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Theoretical Simulation on Dynamics of Macrophase Separation in Styrene-*block*-butadiene Copolymer Driven by Thermooxidative Reactions

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ABSTRACT: A theoretical model has been introduced to elucidate the structure evolution and growth dynamics of macrophase separation in the styrene-*block*-butadiene (SB) diblock copolymer induced by thermooxidative reactions. In the model, the reaction kinetics is combined with the time-dependent Ginzburg−Landau equation (model B) using Flory−Huggins−de Gennes free energy density. Numerical simulations revealed that our kinetic model qualitatively captures the essential features of the experiments reported earlier, including domain morphology and spatiotemporal growth dynamics. Of particular interest is the existence of a plateau (or a hump) in the growth dynamic behavior governed by the competition between chain scission and cross-linking reactions.

Introduction

In a previous paper,[1] we have demonstrated the occurrence of macroscopic phase separation in a commercial grade styrene-*block*-butadiene-*block*-styrene (SBS triblock) copolymer (Kraton 1102) upon exposure to air at elevated temperatures. Thermooxidative reactions occur at unsaturated bonds of polybutadiene segments, causing not only chain scission but also macrophase separation between polystyrene-rich and polybutadiene phases. While the first phase separation advances, the emerging radicals undergo cross-linking, driving macrophase separation to occur for a second time. This second phase separation, termed “cascading phase separation”,[2] takes place within the preformed domains as well as in the matrix. The thermooxidative degradation driven phase separation was confirmed in the as-synthesized SBS triblock and also in the as-synthesized styrene-*block*-butadiene (SB) diblock copolymers. Despite the differences in copolymer types and total molecular weights, the structure and growth dynamics of the three styrene−butadiene block copolymers are strikingly similar to each other.

Another important feature is the reduction of the overall molecular weight of the copolymer due to chain scission and subsequent increase in the molecular weight due to cross-linking. To elucidate the changing trend of the overall molecular weight of the copolymer during thermooxidative degradation, a kinetic equation involving the thermooxidative reaction rate was derived on the basis of a simplified reaction scheme, assuming that the chain scission occurs at the chemical junctions of the block copolymers.[3] Numerical calculations revealed that our kinetic model qualitatively captured the experimental trends such as initial reduction and subsequent increase in molecular weight of polybutadiene (PB) segments. The effect of kinetic parameters on the time-dependent molecular weight of the diblock was demonstrated.[3] Moreover, the thermooxidative reactions not only cause the molecular weight changes but also drive macrophase separation between the constituent polystyrene and polybutadiene segments.

To elucidate the emergence of domain morphology, the nonlinear reaction−diffusion equation is introduced by combining the reaction kinetic equation with the time-dependent Ginzburg−Landau (model B) equation along with the Flory−Huggins−de Gennes free energy density. Numerical simulations have been carried out with emphasis on investigation of effects of reaction rate constants, thermodynamic parameters, and block copolymer compositions on dynamics of macroscopic phase separation in a SB diblock copolymer subjected to the thermooxidative reaction-induced macrophase separation of a SB diblock copolymer.

Theoretical Scheme

In the macrophase separation driven by the thermooxidative reaction, the majority of SB diblock copolymer underwent chain scission, which in turn drives macroscopic phase separation between polystyrene-rich copolymer and pure polybutadiene. When chain scission continues, more and more butadiene segments are detached from the PS-rich copolymer chains. The depletion of butadiene eventually transforms the PS-rich copolymer to the almost pure PS segment, which may be envisaged as equivalent to chain scission occurring near or at the chemical junction. Although the occurrence of chain scission may be equally probable for butadiene segments, the one near the chemical junction is most vulnerable because polystyrene and polybutadiene are inherently immiscible, and thus chain tension would be highest at or near the chemical junction. Furthermore, it is assumed that the film is thin, and the residual amount of butadiene segments in the PS-rich copolymer, if any, is negligibly small and nonreactive; the radical reaction occurs exclusively at the butadiene segments.[3]

Let $\phi_B(\vec{r},t)$ and $\phi_S(\vec{r},t)$ be the local volume fractions of polybutadiene and polystyrene chains at position, $\vec{r}$, and time, t, respectively, assuming the system to be incompressible, viz., $\phi_B(\vec{r},t) + \phi_S(\vec{r},t)$. For a conserved order parameter system, the total free energy of the system is represented as $F = \int_V f\, dV$, where the local free energy of the system, f, may be expressed in the context of

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Flory–Huggins–de Gennes theory,[4,5]

$$\frac{f}{nk_BT} = \chi\phi_B(1-\phi_B) + \frac{\phi_B}{N_B}\ln\phi_B + \frac{1-\phi_B}{N_S}\ln(1-\phi_B) + \frac{1}{36}\left(\frac{a_B^{\,2}}{\phi_B} + \frac{a_S^{\,2}}{1-\phi_B}\right)(\nabla\phi_B)^2 \quad (1)$$

where a_B and a_S are statistical segment length of PB and PS, respectively. The reaction–diffusion process may be modeled by combining the thermooxidative reaction with the time-dependent Ginzburg–Landau equation.[6] The TDGL–model B reads

$$\frac{\partial\phi_B}{\partial t} = \nabla\left(\Lambda_B\nabla\frac{\delta F}{\delta\phi_B}\right) + \eta_B(\vec{r},t) \quad (2)$$

where Λ_B denotes the Onsager coefficient having the form of

$$\frac{1}{\Lambda_B} = \frac{1}{D_BN_B\phi_B} + \frac{1}{D_SN_S\phi_S} \quad (3)$$

with

$$D_B = \frac{D_B^o}{N_B^{\,2}},\quad D_S = \frac{D_S^o}{N_S^{\,2}} \quad (4)$$

where D_B and D_S are self-diffusion coefficients of PB and PS, respectively, and D_B^o and D_S^o are the self-diffusion coefficients of the corresponding monomers. $\eta_B(\vec{r},t)$ is the thermal fluctuation force that satisfies the fluctuation–dissipation theorem as follows:[6]

$$\langle\eta_B(\vec{r},t)\,\eta_B(\vec{r}\,',t')\rangle = -2k_BT\Lambda_B\nabla^2\delta(\vec{r}-\vec{r}\,')\,\delta(t-t') \quad (5)$$

