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Factors Affecting Rates of Comonomer Consumption in Copolymerization Processes with Intermittent Activation

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ABSTRACT: Many controlled polymerization processes proceed via intermittent activation (i.e., by a series of activation/deactivation cycles), and this interrupted growth process may affect not only polydispersities but also (co)polymer microstructure. The computer modeling indicates that, in systems with intermittent and selective activation, rates of consumption of comonomers may be different from conventional systems, and this can result in different copolymer composition, microstructure, and different apparent reactivity ratios. The effect of several parameters such as concentration of the involved reagents, rate constants of homopropagation, cross-propagation, activation, and deactivation on the copolymer composition was studied. Deviations from the conventional systems are predicted for systems such as controlled/living radical polymerization, atom transfer radical polymerization, group transfer radical polymerization, "living" carbocationic polymerization, and other systems with intermittent activation. Use of chiral activators/deactivators may convert *stereoselective* polymerization to *stereoelective* polymerization even in the presence of nonselective initiators. The topology of polymers formed by self-condensing vinyl polymerization (branch distribution) may also depend on the dynamics of exchange reactions.

Introduction

Controlled/living polymerization where control is attained through exchange between an active and a dormant species is one of the most rapidly developing areas of polymer synthesis.[1] This can be traced back to the early reports on the anionic polymerization of dienes where less reactive aggregates played the role of dormant species,[2] to the cationic ring-opening polymerization of cyclic ethers where covalent esters exchanged with much more reactive onium ions,[3] to the group transfer polymerization (GTP) of methacrylates where silyl ketene acetals exchanged with propagating enolate anions,[4] to the "living" carbocationic polymerization where carbocations exchanged with dormant covalent esters or onium ions,[5] and essentially to all controlled/living radical polymerization systems (atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), or degenerative transfer processes with alkyl iodides and dithioesters).[6,7]

The importance of these exchange reactions has been stressed many times and cannot be overemphasized from the point of view of synthetic manipulation and preparation of many well-defined polymers by macromolecular engineering techniques.[1]

The common feature in all of these systems is intermittent activation of the dormant species to short-lived active centers, which after addition of a few (sometimes on average may be even less than one) monomer molecules return to the dormant state. We use the term intermittent with analogy to intermittent windshield wipers in which the period of inactivity can be precisely chosen and controlled. Of course, periods of activity in polymerization may be much less frequent than in the automotive wipers analogy, since in many polymerization systems less than 1 ppm of active species exist, meaning that the proportion of time in which the chain end exists in active state and dormant state is very small ($\sim$1:10^6).

The effect of the dynamics of exchange reactions on the polydispersities and molecular weights of homopolymers formed in systems with intermittent activation has been studied in detail since precise analysis of molecular weight distribution can give deeper insight into the kinetics of exchange processes.[8] The effect of intermittent activation on copolymerization reactions has been much less studied than the corresponding homopolymerizations.[9] The general hypothesis was that reactivity ratios and comonomer consumption in such systems should be nearly identical to those in systems without intermittent activation.[10,11] This belief could be illustrated by an example in which one active center is activated with a different rate than the other one, but it will always react with two comonomers with the same selectivity as in the conventional systems. The differences in activation rates should affect overall rates but should not affect relative comonomer consumption.

This approach has been used to probe the reaction mechanisms and involvement of reactive intermediates in ATRP, NMP, GTP, etc., and reactivity ratios in ATRP and NMP are similar to those in conventional RP, whereas those in GTP close to those determined for anionic polymerization.[9,12−19] Similarly, reactivity ratios in "living" carbocationic systems are close to those in conventional cationic polymerizations.[5] Small differences have been noted but were primarily ascribed to differences in reaction conditions, conversion, precision of measurements, involvement of additives, etc.

Stereocontrol in systems with intermittent activation is a similar issue. Stereoselectivity has been reported in enantiosymmetric systems, where the active R center reacts with R monomer faster than with S. However, stereoelectivity (enantioasymmetric polymerization) always required a chiral, selective initiator to start polymerization of one stereoisomer faster than the other.[20] The question is whether an achiral and nonse-

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Table 1. Values of Exponents of Rate Constants and Concentrations of Reagents[a]

no.	k_{11}	k_{12}	k_{22}	k_{21}	k_{a1}	k_{a2}	k_{d1}	k_{d2}	k_i	k_a	k_d	[M_1]	[M_2]	[R]
1	3	2	3	2	−1	0	5	5	3	−1	5	5	5	0.1
1A	3	**3**	3	3	−1	−1	5	5	3	−1	5	5	5	0.1
1B	3	2	3	2	−1	−1	5	5	3	−1	5	5	5	0.1
1C	3	3	3	3	−1	0	5	5	3	−1	5	5	5	0.1
2A	3	2	3	2	−1	0	5	5	3	−1	5	5	5	0.2
2C	3	2	3	2	−1	0	5	5	3	−1	5	5	5	0.05
2B	3	2	3	2	−1	0	5	5	3	−1	5	5	5	0.5
2D	3	2	3	2	−1	0	5	5	3	−1	5	5	5	0.01
3A	3	1	3	1	−1	0	5	5	3	−1	5	5	5	0.1
3B	3	$^1/_2 \times 10^3$	3	$^1/_2 10^3$	−1	0	5	5	3	−1	5	5	5	0.1
3C	3	2×10^3	3	2×10^3	−1	0	5	5	3	−1	5	5	5	0.1
3D	3	4	3	4	−1	0	5	5	3	−1	5	5	5	0.1
4A	3	2	3	2	−1	1	5	5	3	−1	5	5	5	0.1
4B	3	2	3	2	−1	−2	5	5	3	−1	5	5	5	0.1
5A	3	2	3	2	−2	−1	5	5	3	−1	5	5	5	0.1
5B	3	2	3	2	0	1	5	5	3	−1	5	5	5	0.1
6A	3	2	3	2	−1	0	3	3	3	−1	5	5	5	0.1
6B	3	2	3	2	−1	0	2	2	3	−1	5	5	5	0.1
7A	3	2	3	2	−1	−1	5	4	3	−1	5	5	5	0.1
7B	3	2	3	2	−1	−1	4	5	3	−1	5	5	5	0.1
7C	3	2	3	2	−1	−1	2	3	3	−1	5	5	5	0.1
8A	3	2	3	2	−1	0	5	5	3	−1	5	7	3	0.1
8B	3	2	3	2	−1	0	5	5	3	−1	5	3	7	0.1

[a] Values of k_{11}, k_{12}, k_{22}, k_{21} in M^{-1} s^{-1}; values of k_a, k_d in s^{-1}; concentrations in M (mol/L).

lective initiator can induce stereoelection in systems with intermittent activation when the activator/deactivator (transition-metal complex in ATRP or a capping group like nitroxide in NMP) is chiral.

