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Effect of intramolecular reaction on the branching process of grafting reaction between two reactive polymers

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The kinetic formulation described in a previous paper has been extended to include intramolecular reaction. The extension includes the incorporation of spatial correlation among chain species caused by volume exclusion. The need for consideration of spatial correlation among polymer species is reflected in the self-consistency of the kinetic theory. We provide a general procedure to look into the effect of intramolecular reaction on the branching process. Under a certain approximation in our grafting system, we obtain exact expressions for the weight-average molecular weight and gel point of the system. A thorough discussion is given of the various parameters that are important to the extent of intramolecular reaction and the branching process. It is concluded that intramolecular reaction cannot be simply neglected in the grafting system, since gel point and weight-average molecular weight are fairly sensitive to the extent of intramolecular reaction.

(Keywords: spatial correlation; intramolecular reaction; molecular weight average)

INTRODUCTION

New polymer alloys with improved and desirable properties can be prepared by *in situ* generation of graft copolymer compatibilizer using solution grafting or reactive extrusion[1,2]. Graft copolymers can be produced by: (1) graft polymerization of monomer onto polymer backbones[3,4]; and (2) graft coupling reaction of two reactive polymers[5-7]. Both strategies will lead to a mixture of graft copolymers and ungrafted polymers. In the second scheme, the graft coupling reaction can be classified into three categories according to the numbers of reactive groups on the backbones of the two reactive polymers: (a) one or two reactive groups on both polymers, (b) one or two reactive groups on one polymer and numerous reactive groups on the other polymer, and (c) numerous reactive groups on both polymers. The most complex graft copolymer structures will be produced in the last case. Gelation will occur at a certain extent of grafting reaction.

This work focuses on the effect of intramolecular reaction on the branching process of the graft coupling system of polymers A and B both having a large number of reactive groups (a and b, a reacts with b only). Intramolecular reactions are defined as reactions that happen within any graft copolymer. An example is the graft coupling between cellulose acetate (CA: degree of substitution = 2.45) and styrene maleic anhydride random copolymer (SMA). Intramolecular reactions happen between the hydroxyl and anhydride within any graft copolymer. As a good approximation, the number of reactive groups on both polymers can be considered as infinite so far as the grafting reaction is concerned[8].

BACKGROUND LITERATURE

Theoretical analyses of some monomer polymerization systems and numerous experimental observations indicate that intramolecular reactions account for a finite fraction of the total reaction that delays the growth of molecular weight and the onset of gelation[9-21]. Studies concerned with intramolecular reaction (cyclization) have been mainly on RA_2+RB_f, RA_f ($f=3$-5) systems (condensation polymerization or free-radical polymerization), for example oxypropylene triol and hexamethylene diisocyanate, epoxides and amines, vinyl and divinyl. The properties of the network material formed can be markedly affected by these reactions[17-19,22].

Jacobson and Stockmayer[11] derived the probability and the extent of ring formation in the polymerization of a difunctional monomer using Gaussian conformational statistics for the growing chain. Their theory was further developed by Kilb[13] and applied to polycondensation of an f-functional monomer with a difunctional monomer to predict the gel point in an approximate manner. Frisch[12] gave a slightly different expression for the gel point in the same system. Stepto examined the theories of Kilb and Frisch experimentally, and gave a more accurate condition for the gel point in an RA_2+RB_f system[16,23]. Statistical methods are used in deriving the equations for the gel point in those theories. No attention is paid to the molecular weight averages of

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*To whom correspondence should be addressed at: Midwest Grain Products, Inc., 1300 Main, Atchison, KS 66002-0130, USA these systems. The problem with these theories is that the physical meaning of the model parameters defined in the theories is not clearly defined.

The kinetic approach has been extended to include intramolecular reactions in a non-linear polymerization system[24]. In a self-polymerization, the rate of intramolecular reaction is written as

$$r^{\mathrm{cyc}}_{n,j} = k\bar{Z}_{n,j}[C_{n,j}] \tag{1}$$

where $\bar{Z}_{n,j}$ is the probability that a molecule of chain length n undergoes cyclization by intramolecular reaction of two functional groups separated by j repeat units. Monte Carlo simulation[24] was developed to look at the value of $\bar{Z}_{n,j}$ in relation to n and j. Kumar *et al.*[20] made distinctions of the same molecular weight chain with different ring numbers. Kinetic equations were written out with additional balance equations for those ring species. A numerical method was used to determine the effect of the intramolecular reaction. Several studies have also described the details of the probability of intramolecular cyclization for the vinyl–divinyl polymerization system[18,25,26]. The terms 'primary cyclization' and 'secondary cyclization' were used to distinguish different types of cyclizations. Tobita and Hamielec[25], Dotson *et al.*[26] and Zhu *et al.*[27] derived expressions for the probability of primary cyclization and secondary cyclization. Dotson *et al.*[26] gave a qualitative discussion on the incorporation of intramolecular reaction into the recursive method.

Despite extensive studies conducted on the influence of intramolecular reaction in several monomeric polymerization systems, there is still a lack of a general procedure in a complete sense. Also missing is the presence of spatial correlation among polymer species when we consider the presence of intramolecular reactions. The system has to be moved away from the ideal case of complete randomness because of the excluded volume effect, that is, the collisions leading to intramolecular reaction cannot lead to intermolecular reactions at the same time. Every polymer species creates its own local environment and probably causes the non-uniformity of the system as a whole. As a first-order approximation, the composition of polymer species can still be considered as uniform down to the scale of the polymer species. At the extreme of high probability of intramolecular reaction, there can be compositional heterogeneity. So far, no attention has been paid to such a stochastic correlation in both the statistical and kinetic approaches.

PRESENT WORK

Graft coupling reaction of our system[8] starts with long-chain reactive polymers. The large numbers of reactive groups on the two reactive polymers call for an analysis of the extent of intramolecular reaction of the graft copolymers. It turned out to be a good system for us to study the effect of intramolecular reaction on the branching process. Monodisperse reactive polymers are considered.

THEORETICAL DEVELOPMENTS

Probability of intramolecular reaction

The probability of intramolecular reaction is different for different graft copolymers. The probability of intramolecular reaction for a reaction group depends on its location on the chain segment and the position of grafting linkage. For a graft copolymer, it is an average of all the reactive groups on the graft copolymer. It is further an average over all the structural isomers of a graft copolymer if no distinction is made between the structural isomers in the kinetic expression. Such a mean approach simplifies mathematical description, otherwise the numbers of kinetic equations will be vastly increased. In the following development we use such a simplification.

There is a statistically equivalent mean volume (from the probability of intramolecular reaction) if we focus on one chain segment of a graft copolymer. The local environment around the chain segment of the graft copolymer is sketched conceptually in *Figure 1*, by considering (a) every ungrafted chain and every chain segment of the graft copolymer as a structural unit and (b) clustering solvent molecules as clusters having the total volume of solvent that existed in that mean volume. Such clustering is intended to make the concept more straightforward. The probability of intramolecular reaction for the central unit A is obtained by counting the B units surrounding it, how many of them are connected to it and how many of them are not. The same is true for the probability of intramolecular reaction of the central unit B. The equivalent numbers of structural units of that coordination ball depend on chain configuration and dilution.