The variational derivative of the total free energy may be expressed as

$$\frac{\delta F}{\delta\phi_B} = \chi(1-2\phi_B) + \frac{1+\ln\phi_B}{N_B} - \frac{1+\ln(1-\phi_B)}{N_S} - \frac{1}{18}\left(\frac{a_B^{\,2}}{\phi_B} + \frac{a_S^{\,2}}{\phi_S}\right)(\nabla^2\phi_B) + \frac{1}{36}\left(\frac{a_B^{\,2}}{\phi_B^{\,2}} - \frac{a_S^{\,2}}{\phi_S^{\,2}}\right)(\nabla\phi_B)^2 \quad (6)$$

It should be noted that the effect of chemical reaction is reflected in the change of degree of polymerization of polybutadiene (N_B in eq 6), which, in turn, modifies the diffusion and hence the emerging structure during phase decomposition. The average degree of polymerization of polybutadiene chains may be modeled in the framework of the competition between the oxidative chain scission and the cross-linking in what follows:[3]

$$\frac{dN_B}{dt} = -k_s[O_2]N_B + k_pN_B^{\,2}\left(1-\frac{1}{N_B}\right)^m\left(\frac{1}{N_B}\right)^n \quad (7)$$

where m and n are the reaction kinetic exponents and t is time. k_s and k_p are kinetic constants for chain scission and cross-linking, respectively. Physically, the first term on the right-hand side of eq 7 is due to the oxidative reaction leading to the chain scission, and the second term represents the cross-linking reaction. Since oxygen radicals are needed in the oxidative reaction, its concentration should be accounted for in the chain scission part. Further, the reduction in molecular weight depends on the active oxygen concentration as follows:[7,8]

$$-\frac{d[O_2]}{dt} = k_i[O_2] \quad (8)$$

where k_i is a kinetic constant for oxidation and $[O_2]$ denotes the concentration of active oxygen. It should be noted that eqs 2, 7, and 8 may be nondimensionalized in the numerical calculations. However, regarding the size estimation, one can convert these dimensionless parameters back to the actual dimensions through the relationships $t = (\Lambda/l^2)t'$; $k_j = (l^2/\Lambda)k_j'$; $a_B = a_B'/l$; $a_S = a_S'/l$; $x = x'/l$, and $y = y'/l$, where l is the length scale and j represents the type of reactions such as chain scission or cross-linking. The prime symbols are in real units, and Λ may be treated as constant for simplicity.

The dynamics of phase separation can be investigated by solving eqs 2 and 7 simultaneously. The interaction parameter of the PS/PB pair, reported by Roe and Zin,[9] i.e., $\chi = -0.0652 + 48.8/T$, was used in the calculation. The numerical simulation was performed on a two-dimensional square lattice (128 × 128) using a finite difference scheme for spatial steps and an explicit method for temporal steps with a periodic boundary condition. Various time and spatial grid sizes were employed to ensure the stability of the numerical computations.

To compare with the light scattering experiments, the structure factor, $S(\vec{q},t')$, has been calculated via Fourier transform of local concentration fluctuations in the form of

$$S(\vec{q},t') = F[\phi(\vec{r}_1,t')\,\phi(\vec{r}_2,t')] \quad (9)$$

where $\vec{q}$ is the scattering wave vector, and its magnitude is defined as $q = (4\pi/\lambda)\sin(\theta/2)$ in which λ and θ are wavelength of incident light and scattering angle in the medium, respectively. Since the calculated structure factor corresponds to the theoretical scattering pattern, it may be compared with the experimental light scattering results.[1]

Simulations on Dynamics of Phase Separation

1. Effects of Reaction Kinetics. We have demonstrated experimentally the emergence of macrophase-separated domains during the course of thermooxidative reaction at the disordered state of the SB diblock copolymer.[1] It was shown that the emergence of structure was governed by the kinetics of oxidation, chain scission, and cross-linking reactions underlying the thermooxidative decomposition. Since it is impractical to experimentally determine these kinetic parameters individually, we turn our attention to theoretical elucidation on the role of each kinetic parameter in the temporal evolution of domain morphology.

(i) Effect of k_i. In the simulation, the initial volumetric concentration of polybutadiene was simply taken as the volume fraction of butadiene in the diblock copolymer, i.e., $\phi_B = 0.68$. On the basis of the GPC molecular weight data of the SB diblock copolymer, the degree of polymerization of polystyrene chain (N_S) and the initial degree of polymerization of polybutadiene chain (N_B) were estimated to be 90 and 370, respectively. Other representative parameters used in the oxidative reaction of the SB diblock copolymer are provided in the caption of Figure 1.

