

# Substitution effects and average molecular weights in non-linear stepwise polymerization

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The authors' method of calculating average molecular weights, in the pre-gel region, for stepwise polymerization of polyfunctional monomers, is extended to systems where the functional groups exhibit unequal reactivities induced by substitution effects in the course of the reaction.

**Keywords** Stepwise polymerization; average molecular weights; substitution effect

## INTRODUCTION

In a preceding paper<sup>1</sup>, we derived the general expressions of average molecular weights, in the pre-gel region, for systems with intrinsically unequal reactive functional groups. Now, we deal with systems exhibiting substitution effects. In such systems, the probability of forming a bond between two unreacted coreactive sites borne by two monomers depends on the structure of the two molecules of which the monomers are part, respectively. According to their range of action, the substitution effects of reacted sites on neighbouring unreacted ones are classified into first-shell, second-shell, etc.<sup>2</sup> We have a first-shell substitution effect (FSSE) if the probability of a site reacting depends only on the status (reacted or not) of the remaining sites on a given monomer and is independent of the configuration of the rest of the molecule of which this monomer is a part. As the substitution effect of a given reacted site on other sites borne on distant monomers (second-shell, third-shell, etc.) is, fortunately, of much smaller magnitude, in this paper, stepwise polymerization of polyfunctional monomers exhibiting only a FSSE (first-shell substitution effect) will be considered.

Gordon and coworkers<sup>2-5</sup> have played a great part in the analysis of systems with substitution effects. Using the theory of branching processes, this author and his school showed the influence of substitution effects on polymer distribution<sup>6</sup> and on some network properties<sup>7,8</sup>. More recently, Miller and Macosko extended their recursive method<sup>9,10</sup> to take into account the FSSE in the description of different non-linear stepwise polymerizations<sup>11</sup>.

If the reaction rate of sites borne by a given monomer increases with the number of reacted sites, the substitution effect is said to be positive, and in the opposite case, negative. The sense (positive or negative) of the substitution effect and its magnitude depend on the type of reaction considered and its experimental conditions (solvent, temperature, etc.). So, in a reaction with an acid

group (esterification), tris(hydroxymethyl)ethane exhibits a positive FSSE whereas by reacting with an isocyanate (urethanization) it exhibits a negative FSSE<sup>12</sup>. Moreover the magnitude of this effect varies as a function of the nature of the solvent and the range of temperature. A given polyfunctional monomer will present a linear FSSE if the measure of the substitution effect needs a single dimensionless parameter  $N$ , such that  $N^i$  is the factor multiplying the reaction rate constant  $K$  of the site when  $i$  previously reacted sites are borne by the considered monomer. It is evident that the presence of substitution effects, according to their positive or negative senses, give opposing modifications of various network molecular parameters, such as the reaction extent at gelation<sup>2,3,11,13,14</sup>. Negative substitution effects promote growth of linear chains at the expense of branching and delay the gelation threshold. In this study, we derive expressions of average molecular weights for the stepwise polymerization of very general systems exhibiting substitution effects. These averages will be given by analytical expressions, morphologically identical to those of equireactive and intrinsic non-equireactive systems. The loss of mass by elimination of by-product is also taken into account.

## CHARACTERISTICS OF THE SYSTEM AND KINETICS

Consider the stepwise polymerization of polyfunctional monomers bearing A and (or) B functional groups, some or all of the monomers exhibiting only first substitution effect, i.e. the reactivity of an unreacted site of a given monomer depends on the number of reacted A and B sites borne by this monomer.

Examine a very general system consisting of  $n$  different monomer types and let  $i$  be a type of monomer called  $i$  monomer. An  $i$  monomer is defined by its molecular weight  $M_i$  and its  $f_i$  reactive sites characterized by the vector  $f_i$ :

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$$f_i = [f_{A,i}, f_{B,i}] \quad f_i = f_{A,i} + f_{B,i}$$

where  $f_{A,i}$  and  $f_{B,i}$  are respectively the numbers of A and B sites borne by one  $i$  monomer.