Figure 2 illustrates the naming of structural units. Units of the other type connected directly to the focused unit in the centre are called first neighbours, units of the other type connected next to the focused unit are called second neighbour, and so forth. The units connected directly to the central unit have more chance to react intramolecularly than units not directly connected to it. The probability of intramolecular reaction is different locally for the centre of interest of structural unit A or B on the same graft copolymer.

Mean probabilities of intramolecular reaction of the chain segments of a simple graft copolymer. Let us look first at the mean probability of intramolecular reaction of a simple graft copolymer (one A chain and one B chain) before arriving at the general expression for the probability of intramolecular reaction of any graft

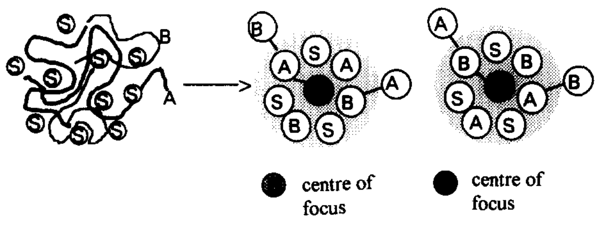

Figure 1 2D model representation of the macroscopic environment of a graft copolymer. S: solvent clusters; A: chain A; B: chain B

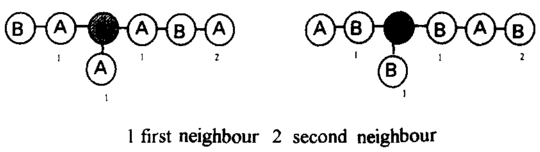

Figure 2 Naming of the chain segments of a graft copolymer

copolymer. Let us assume for the sake of simplicity that the constitutional units on chain A and B have the same volume and the same chain flexibility. Let n_A, n_B be the total moles of polymer A and polymer B, N_A, N_B be the total number of constitutional units on chains A and B, N_a, N_b the numbers of constitutional units each bearing one reactive group a and b, φ_a, φ_b and φ_s the number fractions of constitutional units having reactive groups a and b excluding solvent and the equivalent number fraction of solvent in the system, v_A and v_B the numbers of constitutional units carried by each reactive group of chains A and B respectively ($v_A = N_A/N_a$, $v_B = N_B/N_b$). Both v_A and v_B are equal to one when each constitutional unit has one reactive group. *Figure 3* illustrates the structure of one isomer of a simple graft copolymer.

Let $P^k_{a_ib_j}$ be the probability of an a_i reactive group meeting with a b_j reactive group for the k type isomer, $\bar{P}_a$ the mean probability of $\{a_i\}$ reactive groups meeting with $\{b_j\}$ reactive groups, $\bar{P}_b$ the mean probability of $\{b_j\}$ reactive groups meeting with $\{a_i\}$ reactive groups for the simple graft copolymer. We have

$$\bar{P}_a = \frac{\sum_{k=1}^{n_{iso}} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} P^k_{a_ib_j}}{N_a n_{iso}} \qquad (2)$$

$$\bar{P}_b = \frac{\sum_{k=1}^{n_{iso}} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} P^k_{a_ib_j}}{N_b n_{iso}} \qquad (3)$$

where n_{iso} is the total number of isomers of a simple graft copolymer. It is assumed here that there is an equal probability of the formation of any particular isomer. If we define Z as the number of constitutional units in the coordination sphere surrounding a constitutional unit, the mean probabilities of intramolecular reaction for chains A and B of the simple graft copolymer become

$$\lambda^A_{11} = \frac{\bar{P}_a}{Z\varphi_b} \qquad (4)$$

$$\lambda^B_{11} = \frac{\bar{P}_b}{Z\varphi_a} \qquad (5)$$

where

$$\varphi_a = \frac{N_a}{N_A + N_B x}(1 - \varphi_s) \qquad (6)$$

$$\varphi_b = \frac{N_b x}{N_A + N_B x}(1 - \varphi_s) \qquad (7)$$

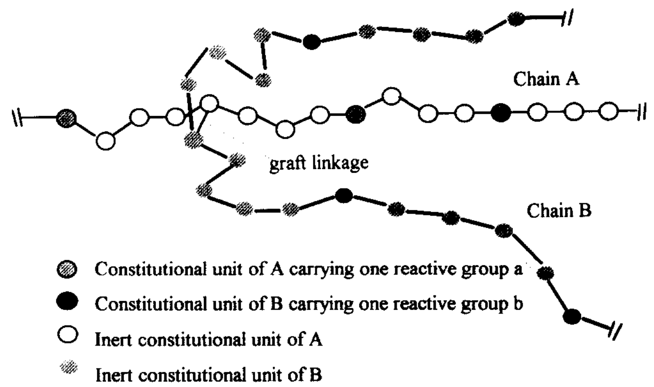

Figure 3 Structure of one isomer of a simple graft copolymer

and subscript 11 stands for one A chain and one B chain. In writing down equations (4)–(7) we have assumed that there is no compositional heterogeneity down to the scale of the surroundings of a constitutional unit. Such an assumption is valid unless there is a very high degree of branching or excluded volume effect. If we define

$$\Theta_A = 1/\lambda^A_{11} \qquad (8)$$

$$\Theta_B = 1/\lambda^B_{11} \qquad (9)$$

we have

$$\Theta_B = x\Theta_A \qquad (10)$$

where x is the molar ratio defined by

$$x = n_B/n_A \qquad (11)$$

Therefore we know that Θ_A and Θ_B are the numbers of chains A and B in the statistically equivalent mean volume including segment A and segment B of the simple graft copolymer.

Mean probabilities of intramolecular reaction of the chain segments of any graft copolymer. On the basis of equations (4) and (5) and the definition of Θ_A and Θ_B we can do a simple computation and generalize the mean probabilities of intramolecular reaction λ^A_{ij} and λ^B_{ij} of any graft copolymer into

$$\lambda^A_{ij} = \frac{(i+j-1)/i}{\Theta_B}(1 + \delta_2 + \delta_3 + \cdots) \qquad (12)$$

$$\lambda^B_{ij} = \frac{(i+j-1)/j}{\Theta_A}(1 + \delta_2 + \delta_3 + \cdots) \qquad (13)$$

δ_2, δ_3... are contributions from the second neighbour and the third neighbour, and so forth. Equations (12) and (13) are obtained under the assumption of an independent Gaussian distribution for each chain segment of the graft copolymer. The ring effect is not considered. There is a certain amount of error associated with the above two equations.

System probability of intramolecular reaction. The contribution to the system probability of intramolecular reaction for a graft copolymer λ_{ij} is independent of whether chain A or chain B is focused upon. It satisfies

$$\lambda_{ij} = i\bar{C}_{ij}\lambda^A_{ij} = \frac{j\bar{C}_{ij}}{x}\lambda^B_{ij} \qquad (14)$$

The system probability of intramolecular reaction λ satisfies

$$\lambda = \sum_{ij} \lambda_{ij} \qquad (15)$$

Equation (14) will always hold no matter how the species probability of intramolecular reaction of the chain segment is modelled.

Kinetic formulation

Intramolecular reaction does not contribute to the growth in molecular weight of the system. It has to be excluded in the kinetic equations that describe the development of polymer species. The kinetic equation in the presence of intramolecular reaction has the general form

$$\frac{d\bar{C}_{ij}}{dE}=P^{g}_{ij}-P^{c}_{ij} \qquad (16)$$

$$E=-\ln(1-f_{A}) \qquad (17)$$

which is the same as in the case of no intramolecular reaction[8].