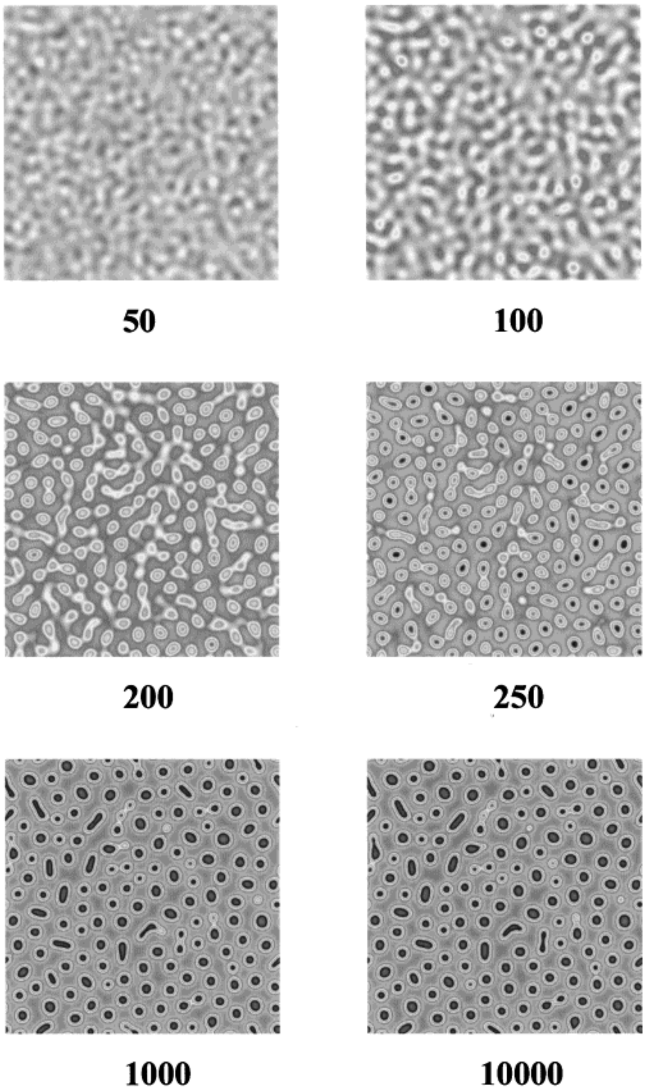

Figure 1. Temporal evolution of phase-separated domains in a SB diblock copolymer induced by thermooxidative degradation at 160 °C with $N_{B0} = 370$, $N_S = 90$, $\phi_B = 0.68$, $\chi = 0.0475$, $a_B = a_S = 0.4$, $D_B^\circ = 1,000$, $D_S^\circ = 500$, $k_i = 0.005$, $k_s = 0.2$, $k_p = 0.2$, $m = 0.5$, and $n = 1.5$.

In the simulation, sizable thermal fluctuation was imparted to trigger the thermooxidative reaction. As shown in Figure 1, a spinodal-like interconnected structure emerges shortly after initiating the oxidative reaction. At 160 °C, the blend is practically in the unstable region; thus, it comes no surprise that the initial SD structure is evident in our numerical simulation. Subsequently, the interconnected structure breaks down into smaller domains due to the instability of the system. At about $t = 250$ small dark droplets appear inside the existing domains that evolve to the final droplet texture. Note that the dark color represents a high polystyrene concentration. With the progression of time, the structures remain virtually the same from the time steps of 1000−10 000, implying that the size of the phase-separated droplets is probably fixed due to the formation of polybutadiene networks.

Next, the temporal evolution of structure factor (i.e., the scattering pattern) was calculated through Fourier inversion. As time progresses, a diffuse scattering halo develops and gets sharper (Figure 2). The scattered intensity increases while the scattering halo collapses to a smaller diameter, suggesting an increase in an average length scale or domain size. To examine the growth dynamics, q_m was plotted against time in the double-logarithmic scale (Figure 3). It is seen that q_m appears essentially constant in the early period. In the intermediate stage, q_m decreases with time. The slope, however, is rather small for the case of $k_i = 0.005$ (the middle curve). An interesting feature is that there appears a small hump (or a peak) in the vicinity of 250 time steps. Incidentally this time step corresponds to the period where small dark droplets appear during the course of structure evolution (see Figure 1). After 1000 time steps, the q_m levels off monotonically. Similar simulations have been undertaken using different rates of the oxidative reaction, viz., $k_i = 0.001$ and 0.1.

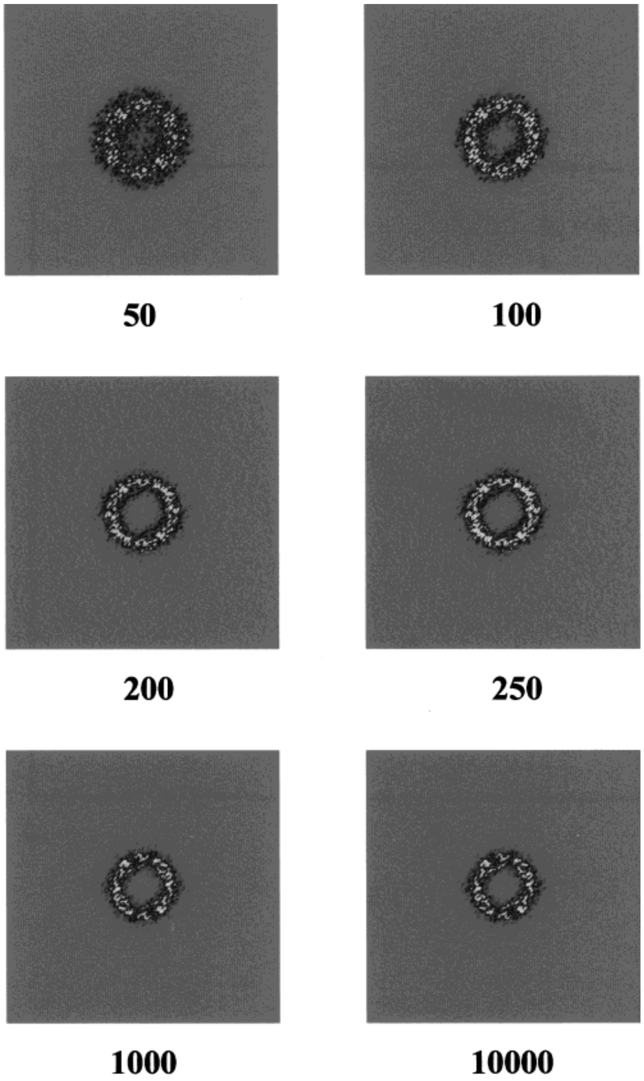

Figure 2. Temporal evolution of the corresponding scattering halo in the SB diblock copolymer induced by thermooxidative degradation at 160 °C. The conditions for the simulation were the same as in Figure 1.

Since k_i represents the rate of reduction in active oxygen concentration, a small k_i value represents a process in which the active oxygen concentration decays slowly, without appreciably affecting the cross-linking reaction. Temporal evolutions of wavenumber maxima for two other k_i values are shown together with that of $k_i = 0.005$ in Figure 3. At the early stage of phase separation, q_m is essentially constant for all the three curves. However, the slopes in the later stages are strongly dependent on the k_i values. The smaller the k_i, the steeper is the slope of the temporal growth curve.

