Average functionalities of macromolecules in stepwise polyfunctional polymerization

Dominique Durand and Claude-Marcel Bruneau
Laboratoire de Physico-Chimie Macromoléculaire, Equipe de Recherche Associée au C.N.R.S., Universite du Maine Faculté des Sciences, Route de Laval, 72017 *Le Mans Cedex, France*

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General expressions are derived for the average functionalities of macromolecules in stepwise polyfunctional polymerization, in particular for systems composed of monomers endowed with both A and B coreactive functional groups. Knowing the molecular distribution functions the weight average functionalities are calculated directly, on the basis of a new method using the propagation expectation.

Keywords Polymerization; macromolecule; molecular distribution; propagation; monomer; functional group

INTRODUCTION

The average functionalities of macromolecules synthesized by stepwise polyfunctional polymerization in the pre-gel region are very important parameters in characterizing such systems. Practically, many industrial macromolecular networks are the result of the condensation of polyfunctional oligomers with appropriate bifunctional reagents. To predict the gel point of such systems, it is necessary to know the different weight average functionalities of reactive species, which are particularly difficult to estimate when oligomers or pre-polymers are the starting materials.

Such average functionalities may be calculated from molecular distribution functions giving the molar and weight fractions of the different species according to their functionalities. But, as with the determination of weight average molecular weight, summation of the molecular distribution functions by Flory and Stockmayer's method[1-3] is tedious or impossible in complex systems when the molecular distribution functions are unknown. In a preceding paper[4], we proposed a new method to compute directly and readily the general expressions of average molecular weights for condensation polymerization of polyfunctional monomers without knowing the molecular distribution functions and without requiring the probability generating functions, but by using the propagation expectation. Here, we use an identical method to calculate directly the average functionalities.

Firstly, in all the derivations described below, we retain the assumptions of an ideal network polymerization: (1) equal and independant reactivity of all functional groups of the same type; (2) no intramolecular reactions in finite species; (3) no side reactions. In this study, we examine two kinds of systems: (i) the order I systems which consist of monomers having identical reactive groups and (ii) the order II systems which consist of monomers bearing functional groups which belong to two distinct coreactive species A and B, in such systems, the monomers may carry together A and B groups (e.g. hydroxyacids).

ORDER I SYSTEMS

Characteristics of the system

If we consider a very general system initially composed of n different types of monomers and let n_i be the number of monomers of type i, called i-monomers with the functionality f_i. The molar fractions of the i-monomers ν_i and the fraction of sites belonging to the i-monomers ρ_i, called i-sites, are:

$$\nu_i = \frac{n_i}{\sum_{i=1}^{n} n_i} \quad ; \quad \rho_i = \frac{\nu_i f_i}{\sum_{i=1}^{n} \nu_i f_i}$$

Let p be the reaction extent, i.e. the fraction of reacted sites.

The number and weight average functionalities of the monomers constituting the initial system (or the number and weight average functionalities of the molecules at $p = 0$) may be written:

$$\bar{f}_{no} = \sum_{i=1}^{n} \nu_i f_i \quad ; \quad \bar{f}_{wo} = \sum_{i=1}^{n} \rho_i f_i$$

Number average functionality

By definition, the number average functionality of the molecules at extent of rection p is the total number of unreacted sites over the number of molecules present at this extent of reaction.

$$\bar{f}_n = \frac{(1-p)\sum_{i=1}^{n} n_i f_i}{\sum_{i=1}^{n} n_i - \frac{1}{2}p\sum_{i=1}^{n} n_i f_i} = \frac{(1-p)\bar{f}_{no}}{1 - p\bar{f}_{no}/2} \qquad (1)$$

This relation is only valid in the pre-gel region.

Weight average functionality

By analogy with the weight average molecular weight

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which may be defined as the expected weight of the molecule of which a monomer unit picked at random is a part[1,4,5] and, following Miller *et al.*[8], we shall define the weight average functionality as the expected functionality of the molecule of which an unreacted functional group picked at random is a part.

