# Mean Field Theory for Phase Separation during Polycondensation Reactions and Calculation of Structure Factors for Copolymers of Arbitrary Architecture

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ABSTRACT: We consider the variation in miscibility during a polycondensation reaction which forms a random multiblock copolymer. Taking a "Markov chain" model for the reacting polymer system, we apply the random phase approximation and calculate the spinodal as a function of degree of reaction. In order to achieve this, we develop a formalism for the calculation of structure factors of polymers of arbitrary complexity. Taking a model two-component system, we show that phase separation may begin at an early stage in the reaction process, while the chains are still short. We also show that in the earliest stages of reaction, this model system becomes more miscible with extent of reaction. Finally, we generalize the theory to branched Markov systems.

## 1. Introduction

Random multiblock copolymers are industrially useful because of the toughness conferred by their phase-separated microstructure. Typically, hard and soft polymeric segments with reactive end groups are mixed together, their reaction yielding long copolymers. Phase separation is driven by the increasing degree of polymerization during the reaction, but it has been shown by Elwell et al.,[1] working on a polyurethane based system, that this frequently begins to occur at quite small degrees of conversion of about 50−60% when the polymer chains are still quite short. In order to achieve a better understanding of the parameters that govern this phase separation, we present a mean field theory that describes the reacting multiblock system.

Our description of the system is based on the simple "Markov chain" model,[2] which is a mathematical description of a polymerization process in which chains are formed by the reaction of two or more types of "monomer". Monomers are added to the chain in some random fashion. The theory gives a mathematical expression for the probability distribution of monomers along each chain.

The "first-order" Markov theory assumes that the probability of finding a particular monomer at a given point of the chain is determined only by the nature of the preceding monomer. This is not a trivial assumption. It requires the chemistry to be such that the reactivity of each monomer is not affected by adjacent monomers. This will be a poor approximation for small monomeric species. Another requirement is that the reaction mixture be of an essentially uniform composition. If large fluctuations in the composition persist over the time scale of the reaction, then it is possible for sections of the chain to be formed in regions with significantly different composition, leading to a degree of "blockiness" in the chains. This effect has been discussed to some extent by Leibler and Fredrickson[3] for the case of single chains growing in a fluctuating solution of monomers (as in a free-radical-induced polymerization with a small number of free radicals).

In this paper we consider a melt of polymeric "blocks" with reactive end groups. The blocks react in some random fashion to form long chains. We assume that the reaction is a Markov process and equate the "blocks" with the Markov chain "monomers". Since each block has reactive end groups, any block has the potential to react at all stages of the process and the model is thus similar to polycondensation, rather than free-radical reactions.

We apply the random phase approximation (RPA)[4] to this Markov chain system and use this to calculate the spinodal. A moderate amount of work (see, for example, ref 5 for a list of references) has already been done on random block copolymer systems, taking Markov chains or distributions with no adjacent monomer correlations as the model. These works have centered on very long polymers (i.e., systems in which the reaction is very nearly completed). They have generally relied on the monomer species being "symmetric" (i.e., different monomer species are identical in their volume and step length but have the tendency to phase segregate, modeled by the Flory $\chi$ parameter). The only work to date considering Markov chains composed from polymeric blocks instead of small monomers (Leibler, Fredrickson, and Milner[6]) also takes the long chain, symmetric block limit.

In contrast to these works, we wish to describe the system as the reaction proceeds, in particular considering whether an instability to phase segregation will occur during the reaction. This means that we do not use the long chain limit but allow for chain termination. Notice that if phase segregation does occur, it may jeopardize the requirement of a uniform reaction mixture, so that the Markov chain model may break down.

We also wish to describe systems in which the blocks (or Markov monomers) are not symmetric in their volume or geometry. In order to achieve this, it is necessary to formalize a method for calculating scattering functions of block copolymers of arbitrary architecture. In addition to being of direct relevance to the present calculation, the method is extremely useful for rapid and systematic calculations of polymer scattering functions. Although the method is implicit in a number of scattering function calculations for complicated copolymer structures,[7] the method has not been formally

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presented in the literature, so an Appendix is devoted to this task.

The paper is organized as follows. Section 2 deals with general issues for the application of the RPA to complex and polydisperse polymers. In section 3 we develop a general theory for reacting polymer systems and then apply it to a specific example in section 4. In section 5 we consider one possible extension of the theory to branched Markov systems.

## 2. RPA for Complex Copolymers

We begin by summarizing the main results of the random phase approximation for polymer blends.[4,7] For simplicity, we consider an incompressible blend containing monomers of only two types (A and B) and assume that each monomer occupies the same volume $v_0$. The total volume of the system is $\Omega$. If the position of the $l$th monomer on chain $\alpha$ is $\mathbf{r}_l^\alpha$, then we can define the density of A monomers as

$$\rho^{A}(\mathbf{r}) = \sum_{\alpha,l} y_l^\alpha \delta(\mathbf{r} - \mathbf{r}_l^\alpha) \tag{1}$$

with Fourier transform

$$\begin{aligned}\rho^{A}_{\mathbf{q}} &= \int_\Omega \exp(i\mathbf{q}\cdot\mathbf{r})\, \rho^{A}(\mathbf{r})\, d^3\mathbf{r} \\ &= \sum_{\alpha,l} y_l^\alpha \exp(i\mathbf{q}\cdot\mathbf{r}_l^\alpha)\end{aligned} \tag{2}$$

where $y_l^\alpha = 1$ if monomer $l$ on chain $\alpha$ is an A monomer, and $y_l^\alpha = 0$ if it is a B monomer. Similarly

$$\rho^{B}_{\mathbf{q}} = \sum_{\alpha,l} (1 - y_l^\alpha) \exp(i\mathbf{q}\cdot\mathbf{r}_l^\alpha) \tag{3}$$

The main result of the RPA for an incompressible blend is that the scattering structure factor is given by

$$\begin{aligned}S(\mathbf{q}) &= \frac{v_0\langle \rho^{A}_{\mathbf{q}} \rho^{A}_{-\mathbf{q}}\rangle}{\Omega} \\ &= \left(\frac{1}{S_{\mathrm{inc}}(\mathbf{q})} - 2\chi\right)^{-1}\end{aligned} \tag{4}$$

where $\chi$ is the Flory interaction parameter and $S_{\mathrm{inc}}(\mathbf{q})$ is the structure factor for a noninteracting incompressible system,

$$S_{\mathrm{inc}}(\mathbf{q}) = \frac{s_0^{AA} s_0^{BB} - (s_0^{AB})^2}{s_0^{AA} + s_0^{BB} + 2 s_0^{AB}} \tag{5}$$

$s_0^{AA}$, $s_0^{BB}$, and $s_0^{AB}$ are the structure factors for the blend in the noninteracting limit (i.e., with $\chi = 0$ and no excluded volume interactions), for example

$$s_0^{AA} = \frac{v_0\langle \rho^{A}_{\mathbf{q}} \rho^{A}_{-\mathbf{q}}\rangle_0}{\Omega} \tag{6}$$

where $\langle ... \rangle_0$ denotes an average over chain conformations in the absence of interactions.

If $\chi$ becomes large enough, then $S(\mathbf{q})$ as defined in eq 4 will diverge at some wavenumber $\mathbf{q} = \mathbf{q}^*$, which lies at the maximum of $S_{\mathrm{inc}}(\mathbf{q})$. The critical value of $\chi$ is given by

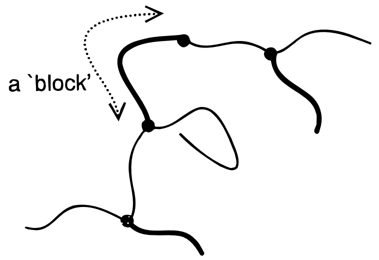

**Figure 1.** Illustrating the splitting of a polymer into "blocks". Each circle represents a block division.

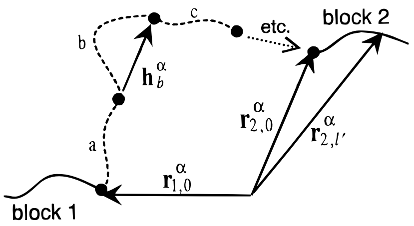

**Figure 2.** Showing the variables that relate to two given blocks in a chain.

$$\chi_S = \frac{1}{2\max_{\mathbf{q}}[S_{\mathrm{inc}}(\mathbf{q})]} \tag{7}$$

This point of instability is the spinodal. Physically, the divergence of the structure factor indicates that concentration fluctuations at these wavelengths become unstable and will grow.

**Structure Factors for Arbitrary Architecture.** We now summarize a method for calculating the structure factors of polymers of complex form, subject to certain assumptions about their nature. The method is similar to that used by Benoit and Hadziioannou[4] for calculating structure factors of comblike, starlike, and multiblock copolymers. A full derivation is presented in Appendix A, and an example application is given in Appendix B.

Central to the method is the assumption that each chain can be divided into "blocks", as illustrated in Figure 1. A "block" is simply a segment of chain. The choice of blocks will be governed by the structure of the polymer chain. It is generally convenient for individual blocks to contain only monomers of one type and to make block divisions at branch points. The aim is to write the structure factors for the system in terms of quantities that relate to the properties of the blocks.

The definition of structure factors in eq 6 involves a sum over all monomer pairs. We replace this with a double sum over *blocks*, $\gamma$.

$$s_0^{AA} = \frac{v_0}{\Omega} \sum_{\substack{\text{blocks}\\ \gamma,\gamma'}} s_{\gamma\gamma'}^{AA} \tag{8}$$

where $s_{\gamma\gamma'}^{AA}$ is the contribution to $s_0^{AA}$ from a pair of blocks $(\gamma, \gamma')$. We note that block pairs on separate chains do not contribute to the sum.