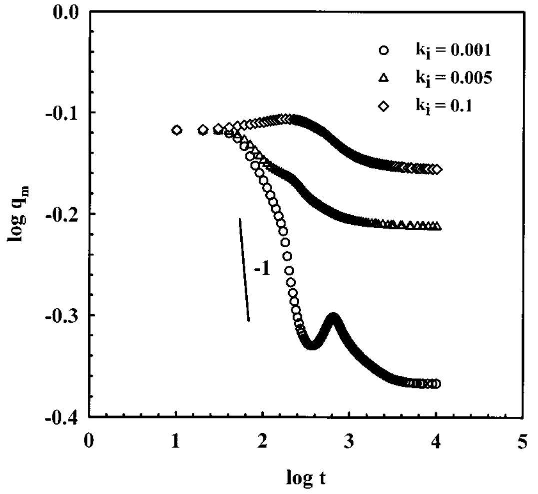

Figure 3. Temporal change of scattering wavenumber maximum in the SB diblock copolymer induced by thermooxidative degradation at 160 °C, demonstrating the effect of the reaction kinetics of radical initiation, k_i, on the growth dynamics.

It is of particular interest to note that the slope becomes positive in some parts of the intermediate stage of phase separation for $k_i = 0.001$, implying that the interdomain distance decreases within the corresponding period. Kyu and Lee[10] reported a similar observation for an epoxy/liquid rubber blend subjected to the cross-linking reaction. A unique feature in the present system is that either an inflection or a hump can be seen in the intermediate stages of growth. It can also be noted that the wavenumber maximum approached a constant value at very late stages due to the network formation.

(ii) Effect of k_s. We shall now consider the role of the reaction rate constant of chain scission, k_s, in the morphology development during thermooxidative decomposition of the SB diblocks. A large k_s implies a rapid chain scission; thus, the average molecular weight of polybutadiene chains declines drastically. In Figure 4 is shown the temporal evolution of macroscopically phase separated domains of the SB diblock copolymer for the case of $k_s = 0.4$. Note that the average molecular weight of polybutadiene dropped to a very low level with the progressive chain breakup. The lowering of molecular weight tends to suppress the UCST to a lower temperature;[3] therefore, the contrast between the two phases becomes less distinct while the initial spinodal-like (or bicontinuous) structure continues to grow. This is due to the fact that the supercooling (i.e., the difference between the UCST point and the reaction temperature) gets smaller incrementally. Since the length scale is inversely proportional to the supercooling, the decreasing supercooling leads to a larger structure. When the UCST curve falls below the reaction temperature, phase dissolution takes place.[3] This scenario is indeed captured in the simulation, revealing a nearly complete homogenization at 250 time steps (see the picture at 250 steps in Figure 4).

As demonstrated in a previous paper,[3] when cross-linking reaction becomes dominant with continued elapsed time, the average molecular weight increases again. Consequently, the UCST coexistence curve moves up asymmetrically to a higher temperature and eventually surpasses the reaction temperature. This event drives phase separation for a second time, showing small droplets, representative of polystyrene-rich domains in the blend. These droplet structures cease to grow due to the network formation. This second phase separation is consistent with our experimental observation of the styrene–butadiene block copolymers.[3]

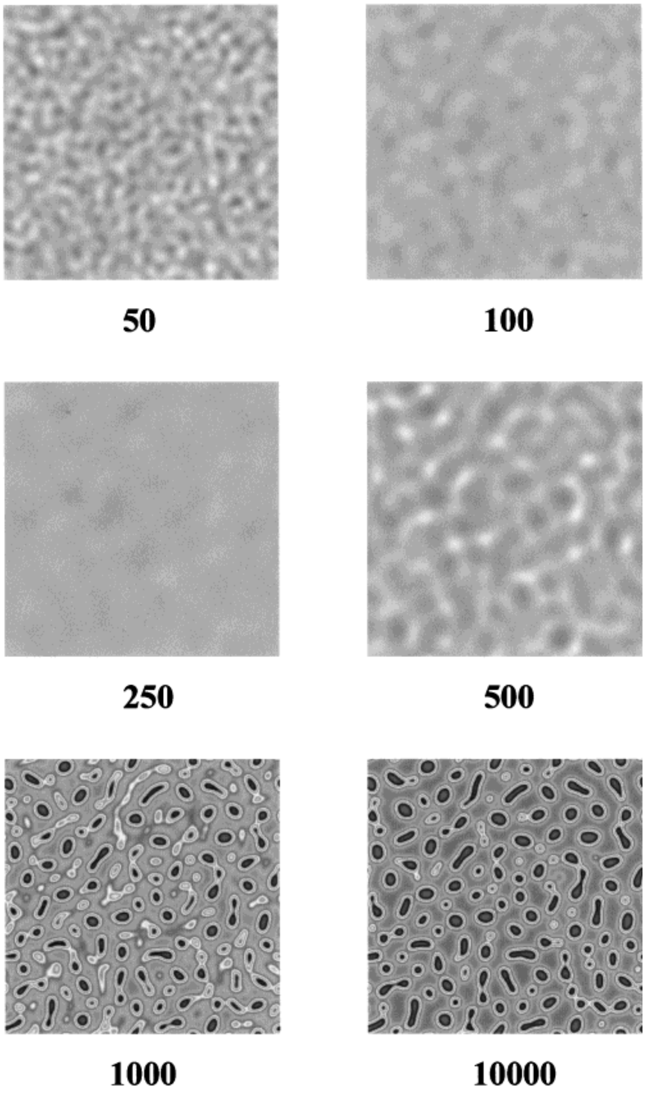

Figure 4. Temporal evolution of phase-separated domains in a SB diblock copolymer induced by thermooxidative degradation at 160 °C with $k_s = 0.4$. All other conditions for the simulation were the same as in Figure 1.

The above observation can be verified on the basis of structure factor through Fourier transformation of the concentration fluctuations. As shown in Figure 5, the scattering halo first collapses rapidly toward the center, suggestive of the structural growth. Again, the increase in domain size may be attributed to the decreasing supercooling caused by the suppression of the UCST.[3] Another interesting observation is that the contrast between the two phases diminishes due to the domination by the phase dissolution process when the UCST falls below the reaction temperature. When the second phase separation is initiated, the halo shifts to a larger scattering angle, suggesting the decrease in the average interdomain distance (or size). Subsequently, the domains show a slight growth as the system has been virtually fixed by the network formation. The present finding is unique which is drastically different from those of the thermal quench systems.

