Intrinsic unequal reactivity and average molecular weights in non-linear stepwise polymerization

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The general expressions of average molecular weights in the pre-gel region, for stepwise polymerization of polyfunctional monomers endowed with both A and B coreactive functional groups, are extended to systems where some or all of the B groups react at different rates. The method of calculation is always based on the propagation expectation and the presence of by-product in the reactions is taken into account.

Keywords Stepwise polymerization; average molecular weights; intrinsic unequal reactivity

INTRODUCTION

Recently, we derived, by a new method, the general expressions of average molecular weights, in the pre-gel region, for stepwise polymerization of polyfunctional monomers with and without condensation by-products[1,2]. In particular, we computed the average molecular weight in systems consisting of mixed monomers endowed with both A and B coreactive functional groups. In the preceding works, we consider the following assumptions: (i) equal reactivity of functional groups of the same type; (ii) no intramolecular reaction on finite species; (iii) no side reactions. In this paper, we treat the effect of intrinsic unequal reactivity between functional groups on the average molecular weights. In fact, many networks made by polycondensation involve monomers having functional groups of unequal reactivity; for example, polyester networks made from glycerine or polyurethane networks formed with 2,4-toluene diisocyanate. We examine in detail a very general system consisting of different types of monomers bearing A and/or B functional groups, where some or all of the B sites react at different rates, the A sites being able to react only with the B sites and *vice versa*. In this study, we also take into account the loss of mass by elimination of by-product.

CHARACTERISTICS OF THE SYSTEM AND KINETICS

Consider a very general system consisting of n different monomer types and m B site species distinguished by their reaction rates. Let i be a type of monomer, called i monomer, and B_j a species of B site called B_j site. An i monomer is defined by its molecular weight M_i and its f_i different reactive sites characterized by the vector f_i:

$$f_i=[f_{A,i}, f_{B_1,i}, \ldots, f_{B_j,i}, \ldots, f_{B_m,i}]$$

where $f_{A,i}$ ($f_{B_j,i}$) is the number of A (B_j) sites borne by one i monomer. Put

$$f_i=f_{A,i}+f_{B,i}$$

with

$$f_{B,i}=\sum_{j=1}^{m} f_{B_j,i}$$

Let v_i and w_i be respectively the mole and weight fractions of the i monomers. Let $\rho_{A,i}$, $\rho_{B_j,i}$ and $\rho_{B,i}$ be the respective fractions of A sites, B_j sites and B sites belonging to the i monomers called respectively A,i sites, B_j,i sites and B_j sites, defined by the following equations:

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

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

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

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

The number average and weight average functionalities of the monomers used in this paper are defined by the following equations:

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

$$\bar{f}_{wA0}=\sum_i \rho_{A,i} f_{A,i} \quad \bar{f}_{wB_j0;B_j}=\sum_i \rho_{B_j,i} f_{B_j,i}$$

$$\bar{\varphi}_{wB_j0}=\sum_i \rho_{A,i} f_{B_j,i} \quad \bar{\phi}_{wA0;B_j}=\sum_i \rho_{B_j,i} f_{A,i}$$

The number average and weight average molecular weights of the monomers are:

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

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

In a system with unequal reactivity, the reaction extent, at any time, will be given by the following vectors:

$$\mathrm{p}=[p_A,p_B]$$

$$\mathrm{p}_A=[p_{AB_1},\ldots,p_{AB_j},\ldots,p_{AB_m}] \quad p_A=\sum_j p_{AB_j}$$

$$\mathrm{p}_B=[p_{B_1A},\ldots,p_{B_jA},\ldots,p_{B_mA}] \quad p_B=\sum_j \rho_{B_j} p_{B_jA}$$

where p_A and p_B are the respective fractional conversions of A and B sites; and p_{AB_j} and p_{B_jA} the respective fractional conversions of A sites linked to B_j sites and B_j sites linked to A sites.

