$u^1 = (1 - p_1 + p_1 u^2)^{f_1 - 1} \quad (174)$$

$$u^2 = (1 - p_2 + p_2 u^1)^{f_2 - 1}. \quad (175)$$

It is immediately seen that u^1 and u^2 are equal to the non-zero components of the matrix of extinction probabilities previously computed by the kinetic method through eqs (136) and (137), taking into account the equivalence relations (171) and (172):

$$u^1 = v_{21} \quad (176)$$

$$u^2 = v_{12}. \quad (177)$$

A relation similar to eq. (61) can generally be written for each repeating unit:

$$\bar{T}^M(1_G, \xi) = U^M F_0^M[u + \xi(1^N - u)]. \quad (178)$$

Note that in classical TBP there is no systematic way of taking into account the pendant end-groups in each repeating unit, so as to add their mass when molecular weights or weight fractions are needed. However, in the alternating polycondensation discussed here, one would write eqs (146) and (147) for \bar{G}^1 and \bar{G}^2 using a probabilistic reasoning, and then eqs (156)–(158) for predicting weight fraction of sol, weight fraction of pendant material and Langley's factor would follow. Thus, there is an exact mathematical equivalence between the kinetic approach and the probabilistic description based on TBP, in the case of this alternating polycondensation.

It is also possible to use TBP for predicting gel structure with monomers which may have more than one elastically active junction. In that case, it is necessary to introduce the vectorial discrete transforms of the normalized distributions of numbers of repeating units $U^1 \dots U^N$ directly linked to each junction G^{MJ} , which we will name $F_0^{MJ}(\zeta)$.

The probability that a tree with a junction G^{MJ} at its root does not lead to infinity is $F_0^{MJ}(u)$. So, the generalization of eq. (178) is

$$\begin{aligned} \bar{T}^{MJ}(1_G, \xi) = U^M \rho^{MJ} \prod_{K=1}^{J^M} [F_0^{MK}(u)(1 - \xi) + \xi]^{g^{MK}} \\ \times F_0^{MJ}[u + \xi(1^N - u)]. \end{aligned} \quad (179)$$

If needed, it is possible to predict the dependence of the numbers of end-groups by a probabilistic reasoning and to write expressions for the $\bar{T}^{MJ}(\alpha, \xi)$.

NUMERICAL CASE STUDIES

The practical performance of the mathematical treatment just described was checked by simulating

the cure of a tetraepoxide with a primary diamine, a system of practical importance in the field of composite materials. The same simplified kinetic scheme used by Tsou and Peppas (1988) was chosen, so that the results could be compared with an earlier treatment by TBP.

We took the ratios of kinetic constants of epoxy reaction with secondary and primary amines $k_s/k_p = 0.2$ (a value of 0.5 would correspond to equal reactivity of each hydrogen) and of etherification to addition to primary amines $k_e/k_p = 0.055$, giving a certain character of polyaddition (See Table 3). Molecular weights of monomers were taken as the corresponding values of 4,4'-diaminodiphenylsulphone and tetraglycidyl-4,4'-diaminodiphenylmethane, $M^1 = 248$ and $M^2 = 422$, respectively. $M_i = 0$ for all $i = 1, 5$, since there is no liberation of by-products.

In Fig. 1, the evolution of weight fraction of sol as a function of epoxide conversion is shown, and in Fig. 2 weight-average molecular weight of sol vs epoxide conversion are shown. In both figures, three different values of the initial molar ratio of active hydrogens in amines to epoxide group r were used ($r = 1$ is the value for stoichiometric balance in the absence of etherification).

Newton iteration for computing the curves after gelation converged without problems, except at the end of the reaction, when the concentration of pri-

mary amines becomes virtually nil and this brings about some numerical problems due to round-off.

Results by TBP are shown for comparison purposes in Figs 3 and 4. There are some slight differences relatively to the more correct results of the kinetic treatment in the presence of the etherification reaction, mostly as far as post-gel molecular weights are concerned. It would be difficult to detect these differences experimentally. In the absence of the etherification reaction, the results would be exactly the same for this chemical system [for a further discussion of the differences between the two approaches, see the recent paper by Sarmoria and Miller (1991)].

Of course, TBP breaks down for irreversible polyadditions: it predicts that MWD for a polyaddition without termination is a Schulz-Flory distribution instead of a Poisson's distribution.

Some care is required in order to use our approach for predicting gel structure and its elastic properties, because the monomers contain reasonably long flexible chains and so are not point-like. The diamine monomer U^1 contains $\rho^{11} = 2$ junctions G^{11} of a single kind, which may be identified with the nitrogen atoms. Each of them is initially attached to $f_1^{11} = 1$ primary amine groups A_1 and to no other reactive groups ($f_2^{11} = \dots = f_s^{11} = 0$). The two junctions are linked by an inert chain L^{111} , which can become elastically active, and therefore $g^{111} = 1$ (Fig. 5).

The N, N', N'', N''' tetraglycidyl monomer U^2 is supposed to contain $\rho^{21} = 2$ junctions G^{21} of a single

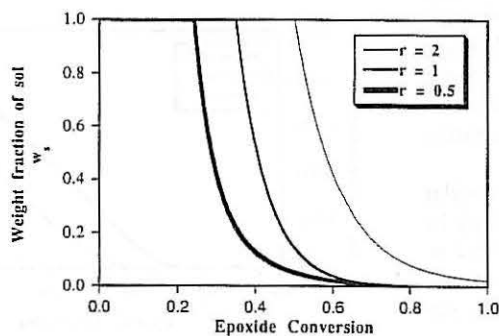


Fig. 1. Weight fraction of sol w_s vs epoxide conversion in the curing of a tetraepoxide by a diamine (kinetic parameters in Table 3) for three different values of initial molar ratio of active hydrogens in amines and to epoxide groups r .