The propagation expectation, ξ, that we may consider here as the mean expectation of reappearance of a structure consisting of a functional group and its chemical link to monomer, in all the paths which start from such a structure, is[6]:

$$\xi=\sum_{i=1}^{n}\rho_i p\sum_{i=1}^{n}\rho_i(f_i-1)=p(\bar{f}_{wo}-1)$$

The expected number of (link, site) structures in all the paths which start from such a structure selected at random is:

$$\eta=1/(1-\xi)$$

All the sites having equal reactivity, the expected number of unreacted sites in all the chains issuing from a (link, site) structure selected at random is:

$$s=\eta(1-p)$$

The expected functionality of the molecule of which an unreacted i-site selected at random, is a part, may be written:

$$\psi_i=1+(f_i-1)s$$

The weight average functionality being the expected functionality of the molecule of which any selected unreacted site is a part, we have:

$$\bar{f}_w=\sum_{i=1}^{n}\gamma_i\psi_i$$

γ_i being the probability of picking at random an unreacted i-site among the unreacted sites:

$$\forall i.\quad \gamma_i=\frac{\rho_i(1-p)}{(1-p)},\quad \gamma_i=\rho_i \qquad \forall p\neq 1$$
$$\gamma_i=0 \qquad \text{at } p=1$$

$$\bar{f}_w=1+\frac{(\bar{f}_{wo}-1)(1-p)}{1-p(\bar{f}_{wo}-1)} \tag{2}$$

Alternatively:

$$\bar{f}_w=\bar{f}_{wo}+\frac{p(\bar{f}_{wo}-1)(\bar{f}_{wo}-2)}{1-p(\bar{f}_{wo}-1)}$$

it should be noted above, that the weight average functionality diverges where $p=1/(\bar{f}_{wo}-1)$, i.e. at the gel point.

ORDER II SYSTEMS

Characteristics of the system

If we consider a general system initially consisting of n different types of monomers and let n_i be the number of moles of monomers of type i (i-monomers) having the functionality f_i:

$$f_i=f_{Ai}+f_{Bi}$$

where f_{Ai} and f_{Bi} are respectively the number of A-functional groups and B-functional groups borne by the i-monomer, one of the two functionalities may be equal to zero if the i-monomer bears only A-sites or B-sites. In such systems the A-sites can react only with the B-sites and *vice-versa*. Let ν_i be the molar fraction of the i-monomers, and ρ_{Ai} and ρ_{Bi} the respective fractions of A-sites and B-sites belonging to the i-monomers, called respectively A_i-sites and B_i-sites:

$$\nu_i=\frac{n_i}{\sum_{i=1}^{n}n_i}\qquad \rho_{Ai}=\frac{\nu_i f_{Ai}}{\sum_{i=1}^{n}\nu_i f_{Ai}}\qquad \rho_{Bi}=\frac{\nu_i f_{Bi}}{\sum_{i=1}^{n}\nu_i f_{Bi}}$$

The extent of reaction is measured by the fraction p_A of reacted A-sites or the fraction p_B of reacted B-sites.

The different number and weight average functionalities of the initial monomers, or of the molecules at $p_A=0$, are defined by the following expressions:

$$\bar{f}_{nAo}=\sum_{i=1}^{n}\nu_i f_{Ai}\qquad \bar{f}_{nBo}=\sum_{i=1}^{n}\nu_i f_{Bi}$$

$$\bar{f}_{wAo}=\sum_{i=1}^{n}\rho_{Ai}f_{Ai}\qquad \bar{f}_{wBo}=\sum_{i=1}^{n}\rho_{Bi}f_{Bi}$$

$$\varphi_{wAo}=\sum_{i=1}^{n}\rho_{Bi}f_{Ai}\qquad \varphi_{wBo}=\sum_{i=1}^{n}\rho_{Ai}f_{Bi}$$

The stoichiometric ratio r_0 of the total number of A-sites to the total number of B-sites, (or the number of unreacted A-sites to unreacted B-sites at $p_A=0$)

$$r_0=\sum_{i=1}^{n}\nu_i f_{Ai}/\sum_{i=1}^{n}\nu_i f_{Bi}$$

gives relations between some sizes relative to A-sites and B-sites.