Consider the case where the two blocks are different, $\gamma \neq \gamma'$, but on the same chain. Figure 2 shows two blocks, labeled 1 and 2, which are separated by a number of other blocks (labeled $\gamma$ = a, b, c, ..., etc.). The end-to-end vector of block $\gamma$ is $\mathbf{h}_\gamma^\alpha$, and the position of monomer $l$ on block $\gamma$ is $\mathbf{r}_{\gamma,l}^\alpha$. Thus, the end monomers of blocks 1 and 2 are $\mathbf{r}_{1,0}^\alpha$ and $\mathbf{r}_{2,0}^\alpha$ respectively. It is shown in Appendix A that, subject to certain conditions, the contribution to $s_0^{AA}$ from these two blocks may be written as

$$s_{12}^{AA} = H_1^A H_2^A \prod_{\gamma=a,b,...} G_\gamma \tag{9}$$

where we have defined the following quantities for *each block* in the chain.

$$G_\gamma = \langle \exp(i\mathbf{q}\cdot\mathbf{h}_\gamma^\alpha)\rangle_0 \tag{10}$$

$$H_\gamma^A = \sum_{\substack{l \\ (\text{block } \gamma)}} y_{\gamma,l}^\alpha \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_{\gamma,l}^\alpha - \mathbf{r}_{\gamma,0}^\alpha))\rangle_0 \tag{11}$$

The product over the $G_\gamma$ in eq 9 describes the effect on the structure factor of the chain between two blocks. We shall call $G_\gamma$ the "propagator" for a given block $\gamma$. The actual contribution of each block to $s_{12}^{AA}$ is determined by the quantities $H_1^A$ and $H_2^A$. We shall call quantities like $H_\gamma^A$ the "coterm" for each block.

The important point is that each term in the structure factor (8) involving separate blocks ($\gamma \neq \gamma'$) can be written as a product of the coterms for the two blocks, and the propagators for the blocks in between. This greatly simplifies the algebra for the calculation of structure factors and also provides a convenient notation.

The same-block terms with $\gamma = \gamma'$ in eq 8 are all of form

$$s_{\gamma\gamma}^{AA} = J_\gamma^{AA} = \sum_{\substack{l,l' \\ \text{in block } \gamma}} y_{\gamma,l}^\alpha y_{\gamma,l'}^\alpha \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_{\gamma,l'}^\alpha - \mathbf{r}_{\gamma,l}^\alpha))\rangle_0 \tag{12}$$

We shall call $J_\gamma^{AA}$ the "self-term" for block $\gamma$.

To summarize, eq 8 is a sum over terms similar to those in (9) and (12). $s_0^{AA}$ is thus completely expressed in terms of the $G_\gamma$, $H_\gamma^A$, and $J_\gamma^{AA}$ of the blocks. Coterms and self-terms involving "B" monomers are defined in an analogous manner, leading to expressions for $s_0^{AA}$ and $s_0^{BB}$.

This technique is extremely useful because the propagator, coterm, and self-term for a given block type (e.g., "Gaussian coil" or "rod") need only be calculated once (the results for a Gaussian coil are presented in Appendix B). It then becomes straightforward to obtain structure factors for polymers containing any arrangement of such blocks. An example of this is given in Appendix B, where the structure factors of a Gaussian H-shaped polymer are derived.

**Preaveraging in the Structure Factor for Random Systems.** Care is required when applying the RPA to random or polydisperse systems such as the Markov chain system, which is the main subject of this paper. We must, at some point in the calculation, average over the possible structure of each chain. The most rigorous method is to leave this to the very end of the calculation and perform the average on the final result. However, in some cases it is reasonable to perform the averages at an earlier stage, and this can greatly simplify the algebra involved. One possibility is to perform this average when calculating the structure factors such as $s_0^{AA}$ but we must be careful that this is justified.

The essential point is that structure factors like $s_0^{AA}$ involve a sum over the chains in the system. In the "thermodynamic limit", the number of chains is large and so it may be reasonable to say that this sum constitutes an *average* over the properties of the chains. We denote this average by $\overline{(...)}$

$$\begin{aligned} s_0^{AA} &= \frac{v_0}{\Omega}\sum_\alpha s_\alpha^{AA} \\ &\equiv \frac{n v_0}{\Omega}\overline{s_\alpha^{AA}} \end{aligned} \tag{13}$$

where $s_\alpha^{AA}$ is the contribution to $s_0^{AA}$ from chain α. Care is required in making this approximation. In fact, in any given system the sum over the chains will not be exactly the same as the average value of the sum. More importantly, the deviation of the sum from the average will be a fixed quantity for that system. This is because the structure of any particular chain is actually fixed and will not change. The structure of each chain is a "quenched" variable. In making the above approximation, we neglect any possible effects due to the deviation of the structure factors from their average value.

In most cases, the approximation is still valid, at least in the mean field limit. This is because the typical deviation of the sum from its mean is negligible when compared to the overall size of the sum. If the number of chains is $n$, then the sum is of order $n$, while the typical deviation of the sum from its mean is of order $n^{1/2}$. Because the number of chains is generally large, the deviation from the mean is usually negligible when compared to the overall size of the sum.

There are cases when this argument breaks down. For example, in a network each chain is localized in space by its cross-link constraints. The first moment average, $\langle\rho_\mathbf{q}\rangle_0$, of the density is not necessarily zero (there is no translational symmetry). However, when we average over the quenched variables (the cross-links), translational symmetry is returned and $\overline{\langle\rho_\mathbf{q}\rangle_0} = 0$. In this case, then, $\langle\rho_\mathbf{q}\rangle_0$ is typically of order $n^{1/2}$ and is entirely due to deviations from the mean of the quenched average, which is zero. The preaveraging of this structure factor is clearly not valid and would miss some of the important physics.[8]

More generally, before preaveraging a structure factor, one must first be sure that deviations from the mean in the sum over chains will not contribute significantly to the result of the calculation. This is in fact the case for our calculation for Markov chains because, in order to calculate the mean-field spinodal, we require only the second-order coefficient in the free energy functional $F\{\rho_\mathbf{q}\}$.

**Effect of Polydispersity on the Binodal.** A further complication is that the transition at the spinodal may be preempted by a first-order transition (at the binodal). The spinodal is the point of local instability to small fluctuations, which are well characterized by the single density order parameter, $\rho_\mathbf{q}$. However, the binodal is the point where the global free energy minimum is lower than the local free energy. To rigorously calculate the binodal requires a fuller description of the system than a free energy functional in a single-order parameter. This is because the randomness in the reacting Markov system gives a wide range of molecule types. A proper description, particularly when considering macrophase separation, requires the coexistence conditions for each molecule type in the system, and there should be as many order parameters as molecule types. Put another way, the same compositions of coexisting phases could be obtained by many different rearrangements of the molecule types between the phases. Not all of these arrangements would have the same free energy. A description of the system in terms of the monomer composition alone is therefore not sufficient when considering the binodal,[9] so the binodal is a difficult object to calculate. We note that a transition at the binodal may be biased toward macrophase separation.

Nevertheless, the spinodal is still a useful object, particularly in industrial polycondensation systems. This is because there are generally kinetic barriers toward phase separation at the binodal, particularly toward the nucleation mechanism typical of macrophase separation. It is possible (and often advantageous) to design reacting systems so that the binodal region is passed rapidly without significant phase segregation, to reach the spinodal where the kinetic barriers are absent. Furthermore, the nature of the transition at the spinodal will give some indication of the likely nature of any transition at the binodal. Finally, the second-order coefficient of the free energy functional may be useful in future considerations of the dynamics of phase separation.

## 3. RPA for Markov Chains

The statistics of a Markov chain are determined entirely by the square matrix whose coefficients $p_{\alpha\beta}$ give the conditional probability that if a given monomer is of type $\beta$, then the following monomer in the chain will be of type $\alpha$. Thus, for a two-component system with blocks of type A or B, the probability matrix is

$$\mathbf{P} = \begin{bmatrix} p_{\mathrm{AA}} & p_{\mathrm{AB}} \\ p_{\mathrm{BA}} & p_{\mathrm{BB}} \end{bmatrix} \tag{14}$$

In the long chain limit, a monomer of some kind must follow the first, so that $\sum_\alpha p_{\alpha\beta} = 1$ for all $\beta$. This reduces the number of independent coefficients in the matrix **P**. If there is some possibility of the chain terminating after each monomer, for example if the reaction is not completed, then the chains are not typically “long”. The coefficients $p_{\alpha\beta}$ are then strictly independent, subject to the condition $\sum_\alpha p_{\alpha\beta} \le 1$, and must be determined from some model involving the number ratios and relative reactivities of each species in the reaction bath.

We now define the probability vector $\mathbf{z}_\gamma$, whose coefficients $z_{\gamma\alpha}$ give the probability that the monomer $\gamma$ on the chain is of type $\alpha$. If $\mathbf{z}_\gamma$ is known for some monomer $\gamma$, then the matrix **P** gives $\mathbf{z}_{\gamma+1}$, via

$$\mathbf{z}_{\gamma+1} = \mathbf{P}\cdot\mathbf{z}_\gamma \tag{15}$$

and so the probability distribution of all the monomers down the chain is determined.

$$\mathbf{z}_{\gamma+n} = \mathbf{P}^n\cdot\mathbf{z}_\gamma \tag{16}$$

Thus the statistics of monomer−monomer correlations along a chain can be obtained.

We now develop a formalism for treating Markov chains using the random phase approximation. We shall present the theory for a simple two-component system, though the extension to more complex systems will become apparent.

Consider a system containing two block types. Each is polymeric in nature and has reactive end groups that allow reaction between any two blocks. The probabilities of reaction between different species are given by the matrix in eq 14. To keep the calculation simple, we suppose that each block type is uniform and contains only one type of monomer, either A or B. We also assume that when two blocks react, the internal configurations of each block remain independent of those of the other. In other words, the reaction point forms a freely rotating joint.