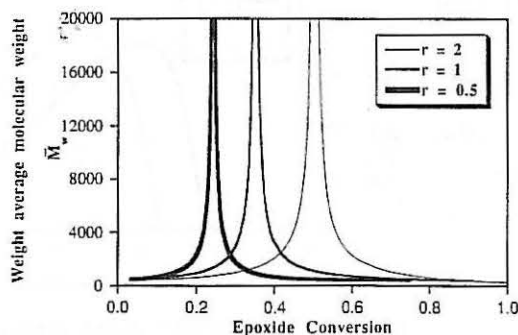


Fig. 2. Weight-average molecular weight of sol \bar{M}_w vs epoxide conversion, for three different values of initial molar ratio of active hydrogens in amines to epoxide groups r .

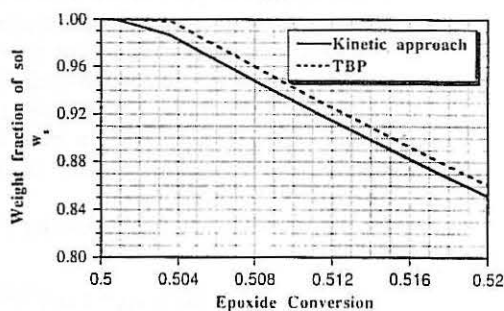


Fig. 3. Comparison between weight fraction of sol w_s as predicted by kinetic approach and by TBP, for the curing of a tetraepoxide with a diamine.

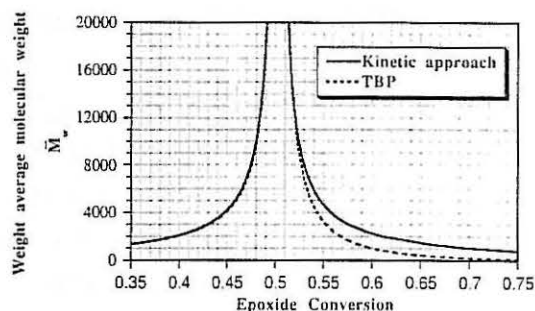


Fig. 4. Comparison between weight-average molecular weight of sol \bar{M}_w as predicted by kinetic approach and by TBP, for the curing of a tetraepoxide with a diamine.

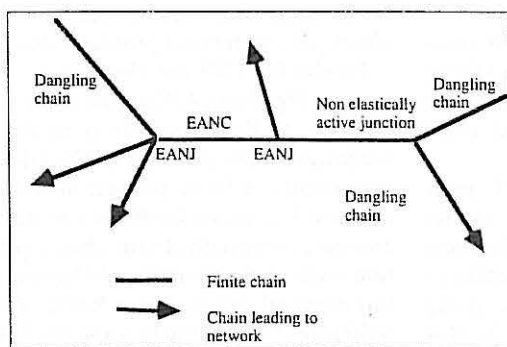


Fig. 5. Elastically active junctions and chains.

kind, which may be identified with the nitrogen atoms. Each of them is initially attached to two epoxide groups A_2 , and so $f_2^{21} = 2$ and to no other reactive groups ($f_1^{21} = f_3^{21} = \dots = f_5^{21} = 0$). The two junctions are linked by an inert chain L^{21} , which can become elastically active, and therefore $g^{211} = 1$.

Tsou and Peppas (1988) presented a slightly different model of the elastic behavior of the tetraepoxide repeating unit. The nitrogen atoms and the two $-CH_2-$ groups attached to



were considered to be independent junctions. Each of them can lead to at most three network chains, when the epoxide group reacts with amines or hydroxyls and the resulting hydroxyl group is also etherified. However, the two pairs of chains of methylene groups between nitrogens and $-CH_2-$ groups are too short for being elastically active. Therefore, their concentration must be subtracted from the overall EANC.

It follows from these structures that molecular weights of each monomer can be evenly shared by each of their two junctions, and so $M^{11} = 248/2 = 124$ and $M^{21} = 422/2 = 211$.

The corresponding predictions by TBP were computed using

$$F_0^1 = [a_p + a_s \zeta^2 + a_t (\zeta^2)^2]^2 \quad (180)$$

$$F_0^2 = [e_0 + e_a \zeta^1 + e_e \zeta^2 + e_e \zeta^1 \zeta^2 + e_{ee} (\zeta^2)^2]^4 \quad (181)$$

$$F_0^{11} = a_p + a_s \zeta^2 + a_t (\zeta^2)^2 \quad (182)$$

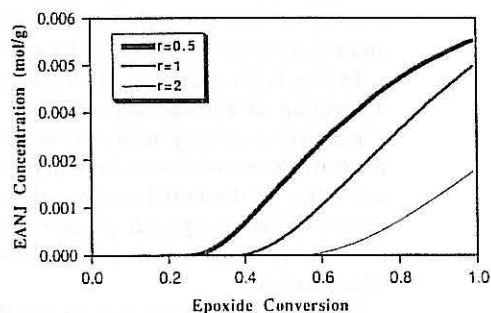
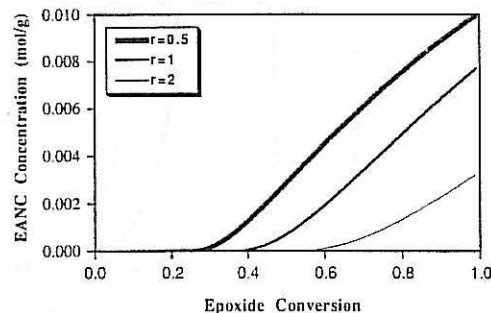
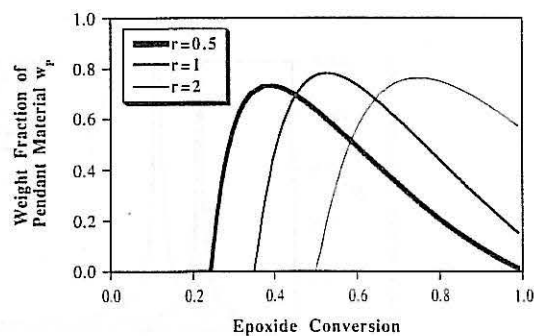
$$F_0^{21} = [e_0 + e_a \zeta^1 + e_e \zeta^2 + e_e \zeta^1 \zeta^2 + e_{ee} (\zeta^2)^2]^2 \quad (183)$$

$$\begin{aligned} \bar{T}^{11}(1_G, \xi) = 2U^1 \{ & [a_p + a_s u^2 + a_t (u^2)^2] (1 - \xi) + \xi \} \\ & \times \{ a_p + a_s [u^2 + \xi(1 - u^2)] \\ & + a_t [u^2 + \xi(1 - u^2)]^2 \} \end{aligned} \quad (184)$$

$$\begin{aligned} \bar{T}^{21}(1_G, \xi) = 2U^2 \{ & [e_0 + e_a u^1 + e_e u^2 + e_e u^1 u^2 \\ & + e_{ee} (u^2)^2] (1 - \xi) + \xi \} \\ & \times \{ e_0 + e_a [u^1 + \xi(1 - u^1)] \\ & + e_e [u^2 + \xi(1 - u^2)] \\ & + e_e [u^1 + \xi(1 - u^1)] [u^2 + \xi(1 - u^2)] \\ & + e_{ee} [u^2 + \xi(1 - u^2)]^2 \}^2. \end{aligned} \quad (185)$$