If $[A]_0$ is the initial moles of A sites and $[A]$ the moles of unreacted A sites remaining after some reaction time t and similarly for B_j, it follows that:

$$p_A=\frac{[A]_0-[A]}{[A]_0} \qquad p_{B_jA}=\frac{[B_j]_0-[B_j]}{[B_j]_0} \qquad p_B=\frac{[B]_0-[B]}{[B]_0}$$

Chemical kinetics and stoichiometry generally allow one to compute all the vector components from any one of them. As usual, let r be the stoichiometric balance:

$$r=\frac{\bar{f}_{nA0}}{\bar{f}_{nB0}}=\frac{p_B}{p_A}=\frac{\rho_{B_j}p_{B_jA}}{p_{AB_j}}$$

The rates of disappearance of the different B site species are given by the m differential equations:

$$\frac{\mathrm{d}[B_j]}{\mathrm{d}t}=-K_j[A]^{\alpha}[B_j]^{\beta_j} \qquad \text{for } 1\leqslant j\leqslant m$$

where K_j is the reaction rate constant between an A site and a B_j site, and α,β_j are the respective orders in A and B_j sites. Solving each equation for $[A]^{\alpha}$, gives:

$$\frac{1}{K_1[B_1]^{\beta_i}}\frac{\mathrm{d}[B_1]}{\mathrm{d}t}=\ldots=\frac{1}{K_j[B_j]^{\beta_j}}\frac{\mathrm{d}[B_j]}{\mathrm{d}t}=\ldots$$

Assuming $\beta_1=\beta_j=1$, for all j, and integrating, we obtain classical relations, first proposed by Case[3] between the fractional conversions of the different B sites where $\rho_j=K_1/K_j$ is the reactivity ratio:

$$(1-p_{B_1A})=\ldots=(1-p_{B_jA})^{\rho_j}=\ldots$$

NUMBER AVERAGE MOLECULAR WEIGHT

Without intramolecular reaction, the number average molecular weight is defined as the total mass over the number of molecules present at considered reaction extent:

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

REAL FUNCTIONALITIES AND PROPAGATION EXPECTATION

To determine more easily the weight average molecular weight, we shall define the notion of real functionalities and compute the propagation expectation with these latter parameters. First, let us partition each monomer in various kinds according to their composition in reacted sites. So, an i monomer will be characterized by the vector $\boldsymbol{k}$ and will be called an $i(\boldsymbol{k})$ monomer:

$$\boldsymbol{k}=[k_A,k_{B_1},\ldots,k_{B_j},\ldots,k_{B_m}]$$

where k_A (k_{B_j}) is the number of reacted A (B_j) sites. Put

$$k=k_A+k_B$$

with

$$k_B=\sum_j k_{B_j}$$

The molar fraction of the $i(k)$ monomer may be written:

$$v_i^{(k)}=\binom{f_{A,i}}{k_A}p_A^{k_A}(1-p_A)^{f_{A,i}-k_A}\prod_j\left[\binom{f_{B_j,i}}{k_{B_j}}p_{B_jA}^{k_{B_j}}(1-p_{B_jA})^{f_{B_j,i}-k_{B_j}}\right]v_i$$

with

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

In the present system, all the sites of the same species being equireactive, the distribution of reacted sites inside each species is given by a binomial probability.

Real functionalities

By definition, the real functionality of a given monomer will be the number of reacted sites borne by this monomer. According to the species A or B of reacted sites, we may define various average real functionalities.

Number average real functionalities. We can write

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

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

$$\bar{f}_{nrA}=\bar{f}_{nrB}$$

where $1\leqslant i\leqslant n$, $\mathbf{0}\leqslant\boldsymbol{k}\leqslant\boldsymbol{f}_i$; $\mathbf{0}$ being a zero vector.

Weight average real functionalities. The definitions of the various weight average real functionalities are the following:

$$\bar{f}_{wrA}=\frac{\sum_{i,k}k_A^2 v_i^{(k)}}{\sum_{i,k}k_A v_i^{(k)}} \qquad \bar{f}_{wrB}=\frac{\sum_{i,k}k_B^2 v_i^{(k)}}{\sum_{i,k}k_B v_i^{(k)}}$$

$$\bar{\phi}_{wrB}=\frac{\sum_{i,k}k_A k_B v_i^{(k)}}{\sum_{i,k}k_A v_i^{(k)}} \qquad \bar{\phi}_{wrA}=\frac{\sum_{i,k}k_B k_A v_i^{(k)}}{\sum_{i,k}k_B v_i^{(k)}}$$

As

$$\sum_{i,k}k_A v_i^{(k)}=\sum_{i,k}k_B v_i^{(k)},\ (\bar{f}_{nrA}=\bar{f}_{nrB}),$$

it is immediately obvious that $\bar{\phi}_{\mathrm{wrA}} = \bar{\phi}_{\mathrm{wtB}}$.