To apply the RPA, we need to calculate the structure factors $s_0^{\mathrm{AA}}$ etc. defined in eq 6. The double sum in this equation is over all the monomers in the system, and we replace this by a double sum over all the “blocks” ($\gamma$, $\gamma'$) in the system:

$$s_0^{\mathrm{AA}} = \frac{v_0}{\Omega}\sum_{\gamma,\gamma'} s_{\gamma\gamma'}^{\mathrm{AA}} \tag{17}$$

Only if the two blocks are of type A will their contribution $s_{\gamma\gamma'}^{\mathrm{AA}}$ be nonzero. We now use the preaveraging approximation. We note that the first sum over the blocks $\gamma$ is a sum over a large number of terms (in a large system). We conclude that this sum can be approximated, to good accuracy, by an average over the possible realisations of the system. This yields

$$s_0^{\mathrm{AA}} = \frac{v_0}{\Omega}\sum_{\gamma}\overline{\Big(\sum_{\gamma'} s_{\gamma\gamma'}^{\mathrm{AA}}\Big)} \tag{18}$$

Only the blocks $\gamma'$ that are on the same chain as block $\gamma$ contribute to $s_{\gamma\gamma'}^{\mathrm{AA}}$. The average is an average over the possible realizations of the chain connected to block $\gamma$. A strategy for calculating the structure factors now presents itself. For each block (or type of block) in the system, we must average over the contributions to the structure factor obtained by interactions between this block and the possible chain conformations connected to it. Because each block in the system has a well-defined probability vector $\mathbf{z}_\gamma$ (each block is either of type A or type B), the probability distribution for the chain connected to it is defined in the Markov chain model by eq 16.

Consider the contribution $\overline{s_{\gamma,\gamma+m}^{\mathrm{AA}}}$ from a block of type A and a second block that is $m$ blocks further down the chain. We can easily calculate the probability that the second block is of type A, since its probability vector $\mathbf{z}_m$ is given by eq 16. However, this is not sufficient information to obtain $\overline{s_{\gamma,\gamma+m}^{\mathrm{AA}}}$, which is dependent not only on whether the second block is of type A, but also on the configurations of the intermediate chain. There are various possibilities for the block sequence in this chain, and we must take account of this.

The averaging is aided by making use of the “propagator” formalism summarized earlier. We define the propagator for an A block to be $G_{\mathrm{A}}$ and the propagator for a B block $G_{\mathrm{B}}$. The total propagator for the intermediate chain is the product of the propagators of all the blocks along that chain. We must average this product, and we achieve this by introducing the matrix

$$\mathbf{G} = \begin{bmatrix} G_{\mathrm{A}} & 0 \\ 0 & G_{\mathrm{B}} \end{bmatrix} \tag{19}$$

We find that if we multiply any Markov vector (such as a probability vector $\mathbf{z}_\gamma$) by the matrix ($\mathbf{G}\cdot\mathbf{P}$), then the resulting vector contains both the probability distribution and the propagator for the next block in the chain, together with any information contained within the original vector. The matrix ($\mathbf{G}\cdot\mathbf{P}$) is thus a matrix "propagator" for one step along a Markov chain. To obtain the propagator for several steps along the chain, we repeatedly multiply the original vector by ($\mathbf{G}\cdot\mathbf{P}$). If the first block is of type A then the vector

$$(\mathbf{G}\cdot\mathbf{P})^{m-1}\begin{pmatrix}1\\0\end{pmatrix} \tag{20}$$

contains the average propagator for the next $m - 1$ connecting blocks, together with the probability distribution for the last of these blocks. To see that the probability distribution is contained within this vector, note that at $\mathbf{q} = \mathbf{0}$, the propagators $G_{\mathrm{A}} = G_{\mathrm{B}} = 1$, so that $\mathbf{G} = \mathbf{I}$, the identity matrix. Equation 20 then reduces to eq 16, the probability distribution for the "($m - 1$)th" block.

We multiply the vector (20) by $\mathbf{P}$ to give the probability distribution for the "$m$th" block. In calculating $\overline{s^{\mathrm{AA}}_{\gamma,\gamma+m}}$, we only require the case where the "$m$ th" block is of type A, so we resolve the resulting vector onto (1 0). We find

$$s^{\mathrm{AA}}_{\gamma,\gamma+m} = H_{\mathrm{A}}^{\ 2}(1 \quad 0)\mathbf{P}\cdot(\mathbf{G}\cdot\mathbf{P})^{m-1}\begin{pmatrix}1\\0\end{pmatrix} \tag{21}$$

where $H_{\mathrm{A}}$ is the coterm of an A block. If we now put all the two-block terms of this form into eq 18 and include the self-terms of all the A blocks, we obtain

$$s_0^{\mathrm{AA}} = \frac{v_0}{\Omega}\sum_{\mathrm{A\ blocks}}\left[J_{\mathrm{A}} + 2H_{\mathrm{A}}^{\ 2}\sum_{m=1}^{\infty}(1 \quad 0)\mathbf{P}\cdot(\mathbf{G}\cdot\mathbf{P})^{m-1}\begin{pmatrix}1\\0\end{pmatrix}\right] \tag{22}$$

where the factor of 2 takes account of the fact that an A block is difunctional and the chain extends from it in both directions. The sum in $m$ is over a geometric progression in ($\mathbf{G}\cdot\mathbf{P}$) and can be carried to infinity because the possibility of chain termination is carried completely within the probability matrix, $\mathbf{P}$. The result is

$$s_0^{\mathrm{AA}} = \frac{n_{\mathrm{A}}v_0}{\Omega}\left[J_{\mathrm{A}} + 2H_{\mathrm{A}}^{\ 2}(1 \quad 0)\mathbf{P}\cdot(\mathbf{I} - \mathbf{G}\cdot\mathbf{P})^{-1}\begin{pmatrix}1\\0\end{pmatrix}\right] \tag{23}$$

The calculation of $s_0^{\mathrm{AB}}$ and $s_0^{\mathrm{BB}}$ proceeds in an identical fashion, giving

$$s_0^{\mathrm{AB}} = \frac{n_{\mathrm{A}}v_0}{\Omega}\left[2H_{\mathrm{A}}H_{\mathrm{B}}(0 \quad 1)\mathbf{P}\cdot(\mathbf{I} - \mathbf{G}\cdot\mathbf{P})^{-1}\begin{pmatrix}1\\0\end{pmatrix}\right] \tag{24}$$

$$s_0^{\mathrm{BB}} = \frac{n_{\mathrm{B}}v_0}{\Omega}\left[J_{\mathrm{B}} + 2H_{\mathrm{B}}^{\ 2}(0 \quad 1)\mathbf{P}\cdot(\mathbf{I} - \mathbf{G}\cdot\mathbf{P})^{-1}\begin{pmatrix}0\\1\end{pmatrix}\right] \tag{25}$$

This solves the problem of the scattering from a two-component Markov chain. The structure factors above may be calculated from a model involving the nature of the component blocks and their relative reactivities. These structure factors should be used in expressions such as (5) when calculating the phase behavior.

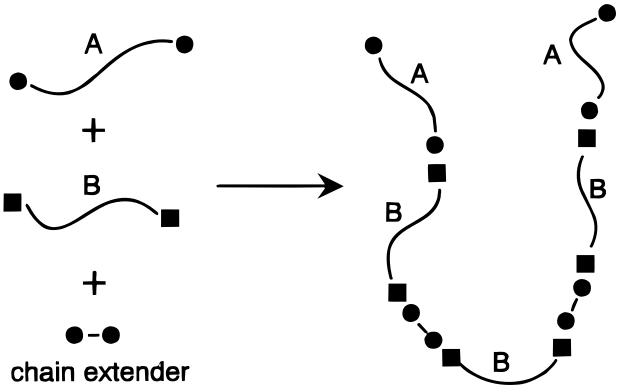

**Figure 3.** Representation of a typical polycondensation reaction.

In the above example with two components, all the matrices are of dimension 2 × 2. The extension to the general $n$ component system is clear. $\mathbf{G}$ and $\mathbf{P}$ are then $n \times n$ matrices, and the probability vectors have $n$ dimensions, but the structure of the resulting expressions is identical to those above. The major difficulty, as $n$ increases, is the calculation of the inverse matrix $(\mathbf{I} - \mathbf{G}\cdot\mathbf{P})^{-1}$, which comes from summing the geometric progression in ($\mathbf{G}\cdot\mathbf{P}$). We shall consider possible extensions to more complicated systems in section 5. We now proceed to complete the calculation of scattering for a simple model A–B system.

## 4. Model Two-Component Markov Chain

The analysis above gives a complete description of any two-component Markov chain. However, there are many free parameters, notably the four components of the probability matrix, and the choice of microscopic model for the two components. We now use the expressions developed to deal with a specific system, illustrated in Figure 3. The reaction chemistry is that of a typical polycondensation reaction, in that there are two reactive groups, which we label ● and ■. All reactions involve the joining of a ● group to a ■ group (there are no ●–● or ■–■ reactions). The system contains three components, an "A block" with reactive end groups of type ●, a "B block" with reactive end groups of type ■, and a "chain extender". The chain extender has reactive groups of type ●, and its function is to allow one "B block" to follow another without an "A block" intervening. We shall assume that the chain extender is otherwise small and that it plays little part in the interactions leading to phase segregation or enhanced scattering in the system. We shall also assume that the reactive groups are present in stoichiometric quantities within the system (there are equal numbers of ● and ■) and that the A and B blocks are both Gaussian polymers, with monomer step length $b$.

