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Branching process of the grafting reaction between two reactive polymers

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Graft coupling between two reactive polymers can lead to the formation of compatibilized blends. There is a need to control the extent of graft coupling if the grafting system is capable of gelation, not just for the control of phase size and morphology, which depend on the amount and structures of graft copolymers in a ternary blend. In this paper, we give a thorough analysis of the molecular characteristics of the grafting system of two reactive polymers each having a large number of reactive groups. A kinetic approach is employed to quantify the molecular characteristics: concentration of individual species, molecular-weight averages and gel point. It is found that the percentage conversions of the reactive polymers to copolymers are quite limited in order to avoid a weight-average molecular weight of the system that is too high. The presence of a high-molecular-weight tail in the polydisperse reactive polymers further limits the extent of the grafting reaction, an undesirable factor in such a grafting system.

(Keywords: grafting reaction; molecular characteristics; kinetics model)

INTRODUCTION

Graft coupling between two reactive polymers can lead to the formation of compatibilized blends with improved and desirable properties[1,2]. The availability of more and more functional polymers, whether they are made by copolymerization or chemical modification, provides opportunities to make new blends by coupling two reactive polymers[3–5]. A different approach has been graft polymerization by a free-radical process[6,7].

In many cases the reactive groups are numerous on both polymers; for instance, polyethylene in the course of free-radical branching. The complexity of graft copolymer structures grows as grafting continues, and gelation occurs when the extent of the grafting reaction goes beyond a certain limit. The weight-average molecular weight (*WAMW*) and the gel point of the resultant polymer mixture are important measures. It is often necessary to stop the grafting reaction at some point to avoid too high a *WAMW* and to avoid further gelation. Another important issue is the phase size and phase homogeneity in ternary blends. Both phase size and homogeneity depend on the structure as well as the amount of graft copolymers in the blends[8–10]. One good example is the control of impact[11] and optical properties of high-impact polystyrene (HIPS) resins[12].

In this study, we look at the branching process during the grafting reaction between two reactive polymers (A and B) each having a large number of reactive groups (a and b); a reacts with b only. So far there has been no theoretical analysis on such a system. Practically, the number of reactive groups on both polymers can be considered infinite when the numbers of reactive groups are large, say, more than 50 (see 'Discussion' section). One of the limitations to fundamental understanding and design of such polymer blend systems is the lack of adequate techniques to characterize the reaction products. *Figure 1* shows one particular example of a grafting system that we studied: the hydroxyl groups on the cellulose acetate (CA) react with the anhydride groups on the styrene–maleic anhydride random copolymer (SMA) to form graft copolymers. There are 85 hydroxyl groups of CA for a number-average molecular weight of 46000, and 90 anhydrides of SMA for a number-average molecular weight of 120000 (8% maleic anhydride in the random copolymer).

BACKGROUND LITERATURE

Over the past decades, many researchers have given theoretical analyses on the branching process of polymerization systems capable of developing a network[13–31]. The analyses can be classified into: statistical, percolation and kinetic. The statistical approach can be classified further into four techniques: (1) Flory and Stockmayer's[13–17] classic combinatorial method, (2) Gordon's[18] cascade theory, (3) Macosko and Miller's[19,20] recursive method, and (4) Durand and Bruneau's[21] approach. Boots *et al.*[24], Bansil *et al.*[25] and Hermann and collaborators[26,27] have proposed percolation models.

In a kinetic approach, generating functions, transformations and continuous variable approximations[32] have been applied to the solution of the batch, free-radical polymerization kinetics for relatively simple systems. A numerical method is possible for a complex system since the advent of stiff ODE (ordinary differential equation)

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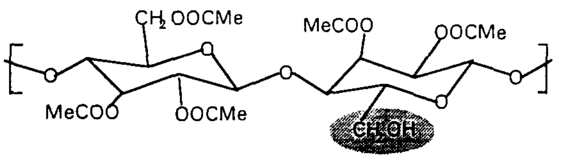
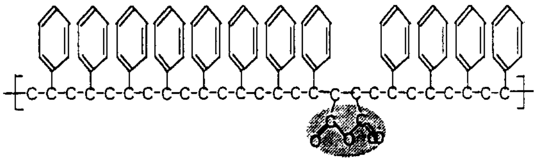


CA (d.s.=2.5, not completely primary hydroxyl)



SMA (the distribution of MA is random)

Figure 1 Structures of cellulose acetate (CA) and styrene–maleic anhydride random copolymer (SMA)

codes[33]. Skeirik and Grulke[34] developed a calculation scheme to reduce the extremely large number of differential equations by grouping chain lengths into equal-sized groups and still retain the flexibility of the initial kinetic formulations.

Kinetic formulation of a non-linear condensation system was referred to briefly without details or development by Stockmayer[14]. Stafford[28] derived a distribution function for a self-condensing $R_1A_{f_1}$, $R_2A_{f_2}$, ... system and considered the special case of $R_1A_{f_1}$, $R_2A_{f_2}$, ..., $R_1B_{g_1}$, $R_2B_{g_2}$, ..., where the total numbers of reactive group A equal the total numbers of B. In a closely related field on the cluster formation or aggregation process, Smoluchowski's coagulation equations have been used to study the formation of clusters in the coaggregation process of particles. Ziff[29] gave a broad discussion on the aggregation kinetics via Smoluchowski's equation. Recently, Tobita and Hamielec[30,31] proposed a pseudo-kinetic rate-constant method to model network formation in free-radical polymerization.

PRESENT WORK

In this study, we look at the branching process during the grafting reaction between two reactive polymers (A and B) having a large number of reactive groups (a and b), where a reacts with b only. A kinetic approach is developed for the grafting system. We focus on the pre-gel region of the grafting system.

THEORETICAL DEVELOPMENT

Grafting reactions are generally heterogeneous since most polymers are immiscible. Heterogeneity complicates the analysis. Theoretical analysis assuming a homogeneous grafting process represents a limiting case. A homogeneous grafting reaction can be found in solution processes. A homogeneous, kinetically controlled, irreversible grafting reaction is considered here. Two assumptions are made in the kinetic approach: (1) equal reactivity of the reactive groups on the polymer backbones; and (2) no intramolecular reaction. The percentage (weight basis) conversion to graft copolymer of a reactive polymer is chosen as a measure of the extent of grafting reaction; that information can be obtained experimentally by extraction studies.