Following the same method as that developed in preceding papers[1,2,4] to compute various weight averages, the weight average functionalities $\bar{f}_{\mathrm{wrA}}$ and $\bar{\varphi}_{\mathrm{wrB}}$ may be defined respectively as the expected real functionalities in A and B sites of the monomers of which any reacted A site, selected at random, is a part. It follows that:

$$\bar{f}_{\mathrm{wrA}} = \sum_i (\rho_{\mathrm{A},i})_{\mathrm{r}} \psi_{\mathrm{rA;A},i}$$

$$\bar{\varphi}_{\mathrm{wrB}} = \sum_i (\rho_{\mathrm{A},i})_{\mathrm{r}} \psi_{\mathrm{rB;A},j}$$

where $\psi_{\mathrm{rA;A},j}$ and $\psi_{\mathrm{rB;A},j}$ are the expected real functionalities in A and B sites of the monomers of which reacted A,i site, selected at random, is a part:

$$\psi_{\mathrm{rA;A},j} = 1 + p_{\mathrm{A}}(f_{\mathrm{A},j} - 1)$$

$$\psi_{\mathrm{rB;A},j} = \sum_j p_{\mathrm{B}_j\mathrm{A}} f_{\mathrm{B}_j,i}$$

and $(\rho_{\mathrm{A},i})_{\mathrm{r}}$ is the probability of finding, from any B site, a reacted A,i site among the reacted A sites:

for all i $\quad (\rho_{\mathrm{A},i})_{\mathrm{r}} = \dfrac{p_{\mathrm{B}}\rho_{\mathrm{A},i}}{p_{\mathrm{B}}}$

$(\rho_{\mathrm{A},i})_{\mathrm{r}} = \rho_{\mathrm{A},i}$ $\quad$ for all $p_{\mathrm{B}} \neq 0$

$(\rho_{\mathrm{A},i})_{\mathrm{r}} = 0$ $\quad$ at $p_{\mathrm{B}} = 0$

It results that

$$\bar{f}_{\mathrm{wrA}} = 1 + p_{\mathrm{A}}(\bar{f}_{\mathrm{wA0}} - 1)$$

$$\bar{\varphi}_{\mathrm{wrB}} = \sum_{i,j} \rho_{\mathrm{A},i} p_{\mathrm{B}_j\mathrm{A}} f_{\mathrm{B},i} = \sum_j p_{\mathrm{B}_j\mathrm{A}} \bar{\varphi}_{\mathrm{wB}_j0}$$

Similarly, the weight average real functionalities in B and A sites of the monomers of which a reacted B_j site, selected at random, is a part, are:

$$\bar{f}_{\mathrm{wrB;B}_j} = \sum_i (\rho_{\mathrm{B}_j,i})_{\mathrm{r}} \psi_{\mathrm{rB;B}_j,i}$$

$$\bar{\varphi}_{\mathrm{wrA;B}_j} = \sum_i (\rho_{\mathrm{B}_j,i})_{\mathrm{r}} \psi_{\mathrm{rA;B}_j,i}$$

where $\psi_{\mathrm{rB;B}_j,i}$ and $\psi_{\mathrm{rA;B}_j,i}$ are the expected real functionalities in B and A sites of the monomers of which a reacted B_j,i site, selected at random, is a part:

$$\psi_{\mathrm{rB;B}_j,i} = 1 + p_{\mathrm{B}_j\mathrm{A}}(f_{\mathrm{B}_j,i} - 1) + \sum_{l \neq j} p_{\mathrm{B}_l\mathrm{A}} f_{\mathrm{B}_l,i}$$

$$= 1 + \sum_j p_{\mathrm{B}_j\mathrm{A}} f_{\mathrm{B}_j,i} - p_{\mathrm{B}_j\mathrm{A}}$$

$$\psi_{\mathrm{rA;B}_j,i} = p_{\mathrm{A}} f_{\mathrm{A},i}$$

and $(\rho_{\mathrm{B}_j,i})_{\mathrm{r}}$ is the probability of finding from any A site a reacted B_j,i site among the reacted B_j sites:

for all j,i $\quad (\rho_{\mathrm{B}_j,i})_{\mathrm{r}} = \dfrac{p_{\mathrm{AB}}\rho_{\mathrm{B}_j,i}}{p_{\mathrm{AB}_j}}$

