# Scattering Properties of Rod−Coil and Once-Broken Rod Block Copolymers

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ABSTRACT: Static and dynamic scattering properties of (a−b) diblock copolymer chains having different architectures are discussed in the framework of the random phase approximation (RPA). The case of a symmetric diblock (50/50) in a solvent satisfying the zero average contrast condition, in the semidilute regime, is considered in detail. We, in particular, calculate the scattering intensity and the relaxation times of linear rod−coil and once-broken rod copolymer chains and compare the results to those already known for classical linear diblock copolymers and to more recent results on ring diblock systems. Both static and dynamic scattering properties show that the microphase separation (MST) occurs for the symmetrical case at ($\chi\Phi N$, $q_mR_{gt}$) = (17.7, 2.9), (8.5, 2.2), and (8.2, 2.5) for ring coil−coil, linear rod−coil, and once-broken rod diblocks, respectively. These results are compared with those for linear diblock copolymers where the MST occurs at (10.5, 2).

## I. Introduction

There has recently been much interest in diblock copolymer systems (a−b) both in solution and in the melt. Most of the published work has focused on the transition from the disordered to ordered phases (microphase separation) leading to the formation of lamellae, hexagonal cylinders, cubic arrays of spheres, gyroid, etc. These morphologies depend on the total degree of polymerization ($N = N_a + N_b$), the Flory−Huggins $\chi_{ab}$ parameter (quantifying the incompatibility between the blocks), and the volume fraction of the a-block, $x$.[1] Thermodynamic interactions—an unfavorable enthalpy of mixing (positive) and a small entropy of mixing—lead to the frustration of the block copolymer chains. This frustration induces the microphase separation, self-assembly, and often fascinating microstructures on length scales of 10−100 nm.

It is of great interest and a challenging task to find new materials that could allow the control of these nanoscale morphologies. One possibility is to take advantage of the self-assembly process in block copolymers and design new architectures with blocks of different morphologies. This can be achieved for instance by designing new diblock copolymers where (i) both blocks are flexible and linked to form ring diblock copolymers, (ii) one block is rigid and the other is flexible to form rod−coil diblock copolymers, and (iii) both blocks are rigid to form so-called once-broken rod diblock copolymers. Figure 1 gives the schematic representation of these different diblock copolymer architectures.

The case where the extremities of the two blocks are flexible and linked to form a ring diblock copolymer has already been studied theoretically.[2] Experimental investigations using small-angle neutron scattering (SANS) are now being conducted to verify the main prediction of this theory—a transition from the disordered to an ordered phase (microphase separation) at ($\chi\Phi N$, $q_mR_{gt}$)

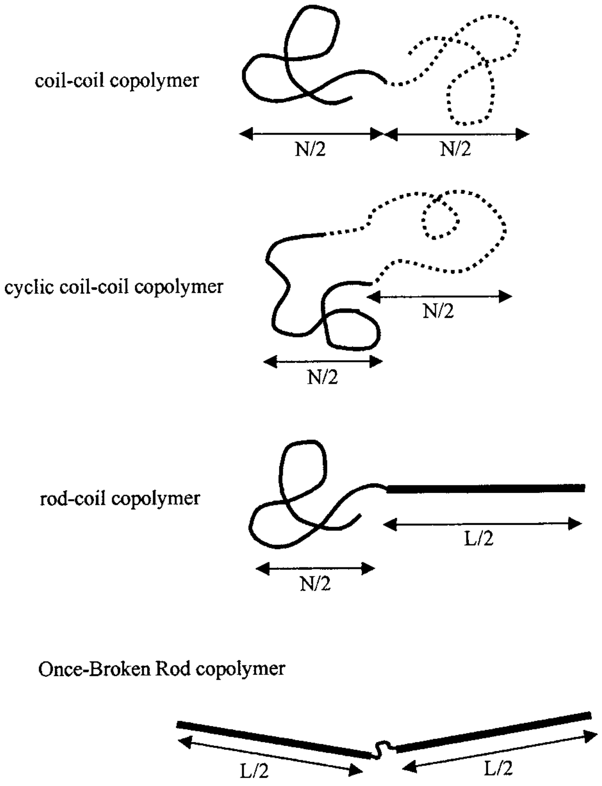

**Figure 1.** Schematic representation of different architecture diblock copolymers.

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= (17.7, 2.9) for a 50/50 diblock copolymer as compared to the classical result for linear diblocks for which ($\chi\Phi N$, $q_{\mathrm{m}}R_{\mathrm{gt}}$) = (10.5, 2.).