Monodisperse case

Kinetic equation. Let A and B represent the two reactive polymers with reactive groups a and b respectively. With the assumptions mentioned above, the kinetic equations that describe the rate of change of the concentration of individual species are described by:

$$\frac{\mathrm{d}C_{ij}}{dt}=\frac{1}{2}\sum_{k=0}^{i}\sum_{l=0}^{i} r_{kl+(i-k)(j-l)}+\frac{1}{2}r_{\frac{1}{2}i\frac{1}{2}j+\frac{1}{2}i\frac{1}{2}j}-r_{ij+ij}-\sum_{p=0}^{\infty}\sum_{q=0}^{\infty} r_{ij+pq} \quad (1)$$

Subscript notation $ij+pq$ means the grafting reaction of component ij with component pq; the left side of the subscript is assigned for A, the right side for B. The term $r_{\frac{1}{2}i\frac{1}{2}j+\frac{1}{2}i\frac{1}{2}j}$ appears when i and j are both even, since there is no component with a non-integer index; the extra r_{ij+ij} term is counted as a self-grafting reaction kills two species simultaneously. Equation (1) can also be written as:

$$\frac{\mathrm{d}C_{ij}}{\mathrm{d}t}=(P^{\mathrm{g}}_{ij}-P^{\mathrm{c}}_{ij})r \quad (2)$$

where P^{g}_{ij} is the fraction of the total reaction rate r for the generation of the graft copolymer ij, and P^{c}_{ij} is the fraction of the total reaction rate for the consumption of the graft copolymer ij.

With the approximation of two reactive polymers having an infinite number of reactive groups, the rate of grafting conversion for polymer A satisfies:

$$C^0_{\mathrm{A}}\frac{\mathrm{d}f_{\mathrm{A}}}{\mathrm{d}t}=(1-f_{\mathrm{A}})r \quad (3)$$

where $1-f_{\mathrm{A}}$ is the fraction of the total reaction rate for the consumption of A. By combining equation (2) with equation (3), we have:

$$\mathrm{d}\bar{C}_{ij}/\mathrm{d}f_{\mathrm{A}}=(P^{\mathrm{g}}_{ij}-P^{\mathrm{c}}_{ij})/(1-f_{\mathrm{A}}) \quad (4)$$

where the reduced concentration $\bar{C}_{ij}$ is defined as:

$$\bar{C}_{ij}=C_{ij}/C^0_{\mathrm{A}} \quad (5)$$

The reduced initial concentration of B becomes:

$$\bar{C}^0_{\mathrm{B}}=C^0_{\mathrm{B}}/C^0_{\mathrm{A}}=x \quad (6)$$

where x is the molar ratio of the two reactive polymers.

The chance for a particular reaction of component ij with component kl to form component $(i+k)(j+l)$ is proportional to $(il+jk)\bar{C}_{ij}\bar{C}_{kl}$. The chance for all reactions to occur at any moment is proportional to $\bar{C}^0_{\mathrm{A}}\bar{C}^0_{\mathrm{B}}$. The fraction of the total reaction rate for the formation of any particular component is the sum of all the chances for the formation of that component divided by the chance of all reactions. The expression for P^{g}_{ij} is generalized as:

$$P^{\mathrm{g}}_{ij}=\frac{1}{2x}\left(\sum_{k=0}^{i}\sum_{l=0}^{i}[k(j-l)+l(i-k)]\bar{C}_{kl}\bar{C}_{(i-k)(j-l)}\right) \quad (7)$$

where the separated plus term in equation (1) is absorbed to give equation (7). Accordingly, the expression for P^{c}_{ij} is generalized as:

$$P^{\mathrm{c}}_{ij}=\frac{1}{x}[(ix+j)\bar{C}_{ij}] \qquad (i=0,1,\ldots,n;\ j=0,1,\ldots,m) \quad (8)$$

where the separated minus term in equation (1) is absorbed to give equation (8).

Concentration of polymer species. The initial conditions of equation (4) are:

$$f_{\mathrm{A}}=0,\quad \bar{C}^0_{\mathrm{A}}=1,\quad \bar{C}^0_{\mathrm{B}}=x,\quad \bar{C}^0_{ij}=0 \qquad (ij\neq 10\neq 01) \quad (9)$$

We can solve equation (4) to have:

$$\bar{C}_{ij}=g_{ij}(1-f_{\mathrm{A}})^{i+j/x}[-\ln(1-f_{\mathrm{A}})]^{i+j-1}\frac{1}{x^{i-1}} \quad (10)$$

where

$$g_{ij}=\frac{1}{2(i+j-1)}\sum_{k=0}^{i}\sum_{l=0}^{j}[k(j-1)+l(i-k)]g_{kl}g_{(i-k)(j-l)} \quad (11)$$

$$(i=1,2,\ldots,m+1;\ j=1,2,\ldots,n+1)$$

and

$$g_{10}=g_{01}=1 \qquad g_{i0}=g_{0j}=0 \quad (12)$$
$$(i=0,2,3,4,\ldots,m+1;\ j=0,2,3,4,\ldots,n+1)$$

Since there is no intramolecular reaction, the total reduced concentration of all species satisfies:

$$\frac{\mathrm{d}\bar{C}_{\mathrm{T}}}{\mathrm{d}t}=\frac{\mathrm{d}(\Sigma_{i=0}^{\infty}\Sigma_{j=0}^{\infty}\bar{C}_{ij})}{\mathrm{d}t}=-\frac{r}{C^0_{\mathrm{A}}} \quad (13)$$

By combining equation (13) with equation (3) and integrating, we have:

$$\bar{C}_{\mathrm{T}}=x+1+\ln(1-f_{\mathrm{A}}) \quad (14)$$

The total reduced concentration of the graft copolymers $\bar{C}_{\mathrm{g}}$ becomes:

$$\bar{C}_{\mathrm{g}}=\bar{C}_{\mathrm{T}}-\bar{C}_{\mathrm{A}}-\bar{C}_{\mathrm{B}}=x+1+\ln(1-f_{\mathrm{A}})-(1-f_{\mathrm{A}})-x(1-f_{\mathrm{A}})^{1/x} \quad (15)$$

Equations (13)–(15) are valid only for grafting conversions before the onset of gelation. Equation (10) is valid for post-gel grafting conversion according to Flory's argument. This is obvious since equation (1) describes species of finite size. The presence of gel does not change the expression for P^{c}_{ij}.

Molecular-weight averages and gel point. The reduced number-average molecular weight (*NAMW*) and weight-average molecular weight (*WAMW*) of all species are calculated by:

$$\frac{\bar{M}_{\mathrm{n}}}{\bar{M}^0_{\mathrm{n}}}=\frac{1+x}{\bar{C}_{\mathrm{T}}} \quad (16)$$

$$\frac{\bar{M}_{\mathrm{w}}}{\bar{M}^0_{\mathrm{w}}}=\frac{\Sigma_{i=0}^{\infty}\Sigma_{j=0}^{\infty}(i+jM_{\mathrm{B}}/M_{\mathrm{A}})^2\bar{C}_{ij}}{1+(M_{\mathrm{B}}/M_{\mathrm{A}})^2x} \quad (17)$$