$(\rho_{\mathrm{B}_j,i})_{\mathrm{r}} = \rho_{\mathrm{B}_j,i}$ $\quad$ *for all* $p_{\mathrm{AB}_j} \neq 0$

$(\rho_{\mathrm{B}_j,i})_{\mathrm{r}} = 0$ $\quad$ at $p_{\mathrm{AB}_j} = 0$

It results that:

$$\bar{f}_{\mathrm{wrB;B}_j} = 1 + \sum_{i,j} \rho_{\mathrm{B}_j,i} p_{\mathrm{B}_j\mathrm{A}} f_{\mathrm{B}_j,i} - p_{\mathrm{B}_j\mathrm{A}}$$

$$= 1 + \sum_j p_{\mathrm{B}_j\mathrm{A}} \bar{f}_{\mathrm{wB}_j\mathrm{0;B}_j} - p_{\mathrm{B}_j\mathrm{A}}$$

$$\bar{\varphi}_{\mathrm{wrA;B}_j} = p_{\mathrm{A}} \sum_i \rho_{\mathrm{B}_j,i} f_{\mathrm{A},i} = p_{\mathrm{A}} \bar{\varphi}_{\mathrm{wA0;B}_j}$$

Finally, the weight average real functionalities in B and A sites of the monomers of which a reacted B site (for all j) selected at random is a part may be written:

$$\bar{f}_{\mathrm{wrB}} = \sum_j (\rho_{\mathrm{B}_j})_{\mathrm{r}} \bar{f}_{\mathrm{wrB;B}_j}$$

$$\bar{\phi}_{\mathrm{wrA}} = \sum_j (\rho_{\mathrm{B}_j})_{\mathrm{r}} \bar{\phi}_{\mathrm{wrA;B}_j}$$

where $(\rho_{\mathrm{B}_j})_{\mathrm{r}}$ is the probability of finding from any A site, a reacted B_j site among the reacted B sites:

$(\rho_{\mathrm{B}_j})_{\mathrm{r}} = \dfrac{p_{\mathrm{AB}_j}}{p_{\mathrm{A}}}$ $\quad$ for all $p_{\mathrm{AB}_j} \neq 0$

$(\rho_{\mathrm{B}_j})_{\mathrm{r}} = 0$ $\quad$ at $p_{\mathrm{AB}_j} = 0$

It follows that:

$$\bar{f}_{\mathrm{wrB}} = 1 + \sum_j p_{\mathrm{B}_j\mathrm{A}} \bar{f}_{\mathrm{wB}_j\mathrm{0;B}_j} - \frac{1}{p_{\mathrm{A}}} \sum_j p_{\mathrm{AB}_j} p_{\mathrm{B}_j\mathrm{A}}$$

$$\bar{\varphi}_{\mathrm{wrA}} = \sum_j p_{\mathrm{AB}_j} \bar{\varphi}_{\mathrm{wA0;B}_j}$$

We can easily check the relation $\bar{\varphi}_{\mathrm{wrA}} = \bar{\varphi}_{\mathrm{wrB}}$.

Propagation expectation

Consider a reacted A site selected at random from the system, and compute the probability of recurrence of such a structure in all the ways which start from this site (out of its monomers), i.e. the propagation expectation ξ. Considering that ϕ_{wrA} and $(\bar{f}_{\mathrm{wrB}} - 1)$ are respectively the expected numbers of reacted A sites and additional reacted B sites borne by any monomer linked directly to any reacted A site and similarly for $\bar{\varphi}_{\mathrm{wrB}}$ and $(\bar{f}_{\mathrm{wrA}} - 1)$, the propagation expectation may be written directly:

$$\xi = \bar{\varphi}_{\mathrm{wrA}} + (\bar{f}_{\mathrm{wrB}} - 1)(1 + \bar{\varphi}_{\mathrm{wrB}} + \bar{\varphi}^2_{\mathrm{wrB}} + \ldots)(\bar{f}_{\mathrm{wrA}} - 1)$$

which becomes:

$$\xi = \bar{\varphi}_{\mathrm{wrA}} + \frac{(\bar{f}_{\mathrm{wrA}} - 1)(\bar{f}_{\mathrm{wrB}} - 1)}{1 - \bar{\varphi}_{\mathrm{wrA}}}$$

With some small changes of notation, the propagation expectation ξ has the same expression as that established in a preceding paper[5].

