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Theoretical Analysis of the Copolymer Composition Equation in Chain Shuttling Copolymerization

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Introduction. The advent of chain shuttling polymerization has expanded the toolbox available to polymer scientists for the preparation of a variety of functional polymer materials such as polymers with narrow polydispersity and olefin block copolymers.[1] At least in one aspect, the chemistry is highlighted for its ability to synthesize block copolymers in a controlled fashion in conjunction with careful selection of reactors and operating strategies.[1−3] One of the key molecular architectures that needs to be controlled in the production of block copolymers is the copolymer composition of each block. It has been hypothesized that the copolymer compositions of instantaneously formed polymers using chain shuttling polymerization are consistent with those using conventional transition-metal-catalyzed polymerization and, thus, can be described by the Mayo−Lewis equation.[4]

$$F_1 = \frac{r_{12}{f_1}^2 + f_1 f_2}{r_{12}{f_1}^2 + 2f_1 f_2 + r_{21}{f_2}^2} \tag{1}$$

Here F_1 is the molar fraction of monomer 1 in the copolymer, r_{12} and r_{21} are the reactivity ratios, and f_i (i = 1, 2) is the molar fraction of monomer, i, in the reactor.

We consider a simple chain shuttling copolymerization scheme that includes catalyst activation and initiation, propagation, irreversible termination such as chain transfer to hydrogen, and reversible reactions between growing and dormant chains. Note that catalyst activation, initiation, and irreversible termination do not affect how monomers are incorporated into the chains; thus, the reactions of interest to copolymer composition are summarized in Table 1. Here in Table 1 M_j is monomer j (j = 1, 2), CSA is chain shuttling agent, Cat* is activated catalyst, $P_i(n)$ is a growing chain with last inserted monomer i (i = 1, 2) and chain length n, $Q_i(n)$ is a dormant chain with last inserted monomer i (i = 1, 2) and chain length n, k_{pij} is the propagation rate coefficient for active center with last inserted monomer i to add monomer j, and k_{CS} is the chain shuttling rate coefficient.

To derive eq 1, F_j (j = 1, 2) is calculated as

$$F_j = \frac{r_{M_j}}{r_{M_1} + r_{M_2}} = \frac{\sum_{i=1}^{2} k_{pij} P_i C_{M_j}}{\sum_{j=1}^{2}\sum_{i=1}^{2} k_{pij} P_i C_{M_j}} = \frac{\sum_{i=1}^{2} k_{pij} \phi_i f_j}{\sum_{j=1}^{2}\sum_{i=1}^{2} k_{pij} \phi_i f_j} \tag{2}$$

Here r_{Mj} (j = 1, 2) is the polymerization rate of monomer j, P_i is the concentration of active center with last inserted monomer i, C_{Mj} is the concentration of monomer j, ϕ_i is the molar fraction of active center with last inserted monomer i, and f_j is the molar fraction of monomer j in the reactor.

The rate of the active center with last inserted monomer i, r_{P_i}, is written as

$$r_{P_i} = -k_{pij} P_i C_{M_j} + k_{pji} P_j C_{M_i} + (-k_{CS} P_i \xi_0 + k_{CS} Q_i \mu_0) \quad (j \neq i) \tag{3}$$

Here ξ_0 is the total concentration of dormant chains, Q_i is the concentration of dormant chains with last inserted monomer i, and μ_0 is the total concentration of active center.

In a conventional transition-metal-catalyzed polymerization, use of the long chain hypothesis (LCH), i.e., the propagation rate is much larger than both the initiation and termination rates, and quasi-steady-state assumption (QSSA) for P_i, i.e., $r_{P_i} = 0$, leads to

$$-k_{pij}\phi_i f_j + k_{pji}\phi_j f_i = 0 \tag{4}$$

Since $\sum_{i=1}^{2} \phi_i = 1$, we have

$$\phi_i = \frac{k_{pji} f_i}{k_{pji} f_i + k_{pij} f_j} \tag{5}$$

Substituting eq 5 into eq 2 leads to the Mayo−Lewis equation as depicted in eq 1.

In a chain shuttling polymerization, however, we must examine the rates of reactions involving both the dormant and growing chains in order to comfortably use eq 5 to determine the active center composition and, subsequently, the copolymer composition equation, i.e., the Mayo−Lewis equation. In case that the reaction rate of the reversible reaction is much smaller than that of propagation, both eq 1 and eq 5 should be adequate. However, the reaction rate of the reversible reaction can be much larger than that of propagation, i.e.

$$k_{CS}\xi_0 \gg k_p C_M \tag{6}$$

Here we use k_p to conceptually represent the overall propagation rate coefficient and C_M the total concentration of monomer in the reactor.