$$p_B=r_0p_A\qquad \bar{f}_{nAo}=r_0\bar{f}_{nBo}$$

$$p_{Bi}f_{Ai}=r_0p_{Ai}f_{Bi}\qquad \varphi_{wA0}=r_0\varphi_{wBo}$$

Number average functionalities

The number average functionalities $\bar{f}_{nA}$ and $\bar{f}_{nB}$ of the molecules at a given extent of reaction p_A (or p_B) are the total number of unreacted A-sites and B-sites respectively over the number of molecules present at this extent of reaction.

$$\bar{f}_{nA}=(1-p_A)\bar{f}_{nAo}/(1-p_A\bar{f}_{nAo}) \tag{3}$$

$$\bar{f}_{nB}=(1-p_B)\bar{f}_{nBo}/(1-p_B\bar{f}_{nBo}) \tag{4}$$

These relations are only valid in the pre-gel region.

Weight average functionalities

We shall use the same method as for the order I systems. The propagation expectation ξ that we consider here as the mean expectation of reappearance of a structure consisting of an A-site with its chemical link to the monomer, in all the paths which start from such a structure is[7]:

$$\xi = \sum_{i=1}^{n} \rho_{Ai} p_A \sum_{i=1}^{n} \rho_{Bi} f_{Ai} + \frac{\sum_{i=1}^{n} \rho_{Ai} p_A \sum_{i=1}^{n} \rho_{Bi}(f_{Bi}-1) p_B \sum_{i=1}^{n} \rho_{Ai}(f_{Ai}-1)}{1 - p_B \sum_{i=1}^{n} \rho_{Ai} f_{Bi}}$$

$$\xi = p_A \bar{\varphi}_{wA_0} + \frac{r_0 p_A^2 (\bar{f}_{wA0}-1)(\bar{f}_{wB_0}-1)}{1 - p_A \bar{\varphi}_{wA_0}}$$

The expected number of (link, A-site) structures in all the paths which start from such a structure selected at random is:

$$\eta_{AA} = 1/(1-\xi)$$

Obviously, we have the same expression if we consider a (link, B-site) structure:

$$\eta_{BB} = 1/(1-\xi)$$

As $\eta_{AA} = \eta_{BB}$, put: $\eta = \eta_{AA} = \eta_{BB}$

The expected numbers of (link, B-site) structures and (link, A-site) structures contained in all the paths starting respectively from a (link, A-site) structure and a (link, B-site) structure selected at random are:

$$\eta_{AB} = \eta_{AA} p_A \frac{\sum_{i=1}^{n} \rho_{Bi}(f_{Bi}-1)}{1 - p_A \sum_{i=1}^{n} \rho_{Bi} f_{Ai}} = \eta\, p_A \frac{\bar{f}_{wB_0}-1)}{1 - p_A \bar{\varphi}_{wA_0}}$$

$$\eta_{BA} = \eta_{BB} p_B(\bar{f}_{wA_0}-1)/(1 - p_B \bar{\varphi}_{wB_0}) = \eta\, p_B(\bar{f}_{wA_0}-1)/(1 - p_B \bar{\varphi}_{wB_0})$$

All the sites of the same type being equireactive, the expected numbers of unreacted A-sites met in all the paths which start from a (link, A-site) structure and a (link, B-site) structure selected at random may be written respectively:

$$s_{AA} = \eta_{AA}(1-p_A) \qquad s_{BA} = \eta_{BA}(1-p_A)$$

In the same way, the expected numbers of unreacted B-sites starting from a (link, B-site) structure and a (link, A-site) structure are:

$$s_{BB} = \eta_{BB}(1-p_B) \qquad s_{AB} = \eta_{AB}(1-p_B)$$

The expected functionalities in A-sites and B-sites of the molecules of which an unreacted A_i-site, selected at random, is a part may be written:

$$\psi_{A.A_i} = 1 + (f_{Ai}-1)s_{AA} + f_{Bi}s_{BA}$$

$$\psi_{B.A_i} = (f_{Ai}-1)s_{AB} + f_{Bi}s_{BB}$$

The weight average functionalities $\bar{f}_{wA}$ and $\bar{\sigma}_{wB}$ being the expected functionalities relative to A-sites and B-sites respectively, of the molecule of which any unreacted A-site, selected at random is a part, may be written:

$$\bar{f}_{wA} = \sum_{i=1}^{n} \gamma_{Ai}\psi_{A.Ai} \qquad \bar{\varphi}_{wB} = \sum_{i=1}^{n} \gamma_{Ai}\psi_{B.Ai}$$