In this paper we analyze such systems and provide evidence that copolymerization with intermittent activation may lead to significant differences in relative comonomer consumption and can yield stereoelective polymerization using nonselective initiators but selective activators. The effect of relative rates of homo- vs cross-propagation, relative rates of activation, deactivation, and concentrations of initiator and monomer on these systems is presented. The implications of the predicted differences may allow further control of macromolecular topology, functionality, and composition. These results may also provide a warning that any potential differences in reactivity ratios, kinetic isotope effects, unusual stereocontrol, and preparation of a variety of topologies are not necessarily related to a different reaction mechanism and involvement of different intermediates, but rather can be attributed to the effect of intermittent activation/deactivation on propagation. Thus, structures of polymers prepared in systems with intermittent activation may be more or less different from those prepared by conventional polymerization techniques without intermittent activation.

Experimental Section

The Predici program was used for kinetic modeling. It employs a discrete h−p method to represent chain length distributions and an adaptive Rothe method as a numerical strategy for time discretization. Concentrations of all species, as well as the distributions of all polymeric species, can be followed. The program has been applied and tested with various free radical polymerizations, including conventional,[21] pulsed laser,[22] ATRP,[23,24] and NMP.[25] Calculations were performed on a personal computer (two 300 MHz processors) running Windows NT and took approximately 1−2 min to complete.

Results of Kinetic Modeling

The aim of this work is to demonstrate whether intermittent activation is a criterion for altering polymer structure in comparison with conventional polymer systems. We have purposely chosen sets of rate constants and reaction conditions that can demonstrate the concept and probe the affect of the most important parameters. Therefore, we varied rate constant by a decade, although concentrations were varied in a smaller range. Eventually, we simulated an ATRP system for copolymerization of two methacrylates that strongly prefer to homopropagate (10-fold) and in which one dormant species is activated 10 times faster than the other.

Table 1 presents values of the exponents of the rate constants of homopropagation (k_{11} and k_{22}), cross-propagation (k_{12} and k_{21}), initiation (k_i), activation (k_a, k_{a1}, k_{a2}), and deactivation (k_d, k_{d1}, k_{d2}) for both an initiator and a macromolecular species. Both activation and deactivation in this scheme are considered as unimolecular processes. (For bimolecular processes, this would correspond to the product of the corresponding rate constant and the concentration of activator/deactivator; cf. later case of ATRP). No termination is considered at this stage. The initiator (R) is nonselective and reacts with the same rate constant with both comonomers (M_1 and M_2). Scheme 1 illustrates this simplified system.

The first case (no. 1 in Table 1) describes a system in which both homopropagation rate constants are 10 times higher than the corresponding cross-propagation rate constants. Activation of one active center is 10 times faster than the other one, and deactivation is nonselective. Initiator reacts with both comonomers with the rate constant equal to the homopropagation rate constant, and activation/deactivation resembles macromolecular systems. Initial concentrations of both comonomers are equal to 5 M, and the concentration of initiator is 0.1 M, i.e., targeting final DP = 100. This system corresponds to conditions for azeotropic copolymerization in conventional radical polymerization, and any deviation from the same rate of comonomer consumption is easy to observe on concentration vs overall conversion plots. We subsequently varied different parameters to observe the magnitude of any deviation and compare it with the ideal case 1A, in which the rate constants of homo- and cross-propagation are equal, and activation and deactivation rate constants are identical

Scheme 1. Simplified Scheme for Copolymerization with Intermittent Activation

Initiation

$$R \underset{k_d}{\overset{k_a}{\rightleftharpoons}} R^{\bullet}$$

$$R^{\bullet} + M_1 \xrightarrow{k_i} P_1^{\bullet}$$

$$R^{\bullet} + M_2 \xrightarrow{k_i} P_2^{\bullet}$$

Propagation

$$P_1 \underset{k_{d1}}{\overset{k_{a1}}{\rightleftharpoons}} P_1^{\bullet}$$

$$P_2 \underset{k_{d2}}{\overset{k_{a2}}{\rightleftharpoons}} P_2^{\bullet}$$

$$P_1^{\bullet} + M_1 \xrightarrow{k_{11}} P_1^{\bullet}$$

$$P_1^{\bullet} + M_2 \xrightarrow{k_{12}} P_2^{\bullet}$$

$$P_2^{\bullet} + M_2 \xrightarrow{k_{22}} P_2^{\bullet}$$

$$P_2^{\bullet} + M_1 \xrightarrow{k_{21}} P_1^{\bullet}$$

for both comonomers. The altered values are bold in Table 1.

The kinetics of the reaction can be followed by variation of the concentration of each remaining monomer vs time, as well as their ratio, and the difference between them vs overall conversion. Since time varies for the corresponding parameters, the time dependence provides a less clear picture. We selected dependence vs conversion for the latter plots, which better illustrate the effect of the various parameters.