As the reversible reaction between dormant and growing chains becomes dominant, using QSSA for P_i leads to

$$-k_{CS}\phi_i \mu_0 \xi_0 + k_{CS}\psi_i \xi_0 \mu_0 = 0 \tag{7}$$

i.e.

$$\phi_i = \psi_i \tag{8}$$

Here ψ_i is the molar fraction of dormant chains that have last inserted monomer i. Note that the active center and the dormant chains have the same composition. In the case of a single catalyst, eqs 5 and 8 can be simultaneously satisfied as the equilibrium term involving both growing and dormant chains cancel while the swap rates of active center ended with different monomer types through propagation are about the same; thus, the Mayo−Lewis equation (cf. eq 1) is still valid. Note that this case is similar to reported "living" free radical copolymerization systems, in which only one active center,

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i.e., radical, exists. It has been reported that the Mayo–Lewis equation can satisfactorily describe the copolymer composition of the resulting polymers in various "living" free radical polymerization systems.[5–10]

However, when dual catalysts are utilized in chain shuttling polymerization, we find that the Mayo–Lewis equation may fail to describe the copolymer composition of polymers originated from each catalyst. Note that the reactions important to copolymer composition are still the same as those in Table 1, but each reaction could involve dual catalysts. First, the Mayo–Lewis equation is still valid when chain shuttling rate is relatively small compared to propagation rate. However, when this condition is violated, following the same approach for the derivation of eq 8, we have

$$\phi_i^{(j)} = \psi_i \tag{9}$$

Here $\phi_i^{(j)}$ is the molar fraction of active center originated from catalyst j (j = 1, 2) with last inserted monomer i (i = 1, 2).

Equation 9 shows that the active centers of dual catalysts shall have the same composition as the dormant chains. Thus, in this case, eq 5 is inadequate to estimate the active center composition for each catalyst. Consequently, the Mayo–Lewis equation does not hold under these conditions. As a rule of thumb for an ideal continuous stirred tank reactor (CSTR), assuming that the concentration of feed monomer is 10 mol/L with a conversion of 90% in the reactor while the number average degree of polymerization, DP_n, of the resulting polymers is 1000, the concentration of dormant chains in the reactor would be in the range of 0.009 mol/L. Implementing eq 6 leads to

$$\frac{k_{CS}}{k_p} \gg 111 \tag{10}$$

Thus, when the ratio of k_{CS} to k_p is greater than 111 and dual catalysts are used, it would be alerted that the Mayo–Lewis equation may not be applicable.

Results and Discussion. To substantiate the analysis carried out in the previous section, it is possible to examine special systems through the analytical method. For example, it would be appropriate to investigate a batch system at constant monomer composition to understand how the copolymer composition evolves for a chain shuttling polymerization by using the transient analysis.[11] Nevertheless, we are more interested in a commercial production of chain shuttling polymerization. Thus, we conducted numerical simulations of a CSTR at steady state using Predici software to examine the theoretical analysis in the previous section.[12] First, we consider a single catalyst case. The simulation conditions are summarized in Table 2. Note that in Table 2 the kinetic rate coefficients for each catalyst are labeled using a superscript (i) (i = 1, 2). Rigorously, the instantaneously formed copolymer composition is calculated via eq 2. In the simulation, we maintain the amount of CSA in the feed constant while varying the chain shuttling rate coefficient over a wide range of values to ensure that both $k_{CS}\xi_0 \gg k_p C_M$ and $k_{CS}\xi_0 \ll k_p C_M$ cases are included. Figure 1a shows the comparison of copolymer compositions calculated using eq 2 and the Mayo–Lewis equation. Figure 1b shows both the

Table 1. Reactions Important for Copolymer Composition in Chain Shuttling Copolymerization

propagation	$P_i(n) + M_j \xrightarrow{k_{pij}} P_j(n+1)$
reversible reaction between chain transfer agent and growing chains	$P_i(n) + CSA \overset{k_{CS}}{\rightleftarrows} Q_i(n) + Cat^*$
reversible reaction between dormant and growing chains	$P_i(n) + Q_j(m) \overset{k_{CS}}{\rightleftarrows} P_j(m) + Q_i(n)$