The difference in volume exclusion among polymer species results in spatial correlation among them. Such spatial correlation has to be considered in the kinetic description to keep it self-consistent. The probabilities for the generation and consumption of individual species including the probability of intramolecular reaction are formulated as

$$P^{g}_{ij}=\frac{1}{2x}\sum_{k=0}^{i}\sum_{l=0}^{j}[k(j-l)(1-\lambda^{A}_{kl})(1-\lambda^{B}_{(i-k)(j-l)})\beta + l(i-k)(1-\lambda^{B}_{kl})(1-\lambda^{A}_{(i-k)(j-l)})\beta]\bar{C}_{kl}\bar{C}_{(i-k)(j-l)} \qquad (18)$$

$$P^{c}_{ij}=\frac{1}{x}[i\bar{C}_{ij}(1-\lambda^{A}_{ij})x+j\bar{C}_{ij}(1-\lambda^{B}_{ij})] \qquad (19)$$

where

$$\beta=\frac{1}{\sum_{pq}(1-\lambda^{A}_{pq})p\bar{C}_{pq}}=\frac{1}{\sum_{pq}(1-\lambda^{B}_{pq})q\bar{C}_{pq}/x}=\frac{1}{1-\lambda} \qquad (20)$$

β is a normalization factor that reflects the disturbance of species distribution away from complete randomness, due to differences in volume exclusion among polymeric species. The spatial correlation is thus included in equations (18) and (19). The kinetic expression is self-consistent only after we have incorporated the spatial correlation through such a normalization procedure. It is consistent that, in summing the concentration of each polymer species, the change of total polymer concentration satisfies equation (31), which is arrived at directly from the definition of the system probability of intramolecular reaction.

Weight-average molecular weight (WAMW) and gel point

Equations (16)–(20) complete the description of the grafting process taking into account the presence of intramolecular reactions. From a control point of view, we need to know the gel point and the system molecular weight averages, particularly the weight-average molecular weight. Under some approximation, we can have a detailed discussion on the effect of intramolecular reaction on the gel point and the WAMW of the grafting system without the need for numerical simulation. Let us assume that the probability of intramolecular reaction comes mainly from the first neighbour in our system. Under such simplification, we can introduce a generating function to avoid numerical simulation. Both gel point and molecular weight averages are obtained in a closed form.

Let us define the generating function as

$$G(A,B,E)=\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}A^{i}B^{j}\bar{C}_{ij}(E) \qquad (21)$$

$\bar{C}_{ij}(E)$ is the reduced concentration as defined in a previous publication[8]. By multiplying equation (16) by $A^{i}B^{j}$ and summing all i and j, we can convert equation (16) into a non-linear first-order partial differential equation

$$\begin{aligned}F=G_{E}+AG_{A}+\frac{1}{x}BG_{B}-\frac{2}{\Theta_{B}}(AG_{A}+BG_{B}-G)\\ -\frac{\beta}{x}[AG_{A}BG_{B}-(AG_{A}BG_{B}+A^{2}G_{A}^{2}-AG_{A}G)/\Theta_{A}\\ -(AG_{A}BG_{B}+B^{2}G_{B}^{2}-BG_{B}G)/\Theta_{B}\\ +(AG_{A}+BG_{B}-G)^{2}/\Theta_{A}\Theta_{B}]=0\end{aligned} \qquad (22)$$

The initial condition of equation (22) satisfies

$$G(A,B,0)=A+xB \qquad (23)$$

G_{E}, G_{A}, G_{B} are partial derivatives. We can convert the first-order non-linear partial differential equation into a series of characteristic ordinary differential equations using the method of characteristics. The characteristic ordinary differential equations cannot be solved in a compact form. We can, however, obtain the solution in a serial form.

The WAMW is defined as

$$\bar{M}_{W}=\frac{\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}(iM_{A}+jM_{B})^{2}\bar{C}_{ij}}{M_{A}+xM_{B}} \qquad (24)$$

By expanding the square term and recalling the definition of generating function, we have

$$\frac{\bar{M}_{W}}{\bar{M}^{0}_{W}}=\frac{\frac{\partial}{\partial A}(AG_{A})+2\frac{M_{B}}{M_{A}}G_{AB}+\left(\frac{M_{B}}{M_{A}}\right)^{2}\frac{\partial}{\partial B}(BG_{B})}{1+x(M_{B}/M_{A})^{2}} \qquad (25)$$

in its reduced form at $A=B=1$. We see from equation (25) that expressions for AG_{A}, AG_{B} instead of G are needed to get an expression for the reduced WAMW.

We can write the expressions for AG_{A} and BG_{B} into serial forms of the Taylor expansion (see appendix for explanation):

$$\begin{aligned}AG_{A}=\zeta\Bigg[1+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^{i}E^{j}a_{ij}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^{i}E^{j}b_{ij}\\ +\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^{i}(\eta-1)^{j}E^{k}c_{ijk}\Bigg]\end{aligned} \qquad (26)$$

$$\begin{aligned}BG_{B}=x\eta\Bigg[1+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^{i}E^{j}a_{ij}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^{i}E^{j}b_{ij}\\ +\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^{i}(\eta-1)^{j}E^{k}c_{ijk}\Bigg]\end{aligned} \qquad (27)$$

ζ and η are functions of A, B and E. Other terms in the general Taylor series should not exist for this particular case. Such expressions are deduced from the characteristic equations. The first two coefficients of $\{a_{1j}\}$ and $\{b_{1j}\}$ are found to be:

$$a_{11}=b_{11}=\frac{1}{\Theta_{B}} \qquad (28)$$

$$a_{12}=b_{12}=-\frac{1}{2\Theta_{B}^{2}}+\frac{1+x}{\Theta_{B}^{3}} \qquad (29)$$

The coefficients of the series decrease rapidly with Θ_{B}. Retaining a few terms is often enough for representing the whole series when Θ_{B} is large. The reduced WAMW is related further to $\zeta_A, \zeta_B, \eta_A, \eta_B$ at $A=B=1$. We also have

$$\zeta|_{A=B=1}=\eta|_{A=B=1}=1 \tag{30}$$

We see from equation (30) that only terms with coefficients $\{a_{1j}\}$ and $\{b_{1j}\}$ are actually needed for calculating WAMW.

In order to obtain the coefficients as well as ζ_A, ζ_B, η_A, η_B at $A=B=1$, we need to obtain the expression of β (equation (22)) in relation to E. Although the functional form of $\beta(E)$ is contained in the characteristic equations, it can be derived separately. From the consideration of reduced total molar concentration, we have in the case of grafting reaction with intramolecular reaction

$$\frac{\mathrm{d}\bar{C}_T}{\mathrm{d}E}=-(1-\lambda) \tag{31}$$

where $\bar{C}_T$ is the reduced concentration of all polymer species (see definition in ref. 8). With the approximation of first neighbour contribution only to the probability of intramolecular reaction, we have from equations (12)–(15)

$$\lambda=(1+x-\bar{C}_T)/\Theta_B \tag{32}$$

By substituting equation (32) into equation (31) and solving with the initial condition $\bar{C}_T(0)=1+x$, we have

$$\bar{C}_T=1+x+\Theta_B(e^{-E/\Theta_B}-1) \tag{33}$$

Substituting equation (33) into equation (32), we have

$$\lambda=1-e^{-E/\Theta_B} \tag{34}$$

We have from the definition of β

$$\beta=e^{E/\Theta_B} \tag{35}$$

The correctness of equations (33) and (35) can be verified directly from one of the characteristic equations in the appendix (equation (A13)).