If all the B sites are equireactive, it follows that:

$$\bar{\varphi}_{\mathrm{wrA}}=p_{\mathrm{A}}\bar{\varphi}_{w\mathrm{A}0}$$

$$(\bar{f}_{w\mathrm{rB}}-1)=p_{\mathrm{B}}(\bar{f}_{w\mathrm{B}0}-1)$$

which gives the classical propagation expectation of an equireactive system[6]. The gel point is the reaction extent such as $\xi=1$.

WEIGHT AVERAGE MOLECULAR WEIGHT

As in Macosko and Miller's studies[7] and in our preceding papers[1,2], the weight average molecular weight is defined here 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 the $i(k)$ monomers is:

$$w_i^{(k)}=\frac{(M_i-k_{\mathrm{A}}M_{e\mathrm{A}}-k_{\mathrm{B}}M_{e\mathrm{B}})\nu_i^{(k)}}{\bar{M}_{n0}-\bar{f}_{n\mathrm{rA}}M_e}$$

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_j site (or an A site), selected at random, are:

$$\rho_{\mathrm{A},i} \qquad \rho^*_{\mathrm{B},i}=\sum_j\frac{p_{\mathrm{AB}_j}}{p_{\mathrm{A}}}\rho_{\mathrm{B}_j,i}$$

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_j site), selected at random, are:

$$\frac{\bar{f}_{\mathrm{wrB}}-1}{1-\bar{\varphi}_{\mathrm{wrB}}}\rho_{\mathrm{A},i} \qquad \frac{\bar{f}_{\mathrm{wrA}}-\mathrm{A}}{1-\varphi_{\mathrm{wrA}}}\rho^*_{\mathrm{B},i}$$

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

$$(\eta_{A,i})_{\mathrm{r}}=\eta\left(\rho^*_{\mathrm{B},i}+\frac{\bar{f}_{\mathrm{wrB}}-1}{1-\bar{\varphi}_{\mathrm{wrA}}}\rho_{\mathrm{A},i}\right)$$

$$(\eta_{\mathrm{B}_j,i})_{\mathrm{r}}=\eta\left(\rho_{\mathrm{A},i}+\frac{\bar{f}_{\mathrm{wrA}}-1}{1-\bar{\varphi}_{\mathrm{wrA}}}\rho^*_{\mathrm{B},i}\right)$$

with $\eta=1/(1-\xi)$. This expression is the same whatever the B_j species, so we put:

$$(\eta_{\mathrm{B}_j,i})_{\mathrm{r}}=(\eta_{\mathrm{B},i})_{\mathrm{r}}$$

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:

$$(\mu_{\mathrm{A}})^*_{\mathrm{r}}=\sum_i(\eta_{\mathrm{A},i})_{\mathrm{r}}M_i=\eta\left(\bar{M}^*_{s\mathrm{B}0}+\frac{\bar{f}_{\mathrm{wrB}}-1}{1-\bar{\Phi}_{\mathrm{wrA}}}\bar{M}_{s\mathrm{A}0}\right)$$

$$(\mu_{\mathrm{B}})^*_{\mathrm{r}}=\sum_i(\eta_{\mathrm{B},i})_{\mathrm{r}}M_i=\eta\left(\bar{M}_{s\mathrm{A}0}+\frac{\bar{f}_{\mathrm{wrA}}-1}{1-\bar{\Phi}_{\mathrm{wrA}}}\bar{M}^*_{s\mathrm{B}0}\right)$$

with

$$\bar{M}^*_{s\mathrm{B}0}=\sum_i\rho^*_{\mathrm{B},i}M_i \qquad \bar{M}_{s\mathrm{A}0}=\sum_i\rho_{\mathrm{A},i}M_i$$