Let  $v_i$  and  $w_i$  be respectively the mole and weight fractions of the  $i$  monomers. The respective fractions of A sites and B sites belonging to the  $i$  monomers, called respectively  $A_{,i}$  sites and  $B_{,i}$  sites, are:

$$\rho_{A,i} = v_i f_{A,i} / \sum_i v_i f_{A,i}$$

$$\rho_{B,i} = v_i f_{B,i} / \sum_i v_i f_{B,i}$$

The various number average and weight average functionalities and molecular weights are given by the following equations:

$$\bar{f}_{nA0} = \sum_i v_i f_{A,i} \quad \bar{f}_{nB0} = \sum_i v_i f_{B,i}$$

$$\bar{f}_{wA0} = \sum_i \rho_{A,i} f_{A,i} \quad \bar{f}_{wB0} = \sum_i \rho_{B,i} f_{B,i}$$

$$\bar{\varphi}_{wA0} = \sum_i \rho_{B,i} f_{A,i} \quad \bar{\varphi}_{wB0} = \sum_i \rho_{A,i} f_{B,i}$$

$$\bar{M}_{n0} = \sum_i v_i M_i \quad \bar{M}_{w0} = \sum_i w_i M_i$$

Let  $M_{eA}$  and  $M_{eB}$  be the respective contributions of an A site and a B site to the molecular weight  $M_e$  of the by-product from any bond between an A site with a B site ( $M_e = M_{eA} + M_{eB}$ ).

The reaction extent, at any time, will be given by the vector  $p$ :

$$p = [p_A, p_B]$$

where  $p_A$  and  $p_B$  are the respective fractional conversions of A and B sites.

Let  $r$  be the stoichiometric balance:

$$r = \frac{\bar{f}_{nA0}}{\bar{f}_{nB0}} = \frac{p_B}{p_A} = \frac{\bar{\varphi}_{wB0}}{\bar{\varphi}_{wA0}}$$

Let us partition each monomer according to its composition of reacted sites. So, an  $i$  monomer will be characterized by the vector  $k$  and will be called an  $i(k)$  monomer:

$$k = [k_A, k_B] \quad k = k_A + k_B$$

where  $k_A$  ( $k_B$ ) is the number of reacted A (B) sites.

Let  $v_i^{(k)}$  be the molar fraction of the  $i(k)$  monomers:

$$v_i^{(k)} = \gamma_i^{(k)} v_i$$

where  $\gamma_i^{(k)}$  is the fraction of  $i$  monomers with  $k_A$  reacted A sites and  $k_B$  reacted B sites. If all the A sites and B sites react with the same rate (i.e. without substitution effect),  $\gamma_i^{(k)}$  is composed of two binomial probabilities:

$$\gamma_i^{(k)} = \binom{f_{A,i}}{k_A} p_A^{k_A} (1-p_A)^{f_{A,i}-k_A} \binom{f_{B,i}}{k_B} p_B^{k_B} (1-p_B)^{f_{B,i}-k_B}$$

with

$$\binom{n}{p} = \frac{n!}{p!(n-p)!}$$

To take into account the substitution effect, we must know at each reaction extent and for each  $i$  monomer the values of  $\gamma_i^{(k)}$  for each  $k$ . The determination of the  $\gamma_i^{(k)}$  values as a function of reaction extent may be found numerically by using the kinetics of the system and, in simple cases, analytical results can be obtained.

In some particular cases, the fractions of each different substituted monomer can be determined experimentally and, in this way, the values of the rate constants can be derived. So, for example, if a monomer bearing only A sites is present and exhibits a FSSE, the characterization of the distribution of the various reaction products of this monomer with a coreactive monofunctional monomer allows one to determine, from an appropriate kinetic scheme, the values of the rate constants and thus the substitution parameters; the separation of the compounds as a function of substitution extent may be obtained by gel permeation chromatography<sup>12,15</sup>.