With the expression of $\beta(E)$ beforehand, we have at $A=B=\zeta=\eta=1$

$$\zeta_A=\frac{\tilde{B}(\tilde{L}+\tilde{F}\tilde{K}/\tilde{A})+\tilde{K}(\tilde{E}-\tilde{F}\tilde{B}/\tilde{A})}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{36}$$

$$\eta_A=\frac{\tilde{F}\tilde{K}+\tilde{A}\tilde{L}}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{37}$$

$$\zeta_B=\frac{\tilde{B}(\tilde{D}+\tilde{F}\tilde{C}/\tilde{A})+\tilde{C}(\tilde{E}-\tilde{F}\tilde{B}/\tilde{A})}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{38}$$

$$\eta_B=\frac{\tilde{F}\tilde{C}+\tilde{A}\tilde{D}}{\tilde{A}\tilde{E}-\tilde{F}\tilde{B}} \tag{39}$$

where

$$\tilde{A}=1+\tilde{c}\int_0^E \beta\,\mathrm{d}E-\tilde{b}\int_0^E \beta\sum_{i=1}^{\infty} a_{1i}E^i\,\mathrm{d}E \tag{40a}$$

$$\tilde{B}=\tilde{a}\int_0^E \beta\,\mathrm{d}E+\tilde{b}\int_0^E \beta\sum_{i=1}^{\infty} b_{1i}E^i\,\mathrm{d}E \tag{40b}$$

$$\tilde{C}=\tilde{o}\int_0^E \beta\,\mathrm{d}E \tag{40c}$$

$$\tilde{D}=1+\tilde{g}\int_0^E \beta\,\mathrm{d}E \tag{40d}$$

$$\tilde{E}=1+\tilde{n}\int_0^E \beta\,\mathrm{d}E-\tilde{r}\int_0^E \beta\sum_{i=1}^{\infty} b_{1i}E^i\,\mathrm{d}E \tag{40e}$$

$$\tilde{F}=\tilde{q}\int_0^E \beta\,\mathrm{d}E+\tilde{r}\int_0^E \beta\sum_{i=1}^{\infty} a_{1i}E^i\,\mathrm{d}E \tag{40f}$$

$$\tilde{K}=1+\tilde{d}\int_0^E \beta\,\mathrm{d}E \tag{40g}$$

$$\tilde{L}=\tilde{p}\int_0^E \beta\,\mathrm{d}E \tag{40h}$$

$$\tilde{a}=1-(1+x)/\Theta_B+2x/\Theta_B^2 \tag{41a}$$

$$\tilde{b}=1-(3+x)/\Theta_B+2(1+x)/\Theta_B^2 \tag{41b}$$

$$\tilde{c}=\tilde{a}-\tilde{b} \tag{41c}$$

$$\tilde{d}=1/\Theta_B-2/\Theta_B^2 \tag{41d}$$

$$\tilde{g}=1/\Theta_B-2x/\Theta_B^2 \tag{41e}$$

$$\tilde{n}=2/\Theta_B-2x/\Theta_B^2 \tag{41f}$$

$$\tilde{o}=x\tilde{d} \tag{41g}$$

$$\tilde{p}=\tilde{g}/x \tag{41h}$$

$$\tilde{q}=\tilde{a}/x \tag{41i}$$

$$\tilde{r}=\tilde{q}-\tilde{n} \tag{41j}$$

$\partial(AG_A)/\partial A$, $\partial(BG_B)/\partial B$, G_{AB} are related to $\zeta_A, \zeta_B, \eta_A, \eta_B$ by

$$\frac{\partial}{\partial A}(AG_A)=\left(1+\sum_{i=1}^{\infty} a_{1i}E^i\right)\zeta_A+\eta_A\sum_{i=1}^{\infty} b_{1i}E^i \tag{42}$$

$$\frac{\partial}{\partial B}(BG_B)=x\left(1+\sum_{i=1}^{\infty} b_{1i}E^i\right)\eta_B+x\zeta_B\sum_{i=1}^{\infty} a_{1i}E^i \tag{43}$$

$$\begin{aligned}G_{AB}&=\frac{\partial}{\partial B}(AG_A)=\frac{\partial}{\partial A}(BG_B)\\&=\left(1+\sum_{i=1}^{\infty} a_{1i}E^i\right)\zeta_B+\eta_B\sum_{i=1}^{\infty} b_{1i}E^i\\&=x\left(1+\sum_{i=1}^{\infty} b_{1i}E^i\right)\eta_A+x\zeta_A\sum_{i=1}^{\infty} a_{1i}E^i\end{aligned} \tag{44}$$

at $A=B=\zeta=\eta=1$. The reduced WAMW of equation (25) is calculated with the results of equations (36)–(44). The common denominator associated with the WAMW connects to the condition of gelation:

$$\tilde{A}\tilde{E}-\tilde{F}\tilde{B}=0 \tag{45}$$

We have thus obtained the condition of gelation and expressions for the WAMW and probability of intramolecular reaction of the system. The results reduce to the situation of grafting with no intramolecular reaction if Θ_B (or Θ_A) goes to infinity.

Model parameter in relation to chain characteristics and dilution

Θ_B is related to chain characteristics and dilution by (from equations (5) and (9))

$$\Theta_B=\frac{xZN_aN_bn_{iso}(1-\varphi_s)}{(N_A+N_Bx)\sum_{k=1}^{n_{iso}}\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}P^k_{a_ib_j}} \tag{46}$$

For chains of Gaussian distribution, we have

$$P^k_{a_ib_j}\approx\left(\frac{3}{2\pi N_{a_ib_j}b^2}\right)^{3/2}V_{sphere} \tag{47}$$

where $N_{a_ib_j}$ are the numbers of statistical equivalent units between the two reactive groups, b is the length of the statistically equivalent unit and V_{sphere} is the volume of the coordination sphere. The exponential term is omitted since it is very close to that for large $N_{a_ib_j}$. Let the radius of the coordination sphere l be expressed by

$$l = kb \tag{48}$$

The volume of the coordination sphere becomes

$$V_{\text{sphere}} = \frac{4}{3}\pi k^3 b^3 \tag{49}$$

By substituting equation (49) into equation (48), we have

$$P^k_{a_ib_j} \approx 1.38 k^3 N_{a_ib_j}^{-3/2} \tag{50}$$

We see from equation (50) that the effect of chain flexibility is reflected in k. k is related to fixed bond angle, rotational potential barrier and steric interactions resulting in the interdependence of rotations about neighbouring bonds[28]. The statistical equivalent numbers of structural units satisfy

$$N_{a_ib_j} = k(iv_a + jv_b) \tag{51}$$

Let $\bar{S}(N_a, N_b, v_b/v_a)$ be the average of the double summation taken over all the isomers. We have

$$S(N_a, N_b, v_b/v_a) = \frac{1}{n_{\text{iso}}} \sum_{k=1}^{n_{\text{iso}}} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \left(i + \frac{v_b}{v_a} j\right)_k^{-1.5} \tag{52}$$