In these expressions, variables a_p , a_s and a_t are, respectively, concentrations of primary, secondary and tertiary amines, normalized by initial primary amine concentration. e_0 , e_a , e_e and e_{ee} are, respectively, concentrations of unreacted epoxides, epoxides which have reacted with an amine and epoxides which have reacted with one and two epoxide groups, normalized by initial epoxide concentration. They are computed as functions of primary amine conversion according to Tsou and Peppas (1988).

In Figs 6–8, the predicted changes of concentrations of EANJ, EANC and weight fraction of pendant materials vs epoxide conversion are shown.

Fig. 6. EANJ vs epoxide conversion for three different values of molar ratio of active hydrogens in amines to epoxide groups r , for the curing of a tetraepoxide with a diamine.Fig. 7. EANC vs epoxide conversion for three different values of molar ratio of active hydrogens in amines to epoxide groups r , for the curing of a tetraepoxide with a diamine.Fig. 8. Weight fraction of pendant material vs epoxide conversion for three different values of molar ratio of active hydrogens in amines to epoxide groups r , for the curing of a tetraepoxide with a diamine.

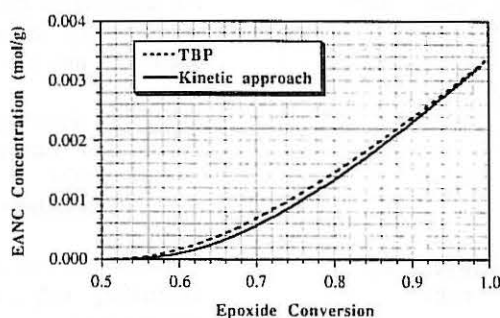


Fig. 9. Comparison between EANC as predicted by kinetic approach and by TBP, for the curing of a tetraepoxide with a diamine ($r = 2$).

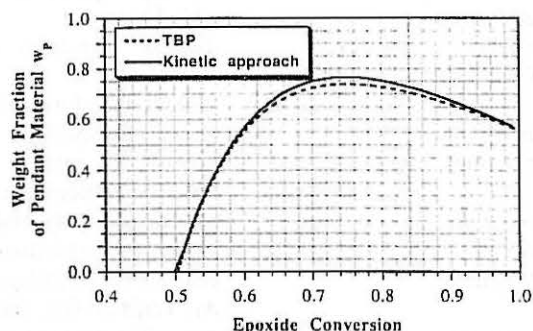


Fig. 10. Comparison between weight fraction of pendant material as predicted by kinetic approach and by TBP, for the curing of a tetraepoxide with a diamine ($r = 2$).

A comparison with results obtained through the use of TBP and of kinetic approach is shown in Figs 9 and 10. Numerical differences between the predictions of the kinetic approach and TBP are small for this chemical system, as for the weight-average molecular weight and fraction of sol. It would be necessary to have a much greater relative importance of the polyetherification of epoxides with hydroxyls to find larger errors in TBP predictions.

CONCLUSIONS

This work has removed the main drawbacks preventing the kinetic approach to have a more widespread use in polymer science and engineering when dealing with non-linear polymerizations: prediction of gel properties became possible and the whole treatment is free from the need of an analytical solution to the mass balance equations of polymer species and pseudo-species, making possible the analysis of complex chemical systems.

A radically different description of molecular structure is needed in order to compute properties of sol, such as average gyration radius and light-scattering properties, which can only be done, for the moment, using TBP (Burchard, 1982). The same problem arises in the modelling of reversible copolymerization systems.

Computations taking into account loop formation (a limited number of small loops) still need to be tried.

It cannot be assessed for the moment whether the increase in complexity coming from the expected large number of pseudo-repeating units and reactive groups can lead to reasonable computing times, and nothing is known from the comparative performance of Monte-Carlo methods.

Also, some automatic means of defining molecular fragments and computing stoichiometric coefficients taking account of intramolecular reactions seems important, in order to allow a realistic modelling of most polycondensation reactions and non-linear radical polymerizations.

There still remains a huge amount of work to be done in the modelling of complex radical polymerizations using the approach just described, although no insurmountable obstacles are likely to exist.

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NOTATION

| | |
|---|--|
| \mathbf{a} | vector of numbers of end-groups |
| a_i | number of end-groups A_i |
| a_p | mole concentration of primary amines, normalized by initial primary amine concentration |
| a_s | mole concentration of secondary amines, normalized by initial primary amine concentration |
| a_t | mole concentration of tertiary amines, normalized by initial primary amine concentration |
| A_i | mole concentration of end-groups A_i ($i = 1, G$) |
| e_0 | mole concentration of unreacted epoxides, normalized by initial epoxide concentration |
| e_a | mole concentration of epoxides which have reacted with one amine, normalized by initial epoxide concentration |
| e_e | mole concentration of epoxides which have reacted with one epoxide, normalized by initial epoxide concentration |
| e_{ee} | mole concentration of epoxides which have reacted with two epoxide groups, normalized by initial epoxide concentration |
| f_i^m | number of end-groups A_i in monomer m |
| f_i^{MJ} | number of end-groups A_i attached to junction G^{MJ} in monomer M |
| $F(t, \sigma_1, \dots, \sigma_G, \bar{P}, \Lambda_1, \dots, \Lambda_G)$ | right-hand side of eq. (20) |
| $F_0^M(\zeta)$ | link probability generating function of repeating units U^M in the root of a tree |