Figure 1 portrays comonomer concentration vs time (Figure 1A) and vs overall conversion (Figure 1B) for the initial case no. 1 and for systems in which activation is nonselective but the propagation step is selective (case 1B), or activation is selective but propagation is not (case 1C), as well as the ideal case (1A). Only in case 1 can differences in consumption of two comonomers be observed. Figure 1C presents the resulting difference between concentrations of comonomers ($[M]_1 - [M]_2$) and their ratios ($[M]_1/[M]_2$) vs overall conversion. As clearly seen in Figure 1C, both selective propagation and selective activation are needed in order to observe deviation from the identical rates of comonomer consumption seen for the ideal case without intermittent activation. The largest difference is observed at relatively low conversion, and this difference progressively decreases, because in the end, both comonomers must be fully consumed. The maximum difference between concentrations of comonomers is significantly higher than the concentration of end groups (0.1 M).

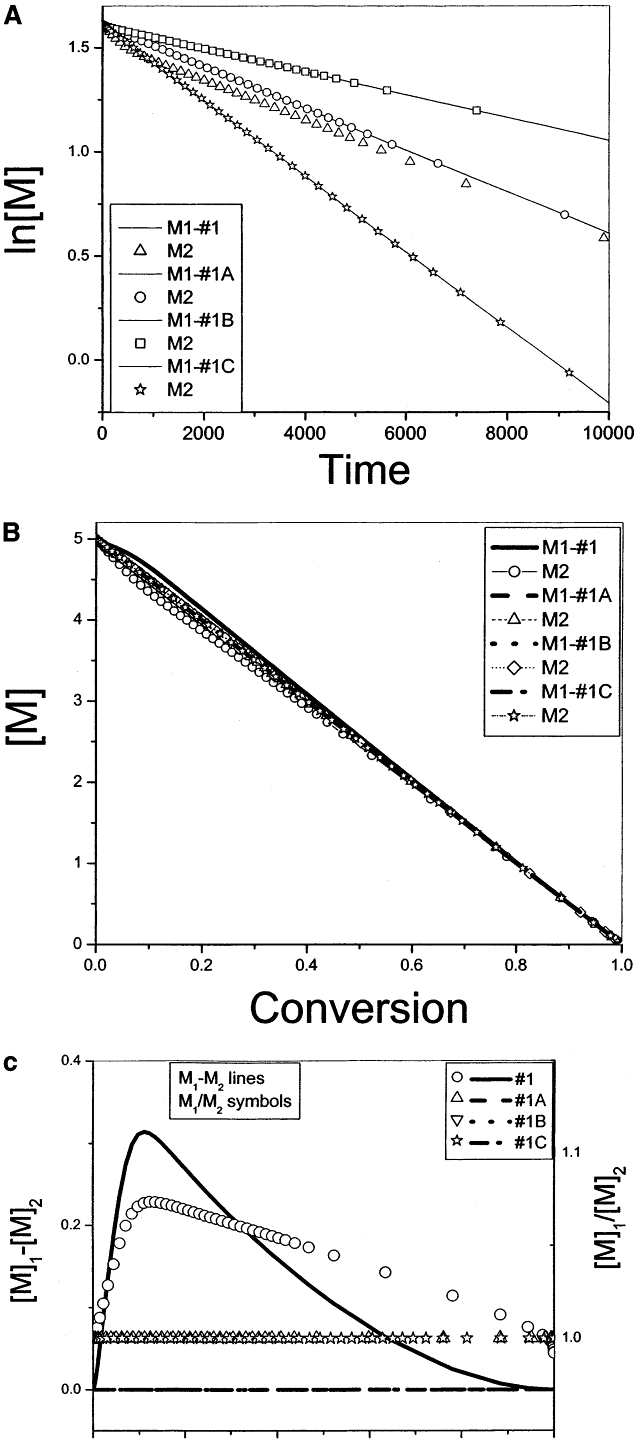


Figure 1. (A) Semilogarithmic dependence of comonomers concentrations on time for systems 1, 1A, 1B, and 1C from Table 1. (B) Dependence of comonomers concentrations on total conversion for systems 1, 1A, 1B, and 1C from Table 1. (C) Dependence of the difference in comonomers concentrations and their ratio on total conversion for systems 1, 1A, 1B, and 1C from Table 1.

Figure 2 presents the effect of the concentration of initiator on the magnitude of deviation of monomer consumption from the ideal case. To reduce the effect of the end groups, the ratio of the difference in comonomer concentration is divided by the initial initiator concentration. The absolute values of the deviation increase with the initiator concentration, but their ratio to the overall concentration of end groups (i.e., initiator) slightly decreases. Nevertheless, the difference in comonomer consumption exceeds by a fewfold (2−3 times) the concentration of end groups and therefore cannot be ascribed to the effect of the end groups alone. The point of maximum deviation moves toward higher conversion with increasing initiator concentration but eventually disappears when both comonomers are fully consumed.

Figure 3 presents the effect of changes in the ratio of homopropagation to cross-propagation rate constants

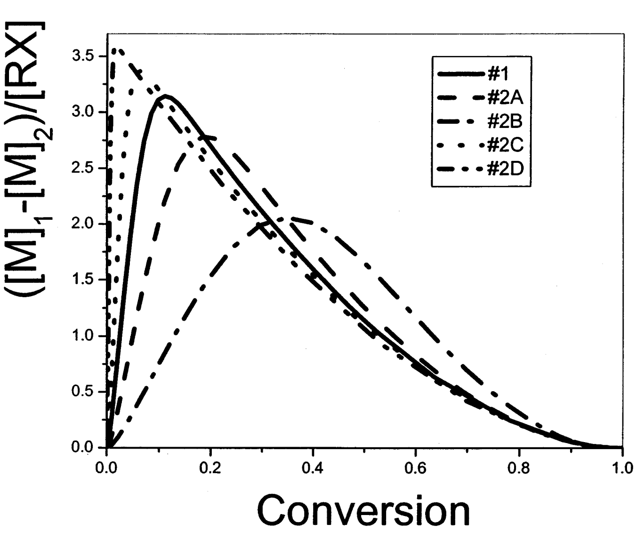


Figure 2. Dependence of the ratio of the difference in comonomers concentrations to the total initiator concentration on conversion for systems 1, 2A, 2B, 2C, and 2D from Table 1.