The self-assembly process in rod–coil diblock copolymers is controlled not only by the microphase separation of the blocks but also by the tendency of the rigid segments to form anisotropic liquid-crystalline domains. This competition between the flexibility of one block and the rigidity of the other can lead to morphologies that are distinctly different from those commonly observed in classical coil–coil diblock copolymers.[3,4] The stiffness asymmetry in rod–coil diblocks results in an increase of the Flory–Huggins $\chi$-parameter over that of coil–coil diblock copolymers as has been shown experimentally.[3,4] An important consequence of this enhancement is that rod–coil diblock systems self-assemble into microphase separation structures at relatively small degrees of polymerization ($N$)[5] and therefore at length scales that are not attainable with traditional coil–coil diblock copolymers. In this respect, microphase separation results typically in morphologies with domain sizes between 10 and 100 nm in coil–coil diblock copolymers and a few nanometers for rod–coil diblock oligomers.

The case of diblock copolymers made of two rigid segments (the once-broken diblock rod) where the two rods can, in addition, be chemically different has never been investigated either experimentally or theoretically. The only analogous system that has been studied to date is an a–b–a triblock made of poly($\gamma$-benzyl-L-glutamate) (PBLG) as the rigid a-block and poly(isoprene) (PI) as the flexible b-component.[6] In that work, the synthesis of the triblock (PBLG)–(PI)–(PBLG) has been described, and the results obtained from viscosity and circular dichroism data are in good agreement with the once-broken rod viscosity model.[7]

In this article, we focus primarily on diblock copolymers having different architectures that may lead to interesting nanoscale structures. We, in particular, calculate the scattering intensity and the relaxation times of linear rod–coil and once-broken rod copolymers using the RPA. The calculations have been carried out, for the sake of simplicity, for the cases of symmetric diblocks (50/50) in a solvent satisfying the zero average contrast condition (ZAC). We show that the static and the dynamic properties and, a fortiori, the morphologies in the ordered phases are very sensitive to the intrinsic rigidity of the blocks (rod–coil or once-broken rod). These calculations are compared to the well-known results for linear and ring coil–coil diblock copolymer systems.[2,8]

## II. Theoretical Background

The general formalism using the RPA for the static and the dynamic scattering functions for multicomponent systems was developed by Benoît, Akcasu, and Benmouna.[9] Particular attention has been given to the dynamic properties of ternary mixtures consisting of two homopolymers and a solvent and to linear diblock copolymers in solution.[10] Experimental investigations using quasi-elastic light scattering and neutron spin echo have been carried out on homopolymer mixtures in solution[11] and on linear diblock copolymer systems.[8,12] Most of the experimental results are in good agreement with theoretical RPA predictions on the structure and the dynamics of block copolymers.

In the present work, we extend the developed formalism to the case of rod–coil and once-broken rod diblock copolymer systems in solution and in the melt. The mean-field model presented in this paper is valid for any diblock copolymer chain (any block composition). We discuss mainly the symmetrical case (50/50 composition of the blocks) where the relations are relatively simple and the effects of architecture are more pronounced.