By counting the numbers of isomers, we have for even numbers of N_a, N_b

$$n_{\text{iso}} = (N_a/2 + 1)(N_b/2 + 1) \tag{53}$$

Equation (46) becomes

$$\Theta_B = \frac{xZ(1-\varphi_s)v_a^{0.5}}{1.38k^{1.5}\left(\frac{1}{N_b} + x\frac{v_b}{v_a}\frac{1}{N_a}\right)\bar{S}(N_a, N_b, v_b/v_a)} \tag{54}$$

RESULTS AND DISCUSSION

Order of magnitude of Θ_B

Several qualitative conclusions are deduced from equation (54). (a) Θ_B is directly proportional to dilution in a theta solvent. A good solvent expands the coil, it results in a smaller k value and therefore higher Θ_B. (b) Θ_B is very sensitive to the flexibility of the chain, this is shown by the 1.5 power dependence. (c) Θ_B increases with the numbers of inert units on the chain, but the influence of inert spacing on Θ_B is much less sensitive than chain flexibility. (d) The change in molar ratio also affects Θ_B; Θ_B increases with x. (e) The numbers of reactive groups on chain A and chain B affect Θ_B. The numbers of reactive groups on chain A and chain B are perhaps the most important parameter since they connect to the dimensions of chain A and chain B. Apparently, many factors contribute to Θ_B. A complete discussion of the various factors and their combinations is cumbersome. The importance of equation (54) is in estimating the order of magnitude of Θ_B given the assumptions that have been made in arriving at the equation.

Special case: $N_A = N_B$, $v_a = v_b$. Let us look at a special case of equal numbers of reactive groups and inert spacing on chain A and chain B. Let

$$\Theta = \Theta_A + \Theta_B \tag{55}$$

We see from equations (10) and (54) that Θ is independent of x. We can, therefore, choose Θ as the model parameter and see the effect of molar ratio on a common basis.

A particular set of parameters is chosen for a semi-quantitative estimation of the change of Θ value with the numbers of reactive groups, the parameters are:

$$v_a = v_b = 10;\ \varphi_s = 0;\ z = 12;\ k = 1.0$$

The selection for the coordination number is 12. No ring size prohibition is needed in the calculation of Θ since the smallest ring will contain 20 constitutional units for the particular set of parameters[26].

Figure 4 shows the change of Θ with N (reactive groups on chain A or chain B) of a random flight chain in the absence of solvent. Θ increases with N. Therefore the probability of intramolecular reaction decreases with increasing numbers of reactive groups on the chains. Θ falls in the range 50–160 for the numbers of N selected. Flory has given an accurate calculation of the reduced mean-square end-to-end distance ($\langle r\rangle^2/nl^2$) for several polymers in the unperturbed state, following his complete theory of Rotational Isomeric State (RIS)[29]. It has the value of 6 for polyethylene, 8 for syndiotactic poly(methyl methacrylate) (PMMA) and 10 for isotactic PMMA in the asymptotic limit of coarse-grained Gaussian chain[30]. The corresponding k is equal to 1/6, 1/8 and 1/10 respectively. Θ increases to 370–2350 if we choose k to be 1/6. It drops back to the range 40–235 for a tenfold dilution (φ_s can be considered as volume fraction as a first approximation) in solution grafting reaction and 20–120 for a 20-fold dilution. The above analysis is based purely on the assumptions of long-chain Gaussian distribution. Such a semi-quantitative analysis is good at least for estimating the order of magnitude of Θ. In a broader sense, we select Θ in the range 10–100. It is very important to point out that the mean probability of intramolecular reaction decreases with chain length.

Probability of intramolecular reaction, gel point and WAMW

Figure 5 shows that the probability of intramolecular reaction of the system increases exponentially with the grafting conversion of polymer A. The system probability of intramolecular reaction decreases as x increases.

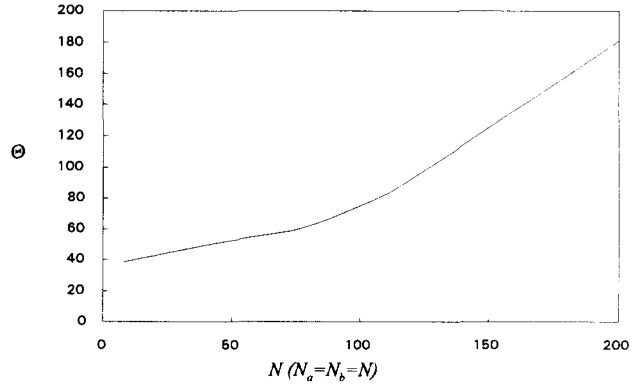

Figure 4 Model parameter Θ in relation to the numbers of reactive groups on chains A and B

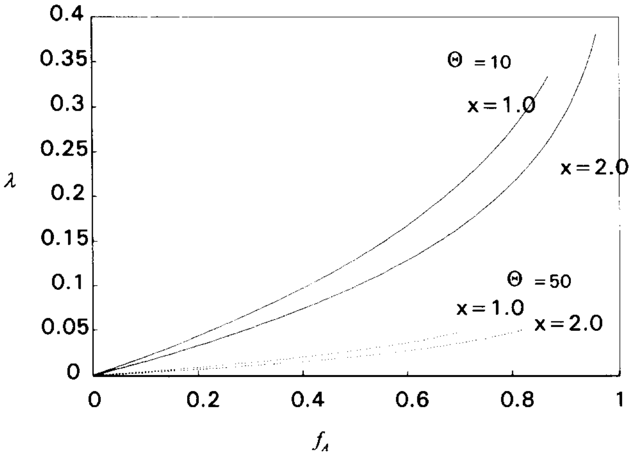

Figure 5 System probability of intramolecular reaction in relation to grafting conversion of polymer A and molar ratio

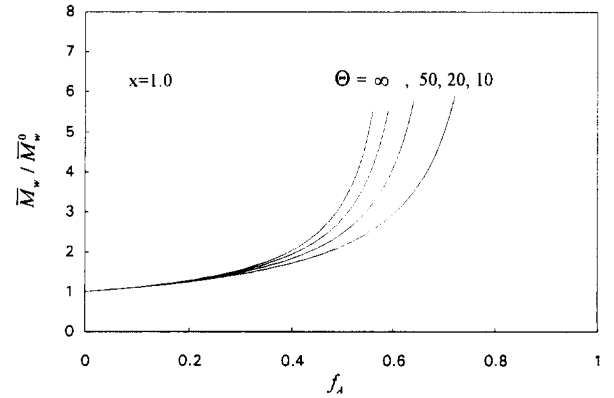

Figure 6 Reduced WAMW in relation to grafting conversion at different Θ with equal molar amounts A and B

Table 1 Effect of Θ on the critical point of grafting conversion at two molar ratios

	f_w^{cri} for Θ =			
x	∞	50	20	10
1.0	0.63	0.67	0.73	0.82
2.0	0.76	0.80	0.85	0.93

Table 2 System probability of intramolecular reaction at f_A^{cri}

	λ at Θ =			
x	∞	50	20	10
1.0	0.0	0.039	0.123	0.290
2.0	0.0	0.047	0.132	0.328

The expressions for the gel point (equation (45)) and the WAMW (equation (25)) contain serial terms with coefficients $\{a_{1i}\}$, $\{b_{1i}\}$. The calculations were made in which terms with coefficients $\{a_{1i}\}$, $(b_{1i}\}$ are dropped except for those with coefficients a_{11}, a_{12}, b_{11}, b_{12}. This is a good approximation for the range of Θ_B, E and x values chosen in the calculations.