We define the number of A blocks (each of polymerization $N_{\mathrm{A}}$) to be $n_{\mathrm{A}}$ (similarly, $N_{\mathrm{B}}$ and $n_{\mathrm{B}}$ for the B blocks). The fraction of chains in the system which are of type A is

$$f_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \tag{26}$$

The specified reaction chemistry dictates that $0 \le f_{\mathrm{A}} \le {}^1\!/_2$. The limit $f_{\mathrm{A}} = {}^1\!/_2$ corresponds to a system with no chain extenders and whose final reacted state is long chains containing alternating A and B blocks. As $f_{\mathrm{A}}$

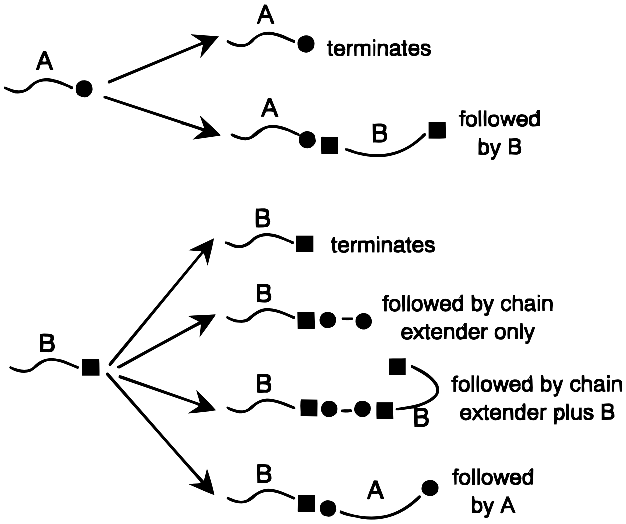

**Figure 4.** Showing the possible arrangements that may follow an A or a B block in the reaction process.

decreases, the average number of adjacent B blocks in the final reacted chain increases.

We also define the volume fraction of A monomers

$$\phi_A = \frac{n_A N_A}{n_A N_A + n_B N_B} \tag{27}$$

and the mean block size

$$N = f_A N_A + f_B N_B \tag{28}$$

The three parameters $\phi_A$ (with $\phi_B = 1 - \phi_A$), $f_A$ (with $f_B = 1 - f_A$), and $N$ are sufficient to completely specify the system at the start of the reaction.

**Probability Matrix.** We now look to write down the probability matrix at a given stage of reaction. Suppose that the reaction rates of all the reactive groups in the system are identical (independent of the molecule carrying the group). Then we can define a *degree of reaction*, $p$, which is the probability at a given time that a given group will have reacted. Clearly $0 \le p \le 1$, with $p = 0$ at the start of the reaction and $p = 1$ when the reaction is completed. Given this assumption, we can write down the components of **P**.

Figure 4 illustrates the possible groups that can follow an A or a B block. An A block can only be followed by a B block, with probability $p$, since the reaction chemistry allows reaction with nothing else. The only alternative is for the chain to terminate. Hence

$$p_{AA} = 0$$

$$p_{BA} = p$$

There are four possibilities following a B block. The chain can terminate immediately or react. If it reacts with a "chain extender", the chain may still terminate after the chain extender, or be followed by another B block. Finally, the B block may react directly with an A block. We find

$$p_{AB} = p\left(\frac{f_A}{f_B}\right)$$

$$p_{BB} = p^2\left(1 - \frac{f_A}{f_B}\right)$$

**Structure Factors.** Substituting these into the results of eqs 23, 24, and 25, we obtain

$$s_0^{AA} = N\left(\frac{\phi_A^{\,2}}{f_A}\right)\left(j_A + \frac{2h_A^{\,2}G_B p^2 f_A}{1 - f_A - p^2 G_B(f_A G_A + 1 - 2f_A)}\right) \tag{29}$$

$$s_0^{AB} = N(\phi_A\phi_B)\left(\frac{2h_A h_B p}{1 - f_A - p^2 G_B(f_A G_A + 1 - 2f_A)}\right) \tag{30}$$

$$s_0^{BB} = N\left(\frac{\phi_B^{\,2}}{f_B}\right)\left(j_B + \frac{2h_B^{\,2}p^2(f_A G_A + 1 - 2f_A)}{1 - f_A - p^2 G_B(f_A G_A + 1 - 2f_A)}\right) \tag{31}$$

In Appendix A, the propagator, coterm, and self-term for Gaussian coils are calculated. Using these results, given in eq 68, we have

$$G_A = \exp\left(-\frac{\phi_A}{f_A}Q^2\right) \tag{32}$$

$$h_A = h_{coil}\left(\frac{\phi_A}{f_A}Q^2\right) \tag{33}$$

and

$$j_A = j_{coil}\left(\frac{\phi_A}{f_A}Q^2\right) \tag{34}$$

where $Q^2 = q^2 b^2 N/6$ is the normalized wavevector. $G_B$, $h_B$, and $j_B$ are defined analogously.

We substitute the structure factors $s_0^{AA}$ etc. into eq 5. For a given initial system (i.e., at fixed $f_A$, $\phi_A$, and $N$) this yields a surface $S_{inc}(\mathbf{q},p)$. Equation 7 indicates that at fixed $p$ (i.e., at a particular stage of the reaction) the spinodal is determined by the maximum of $S_{inc}(\mathbf{q},p)$ with respect to **q**. The position of the maximum along the **q** axis indicates to some extent the nature of the transition, in the event of the spinodal being crossed at this stage of reaction. In Figure 5 we show slices through the surface $S_{inc}(\mathbf{q},p)$ at various degrees of reaction, $p$, for system parameters $\phi_A = 0.7$ and $f_A = 0.2$.

There are two questions that may be answered by examining the surface $S_{inc}(\mathbf{q},p)$. Firstly, by examining whether the maximum value of $S_{inc}(\mathbf{q},p)$ decreases or increases as the reaction proceeds, we can judge whether the system is becoming more or less miscible in terms of the value of $\chi$ at which the spinodal occurs. Even if the value of $\chi$ in the reaction mixture remains constant during the reaction, a phase separation may occur because the spinodal line is moving and may pass this value of $\chi$. Secondly, by noting how the position of the maximum varies with $p$, we can judge whether the reaction mixture is unstable to microphase or bulk phase separation. The initial system, if quenched, would undergo bulk phase separation (since it consists of separate A and B blocks), so the peak in $S_{inc}(\mathbf{q},p = 0)$ is always at zero **q**. As the reaction proceeds, the peak can either remain at zero **q** or shift to nonzero **q** (indicating a preference for microphase separation). The system for which Figure 5 is plotted eventually becomes

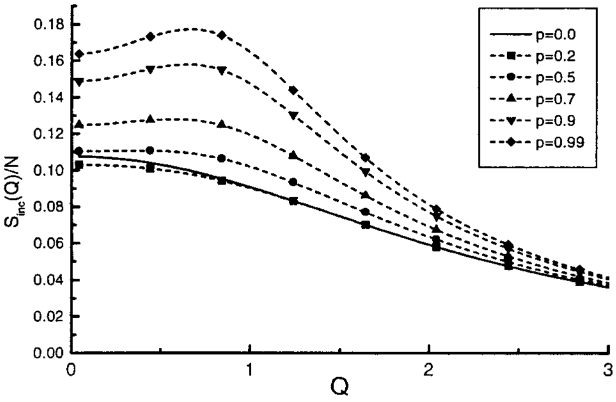

**Figure 5.** Plot of $S_{\text{inc}}(\mathbf{q},p)/N$ at various degrees of reaction, $p$, for the simple two-component system with parameters $\phi_A = 0.7$ and $f_A = 0.2$.

less miscible as the reaction proceeds, and the spinodal crosses to microphase type.

**Results and Discussion.** We begin by addressing the question of how the miscibility of the system changes with the degree of reaction, $p$. In general, it is possible for the miscibility to increase or decrease.

The decrease in miscibility is driven by the joining together of B blocks, which we have allowed by including chain extenders. This leads to sections of chain which consist entirely of B blocks, and these sections grow as the reaction proceeds. The result is an increase of the "effective degree of polymerization", $N_{\text{eff}}$, defined (roughly) as the average size of the $-(\text{A}-\text{B}^n)-$ repeat unit in the copolymer chain. Since the product "$\chi N_{\text{eff}}$" is the relevant parameter determining whether a polymer system is miscible, the increase in $N_{\text{eff}}$ clearly drives the system toward phase segregation.

However, there is a competing process. As the reaction proceeds, the system becomes more "copolymeric" in nature, A blocks becoming joined chemically to B blocks. The tendency of copolymers to make mixtures more compatible thus becomes important. This effect makes the system more miscible.

The result of the competition between these two effects depends upon the system parameters $f_A$ and $\phi_A$ only (since the third parameter, $N$, factorizes out of the structure factors in (29)−(31)). In the very early stages of reaction, the compatiblization due to formation of copolymers is the dominant effect in all systems. This was evident in Figure 5, where the peak in the stucture factor initially decreased in height and is illustrated further in Figure 6. We plot the spinodal $N\chi_S$ as a function of $\phi_A$ at fixed $f_A = 0.168$, taking two values of the degree of reaction, $p = 0$ and $p = 0.2$. We see that the initial effect of the reaction is everywhere to increase $N\chi_S$. The reason for this effect is simple and related to the chosen model. In the early stages of reaction, it is easier to join A blocks to B blocks than to join A to A or B to B. The former is possible via the formation if a single ■−● bond, while the latter requires at least two such bonds (for example, B blocks are joined via a chain extender). The formation of copolymers is thus dominant.

As $p$ increases further, the reaction mixture may become less miscible. Figure 7 shows how the spinodal changes with $p$ at a fixed volume fraction, $\phi_A = 0.7$. After the initial increase in miscibility, the system continues to become more miscible if $f_A$ is large but begins to get less miscible for smaller $f_A$. This is to be expected, since as $f_A$ gets closer to $^1/_2$, the growing copolymers consist more of alternating A and B blocks rather than extended sections of several B blocks. At smaller values of $f_A$, there are typically several B blocks between each A block, so the increase in the effective degree of polymerization becomes more significant.

