Composition Fluctuation Effects in Chain Copolymerization

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ABSTRACT: We discuss the effects of local fluctuations in monomer composition during chain copolymerization reactions on sequence distributions and phase behavior. In particular, we show that near-critical mixtures of type A and B monomers (or macromonomers) with equal reactivity ratios can polymerize to form very blocky random copolymers. We further argue that this blockiness can be sufficient to induce liquid–liquid phase separation or mesophase separation within the reaction medium. Applications to bulk and emulsion polymerizations are briefly discussed.

I. Introduction

The importance of copolymerization was recognized very early in the development of polymer science. Chain copolymerization, in particular, has proven to be an extremely versatile tool for modifying polymer properties, such as impact strength, solvent resistance, and thermal stability, by the incorporation of appropriate comonomers into the chain backbone. Properties can be varied widely, e.g. between elastomeric and brittle, by adjusting the composition of the copolymer or the chemical identity of the constituent monomers.

The traditional scheme for analyzing the reaction kinetics of chain copolymerizations can be found in many standard textbooks on polymer science.[1] Within the so-called first-order Markov model of copolymerization, the reactivity of an active end of a growing chain (free radical, carbenium ion, or carbanion) is assumed to be dictated only by the chemical identity of that end group, and independent of the sequence of monomers added previously. For a copolymerization involving just two types of monomers, A and B, a matrix of four bimolecular reaction rate coefficients, k_{ij}, suffices to characterize the reaction kinetics of the model. Here, k_{ij} is the rate at which a type j (A or B) reactive end combines with a type i monomer to advance the growing chain. With the added assumption of steady-state concentrations of reactive species, rather complete predictions can be made for the composition and sequence-length distributions of the copolymer. These predictions are conventionally expressed in terms of the feed composition of unreacted monomers, f_0 (volume fraction of A-monomers), and two monomer reactivity ratios, denoted by $r_A = k_{AA}/k_{BA}$ and $r_B = k_{BB}/k_{AB}$.

While the above model has proven extremely useful in practice, e.g. for the design and control of polymeric reactors, it is based on a rather restrictive and frequently overlooked assumption: *spatial homogeneity of the reactants and products in the reaction bath*. Theoretical developments beyond the first-order Markov model have almost without exception been concerned with penultimate effects,[2] reversibility of the various propagation reactions (depropagation),[3] or transient (non-steady state) effects[4] but have largely overlooked microstructural changes associated with compositional inhomogeneities within the reaction medium. Experimentally, however, it is well known that significant deviations from the predictions of the first-order Markov model can occur when the copolymer has limited solubility in the reaction bath.[5] Moreover, deviations are prevalent under heterogeneous polymerization conditions, such as those achieved in suspension or emulsion polymerizations.[2,6] Related phenomena are well known in thermosetting materials such as segmented urethanes.[7] Finally, we note that concerns regarding the homogeneity assumption in traditional models of copolymerization are particularly acute in staged emulsion polymerizations, where phase-separated "core–shell" morphologies are explicitly targeted.[8]

In the present paper, we make a first attempt to address some of these issues within the context of a very simple model of reaction and diffusion. Specifically, we address the role of thermally excited spatial and temporal composition fluctuations in the reaction bath on the microstructure of an A–B random copolymer (section II). A scaling analysis is presented in section II.A, while a more quantitative approach is outlined in section II.B. To simplify the calculations and presentation, we restrict consideration to the special case of ideal random copolymerization ($r_A = r_B = 1$) in a bulk mixture of undiluted A and B monomers, but the methods and qualitative results likely have more general applicability to arbitrary reactivity ratios, to bulk solution polymerizations, and to various types of heterogeneous polymerization methods. In section III, we turn our attention to the thermodynamic stability of the reaction bath and assess the conditions for which macro- or mesophase separation can be expected. Finally, in section IV, we summarize our results and discuss the implications of our predictions for more practical situations of heterogeneous polymerization, such as emulsion polymerization.

II. Sequence Distribution Effects

In the present section we consider the idealized situation of the early-time growth of an A–B random copolymer in a reaction medium consisting of an undiluted mixture of A and B monomers. To simplify the analysis, we assume that the reaction bath is isothermal and that the copolymerization is *ideal* with equal reactivity ratios, $r_A = r_B = 1$. Thus, a single bimolecular reaction rate coefficient, $k \equiv k_{ij}$, suffices to describe the rate of addition of monomers by reaction. We also

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assume that the reaction bath is sufficiently large and the reactive species (e.g. free radicals) are sufficiently dilute that there is a significant period of time for which the growing chains propagate independently and without considerable depletion of monomer. In the present section, we restrict our analysis to such times.

The mixture of A and B monomers is taken to be homogeneous on average with a mean composition f_0, defined as the average volume fraction of type A monomers. However, the fluctuations about the mean composition are assumed to be substantial, due to the proximity of the mixture at temperature T, pressure P, and composition f_0 to a liquid–liquid phase boundary. Specifically, we require that the correlation length ξ for composition fluctuations in the mixture greatly exceeds the characteristic size of a monomer, denoted by a. In practice, this condition is most easily met in a mixture near its critical composition.

A. Scaling Picture. Within the context of the above idealized model system, we now turn to a simple scaling analysis of the sequence distribution of A and B monomers that are incorporated into a single growing chain. For this purpose, it is useful to recall the scaling picture of a one-phase binary fluid mixture near its critical point.[9] Such a mixture, in the present case the reaction medium, has its fluctuation and thermodynamic properties dominated by a single length scale—the correlation length for composition fluctuations, ξ. At the critical composition, this length grows as the critical temperature T_c is approached according to[10]

$$\xi \sim a|T - T_c|^{-\nu} \tag{2.1}$$

where $\nu \approx 0.63$ is a universal scaling exponent. Physically, ξ denotes the spatial extent over which fluctuations in composition about the mean composition f_0 are correlated.

To explore these ideas further, it proves convenient to define a composition fluctuation field $\psi(\mathbf{r},t)$ by the expression

$$\psi(\mathbf{r},t) = \phi_A(\mathbf{r},t) - f_0 \tag{2.2}$$

where $\phi_A(\mathbf{r},t)$ is the local volume fraction of type A monomers near position $\mathbf{r}$ at time t and we make the assumption of local incompressibility, i.e. $\phi_A(\mathbf{r},t) + \phi_B(\mathbf{r},t) = 1$. We further define the spatial Fourier transform of $\psi(\mathbf{r},t)$ by

$$\psi(\mathbf{q},t) = \int \mathrm{d}\mathbf{r}\, \exp(i\mathbf{q}\cdot\mathbf{r})\psi(\mathbf{r},t) \tag{2.3}$$

Information about spatial correlations in composition are contained in the "structure factor" or equal-time correlation function of $\psi(\mathbf{q},t)$:

$$S(q) \equiv V^{-1}\langle\psi(\mathbf{q},t)\psi(-\mathbf{q},t)\rangle \tag{2.4}$$

where V is the volume of the reaction bath and the angular brackets denote an equilibrium ensemble average.

With these definitions, the *scaling hypothesis* of critical phenomena[9] can be summarized by the statement that, as regards the singular dependence of thermodynamic and fluctuation properties is concerned, ξ is the only relevant length scale. For example, the free energy density of the near-critical fluid scales as $F \sim k_BT/\xi^3$. Of particular interest here is the scaling form of the structure factor, which for wavelengths greatly exceeding the monomer size a, $qa \ll 1$, can be expressed as

$$S(q) \sim a^{1+\eta}\xi^{2-\eta}G(q\xi) \tag{2.5}$$

where $\eta \approx 0.032$ is a second scaling exponent. The dimensionless scaling function $G(x)$ has the asymptotic behaviors

$$G(x) \sim 1, \quad x \to 0$$

$$G(x) \sim x^{\eta-2}, x \to \infty \tag{2.6}$$

A convenient physical interpretation of the scaling hypothesis is to envision the near-critical monomer mixture as being composed at some instant in time by a close-packed assembly of "blobs" with characteristic radius ξ. The interior of each blob corresponds to a region of fluid with strongly correlated composition, while the compositions of different blobs are essentially uncorrelated. Since the composition fluctuations can occur only to the extent that their energy is of order the thermal energy k_BT, we naturally arrive at the result already given that the free energy density is of order k_BT/ξ^3; i.e. k_BT of energy is assigned per blob.