| | | | |
|-----------------------------|--|--------------------------|---|
| $F_1^M(\zeta)$ | link probability generating function of repeating units U^M not in the root of a tree | \bar{M}_n^{MJ} | number-average molecular weight allocated to junction G^{MJ} |
| g^{MJK} | number of G^{MK} junctions attached to G^{MJ} junction | n | vector of numbers of repeating units |
| G | number of reactive groups | n^i | number of repeating units U^i |
| G_e | small-strain equilibrium shear modulus | N | number of different kinds of repeating units |
| G_{Ne}^0 | small-strain equilibrium shear modulus of uncrosslinked polymer | p | parameter in Schulz-Flory's distribution |
| $G^{MJ}(a, l)$ | mole concentration of units $G^{MJ}(a, l)$ | p_i | conversion of end-group A_i in an alternating polycondensation of two monomers |
| h | empirical parameter used for describing networks with an intermediate behavior between affine and phantom networks | $P(a, n)$ | mole concentration of the set of polymer molecules $P(a, n)$, containing n repeating units and a end-groups of the several possible kinds |
| $H^{MJ}, H^{MJ'}, H^{MJ''}$ | auxiliary functions defined by eqs (69), (70) and (71), respectively | $\bar{P}(\sigma, \zeta)$ | discrete transform of polymer VNMND |
| I^{MJ} | auxiliary function defined by eq. (72) | $\bar{P}(\mu)$ | discrete transform of the NMWD of polymer species |
| j | integer variable going from 0 to ∞ , used for enumerating a set of entities of some kind | Q | volume flow rate |
| J^M | number of distinguishable junctions in repeating unit M | r | initial stoichiometric ratio in an alternating polycondensation of two monomers (ratio of initial concentrations of end-groups A_2 and A_1 , respectively), such as in the case of epoxy resin curing |
| J | average number of repeating units in a Poisson distribution | R | ideal gas constant |
| k_{ij} | bimolecular pseudo-rate constant of the reaction between end-groups A_i and A_j forming a link between the repeating units carrying them | R_j | rate of formation by chemical reaction of j th species |
| k_{ij}^0, k'_{ij} | bimolecular and termolecular (catalysis by hydroxyl groups) rate constants of the reactions between reactive groups A_i and A_j in the kinetic scheme of the cure of an epoxy resin by a diamine | R_V | relative rate of change of volume caused by chemical reaction |
| k_i^* | unimolecular pseudo-rate constant of a reaction of end group A_i that does not form a link between repeating units | S_{kl} | component of the Jacobian of σ_k , as defined by eq. (34) |
| l | vector of numbers of linking groups | S_l^k | auxiliary variables used for computing matrix $[S_{kl}]$, as defined by eq. (35) |
| L_{ij} | mole concentration of linking groups L_{ij} | T | absolute temperature |
| L^{MIJ} | mole concentration of linking groups between junctions L^{MIJ} | T_e | Langley's trapping factor for chain entanglements |
| $M(j)$ | relative molecular mass of j th species | T_e^* | nonnormalized Langley's trapping factor |
| M^{mj} | molecular weight of the repeating unit U^{mj} belonging to monomer class U^m | T_{eMAX}^* | maximum value of nonnormalized Langley's trapping factor |
| \bar{M}_n | number-average molecular weight | $T^{MJ}(a, x)$ | mole concentration of G^{MJ} junctions connected to a end-groups and x network chains |
| \bar{M}_w | weight-average molecular weight | u | vector of the extinction probabilities of repeating units (see below) |
| \bar{M}_z | z -average molecular weight | u^M | extinction probability of repeating unit U^M , i.e. probability that a rooted tree beginning by such an unit is finite |
| M_i | loss of molecular weight of a polymer molecule when one of its end-groups A_i reacts; this loss is supposed to be independent of the nature of this latter reaction | U^n | mole concentration of repeating units U^n ($n = 1, N$) |
| | | v_{ij} | extinction probability of chains starting in a linking unit L_{ij} in the direction going from the repeating unit previously carrying group A_i to the one previously carrying |