A more compact form can be sought by seeking the generating function of equation (1) or equation (4). Let us define the generating function as:

$$G(A,B,Z)=\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}A^iB^j\bar{C}_{ij}(Z) \quad (18)$$

where

$$Z=-\ln(1-f_{\mathrm{A}}) \quad (19)$$

Multiplying equation (4) by A^iB^j and summing for all the i and j we have:

$$G_z=\frac{1}{x}ABG_AG_B-AG_A-\frac{1}{x}BG_B \quad (20)$$

The initial condition becomes

$$G(A,B,0)=A+Bx \quad (21)$$

G_A, G_B and G_Z are the partial derivatives. We can solve it using the method of characteristics[35] with the initial condition of equation (21) (see Appendix). The results are:

$$G(A,B,Z)=\zeta+x\eta-\zeta\eta Z \quad (22)$$

$$A=\zeta\exp[(1-\eta)Z] \quad (23)$$

$$B=\eta\exp[(1-\zeta)Z] \quad (24)$$

$$G_A=\zeta/A \quad (25)$$

$$G_B=x\eta/B \quad (26)$$

The *WAMW* is related to the generating function by:

$$\bar{M}_{\mathrm{w}}=\left.\frac{M_{\mathrm{A}}^2\partial(AG_A)/\partial A+2M_{\mathrm{A}}M_{\mathrm{B}}G_{AB}+M_{\mathrm{B}}^2\partial(BG_B)/\partial B}{M_{\mathrm{A}}G_A+M_{\mathrm{B}}G_B}\right|_{\substack{A=1\\B=1}} \quad (27)$$

By manipulation of equations (23)–(26), we have for the reduced *WAMW*:

$$\frac{\bar{M}_{\mathrm{w}}}{\bar{M}^0_{\mathrm{w}}}=\frac{1+2ZM_{\mathrm{B}}/M_{\mathrm{A}}+x(M_{\mathrm{B}}/M_{\mathrm{A}})^2}{[1+x(M_{\mathrm{B}}/M_{\mathrm{A}})^2](1-Z^2/x)} \quad (28)$$

From equation (28), we have at the critical point of gelation:

$$Z^2=x \quad (29)$$

Substituting the expression for Z, we have

$$-\ln(1-f_{\mathrm{A}}^{\mathrm{cr}})=x^{0.5} \quad (30)$$

Polydisperse reactive polymers

For polydisperse reactive polymers, it is necessary to relate the grafting reaction to the conversion of a reactive polymer by weight. With proper labelling of polymer species, the kinetic expression of equation (1) can be readily extended to accommodate the situation with polydisperse reactive polymers.

Kinetic equation. Let us designate the concentration of a polymer species by:

$$C_{i,i',\ldots;j,j',\ldots}$$

where $i,i',\ldots$ stand for numbers of chains of polymer A of different molecular weight, and $j,j',\ldots$ stand for numbers of chains of polymer B of different molecular weight. The kinetic expression of equation (4) becomes:

$$\frac{\mathrm{d}\bar{C}_{i,i',\ldots;j,j',\ldots}}{\mathrm{d}f_{\bar{M}^0_{\mathrm{nA}}}}=\frac{P^{\mathrm{g}}_{i,i',\ldots;j,j',\ldots}-P^{\mathrm{c}}_{i,i',\ldots;j,j',\ldots}}{1-f_{\bar{M}^0_{\mathrm{nA}}}} \tag{31}$$

where $\bar{M}^0_{\mathrm{nA}}$ is the reference free chain component of polymer A having the molecular weight of the number-average molecular weight of initial polymer A. $\bar{C}_{i,i',\ldots;j,j',\ldots}$ is defined as:

$$\bar{C}_{i,i',\ldots;j,j',\ldots}=C_{i,i',\ldots;j,j',\ldots}/C^0_{\mathrm{A}} \tag{32}$$

With such identification, we can extend $P^{\mathrm{g}}_{i,i',\ldots;j,j',\ldots}$ and $P^{\mathrm{c}}_{i,i',\ldots;j,j',\ldots}$ into:

$$P^{\mathrm{g}}_{i,i',\ldots;j,j',\ldots}=\frac{1}{2x}\sum_{i_{\mathrm{A}}=0}^{i}\sum_{i'_{\mathrm{A}}=0}^{i'}\cdots\sum_{j_{\mathrm{B}}=0}^{j}\sum_{j'_{\mathrm{B}}=0}^{j'}\cdots$$
$$\left[\left(\sum_{k=i,i',\ldots}k_{\mathrm{A}}\bar{M}_{k_{\mathrm{A}}}\right)\left(\sum_{l=j,j',\ldots}(l-l_{\mathrm{B}})\bar{M}_{l_{\mathrm{B}}}\right)+\left(\sum_{l=j,j',\ldots}l_{\mathrm{B}}\bar{M}_{l_{\mathrm{B}}}\right)\left(\sum_{k=i,i',\ldots}(k-k_{\mathrm{A}})\bar{M}_{k_{\mathrm{A}}}\right)\right]$$
$$\bar{C}_{i_{\mathrm{A}},i'_{\mathrm{A}},\ldots;j_{\mathrm{B}},j'_{\mathrm{B}},\ldots}\bar{C}_{i-i_{\mathrm{A}},i'-i'_{\mathrm{A}},\ldots;j-j_{\mathrm{B}},j'-j'_{\mathrm{B}},\ldots} \tag{33}$$

$$P^{\mathrm{c}}_{i,i',\ldots;j,j',\ldots}=\frac{1}{x}\left(x\sum_{k=i,i',\ldots}k\bar{M}_{k_{\mathrm{A}}}+\sum_{l=j,j',\ldots}l\bar{M}_{l_{\mathrm{B}}}\right)\bar{C}_{i,i',\ldots;j,j',\ldots} \tag{34}$$

where x is defined in the same way as in monodisperse case. The reduced molecular weights of free chains and chain segments on the graft copolymers are defined as:

$$\bar{M}_{k_{\mathrm{A}}}=M_{k_{\mathrm{A}}}/\bar{M}^0_{\mathrm{nA}}\qquad\bar{M}_{l_{\mathrm{B}}}=M_{l_{\mathrm{B}}}/\bar{M}^0_{\mathrm{nB}} \tag{35}$$

The initial conditions are:

$$f_{\bar{M}^0_{\mathrm{nA}}}=0$$

except

$$\bar{C}^0_{i,i',\ldots;j,j',\ldots}=0$$
$$\bar{C}^0_{0,k,\ldots;0,0,\ldots}=N^0(\bar{M}_{k_{\mathrm{A}}})\qquad(k=i,i',\ldots,k=1) \tag{36}$$
$$\bar{C}^0_{0,0,\ldots;0,l,\ldots}=xN^0(\bar{M}_{l_{\mathrm{B}}})\qquad(l=j,j',\ldots,l=1)$$

where $N^0(\bar{M}_{k_{\mathrm{A}}})$ and $N^0(\bar{M}_{l_{\mathrm{B}}})$ are, respectively, the number fractions of polymer A and polymer B of a certain molecular weight.