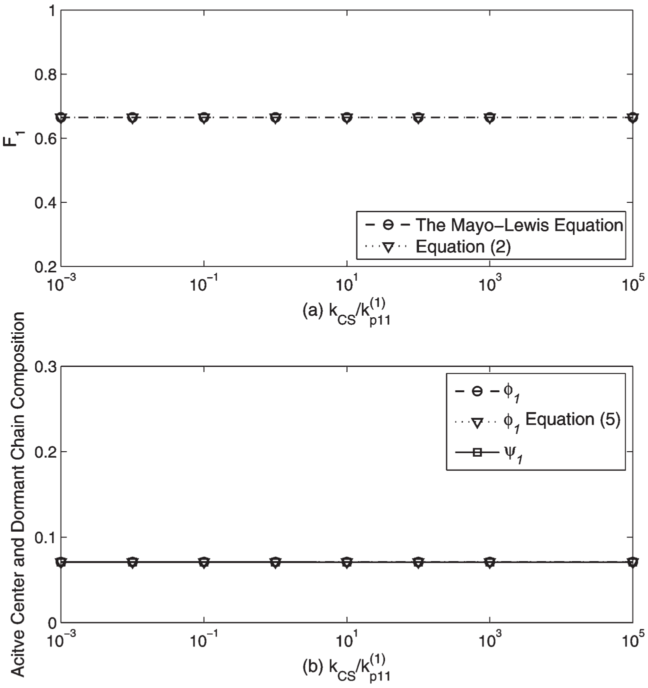

Figure 1. Case studies for a single catalyst in a single CSTR at steady state for a range of chain shuttling rate coefficients. (a) Copolymer composition calculated using the Mayo–Lewis equation and eq 2. (b) Active center and dormant chain compositions.

Table 2. Simulation Conditions for Both Single Catalyst and Dual Catalysts in a Single CSTR[a]

reactor residence time, θ (min)	10
normalized catalyst 1 feed concentration (dimensionless)	1.266×10^2
normalized catalyst 2 feed concentration (dimensionless)	0 (single catalyst case), 84.6 (dual catalyst case)
normalized monomer 1 feed concentration (dimensionless)	1.08×10^8
normalized monomer 2 feed concentration (dimensionless)	6.78×10^7
normalized CSA feed concentration (dimensionless)	1.8×10^3

$$r_{12}^{(1)} = 5,\ r_{21}^{(1)} = 0.3,\ r_{12}^{(2)} = 100,\ r_{21}^{(2)} = 0.05$$

$$\frac{k_{p22}^{(1)}}{k_{p11}^{(1)}} = 0.01,\ \frac{k_{p11}^{(2)}}{k_{p11}^{(1)}} = 0.1,\ \frac{k_{p22}^{(2)}}{k_{p11}^{(1)}} = 0.01$$

$$\frac{k_{CS}}{k_{p11}^{(1)}} = 1 \text{ (baseline)}$$

[a] Here $C_{i,f}$, the feed concentration of species i, is normalized as $C_{i,f}(\text{normalized}) = C_{i,f}k^{(1)}{}_{p11}\theta$.