**II.1. Elastic Scattering.** In diblock copolymer systems, the partial structure factors $S_{ij}(q)$ are calculated in the framework of the RPA, introduced by de Gennes.[13] These partial structure factors are expressed in terms of the "bare" or intramolecular structure factors $S^0_{ij}(q)$ of a single chain (without intermolecular interactions):[14,15]

$$S_{aa}(q) = [S^0_{aa}(q) + \nu_{bb}\Delta S^0(q)]/[1 + \nu_{aa}S^0_{aa}(q) + \nu_{bb}S^0_{bb}(q) + 2\nu_{ab}S^0_{ab}(q) + (\nu_{aa}\nu_{bb} - \nu^2_{ab})\Delta S^0(q)] \quad (1)$$

$$S_{aa}(q) = S_{ba}(q) = [S^0_{ab}(q) - \nu_{ab}\Delta S^0(q)]/[1 + \nu_{aa}S^0_{aa}(q) + \nu_{bb}S^0_{bb}(q) + 2\nu_{ab}S^0_{ab}(q) + (\nu_{aa}\nu_{bb} - \nu^2_{ab})\Delta S^0(q)] \quad (2)$$

where

$$\Delta S^0(q) = S^0_{aa}(q)\, S^0_{bb}(q) - S^{0\ 2}_{ab}(q) \quad (3)$$

$v_{ij}$ ($i$, $j$ = $a$, $b$) are the excluded volume parameters between monomers of type a and b. The "bare" structure factors for diblock copolymer a–b with $N_a$ and $N_b$ degrees of polymerization at the total polymer volume fraction $\Phi = n(N_a + N_b) = nN$ ($n$ = total number of chains with a degree of polymerization $N$) may be written as follows:

$$S^0_{aa}(q) = \Phi(N_a + N_b)P_a(x,q) \quad (4)$$

$$S^0_{bb}(q) = \Phi(N_a + N_b)P_b(1 - x,q) \quad (5)$$

$$S^0_{ab}(q) = S^0_{ba}(q) = \Phi(N_a + N_b)P_{ab}(x,q) \quad (6)$$

where $P_a(x,q)$, $P_b(1 - x,q)$, and $P_{ab}(x,q)$ are the intramolecular form factors for blocks a and b and the intramolecular interference form factor between blocks a and b, respectively. For an ideal copolymer chain, these form factors can be represented by the modified Debye function:

$$P_a(x,q) = \frac{2}{u^4}(\mathrm{e}^{-xu^2} + xu^2 - 1) \quad (7)$$

$$P_b(1 - x,q) = \frac{2}{u^4}(\mathrm{e}^{-(1-x)u^2} + (1 - x)u^2 - 1) \quad (8)$$

$$P_{ab}(x,q) = \left(\frac{1}{2}\right)[P_a(1,q) - P_a(x,q) - P_b(1 - x,q)] \quad (9)$$

where $x$ is the composition of species a within the a–b ($x = N_a/(N_a + N_b)$) copolymer chain and $u = qR_{\mathrm{gt}}$; $R_{\mathrm{gt}}$ is the radius of gyration of the whole diblock copolymer chain and $q = (4\pi/\lambda)\sin(\theta/2)$ is the wavevector with $\lambda$ the wavelength of the scattering radiation and $\theta$ the scattering angle.

We consider the relatively simple case of a diblock copolymer chain in which the two blocks a and b have the same degree of polymerization ($N_a = N_b = N/2$), the same radius of gyration $R_{ga} = R_{gb} = R_g$, the same excluded volume parameter $v_{aa} = v_{bb} = v$, and a slight incompatibility ($\chi \neq 0$) introduced through the interaction parameter $\chi = v_{ab} - v$.

In the framework of the RPA, one can easily generalize the results obtained for linear coil–coil diblocks, given by[16]

$$\frac{I(q)}{\Phi N} = \left(\frac{a_0 - b_0}{2}\right)^2 \frac{[P_{\text{half}}(q) - P_t(q)]}{1 - \left(\frac{\chi \Phi N}{2}\right)[P_{\text{half}}(q) - P_{\text{t}}(q)]} + \left(\frac{a_0 + b_0}{2} - s\right)^2 \frac{P_t(q)}{1 + \left(\nu + \frac{\chi}{2}\right)\Phi N P_{\text{t}}(q)} \tag{10}$$