Temporal scaling curves of scattering wavenumber maxima for different k_s are shown in Figure 6. In the plot with $k_s = 0.4$, three distinct regions can be identi-

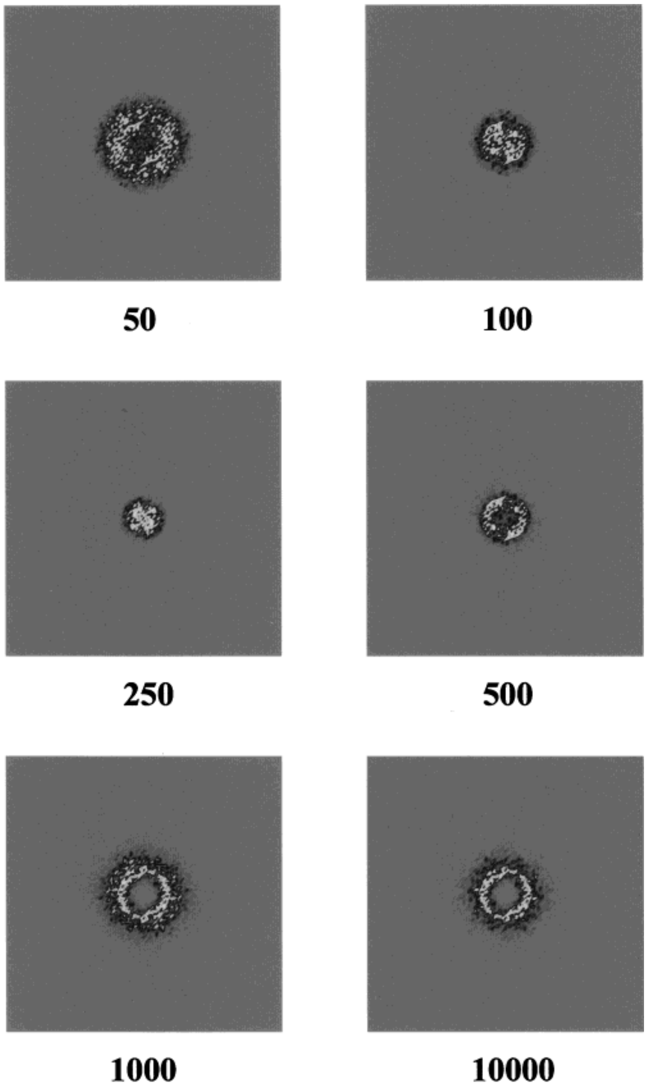

Figure 5. Temporal evolution of the corresponding scattering halo in the SB diblock copolymer induced by thermooxidative degradation at 160 °C, showing the complete phase dissolution and the second phase separation. The conditions for the simulation were the same as in Figure 4.

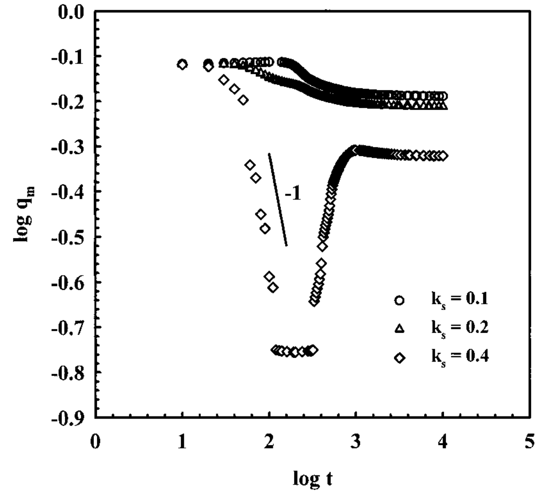

Figure 6. Temporal change of scattering wavenumber maximum in the SB diblock copolymer induced by thermooxidative degradation at 160 °C, demonstrating the effect of the reaction kinetics of chain scission, k_s, on the growth dynamics. The −1 slope is shown to guide the eye.

fied in the growth dynamic curve. Initially, the q_m shows little or no change (0−12 steps). In the region of 12−120 time steps, the q_m decreases drastically with a slope close to approximately −1. In the later region (120−320 steps), the wavenumber maximum is virtually in the main beam; i.e., the length scale of the domains diverges as the UCST approaches the reaction temperature, i.e., the supercooling approaches zero. When the UCST falls below the reaction temperature, phase dissolution occurs. When the cross-linking starts, the wavenumber maximum increases in the third region. As evident in Figure 6, the increase in the scattering wavenumber peak is due to the continuous decease in the interdomain distance rather than the size reduction (see 320−1000 time steps).

With continued elapsed time, the wavenumber maximum levels off and the corresponding structure is effectively fixed. The plot of $k_s = 0.1$ appears relatively simple as compared to that of $k_s = 0.4$. Initially, the wavenumber peak shows a slight increase in the early and intermediate stages, which may be attributed to reduction in interdomain distances or size. It then decreases slightly due to the structural growth driven primarily by thermal relaxation and eventually levels off when cross-linking takes place. It seems that the universal scaling relationship may not be valid in the entire macrophase separation of styrene−butadiene block copolymers driven by the thermooxidative reactions.

One interesting observation in the present simulation is that the growth behavior is profoundly affected by the relative reaction rates of chain scission and cross-linking, showing an inflection in the intermediate stage of the temporal growth curve. The cross-linking driven cessation of the domain growth provides an interesting avenue for morphology control of reactive polymer systems. These features are quite different from those of the regular thermal quench case. Contrary to the general perception, most block copolymers would, if not all, undergo macroscopic phase separation under the thermooxidative environment, particularly upon annealing at the disorder state.