The overall extent of reacted A sites and B sites may be written respectively:

$$p_A = \frac{1}{\bar{f}_{nA0}} \sum_{i,k} k_A \gamma_i^{(k)} v_i$$

$$p_B = \frac{1}{\bar{f}_{nB0}} \sum_{i,k} k_B \gamma_i^{(k)} v_i$$

with  $0 \leq k \leq f_i$ ,  $\mathbf{0}$  being a zero vector.

## NUMBER AVERAGE MOLECULAR WEIGHT

Without intramolecular reaction, the number average molecular weight follows the expression:

$$\bar{M}_n = \frac{\bar{M}_{n0} - p_A \bar{f}_{nA0} M_e}{1 - p_A \bar{f}_{nA0}} = \frac{\bar{M}_{n0} - p_B \bar{f}_{nB0} M_e}{1 - p_B \bar{f}_{nB0}}$$

## REAL FUNCTIONALITIES AND PROPAGATION EXPECTATION

### Real functionalities

The real functionality of a given monomer being the number of reacted sites borne by this monomer<sup>1</sup>, the number average and weight average real functionalities of the monomers are given by the following expressions.

*Number average real functionalities.* We can write

$$\bar{f}_{nA} = \sum_{i,k} k_A v_i^{(k)} = p_A \bar{f}_{nA0}$$

$$\bar{f}_{nB} = \sum_{i,k} k_B v_i^{(k)} = p_B \bar{f}_{nB0}$$

$$\bar{f}_{nA} = \bar{f}_{nB}$$

where  $1 \leq i \leq n$ ,  $\mathbf{0} < k < f_i$ .

*Weight average real functionalities.* We can write

$$\bar{f}_{wA} = \frac{\sum_{i,k} k_A^2 v_i^{(k)}}{\sum_{i,k} k_A v_i^{(k)}} \quad \bar{f}_{wB} = \frac{\sum_{i,k} k_B^2 v_i^{(k)}}{\sum_{i,k} k_B v_i^{(k)}}$$

$$\bar{\varphi}_{wtB} = \frac{\sum_{i,k} k_{AK} k_{BV_i^{(k)}}}{\sum_{i,k} k_{AV_i^{(k)}}} \quad \bar{\varphi}_{wtA} = \frac{\sum_{i,k} k_{BK} k_{AV_i^{(k)}}}{\sum_{i,k} k_{BV_i^{(k)}}$$

with  $\bar{\varphi}_{wtA} = \bar{\varphi}_{wtB}$ .

**Propagation expectation**

The propagation expectation  $\xi$ , which may be considered as the expectation of finding a reacted A site from a reacted A site selected at random, may be written<sup>1</sup>:

$$\xi = \bar{\varphi}_{wtA} + \frac{(\bar{f}_{wtA} - 1)(\bar{f}_{wtB} - 1)}{1 - \bar{\varphi}_{wtA}}$$

The gel point is the reaction extent such as  $\xi = 1$ .

**WEIGHT AVERAGE MOLECULAR WEIGHT**

As previously seen<sup>1</sup>, the weight average molecular weight is defined as the expected weight of the molecule of which a unit of mass picked at random is a part. If the considered reaction gives a by-product, the weight of unit selected at random depends on its branching degree. So, the weight fraction  $w_i^{(k)}$  of the polycondensate consisting of  $i(k)$  monomers is:

$$w_i^{(k)} = \frac{(M_i - k_A M_{eA} - k_B M_{eB}) v_i^{(k)}}{\bar{M}_{n0} - \bar{f}_{wtA} M_e}$$

The expected numbers of  $i$  monomers for which an A site (or a B site) is connected, at first distance, respectively to a reacted B site (or an A site), selected at random, are:

$$\rho_{A,i}^* = \frac{\sum_k k_{AV_i^{(k)}}}{P_A \bar{f}_{nA0}} \quad \rho_{B,i}^* = \frac{\sum_k k_{BV_i^{(k)}}}{P_B \bar{f}_{nB0}}$$