| | | | |
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| | end-group A_i ; it is the fraction of those chains which do not go to infinity | μ | Laplace parameter of discrete transform of molecular weight distributions |
| v^{MJK} | extinction probability of chains starting in a junction G^{MJ} towards a junction G^{MK} ; it is the fraction of those chains which do not go to infinity | μ_e | concentration of elastically effective network junctions (EANJ) |
| | | v_e | concentration of elastically effective network chains (EANC) |
| V | reaction volume | v_{ijk} | number of A_k end-groups formed by reaction of end-group A_i with A_j , which are linked to the repeating unit to which A_i is attached |
| w | weight fraction | | vector of the v_{ij}^* , with $j = 1, G$ (see below) |
| w_p | weight fraction of pendant material | v_i^* | number of A_i end-groups formed by a reaction of end group A_i not leading to an intermolecular link |
| w_s | weight fraction of sol | v_{ij}^* | Laplace parameter associated with number of network chains x |
| W_{ij} | change of volume by reaction of 1 mole of end-groups A_i and A_j | ξ | number of G^{MJ} junctions in repeating unit U^M |
| W_i^* | change of volume by reaction of 1 mole of end-group A_i by a reaction not forming links | ρ^{MJ} | vector of Laplace parameters of the vectorial discrete transform associated with vector a of the numbers of reactive groups of polymer species |
| $\bar{W}^M(\zeta)$ | discrete transform of the distribution with respect to numbers of repeating units of trees with a repeating unit U^M in their root | σ | i th component of vector σ |
| x | number of network chains | σ_i | space time (ratio of reactor volume by inlet volume flow rate) |
| $X_{ij}(a)$ | mole concentration of dangling chains attached to a end-groups, $X_{ij}(a)$ | τ | vector of N auxiliary Laplace parameters used in TBP |
| $X^{MJ}(a)$ | mole concentration of dangling chains attached to a end-groups, $X^{MU}(a)$ | ν | i th component of the vector of auxiliary Laplace parameters ν |
| Z_{kl} | component of the Jacobian of α_k , ($= \partial \log \alpha_k / \partial \log x_{l0}$) as defined by eq. (96) | ν_i | fractions of initial end-groups A_1 and A_2 not leading to network chains |
| $1_G, 1^N$ | vectors with all their G or N components equal to 1 | ϕ_1, ϕ_2 | matrix of the ω_{ijk} , with $k = 1, G$ (see below) |
| 1_{GG} | matrix G by G with all components equal to 1 | ω_{ij} | number of A_k end-groups formed by reaction of end group A_i and A_j in both repeating units they are attached to |
| Greek letters | | ω_{ijk} | mole fraction of subspecies U^{mj} relative to the overall number of repeating units U^m |
| α | vector of Laplace parameters of discrete transform of distributions of concentrations of junctions $G^{MJ}(a, l)$ with respect to their numbers of end-groups a | Ω^{mj} | |
| α_i | i th component of vector α | | |
| $\Gamma_{mn}^{MJijkl\dots}$ | partial derivative of G^{MJ} with respect to $\zeta_{ij}, \zeta_{kl}, \dots$ and $\sigma_m, \sigma_n, \dots$ | Subscripts | |
| ζ | vector of Laplace parameters of the vectorial discrete transform associated with vectors with vector of numbers of repeating units n or numbers of linking groups l | F | feed |
| ζ^i | i th component of vector ζ | g | gel |
| $\lambda_{ijk}^{mnp\dots}$ | moment of NMND of polymer species of order 1 with respect to the numbers of end-groups a_i, a_j, a_k, \dots and of repeating units n^m, n^n, n^p, \dots | s | sol |
| λ_{M_i} | i th order moment of NMWD of polymer species | MAX | upper limit |
| $\Lambda_{ijk}^{mnp\dots}$ | partial derivative of \bar{P} with respect to $\sigma_i, \sigma_j, \sigma_k, \dots$ and $\zeta^m, \zeta^n, \zeta^p, \dots$ | 0 | initial |
| | | Superscripts | |
| | | I, II | labels of the alternative sets of apparent rate constants and stoichiometric coefficients |
| | | — | discrete transform |
| | | Abbreviations | |
| | | A_i | reactive group of i th kind |
| | | EANC | elastically active network chain |

| | |
|----------------|---|
| EANJ | elastically active network junction |
| G^{MJ} | junction in repeating unit U^M |
| $G^{MJ}(a, l)$ | junction G^{MJ} which is attached to a end-groups and l linking groups |
| L_{ij} | group that links two repeating units, formed by reaction of end-groups A_i and A_j |
| L^{MJK} | chain linking G^{MJ} and G^{MK} |
| MWD | molecular weight distribution |
| NMWD | number molecular weight distribution |
| $P(a, n)$ | set of polymer molecules with n repeating units and a end-groups |
| TBP | theory of branching processes |
| U^m | repeating unit of class m |
| U^{mj} | repeating sub-unit of j th kind included in class U^m |
| VNMND | vectorial number molecular distribution of numbers of end-groups and repeating units, obtained from function $P(a, n)$ |
| $X_{ij}(a)$ | dangling chain starting at a linking-group L_{ij} , going towards the repeating unit previously carrying end-group A_j and terminated by a end-groups |
| $X^{MJ}(a)$ | dangling chain starting at a linking-group between junctions L^{MJ} , going towards junction G^{MJ} and terminated by a end-groups |

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- weights M^{m0}, M^{m1}, \dots , is given by
- $$M[\mathbf{P}(\mathbf{a}, \mathbf{n})] = \sum_{m=1}^N \sum_{k=0}^{\infty} M^{mk} n^{mk} + \sum_{i=1}^G M_i a_i. \quad (\text{A1})$$
- The discrete transform of polymer molecular weight distribution is the function
- $$\bar{P}(\mu) = \sum_{j=0}^{\infty} \mu^{M(j)} P_j. \quad (\text{A2})$$
- The index j sweeps all kinds of molecules. Taking into account (A1), this becomes
- $$\begin{aligned} \bar{P}(\mu) = & \sum_{n^{10}=0}^{\infty} \sum_{n^{11}=0}^{\infty} \mu^{n^{10}M^{10} + n^{11}M^{11} + \dots} \dots \sum_{n^{N0}=0}^{\infty} \sum_{n^{N1}=0}^{\infty} \\ & \dots \mu^{n^{N0}M^{N0} + n^{N1}M^{N1} + \dots} \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} \mu^{a_1M_1 + \dots + a_GM_G} P \\ & \times (a_1, \dots, a_G, n^{10}, n^{11}, \dots, n^{N0}, n^{N1}, \dots). \end{aligned} \quad (\text{A3})$$
- Since the probabilities of occurrence of specified vectors of numbers of subclasses of each repeating unit follow multinomial distributions, the mole concentration of polymer with given numbers of end-groups a_1, \dots, a_G and of classes of repeating units $n^{10}, n^{11}, \dots, n^{N0}, \dots$ is given by
- $$\begin{aligned} P(a_1, \dots, a_G, n^{10}, n^{11}, \dots, n^{N0}, \dots) \\ = & \binom{n^1}{n^{10} n^{11} n^{12} \dots} \dots \binom{n^N}{n^{N0} n^{N1} n^{N2} \dots} \\ & \times (\Omega^{10})^{n^{10}} (\Omega^{11})^{n^{11}} \dots (\Omega^{N0})^{n^{N0}} (\Omega^{N1})^{n^{N1}} \\ & \dots P(a_1, \dots, a_G, n^1, n^2, \dots, n^N). \end{aligned} \quad (\text{A4})$$
- Equation (2) is now obtained by substitution of eq. (A4) into eq. (A3), with simplification of the powers of n^1, n^2, \dots, n^N :
- $$\begin{aligned} \bar{P}(\mu) = & \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} \mu^{a_1M_1 + \dots + a_GM_G} \sum_{n^1=0}^{\infty} \\ & \dots \sum_{n^N=0}^{\infty} P(a_1, \dots, a_G, n^1, n^2, \dots, n^N) \\ & \times \sum_{n^{10}=0}^{\infty} \sum_{n^{11}=0}^{\infty} \dots (\mu^{M^{10}} \Omega^{10})^{n^{10}} (\mu^{M^{11}} \Omega^{11})^{n^{11}} \\ & \dots \binom{n^1}{n^{10} n^{11} n^{12} \dots} \dots \sum_{n^{N0}=0}^{\infty} \sum_{n^{N1}=0}^{\infty} (\mu^{M^{N0}} \Omega^{N0})^{n^{N0}} \\ & \times (\mu^{M^{N1}} \Omega^{N1})^{n^{N1}} \dots \binom{n^N}{n^{N0} n^{N1} n^{N2} \dots} \\ = & \sum_{a_1=0}^{\infty} \dots \sum_{a_G=0}^{\infty} \mu^{a_1M_1 + \dots + a_GM_G} \sum_{n^1=0}^{\infty} \\ & \times (\mu^{M^{10}} \Omega^{10} + \mu^{M^{11}} \Omega^{11} + \dots)^{n^1} \\ & \dots \sum_{n^N=0}^{\infty} (\mu^{M^{N0}} \Omega^{N0} + \mu^{M^{N1}} \Omega^{N1} + \dots)^{n^N} \\ & \times P(a_1, \dots, a_G, n^1, n^2, \dots, n^N) \\ = & \bar{P}(\mu^{M_1}, \dots, \mu^{M_G}, \mu^{M^{10}} \Omega^{10} + \mu^{M^{11}} \Omega^{11} \\ & + \dots, \mu^{M^{N0}} \Omega^{N0} + \mu^{M^{N1}} \Omega^{N1} + \dots) \\ = & \bar{P}[\mu^{M_1}, \dots, \mu^{M_G}, \bar{\Omega}^1(\mu), \dots, \bar{\Omega}^N(\mu)] \end{aligned} \quad (\text{A5})$$
- in which
- $$\bar{\Omega}^m(\mu) = \mu^{M^{m0}} \Omega^{m0} + \mu^{M^{m1}} \Omega^{m1} + \dots = \sum_{j=0}^{\infty} \mu^{M^{mj}} \Omega^{mj}. \quad (\text{A6})$$