Next, we consider the probability distribution function of compositions of the blobs. We define the composition of a blob, f, as the instantaneous fluid composition, $\phi_A(\mathbf{r})$, averaged over the blob volume ξ^3. The distribution function for blob compositions, $P_b(f)$, is peaked about the mean composition, f_0, and is expected to be approximately symmetric about f_0. Moreover, the characteristic width of the distribution can be deduced from the structure factor:

$$\langle(f - f_0)^2\rangle \equiv \int_0^1 \mathrm{d}f\,(f - f_0)^2P_b(f) \sim \int_0^\infty \mathrm{d}q\, q^2S(q)(q\xi)^{-2}j_1^{\,2}(q\xi) \tag{2.7}$$

where $j_1(x) = \sin(x)/x^2 - \cos(x)/x$ is the familiar spherical Bessel function. The final expression results from explicitly evaluating $\langle[V_\xi^{-1}\int_{V_\xi}\mathrm{d}\mathbf{r}\ \psi(\mathbf{r},t)]^2\rangle$, where the integral is over the blob volume $V_\xi \sim \xi^3$. In order to estimate the integral in eq 2.7, we next insert the scaling form of the structure factor given in eq 2.5. This leads to the following scaling result for the root-mean-square composition variations among blobs:

$$\delta f_b \equiv \langle(f - f_0)^2\rangle^{1/2} \sim (a/\xi)^{(1+\eta)/2} \tag{2.8}$$

Thus, we are led to the conclusion that the strongly fluctuating monomer composition field in a nearly incompatible mixture of monomers can be approximately described, instantaneously, as a dense collection of blobs of two types: A and B (see Figure 1). These two types of blobs are present in approximately equal proportions and are characterized by compositions that differ by an amount that is of order $\delta f_b \sim (a/\xi)^{(1+\eta)/2}$. In particular, type-A blobs have composition $f_0 + \delta f_b$, while type-B blobs have composition $f_0 - \delta f_b$.

The above scaling picture for the static properties of a near-critical fluid, summarized in Figure 1, can be extended to dynamics.[11] For the purposes of the present paper, we only require information about the characteristic lifetime of a blob. In particular, at equilibrium the various blobs will fade in and out with time. Collective diffusion over distances comparable to ξ will destroy, create, or interchange the two types of blobs. The rates of these various processes must satisfy detail balance conditions such that the time-averaged concen-

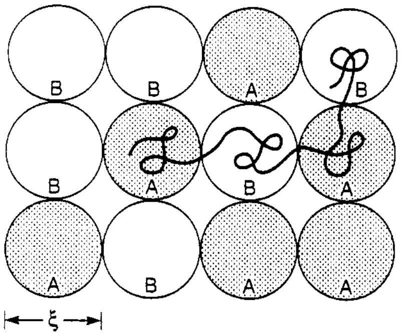

Figure 1. Growth of a "blocky" random copolymer chain in a strongly fluctuating mixture of A and B monomers. The fluid can be divided into blobs of size the concentration correlation length, ξ, each of which can be classified as being either A-rich or B-rich. A growing chain expends of order $g \sim (\xi/a)^2$ monomers in executing a random walk to displace the free radical end a distance comparable to ξ. Thus, provided the reaction is fast compared to the blob lifetime, g corresponds to the characteristic block size of the copolymers.

trations of A and B blobs remain equal and the blob characteristics are preserved. To estimate the blob lifetime, we make use of the well-known Kawasaki-Stokes formula for the collective diffusion coefficient of a near-critical binary fluid mixture[11]

$$D_\psi = k_B T/(6\pi\bar{\eta}\xi) \tag{2.9}$$

where $\bar{\eta}$ is the shear viscosity of the fluid mixture.[12] This expression has the familiar (Einstein) form of diffusivity expressed as a ratio of the thermal energy to a friction coefficient. The relevant friction coefficient has the form expected from Stokes' law applied to a sphere of radius ξ in a fluid with shear viscosity $\bar{\eta}$. The blob lifetime, τ_b, is simply estimated as the time for collective diffusion to remove concentration inhomogeneities over scales of order the blob size:

$$\tau_b \sim \xi^2/D_\psi \sim \bar{\eta}\xi^3/(k_B T) \tag{2.10}$$

We are now in a position to discuss the growth of a copolymer chain in the fluctuating reaction medium of A and B monomers. Our basic picture, summarized in Figure 1, is that subsequent to initiation at $t = 0$, the reactive group (e.g. a free radical) begins to grow a chain from monomers belonging to the interior of a particular blob. Provided that the blob lifetime τ_b is sufficiently long, the initial composition of the copolymer will be $f_0 + \delta f_b$ if the blob containing the reactive group is A-rich or $f_0 - \delta f_b$ if the blob is B-rich. Eventually, after adding a certain number of monomers, g, the propagating chain will have displaced the reactive group by a distance of order ξ, at which point a new blob (with uncorrelated composition) is entered. Thus, within this static picture of frozen blobs (τ_b very large), we expect that *random block copolymers* will be grown with a characteristic block length g and with A-rich and B-rich blocks differing in composition by an amount of order $2\delta f_b$. The placement of A-rich and B-rich blocks along the chain is expected to be random and the mean fraction of A-rich blocks should be $^1/_2$. In order to estimate the block length g within the present static picture, we note that g is the number of monomers that a growing chain must add for its characteristic size, i.e. radius of gyration, to be of order ξ. Since each addition of a monomer, corresponding to a time increment of $1/k$, advances the reactive group by a distance of order the monomer size a, but in a randomly chosen direction, we expect that a random walk is traced out by the monomers participating in the reaction. This suggests the relation $ag^{1/2} \sim \xi$, or

$$g \sim (\xi/a)^2 \tag{2.11}$$

While probably rigorous in the extreme limit of fast reaction, $k \to \infty$, this relation is questionable if the internal dynamics of the chain are operative on the time scale g/k required to add g monomers. Because the solvent is nearly athermal for the growing polymer, we expect that if conformational equilibration is possible during the growth of the chain, then self-avoiding walk statistics would be more appropriate: $g \sim (\xi/a)^{5/3}$.

From the discussion surrounding eq 2.11, it is clear that the above static picture, while correct for $k \to \infty$, is more generally suspect unless certain conditions on time scales are met. Besides the blob lifetime, τ_b, there are two other relevant time scales that must be considered. The first of these, denoted by τ_r, is the time required for a blob to be explored by reaction, i.e. by means of the random walk of the reactive group described above. This time is simply estimated as

$$\tau_r \sim g/k \sim k^{-1}(\xi/a)^2 \tag{2.12}$$

where we have used eq 2.11 for g.

The second time scale that is relevant to microstructural evolution is related to the Brownian dynamics of the growing chain. Specifically, we need an estimate of the time, denoted τ_d, for the reactive end group to explore the volume of a blob, ξ^3, in the *absence* of reaction. At extremely short times, when the growing chain has a radius of gyration much less than ξ, this exploration is dominated by center-of-mass diffusion of the chain. However, for times of order τ_r, when one or more blobs have been explored by the reaction, the chain has grown to an extent that the *internal* Brownian modes control the dynamics of the reactive end group. Building on earlier work,[13] de Gennes[14] examined this situation for both Rouse and reptation models. The restrictions on the dynamics of an end group caused by its connection to the remainder of a chain lead to an unusual diffusive behavior, referred to as "compact exploration". For the present situation of a growing chain under dilute conditions, however, hydrodynamic interactions are unscreened, so it is necessary to generalize the de Gennes approach to the Zimm model.[15]

With the goal of estimating τ_d, we now turn to consider the mean squared displacement, $\langle r^2(t)\rangle$, of the end of a chain of total degree of polymerization N subject to Zimm dynamics. The following scaling form for the displacement of the end in the Zimm model can be explicitly demonstrated:

$$\langle r^2(t)\rangle = 6D_Z t\, H(t/\tau_Z) \tag{2.13}$$

Here, $D_Z \sim k_B T/(\bar{\eta}R_g)$ is the center-of-mass diffusion coefficient of the chain, $\tau_Z \sim \bar{\eta}R_g{}^3/k_B T$ is the longest Zimm relaxation time, R_g is the chain radius of gyration, and $H(x)$ is a dimensionless scaling function. By demanding that for $t/\tau_Z \gg 1$ center-of-mass diffusion is dominant, while $\langle r^2(t)\rangle$ should be N-independent for $t/\tau_Z \ll 1$, the following asymptotic behavior of the scaling function can be deduced:

$$H(x) \sim x^{-1/3}, \quad x \to 0$$

$$H(x) \sim 1, \quad x \to \infty \tag{2.14}$$

It thus follows that the dynamics of the chain end in the "compact exploration" regime, $t/\tau_Z \ll 1$, is described by the scaling expression

$$\langle r^2(t)\rangle \sim (k_B Tt/\bar{\eta})^{2/3} \tag{2.15}$$

An estimate of τ_d is now easily obtained from eq 2.15 by identifying it as the time required for a displacement of order the blob size ξ:

$$\tau_d \sim \bar{\eta}\xi^3/k_B T \tag{2.16}$$

It follows from the scaling equivalence of eqs 2.10 and 2.16 that the blob lifetime and the end exploration time are comparable to within a numerical prefactor; i.e. $\tau_b \sim \tau_d$.