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

$$m_i^{(k)}=M_i+k_{\mathrm{A}}(\mu_{\mathrm{A}})^*_{\mathrm{r}}+k_{\mathrm{B}}(\mu_{\mathrm{B}})^*_{\mathrm{r}}$$

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

$$DL_i^{(k)}=k_{\mathrm{A}}\eta\left(1+\frac{\bar{f}_{\mathrm{wrB}}-1}{1-\bar{\varphi}_{\mathrm{wrA}}}\right)+k_{\mathrm{B}}\eta\left(1+\frac{\bar{f}_{\mathrm{wrA}}-1}{1-\bar{\varphi}_{\mathrm{wrA}}}\right)$$

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

$$m_i^{(k)}=M_i+k_{\mathrm{A}}\eta\left((M^*_{s\mathrm{B}0}-M_e)+\frac{\bar{f}_{\mathrm{wrB}}-1}{1-\varphi_{\mathrm{wrA}}}(\bar{M}_{s\mathrm{A}0}-M_e)\right)$$
$$+k_{\mathrm{B}}\eta\left((\bar{M}_{s\mathrm{A}0}-M_e)+\frac{\bar{f}_{\mathrm{wrA}}}{1-\bar{\varphi}_{\mathrm{wrA}}}(\bar{M}^*_{s\mathrm{B}0}-M_e)\right)$$

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:

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

By using analogous derivations to those developed in Appendix 2 of a preceding paper[2], we obtain:

$$\bar{M}_w=\frac{\bar{M}_{n0}\bar{M}_{w0}-\bar{f}_{n\mathrm{rA}}M_e^2}{\bar{M}_{n0}-\bar{f}_{n\mathrm{rA}}M_e}+\frac{\bar{f}_{n\mathrm{rA}}}{\bar{M}_{n0}-\bar{f}_{n\mathrm{rA}}M_e}\Bigg(2(\bar{M}_{s\mathrm{A}0}$$
$$-M_e)(\bar{M}^*_{s\mathrm{B}0}-M_e)+\frac{1}{1-\bar{\varphi}_{\mathrm{wrA}}}[(\bar{f}_{\mathrm{wrB}}-1)(\bar{M}_{s\mathrm{A}0}$$
$$-M_e)^2+(\bar{f}_{\mathrm{wrA}}-1)(\bar{M}^*_{s\mathrm{B}0}-M_e)^2]\Bigg)$$

with $\bar{f}_{n\mathrm{rA}}=p_{\mathrm{A}}\bar{f}_{n\mathrm{A}0}$, $\bar{f}_{\mathrm{wrA}}-1=p_{\mathrm{A}0}(\bar{f}_{w\mathrm{A}0}-1)$ and

$$\bar{\varphi}_{\mathrm{wrA}}=\sum_j p_{\mathrm{AB}_j}\bar{\varphi}_{w\mathrm{A}0;\mathrm{B}_j}$$

$$\bar{f}_{\mathrm{wrB}}-1=\sum_j p_{\mathrm{B}_j\mathrm{A}}\bar{f}_{w\mathrm{B}_j0;\mathrm{B}_j}-\frac{1}{p_{\mathrm{A}}}\sum_j p_{\mathrm{AB}_j}p_{\mathrm{B}_j\mathrm{A}}$$

The expression for the weight average molecular weight without by-product comes immediately by putting $M_e=0$ in the above equation. The number average and weight average degrees of polymerization $\overline{DP}_n$ and $\overline{DP}_w$ 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 stoichiometric mixture of trifunctional monomers