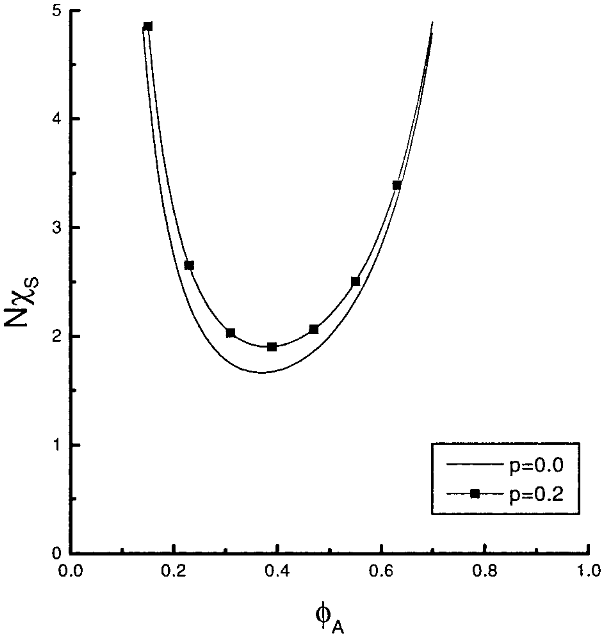

**Figure 6.** Showing how the spinodal for the model Markov system typically changes in the early stages of reaction. The plot is for a fixed value of $f_A = 0.168$.

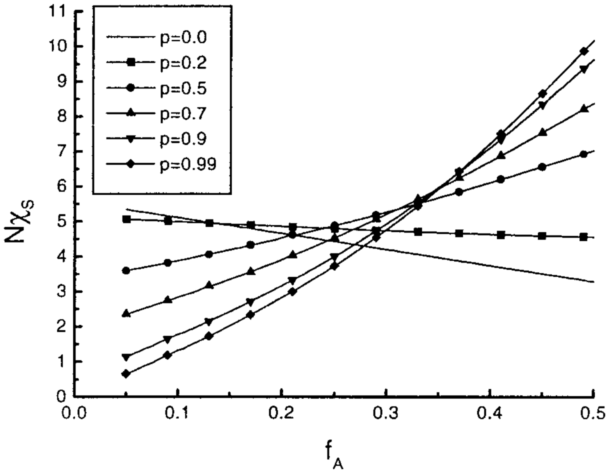

**Figure 7.** Showing the variation of the spinodal with $f_A$ for the model Markov system at fixed $\phi_A = 0.7$ and at various stages of the reaction.

We now turn to the dependence on $\phi_A$ of the spinodal behavior. Varying $\phi_A$ at fixed $f_A$ is equivalent to changing the relative lengths of the two block types. Figure 8 shows how the spinodal changes with $p$ for fixed values $f_A = 0.168$. The system appears to become less miscible at the higher values of $\phi_A$ only. The increasing degree of polymerization of the B chain sections has the most marked effect when the initial B-blocks are small compared to the A-blocks. This is as we would expect, since the position of the spinodal in polymer blends is generally dominated by the smaller, least concentrated component.

To begin to quantify these results, consider the variation with $p$ of the zero-wavevector structure factor

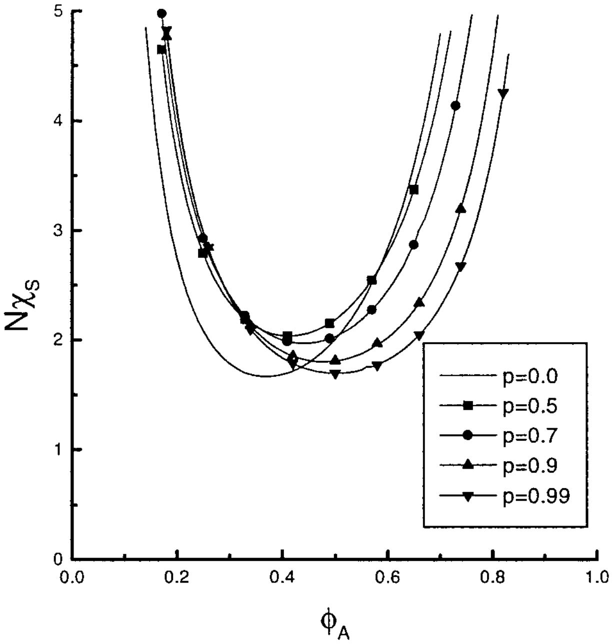

**Figure 8.** Variation of the spinodal with $\phi_A$ for the model Markov system at fixed $f_A = 0.168$ and at different stages of the reaction.

$S_{\rm inc}(\mathbf{q}=\mathbf{0},p)$. If we note how this changes from $p = 0$ to $p = 1$, then we obtain some indication of whether the system has become more or less miscible as the reaction has proceeded. The result will not be exact, since at $p = 1$ the peak in $S_{\rm inc}(\mathbf{q})$ may be at nonzero $\mathbf{q}$. A proper calculation requires numerical maximization of $S_{\rm inc}(\mathbf{q},p)$. Nevertheless, Figure 5 is typical of the structure factors obtained for "microphase" systems in that the peak in the structure factor is only a little higher than the zero $\mathbf{q}$ structure factor. By taking this approach, we obtain an approximate algebraic expression for the crossover.

A series expansion of $S_{\rm inc}(\mathbf{q},p)$ in the normalized wavevector, $Q$, yields, at $p = 0$

$$\frac{S_{\rm inc}}{N} = \frac{\phi_A^{\ 2}(1-\phi_A)^2}{\phi_A^{\ 2} + f_A - 2f_A\phi_A} + O(Q^2) \qquad (35)$$

and at $p = 1$

$$\frac{S_{\rm inc}}{N} = \frac{(1-2f_A)\phi_A^{\ 2}(1-\phi_A)^2}{f_A(1-f_A)} + \{[(f_A^{\ 2} + 10f_A\phi_A - 12f_A^{\ 2}\phi_A - 2\phi_A + 3\phi_A^{\ 2} - 12f_A\phi_A^{\ 2} + 12f_A^{\ 2}\phi_A^{\ 2}) \times \phi_A^{\ 2}(1-\phi_A)^2]/[6f_A^{\ 2}(1-f_A)^2]\}Q^2 + O(Q^4) \qquad (36)$$

Solving the equation $S_{\rm inc}(\mathbf{0},0) = S_{\rm inc}(\mathbf{0},1)$ yields the required expression. We find that the system has become less miscible if

$$f_A < \frac{\phi_A + \phi_A^{\ 2} - \sqrt{\phi_A^{\ 2}(2 - 2\phi_A + \phi_A^{\ 2})}}{4\phi_A - 1} \qquad (37)$$

This is illustrated in Figure 9 showing that, in the high-$\phi_A$, low-$f_A$ region of the phase diagram, the system becomes less miscible by the end of the reaction.

We turn now to the nature of any transition that may occur during the reaction. Because the shape of $S_{\rm inc}(\mathbf{q})$ changes continually with $p$, the nature of the transition depends very much on at what stage of the reaction the transition occurs, and hence on the value of $\chi$. For the moment, then, we simply make some general comments.

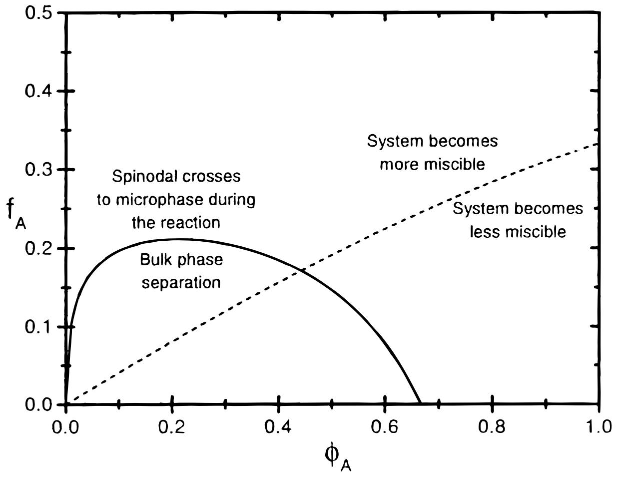

**Figure 9.** Showing the approximate boundaries between the final reaction mixture being susceptible to bulk/microphase separation (solid line) and the mixture becoming more/less miscible as the reaction proceeds (dashed line).

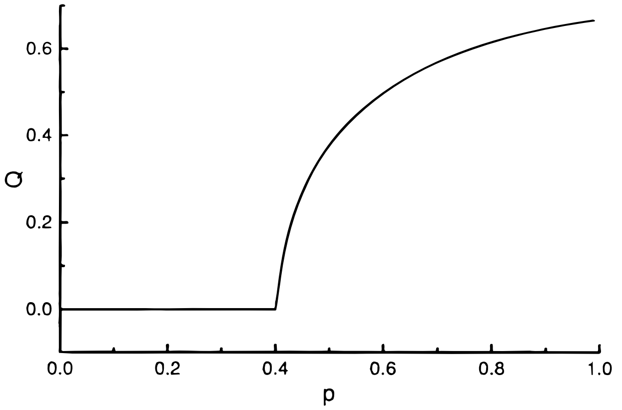

**Figure 10.** Plot of the peak position, $Q^*$; as a function of $p$ for the simple two-component system with parameters $\phi_A = 0.7$ and $f_A = 0.2$.

In terms of the how the position of the peak in $S_{\rm inc}(\mathbf{q})$ may vary as the reaction proceeds, there are only two possibilities. Either the peak will remain at zero wavevector (in which case any transition will definitely be a bulk phase transition) or the peak will shift to nonzero wavevector at some stage of the reaction. The latter was true for the structure factors plotted in Figure 5 and we show in Figure 10 the associated variation of the peak position with degree of reaction. There is a point (known as the Lifshitz point[10]) where the peak moves away from zero wavevector. In practice this point will be passed quickly as the reaction proceeds. If a Lifshitz point is passed, there is some uncertainty as to the nature of the transition. The spinodal may be reached after the peak of $S_{\rm inc}(\mathbf{q})$ has shifted to nonzero wavevectors, giving a transition that is specifically of microphase type. However, if the spinodal is reached at an early stage of the reaction, it may give a transition that is initially of bulk nature. It is impossible to say, without further work, how the reaction then proceeds. A microphase morphology may eventually be obtained, but the bulk phase separation will certainly inhibit bond formation between the A and B blocks.