Having established that the times τ_b and τ_d are equivalent in a scaling sense,[16] we can now assess the significance of these times, collectively denoted by τ_{bd}, and the reaction time τ_r for the microstructure of the copolymer. If the reaction is *fast* compared with collective diffusion or end exploration, i.e. $\tau_r \ll \tau_{bd}$, then the static picture described previously is recovered. In particular, monomers are added to the chain in a frozen medium of correlated concentration blobs. This leads to blocky copolymers with a mean block degree of polymerization g given by eq 2.11; the A-rich blocks have a mean composition $f_0 + \delta f_b$ and the B-rich blocks have a mean composition $f_0 - \delta f_b$ with δf_b given by eq 2.8. We note that the fast reaction limit can be achieved either by starting with a very nearly incompatible monomer mixture, $\xi/a \gg 1$, in which case $\tau_r \sim \xi^2 \ll \tau_{bd} \sim \xi^3$, or (more typically) by fast polymerization kinetics, i.e. k very large.

In contrast, if the reaction kinetics are *slow* relative to cooperative diffusion or end exploration, $\tau_r \gg \tau_{bd}$, the blob composition inhomogeneities fluctuate or are explored by the radical end sufficiently rapidly that random copolymers are grown with *uniform* microstructure. Thus, the composition fluctuations in the reaction bath are temporally averaged on the time scale of monomer addition ($1/k$) and ideal random copolymers of composition f_0 are grown. No long-ranged chemical correlations are incorporated into the chains.

B. Quantitative Approach. Having provided a qualitative picture of how blocky random copolymers might be grown in a strongly fluctuating reaction bath, we now outline a more quantitative approach for describing the evolution of microstructure. Two key objectives are to verify the role of the time scales τ_r, τ_b, and τ_d identified in the above section and to provide explicit crossover formulas between the extreme limits of fast reaction and fast diffusion. Furthermore, the subsequent analysis will highlight certain deficiencies in the scaling picture.

As in the previous section, we consider the growth of a single A–B copolymer with a radical end in a fluctuating bath of A and B monomers. It proves convenient to (temporarily) discretize time into intervals of width $1/k$, the mean time between monomer additions. In particular, the time required for a chain to grow to a degree of polymerization n is denoted by $t_n = n/k$, where, for convenience, we choose the initiation event to correspond to the zero of time. Our next step is to assign to the ith monomer along the chain a stochastic Ising-like variable σ_i that assumes the value +1 if the monomer at that position is type A and −1 if type B. The probability distribution of σ_i, $p_i(\sigma_i)$, can be written as

$$p_i(1) = \int d\mathbf{r}\, \phi_A(\mathbf{r},t_i)\varrho(\mathbf{r},t_i) \tag{2.17}$$

$$p_i(-1) = \int d\mathbf{r}\, \phi_B(\mathbf{r},t_i)\varrho(\mathbf{r},t_i) \tag{2.18}$$

where $\phi_K(\mathbf{r},t)$ (K = A or B) is the volume fraction of type-K monomers and $\varrho(\mathbf{r},t)$ is the radical number density near position $\mathbf{r}$ at time t. We consider only a single radical so that

$$\int d\mathbf{r}\, \varrho(\mathbf{r},t) = 1 \tag{2.19}$$

and insist on local incompressibility ($\sum_K \phi_K(\mathbf{r},t) = 1$); hence, the probability distribution is properly normalized, $\sum_\sigma p_i(\sigma) = 1$. Introducing the composition fluctuation field $\psi(\mathbf{r},t)$ defined in eq 2.2 and spatial Fourier transforms (eq 2.3), $p_i(\sigma)$ can be reexpressed as

$$p_i(1) = f_0 + V^{-1}\sum_{\mathbf{q}} \psi(\mathbf{q},t_i)\varrho(-\mathbf{q},t_i) \tag{2.20}$$

$$p_i(-1) = 1 - f_0 - V^{-1}\sum_{\mathbf{q}} \psi(\mathbf{q},t_i)\varrho(-\mathbf{q},t_i) \tag{2.21}$$

With these definitions, the microstructure of the growing copolymer can be examined by computing moments of the chemical disorder variables. For example,

$$\langle \sigma_i \rangle \equiv \sum_\sigma \sigma \langle p_i(\sigma)\rangle_0 = 2f_0 - 1 \tag{2.22}$$

where $\langle ...\rangle_0$ denotes an equilibrium ensemble average over the fluid and chain dynamical variables contained in ψ and ϱ. The final expression in eq 2.22 follows by noting that $\langle\psi\rangle_0 = 0$, required by the definition eq 2.2. While the first moment provides information only about the mean composition of the copolymer, f_0, the second is useful for studying correlations. In particular,

$$\langle \sigma_i\sigma_j\rangle = \delta_{ij} + (1 - \delta_{ij})\sum_\sigma\sum_{\sigma'} \sigma\sigma' \langle p_i(\sigma)p_j(\sigma')\rangle_0 \tag{2.23}$$

or, more explicitly

$$\langle \sigma_i\sigma_j\rangle = \delta_{ij} + (1 - \delta_{ij})[\langle\sigma_i\rangle\langle\sigma_j\rangle + 4V^{-2}\sum_{\mathbf{k}}\sum_{\mathbf{q}} \langle \psi(\mathbf{k},t_i)\psi(\mathbf{q},t_j)\varrho(-\mathbf{k},t_i)\varrho(-\mathbf{q},t_j)\rangle_0] \tag{2.24}$$

At this point we introduce an *approximation*: namely, because the ψ fluctuations are small in amplitude (although correlated over large distances), we ignore correlations between the dynamics of the radical chain end and the fluctuating composition field. While the diluteness of radicals can be used to argue that the ψ dynamics should be independent of ϱ, the radical dynamics are in general weakly influenced by ψ, which we neglect. The approximation is implemented by breaking the average in eq 2.24; subsequent use of translational invariance leads to

$$\langle \psi(\mathbf{k},t_i)\psi(\mathbf{q},t_j)\varrho(-\mathbf{k},t_i)\varrho(\mathbf{q},t_j)\rangle_0 \approx \delta_{\mathbf{k},-\mathbf{q}}\langle \psi(-\mathbf{q},t_i)\psi(\mathbf{q},t_j)\rangle_0 \langle \varrho(\mathbf{q},t_i)\varrho(-\mathbf{q},t_j)\rangle_0 \tag{2.25}$$

A simple approximation for the first factor, the dynamic structure factor of a near-critical fluid mixture, can be taken to be of the form[11,15]

$$\langle \psi(-\mathbf{q},t_i)\psi(\mathbf{q},t_j)\rangle_0 \approx VS(q) \exp[-\Gamma(q)|t_i - t_j|] \tag{2.26}$$

where $S(q)$ is the structure factor discussed in eq 2.5. (In the analysis below we take $\eta \approx 0$.) The decay rate $\Gamma(q)$ can be written

$$\Gamma(q) = D_\psi q^2 F(q\xi) \tag{2.27}$$

where D_ψ is the collective diffusion coefficient identified in eq 2.9, ξ is the static correlation length, and $F(x)$ is the Kawasaki scaling function[17]

$$F(x) = \frac{3(1+x^2)}{4x^3}[x + (x^2 - 1)\tan^{-1}(x)] \tag{2.28}$$

This function has the asymptotic behaviors

$$F(x) \approx 1, \qquad x \to 0$$
$$F(x) \approx 3\pi x/8, \qquad x \to \infty \tag{2.29}$$

Note also that in writing eq 2.26 we assume a *stationary* distribution of ψ; i.e. we ignore feedback of the reaction on the thermodynamic properties of the bath. The latter effect will be considered in the next section.