(iii) Effect of k_p. Increasing k_p, the kinetic rate constant of cross-linking reaction, is analogous to decreasing the rate of chain scission, k_s. Naturally, a larger k_p is represented by a rapid increase in polybutadiene molecular weight. However, it is seen from Figure 5 of ref 3 that k_p values larger than 0.2 result in only slight decrease in N_B in the early stage. Therefore, two smaller k_p values of 0.05 and 0.1 have been chosen in our investigation. In the first case ($k_p = 0.05$), the temporal evolution of structure is quite similar to those with a larger k_s. As shown in Figures 7a, complete phase dissolution takes place after the initial spinodal decomposition, and then a second phase separation emerges at a later time. In a latter case $k_p = 0.1$, however, the second phase separation commences before the system has reached a complete homogeneous state, thereby showing incomplete phase dissolution (Figure 7b).

Figure 8 shows a plot of wavenumber maximum as a function of time in which the growth dynamic curve for $k_p = 0.05$ exhibits three regions similar to that of $k_s = 0.4$ shown in Figure 6. When the cross-linking reaction starts to dominate over the chain scission, the q_m increases. After reaching a maximum, the q_m decreases slightly before the domain size gets fixed due to the network formation. In the case of $k_p = 0.1$, the maxi-

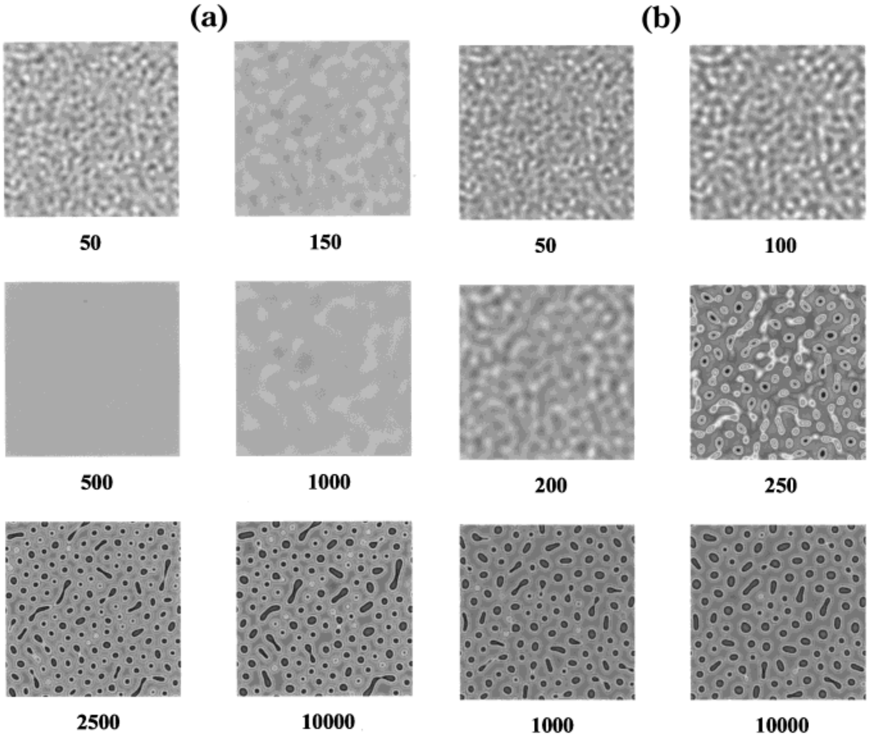

Figure 7. Temporal evolution of phase-separated domains in a SB diblock copolymer induced by thermooxidative degradation at 160 °C with $k_p = 0.05$, showing (a) complete phase dissolution followed by second phase separation and (b) $k_p = 0.1$, showing incomplete phase dissolution. All other conditions for the simulation were the same as in Figure 1.

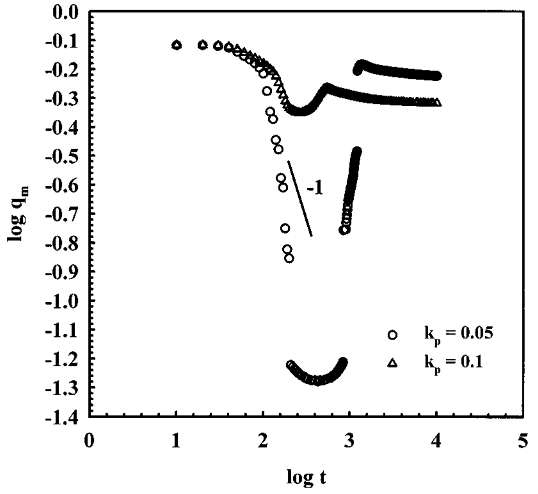

Figure 8. Temporal change of scattering wavenumber maximum in the SB diblock copolymer induced by thermooxidative degradation at 160 °C, demonstrating the effect of the reaction kinetics of cross-linking reaction, k_p, on the growth dynamics.

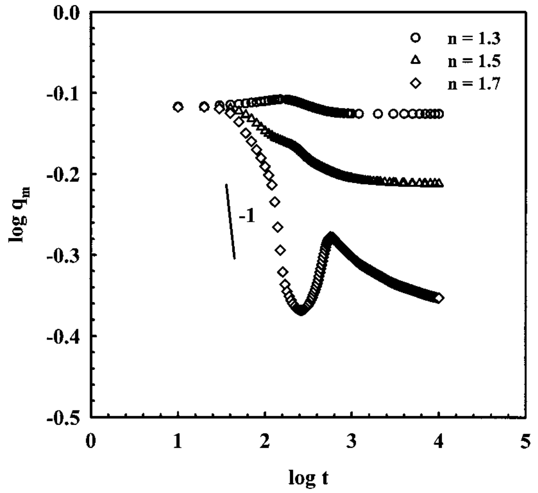

Figure 9. Temporal change of scattering wavenumber maximum in the SB diblock copolymer induced by thermooxidative degradation at 160 °C, demonstrating the effect of the reaction kinetic exponent, *n*, on the growth dynamic behavior.

mum wavenumber increases around 840 time steps after an initial decline of the q_m. The slope of the initial domain growth in the $k_p = 0.1$ case is closer to -1, indicating the sensitivity of kinetic parameter k_p to the growth behavior. In the $k_p = 0.05$ case, the slope is seemingly steeper than -1. However, in view of the limited time interval (less than 1 decade) for which the slope was drawn, it should not be overinterpreted. One plausible explanation is that the depression of the UCST curve, driven by the continued chain scission, makes the supercooling smaller; therefore, the structure gets larger. Concurrently, the structure coarsens driven by the thermal relaxation as in the case of the thermal quench case.[6] The combination of these two effects makes the structure to coarsen much faster than the conventional thermal quench systems; hence, the growth exponent could be larger than unity. Although this unusual growth behavior was observed experimentally in the SB, SBS, and Kraton (mixed SBS/SB) block copolymers, it should be cautioned that the time interval for the slope is too short (less than a decade) to make meaningful argument.[1] Nevertheless, it is evident that the growth behavior strongly depends on the relative rates of chain scission and cross-linking reactions.