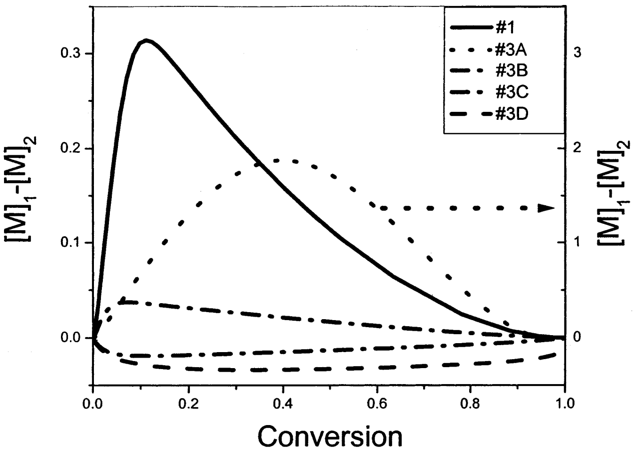


Figure 3. Dependence of the difference in comonomers concentrations on conversion for systems 1, 3A, 3B, and 3C from Table 1.

using the same selectivity of activation ($k_{a2}/k_{a1} = 10$). The magnitude of the deviation from the ideal case strongly depends on the values of k_{11}/k_{12}. The resulting enhancement in concentration of one comonomer reaches nearly 2 M, for $k_{11}/k_{12} = 100$. The magnitude of this deviation decreases when selectivity of the propagation rate constant drops but is still present in systems which tend to alternate; in fact, it is larger (more negative) for $k_{11}/k_{12} = 0.1$ than for $k_{11}/k_{12} = 0.5$.

Analysis of the dynamics and selectivity of activation and deactivation provides a deeper insight into systems with intermittent activation. For this particular case starting conditions were chosen to be similar to those for ATRP of styrene or MMA. This means that the ratio of the activation and deactivation rates is between 10^5 and 10^6, and deactivation is faster than propagation. Figure 4 illustrates that variation of the selectivity of activation has a relatively small effect on deviation from the ideal case. When k_{a2}/k_{a1} increases from 10 to 100, the maximum deviation increases from 0.32 to 0.37 M. When $k_{a2}/k_{a1} = 0.1$, the deviation is of the same magnitude, 0.32 M, but in the opposite direction.

The dynamics of activation also has some effect on the magnitude of the deviation from the ideal case. Slowing down the rate of activation but keeping the same selectivity has very minor effect. However, when activation is faster, then the level of deviation is reduced to a greater degree, as shown in Figure 5.

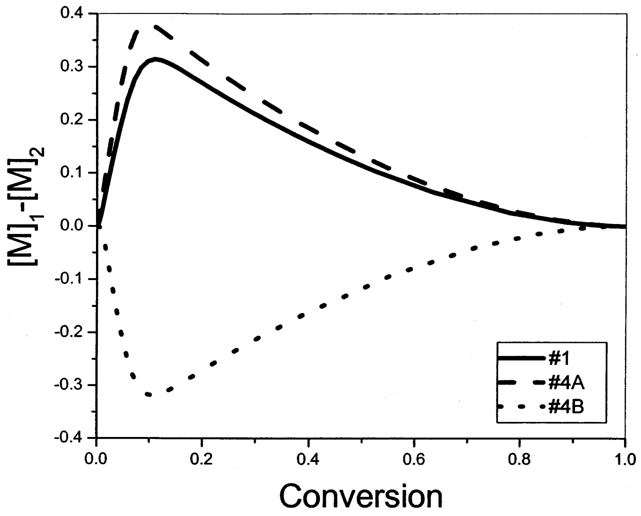


Figure 4. Dependence of the difference in comonomers concentrations on conversion for systems 1, 4A, and 4B from Table 1.

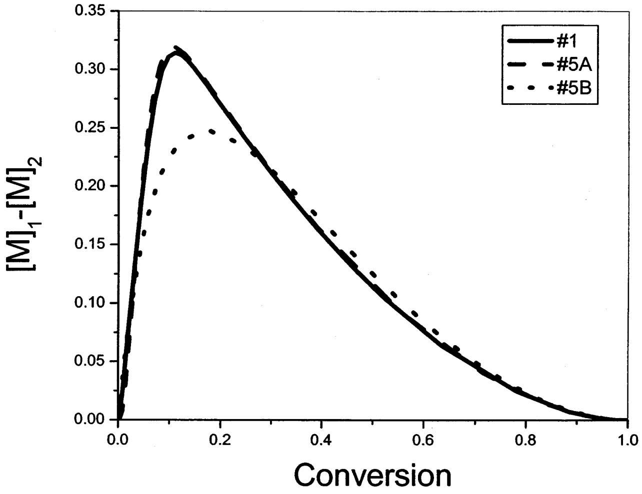


Figure 5. Dependence of the difference in comonomers concentrations on conversion for systems 1, 5A, and 5B from Table 1.

On the contrary, if both rate constants of deactivation get smaller, the magnitude of the deviation decreases. Thus, if the rate constant of deactivation becomes equal to that of homopropagation, deviation drops from 0.32 to 0.12 M. It further drops to 0.04 M (less than end group concentration) for $k_d/k_{11} = 0.1$, as illustrated in Figure 6. The origin of this phenomenon is nonselective initiation. Both active sites are generated with identical probabilities, and they propagate with the same rates before they can be deactivated. Therefore, the contribution of selective activation is diminished with reduction in the rate constant of deactivation. This demonstrates the effect of intermittent activation on chemoselectivity in these systems.