The first question to be asked, then, is whether a shift in the peak of $S_{\rm inc}(\mathbf{q})$ occurs during the reaction. To find an approximate expression for the crossover between the two types of behavior, we look once again at the series expansion at $p = 1$ in eq 36. If the coefficient of $Q^2$ in this expression is positive, then the peak in $S_{\mathrm{inc}}(\mathbf{q})$ at $p = 1$ is definitely at nonzero wavevector, and so a shift from the zero wavevector peak must have occurred at some stage of the reaction. By setting the coefficient of $Q^2$ to zero, we find an approximate expression for the crossover. The peak in $S_{\mathrm{inc}}(\mathbf{q})$ remains at $\mathbf{q} = \mathbf{0}$ if

$$f_A < \frac{6\phi_A^{\,2} - 5\phi_A + \sqrt{2\phi_A(1-\phi_A)}}{1 - 12\phi_A + 12\phi_A^{\,2}} \tag{38}$$

This is illustrated in Figure 9. At high values of $f_A$ the reaction tends toward alternating A and B blocks, giving a tendency for microphase separation. At high values of $\phi_A$, the influence of the monodisperse A blocks on the nature of the transition is highest, and the polydispersity of the sections of chain containing B blocks matters less. Again, a microphase separation is favored toward the end of the reaction.

In conclusion, as the reaction proceeds, the system initially becomes more miscible. After this early increase in miscibility, the behavior depends on $f_A$ and $\phi_A$. At high values of $\phi_A$ and low values of $f_A$ the reacting system becomes less miscible, so that the reaction may drive a phase separation. We note that, for many choices of $f_A$ and $\phi_A$, this decrease in miscibility occurs early on in the reaction, when the chains are still short. This is consistent with the findings of Elwell et al.,[1] who showed that for blends commonly used in industry the phase segregation typically started between $p = 0.5$ and $p = 0.6$. However, we note that they did not explore the variation in behavior with $f_A$ and $\phi_A$.

At other concentrations and ratios of blocks, the system will phase separate only if $\chi$ changes during the reaction. For example, energy released by the chemical reaction may increase the temperature and in lower-critical systems this results in an increase in $\chi$. The nature of the transition also depends on $f_A$ and $\phi_A$ as well as on the value of $p$ when reaction occurs. A simple guide is that at low values of $f_A$ and $\phi_A$ the initial instability will certainly be to a bulk phase transition. At other system parameters, the result is more sensitive to the stage of the reaction at which phase separation occurs. These ideas are summarized in Figure 9, which shows approximately where the boundaries between different types of behavior lie in $(f, \phi_A)$ space.

## 5. Branched Markov Systems

It was pointed out in section 3 that expressions such as eq 23 could be generalized to obtain the scattering functions for many-component systems, by increasing the dimensionality of the vectors and matrices. A possible extension of the theory from the simple system discussed above is to use different "building blocks" in the Markov system, with different propagators, coterms, and self-terms. We have already calculated these for Gaussian coils. Similar expressions exist for rod-like blocks.[11] It is also possible to consider "composite" blocks, containing both A and B monomers. As an example of how the theory may be extended, we look at how branched "blocks" may be incorporated into the Markov chain formalism.

First we pursue a simple example. We calculate the structure factor for a branched polymer formed from difunctional polymer blocks of polymerization $N$ and pointlike $m$ -functional branch points, as illustrated in Figure 11. Bonds are formed between the polymers and branch points with probability $p$.

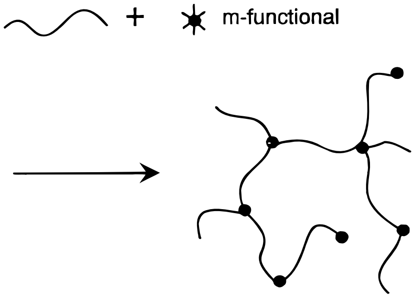

**Figure 11.** Schematic diagram of a reaction between linear polymeric blocks and $m$-functional branch points.

We shall take the preaveraging approximation and assume, as before, that no loops are formed. For each polymer block in the system, the contribution to the structure factor comes from its self-term $J_0$ plus the interactions with other blocks attached to it, involving its coterm $H_0$. At each end of the polymer block, there follows a branch point with probability $p$. The branch point has $(m - 1)$ reactive groups free, and each of these may be connected to a further polymer and more branching with probability $p$. We define $H_{\mathrm{branch}}$ to be the average coterm of the polymer following a branch point. The structure factor for the branched system containing $n$ polymer blocks is thus

$$S \sim n[J_0 + 2(m-1)p^2 H_0 H_{\mathrm{branch}}] \tag{39}$$

But $H_{\mathrm{branch}}$ is easy to calculate. It is simply the coterm for the first polymer block in the branch plus the coterms for the $(m - 1)$ *possible* branches following the first (multiplied by the propagator, $G_0$, for the first block). Because this is a random system, the probability distribution for each of the "sub-branches" is the same as the probability distribution for the whole branch (a similar scheme to this may be found in ref 12). Hence

$$H_{\mathrm{branch}} = H_0 + G_0(m-1)p^2 H_{\mathrm{branch}} \tag{40}$$

Solving for $H_{\mathrm{branch}}$, we have

$$H_{\mathrm{branch}} = \frac{H_0}{1 - (m-1)p^2 G_0} \tag{41}$$

Substituting into eq 39 gives the expression for the structure factor of a branched Markov chain.

$$S \sim n\left[J_0 + \frac{2(m-1)p^2 H_0^{\,2}}{1 - (m-1)p^2 G_0}\right] \tag{42}$$

We can compare this expression with the structure factor $s_0^{\mathrm{AA}}$ for the simple A–B system above, in eq 29. We take the limit $f_A = {}^1\!/_2$ (so that the A and B blocks alternate in the same way as the branch points alternate with the polymer blocks in the present example). Then

$$s_0^{\mathrm{AA}} = N\left(\frac{\phi_A^{\,2}}{f_A}\right)\left(j_{\mathrm{AA}} + \frac{2h_A^{\,2} G_B p^2}{1 - p^2 G_B G_A}\right) \tag{43}$$

and we can see that the factor $(m - 1)$ in the expression (42) plays the same role as the propagator $G_B$ for the B blocks in (43). In effect, the propagator for an $m$-functional branch point is, within the Markov chain formalism,

$$G_{\text{branch}} = (m - 1) \tag{44}$$

An alternative way of reaching the same conclusion is to note that the chain attached to each reactive group on the branch point has exactly the same probability distribution. Thus the branch point simply "multiplies the number of chains" attached to the original one by $(m - 1)$. Notice that this only works because we have pre-averaged the structure factors so the chains attached to the branch point are identical in an average sense. This expression for the propagator should not be used in non-Markov systems, unless each chain attached to the branch point is identical.

In the above analysis, we have assumed that the reaction rate of the groups on a branch point is unaffected by how many of the other groups have already reacted. For small branching groups, this may not be the case. A simple way to overcome this problem is to consider the functionality, $m$, as being the ($p$-dependent) "effective functionality" at a given stage of reaction.

The above Markov chain analysis breaks down mathematically when the determinant of the matrix $(\mathbf{I} - \mathbf{G}\cdot\mathbf{P})$ becomes zero at some wavevector, and the inverse can no longer be taken. By introduction of propagators with values greater than 1, such as $G_{\text{branch}}$, this breakdown of the theory occurs before the degree of reaction $p$ reaches 1. The breakdown can be attributed to the "average" polymerization index of the growing polymers becoming infinite. This point is the theoretical definition of the classical "gel point"[12] and it occurs in this simple system at $p = p_c$, where

$$p_c^{\,2} = \frac{1}{m - 1}$$

We expect, however, that the theory effectively breaks down earlier than this when a significant number of loops appear. Consequently, our theory is applicable only to the earlier stages of reaction, outside the Ginzburg region for the gelation ensemble, calculated by de Gennes[13] to be of order

$$p_c - p = \Delta p \sim N^{-1/3} \tag{45}$$

Within the Ginzburg region we expect percolation statistics to be dominant.

**Model Two-Component Branched System.** The simplest generalization of the two-component system in section 4 to branched systems is illustrated in Figure 12. The 2-functional A blocks are replaced by $m_A$-functional stars (while the B blocks retain their functionality $m_B = 2$). As in section 4, we define the number of A stars (each of total polymerization $N_A$) to be $n_A$ and we retain the definitions of $f_A$, $\phi_A$, and $N$ given in eqs 26, 27, and 28.

In addition to these, it is convenient to define a "valence fraction" $\eta_A$, which is the ratio of reactive groups on the A blocks to the total number of reactive groups in the A and B blocks:

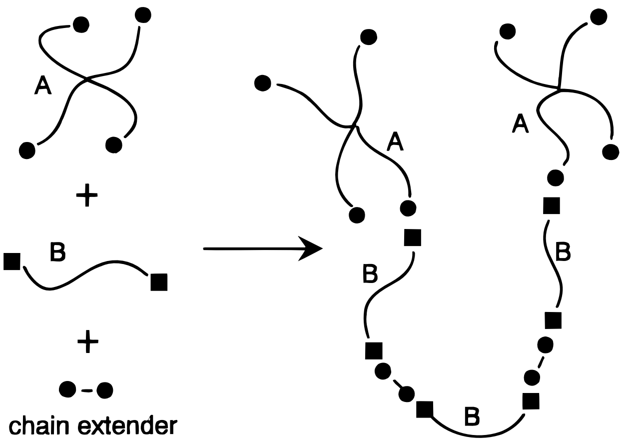

**Figure 12.** Representation of a polycondensation reaction involving four-functional stars.

$$\eta_A = \frac{m_A n_A}{m_A n_A + m_B n_B} \tag{46}$$

Since we impose the constraint that the reactive groups are present in stoichiometric quantities, it is clear that $0 < \eta_A < {}^1/_2$ (while the equivalent constraint on $f_A$ varies with $m_A$). Furthermore, it is apparent that fixing $\eta_A$ while varying $m_A$ ensures a constant average number of adjacent B blocks between A blocks in the final reacted product. Thus, $\eta_A$ is a more natural variable to work with than $f_A$ (though they are identical when $m_A = m_B$), particularly when considering the elements of the probability matrix, $\mathbf{P}$. The relationship between $f_A$ and $\eta_A$ is

$$f_A = \frac{m_B \eta_A}{m_B \eta_A + m_A \eta_B} \tag{47}$$

It is necessary to obtain the propagator, coterm, and self-term of the $m_A$-arm stars. In terms of the results for a single coil given in Appendix B, we can write down these quantities for the star-arms (we remove the molecular weight prefactors for convenience).