Tables 1 and *2* list the grafting conversion and the system probability of intramolecular reaction at gel point. We can see that the critical grafting conversion of a polymer is fairly sensitive to intramolecular reaction even though the system probability of intramolecular reaction is relatively small at the gel point. *Figure 6* shows the change of reduced WAMW with grafting reaction at equal amounts of A and B (molar). The effect of intramolecular reaction gradually shows up with grafting reaction. For example, changes of a few per cent in the grafting conversion of a polymer can lead to substantially different WAMW in the presence of intramolecular reaction at a Θ value of 50, when the desirable WAMW (reduced) is 4.0.

CONCLUSIONS

The kinetic formulation in a previous paper has been extended to include intramolecular reaction for the grafting reaction system of reactive polymers A and B having large numbers of reactive groups. The importance of spatial correlation among chain species, due to difference in volume exclusion for different species, is incorporated into the kinetic theory. We provide a general procedure to look into the effect of intramolecular reaction on the branching process.

We make a distinction for the probability of intramolecular reaction of different graft copolymers. A generating function is introduced to derive the expressions for the system probability of intramolecular reaction, WAMW and gel point in the approximation of the first neighbour contribution only to the probability of intramolecular reaction.

A semi-quantitative discussion is given on the model parameter Θ in relation to chain characteristics and dilution under the assumption of Gaussian distribution. It is shown that Θ can have a broad range depending on the chain characteristics and dilution. Θ increases with the numbers of reactive groups on the chain, therefore of the reduced system probability of intramolecular reaction.

It is found that the gel point is fairly sensitive to intramolecular reaction even though the system probability of intramolecular reaction is relatively small at the gel point. The presence of intramolecular reaction on system weight average molecular weight can be either sensitive or not depending on the value of the system WAMW sought in a practical situation. It is concluded that the presence of intramolecular reaction cannot be simply neglected in the defined grafting system.

REFERENCES

1 Klempner, D. and Frisch, K. C. (eds) 'Polymer Alloys III: Blends, Blocks, Grafts, and Interpenetrating Networks. Polymer Science and Technology', Vol. 20, Plenum, New York, 1981

2 Narayan, R. in 'Emerging Technologies for Materials and Chemicals from Biomass' (eds R. M. Rowell, T. P. Schults and R. Narayan), ACS Symp. Ser. 476, 1990, p. 1

3 Stannett, V. in 'Graft Copolymerization of Lignocellulosic Fibers', (ed. D. N. S. Hon), ACS Symp. Ser. 187, 1982, p. 1

4 Mukherjee, A. K. and Goel, H. R. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* 1985, **C25**(1), 99

5 Cimmino, S., D'Orazio, L., Greco, R., Maglio, G., Malinconico, M., Mancarella, C. *et al. Polym. Eng. Sci.* 1984, **24**, 48

6 Angola, J. C., Fujita, Y., Sakai, T. and Inoue, T. *J. Polym. Sci. B: Polym. Phys.* 1988, **26**, 807

7 Biermann, C. J. and Narayan, R. *Polymer* 1987, **28**, 2176

8 Nie, L., Narayan, R. and Grulke, E. A. *Polymer* in press

9 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
10 Stockmayer, W. H. in 'Advancing Fronts in Chemistry', Reinhold, New York, Vol. I, 1945, p. 61
11 Jacobson, H. and Stockmayer, W. H. *J. Chem. Phys.* 1950, **18**, 1600
12 Frisch, H. L. in '128th Meeting Am. Chem. Soc., Polymer Div., Minneapolis', 1955
13 Kilb, R. W. *J. Phys. Chem.* 1958, **62**, 969
14 Gordon, M. and Scantlebury, G. R. *J. Chem. Soc., B* 1967, 1
15 Dusek, K. *Coll. Czech. Chem. Commun.* 1968, **33**, 1100
16 Stepto, R. F. T. *Disc. Faraday Soc.* 1974, **57**, 69
17 Stepto, R. F. T. *Polymer* 1979, **20**, 1324
18 Dusek, K. and Spevacek, J. *Polymer* 1980, **21**, 750
19 Stanford, J. L. and Stepto, R. F. T. in 'Elastomers and Rubber Elasticity', (eds J. E. Mark and J. Lal), ACS Symp. Ser. 193, 1982, p. 378
20 Kumar, A., Wahal, S., Sastri, S. and Gupta, S. K. *Polymer* 1986, **27**, 583
21 Scranton, A. B. and Peppas, N. K. *J. Polym. Sci.: Part A: Polym. Chem.* 1990, **28**, 39
22 Shah, A. C., Parsons, I. W. and Harward, R. N. *Polymer* 1980, **21**, 825
23 Ahmad, Z., Fasina, A. B. and Stepto, R. F. T. Proc. Rubber '78, Kiev, 1978
24 Plate, N. A. and Noah, O. V. *Adv. Polym. Sci.* 1979, **160**, 277
25 Tobita, H. and Hamielec, A. E. in 'Integration of Fundamental Polymer Science and Technology', Vol. 4 (eds P. J. Lemstra and L. A. Kleintjens), 1989, p. 33
26 Dotson, N. A., Macosko, C. W. and Tirrell, M. in 'Synthesis, Characterization, and Theory of Polymeric Networks and Gels' (ed. S. M. Aharoni), 1992, p. 319
27 Zhu, S., Hamielec, A. E. and Pelton, R. H. *Makromol. Chem., Theory Simul.* 1993, **2**, 587
28 Freed, K. F. 'Renormalization Group Theory of Macromolecules', John Wiley, New York, 1987
29 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley, New York, 1969
30 Flory, P. J. in 'Selected Works of Paul J. Flory', Vol. 1 (eds L. Mandelkern, J. E. Mark, U. W. Suter and D. Y. Yoon), 1975, p. 6

APPENDIX

Serial solution of the characteristic equations

The characteristic equations of equation (22) are:

$$\begin{aligned}\frac{\mathrm{d}A}{\mathrm{d}S}=F_{G_A}=A-2A/\Theta_B-[&ABG_B-ABG_B/\Theta_B\\ &-(ABG_B+2A^2G_A-AG)/\Theta_A\\ &+2A(AG_A+BG_B-G)/\Theta_B\Theta_A]\beta/x\end{aligned}\qquad\text{(A1)}$$

$$\begin{aligned}\frac{\mathrm{d}B}{\mathrm{d}S}=F_{G_B}=B/x-2B/\Theta_B-[&ABG_A-ABG_A/\Theta_A\\ &-(ABG_A+2B^2G_B-BG)/\Theta_B\\ &+2B(AG_A+BG_B-G)/\Theta_B\Theta_A]\beta/x\end{aligned}\qquad\text{(A2)}$$

$$\frac{\mathrm{d}E}{\mathrm{d}s}=F_{G_E}=1\qquad\text{(A3)}$$

$$\begin{aligned}\frac{\mathrm{d}G_A}{\mathrm{d}s}=&-(F_A+G_AF_G)=-G_AF_G\\ &-\Big\{G_A-\frac{2G_A}{\Theta_B}-[BG_BG_A(1-1/\Theta_B)\\ &-(BG_BG_A+2AG_A^2-G_AG)/\Theta_A\\ &+2G_A(AG_A+BG_B-G)/\Theta_B\Theta_A]\frac{\beta}{x}\Big\}\end{aligned}\qquad\text{(A4)}$$