A simple approximation for the dynamical correlations of ϱ can also be constructed. By restricting the times t_i and t_j to be sufficiently long so that many monomers have been added, i.e. kt_i, $kt_j \gg g \gg 1$, the "compact exploration" regime of the radical chain end is appropriate. Further assuming that the dynamics associated with reaction (random advancement of the end by addition of monomers) proceeds *independently* of the diffusive end exploration,[18] we arrive at the simple expression

$$\langle \varrho(\mathbf{q},t_i)\varrho(-\mathbf{q},t_j)\rangle_0 \approx \exp\{-(q^2/6)[\langle r^2(|t_i - t_j|)\rangle + ka^2|t_i - t_j|]\} \tag{2.30}$$

where $\langle r^2(t)\rangle$ is the diffusive mean-squared displacement of the end discussed in eq 2.13. In eq 2.30, we have assumed reactive jumps of the end by distances of order the monomer size a every time interval $1/k$, leading to a "diffusion coefficient" of $ka^2/6$. Finally, inserting eq 2.15 for compact exploration, we have to within a numerical constant c

$$\langle \varrho(\mathbf{q},t_i)\varrho(-\mathbf{q},t_j)\rangle_0 \approx \exp\{-(q^2/6)[c(k_BT|t_i - t_j|/\bar{\eta})^{2/3} + ka^2|t_i - t_j|]\} \tag{2.31}$$

Gathering these various approximations, the monomer sequence correlation function can be written for $i \neq j$ as

$$\langle \sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle \approx 4\int \frac{d\mathbf{q}}{(2\pi)^3}S(q) \times \exp\{-\Gamma(q)|t_i - t_j| - (q^2/6)[c(k_BT|t_i - t_j|/\bar{\eta})^{2/3} + ka^2|t_i - t_j|]\} \tag{2.32}$$

Next, we scale q in the integral by $1/\xi$ ($\tilde{q} = q\xi$) and the t_i's by τ_r ($\tilde{t}_i = t_i/\tau_r$), defined in eq 2.12. Finally, insertion of the scaling forms for $S(q)$ given in eq 2.5 and $\Gamma(q)$ given in eq 2.27 leads to

$$\langle \sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle \sim (a/\xi)\int d\tilde{\mathbf{q}}\; G(\tilde{q}) \times \exp\{-(\lambda/6\pi)\tilde{q}^2F(\tilde{q})|\tilde{t}_i - \tilde{t}_j| - (\tilde{q}^2/6)[c\lambda^{2/3}|\tilde{t}_i - \tilde{t}_j|^{2/3} + |\tilde{t}_i - \tilde{t}_j|]\} \tag{2.33}$$

where we have introduced the diffusion time scale $\tau_{bd} \equiv \tau_b \sim \tau_d$ identified in the last section through the dimensionless ratio

$$\lambda \equiv \tau_r/\tau_{bd} \tag{2.34}$$

The dependence of the chemical correlations on the ratio of time scales λ is now readily apparent. To leading order for $\lambda \ll 1$, i.e. *fast reaction*, eq 2.33 reduces to

$$\langle \sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle \sim \frac{a}{\xi}\int_0^\infty dx\, x^2G(x)\exp[-(x^2/6)|\tilde{t}_i - \tilde{t}_j|] \tag{2.35}$$

A simple choice would be to adopt an Ornstein–Zernike (OZ) form for the structure factor, $G(x) \sim 1/(1+x^2)$, and then numerically evaluate the integral in eq 2.35. However, for $|\tilde{t}_i - \tilde{t}_j| \gg 1$ the asymptotic behavior of the integral is controlled by $G(0)$; hence, the decay of the correlation function for large $|i-j|$ is given by

$$\langle \sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle \sim (a/\xi)g^{3/2}|i-j|^{-3/2} \sim (\xi/a)^2|i-j|^{-3/2} \tag{2.36}$$

where g is the mean block length *defined* by eq 2.11 of the previous section.

The long-ranged *algebraic* decay of the correlation function in this static limit of fast reaction is unusual—exponential decay is obtained from conventional models of chain copolymerization in homogeneous media. Moreover, it highlights a deficiency in our scaling picture of the last section. While the correlations between the monomers i and j are reduced to a small value, a/ξ, when i and j are separated by a distance $g \sim (\xi/a)^2$ along the chain, these residual correlations die off very slowly with increasing separation. Indeed, the decay is so slow that the average block size $\bar{g}$ defined by the relation

$$\bar{g} = \frac{\sum_{i\neq}\sum_{j}|i-j|[\langle\sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle]}{\sum_{i\neq}\sum_{j}[\langle\sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle]} \tag{2.37}$$

does not exist! Thus, our physical picture of the copolymer as a random multiblock chain with average block size g is slightly flawed; correlations in chemical sequence persist well beyond the distance g. Nevertheless, eq 2.33 or (for $\lambda \ll 1$) eq 2.35 provides access to any questions about microstructure that can be addressed at the pair correlation level.

The correlations of *nearest neighbors* in the fast reaction limit, $\lambda \ll 1$, can also be extracted from eq 2.35. By inserting the OZ form of $G(x)$, we find for $a/\xi \ll 1$

$$\langle \sigma_i\sigma_{i+1}\rangle - \langle\sigma_i\rangle\langle\sigma_{i+1}\rangle \sim (a/\xi)\int_0^\infty dx\, x^2(1+x^2)^{-1}\exp[-(1/6)(a/\xi)^2x^2] \sim 1 \tag{2.38}$$

indicating that neighboring monomers are strongly correlated. Thus, our "cartoon" of copolymer microstructure in the static (fast reaction) limit should be modified. Chains have nearly perfect local correlations (i.e. A following A and B following B), but due to A–B and B–A defects, the correlations ultimately decay algebraically according to eq 2.36. These strong local correlations arise from the fact that a critical fluid mixture has composition fluctuations of amplitude much larger than $\delta f_b \sim (a/\xi)^{1/2}$ (estimated in eq 2.8) when probed at scales smaller than ξ. Thus, the simple approach of assuming uniform compositions of $f_0 \pm \delta f_b$ within blobs seriously underestimates the strength of short-ranged correlations that are built up in the copolymer.

In order to examine these microstructural issues a bit further, we turn to consider the distribution of "block" compositions along the chain. For this purpose, we focus on a contiguous sequence of L monomers at some arbitrary location along the chain. The deviation of the composition of this L-monomer block from the average composition f_0 can be expressed as

$$\delta f_L = \frac{1}{2L}\sum_{i=1}^{L}(1 + \sigma_i) - f_0 \qquad (2.39)$$

With some straightforward algebra, it is easy to show that the mean composition deviation $\langle \delta f_L \rangle$ vanishes, but the mean-squared deviation is given by

$$\langle(\delta f_L)^2\rangle = \frac{1}{L}f_0(1 - f_0) + \frac{1}{4L^2}\sum_{i\neq}^{L}\sum_{j}^{L}[\langle\sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle] \qquad (2.40)$$

The first term on the right-hand side of this expression represents the natural fluctuations in composition that are present even when the reaction medium is homogeneous; the second term describes the additional composition fluctuations associated with the "blockiness" caused by the inhomogeneous medium.

Next, we note that eqs 2.35, 2.36, and 2.38 imply that the correlation function can be written for $\lambda \ll 1$ in the scaling form

$$\langle\sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle \sim \frac{a}{\xi}\Phi((a/\xi)^2|i - j|) \qquad (2.41)$$

with

$$\Phi(x) \sim x^{-1/2}, \qquad x \ll 1$$

$$\Phi(a) \sim x^{-3/2}, \qquad x \to \infty \qquad (2.42)$$

By using this result to estimate the double sum in eq 2.40, we find a contribution that dominates the first term on the right-hand side of that equation by a factor of ξ/a, namely

$$\langle(\delta f_L)^2\rangle \sim \frac{1}{L}(\xi/a) \qquad (2.43)$$

Thus, while random copolymerization in a homogeneous medium leads to root-mean-squared composition fluctuations that are of order $L^{-1/2}$ for a block of length L, copolymerization in an inhomogeneous medium enhances these block composition fluctuations by a factor of $(\xi/a)^{1/2}$. Of particular interest is the special case of $L = g \sim (\xi/a)^2$. Substitution into eq 2.43 leads to $\langle(\delta f_g)^2\rangle^{1/2} \sim (a/\xi)^{1/2} \sim \delta f_b$. In words, the composition fluctuations for a "block" of g monomers coincides in a scaling sense with the root-mean-squared composition variations among blobs computed in eq 2.8. Thus, aside from the reservations expressed above concerning local copolymer microstructure, consistent results are obtained by envisioning the copolymer at large scales as a random multiblock chain with block length $g \sim (\xi/a)^2$ and block compositions $f_0 \pm \delta f_b$.