The expected numbers of  $i$  monomers for which an A site (or a B site) is connected, at first distance, respectively to a reacted A site (or a B site), selected at random, are:

$$\frac{\bar{f}_{wtB} - 1}{1 - \varphi_{wtB}} \rho_{A,i}^* \quad \frac{\bar{f}_{wtA} - 1}{1 - \bar{\varphi}_{wtA}}$$

The expected number of  $i$  monomers contained in all the paths which start from a reacted A site and a reacted B site selected at random, are respectively:

$$(\eta_{A,i})_r = \eta \left( \rho_{B,i}^* + \frac{\bar{f}_{wtB} - 1}{1 - \bar{\varphi}_{wtA}} \rho_{A,i}^* \right)$$

$$(\eta_{B,i})_r = \eta \left( \rho_{A,i}^* + \frac{\bar{f}_{wtA} - 1}{1 - \bar{\varphi}_{wtA}} \rho_{B,i}^* \right)$$

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

Without by-product, the expected molecular weights of all the monomers which form the chains issued from a reacted A site and a reacted B site are respectively:

$$(\mu_A)_r^* = \sum_i (\eta_{A,i})_r M_i = \eta \left( \bar{M}_{sB0}^* + \frac{\bar{f}_{wtB} - 1}{1 - \bar{\varphi}_{wtA}} \bar{M}_{sA0}^* \right)$$

$$(\mu_B)_r^* = \sum_i (\eta_{B,i})_r M_i = \eta \left( M_{sA0}^* + \frac{\bar{f}_{wtA} - 1}{1 - \bar{\varphi}_{wtA}} \bar{M}_{sB0}^* \right)$$

with

$$\bar{M}_{sB0}^* = \sum_i \rho_{B,i}^* M_i \quad \bar{M}_{sA0}^* = \sum_i \rho_{A,i}^* M_i$$

And, always without by-product, the expected weight of the molecule of which an  $i(k)$  monomer selected at random, is a part may be written:

$$m_i^{(k)} = M_i + k_A (\mu_A)_r^* + k_B (\mu_B)_r^*$$

The expected number of links in the molecule of which an  $i(k)$  monomer selected at random is a part, is:

$$DL_i^{(k)} = k_A \eta \left( 1 + \frac{\bar{f}_{wtB} - 1}{1 - \bar{\varphi}_{wtA}} \right) + k_B \eta \left( 1 + \frac{\bar{f}_{wtA} - 1}{1 - \bar{\varphi}_{wtA}} \right)$$

The expected weight of condensate issued from the formation of such a molecule is  $DL_i M_e$  and taking into account the loss of weight due to the condensate, the expected weight of the molecule of which an  $i(k)$  monomer, selected at random, is a part, may be written:

$$m_i^{(k)} = M_i + k_A \eta \left( (\bar{M}_{sB0}^* - M_e) + \frac{\bar{f}_{wtB} - 1}{1 - \bar{\varphi}_{wtA}} (\bar{M}_{sA0}^* - M_e) \right)$$

$$+ k_B \eta \left( (\bar{M}_{sA0}^* - M_e) + \frac{\bar{f}_{wtA} - 1}{1 - \bar{\varphi}_{wtA}} (\bar{M}_{sB0}^* - M_e) \right)$$

The weight average molecular weight of the copolycondensate being the expected weight of the molecule of which any unit of mass is a part, it follows that:

$$\bar{M}_w = \sum_{i,k} w_i^{(k)} m_i^{(k)}$$

It results that:

$$\bar{M}_w = \frac{\bar{M}_{n0} \bar{M}_{w0} - \bar{f}_{wtA} M_e^2}{\bar{M}_{n0} - \bar{f}_{wtA} M_e} + \frac{\bar{f}_{wtA} \eta}{\bar{M}_{n0} - \bar{f}_{wtA} M_e} \left( 2(\bar{M}_{sA0}^* - M_e)(\bar{M}_{sB0} - M_e) + \frac{1}{1 - \bar{\varphi}_{wtA}} [(\bar{f}_{wtB} - 1)(\bar{M}_{sA0}^* - M_e)^2 + (\bar{f}_{wtA} - 1)(\bar{M}_{sB0}^* - M_e)^2] \right)$$

The expression for the weight average molecular weight without by-product comes immediately by putting  $M_e = 0$  in the above equation.