$$\begin{aligned}\frac{\mathrm{d}G_B}{\mathrm{d}s}=&-(F_B+G_BF_G)=-G_BF_G\\ &-\Big\{\frac{G_B}{x}-\frac{2G_B}{\Theta_B}-[AG_BG_A(1-1/\Theta_A)\\ &-(AG_AG_B+2BG_B^2-G_BG)/\Theta_B\\ &+2G_B(AG_A+BG_B-G)/\Theta_B\Theta_A]\frac{\beta}{x}\Big\}\end{aligned}\qquad\text{(A5)}$$

$$\begin{aligned}\frac{\mathrm{d}G_E}{\mathrm{d}s}=&-(F_E+G_EF_G)=-G_EF_G\\ &+\frac{\Theta_B}{\mathrm{d}E}[ABG_AG_B-(ABG_AG_B+A^2G_A^2-AG_AG)/\Theta_A\\ &-(ABG_AG_B+B^2G_B^2-BG_BG)/\Theta_B\\ &+(AG_A+BG_B-G)^2/\Theta_A\Theta_B]/x\end{aligned}\qquad\text{(A6)}$$

$$\begin{aligned}\frac{\mathrm{d}G}{\mathrm{d}s}=\sum_{i=A,B,E}G_iF_{G_i}=&-\frac{2G}{\Theta_B}\\ &-\{ABG_AG_B(1-1/\Theta_A-1/\Theta_B)\\ &-(A^2G_A^2/\Theta_A+B^2G_B^2/\Theta_B)\\ &+[(AG_A+BG_B)^2-G^2]/\Theta_A\Theta_B\}\frac{\beta}{x}\end{aligned}\qquad\text{(A7)}$$

where

$$\begin{aligned}F_G=2/\Theta_B-[&AG_A/\Theta_A+BG_B/\Theta_B\\ &-2(AG_A+BG_B-G)/\Theta_A\Theta_B]\beta/x\end{aligned}\qquad\text{(A8)}$$

Equation (A6) needs not to be considered in the solution since G_E does not appear in the rest of the equations. Dividing equations (A1), (A2), (A4), (A5) and (A7) by equation (A3), we have

$$\begin{aligned}\frac{\mathrm{d}\ln A}{\mathrm{d}E}=1-\frac{2}{\Theta_B}-\Bigg[&BG_B-\frac{BG_B}{\Theta_B}-\frac{BG_B+2AG_A-G}{\Theta_A}\\ &+\frac{2(AG_A+BG_B-G)}{\Theta_B\Theta_A}\Bigg]\frac{\beta}{x}\end{aligned}\qquad\text{(A9)}$$

$$\begin{aligned}\frac{\mathrm{d}\ln B}{\mathrm{d}E}=\frac{1}{x}-\frac{2}{\Theta_B}-\Bigg[&AG_A\left(1-\frac{1}{\Theta_A}\right)\\ &-\frac{AG_A+2BG_B-G}{\Theta_B}+\frac{2(AG_A+BG_B-G)}{\Theta_B\Theta_A}\Bigg]\frac{\beta}{x}\end{aligned}\qquad\text{(A10)}$$

$$\begin{aligned}\frac{\mathrm{d}\ln G_A}{\mathrm{d}E}=-\{1-2/\Theta_B-[&BG_B(1-1/\Theta_B)\\ &-(BG_B+2AG_A-G)/\Theta_A\\ &+2(AG_A+BG_B-G)/\Theta_B\Theta_A]\beta/x\}-F_G\end{aligned}\qquad\text{(A11)}$$

$$\begin{aligned}\frac{\mathrm{d}\ln G_B}{\mathrm{d}E}=-\{1/x-2/\Theta_B-[&AG_A(1-1/\Theta_A)\\ &-(AG_A+2BG_B-G)/\Theta_B\\ &+2(AG_A+BG_B-G)/\Theta_B\Theta_A]\beta/x\}-F_G\end{aligned}\qquad\text{(A12)}$$

$$\begin{aligned}\frac{\mathrm{d}G}{\mathrm{d}E}=-2G/\Theta_B-\{&ABG_AG_B(1-1/\Theta_A-1/\Theta_B)\\ &-(A^2G_A^2/\Theta_A+B^2G_B^2/\Theta_B)\\ &+[(AG_A+BG_B)^2-G^2]/\Theta_A\Theta_B\}\beta/x\end{aligned}\qquad\text{(A13)}$$

The initial conditions are:

$$E=0;\ A=\zeta,\ B=\eta,\ G_A=1,\ G_B=x,\ G=\zeta+x\eta\qquad\text{(A14)}$$

No analytical solution is obtained for G. We have from equation (A9) and equation (A11)

$$\frac{\mathrm{d}\ln(AG_{\mathrm{A}})}{\mathrm{d}E}=-F_{\mathrm{G}} \tag{A15}$$

We have from equation (A10) and equation (A12)

$$\frac{\mathrm{d}\ln(BG_{\mathrm{B}})}{\mathrm{d}E}=-F_{\mathrm{G}} \tag{A16}$$

We see from the inspection of equations (A13), (A15) and (A16) that G, AG_{A} and BG_{B} are functions of E, ζ and η. Integrating equations (A15) and (A16), we have

$$\frac{AG_{\mathrm{A}}}{\zeta}=\frac{BG_{\mathrm{B}}}{x\eta}=f(E,\zeta,\eta) \tag{A17}$$

Integrating equations (A9), (A10) and (A15), we have

$$\begin{aligned}\ln\frac{A}{\zeta}=\left(1-\frac{2}{\Theta_{\mathrm{B}}}\right)E-\int_0^E &\{[BG_{\mathrm{B}}-BG_{\mathrm{B}}/\Theta_{\mathrm{B}}\\ &-(BG_{\mathrm{B}}+2AG_{\mathrm{A}}-G)/\Theta_{\mathrm{A}}\\ &+2(AG_{\mathrm{A}}+BG_{\mathrm{B}}-G)/\Theta_{\mathrm{B}}\Theta_{\mathrm{A}}]\beta/x\}\,\mathrm{d}E\end{aligned} \tag{A18}$$

$$\begin{aligned}\ln\frac{B}{\eta}=\left(\frac{1}{x}-\frac{2}{\Theta_{\mathrm{B}}}\right)E-\int_0^E &\{[AG_{\mathrm{A}}-AG_{\mathrm{A}}/\Theta_{\mathrm{A}}\\ &-(AG_{\mathrm{A}}+2BG_{\mathrm{B}}-G)/\Theta_{\mathrm{B}}\\ &+2(AG_{\mathrm{A}}+BG_{\mathrm{B}}-G)/\Theta_{\mathrm{B}}\Theta_{\mathrm{A}}]\beta/x\}\,\mathrm{d}E\end{aligned} \tag{A19}$$

$$\begin{aligned}\ln\frac{AG_{\mathrm{A}}}{\zeta}=\frac{2E}{\Theta_{\mathrm{B}}}-\int_0^E &\{[AG_{\mathrm{A}}/\Theta_{\mathrm{A}}+BG_{\mathrm{B}}/\Theta_{\mathrm{B}}\\ &-2(AG_{\mathrm{A}}+BG_{\mathrm{B}}-G)/\Theta_{\mathrm{B}}\Theta_{\mathrm{A}}]\beta/x\}\,\mathrm{d}E\end{aligned} \tag{A20}$$