Selectivity of exchange may be accomplished by either selective activation or selective deactivation. Figure 7 presents data obtained for a system in which both activation rate constants are identical but deactivation is selective. The net result is identical to the starting case with 10-fold faster activation but nonselective deactivation. When both rate constants of deactivation

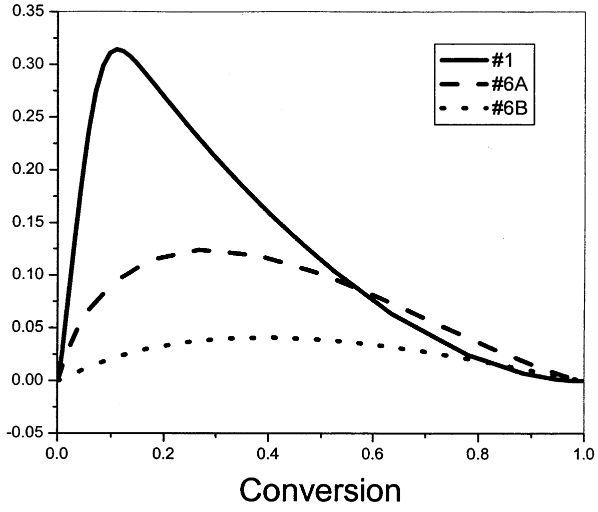


Figure 6. Dependence of the difference in comonomers concentrations on conversion for systems 1, 6A, and 6B from Table 1.

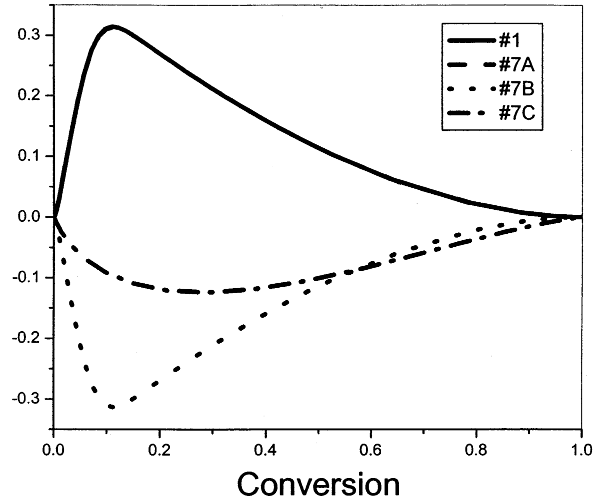


Figure 7. Dependence of the difference in comonomers concentrations on conversion for systems 1, 7A, 7B, and 7C from Table 1.

are reduced, the magnitude of deviation also drops, in agreement with the previously discussed case. The data for cases 1 and 7A overlap, since the equilibrium constants are respectively the same. Moreover, when the equilibrium constants for both comonomers are the same, even if the values of k_{a1} and k_{a2} are different, no deviation is observed.

The magnitude of deviation also depends on the initial monomer ratio. However, the divergence from the ideal system is more difficult to observe than in copolymerization of an equimolar mixture, since the system is not symmetrical. In Figure 8A differences from the corresponding ideal systems without exchange are shown as dotted lines. The deviations are more significant at the early stage of the copolymerization when the monomer present in excess is activated slower; on the other hand, the maximum effect shifts toward higher conversion when the faster activated monomer is present at higher initial concentration (cases 8A and 8B). This is even more clearly seen in Figure 8B, where differences between cases 8A and 8B and the ideal systems (equal rates of activation and deactivation for both species) are plotted as a function of conversion. An excess of the more slowly activated monomer (70%) leads to smaller

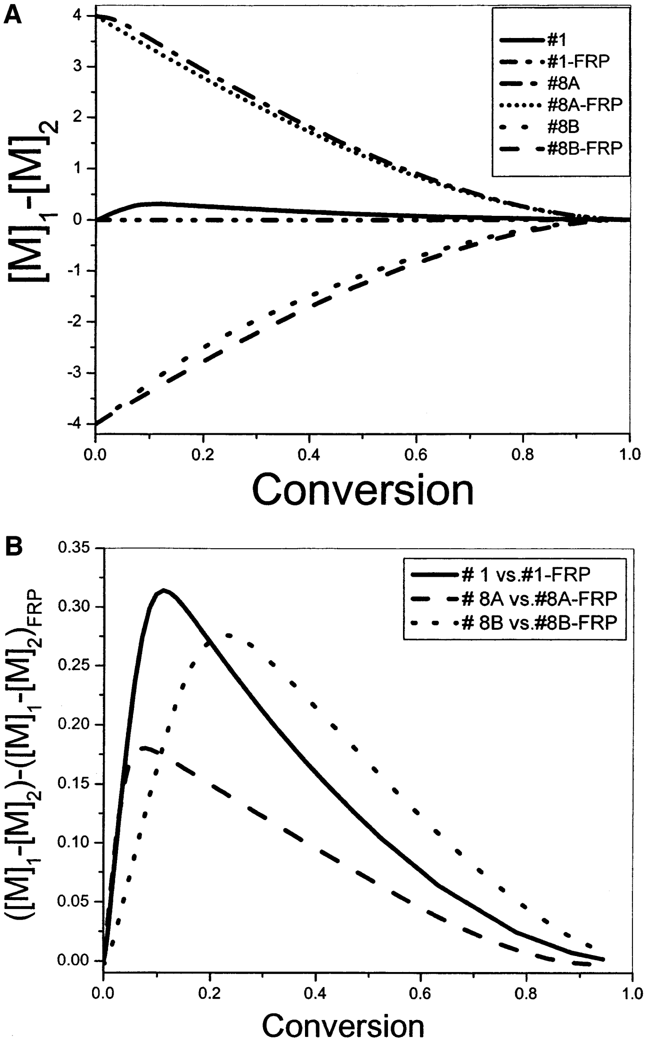


Figure 8. (A) Dependence of the difference in comonomers concentrations on conversion for systems 1, 8A, and 8B from Table 1. (B) Dependence of the relative difference in comonomers concentrations for systems with intermittent activation and the ideal copolymerization at initial comonomer ratios 50:50, 30:70, and 70:30 on conversion for systems 1, 6A, and 6B from Table 1.

and earlier deviation from the ideal case. Excess of the faster activated monomer shifts the maximum of the deviation to higher conversion, but the magnitude is still smaller than seen for the copolymerization of an equimolar ratio on monomers.