Next, we examine the asymptotic behavior of the correlation function in the limit of *slow reaction*, i.e. $\lambda \gg 1$. This regime can be examined by dropping the third term in the exponent of eq 2.33 and considering various special cases. For $\lambda \gg 1$, it is easy to show that the asymptotic decay of the correlation function for large $|i - j|$ is dominated by the first term (cooperative diffusion) in the exponent of eq 2.33. In particular, we find the limiting behavior

$$\langle\sigma_i\sigma_j\rangle - \langle\sigma_i\rangle\langle\sigma_j\rangle \sim (\xi/a)^2\lambda^{-3/2}|i - j|^{-3/2} \qquad (2.44)$$

which is reduced from the algebraic decay found in the fast reaction limit by a factor of $\lambda^{-3/2} \ll 1$. Thus, the large distance decay of the correlation function in the slow reaction limit is limited by the finite lifetime of the concentration blobs. The correlations become dramatically reduced as $\lambda = \tau_r/\tau_{bd}$ is increased because the local concentration field experienced by a radical is time-averaged by the flickering in and out of the concentration blobs.

The nearest neighbor correlations in the slow reaction limit are slightly more interesting. If $\lambda \gg (\xi/a)^2 \gg 1$, then again the first term in the exponent of eq 2.33 dominates and we can write

$$\langle\sigma_i\sigma_{i+1}\rangle - \langle\sigma_i\rangle\langle\sigma_{i+1}\rangle \sim \frac{a}{\xi}\int_0^\infty dx\, x^2G(x)\exp[-(\lambda/6\pi)x^2F(x)(a/\xi)^2] \qquad (2.45)$$

Because $\lambda(a/\xi)^2 \gg 1$ in this regime, the integral is dominated by the small-x behavior of the integrand, leading to

$$\langle\sigma_i\sigma_{i+1}\rangle - \langle\sigma_i\rangle\langle\sigma_{i+1}\rangle \sim (\xi/a)^2\lambda^{-3/2} \ll 1 \qquad (2.46)$$

Alternatively, if $1 \ll \lambda \ll (\xi/a)^2$, then the second term in the exponent of eq 2.33 (representing end exploration dynamics) dominates the integral and we have

$$\langle\sigma_i\sigma_{i+1}\rangle - \langle\sigma_i\rangle\langle\sigma_{i+1}\rangle \sim \frac{a}{\xi}\int_0^\infty dx\, x^2G(x)\exp[-(c/6)x^2\lambda^{2/3}(a/\xi)^{4/3}] \qquad (2.47)$$

In this case, however, $\lambda^{2/3}(a/\xi)^{4/3} \ll 1$, so the large-$x$ behavior of the integrand is crucial. Inserting the OZ form for $G(x)$, we find

$$\langle\sigma_i\sigma_{i+1}\rangle - \langle\sigma_i\rangle\langle\sigma_{i+1}\rangle \sim (a/\xi)^{1/3}\lambda^{-1/3} \ll 1 \qquad (2.48)$$

Thus, the nearest neighbor correlations in both cases of $1 \ll \lambda \ll (\xi/a)^2$ and $\lambda \gg (\xi/a)^2$ are considerably reduced over the fast reaction limit where neighbor correlations were of order unity (cf. eq 2.38).

In more general cases of competitive diffusion and reaction, e.g. $\tau_r \sim \tau_{bd}$, the above asymptotic forms do not apply, but eq 2.33 could be numerically integrated to examine the crossover behavior between the fast and slow reaction limits. We do not attempt this here, but simply comment that the crossover will be smooth and should occur when λ is of order unity, as indicated by comparison of eqs 2.36 and 2.44.

III. Thermodynamic Stability

Next, we turn to consider the thermodynamic consequences of the blocky random copolymers that are grown in the strong fluctuating reaction medium. While blocky random copolymers destabilize the reaction bath to phase separation, as explicitly demonstrated below, ideal random copolymers (grown in the slow reaction limit) are unable to act in this manner. Thus, we restrict consideration in the following to the fast reaction limit, i.e. $\lambda \ll 1$.

Previous theoretical studies[19] of random block copolymer *melts* indicate that such systems possess very rich phase behavior, distinct from more conventional block copolymers (diblocks, triblocks, etc.) with narrow block size and molecular weight distributions. If the A- and B-rich blocks tend to alternate along the chain (alternating multiblock copolymer), it can be demonstrated[19] that the first instability of a homogeneous melt on cooling is to a *mesophase* (a disorder–order phase transition). If the two types of blocks have comparable degrees of polymerization, M, then local *lamellar* ordering is expected and the mesophase separation threshold can be estimated as

$$\chi_b M \approx 10 \tag{3.1}$$

where χ_b is the effective Flory χ parameter between monomers of the A-rich and B-rich *blocks*. In particular, $\chi_b = \chi(\Delta f)^2$, where χ is the A–B Flory χ parameter and Δf is the composition difference between the two types of blocks. Hence, $\chi_b = \chi$ if the blocks are pure A and pure B.

In contrast, a melt of chains with mean block length M and where the A-rich and B-rich blocks are placed in completely *random* sequences along the chains is prone to *liquid–liquid phase separation* on cooling.[19] The phase transition is located in mean-field theory at

$$\chi_b M = \frac{1}{2f_A(1 - f_A)} \tag{3.2}$$

where f_A is the mean fraction of A-rich blocks. This liquid–liquid separation, first identified by Scott[20] for ordinary (nonblocky) random copolymers, can be simply explained. An ensemble of multiblock chains with finite length will naturally possess a distribution in the compositions, c_A, of individual chains. A statistical number of chains will have more type-A blocks than would a chain of the mean composition f_A; correspondingly, a comparable number of chains will have an excess of type-B blocks. The probability distribution function for c_A approaches a Gaussian in the limit that the average number of blocks per chain, Q, gets very large (central limit theorem), with a mean of f_A and a variance given by

$$\langle(\delta c_A)^2\rangle = f_A(1 - f_A)/Q \tag{3.3}$$

The liquid–liquid separation arises from a partitioning of this distribution: chains enriched in A by an amount of order $\langle(\delta c_A)^2\rangle^{1/2}$ separate from the chains depleted in A by a comparable amount. From Flory–Huggins theory,[14] we expect that a mixture of equal amounts of two homopolymers with equal overall lengths $N = MQ$ will phase separate when $\chi_c N \approx 2$, where χ_c is the effective Flory χ between monomers of *chains* drawn from the two halves of the Gaussian distribution. Since their compositions differ by order $\langle(\delta c_A)^2\rangle^{1/2}$, this leads to $\chi_c \sim \chi_b f_A(1 - f_A)/Q$. Combining these results recovers the separation threshold given in eq 3.2.

While the first instability of a homogeneous melt of random block copolymers with uncorrelated block sequences is to liquid–liquid phase separation, it can be shown[19] that subsequent cooling of a high molecular weight melt ($Q \gg 1$) leads very rapidly to the formation of a mesophase (likely without long-ranged order). Indeed, $\chi_b M$ need only be increased above the threshold given in eq 3.2 by an amount of order $1/Q \ll 1$ for the coexisting liquid phases to lose stability to a single mesophase.

Next, we apply the above considerations to a *melt* of the blocky copolymers that are grown in the fluctuating reaction bath of the last section. Because there is no bias toward alternation of A- and B-rich blocks during chain growth, we anticipate that liquid–liquid separation (rather than mesophase separation) will first occur upon cooling. For a melt of chains with degree of polymerization N, the variance of chain compositions has already been calculated in eq 2.43 (setting $L = N$):

$$\langle(\delta f_N)^2\rangle \sim \frac{1}{N}(\xi/a) \tag{3.4}$$

Separation of the melt into two liquid phases of compositions $f_0 \pm \langle(\delta f_N)^2\rangle^{1/2}$ is thus expected when $\chi_c N \approx 2$, where the effective χ_c is given by $\chi_c = \chi\langle(\delta f_N)^2\rangle$ and χ is the A–B Flory parameter. Combining these results leads to the phase separation criterion

$$\chi \sim a/\xi \ll 1 \tag{3.5}$$

Note that the same result can be obtained by direct use of eq 3.2 with the following replacements: $g \sim (\xi/a)^2$ for the block size M, $\chi(\delta f_b)^2 \sim \chi(a/\xi)$ for χ_b, and $f_A \approx 1/2$ (half the "blocks" are A-rich).