We have from the definition of the generating function

$$AG_{\mathrm{A}}|_{A=B=1}\equiv 1 \tag{A21}$$

$$BG_{\mathrm{B}}|_{A=B=1}\equiv x \tag{A22}$$

From equations (A18) and (A19), we have

$$\zeta|_{A=B=1}=1 \tag{A23}$$

$$\eta|_{A=B=1}=1 \tag{A24}$$

With the requirements of equations (A14), (A21), (A22), (A23) and equation (A24), $f(E,\zeta,\eta)$ of equation (A17) satisfies

$$f(0,\zeta,\eta)=1 \tag{A25}$$

$$f(E,1,1)=1 \tag{A26}$$

We must have for the Taylor expansion of $f(E,\zeta,\eta)$:

$$\begin{aligned}f(E,\zeta,\eta)=1+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^iE^ja_{ij}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^iE^jb_{ij}\\ +\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^jE^kc_{ijk}\end{aligned} \tag{A27}$$

By substituting equation (A27) into equation (A17), we have

$$\begin{aligned}AG_{\mathrm{A}}=\zeta\Bigg[1+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^iE^ja_{ij}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^iE^jb_{ij}\\ +\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^jE^kc_{ijk}\Bigg]\end{aligned} \tag{A28}$$

$$\begin{aligned}BG_{\mathrm{B}}=x\eta\Bigg[1+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\zeta-1)^iE^ja_{ij}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(\eta-1)^iE^jb_{ij}\\ +\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\sum_{k=1}^{\infty}(\zeta-1)^i(\eta-1)^jE^kc_{ijk}\Bigg]\end{aligned} \tag{A29}$$

The system WAMW is related to $\partial(AG_{\mathrm{A}})/\partial A$, G_{AB} and $\partial(BG_{\mathrm{B}})/\partial B$ at $\zeta=\eta=1$. The terms with coefficients c_{ijk} are not needed for obtaining the system WAMW, only terms with coefficients a_{1i}, b_{1i} $(i=1,2,\ldots)$ are actually needed for the molecular weight average. $\partial(AG_{\mathrm{A}})/\partial A$, G_{AB} and $\partial(BG_{\mathrm{B}})/\partial B$ are related further to ζ_{A}, ζ_{B}, η_{A}, η_{B} at $\zeta=\eta=1$. The coefficients of a_{1i}, b_{1i} $(i=1,2,\ldots)$ and ζ_{A}, ζ_{B}, η_{A}, η_{B} at $\zeta=\eta=1$ are obtained simultaneously by taking partial derivatives of equations (A18)–(A20) with A and B where we have already substituted equation (A28) and equation (A29) into them. ζ and η are independent variables that are taken out of the integrals before we take the partial derivatives. We need also to substitute the results of $G_{\mathrm{A}}=1$, $G_{\mathrm{B}}=x$ at $\zeta=\eta=1$. From the partial derivatives of equation (A18) and equation (A19), we obtain the expression for ζ_{A}, η_{A} and ζ_{B}, η_{B}. Substituting these expressions into the partial derivative of equation (A20), we have

$$\sum_{i=1}^{\infty}g_iE^i=0\qquad\left(\text{from }\frac{\partial}{\partial A}\right) \tag{A30}$$

$$\sum_{i=1}^{\infty}h_iE^i=0\qquad\left(\text{from }\frac{\partial}{\partial B}\right) \tag{A31}$$

We recover the coefficients of a_{1i}, b_{1i} $(i=1,2,\ldots)$ by setting $g_i=h_i=0$ $(i=1,2,\ldots)$; in return, ζ_{A}, η_{A} and ζ_{B}, η_{B} are obtained. Coefficients of a_{11}, a_{12}, b_{11}, b_{12} were shown in equation (20) and equation (21). The expressions for ζ_{A}, η_{A} and ζ_{B}, η_{B} were shown in equations (29)–(32). In order to get the results of equation (A30) and equation (A31), we need to expand the results of several integrals from the partial derivatives of equations (A18)–(A20) into serial forms. These are:

$$\int_0^E\beta\,\mathrm{d}E=\sum_{i=1}^{\infty}\frac{1}{i!}\left(\frac{1}{\Theta_{\mathrm{B}}}\right)^{i-1}E^i \tag{A32}$$

$$\sum_{i=1}^{\infty}\int_0^E a_{1i}E^i\beta\,\mathrm{d}E=\sum_{i}\sum_{j=1}^{\infty}\frac{a_{1i}\Theta_B^{1-j}}{(i+j)(j-1)!}E^{i+j} \tag{A33}$$

$$\sum_{i=1}^{\infty}\int_0^E b_{1i}E^i\beta\,\mathrm{d}E=\sum_{i}\sum_{j=1}^{\infty}\frac{b_{1i}\Theta_B^{1-j}}{(i+j)(j-1)!}E^{i+j} \tag{A34}$$

Detailed manipulations are tedious but straightforward, and are therefore not included here.

NOMENCLATURE

a_{ij}, b_{ij}	Parameters in Taylor expansion
b	Length of the statistically equivalent unit
$\bar{C}_{ij}$	Reduced molar concentration of polymer species having i A chains and j B chains
E	Variable relating to grafting conversion of polymer A
f_{A}	Fraction of polymer A found in graft copolymers
$f_{\mathrm{A}}^{\mathrm{crit}}$	Fraction of A found in graft copolymers at the gel point

n_A, n_B	Total moles of polymer A and B in the system
N_A, N_B	Constitutional units of polymers A and B
$N_{a_i b_j}$	Numbers of statistical equivalent units between two reactive groups with coarse-grained Gaussian distribution
n_{iso}	Total numbers of isomers that can be constructed out of a simple graft copolymer
$\bar{p}_a$	Mean probability of $\{a_i\}$ reactive groups meeting with $\{b_j\}$ reactive groups of a simple graft copolymer
$\bar{p}_b$	Mean probability of $\{b_j\}$ reactive groups meeting with $\{a_i\}$ reactive groups of a simple graft copolymer
P_{ij}^g, P_{ij}^c	Fraction of grafting reaction for the generation and consumption of polymer species having i A chains and j B chains
$P_{a_i b_j}^k$	Probability of a_i reactive group meeting with b_j reactive group for a k isomer
v_A, v_B	Numbers of constitutional units carried by each reactive group of polymers A and B
V_{sphere}	Volume of coordination sphere
x	Molar ratio of polymer A to polymer B
Z	Number of constitutional units of the coordination sphere
β	Normalization factor
Θ(or Θ_A or Θ_B)	Model parameter
φ_S	Equivalent number fraction of solvent in the reaction system
φ_a, φ_b	Number fraction of constitutional units containing reactive group a of chain A and reactive group b of chain B in the reaction system excluding solvent
$\lambda_{11}^A, \lambda_{11}^B$	Mean probability of intramolecular reaction for reactive groups on chain A and chain B of a simple graft copolymer
$\lambda_{ij}^A, \lambda_{ij}^B$	Mean probability of intramolecular reaction for reactive groups on chain A and chain B of any graft copolymer having i A chains and j B chains
λ_{ij}	Contribution to the system probability of intramolecular reaction of the graft copolymer having i A chains and j B chains
λ	System probability of intramolecular reaction