We have also performed simulation of a case very similar to ATRP of methacrylates catalyzed by the CuBr/bpy system. The same concentrations of comonomers and initiators were used as in case 1 (Table), but initial values for the concentration of the catalyst components, 0.1 M of Cu(I) and 0.01 M of Cu(II) species, were used. The values of the rate constants were similar, as in case 1 (Table 1), but bimolecular rate constants of activation were $k_{a1} = k_a = 1\ M^{-1}\ s^{-1}$, $k_{a2} = 10\ M^{-1}\ s^{-1}$, and $k_d = k_{d1} = k_{d2} = 10^7\ M^{-1}\ s^{-1}$. In addition, we included termination steps with values $k_{t0} = k_{tc} = k_{td} = 10^7$ and $10^8\ M^{-1}\ s^{-1}$, as depicted in Scheme 2.

Thus, homopropagation is 10 times faster than cross-propagation, and activation of the second comonomer is 10 times faster than the first one. This might be the case in a system containing methacrylates with a chiral moiety, which should obey some stereoselectivity. In the presence of a nonselective initiator and a nonselective

Scheme 2. ATRP Scheme for Copolymerization with Intermittent Activation and Termination

Initiation

$$\mathrm{R\text{-}X + Cu^{I}X/L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} R^{\bullet} + Cu^{II}X_2/L}$$

$$\mathrm{R^{\bullet} + M_1 \xrightarrow{k_i} P_1^{\bullet}}$$

$$\mathrm{R^{\bullet} + M_2 \xrightarrow{k_i} P_2^{\bullet}}$$

Propagation

$$\mathrm{P_1\text{-}X + Cu^{I}X/L \underset{k_{d1}}{\overset{k_{a1}}{\rightleftharpoons}} P_1^{\bullet} + Cu^{II}X_2/L}$$

$$\mathrm{P_2\text{-}X + Cu^{I}X/L \underset{k_{d2}}{\overset{k_{a2}}{\rightleftharpoons}} P_2^{\bullet} + Cu^{II}X_2/L}$$

$$\mathrm{P_1^{\bullet} + M_1 \xrightarrow{k_{11}} P_1^{\bullet}}$$

$$\mathrm{P_1^{\bullet} + M_2 \xrightarrow{k_{12}} P_2^{\bullet}}$$

$$\mathrm{P_2^{\bullet} + M_2 \xrightarrow{k_{22}} P_2^{\bullet}}$$

$$\mathrm{P_2^{\bullet} + M_1 \xrightarrow{k_{21}} P_1^{\bullet}}$$

Termination

$$\mathrm{2\,R^{\bullet} \xrightarrow{k_{t0}} D_2}$$

$$\mathrm{P_n^{\bullet} + P_m^{\bullet} \xrightarrow{k_{tc}} D_{n+m}}$$

$$\mathrm{P_n^{\bullet} + P_m^{\bullet} \xrightarrow{k_{td}} D_n + D_m}$$

activator, stereoselection but *no stereoelection* could be observed. However, when using an achiral initiator but a catalyst with a chiral ligand, one can expect either selective activation or deactivation. The rate constants correspond to the first system depicted in Figure 1 but with both activation and deactivation processes occurring as bimolecular reactions and with radical termination reactions involved.

As shown in Figure 9A, this system behaves like the first analyzed model system, indicating that termination reactions have a small effect on overall comonomer consumption.

However, when termination becomes faster ($k_t = 10^8$ M^{-1} s^{-1}), a slightly weaker deviation is observed than for case no. 1 (cf. Figure 9B).

Understanding the Origin of the Deviations. Differences in relative rates of comonomer consumption between systems with and without intermittent activation may be ascribed either to the late establishment of the equilibrium between dormant and active sites of the equilibrium between cross-propagation steps.

Figure 10 represents values of the quotients of rates of activation and deactivation for the standard case 1 and for the ATRP system with termination, together with the deviation in relative monomer concentration. The equilibrium between active and dormant species for both comonomers is reached at a very early stage of copolymerization reaction (<5% monomer conversion) whereas the magnitude of deviation still increases and reaches the maximum at >10% conversion.

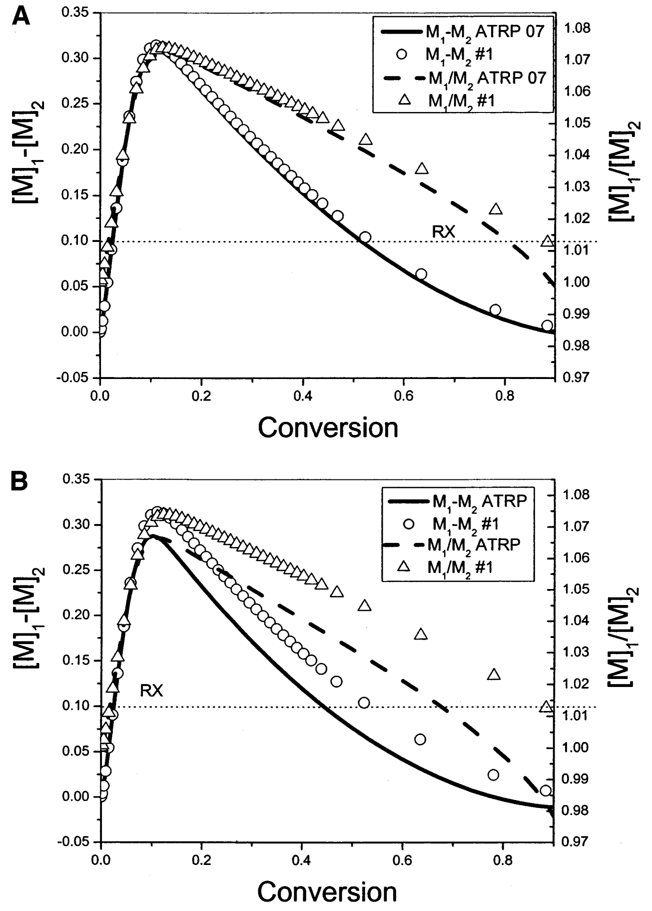


Figure 9. (A) Dependence of the difference in comonomers concentrations and their ratio on conversion for system 1 from Table 1 and the ATRP system with slower rate constant of termination ($k_t = 10^7$ M^{-1} s^{-1}). (B) Dependence of the difference in comonomers concentrations and their ratio on conversion for system 1 from Table 1 and the ATRP system with faster rate constant of termination ($k_t = 10^8$ M^{-1} s^{-1}).