Concentration of polymer species. The analytical solution of equation (31) for the concentration of polymer species becomes:

$$\bar{C}_{i,i',\ldots;j,j',\ldots}=g_{i,i',\ldots;j,j',\ldots}\frac{1}{x^{\alpha}}(1-f_{\bar{M}^0_{\mathrm{nA}}})^{\delta+\varepsilon/x}[-\ln(1-f_{\bar{M}^0_{\mathrm{nA}}})]^{\beta+\gamma} \tag{37}$$

with

$$g_{0,k,\ldots;0,0,\ldots}=\begin{cases}N^0(\bar{M}_{k_{\mathrm{A}}}) & k=1\\ 0 & k\neq 1\end{cases}\qquad(k=i,i',\ldots)$$
$$g_{0,0,\ldots;0,l,\ldots}=\begin{cases}N^0(\bar{M}_{l_{\mathrm{B}}}) & l=1\\ 0 & l\neq 1\end{cases}\qquad(l=j,j',\ldots) \tag{38}$$

$$g_{i,i',\ldots;j,j',\ldots}=\frac{1}{2(\beta+\gamma)}\sum_{i_{\mathrm{A}}=0}^{i}\sum_{i'_{\mathrm{A}}=0}^{i'}\cdots\sum_{j_{\mathrm{B}}=0}^{j}\sum_{j'_{\mathrm{B}}=0}^{j'}\cdots$$
$$\left[\left(\sum_{k=i,i',\ldots}k_{\mathrm{A}}\bar{M}_{k_{\mathrm{A}}}\right)\left(\sum_{l=j,j',\ldots}(l-l_{\mathrm{B}})\bar{M}_{l_{\mathrm{B}}}\right)+\left(\sum_{l=j,j',\ldots}l_{\mathrm{B}}\bar{M}_{l_{\mathrm{B}}}\right)\left(\sum_{k=i,i',\ldots}(k-k_{\mathrm{A}})\bar{M}_{k_{\mathrm{A}}}\right)\right] \tag{39}$$
$$g_{i_{\mathrm{A}},i'_{\mathrm{A}},\ldots;j_{\mathrm{B}},j'_{\mathrm{B}},\ldots}g_{i-i_{\mathrm{A}},i'-i'_{\mathrm{A}},\ldots;j-j_{\mathrm{B}},j'-j'_{\mathrm{B}},\ldots}$$

where for ease of notation we have written:

$$\alpha=\sum_{k=i,i',\ldots}k-1\qquad\beta=\sum_{k=i,i',\ldots}k\qquad\gamma=\sum_{l=j,j',\ldots}l-1$$
$$\delta=\sum_{k=i,i',\ldots}k\bar{M}_{k_{\mathrm{A}}}\qquad\varepsilon=\sum_{l=j,j',\ldots}l\bar{M}_{l_{\mathrm{B}}}$$

Stockmayer[16] has given a compact form for the concentration of species in a multicomponent polymerization system of $\{\mathrm{A}_{f,i}\}+\{\mathrm{B}_{g,j}\}$ through classic combinatorial derivation. By referring to his result, we have a neat expression for the $g_{i,i',\ldots;j,j',\ldots}$ of equation (39). The new expression:

$$g_{i,i',\ldots;j,j',\ldots}=\prod_{k=i,i',\ldots}\frac{[\bar{M}_{k_{\mathrm{A}}}N^0(\bar{M}_{k_{\mathrm{A}}})]^k}{k!}\prod_{l=j,j',\ldots}\frac{[\bar{M}_{l_{\mathrm{B}}}N^0(\bar{M}_{l_{\mathrm{B}}})]^l}{l!}\left(\sum_{k=i,i',\ldots}\bar{M}_{k_{\mathrm{A}}}k\right)^{\gamma}\left(\sum_{l=j,j',\ldots}\bar{M}_{l_{\mathrm{B}}}l\right)^{\alpha} \tag{40}$$

is obtained in the limit of polymers having an infinite number of reactive groups. The percentage grafting conversion $f^{\mathrm{w}}_{\mathrm{A}}$ is related to $f_{\bar{M}^0_{\mathrm{A}}}$ by

$$f^{\mathrm{w}}_{\mathrm{A}}=1-\frac{\Sigma_{k=i,i',\ldots}M_{k_{\mathrm{A}}}C_{0,k,\ldots;0,0,\ldots}}{\bar{M}^0_{\mathrm{nA}}C^0_{\mathrm{A}}}$$
$$=1-\sum_{k=i,i',\ldots}\bar{M}_{k_{\mathrm{A}}}\bar{C}_{0,k,\ldots;0,0,\ldots}$$
$$=1-\sum_{k=i,i',\ldots}\bar{M}_{k_{\mathrm{A}}}N^0(\bar{M}_{k_{\mathrm{A}}})(1-f_{\bar{M}^0_{\mathrm{nA}}})^{\bar{M}_{k\mathrm{A}}} \tag{41}$$

Molecular-weight averages and gel point. The reduced *NAMW* and *WAMW* of the grafting system satisfy:

$$\frac{\bar{M}_{\mathrm{n}}}{\bar{M}_{\mathrm{n}}^{0}}=\frac{1+x}{\bar{C}_{\mathrm{T}}}=\frac{1+x}{1+x+\ln(1-f_{\bar{M}_{\mathrm{nA}}^{0}})} \tag{42}$$

$$\frac{\bar{M}_{\mathrm{w}}}{\bar{M}_{\mathrm{w}}^{0}}=\frac{1}{(\bar{M}_{\mathrm{wA}}^{0}/\bar{M}_{\mathrm{nA}}^{0})+x(\bar{M}_{\mathrm{wB}}^{0}/\bar{M}_{\mathrm{nB}}^{0})(\bar{M}_{\mathrm{nB}}^{0}/\bar{M}_{\mathrm{nA}}^{0})^{2}}$$
$$\times\sum_{i=0}^{\infty}\sum_{i'=0}^{\infty}\cdots\sum_{j=0}^{\infty}\sum_{j'=0}^{\infty}\cdots\left(\sum_{k=i,i',\ldots}k\bar{M}_{k_{\mathrm{A}}}+\frac{\bar{M}_{\mathrm{nB}}^{0}}{\bar{M}_{\mathrm{nA}}^{0}}\sum_{l=j,j',\ldots}l\bar{M}_{l_{\mathrm{B}}}\right)^{2}\bar{C}_{i,i',\ldots;j,j',\ldots} \tag{43}$$

Again, we can introduce a generating function to reduce equation (43) into a compact form. Let:

$$G=\sum_{i=0}^{\infty}\sum_{i'=0}^{\infty}\cdots\sum_{j=0}^{\infty}\sum_{j'=0}^{\infty}\cdots[A_i^iA_{i'}^{i'}\ldots B_j^jB_{j'}^{j'}\ldots\bar{C}_{i,i',\ldots;j,j',\ldots}(E)] \tag{44}$$

be the generating function in the polydisperse case, where:

$$E=-\ln(1-f_{\bar{M}_{\mathrm{nA}}^{0}}) \tag{45}$$

By multiplying equation (31) by $A_i^iA_{i'}^{i'}\ldots B_j^jB_{j'}^{j'}\ldots$ and summing for all the species, we have:

$$G_E=\frac{1}{x}\sum_m\sum_n\bar{M}_{A_m}\bar{M}_{B_n}A_mB_nG_{A_m}G_{B_n}-\sum_m\bar{M}_{A_m}A_mG_{A_m}$$
$$-\frac{1}{x}\sum_n\bar{M}_{B_n}B_nG_{B_n}\ (m=i,i',\ldots;\ n=j,j',\ldots) \tag{46}$$