Since the reaction bath was assumed to be a nearly critical mixture of A and B monomers prior to the initiation event, we conclude that χ must be very close to the spinodal, given in mean-field theory by $\chi_s \approx 1/[2f_0(1 - f_0)]$. However, if the reaction is allowed to go to completion, transforming all the monomers to random block copolymer, it follows that such an O(1) value of χ is well beyond the threshold eq 3.5 for liquid–liquid separation. Thus, the homogeneous (but fluctuating) reaction bath must become thermodynamically unstable well before the reaction has gone to completion. Indeed, as will be demonstrated explicitly below, a driving force for phase separation can already appear in either the dilute or semidilute regimes of copolymer concentration.

To this end, we now examine the reaction bath at the early stages of conversion. For simplicity, we imagine that the free-radical volume fraction is fixed at a very small value, $\phi_r \ll 1$, e.g. after a pulse of ultraviolet radiation, and we ignore termination processes and diffusion limitations. Because phase separation will be seen to occur at very low conversion where chain propagation is dominant, these assumptions are actually quite realistic. Under such conditions, the volume-averaged total fraction of monomers, ϕ_m, decays exponentially in time

$$\phi_m(t) = \exp(-\phi_r k t) \tag{3.6}$$

while the average degree of polymerization of the blocky copolymers, N, rises according to

$$N(t) = [1 - \exp(-\phi_r k t)]/\phi_r \tag{3.7}$$

At time t, for the purpose of assessing the thermodynamic stability of the bath, we envision the system as a pseudo-four-component system: unreacted monomer A, unreacted monomer B, copolymer of composition $f_0 + \langle(\delta f_N)^2\rangle^{1/2}$, and copolymer of composition $f_0 - \langle(\delta f_N)^2\rangle^{1/2}$. Labeling these species as components 1–4, respectively, the free energy density can be written in mean-field theory as (expressed in units of the total density)

$$F_V = \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + \frac{\phi_3}{N} \ln \phi_3 + \frac{\phi_4}{N} \ln \phi_4 + \chi\phi_A\phi_B \tag{3.8}$$

In this equation, the ϕ_i, $i = 1, ..., 4$, represent the volume fractions of the four species and the overall A and B volume fractions are given by

$$\phi_A = \phi_1 + \phi_3(f_0 + \langle(\delta f_N)^2\rangle^{1/2}) + \phi_4(f_0 - \langle(\delta f_N)^2\rangle^{1/2}) \tag{3.9}$$

$$\phi_B = 1 - \phi_A \tag{3.10}$$

Next, we expand F_V about the *uniform* compositions of the four species according to

$$\phi_1(\mathbf{r},t) = f_0\phi_m(t) + \delta\phi_1(\mathbf{r},t) \tag{3.11}$$

$$\phi_2(\mathbf{r},t) = (1 - f_0)\phi_m(t) + \delta\phi_2(\mathbf{r},t) \tag{3.12}$$

$$\phi_3(\mathbf{r},t) = \frac{1}{2}[1 - \phi_m(t)] + \delta\phi_3(\mathbf{r},t) \tag{3.13}$$

$$\phi_4(\mathbf{r},t) = \frac{1}{2}[1 - \phi_m(t)] + \delta\phi_4(\mathbf{r},t) \tag{3.14}$$

We then invoke incompressibility, $\Sigma_i\delta\phi_i = 0$, to eliminate $\delta\phi_4$ and ignore fluctuations in the total monomer concentration that are only weakly coupled to the critical mode, i.e. $\delta\phi_m = \delta\phi_1 + \delta\phi_2$. By defining the two new fluctuation fields

$$m(\mathbf{r},t) \equiv \delta\phi_1 + \delta\phi_3(f_0 + \langle(\delta f_N)^2\rangle^{1/2}) + \delta\phi_4(f_0 - \langle(\delta f_N)^2\rangle^{1/2}) \tag{3.15}$$

$$\psi(\mathbf{r},t) \equiv (1 - f_0)\delta\phi_1 - f_0\delta\phi_2 \tag{3.16}$$

the free energy density is given to harmonic order in m and ψ by

$$F_V = \frac{\psi^2}{2f_0(1 - f_0)\phi_m(t)} + \frac{(m - \psi)^2}{2N(t)\langle(\delta f_N)^2\rangle[1 - \phi_m(t)]} - \chi m^2 \tag{3.17}$$

Physically, it is clear from the above definitions that m represents fluctuations in the *total* species-A volume fraction (both monomeric and polymeric), while ψ describes fluctuations in the strictly *monomeric* species-A composition field.

The thermodynamic stability of the reaction medium can now be assessed by searching for soft modes of the quadratic form eq 3.17. From the condition that the determinant of the coefficient matrix vanish, we obtain the following result for the location of the *spinodal* for liquid–liquid phase separation, $\chi = \chi_s$:

$$\chi_s = \frac{1}{2f_0(1 - f_0)\phi_m(t)[1 + \alpha(t)]} \tag{3.18}$$

where

$$\alpha(t) \equiv \frac{N(t)\langle(\delta f_N)^2\rangle[1 - \phi_m(t)]}{f_0(1 - f_0)\phi_m(t)} \tag{3.19}$$

The critical mode, w, is the following linear combination of m and ψ:

$$w(\mathbf{r},t) = [1 + \alpha(t)]m(\mathbf{r},t) + \psi(\mathbf{r},t) \tag{3.20}$$

and F_V behaves near the spinodal as (ignoring the noncritical mode)

$$F_V \approx \frac{(1 + \alpha)^2(\chi_s - \chi)}{(2 + 2\alpha + \alpha^2)^2} w^2 \tag{3.21}$$

The time-dependent function $\alpha(t)$, defined in eq 3.19, can be reexpressed to within a leading constant by insertion of eqs 3.4 and 3.6:

$$\alpha(t) \sim \frac{\xi[\exp(\phi_r kt) - 1]}{af_0(1 - f_0)} \tag{3.22}$$

According to eq 3.18, the spinodal thus varies from $\chi_s \approx 1/[2f_0(1 - f_0)] \sim 1$ at $t = 0$, the threshold for the unreacted *pure* monomer mixture, to $\chi_s \sim a/\xi \ll 1$ at $t = \infty$, the threshold for the random copolymer *melt* previously estimated in eq 3.5. At a fixed value of χ, we can identify the *time* t_s at which the reaction bath becomes unstable by noting that in mean-field theory

$$1/[2f_0(1 - f_0)] - \chi \sim (a/\xi)^2 \tag{3.23}$$

Then, for very small radical concentrations, $\phi_r \ll 1$, the spinodal condition $\chi = \chi_s$ leads to

$$\phi_r kt_s \sim f_0^2(1 - f_0)^2(a/\xi)^3 \tag{3.24}$$

Since $N(t) \approx kt$ for $\phi_r kt \ll 1$, the degree of polymerization attained at the instability, N_s, scales as

$$N_s \sim f_0^2(1 - f_0)^2(a/\xi)^3/\phi_r \tag{3.25}$$

Moreover, the volume fraction of polymer at the spinodal scales as $\phi_r kt_s \sim (a/\xi)^3 \ll 1$. Assuming ideal chain conformations (cf. eq 2.11), the overlap threshold at the spinodal is

$$\phi_s^* \sim N_s^{-1/2} \sim (\xi/a)^{3/2}\phi_r^{1/2} \tag{3.26}$$

Thus, the instability occurs in the *dilute* regime if $(a/\xi)^9 \ll \phi_r \ll 1$ and in the *semidilute*, overlapped chain regime if $\phi_r \ll (a/\xi)^9$. This is a consequence of larger polymers being grown as the radical concentration ϕ_r is reduced; cf. eq 3.25. Overall, our estimates suggest that a near-critical mixture of A and B monomers will become unstable to liquid–liquid phase separation after a surprisingly small extent of conversion to random copolymer, of order $(a/\xi)^3$. The reaction bath at this separation threshold will be either a dilute or a semidilute solution of copolymer, depending on the value of the radical concentration ϕ_r.

We should emphasize that the above actually corresponds to a very *conservative* estimate of the threshold to phase separation. In our analysis, notably in evaluating the dispersion of random copolymer compositions, $\langle(\delta f_N)^2\rangle$, it was assumed that the correlation length of the reaction bath ξ remained fixed at its initial value set by χ (cf. eq 3.23). However, as the reaction proceeds and the thermodynamic compatibility of the medium is reduced, the correlation length will actually grow continuously larger. This would produce phase separation in a time shorter than that estimated in eq 3.24 and hence yield shorter chains than indicated in eq 3.25. However, we expect this growth in ξ to be held back to some extent by the critically slowed dynamics of the concentration mode $w(\mathbf{r},t)$. Thus, particularly in situations where the reaction kinetics are extremely fast, our estimates should be quite reasonable.