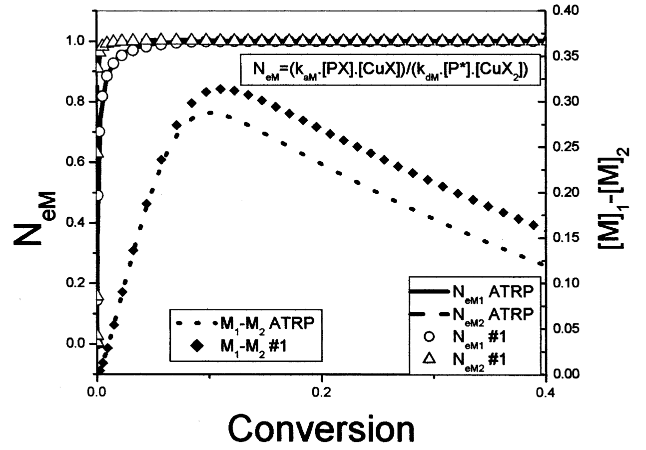


Figure 10. Dependence of the difference in comonomers concentrations and ratio of activation/deactivation rates for both chain ends on conversion for system 1 from Table 1 and the ATRP system with faster rate constant of termination ($k_t = 10^8$ M^{-1} s^{-1}).

Surprisingly, the rates of cross-propagation are not equal, and they only reach equilibrium when the deviation reaches the maximum value. Once the equilibrium is attained, the magnitude of the deviation decreases, and the system attempts to self-correct. Thus, it seems that the origin of the observed deviations is in the slow establishment of the cross-propagation equilibrium. This is also associated with different concentrations of active centers, since the deviation disappears, when the equilibrium constants are the same. We analyzed in the

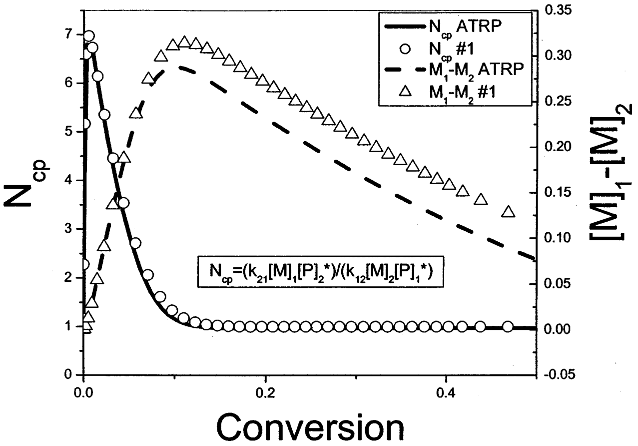


Figure 11. Dependence of the difference in comonomers concentrations and ratio of cross-propagation rates on conversion for system 1 from Table 1 and the ATRP system with faster rate constant of termination ($k_t = 10^8$ M^{-1} s^{-1}).

same way the other systems discussed earlier, and in all of them, the deviation started to decrease once the cross-propagation equilibrium is established.

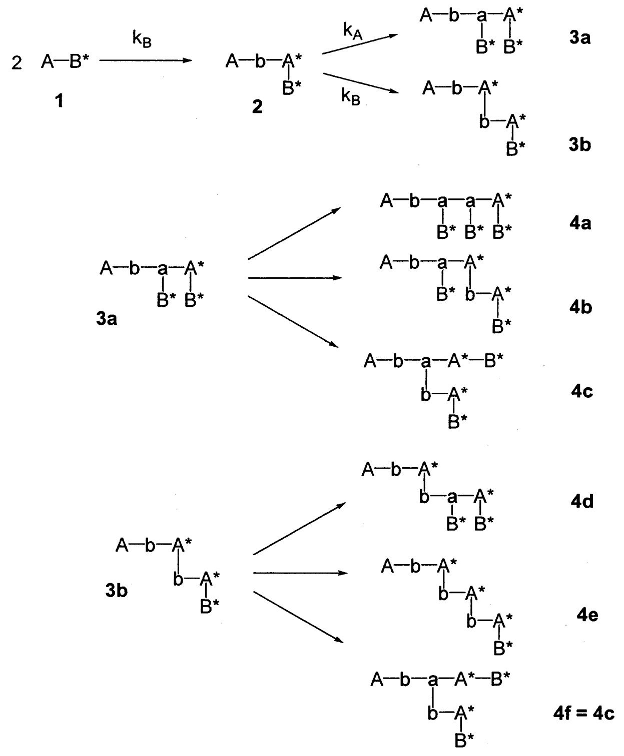
This may suggest that data collected at low conversion may give erroneous reactivity ratios. We have previously discussed the potential deviation originating from the selective initiation,[9] but this affect may be additionally magnified by the selective activation/deactivation steps.

Relations to Real Systems. The analyzed systems suggest that intermittent activation may enhance stereocontrol and convert stereoselection to stereoelection, when chiral mediators (ligands in ATRP or chiral nitroxides in NMP) are used in conjunction with racemic mixtures of comonomers. This stereoelection does not require involvement of any special (nonradical) intermediates, just conventional free radicals and conventional stereoselectivities. However, the presence of a chiral mediator is not sufficient to observe any effects on for example tacticity.