The initial condition of equation (36) becomes:

$$G|_{E=0}=\sum_m A_mN^0(\bar{M}_{A_m})+x\sum_n B_nN^0(\bar{M}_{B_n}) \tag{47}$$

The system's *WAMW* is related, at $A_m=B_n=1$, to the generating function by:

$$\bar{M}_{\mathrm{w}}=\left(\sum_m M_{A_m}^2\partial(A_mG_{A_m})/\partial A_m+2\sum_m\sum_{m'}M_{A_m}M_{A_{m'}}G_{A_mA_{m'}}\right.$$
$$+2\sum_m\sum_n M_{A_m}M_{B_n}G_{A_mB_n}+2\sum_n\sum_{n'}M_{B_n}M_{B_{n'}}G_{B_nB_{n'}}$$
$$\left.+\sum_n M_{B_n}^2\partial(B_nG_{B_n})/\partial B_n\right)\left(\sum_m M_{A_m}G_{A_m}+\sum_n M_{B_n}G_{B_n}\right)^{-1} \tag{48}$$

We can solve the generating equation using the method of characteristics. We have from the generating function (see Appendix):

$$\frac{\bar{M}_{\mathrm{w}}}{\bar{M}_{\mathrm{w}}^{0}}=\left(1+x\frac{\bar{M}_{\mathrm{wB}}^{0}}{\bar{M}_{\mathrm{wA}}^{0}}\frac{\bar{M}_{\mathrm{nB}}^{0}}{\bar{M}_{\mathrm{nA}}^{0}}+2E\frac{\bar{M}_{\mathrm{wB}}^{0}}{\bar{M}_{\mathrm{nA}}^{0}}\right)$$
$$\times\left[\left(1+x\frac{\bar{M}_{\mathrm{wB}}^{0}}{\bar{M}_{\mathrm{wA}}^{0}}\frac{\bar{M}_{\mathrm{nB}}^{0}}{\bar{M}_{\mathrm{nA}}^{0}}\right)\left(1-\frac{E^2}{x}\frac{\bar{M}_{\mathrm{wA}}^{0}}{\bar{M}_{\mathrm{nA}}^{0}}\frac{\bar{M}_{\mathrm{wB}}^{0}}{\bar{M}_{\mathrm{nB}}^{0}}\right)\right]^{-1} \tag{49}$$

At the critical point of gelation we have

$$-\ln(1-f_{\bar{M}_{\mathrm{nA}}^{0}}^{\mathrm{cr}})=\left(\frac{x}{(\bar{M}_{\mathrm{wA}}^{0}/\bar{M}_{\mathrm{nA}}^{0})(\bar{M}_{\mathrm{wB}}^{0}/\bar{M}_{\mathrm{nB}}^{0})}\right)^{1/2} \tag{50}$$

$(f_{\mathrm{A}}^{\mathrm{w}})^{\mathrm{cr}}$ and $f_{\bar{M}_{\mathrm{nA}}^{0}}^{\mathrm{cr}}$ are related through equation (41). Equation (49) can be obtained from Stockmayer's expression[16] in the case of two reactive polymers having infinite number of reactive groups when percentage conversion is used as a measure of the extent of reaction. The result is different from Stafford's expression[28].

Average numbers of graft linkages on each polymer A segment of the graft copolymers

The average numbers of graft linkages on each polymer A segment of the graft copolymers ($\bar{n}_{\mathrm{A}}^{\mathrm{a}}$) is defined as:

$$\bar{n}_{\mathrm{A}}^{\mathrm{a}}=\frac{C_{\mathrm{a}}^{0}f_{\mathrm{a}}}{C_{\mathrm{A}}^{0}f_{\mathrm{A}}} \tag{51}$$

The conversion of reactive groups is related to the conversion of polymer A having a molecular weight of $\bar{M}_{\mathrm{nA}}^{0}$ by:

$$C_{\mathrm{a}}^{0}f_{\mathrm{a}}=-C_{\mathrm{A}}^{0}\ln(1-f_{\bar{M}_{\mathrm{nA}}^{0}}) \tag{52}$$

Substituting equation (52) into equation (51), we have:

$$\bar{n}_{\mathrm{A}}^{\mathrm{a}}=\frac{-\ln(1-f_{\bar{M}_{\mathrm{nA}}^{0}})}{f_{\mathrm{A}}} \tag{53}$$

DISCUSSION

Monodisperse reactive polymers

Table 1 lists the grafting conversion of polymer A at the gel point at different molar ratios. The gel point is delayed to higher grafting conversion as the molar ratio of polymer B to polymer A increases. Controlling the relative amount of A and B can be used as a means for regulating the grafting process.

Figure 2 shows the change of the reduced concentration of all graft copolymers with grafting reaction at different molar ratios. The plot in *Figure 2* stops at the gel point since equation (15) is valid only in the pre-gel region.

Table 1 Change of the critical grafting conversion of A with molar ratio

x	1.0	1.5	2.0	3.0	6.0	12.0
$f_{\mathrm{A}}^{\mathrm{cr}}$	0.63	0.71	0.76	0.82	0.91	0.97

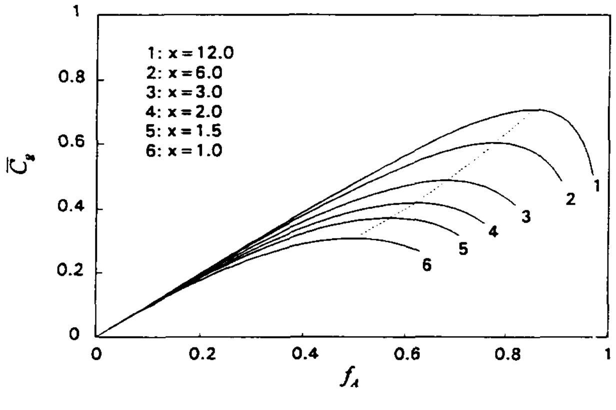


Figure 2 Reduced concentration of graft copolymers in relation to grafting conversion and molar ratio

The delay of the gel point with an increase of molar ratio is partly explained by the existence of more graft copolymers. The dotted curve in *Figure 2* corresponds to the maximum concentration of all graft copolymers at different molar ratios.