APPENDIX A: RELATION BETWEEN DISCRETE TRANSFORMS OF MOLECULAR WEIGHT DISTRIBUTION AND OF NUMBER MOLECULAR WEIGHT DISTRIBUTION

The molecular weight $M[\mathbf{P}(\mathbf{a}, \mathbf{n})]$ of a molecule $\mathbf{P}(\mathbf{a}, \mathbf{n})$ containing (n^{m0}, n^{m1}, \dots) repeating units of subclasses U^{m0}, U^{m1}, \dots , of repeating units U^m , with molecular

APPENDIX B: KINETIC SCHEME AND STOICHIOMETRIC COEFFICIENTS IN THE RADICAL COPOLYMERIZATION OF N VINYL COMPOUNDS

Tables 5-12 summarize the description of a radical copolymerization of an arbitrary number of monomers, ac-

Table 5. Description of reactive groups

| Group A_i | Description | Index i |
|-------------|---|----------------|
| B_k | Monomer, containing f_k double bonds | k |
| C_k | Set of f_k double bonds in a repeating unit coming from a monomer which has undergone a transfer reaction | $k + N$ |
| D_k | Pendant double bond coming from B_k | $k + 2N$ |
| E_k | Intact polymerized fragment coming from monomer | $k + 3N$ |
| R_{0k}^1 | Radical formed by addition of a primary radical to B_k | $k + 4N$ |
| R_{0k}^2 | Radical formed by transfer to monomer B_k | $k + 5N$ |
| R_{0k}^3 | Radical site formed by transfer to polymer in a site E_k | $k + 6N$ |
| R_{kl}^1 | Radical ending by units coming from B_k and B_l | $(k + 6)N + l$ |
| I | Initiator | $N^2 + 7N + 1$ |
| I^* | Primary radical | $N^2 + 7N + 2$ |
| S | Solvent or chainlength regulator | $N^2 + 7N + 3$ |

Table 6. Stoichiometry of initiation reactions

| Reaction | i | k_i^* | \bar{v}_i^* |
|---|----------------|-----------------------------|---|
| $I \rightarrow I^*$ | $N^2 + 7N + 1$ | $2\phi k_d$ | $\frac{\sigma_{i+1}}{\sigma_i}$ |
| $I^* + B_k \rightarrow R_{0k}^1 + (f_k - 1)D_k$ | $N^2 + 7N + 2$ | $f_k k_{p1}^0 A_k$ | $\frac{1}{\sigma_i}$ |
| $I^* + C_k \rightarrow R_{0k}^1 + (f_k - 1)D_k$ | $N^2 + 7N + 2$ | $f_k k_{p1}^0 A_k$ | $\frac{1}{\sigma_i}$ |
| $I^* + D_k \rightarrow R_{0k}^1$ | $N^2 + 7N + 2$ | $k_{p1}^1 A_k + 4N$ | $\frac{1}{\sigma_i}$ |
| $B_k + I^* \rightarrow R_{0k}^1 + (f_k - 1)D_k$ | k | $f_k k_{p1}^0 A_{N^2+7N+2}$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{i+4N}}{\sigma_i}$ |
| $C_k + I^* \rightarrow R_{0k}^1 + (f_k - 1)D_k$ | $k + N$ | $f_k k_{p1}^0 A_{N^2+7N+2}$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{i+4N}}{\sigma_i}$ |
| $D_k + I^* \rightarrow R_{0k}^1$ | $k + 2N$ | $k_{p1}^1 A_{N^2+7N+2}$ | $\frac{\sigma_{i+4N}}{\sigma_i}$ |