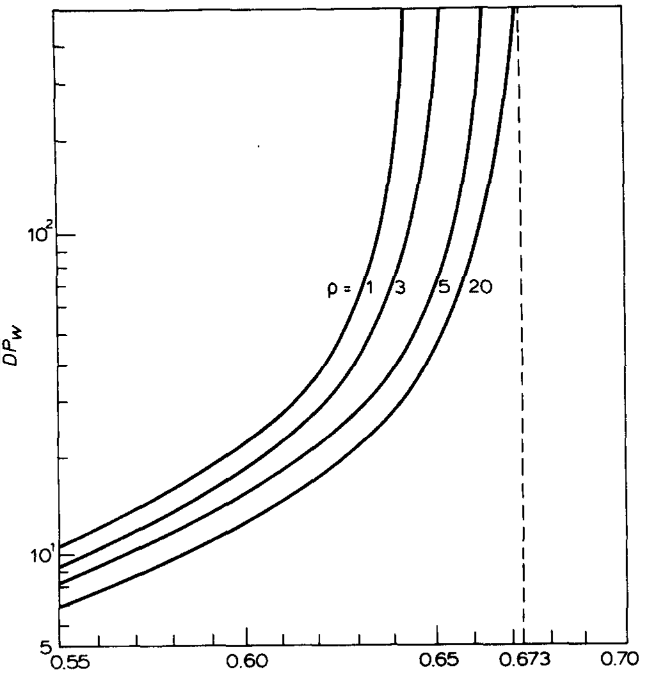

Figure 1 Weight average degree of polymerization $\overline{DP}_w$ vs. reaction extent P_A for a copolycondensate $[R(A)_2]/[R'(B_1)_1(B_2)_3]$ in the initial stoichiometric ratio $r = 0.8$ and for different reactivity ratios $\rho = K_1/K_2$

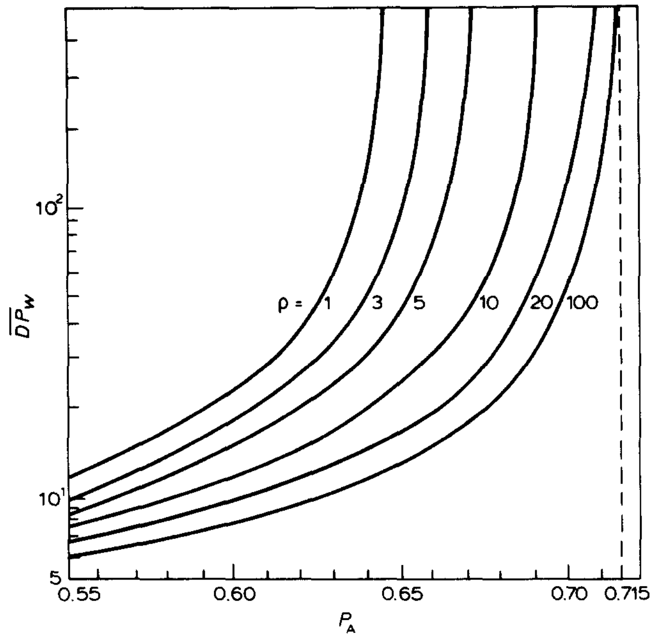

Figure 2 Weight average degree of polymerization $\overline{DP}_w$ vs. reaction extent p_A for a copolycondensate $[R(A)_2]/[R'(B_1)_2(B_2)_2]$ in the stoichiometric ratio $r = 0.8$ and for different reactivity ratios $\rho = K_1/K_2$

$[R(B_1)_2B_2]$ with bifunctional monomers $[R'(A)_2]$, we again find, after some trivial steps, the same result as Miller and Macosko[7]. If all the B sites react with the same rate, we obtain a weight average molecular weight expression which agrees with that given in ref. 2.

For example, we have computed the evolution of the weight average degree of polymerization $\overline{DP}_w$ as a function of reaction extent p_A in a copolycondensate made from a mixture of bifunctional monomers $[R(A)_2]$ with tetrafunctional monomers $[R'(B_1)_{f_{B_1}}(B_2)_{f_{B_2}}]$, $f_{B_1}+f_{B_2}=4$, in the initial stoichiometric ratio $r = 0.8$ and for different reactivity ratios $\rho = K_1/K_2$. *Figures 1* and *2* depict systems with respectively $f_{B_1}=1$ and $f_{B_1}=2$. The curves shift to the right with increasing ρ because the reaction extent at the gel point increases as the B_1 and B_2 sites differ in reactivity[5]. The upper limits of the reaction extents at the gel point with increasing ρ are respectively 0.673 (*Figure 1*) and 0.715 (*Figure 2*)[5].

CONCLUSION

This paper gives the general expressions of average molecular weights for condensation polymerization involving eliminated species in the case of systems composed of mixed monomers bearing coreactive A and B sites, where the B sites may be of unequal intrinsic reactivity. The following paper deals with systems having monomers exhibiting substitution effects[8].

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