The number and weight average degrees of polymerization  $\overline{DP}12^n$  and  $\overline{DP}12^w$  are obtainable from the corresponding  $\bar{M}_n$  and  $\bar{M}_w$  expressions by putting  $M_i = 1$  (for all  $i$ ) and  $M_e = 0$ .

In the particular case of a copolycondensate made from a mixture of  $f$ -functional monomers  $[R(A)12^f]$  with bifunctional monomers  $[R(B)12^2]$ , we again find the same result as Miller and Macosko<sup>11</sup>.

For example, consider a copolycondensate made from a mixture of bifunctional monomer  $[R(A)_2]$  with a trifunctional monomer  $[R'(B)_3]$  exhibiting a linear first substitution effect characterized by the parameter  $N$  such

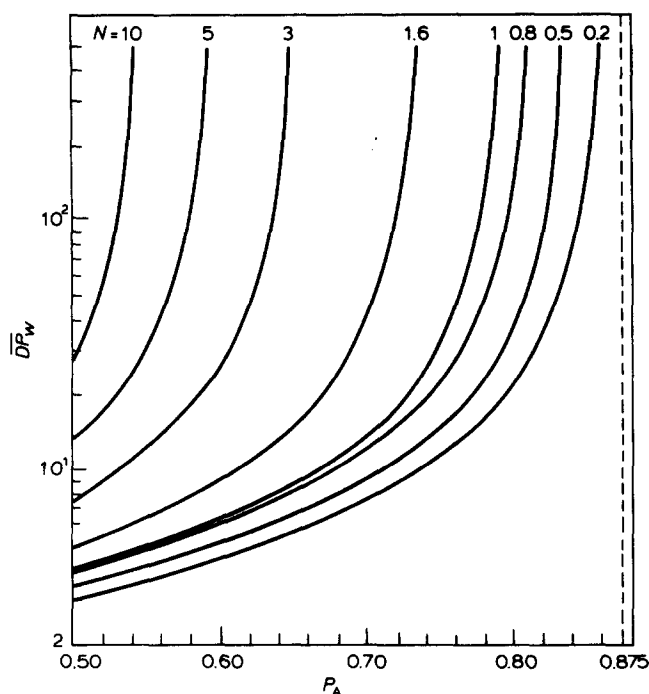


Figure 1 Weight average degree of polymerization  $\overline{DP}_w$  vs. reaction extent  $p_A$  for a copolycondensate  $[R(A)_2]/[R'(B)_3]$  in the initial stoichiometric ratio  $r = 0.8$  and for different linear substitution parameters  $N$  on  $[R'(B)_3]$  monomers

that, with  $K$  denoting the rate constant of a site belonging to any unreacted monomer,  $KN$  and  $KN^2$  are the rate constants of sites belonging respectively to monosubstituted and bisubstituted monomers. In such a system, the fractions of each different substituted monomer can be derived easily from an appropriate classical kinetic scheme<sup>7</sup>. So, Figure 1 shows the evolution of the weight average degree of polymerization of such a copolycondensate, as a function of reaction extent  $p_A$ , in the stoichiomet-

ric ratio  $r = 0.8$  and for different substitution parameters  $N$ . A negative substitution effect delays the divergence of  $\overline{DP}_w$  and consequently the gel point, and inversely a positive substitution effect advances the divergence of  $\overline{DP}_w$ . The lower and upper limits of the reaction extents  $p_A$  at the gel point with increasing and decreasing  $N$  are respectively 0.500 and 0.875.<sup>7</sup>

## CONCLUSION

The method proposed in these papers to compute the weight average molecular weights for polycondensation of multifunctional reactants bearing functional groups exhibiting unequal intrinsic or induced reactivity is very general and leads to analytical expressions morphologically identical.

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