$$G_{\text{arm}} = \exp\left(-\frac{\phi_A}{m_A f_A} Q^2\right) \tag{48}$$

$$h_{\text{arm}} = h_{\text{coil}}\left(\frac{\phi_A}{m_A f_A} Q^2\right) \tag{49}$$

and

$$j_{\text{arm}} = j_{\text{coil}}\left(\frac{\phi_A}{m_A f_A} Q^2\right) \tag{50}$$

Any path between two of the star's reactive groups passes through two arms and the branch point, so the propagator for the A star is

$$G_A = (m_A - 1) G_{\text{arm}}^{\;2} \tag{51}$$

The coterm and self-term, calculated by similar reasoning, are

$$\frac{H_A}{N_A} = h_A = \frac{[1 + (m_A - 1)G_{\text{arm}}]h_{\text{arm}}}{m_A} \tag{52}$$

$$\frac{J_A}{N_A^2} = j_A = \frac{j_{arm} + (m_A - 1)h_{arm}^2}{m_A} \tag{53}$$

In terms of these, the bare structure factors for the branched two-component system are

$$s_0^{AA} = N\left(\frac{\phi_A^2}{f_A}\right)\left(j_A + \frac{m_A h_A^2 G_B p_A^2 \eta_A}{1 - \eta_A - p^2 G_B(\eta_A G_A + 1 - 2\eta_A)}\right) \tag{54}$$

$$s_0^{AB} = N(\phi_A \phi_B)\left(\frac{m_A m_B}{m_A f_A + m_B f_B}\right) \times \left(\frac{h_A h_B p}{1 - \eta_A - p^2 G_B(\eta_A G_A + 1 - 2\eta_A)}\right) \tag{55}$$

$$s_0^{BB} = N\left(\frac{\phi_B^2}{f_B}\right)\left(j_B + \frac{m_B h_B^2 p^2(\eta_A G_A + 1 - 2\eta_A)}{1 - \eta_A - p^2 G_B(\eta_A G_A + 1 - 2\eta_A)}\right) \tag{56}$$

These may be substituted into (5) to yield a surface $S_{inc}(\mathbf{q},p)$ as before. We note that for $m_A = 2$ these results reduce to those found in section 4.

The mathematical breakdown of the theory occurs at the percolation limit, found as the point where the denominator

$$1 - \eta_A - p^2 G_B(\eta_A G_A + 1 - 2\eta_A)$$

is zero at $\mathbf{q} = \mathbf{0}$. This gives

$$p_c^2 = \frac{1 - \eta_A}{1 + \eta_A(m_A - 3)} \tag{57}$$

In Figures 13 ($m_A = 3$) and 14 ($m_A = 4$) we plot $S_{inc}$ for the same parameters $\phi_A = 0.7$ and $\eta_A = 0.2$ as in figure 5. The curves are plotted for degrees of reaction up to the percolation limit. It can be seen that the curves are similar and any effect of the branch points is subtle, which broadly justifies the use of the primary variable $\eta_A$ rather than $f_A$.

We now apply the same methods as in section 4 to ascertain the effect of the variables $\phi_A$ and $\eta_A$ on the misciblity and tendency to microphase separate, obtaining the results for different numbers of star arms, $m_A$. In order to make a reasonable comparison, we compare systems with different $m_A$ at the same degree of reaction, $p$ ($<p_c$).

The method used to determine whether the system has become more or less miscible at a given degree of reaction was to find the approximate crossover, $S_{inc}(\mathbf{0},0) = S_{inc}(\mathbf{0},p)$. We find that in terms of this criterion, the crossover is independent of $m_A$ and lies at

$$\eta_A = \{\phi_A + (2p - 1)\phi_A^2 - \sqrt{\phi_A^2(1 + p^2 - 2(p^2 - p + 1)\phi_A + (2p^2 - 2p + 1)\phi_A^2)}\}/[2\phi_A^2(p - 1) + 2(p + 1)\phi_A - p] \tag{58}$$

The lack of dependence on $m_A$ is a suprising result, since in general the shape of the curve $S_{inc}$ $(\mathbf{0},p)$ varies with $m_A$.

This line is plotted in Figure 15 for $p = 0.55$, along with the crossover between macrophase and microphase spinodals at this degree of reaction. The latter is found using the same method as in section 4 and is found to vary with $m_A$. A higher value of $m_A$ favors microphase separation. The reason for this is that increasing $m_A$ reduces the radius of gyration of the A stars while keeping the molecular weight constant. The influence of the monodisperse A stars is then increased at higher wavevectors.

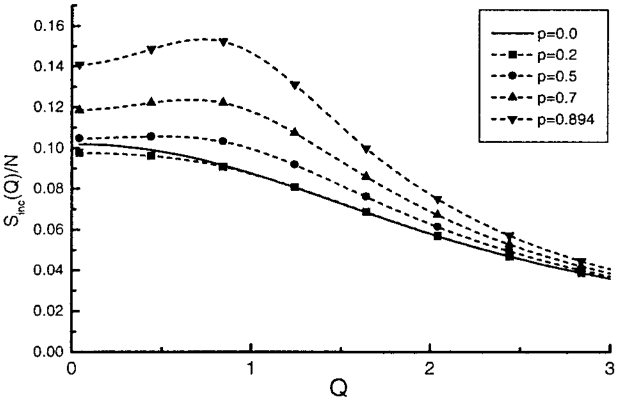

**Figure 13.** Plot of $S_{inc}(\mathbf{q},p)/N$ at various degrees of reaction, $p$, for the branched two-component system with parameters $m_A = 3$, $\phi_A = 0.7$, and $\eta_A = 0.2$.

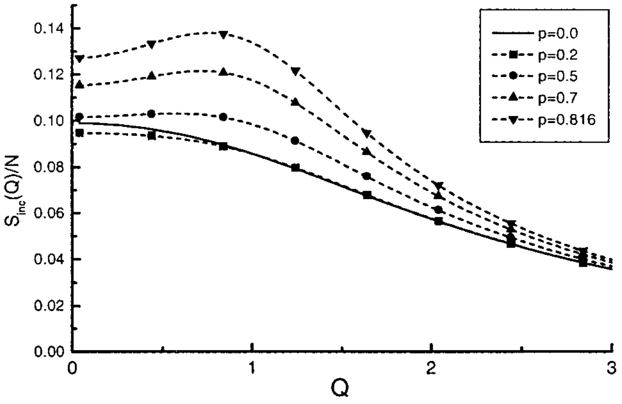

**Figure 14.** Plot of $S_{inc}(\mathbf{q},p)/N$ at various degrees of reaction, $p$, for the branched two component system with parameters $m_A = 3$, $\phi_A = 0.7$, and $\eta_A = 0.2$.

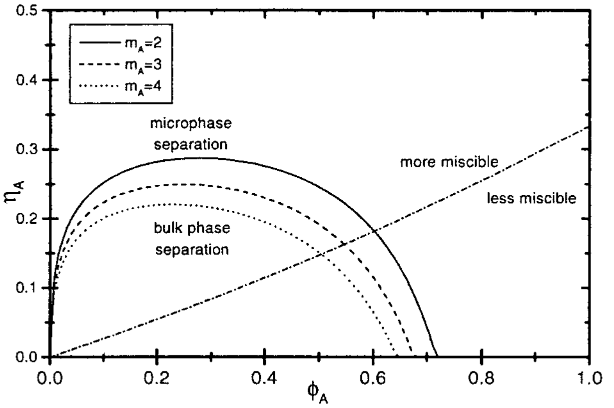

**Figure 15.** Showing the approximate boundaries between the reaction mixture at $p = 0.55$ being susceptible to bulk/microphase separation and the mixture being more/less miscible than the initial system.

## 6. Conclusions

In this paper we have developed a systematic method of applying the random phase approximation to reacting

Markov chains. We carried the calculation through for a simple two-component system and showed that predictions could be made for the miscibility of the system as a function of the degree of reaction. These predictions were consistent with the results of Elwell et al.,[1] showing that phase separation may occur at early stages of reaction. However, not all systems become less miscible as the reaction proceeds. In fact, at the earliest stages of reaction all our model systems became more miscible in terms of the Flory $\chi$ parameter. Some semiquantitative predictions were made for the nature of any transition at different stages of the reaction. In the last section we showed that the theory could be extended to include more complicated reacting species, such as those containing branch points.

There are many further Markov chain systems to which the theory could be applied, each characterized by different reacting species. More work is required on the phase behavior as a function of the system parameters and the point of the reaction at which phase separation occurs. Finally, no mention has been made of the effect of the chain dynamics on the phase separation and subsequent reaction. The latter point will be complicated by the fact the reaction continues to proceed as the phase separation occurs, so that the free energy functional is continually modified with time and the chain dynamics also change. Furthermore, there may be some coupling between fluctuations in composition and the reaction probabilities, so that the Markov chain theory may have to be modified. In view of these difficulties, the simplest quantitative test of this theory may involve avoiding the phase separation altogether (e.g., by reacting hydrogenated and deuterated blocks of the same basic chemistry) and measuring the scattering functions. Confirmation of the predicted trends in phase separation with system parameters would also be very welcome.

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## A. Derivation of Structure Factors for Arbitrary Architecture

In this Appendix we present in full the method for calculating the structure factors of polymers of complex form, subject to certain assumptions about their nature. The method is similar to that used by Benoit and Hadziioannou[7] for calculating structure factors of comblike, starlike, and multiblock copolymers. We shall describe the calculation of $s_0^{\mathrm{AA}}$,

$$s_0^{\mathrm{AA}} = \frac{v_0}{\Omega}\sum_{\substack{\alpha,l\\ a',l'}} y_l^{\ \alpha} y_{l'}^{\ \alpha'} \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_l^{\ \alpha} - \mathbf{r}_{l'}^{\ \alpha'}))\rangle_0 \tag{59}$$

The extension to $s_0^{\mathrm{AB}}$ and $s_0^{\mathrm{BB}}$ is then obvious.