Figure 3 shows the change of the reduced *WAMW* with the grafting conversion of A. Controlling the *WAMW* of the system is more important since solution or melt viscosity is closely related to the *WAMW* of the system[10]. In equation (28), the *WAMW* is also a function of molecular weight ratio M_B/M_A of the two reactive polymers. This factor is less sensitive to the change of *WAMW* in comparison to molar ratio and grafting conversion. However, the composition of the system (w_A) is much affected by that ratio since w_A, x and M_B/M_A are related by:

$$x\frac{M_B}{M_A}=\frac{w_A}{1-w_A} \qquad (54)$$

From the discussion on monodisperse reactive polymers, two important things are found: (a) the grafting conversions of the reactive polymers are quite limited in order to avoid gelation; and (b) grafting reaction should be stopped long before the system starts to gel to avoid too high a *WAMW* of the reaction products.

Effect of polydispersity

The effect of polydispersity on the branching process comes from two factors: (a) polydispersity index (*PDI*); and (b) molecular-weight distribution function. It is important to point out that only the distribution function of polymer A is needed in reference to the percentage conversion of A.

Several known distribution functions are commonly used in the discussion of molecular-weight distributions of linear polymers. The two-parameter Schulz and the Wesslau (log-normal) distributions are two of the representative distribution functions[36]. The former has a theoretical basis; the latter has the feature of high-molecular-weight tail. The two distribution functions are:

$$\text{Schulz} \qquad W(M)=\frac{(-\ln a)^{b+2}}{\Gamma(b+2)}M^{b+1}a^M \qquad (55)$$

$$\text{Wesslau} \qquad W(M)=\frac{1}{\sigma\sqrt{\pi}M}\exp\left[-\frac{1}{\sigma^2}\ln^2\left(\frac{M}{M_p}\right)\right] \qquad (56)$$

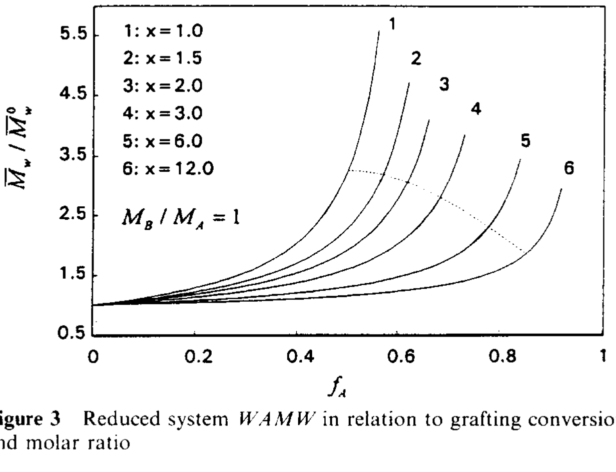


Figure 3 Reduced system *WAMW* in relation to grafting conversion and molar ratio

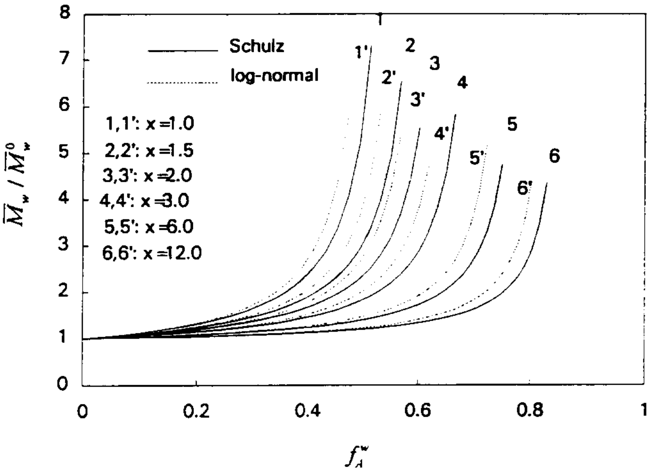


Figure 4 Reduced system *WAMW* of the Schulz and Wesslau (log-normal) distribution functions of *PDI* = 2 in relation to grafting conversion and molar ratio

Table 2 Effect of polydispersity of the reactive polymers on the critical grafting conversion of A at various molar ratio ($PDI_A = PDI_B$)

	PDI				
		Schulz		Log-normal	
x	1.0	2.0	3.0	2.0	3.0
1.0	0.63	0.56	0.54	0.52	0.47
1.5	0.71	0.61	0.59	0.58	0.53
2.0	0.76	0.66	0.63	0.62	0.56
3.0	0.82	0.71	0.68	0.68	0.61
6.0	0.91	0.80	0.77	0.77	0.70
12.0	0.97	0.87	0.83	0.84	0.78

The main objective here is to have a better understanding on the effect of polydispersity, and in particular the presence of a high-molecular-weight tail, on the branching process.

In the case of the Schulz distribution, f_A^w and $f_{\bar{M}_{nA}^0}$ are related analytically by:

$$-\ln(1-f_{\bar{M}_{nA}^0})=(b_A+1)[(1-f_A^w)^{1/(b_A+2)}-1] \qquad (57)$$

For the log-normal distribution, simple numerical calculation is needed for f_A^w and $f_{\bar{M}_{nA}^0}$ through the following equation:

$$f_A^w=1-\int_0^{\infty}(1-f_{\bar{M}_{nA}^0})^{M/\bar{M}_{nA}^0}W_A(M)\,\mathrm{d}M \qquad (58)$$

Table 2 lists the grafting conversions of A at the gel point for the Schulz distribution. The critical grafting conversion decreases with polydispersity if A and B have the same polydispersity index (*PDI*), i.e. at equal molar amounts of A and B, the critical grafting conversion is 63% for monodisperse polymer, but the critical grafting conversion is 56% at a *PDI* of 2.0, 54% at *PDI* of 3.0. The differences of critical grafting conversion are small when *PDI* increases from 2.0 to 3.0. In case of the log-normal distribution of A, the critical grafting conversion of A is reduced further in comparison to the Schulz distribution at the same *PDI*. The effect of *PDI*

Table 3 Effect of *PDI* of A on the critical grafting conversion of A at various molar ratio ($PDI_B = 1.0$)

	PDI				
		Schulz		Log-normal	
x	1.0	2.0	3.0	2.0	3.0
1.0	0.63	0.66	0.68	0.67	0.60
1.5	0.71	0.71	0.73	0.72	0.67
2.0	0.76	0.75	0.77	0.75	0.70
3.0	0.82	0.80	0.80	0.79	0.75
6.0	0.91	0.87	0.87	0.85	0.82
12.0	0.97	0.92	0.91	0.90	0.88

on critical conversion is far more sensitive with log-normal distribution. From equation (50), it is obvious that increasing the polydispersity of B will reduce the critical grafting conversion at fixed polydispersity of A. *Table 3* lists the critical conversion of A with monodisperse B. The effect of polydispersity of A alone is to increase the critical grafting conversion of A when the molar ratio is close to 1.0 and to decrease it when the molar ratio is much more than 1.0. The change of critical grafting conversion of polymer A depends on the polydispersities of both polymers, and also on composition. The critical grafting conversion is quite sensitive to the presence of a high-molecular-weight tail.