There are reports on selective capping of styryl radicals with chiral nitroxides.[26,27] Similar observations have been made with *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN) and acrylates. The ratio of diastereomers is 2.8:1 for methyl 2-propionate alkoxyamine[28] and 5:1 for *tert*-butyl 2-propionate alkoxyamine.[29] For both systems, deactivation seems to be nonselective, and the enantiomeric enrichment originates in selective activation. This is in contrast to 1-phenylethyl derivatives of DEPN, where the distereomeric enrichment is due to selective coupling, since diastereomeric alkoxyamines with DEPN moieties are present at different concentrations but both cleave with the same rate.[28,30] Regardless, for all these systems, no stereocontrol of the polymer chain and no effect on tacticity was observed. It will be interesting in the future to study similar systems using chiral monomers and chiral capping agents. In fact, a preliminary report on ATRP using chiral ligands and chiral monomers has been published.[31] A small degree of stereoelection has been reported despite using an achiral initiator. It is difficult to elucidate whether the optical activity originated only from the chiral end group and selective capping or also from an additional stereoelection process.

A similar case is the synthesis of hyperbranched polymers by self-condensing vinyl polymerization (SCVP)[32] of unimers, i.e., vinyl monomers which contain initiating sites.[33] The degree of branching in the SCVP of 2-(2-bromopropionyloxy)ethyl acrylate depends very strongly on the reaction conditions and on the concentration of deactivator.[34,35] The concentration of deactivator in solution can be controlled by either temperature or ligand. At higher temperatures $CuBr_2$/bpy is more soluble in the reaction medium and highly branched polymers are formed, whereas at lower temperature deactivator concentration is low, and consequently deactivation is too slow, and linear polymers are obtained. Branching also strongly depends on the ligand used and is higher for complexes formed with bpy containing alkyl substituents than for complexes with less soluble unsubstituted bpy.

Scheme 3. Formation of Hyperbranched Polymers in Self-Condensing Vinyl Polymerization for AB* Monomers



In Scheme 3, A represents a double bond and B* a pendant alkyl halide which is reversibly activated. Incorporation of the alkyl halide leads to structure b and transfer of the halide to a double bond to form A*. A double bond can react with either B* or A* unit leading to either b or a units and (re)generating A* unit. In the most simple case, activity of A* and B* may be identical, leading to the same values for rate constants k_A and k_B. If the deactivation happens very quickly, then both A* and B* units will react with the same probabilities leading to structures like 4b, 4c, and 4d in Scheme 3. However, if deactivation happens very slowly, then the A* species will continue to react with A units resulting in a segment with linear polymer units (4a). The topology therefore depends on the rate of deactivation (i.e., on the concentration of deactivator). Without sufficient deactivator nearly linear chains are formed but in the presence of large amounts of deactivator in solution, linear chain growth is interrupted to yield Br-terminated oligomers where each initiation site can be randomly activated.

In SCVP of 2-(2-bromopropionyloxy)ethyl acrylate, the reactivation can occur at Br atoms either at the chain end or at the pendant units. Since the latter are present at much higher concentration, the result is the formation of highly branched systems. The proportion of branched units increases with temperature and solubility of ligands. At 50 °C, the degree of branching was below 20% with 2,2′-bipyridine but over 45% with di-4,4′-*tert*-butyl-2,2′-bipyridine and 50% with di-4,4′-nonyl-2,2′-bipyridine.[35] This example clearly demonstrates that chemoselectivity can be affected in systems with variable intermittent activation/deactivation.

Results of simulations indicate that there is some possibility of affecting the apparent reactivity ratios. Although measurement of reactivity ratios for several ATRP copolymerizations showed values similar to conventional radical polymerizations, small differences were observed.[9] The possible reasons for these differences were considered to originate from different reaction conditions, such as conversion, temperature, effect of end group (either using selective initiator or selective capping agent), potential complexation with transition metal complexes (weak Lewis acids), and imprecision of the experimental data. However, as demonstrated in this paper, intermittent activation may affect the relative rates of comonomer consumption and hence the apparent reactivity ratios. The differences will be largest for systems with a tendency for homopropagation but are also noticeable in systems with a tendency toward alternating copolymerization. Intermittent activation can potentially result in a small variation in kinetic isotope effects (copolymerization of “comonomers” with ^{1}H vs ^{2}H and ^{12}C vs ^{13}C isotopes) due to selective activation.

The reported effects can be obviously magnified, and even become dominant, when additional interactions are included. For example, complexation with Lewis acids leads to well-defined alternating styrene/methyl methacrylate copolymers using the RAFT technique.[36] Copolymerization of macromonomers is affected by solvent and structure of (macro)initiator, since diffusion becomes controlling factor in some systems.[18,37−39]

Therefore, conclusions on the nature of active centers and the mechanism, based solely on measurements of apparent reactivity ratios, may not be fully reliable, unless rate constants for the activation and deactivation steps are measured for both types of active centers. In addition, penultimate effects should be also considered.

Conclusions

The modeling studies, and some earlier reported experimental results, have demonstrated that a copolymerization that proceeds through an intermittent activation/deactivation process can influence relative rates of comonomer consumption. The effect is stronger when homopropagation is faster than cross-propagation; however, it is still noticeable for systems with a tendency toward alternating copolymerization. The prerequisite for an observable difference in reactivity ratio is a difference in either the activation or the deactivation steps. The degree of deviation from ideal systems increases with concentration of initiator and exceeds by severalfold the concentration of end groups. It is generally larger at lower monomer conversion, and the effect nearly disappears for systems with very slow deactivation, i.e., systems that resemble conventional polymerizations when initiation is nonselective.

Polymerization by intermittent activation processes can affect not only copolymer composition but also the topology of chains in self-condensing vinyl polymerization. It can also convert stereoselective polymerization to stereoelective polymerization. These systems are currently under study, and results will be reported in the near future.

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