(iv) Effect of *n*. The effect of *n* on the growth dynamics may be demonstrated in the plot of the temporal evolution of maximum wavenumber (Figure 9). It is apparent from eq 7 that the cross-linking of polybutadiene chains depends on the value of *n*. That is to say the smaller the *n* value, the faster increase in the polybutadiene molecular weight. In the case of $n =$

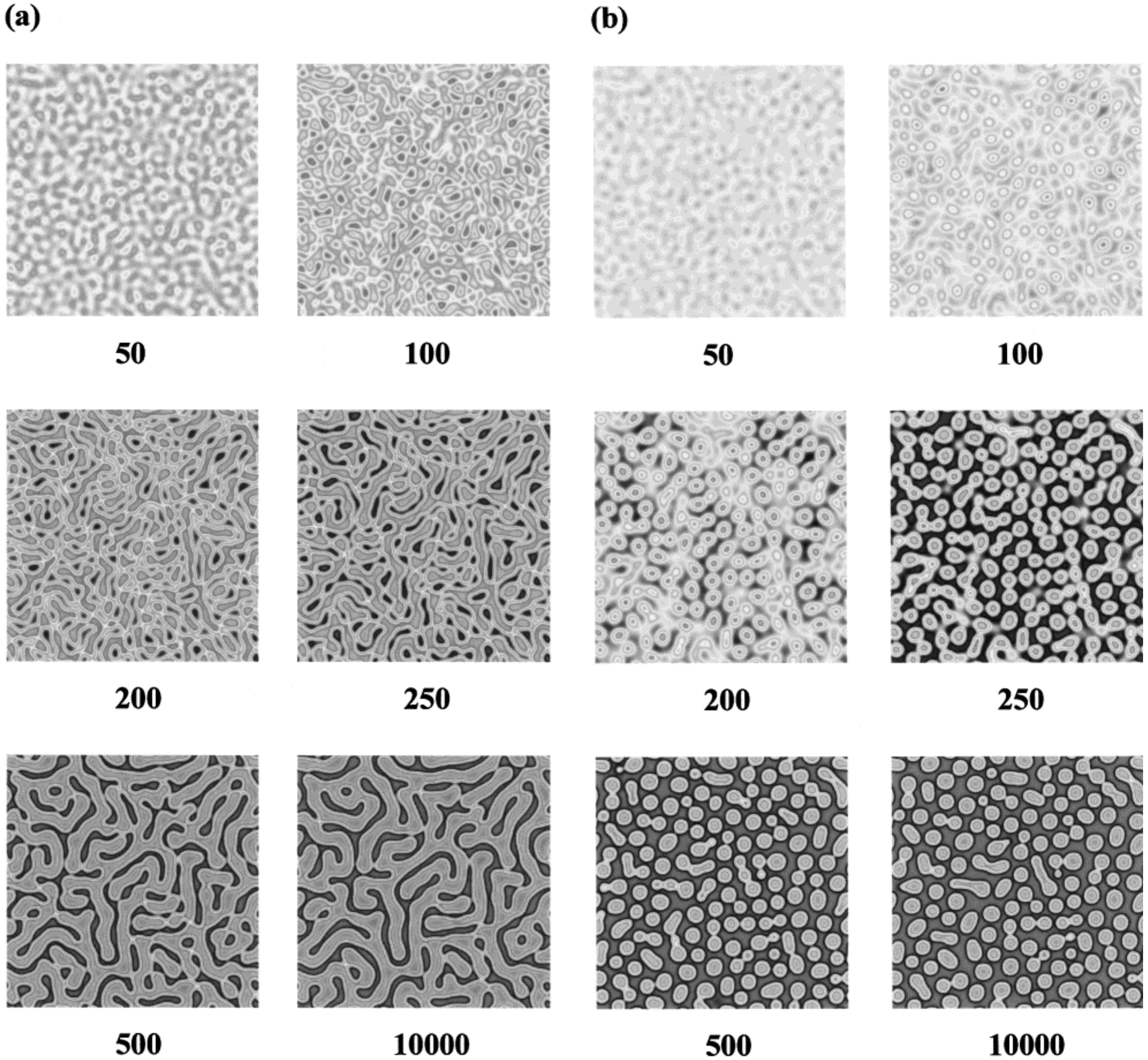

Figure 10. Effect of volume fraction of polybutadiene in the SB diblock copolymer on the emergence of domains morphology subjected to thermooxidative reaction at 160 °C: (a) 50/50 and (b) 70/30 SB diblock copolymers in comparison with that of the 32/68 compositions in Figure 1.

1.7, where the cross-linking reaction is slow relative to the chain scission, the phase-separated domains grow rapidly. The reduction in molecular weight due to the dominant chain scission makes the supercooling smaller; thus, the magnitude of q_m decreases faster, reaching the kinetic exponent close to unity. When the UCST falls below the reaction temperature, phase dissolution occurs. At a later time, the hump appears in the vicinity of 250 time units for all n values investigated. The location of the hump or peak depends on the relative rates of chain scission and cross-linking reactions. When the cross-linking becomes dominant, the growth continues until the structure has been fixed by the network formation. With a smaller n value of 1.3, the cross-linking reaction is so dominant that there appears little or no time for the domains to coarsen.