Figure 4 shows the reduced *WAMW* of the two distributions in relation to grafting conversion and molar ratio ($PDI = 2.0$). The molecular weight take-off is earlier for the log-normal distribution than for the Schulz distribution. The tailing in the log-normal distribution is responsible for it.

It is very desirable to take a look at the change of molecular-weight distribution with grafting reaction. The difference between the molecular-weight distribution of the graft copolymers and that of the remaining free A and B tends to widen as the grafting reaction continues. Unfortunately, simulating the change of molecular-weight distribution is not possible in a practical time limit.

Average numbers of graft linkages of each polymer A segment of the graft copolymers

In the case of the Schulz distribution, the average numbers of graft linkages $\bar{n}_A^a$ of each polymer A segment of the graft copolymers becomes:

$$\bar{n}_A^a = [(1-f_A^w)^{1/(b_A+2)} - 1]\frac{b_A+1}{1-(1-f_A^w)^{(b_A+1)/(b_A+2)}} \quad (59)$$

Numerical solution is needed for the log-normal distribution.

Figure 5 shows the average numbers of graft linkages of each polymer A segment of the graft copolymers for the two distributions in relation to the grafting conversion of A. We can see that the average number of functional groups consumed is less than 2.5 when the grafting conversion of A is below 80% by weight. Therefore, the amount of reactive groups consumed is very small. If the reactive groups on both A and B number 50, then at 80% conversion, the percentage conversion of reactive groups of the grafted chain is less than 5%. Therefore the numbers of reactive groups consumed can be neglected without causing much error in the approximation of polymer chains having an infinite number of reactive groups.

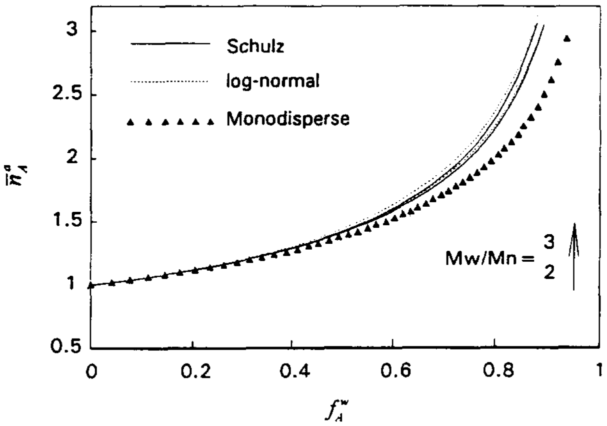


Figure 5 Increase of the average numbers of linkages on the polymer A chain of the graft copolymers with the grafting conversion of A

This study neglects the presence of intramolecular reactions that might be significant. The kinetic approach can be extended to take into account the presence of intramolecular reactions. A study of its effect on the branching process of our grafting system is shown separately.

CONCLUSIONS

We have developed a kinetic approach for quantifying the concentration of individual species and determining the molecular-weight averages and gel point in the grafting reaction of two reactive polymers having large numbers of reactive groups. The concentrations of polymer species are obtained by solving directly the kinetic equations. Generating functions are used to derive the expressions for the system's molecular-weight averages and condition of gelation.

A thorough discussion is given to look at the molecular characteristics of the defined grafting system. The analysis makes clear how the various parameters affect the branching process of the grafting system. It is concluded that the percentage conversions of the two reactive polymers are quite limited in order to avoid too high a *WAMW* of the reaction products. The presence of a high-molecular-weight tail in the polydisperse reactive polymers further limits the extent of grafting reaction.

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APPENDIX

In order to solve the first-order non-linear partial differential equations in the case of polydispersive reactive polymers, let us rearrange the partial differential equation into:

$$G_E=\frac{1}{x}\sum_m\sum_n \bar{M}_{A_m}\bar{M}_{B_n}A_mB_nG_{A_m}G_{B_n}-\sum_m \bar{M}_{A_m}A_mG_{A_m}$$

$$-\frac{1}{x}\sum_n \bar{M}_{B_n}B_nG_{B_n} \qquad \text{(A.1)}$$

$$(m=i,i',\ldots;\ n=j,j',\ldots)$$

The characteristic equations are:

$$\frac{\mathrm{d}A_m}{\mathrm{d}s}=A_m\bar{M}_{A_m}-A_m\bar{M}_{A_m}\sum_n B_n\bar{M}_{B_n}G_{B_n}/x \qquad \text{(A.2)}$$

$$\frac{\mathrm{d}B_n}{\mathrm{d}s}=\left(B_n\bar{M}_{B_n}-B_n\bar{M}_{B_n}\sum_m A_m\bar{M}_{A_m}G_{A_m}\right)/x \qquad \text{(A.3)}$$

$$\mathrm{d}E/\mathrm{d}s=1 \qquad \text{(A.4)}$$

$$\frac{\mathrm{d}G}{\mathrm{d}s}=-\left(\sum_m\sum_n \bar{M}_{A_m}\bar{M}_{B_n}A_mB_nG_{A_m}G_{B_n}\right)/x \qquad \text{(A.5)}$$

$$\frac{\mathrm{d}G_{A_m}}{\mathrm{d}s}=-\left(\bar{M}_{A_m}G_{A_m}-\bar{M}_{A_m}G_{A_m}\sum_n B_n\bar{M}_{B_n}G_{B_n}/x\right) \qquad \text{(A.6)}$$

$$\frac{\mathrm{d}G_{B_n}}{\mathrm{d}s}=-\left(\bar{M}_{B_n}G_{B_n}-\bar{M}_{B_n}G_{B_n}\sum_m A_m\bar{M}_{A_m}G_{A_m}\right)/x \qquad \text{(A.7)}$$

$$\mathrm{d}G_E/\mathrm{d}s=0 \qquad \text{(A.8)}$$

The initial conditions become:

$$s=0 \qquad E=0 \qquad A_m=\zeta_m \qquad B_n=\eta_n$$

$$G_{A_m}=N^0(\bar{M}_{A_m}) \qquad G_{B_n}=xN^0(\bar{M}_{B_n})$$

$$G=\sum_m\zeta_mN^0(\bar{M}_{A_m})+x\sum_n\eta_nN^0(\bar{M}_{B_n}) \qquad \text{(A.9)}$$

$$(m=i,i',\ldots;\ n=j,j',\ldots)$$

Solving equations (A.2)–(A.8), we have:

$$G=\sum_m\zeta_mN^0(\bar{M}_{A_m})+x\sum_n\eta_nN^0(\bar{M}_{B_n})$$

$$-E\sum_m\sum_n\zeta_m\eta_nN^0(\bar{M}_{A_m})N^0(\bar{M}_{B_n})\bar{M}_{A_m}\bar{M}_{B_n} \qquad \text{(A.10)}$$