Another concern is the use of mean-field estimates for locating the instability. While it is straightforward to correct such estimates for copolymer solutions at thermodynamic equilibrium, e.g. with blob arguments,[21] in the present case of a complex mixture driven far from equilibrium by a rapid chemical reaction it is not obvious that such methods apply. Moreover, critical systems often recover mean-field-like behavior when strongly driven, e.g. by shear, magnetic, or electric fields.[22] Thus, in the absence of experiment and lacking a better theoretical approach, we rely on simple mean-field theory.

Once the reaction has progressed to the point where the mixture of monomers and copolymer becomes thermodynamically unstable, the time evolution of the system becomes very complicated. Phase separation is initiated and the subsequent growth of copolymer chains takes place in a medium that becomes increasingly inhomogeneous with time. As a result, the copolymers become even blockier, the compatibility of the mixture is lessened, and phase separation is driven even more forcefully. Added to this autocatalytic response is a thermodynamic complexity. While the initial instability for a solution of random multiblock copolymers is to liquid–liquid phase separation, very rapidly after the copolymerization reaction effects a "quench" below the spinodal, a second instability to mesophase separation is encountered.[19] The wavelengths of the growing concentration modes are thus shortened and stabilized at a finite value and the character of the free energy changes considerably from the expression given in eq 3.21. Ultimately, the reaction is quenched either through termination processes or by depletion of monomer with associated diffusion limitations. The system at such a point consists of random multiblock chains, self-assembled into a mesophase (lacking long-range order and with local symmetry dictated by the mean composition f_0), and with a broad distribution of block sizes that reflect not only conditions within the initial fluctuating reaction bath but also the complex dynamical trajectory to the final mesophase. Added complexity arises if one or more structural arrest mechanisms, such as crystallization or vitrification, are operative and can disrupt or terminate this dynamical trajectory.

While a quantitative description of such events would be quite difficult to develop, the very early time evolution of the system immediately after crossing the spinodal boundary is amenable to a simple Cahn–Hilliard-type analysis.[23] Such an analysis is appropriate for mixtures at the critical composition but probably also applies to off-critical mixtures because no time is afforded for nucleation events in the case of very fast reaction. Thus, regardless of the composition f_0, we make the simplifying assumption that the bath remains nearly homogeneous until the spinodal boundary is traversed and spinodal decomposition is initiated.

For the purpose of constructing a Cahn–Hilliard theory, it is necessary to augment the free energy given in eq 3.21 with "square gradient" terms that penalize spatial composition variations. In order to keep the analysis tractable, we neglect other than the critical mode $w(\mathbf{r},t)$ (valid for times sufficiently close to t_s) and assume that the solvent contributions to the square gradient coefficients can be computed as polymeric contributions, but with $N = 1$. The latter assumption is correct in a scaling sense but makes numerical errors comparable to those associated with dropping the prefactor in scaling expressions like eq 3.22. Since our goal is simply to derive scaling results for the maximum growth rate and wavenumber of unstable modes at times slightly exceeding t_s, we shall ignore such constant prefactors in the following.

After a straightforward calculation, the augmented free energy functional can be written

$$F[w] = \frac{(1+\alpha)^2}{(2+2\alpha+\alpha^2)^2}\int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left[(\chi_s - \chi) + q^2\kappa\chi_s\frac{1+\alpha N}{1+\alpha}\right]w(\mathbf{q},t)w(-\mathbf{q},t) \quad (3.27)$$

where $\kappa = b^2/18$, with $b \sim a$ the copolymer statistical segment length. The field $w(\mathbf{q},t)$ is the spatial Fourier transform of the field $w(\mathbf{r},t)$ and the parameters α, χ_s, and N appearing in this expression have explicit time dependence as previously indicated. Expanding these time-dependent quantities to leading order in $k(t - t_s) \ll 1$ and to leading order in $a/\xi \ll 1$, eq 3.27 is considerably simplified:

$$F[w] = \frac{1}{8}\int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}[-\beta(t-t_s) + \gamma q^2]w(\mathbf{q},t)q(-\mathbf{q},t) \quad (3.28)$$

The time-independent quantities β and γ appearing in this expression are defined by

$$\beta \equiv \frac{\xi\phi_r k}{af_0^2(1-f_0)^2} \quad (3.29)$$

$$\gamma \equiv \frac{\kappa}{f_0(1-f_0)}\begin{cases}1, & (a/\xi)^5 \ll \phi_r \ll 1\\ f_0^4(1-f_0)^4(a/\xi)^5\phi_r^{-1}, & \phi_r \ll (a/\xi)^5\end{cases} \quad (3.30)$$

We note that the condition $\phi_r \ll (a/\xi)^5$ corresponds to a situation where $\alpha(t_s)N_s \gg 1$, while $\phi_r \gg (a/\xi)^5$ corresponds to $\alpha(t_s)N_s \ll 1$. From eqs 3.22 and 3.24, it is also clear that $\alpha(t_s) \sim f_0(1 - f_0)(a/\xi)^2 \ll 1$.

We note that the condition $\phi_f \ll (a/\xi)^5$ corresponds to a situation where $\alpha(t_s)N_s \gg 1$, while $\phi_r \gg (a/\xi)^5$ corresponds to $\alpha(t_s)N_s \ll 1$. From eqs 3.22 and 3.24, it is also clear that $\alpha(t_s) \sim f_0(1 - f_0)(a/\xi)^2 \ll 1$.

As a next step, we make note of the fact that $w(\mathbf{q},t)$ is a *conserved* concentration mode and thus should satisfy relaxational dynamics of the form

$$\frac{\partial}{\partial t}w(\mathbf{q},t) = -q^2\Lambda\frac{\delta F}{\delta w(-\mathbf{q},t)} \quad (3.31)$$

where Λ is an Onsager kinetic coefficient for the mode. Because the initial instability will subsequently be shown to involve composition modes with wavelengths that are much larger than the radius of gyration of the chains at time t_s, it is appropriate to take Λ to be a constant rather than a q-dependent function as in the theory of spinodal decomposition for polymer blends.[24,25] For simplicity, we also neglect hydrodynamic coupling of w to the total momentum density, which is capable of renormalizing Λ. Such coupling is probably not very effective in the present situation due to the anticipated high viscosity of the copolymer reaction bath.

Integrating eq 3.31 (with eq 3.28) from the time t_s at which the spinodal to liquid–liquid separation is traversed to a slightly later time t, we obtain

$$w(\mathbf{q},t) = w_s(\mathbf{q}) \exp\left\{\frac{q^2\Lambda}{4}[(\beta/2)(t - t_s)^2 - \gamma(t - t_s)q^2]\right\} \quad (3.32)$$

where $w_s(\mathbf{q})$ is the initial amplitude of the mode at time t_s, assumed to be thermally populated. By maximizing the argument of the exponential with respect to q, we find that the fastest growing modes are those with the wavenumber q_m given by

$$q_m = [\beta/(4\gamma)]^{1/2}(t - t_s)^{1/2} \quad (3.33)$$

These fastest modes grow according to

$$w(q_m,t) \sim \exp\left[\frac{\Lambda\beta^2(t - t_s)^3}{64\gamma}\right] \quad (3.34)$$

As expected in a translationally invariant and isotropic system, the growth rate is independent of the direction of the unstable mode but is sensitive only to the wavelength, $2\pi/q$.

By inserting the two different forms of γ given in eq 3.30, depending on the magnitude of the radical concentration, explicit scaling predictions can be made for the initial wavenumber and maximum growth rate as the spinodal is traversed. For $(a/\xi)^5 \ll \phi_r \ll 1$, we find

$$q_m \sim \left[\frac{\xi\phi_r k(t - t_s)}{af_0(1 - f_0)\kappa}\right]^{1/2} \quad (3.35)$$

and

$$\ln w(q_m,t) \sim \frac{\Lambda\xi^2(\phi_r k)^2(t - t_s)^3}{a^2 f_0^{\,3}(1 - f_0)^3\kappa} \quad (3.36)$$

Alternatively, for lower radical concentrations, $\phi_r \ll (a/\xi)^5$, we find

$$q_m \sim (\xi/a)^3\left[\frac{\phi_r^{\,2}k(t - t_s)}{\kappa f_0^{\,5}(1 - f_0)^5}\right]^{1/2} \quad (3.37)$$

and

$$\ln w(q_m,t) \sim \frac{\Lambda\xi^7\phi_r^{\,3}k^2(t - t_s)^3}{a^7\kappa f_0^{\,7}(1 - f_0)^7} \quad (3.38)$$

While characteristic of the early-stage growth of concentration inhomogeneities, the above formulas will fail once the spinodal pattern grows large enough in amplitude that terms beyond harmonic order in the free energy eq 3.28 begin to contribute. Perhaps more important in limiting the applicability of the above predictions, however, is the crossing of the liquid–liquid to mesophase boundary as the reaction proceeds. As discussed previously, the free energy changes character at this boundary,[19] stabilizing modulated composition waves of finite wavelength.