Table 7. Stoichiometry of propagation reactions

| Reaction | i | j | k_{ij} | \bar{v}_{ij} | \bar{v}_{ji} |
|--|----------|----------------|-----------------|---|----------------------------------|
| $B_k + R_{lm}^1 \rightarrow (f_k - 1)D_k + R_{mk}^1 + E_m$ | k | $(l + 6)N + m$ | $f_k k_{p1m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+3N}}{\sigma_j}$ |
| $B_k + R_{0m}^1 \rightarrow (f_k - 1)D_k + R_{mk}^1 + E_m$ | k | $m + 4N$ | $f_k k_{p0m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+3N}}{\sigma_j}$ |
| $B_k + R_{0m}^2 \rightarrow (f_k - 1)D_k + R_{mk}^1 + C_m$ | k | $m + 5N$ | $f_k k_{p0m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+N}}{\sigma_j}$ |
| $B_k + R_{0m}^3 \rightarrow (f_k - 1)D_k + R_{mk}^1 + E_m$ | k | $m + 6N$ | $f_k k_{p0m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $C_k + R_{lm}^1 \rightarrow (f_k - 1)D_k + R_{mk}^1 + E_m$ | $k + N$ | $(l + 6)N + m$ | $f_k k_{p1m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+3N}}{\sigma_j}$ |
| $C_k + R_{0m}^1 \rightarrow (f_k - 1)D_k + R_{mk}^1 + E_m$ | $k + N$ | $m + 4N$ | $f_k k_{p0m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+3N}}{\sigma_j}$ |
| $C_k + R_{0m}^2 \rightarrow (f_k - 1)D_k + R_{mk}^1 + C_m$ | $k + N$ | $m + 5N$ | $f_k k_{p0m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+N}}{\sigma_j}$ |
| $C_k + R_{0m}^3 \rightarrow (f_k - 1)D_k + R_{mk}^1$ | $k + N$ | $m + 6N$ | $f_k k_{p0m}^1$ | $\frac{\sigma_{i+1}^{f_{i-1}} \sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $D_k + R_{lm}^1 \rightarrow R_{mk}^1 + E_m$ | $k + 2N$ | $(l + 6)N + m$ | k_{p0m}^2 | $\frac{\sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+3N}}{\sigma_j}$ |
| $D_k + R_{0m}^1 \rightarrow R_{mk}^1 + E_m$ | $k + 2N$ | $m + 4N$ | k_{p0m}^2 | $\frac{\sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+3N}}{\sigma_j}$ |
| $D_k + R_{0m}^2 \rightarrow R_{mk}^1 + C_m$ | $k + 2N$ | $m + 5N$ | k_{p0m}^2 | $\frac{\sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{\sigma_{m+N}}{\sigma_j}$ |
| $D_k + R_{0m}^3 \rightarrow R_{mk}^1$ | $k + 2N$ | $m + 6N$ | k_{p0m}^2 | $\frac{\sigma_{(m+6)N+k}}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |

Table 8. Stoichiometry of terminations by combination

| Reaction | <i>i</i> | <i>j</i> | k_{ij} | \bar{v}_{ij} | \bar{v}_{ji} |
|---|--------------|--------------|--------------------|----------------------|----------------------|
| $R_{kl}^1 + R_{mn}^1 \rightarrow \text{products}$ | $(k+6)N + l$ | $(m+6)N + n$ | $k_{t_{kmn}}^{11}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{kl}^1 + R_{0m}^1 \rightarrow \text{products}$ | $(k+6)N + l$ | $m + 4N$ | $k_{t_{cm}}^{11}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{kl}^1 + R_{0m}^2 \rightarrow \text{products}$ | $(k+6)N + l$ | $m + 5N$ | $k_{t_{cm}}^{12}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{kl}^1 + R_{0m}^3 \rightarrow \text{products}$ | $(k+6)N + l$ | $m + 6N$ | $k_{t_{cm}}^{13}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{0m}^1 + R_{0n}^1 \rightarrow \text{products}$ | $m + 4N$ | $n + 4N$ | $k_{t_{mn}}^{11}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{0m}^1 + R_{0n}^2 \rightarrow \text{products}$ | $m + 4N$ | $n + 5N$ | $k_{t_{mn}}^{12}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{0m}^1 + R_{0n}^3 \rightarrow \text{products}$ | $m + 4N$ | $n + 6N$ | $k_{t_{mn}}^{13}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{0m}^2 + R_{0n}^2 \rightarrow \text{products}$ | $m + 5N$ | $n + 5N$ | $k_{t_{mn}}^{22}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{0m}^2 + R_{0n}^3 \rightarrow \text{products}$ | $m + 5N$ | $n + 6N$ | $k_{t_{mn}}^{23}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |
| $R_{0m}^3 + R_{0n}^3 \rightarrow \text{products}$ | $m + 6N$ | $n + 6N$ | $k_{t_{mn}}^{33}$ | $\frac{1}{\sigma_i}$ | $\frac{1}{\sigma_j}$ |

Table 9. Stoichiometry of terminations by dismutation

| Reaction | <i>i</i> | k_i^* | \bar{v}_i^* |
|---|--------------|----------------------------------|----------------------|
| $R_{kl}^1 + R_{mn}^1 \rightarrow \text{products}$ | $(k+6)N + l$ | $k_{id_{kmn}}^{11} A_{(m+6)N+n}$ | $\frac{1}{\sigma_i}$ |
| $R_{kl}^1 + R_{0m}^1 \rightarrow \text{products}$ | $(k+6)N + l$ | $k_{id_{cm}}^{11} A_{m+4N}$ | $\frac{1}{\sigma_i}$ |
| $R_{kl}^1 + R_{0m}^2 \rightarrow \text{products}$ | $(k+6)N + l$ | $k_{id_{cm}}^{12} A_{m+5N}$ | $\frac{1}{\sigma_i}$ |
| $R_{kl}^1 + R_{0m}^3 \rightarrow \text{products}$ | $(k+6)N + l$ | $k_{id_{cm}}^{13} A_{m+6N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0m}^1 + R_{0n}^1 \rightarrow \text{products}$ | $m + 4N$ | $k_{id_{mn}}^{11} A_{m+4N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0m}^1 + R_{0n}^2 \rightarrow \text{products}$ | $m + 4N$ | $k_{id_{mn}}^{12} A_{m+5N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0m}^1 + R_{0n}^3 \rightarrow \text{products}$ | $m + 4N$ | $k_{id_{mn}}^{13} A_{m+6N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0m}^2 + R_{0n}^2 \rightarrow \text{products}$ | $m + 5N$ | $k_{id_{mn}}^{22} A_{m+5N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0m}^2 + R_{0n}^3 \rightarrow \text{products}$ | $m + 5N$ | $k_{id_{mn}}^{23} A_{m+6N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0m}^3 + R_{0n}^3 \rightarrow \text{products}$ | $m + 6N$ | $k_{id_{mn}}^{33} A_{m+6N}$ | $\frac{1}{\sigma_i}$ |

cording to the general approach developed in the body of this paper. The following assumptions were used:

(a) Chemical initiation by a single monofunctional initiator I ;

(b) Equal reactivity of all double bonds in each monomer, changing as soon as one of these bonds has reacted, but not changing reactivity any further—this is needed for describing reactions of monovinyl and divinyl compounds;

(c) No primary radical termination and no transfer to the initiator;

(d) Dependence of propagation rate constants on the chemical nature of the *two* units in the chain end;

(e) Dependence of termination and transfer rate constants on the chemical nature of the *last* units in the chain end;

These assumptions can easily be relaxed in order to accommodate more complex reaction schemes, provided that no

Table 10. Stoichiometry of transfers to monomers

| Reaction | <i>i</i> | k_i^* | \bar{v}_i^* |
|--|--------------|-----------------------------|----------------------------------|
| $B_k + R_{lm}^1 \rightarrow R_{0k}^2$ | <i>k</i> | $k_{M_{lm}}^1 A_{(m+6)N+n}$ | $\frac{\sigma_i + 5N}{\sigma_i}$ |
| $B_k + R_{0m}^1 \rightarrow R_{0k}^2$ | <i>k</i> | $k_{M_{0m}}^1 A_{m+4N}$ | $\frac{\sigma_i + 5N}{\sigma_i}$ |
| $B_k + R_{0m}^2 \rightarrow R_{0k}^2$ | <i>k</i> | $k_{M_{0m}}^2 A_{m+5N}$ | $\frac{\sigma_i + 5N}{\sigma_i}$ |
| $B_k + R_{0m}^3 \rightarrow R_{0k}^2$ | <i>k</i> | $k_{M_{0m}}^3 A_{m+6N}$ | $\frac{\sigma_i + 5N}{\sigma_i}$ |
| $R_{kl}^1 + B_m \rightarrow \text{products}$ | $(k+6)N + l$ | $k_{M_{lm}}^1 A_m$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^1 + B_m \rightarrow \text{products}$ | $k + 4N$ | $k_{M_{lm}}^1 A_m$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^2 + B_m \rightarrow \text{products}$ | $k + 5N$ | $k_{M_{lm}}^2 A_m$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^3 + B_m \rightarrow \text{products}$ | $k + 6N$ | $k_{M_{lm}}^3 A_m$ | $\frac{1}{\sigma_i}$ |

Table 11. Transfers to polymer

| Reaction | <i>i</i> | k_i^* | \bar{v}_i^* |
|--|--------------|-----------------------------|----------------------------------|
| $E_k + R_{lm}^1 \rightarrow R_{0k}^3$ | $k + 3N$ | $k_{P_{lm}}^1 A_{(l+6)N+m}$ | $\frac{\sigma_i + 3N}{\sigma_i}$ |
| $E_k + R_{0m}^1 \rightarrow R_{0k}^3$ | $k + 3N$ | $k_{P_{0m}}^1 A_{m+4N}$ | $\frac{\sigma_i + 3N}{\sigma_i}$ |
| $E_k + R_{0m}^2 \rightarrow R_{0k}^3$ | $k + 3N$ | $k_{P_{0m}}^2 A_{m+5N}$ | $\frac{\sigma_i + 3N}{\sigma_i}$ |
| $E_k + R_{0m}^3 \rightarrow R_{0k}^3$ | $k + 3N$ | $k_{P_{0m}}^3 A_{m+6N}$ | $\frac{\sigma_i + 3N}{\sigma_i}$ |
| $R_{kl}^1 + E_m \rightarrow \text{products}$ | $(k+6)N + l$ | $k_{P_{lm}}^1 A_{m+3N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^1 + E_m \rightarrow \text{products}$ | $k + 4N$ | $k_{P_{lm}}^1 A_{m+3N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^2 + E_m \rightarrow \text{products}$ | $k + 5N$ | $k_{P_{lm}}^2 A_{m+3N}$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^3 + E_m \rightarrow \text{products}$ | $k + 6N$ | $k_{P_{lm}}^3 A_{m+3N}$ | $\frac{1}{\sigma_i}$ |

Table 12. Transfers to solvent

| Reaction | <i>i</i> | k_i^* | \bar{v}_i^* |
|--------------------------------|----------------|---------------|----------------------|
| $R_{kl}^1 + S \rightarrow I^*$ | $(k+6)N + l$ | $k_{S_i}^1 S$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^1 + S \rightarrow I^*$ | $k + 4N$ | $k_{S_i}^1 S$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^2 + S \rightarrow I^*$ | $k + 5N$ | $k_{S_i}^2 S$ | $\frac{1}{\sigma_i}$ |
| $R_{0k}^3 + S \rightarrow I^*$ | $k + 6N$ | $k_{S_i}^3 S$ | $\frac{1}{\sigma_i}$ |
| $R_{kl}^1 + S \rightarrow I^*$ | $N^2 + 7N + 2$ | $k_{S_i}^1 S$ | σ_i |
| $R_{0k}^1 + S \rightarrow I^*$ | $N^2 + 7N + 2$ | $k_{S_i}^1 S$ | σ_i |
| $R_{0k}^2 + S \rightarrow I^*$ | $N^2 + 7N + 2$ | $k_{S_i}^2 S$ | σ_i |
| $R_{0k}^3 + S \rightarrow I^*$ | $N^2 + 7N + 2$ | $k_{S_i}^3 S$ | σ_i |

molecular break-up occurs in the middle of a chain (such as β -scission of radicals).

There was no attempt to follow the number of initiator fragments per molecule, as well as transfer reactions of those fragments, but this could also be done without much added difficulty. For this reason, primary radicals coming from the initiator or from the solvent were not distinguished.

Notice also that initiator *I* is taken as "polymer" species with zero repeating units and a single group *I* (see Table 5). Monomer *k* is a species with a single repeating unit *U_k* and one kind of reactive groups *B_k*, the set of its *f_k* double bonds and the remaining molecule, which can undergo transfer reactions.