γ_{Ai} being the probability of picking at random an unreacted A_i-site among the unreacted A-sites:

$$\forall i,\ \gamma_{Ai} = \frac{\rho_{Ai}(1-p_A)}{(1-p_A)} \qquad \gamma_{Ai} = \rho_{Ai}, \quad \forall p_A \neq 1\gamma_{Ai}$$

$$\gamma p_A = 0, \text{ at } p_A = 1$$

$$\bar{f}_{wA} = 1 + \eta(\bar{f}_{wA_0}-1)(1-p_A)\left[\frac{1 + p_A\bar{\varphi}_{wA_0}}{1 - p_A\bar{\varphi}_{wA_0}}\right] \tag{5}$$

$$\bar{\varphi}_{wB} = \eta(1 - r_0 p_A)\left(\frac{p_A(\bar{f}_{wA_0}-1)(\bar{f}_{wB_0}-1}{1 - p_A\bar{\varphi}_{wA_0}} + \frac{\bar{\varphi}_{wA_0}}{r_0}\right)$$

Alternatively:

$$\bar{\varphi}_{wB} = \frac{1 - r_0 p_A}{r_0 p_A}\,\frac{\xi}{1-\xi} \tag{6}$$

In the same way, the expected functionalities in B-sites and A-sites of the molecules of which an unreacted B_i-site, selected at random, is a part, are:

$$\psi_{A.Bi} = f_{Ai}s_{AA} + (f_{Bi}-1)s_{BA}$$

$$\psi_{B.Bi} = 1 + f_{Ai}s_{AB} + (f_{Bi}-1)s_{BB}$$

These expressions lead to the weight average functionalities $\bar{f}_{wB}$ and $\bar{\varphi}_{wA}$:

$$\bar{f}_{wB} = \sum_{i=1}^{n} \gamma_{Bi}\psi_{B.Bi} \qquad \bar{\varphi}_{wA} = \sum_{i=1}^{n} \gamma_{Bi}\psi_{A.Bi}$$

γ_{Bi} being the probability of picking at random an unreacted B_j-site among the unreacted B-sites:

$$\forall i,\ \gamma_{Bi} = \frac{\rho_{Bi}(1-p_B}{(1-p_B)} \qquad \gamma_{Bi} = \rho_{Bi} = \rho_{Bi}, \quad \forall p_B \neq 1$$

$$\gamma_{Bi} = 0, \quad \text{at } p_B = 1$$

$$\bar{f}_{wB} = 1 + \eta(\bar{f}_{wB_0}-1)(1 - r_0 p_A\left[\frac{1 + p_A\bar{\varphi}_{wA_0}}{1 - p_A\bar{\varphi}_{wA_0}}\right] \tag{7}$$

$$\bar{\varphi}_{wA} = \eta(1-p_A)\left[\frac{r_0 p_A(\bar{f}_{wA_0}-1)(\bar{f}_{wB_0}-1)}{1 - p_A\bar{\varphi}_{wA_0}} + \bar{\varphi}_{wA_0}\right]$$

$$\bar{\varphi}_{wA} = \frac{1-p_A}{p_A}\,\frac{\xi}{1-\xi} \tag{8}$$

Note the following relations:

$$\bar{\varphi}_{wA} = r\bar{\varphi}_{wB} \qquad \frac{(\bar{f}_{wA}-1}{r(\bar{f}_{wB}-1)} = \frac{(\bar{f}_{wA_0}-1)}{r_0(\bar{f}_{wB_0}-1)}$$

where $r = r_0(1-p_A)/(1-r_0 p_A)$

r is the stoichiometric ratio of the number of unreacted A-sites to the number of unreacted B-sites at the extent of reaction p_A.