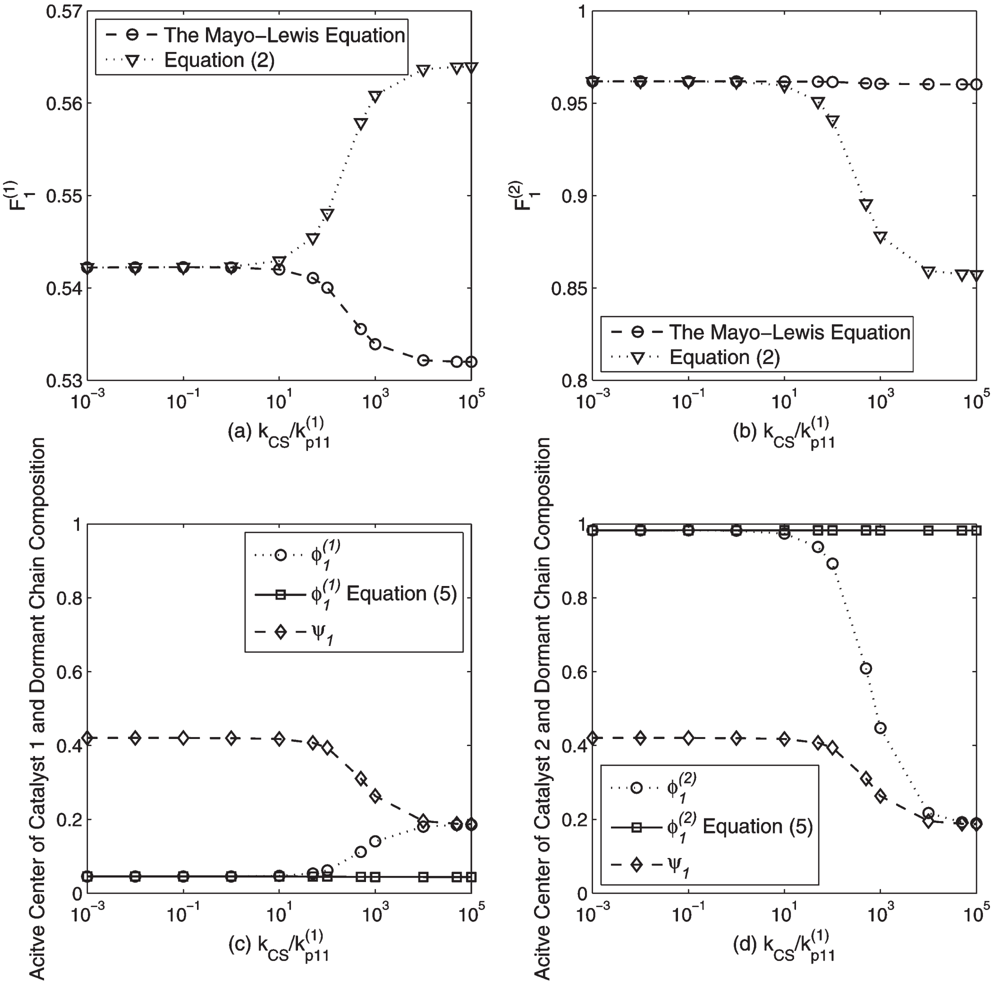

Figure 2. Case studies for dual catalysts in a single CSTR at steady state for a range of chain shuttling rate coefficients. (a) Copolymer composition calculated using the Mayo–Lewis equation and eq 2 for polymers formed through catalyst 1. (b) Copolymer composition calculated using the Mayo–Lewis equation and eq 2 for polymers formed through catalyst 2. (c) Active center of catalyst 1 and dormant chain composition. (d) Active center of catalyst 2 and dormant chain composition.

active center and dormant chain compositions. As a comparison, the active center composition using eq 5 is also shown. It appears that in the single catalyst case the presence of CSA does not affect the active center composition, and the Mayo–Lewis equation is still applicable. It has also been observed that the active center composition is always the same as the dormant chain composition no matter the magnitude of chain shuttling rate coefficient. Similarly, for a "living" free radical copolymerization, numerical simulations have drawn the same conclusions. For example, Feldermann et al.[7] conducted numerical simulations to investigate the effect of reversible addition–fragmentation chain transfer radical copolymerization (RAFT) on the copolymer composition and concluded that, once chain equilibration involving macro-RAFT agent and growing chains is established, the copolymer compositions using the RAFT process and the corresponding conventional free radical polymerization are similar. In essence, the composition of radicals in the RAFT process can be determined by eq 3 if the addition chain transfer rate coefficient is large and the argument in this Communication is also applicable.

By contrast, simulation of the use of dual catalysts reveals different behavior. The simulation parameters are summarized in Table 2, and again, we consider the steady-state operation in a single CSTR. Parts a and b of Figure 2 show the comparison of copolymer composition of instantaneously formed polymers originating from catalysts 1 and 2 using eq 2 and the Mayo–Lewis equation, respectively. When chain shuttling rate is much smaller than propagation rate, copolymer composition calculated using the Mayo–Lewis equation is consistent with that calculated rigorously using eq 2. However, as chain shuttling rate coefficient increases such that chain shuttling rate is much larger than that of propagation, the predictions from the Mayo–Lewis equation deviate significantly from those calculated rigorously. Figure 2c,d shows both the active center and dormant chain compositions. As a comparison, the active center composition using eq 5 is also shown. When the chain shuttling rate is much smaller than propagation rate, the active center composition for each catalyst is consistent with predictions using eq 5. In contrast with the single catalyst case, the dormant chain composition does not coincide with either active center composition and is in between the two. As chain shuttling rate increases, the three compositions for active centers 1 and 2 and the dormant chains start to and eventually merge together, consistent with the analysis of eq 9.

Conclusions. We report a theoretical analysis on the copolymer composition for chain shuttling copolymerization and point out that the Mayo–Lewis equation could potentially be invalid for dual catalysts. As a rule of thumb, for feed monomer concentration of 10 mol/L with conversion 90% and a targeted DP_n of 1000 in a CSTR using dual catalysts, the ratio of k_{CS} to k_p greater than 111 could raise the alarm that the Mayo−Lewis equation may fail. Our numerical simulations support our findings: (1) the presence of CSA has no impact on active center composition using a single catalyst and, thus, the Mayo−Lewis equation is still valid; (2) the presence of CSA could potentially alter active center composition for dual catalysts when the chain shuttling rate is much higher than the propagation rate and, thus, the Mayo−Lewis equation does not hold.

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