2. Effect of Volume Fraction of Butadiene Block. One of the major advantages of the present theoretical model is that one may perform numerical experiments by varying the individual parameter as opposed to the tedious synthesis of block copolymers with different volume fractions of butadiene blocks. We first investigated the thermooxidative reaction-induced phase decomposition of a diblock copolymer with a volume fraction of $\phi_B = 0.5$, having lamellar microdomains. As shown in Figure 10a, a typical SD process was observed showing a bicontinuous structure at the early stage that grows via coalescence with time. There was only slight change after 500 steps, reflecting the slow diffusion of the high molecular weight species. The final structure remains bicontinuous, suggesting self-similarity of the system.

In the case of a diblock copolymer with $\phi_B = 0.3$, polybutadiene was the minority component. We again observed the interconnected bicontinuous structure initially, but it quickly transforms to a droplet texture. These bright droplets correspond to the polybutadiene-rich phase dispersed in the PS matrix (Figure 10b). The present domain morphology is just the opposite of Figure 1 where the PS domains are dispersed in the continuum of PB. It is reasonable to infer that the change in the compositions of SB diblock from 32:68 to 70:30 makes phase inversion to occur, thereby showing the reversal of the bright and dark color of the domains,

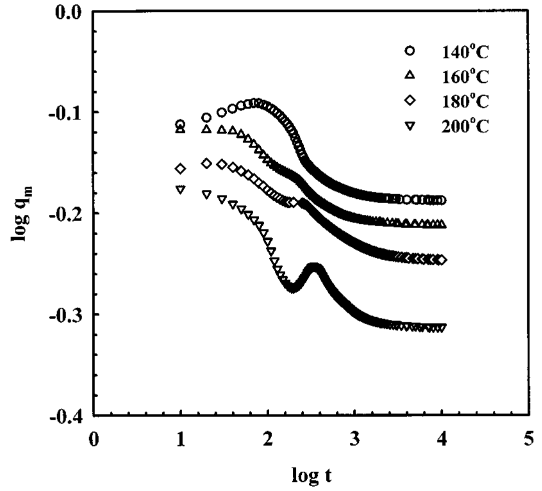

Figure 11. Temporal change of calculated scattering wavenumber maximum in the SB diblock copolymer induced by thermooxidative degradation at 160 °C, demonstrating the effect of reaction temperature on the growth dynamic behavior.

representing the dispersion of polybutadiene domains in the matrix of polystyrene.

3. Effect of Reaction Temperature. Decomposition temperature is another most important variable that affects the phase separation and chemical kinetics. In the present investigation, the effect of reaction temperature is expressed through the Flory–Huggins χ interaction parameter and the monomeric diffusion coefficients used. Note that the Flory–Huggins χ interaction parameter is inversely proportional to absolute temperature. In thermal quench systems, the interdomain distance, r, is proportional to the reciprocal of quench depth or supercooling, ΔT, i.e., the difference between the reaction temperature and the coexistence point of the final cross-linked system.[6] Since the thermodynamic driving force, i.e., the supercooling, is smaller at the higher reaction temperature, the length scale (or the interdomain distance) is larger. This is exactly what one observes in the simulations in the temperature range investigated, e.g., 140–200 °C (Figure 11).

4. Size Estimation. Although it is not our intention to match the simulation with the experimental results, it may be instructive to estimate the length scale. Regarding the comparison of the domain size, the dimensionless units may be converted to real units through the relationships $t = (\Lambda/l^2)t'$, $k_j = (l^2/\Lambda)k_j'$, $x = x'/l$, and $y = y'/l$, where l is the length scale and j represents the type of reactions. The prime symbols are in real units. If one assumes the mutual diffusivity of the system is 10^{-10} cm^2/s and the characteristic time is 0.001, the estimated length scale would be 1 μm, which gives the picture frame to be 128 μm. Hence, the average domain size would be 8.5 μm, which is somewhat smaller than that in some experiments,[1,3] but the order of magnitude is within the experimental range (10–50 μm). A possible reconciliation is that the light scattering experiment represents the 3D case, so the degree of freedom for the growth process would be higher than that of the 2D simulation. Consequently, the macrophase-separated domains could grow in the experiment to a larger dimension relative to that in the 2D simulation.[1,3] The comparison between the calculated domain pattern and the observed morphology suggests that the present simulation qualitatively shows some similar features of the macrophase-separated domains in the SB block copolymer that is driven by the complex thermooxidative reaction involving the competition between the chain scission and the cross-linking. There is no doubt that the dimensionality of growth exponent may be important, but the 3D simulation was not undertaken here because no universal scaling is expected to be valid for the entire growth of the macroscopic phase separation of the SB diblock copolymer.

Conclusions

A novel theoretical model for reaction kinetics and phase separation dynamics of SB diblock copolymer has been established on the basis of a simplified reaction scheme. The macroscopic phase separation of SB diblock copolymer is modeled as the macrophase separation between the constituent polystyrene and polybutadiene generated by the chain scission in the aforementioned SB diblock copolymer. The behavior of molecular weight change in polybutadiene is determined by the competition between the chain scission and cross-linking reactions during thermal oxidative degradation. Although the simulated results capture some qualitative features of the observed domain morphology and the experimental growth dynamics, the present theoretical approach would be more rigorous if the dimensionality of growth were taken into consideration in the simulation. The growth rate was found to be strongly dependent on kinetic parameters, implying the important role of molecular weight on controlling dynamic aspects of phase separation in reactive polymeric systems. Of particular interest is that the 50:50 SB block shows a spinodal-like bicontinuous morphology, whereas the 32/68 and 70/30 compositions exhibit droplet morphology in which phase inversion takes place. In the study of the effect of reaction temperature, it was found that the higher the reaction temperature, the larger the domain size. This observation may be ascribed to the smaller supercooling that leads to the larger length scale. Another interesting feature is the appearance of a hump (plateau or peak) in the simulated curves of wavenumber maximum vs time, which has not been seen in any thermal quench systems. There seems no universal scaling relationships exist in the macroscopic phase separation of SB diblock copolymer. To the best of our knowledge, the present study is probably the first to model the macroscopic phase separation in the block copolymers driven by the thermooxidative chain scission and cross-linking reactions.

References and Notes

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