All these weight average functionalities (5) to (8) diverge at the gel point, i.e. for the reaction extent:

$$(p_A)_c = \frac{1}{\bar{\varphi}_{wA_0} + [r_0(\bar{f}_{wA_0}-1)(\bar{f}_{wB_0}-1)]^{1/2}}$$

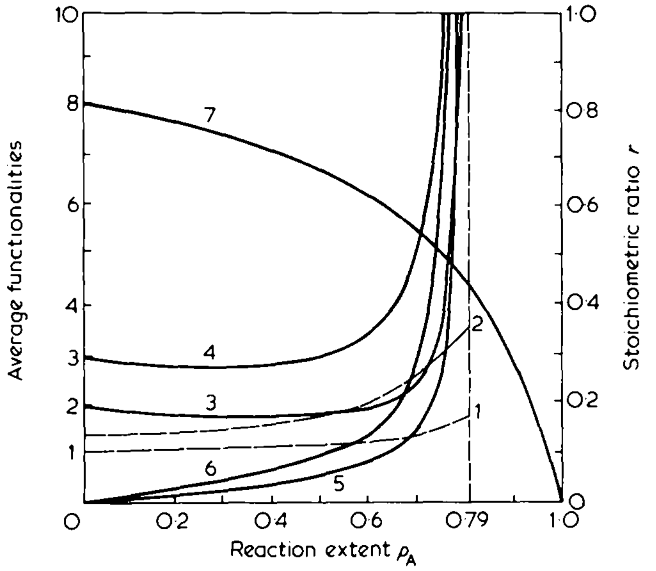

Figure 1 Evolution of the various average functionalities: 1 $\bar{f}_{nA}$, 2 $\bar{f}_{nB}$, 3 $\bar{f}_{wA}$, 4 $\bar{f}_{wB}$, 5 $\bar{\phi}_{wA}$, 6 $\bar{\phi}_{wB}$ and the stoichiometric ratio 7 r as a function of reaction extent p_A for a copolycondensate $R(A)_2/R'(B)_3$ in the initial stoichiometric ratio $r_0 = 0.8$

For complete reaction of the B-groups ($p_B = 1, p_A = 1/r_0$), we have the expressions:

$$\bar{f}_{wA} = 1 + \eta\left(\frac{r_0 - 1}{r_0}\right)(\bar{f}_{wA_o} - 1)\left(\frac{r_0 + \bar{\varphi}_{wA_o}}{r_0 - \bar{\varphi}_{wA_o}}\right) \qquad \bar{\varphi}_{wB} = 0$$

$$\bar{f}_{wB} = 0 \qquad \bar{\varphi}_{wA} = 0$$

with:

$$\eta = 1/(1-\xi),\ \xi = (\bar{\varphi}_{wA_o}/r_0) + [(\bar{f}_{wA_o} - 1)(\bar{f}_{wB_o} - 1)/(r_0 - \bar{\varphi}_{wA_o})]$$

If in the original mixture, no monomers with A and B groups on the same molecule are present, we find again at $p_B = 1$ the expression of $\bar{f}_{wA}$ obtained recently by Miller *et al.*[8] by using their recursive method.

$$\bar{f}_{wA} = 1 + \frac{(r_0 - 1)(\bar{f}_{wA_o} - 1)}{r_0 - (\bar{f}_{wA_o} - 1)(\bar{f}_{wB_o} - 1)} \qquad \text{at } p_B = 1)$$

As an example, assuming that no intramolecular reaction occurs before gelation, the various average functionalities in the case of a copolycondensate made from a mixutre of bifunctional monomers $(R(A)_2$ with trifunctional monomers $R'(B)_3$ in the initial stoichiometric ratio $r_0 = 0.8$, may be computed. *Figure 1* shows the evolution of these various average functionalities $\bar{f}_{nA}$, $\bar{f}_{nB}$, $\bar{f}_{wA}$, $\bar{f}_{wB}$, $\bar{\varphi}_{wA}$, $\bar{\varphi}_{wB}$ and the stoichiometric ratio r as a function of reaction extent p_A.

CONCLUSION

The general expression of average functionalities of macromolecules in stepwise polyfunctional polymerization has been derived by a direct method without knowing the molecular distribution functions and without requiring the probability generating functions. This technique may be applied to systems having unequally reactive groups (intrinsic or induced unequal reactivities).

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