$$A_m=\zeta_m\exp\left[\bar{M}_{A_m}E\left(1-\sum_n\eta_nN^0(\bar{M}_{B_n})\bar{M}_{B_n}\right)\right] \qquad \text{(A.11)}$$

$$B_n=\eta_n\exp\left[\frac{\bar{M}_{B_n}E}{x}\left(1-\sum_m\zeta_mN^0(\bar{M}_{A_m})\bar{M}_{A_m}\right)\right] \qquad \text{(A.12)}$$

$$G_{A_m}=\zeta_mN^0(\bar{M}_{A_m})/A_m \qquad \text{(A.13)}$$

$$G_{B_n}=x\eta_nN^0(\bar{M}_{B_n})/B_n \qquad \text{(A.14)}$$

$$(m=i,i',\ldots;\ n=j,j',\ldots)$$

Apparently $\zeta_m=\eta_n=1$ when $A_m=B_n=1$. By taking derivatives of equation (A.11) and equation (A.12) with respect to A_m and solving the resultant equations at $A_m=B_n=1$, we have:

$$\sum_m N^0(\bar{M}_{A_m})\bar{M}_{A_m}\frac{\partial\zeta_m}{\partial A_m}=\frac{N^0(\bar{M}_{A_m})\bar{M}_{A_m}}{1-E^2PDI_\mathrm{A}PDI_\mathrm{B}/x} \qquad \text{(A.15)}$$

$$\sum_n N^0(\bar{M}_{B_n})\bar{M}_{B_n}\frac{\partial\eta_n}{\partial A_m}=\frac{N^0(\bar{M}_{A_m})\bar{M}_{A_m}PDI_\mathrm{B}E}{x-E^2PDI_\mathrm{A}PDI_\mathrm{B}} \qquad \text{(A.16)}$$

By taking derivatives of equation (A.11) and equation (A.12) with respect to B_n and solving the resultant equations at $A_m=B_n=1$, we have:

$$\sum_m N^0(\bar{M}_{A_m})\bar{M}_{A_m}\frac{\partial\zeta_m}{\partial B_n}=\frac{N^0(\bar{M}_{B_n})\bar{M}_{B_n}PDI_\mathrm{A}E}{1-E^2PDI_\mathrm{A}PDI_\mathrm{B}/x} \qquad \text{(A.17)}$$

$$\sum_n N^0(\bar{M}_{B_n})\bar{M}_{B_n}\frac{\partial\eta_n}{\partial B_n}=\frac{N^0(\bar{M}_{B_n})\bar{M}_{B_n}}{1-E^2PDI_\mathrm{A}PDI_\mathrm{B}/x} \qquad \text{(A.18)}$$

$$(m=i,i',\ldots;\ n=j,j',\ldots;\ m'=i,i',\ldots;\ n'=j,j',\ldots)$$

Here PDI_A and PDI_B are the polydispersity indices of polymer A and polymer B. Equation (48) is equivalent to:

$$\bar{M}_w = \left[\sum_m M_{A_m}^2 G_{A_m} + \sum_m M_{A_m} \frac{\partial}{\partial A_m} \left(\sum_{m'} M_{A_{m'}} G_{A_{m'}} \right) + 2 \sum_m M_{A_m} \frac{\partial}{\partial A_m} \left(\sum_n M_{B_n} G_{B_n} \right) + \sum_n M_{B_n} \frac{\partial}{\partial B_n} \left(\sum_{n'} M_{B_{n'}} G_{B_{n'}} \right) + \sum_n M_{B_n}^2 G_{B_n} \right] \left(\sum_m M_{A_m} G_{A_m} + \sum_n M_{B_n} G_{B_n} \right)^{-1} \tag{A.19}$$

The partial derivatives in equation (A.19) are taken from equation (A.13) and equation (A.14). By substituting terms of equations (A.15)–(A.18) into equation (A.19) and with further manipulation, we arrive at the result of equation (49).

The results for monodisperse reactive polymers can be derived using the same procedures or from equation (49).

NOMENCLATURE

A, B	storage index of the generating function for monodisperse polymer A and B
A_m, B_n	storage index of the generating function for polydisperse polymer A and B
C_A^0, C_B^0	initial molar concentration of polymer A and B
$\bar{C}_g$	reduced concentration of graft copolymers
C_{ij}	molar concentration of polymer species containing i A chains and j B chains
$\bar{C}_{ij}$	reduced molar concentration of polymer species having i A chains and j B chains
$\bar{C}_T$	reduced concentration of all polymer species
$C_{i,i',\ldots;j,j',\ldots}$, $\bar{C}_{i,i',\ldots;j,j',\ldots}$	concentration of polymer species having $i,i',\ldots$ numbers of polymer A of different molecular weight and $j,j',\ldots$ numbers of polymer B of different molecular weight, and its reduced form
E	variable relating to grafting conversion of polydisperse polymer A
f_A	molar fraction of polymer A found in graft copolymers
f_A^{cr}	grafting conversion of A at gel point (molar basis)
f_A^w	grafting conversion of polymer A (weight basis)
$f_{\bar{M}_{nA}^0}$	grafting conversion of the reference free chain component of polymer A having a molecular weight equivalent to the number-average molecular weight of the initial A
$G(A,B,Z)$, G	generating function in case of monodisperse and polydisperse reactive polymers
G_I, ($I = A$, B, A_m, B_n, Z)	partial derivative of the generating function
M_A, M_B	molecular weight of monodisperse polymer A and B
$\bar{M}_{k_A}$, $\bar{M}_{l_B}$	reduced molecular weight of the free chain component of polymer A and polymer B
$\bar{M}_n$	number-average molecular weight of reaction product
$\bar{M}_n^0$	initial number-average molecular weight of reaction product
$\bar{M}_w$	weight-average molecular weight of reaction product
$\bar{M}_w^0$	initial weight-average molecular weight of reaction product
$N^0(\bar{M}_{k_A})$, $N^0(\bar{M}_{l_B})$	molar fraction of chain component of the initial polymer A having molecular weight of $\bar{M}_{k_A}$ and polymer B having molecular weight of $\bar{M}_{l_B}$
$\bar{n}_A^a$	average numbers of linkages of polymer A segment of the graft copolymers
P_{ij}^g, P_{ij}^c	fraction of grafting reaction for the respective generation and consumption of polymer species having i A chains and j B chains
$P_{i,i',\ldots;j,j',\ldots}^g$, $P_{i,i',\ldots;j,j',\ldots}^c$	probability of grafting reaction for the respective generation and consumption of species having $i,i',\ldots$ numbers of polymer A of different molecular weight and $j,j',\ldots$ numbers of polymer B of different molecular weight
w_A	weight fraction of polymer A in mixture of polymer A and polymer B
$W(M)$	weight-fraction molecular-weight distribution function
Z	variable relating to grafting conversion of monodisperse polymer A
r	grafting reaction rate of the system
x	molar ratio of polymer A to polymer B
ζ, η, ζ_m, η_n	implicit variables
$\Gamma(b+2)$	gamma function