Assuming that the early stages of phase separation can be captured, it should be possible to subject these scaling predictions to an experimental test. The spinodal instability should be clearly evident in a light scattering experiment where a peak will arise in the structure factor (equal-time concentration correlation function) at a wavenumber corresponding to q_m. The movement of q_m to *larger* rather than smaller values (as is typical in conventional spinodal decomposition experiments) according to $q_m \sim (t - t_s)^{1/2}$ should be quite striking. Moreover, the strong predicted dependence of the maximum wavenumber and growth rate on the initial correlation length of the reaction bath, ξ, and the free-radical concentration, ϕ_r, could be easily tested since both of these parameters are experimentally adjustable over a broad range.

IV. Discussion

In the present paper we have argued that a mixture of two types of polymerizable monomers in close proximity to a liquid–liquid phase boundary will react to produce "blocky" random copolymers. The nature of the backbone correlations (microstructure) frozen into the copolymers, examined in some detail in section II, reflects the statistical properties of thermal composition fluctuations in the reaction bath and a competition between reaction and diffusion for spatial displacement of free radicals. We further argued in section III that the blocky copolymers can have the effect of destabilizing the reaction bath to phase separation, even at very early stages of conversion where the reaction bath is either dilute or semidilute in copolymer. Scaling predictions were made for the location of the instability, i.e. elapsed time, copolymer concentration, and molecular weight, as well as for quantitative features of the initial growth mode. Experiments that vary temperature (hence correlation length) and free-radical concentration are likely to provide the most sensitive tests of the present theory. While the near-critical conditions required to produce significant blockiness may be difficult to achieve in conventional monomer mixtures, we anticipate that the use of *macromonomers* will greatly expand the class of chemical systems for which the above phenomena can be experimentally observed.

While directly relevant to bulk copolymerizations carried out under isothermal conditions and for nearly equal reactivity ratios, our approach could be straightforwardly extended to situations where an additional solvent component is present or to monomers with unequal reactivity ratios. Another important extension would be to batch copolymerizations, particularly with unequal reactivity ratios, where the bath becomes depleted in one monomer species as the reaction progresses. The "bootstrap effect",[26] where comonomers are speculated to partition between solvent-rich and polymer-rich phases, may also be amenable to treatment by methods similar to those used here. Perhaps more interesting, however, is to speculate on related phenomena in emulsion copolymerizations.

In emulsion polymerization with a water-soluble initiator and nearly water-insoluble comonomers, chain growth takes place predominantly within micelles swollen by the two types of monomers. If the hydrophobic surfactant tails within the interior of the micelles have comparable affinity for the A and B monomers and the micelles are swollen to a size greatly exceeding the correlation length ξ, then the scenario outlined in sections II and III is largely preserved. Namely, blocky random copolymers are grown within the micelles and macrophase (and ultimately mesophase) separation occurs after the copolymer concentration within the particles builds up to the threshold estimated in section III. We note, however, that our estimate for the time required for this to occur must be modified to account for the continuous flux of new solvent into the particles as the reaction proceeds.

If the surfactant tails have similar affinity for the two monomer species but the micelle diameter is comparable to ξ, the finite size of the "reaction vessel" will likely influence the copolymer microstructure. One possibility is that the population of micelles will partition, with some micelles possessing an A-rich interior, and others B-rich interiors. Polymerization under such conditions would yield copolymers with relatively homogeneous microstructure, but a bimodal distribution of compositions. Clearly the combination of finite-size effects on critical fluctuations and chemical reaction could lead to interesting and possibly unexpected latex morphologies.

Potentially even more interesting is the situation where the surfactant tails are *selective* for one of the monomers, e.g. A. Then the micelle interiors would be enriched to some extent in monomer A, homogeneously if the micelle size is comparable to ξ, or inhomogeneously if the swollen micelles are larger than ξ. In the latter case, A-rich blobs would coat the inside surface of each micelle (a wetting layer), contributing additional heterogeneity to copolymer chains that were grown near the surface.

Overall, much remains to be understood about such situations in which reaction, diffusion, phase separation, wetting, and confinement all participate in determining copolymer microstructure and particle morphology. Increased experimental and theoretical attention paid to this exciting area could yield both intellectual and practical dividends.

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References and Notes

(1) Odian, G. *Principles of Polymerization*; Wiley-Interscience: New York, 1981.

(2) *Copolymerization*; Ham, G. E., Ed.; Wiley-Interscience: New York, 1964.

(3) Lowry, G. G. *J. Polym. Sci.* **1960**, *42*, 463.

(4) Dionisio, J. M.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 701. O'Driscoll, K. F.; Kale, L. T.; Garcia Rubio, L. H.; Reilly, P. M. *J. Polym. Sci.* **1984**, *A22*, 2777.

(5) Suggate, J. R. *Makromol. Chem.* **1979**, *180*, 679. Pichot, C.; Guyot, A.; Strazielle, C. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2269. Ledwith, A.; Galli, G.; Chiellini, E.; Solaro, R. *Polym. Bull.* **1979**, *1*, 491.

(6) Doiuchi, T.; Minoura, Y. *Macromolecules* **1977**, *10*, 261.

(7) Bras, W.; Derbyshire, G. E.; Bogg, D.; Cooke, J.; Elwell, M. J.; Komanschek, B. U.; Naylor, S.; Ryan, A. J. *Science* **1995**, *267*, 996.

(8) Lee, S.; Rudin, A. In *Polymer Latexes*; Daniels, E. S., Sudol, E. D., El-Aasser, M. S., Eds.; ACS Symposium Series 492; Washington, DC, 1992; p 234; *Makromol. Chem., Rapid Commun.* **1989**, *10*, 655. Sundberg, D. C.; Casassa, A. P.; Pantazopoulos, J.; Muscato, M. R. *J. Appl. Polym. Sci.* **1990**, *40*, 1425.

(9) Ma, S.-K. *Modern Theory of Critical Phenomena*; Benjamin-Cummings: Reading, MA, 1976.

(10) In the present paper we use the symbol $\sim$ to imply "scales as". A numerical coefficient in the expression following the symbol is either unknown or omitted.

(11) Hohenberg, P. C.; Halperin, B. I. *Rev. Mod. Phys.* **1977**, *49*, 435.

(12) We neglect the very weak critical anomaly of the shear viscosity $\bar{\eta}$ in all of our estimates. See ref 11 for more details.

(13) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1973**, *58*, 5009; **1974**, *60*, 866, 878. Doi, M. *Chem. Phys.* **1975**, *9*, 455; **1975**, *11*, 107, 115.

(14) de Gennes, P.-G. *J. Chem. Phys.* **1982**, *76*, 3316, 3322.

(15) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.

(16) Note that τ_b and τ_d may differ significantly if the numerical prefactor relating them is not O(1). In such cases it may prove necessary to consider τ_b and τ_d separately rather than τ_{bd}. We ignore such situations in the following.

(17) Kawasaki, K. *Ann. Phys.* **1970**, *61*, 1.

(18) This separability is not obvious, except when the reaction and diffusion processes have very different time scales. Because relaxing the assumption requires a rather involved analysis that will take us far from our present objectives, we defer it to future work.

(19) Fredrickson, G. H.; Milner, S. T.; Leibler, L. *Macromolecules* **1992**, *25*, 6341.

(20) Scott, R. *J. Polym. Sci.* **1952**, *9*, 423.

(21) Fredrickson, G. H.; Leibler, L. *Macromolecules* **1989**, *22*, 1238.

(22) Onuki, A.; Kawasaki, K. *Ann. Phys.* **1979**, *121*, 456.

(23) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258.

(24) de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.

(25) Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996. Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.

(26) Harwood, H. J. *Makromol. Chem., Macromol. Symp.* **1987**, *10/11*, 331. Semchikov, Y. D.; Smirnova, L. A.; Knyazeva, T. Y.; Bulgakova, S. A.; Sherstyanykh, V. I. *Eur. Polym. J.* **1990**, *26*, 883.

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