The first simplification to be made is that each polymer chain in the system is independent in the absence of interactions. This means that the contribution to $s_0^{\mathrm{AA}}$ from nonidentical chains ($\alpha \neq \alpha'$) is zero. Equation 59 becomes

$$s_0^{\mathrm{AA}} = \frac{v_0}{\Omega}\sum_{\alpha} s_\alpha^{\mathrm{AA}} \tag{60}$$

where $s_\alpha^{\mathrm{AA}}$ is the contribution to $s_0^{\mathrm{AA}}$ from the chain $\alpha$;

$$s_\alpha^{\mathrm{AA}} = \sum_{l,l'} y_l^{\ \alpha} y_{l'}^{\ \alpha} \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_{l'}^{\ \alpha} - \mathbf{r}_l^{\ \alpha}))\rangle_0 \tag{61}$$

To proceed, we replace the double sum over monomers $l$ in (61) by a sum over *blocks*, $\gamma$.

$$s_\alpha^{\mathrm{AA}} = \sum_{\substack{\text{blocks}\\ \gamma,\gamma'}} s_{\gamma\gamma'}^{\mathrm{AA}} \tag{62}$$

where $s_{\gamma\gamma'}^{\mathrm{AA}}$ is the contribution to $s_\alpha^{\mathrm{AA}}$ from a pair of blocks ($\gamma$, $\gamma'$).

Consider the case where the two blocks are different, $\gamma \neq \gamma'$. Figure 2 shows two blocks, labeled 1 and 2, which are separated by a number of other blocks (labeled $\gamma$ = a, b, c, ..., etc.). The end-to-end vector of block $\gamma$ is $\mathbf{h}_\gamma^\alpha$ and the position of monomer $l$ on block $\gamma$ is $\mathbf{r}_{\gamma,l}^\alpha$. Thus, the end monomers of blocks 1 and 2 are $\mathbf{r}_{1,0}^\alpha$ and $\mathbf{r}_{2,0}^\alpha$ respectively. The contribution to $s_\alpha^{\mathrm{AA}}$ from these two blocks is

$$\begin{aligned} s_{12}^{\mathrm{AA}} &= \sum_{\substack{\text{monomers } l\\ \text{in block 1.}\\ \text{monomers } l'\\ \text{in block 2}}} y_{1,l}^\alpha y_{2,l'}^\alpha \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_{2,l'}^\alpha - \mathbf{r}_{1,l}^\alpha))\rangle_0 \\ &= \sum_{l,l'} y_{1,l}^\alpha y_{2,l'}^\alpha \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_{2,l'}^\alpha - \mathbf{r}_{2,0}^\alpha)) \times \\ &\qquad [\prod_{\gamma=\mathrm{a,b,\ldots}} \exp(i\mathbf{q}\cdot\mathbf{h}_\gamma^\alpha)] \exp(i\mathbf{q}\cdot(\mathbf{r}_{1,0}^\alpha - \mathbf{r}_{1,l}^\alpha))\rangle_0 \end{aligned} \tag{63}$$

To proceed further, it is vital that there is no correlation between the internal configurations of any two blocks. For example, this method will not work if a rodlike polymer is divided in two, because there is a correlation in the orientation of each half-rod. The method also breaks down in cases where topological interactions affect the overall chain structure, for example, if there are “rings” present in the polymer. Other than these restrictions, the choice of blocks is quite arbitrary. The configuration of each block is then independent under $\langle ...\rangle_0$; so the above expression factorizes and can be written in a straightforward manner:

$$s_{12}^{\mathrm{AA}} = H_1^{\mathrm{A}} H_2^{\mathrm{A}} \prod_{\gamma=\mathrm{a,b,\ldots}} G_\gamma \tag{64}$$

where we have defined the following quantities for *each block* in the chain.

$$G_\gamma = \langle \exp(i\mathbf{q}\cdot\mathbf{h}_\gamma^\alpha)\rangle_0 \tag{65}$$

$$H_\gamma^{\mathrm{A}} = \sum_{\substack{l\\ (\text{block } \gamma)}} y_{\gamma,l}^\alpha \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_{\gamma,l}^\alpha - \mathbf{r}_{\gamma,0}^\alpha))\rangle_0 \tag{66}$$

These are the propagator and coterm defined in eqs 10 and 11. Each term in the single chain structure factor (62) involving separate blocks ($\gamma \neq \gamma'$) can be written as a product of the coterms for the two blocks, and the propagators for the blocks in between.

The same-block terms with $\gamma = \gamma'$ in eq 62 are all of form

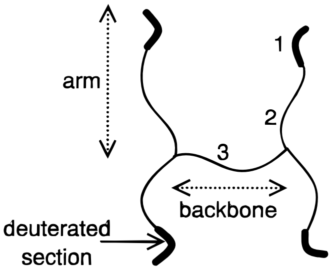

**Figure 16.** Gaussian "H-polymer" with deuterated arm ends.

$$s_{\gamma\gamma}^{\mathrm{AA}} = J_{\gamma}^{\mathrm{AA}} = \sum_{\substack{l,l' \\ \text{in block } \gamma}} y_{\gamma,l}^{\alpha} y_{\gamma,l'}^{\alpha} \langle \exp(i\mathbf{q}\cdot(\mathbf{r}_{\gamma,l'}^{\alpha} - \mathbf{r}_{\gamma,l}^{\alpha}))\rangle_0 \quad (67)$$

We shall call $J_{\gamma}^{\mathrm{AA}}$ the "self-term" for block $\gamma$.

This technique is extremely useful because the propagator, coterm, and self-term for a given block type (e.g., "Gaussian coil" or "rod") need only be calculated once. It then becomes straightforward to obtain structure factors for polymers containing any arrangement of such blocks. The procedure is best clarified by example. We shall now derive the structure factor for an example molecule using this simple method.

### B. Structure Factors of a Gaussian H-Polymer

We now calculate the expected scattering properties of an incompressible blend of H-shaped polymers such as the one shown in Figure 16. The end of each arm of the H-polymer is deuterated (A monomers), and the rest of the chain is undeuterated (B monomers). We thus divide the chain into blocks as follows. The deuterated ends are blocks of type 1, with polymerization index $N_1$. The undeuterated sections of arm are blocks of type 2, with polymerization index $N_2$. Finally, the backbone is a block of type 3, with polymerization $N_3$.

First is necessary to calculate the propagator, coterm, and self-term for a Gaussian block. Consider a block that is a Gaussian coil of monomer step-length $b$ and molecular weight $M$. The calculation is done using the standard method for calculation of structure factors.[14] We define a normalized wavevector $Q_M$ such that ${Q_M}^2 = q^2b^2M/6$. The sums over monomers in eqs 11 and 12 are replaced by integrals. It is convenient to factorize out the molecular weight prefactors, so we write

$$\begin{aligned} G_{\mathrm{coil}} &= \exp(-{Q_M}^2) \\ H_{\mathrm{coil}} &= M h_{\mathrm{coil}}({Q_M}^2) \qquad (68) \\ J_{\mathrm{coil}} &= M^2 j_{\mathrm{coil}}(-{Q_M}^2) \end{aligned}$$

where

$$h_{\mathrm{coil}}(Q_M^2) = \frac{1}{M}\int_0^M \exp\left(-\frac{q^2b^2l}{6}\right)\mathrm{d}l = \frac{1}{{Q_M}^2}(1 - \exp(-{Q_M}^2)) \quad (69)$$

and

$$j_{\mathrm{coil}}(Q_M^2) = \frac{1}{M^2}\int\int_0^M \exp\left(-\frac{q^2b^2|l-l'|}{6}\right)\mathrm{d}l\,\mathrm{d}l' = \frac{2}{{Q_M}^4}(\exp(-{Q_M}^2) - 1 + {Q_M}^2) \quad (70)$$

$j_{\mathrm{coil}}$ is the Debye structure factor for a Gaussian polymer chain. In the above expressions, $M$ may be replaced by the relevant molecular weight to give the propagator, coterm, and self-term for each block.

$s_{\alpha}^{\mathrm{AA}}$ is calculated as follows. Each deuterated section has a self-interaction term $J_1$ and interacts with the other three via the propagators of the undeuterated chain. We thus find

$$s_{\alpha}^{\mathrm{AA}} = 4\{J_1 + {H_1}^2 \times {G_2}^2(1 + 2G_3)\} \quad (71)$$

We shall not expand this expression further, but simply note that the propagators, self-terms, and coterms are all of the Gaussian chain form. The notation in terms of the propagators, coterms, and self-terms provides a convenient shorthand. $s_{\alpha}^{\mathrm{AB}}$ and $s_{\alpha}^{\mathrm{BB}}$ are calculated in an identical fashion. These are

$$\begin{aligned} s_{\alpha}^{\mathrm{AB}} &= 4H_1\{H_2(1 + G_2 + 2G_2G_3) + H_3G_2\} \\ s_{\alpha}^{\mathrm{BB}} &= 4J_2 + J_3 + 4{H_2}^2(1 + 2G_3) + 8H_2H_3 \quad (72) \end{aligned}$$

Particular care is required when deciding on the numerical prefactors of coterm combinations. In $s_{\alpha}^{\mathrm{AB}}$, the double sum over blocks includes one sum over all A blocks and one sum over all B blocks. Each block pair is counted only once. For example, the contribution from the 1−3 pairs is $4H_1H_3G_2$, i.e., counting one for each pair. In $s_{\alpha}^{\mathrm{BB}}$, the double sum is a sum twice over all B blocks. Each block pair is counted twice; so the contribution from the 2−3 pairs is $8H_2H_3$.

These results may be substituted into eq 5 to obtain the expected structure factor for an incompressible blend of H-polymers such as the one in Figure 16.

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