to other diblock copolymer morphologies. In eq 10, $a_0$, $b_0$, and $s$ are respectively the scattering lengths for each monomer and the solvent in the case of neutron scattering and can be related to the indices of refraction of the monomers and solvent in the light scattering case. The only difference between the different copolymer systems is in the inherent form factors $P_t(q)$ and $P_{\text{half}}(q)$. These quantities are, of course, sensitive to the chain architecture and reflect the entropic interactions of its monomers. The total form factor $P_t(q)$ is

$$P_t(q) = \left(\frac{1}{4}\right) [P_{\text{half}}(q,\text{block}_a) + P_{\text{half}}(q,\text{block}_b) + 2P_{ab}(q)] \tag{11}$$

where $P_{\text{half}}(q,\text{block}_a)$, $P_{\text{half}}(q,\text{block}_b)$, and $P_{ab}(q)$ are the form factors of block a, block b, and the intramolecular interference between blocks a and b, respectively.

Equation 10 is comprised of two terms with different physical interpretations. The scattering due the local composition is completely decoupled from that due to the total concentration fluctuations of the polymer in the solvent. Consequently, one can directly access each of these terms in scattering experiments by properly choosing the parameters $a$, $b$, and $s$. Obviously, the composition fluctuations are of more interest in these systems and can be directly measured under zero average contrast conditions (ZAC),[9,15] that is, when $(a_0 + b_0)/2 = s$. In this case, eq 10 reduces to

$$\frac{I_{\text{ZAC}}(q)}{\Phi N} = \left(\frac{a_0 - b_0}{2}\right)^2 \frac{P_{\text{half}}(q) - P_t(q)}{1 - \left(\frac{\chi \Phi N}{2}\right)[P_{\text{half}}(q) - P_{\text{t}}(q)]} \tag{12}$$

Equation 12 applies to any symmetrical diblock copolymer in which both blocks have the same form factors. This is the case for the linear coil–coil, ring coil–coil, and once-broken rod systems. For these three systems, we need only to substitute the form factor of one block $P_{\text{block},a}(q) = P_{\text{block},b}(q) = P_{\text{half}}(q)$ and the total form factor $P_{\text{t}}(q)$ for the whole diblock into eq 12. For the symmetrical rod–coil system, the scattering function is more complicated since $P_{\text{block},a}(q) \neq P_{\text{block},b}(q)$. This case is discussed in section IV. The first three cases are given as follows:

**(i) Linear Coil–Coil Diblock.** For the linear coil–coil diblock copolymers, we use as usual the Debye function for the form factors:

$$P_{\text{t,lin}}(q) = \frac{2}{u^4}(\mathrm{e}^{-u^2} + u^2 - 1) \tag{13}$$

$$P_{\text{half,lin}}(q) = \frac{8}{u^4}\left(\mathrm{e}^{-u^2/2} + \frac{u^2}{2} - 1\right) \tag{14}$$

where $u = qR_{\text{gt}}$ and $R_{\text{gt}}$ is the total radius of gyration of the whole block copolymer.

**(ii) Ring Coil–Coil Diblock.** For ring coil–coil copolymers, the total form factor $P_{\text{t,ring}}(q)$ is given by the Cassasa function:[17]

$$P_{\text{t,ring}}(q) = \frac{2}{u}\mathrm{e}^{-u^2/4}\int_0^{u/2} \mathrm{e}^{x^2}\,\mathrm{d}x \tag{15}$$

The calculation of the half form factor $P_{\text{half,ring}}(q)$ can be made in a similar way, leading to the following expression:[2,10f]

$$P_{\text{half,ring}}(q) = \frac{4[1 - \mathrm{e}^{-u^2/4}]}{u^2} \tag{16}$$

**(iii) Once-Broken Rod Diblock.** The total form factor for a 50/50 once-broken rod of length $L$ (each block is $L/2$ in length) was calculated by Pecora[17] and reads

$$P_{\text{rod-rod}}(q) = \frac{1}{2}\left[P_{\text{half,rod}} + \frac{1}{u\sqrt{3}}\left(\int_0^{u\sqrt{3}} \frac{\sin x}{x}\,\mathrm{d}x\right)^2\right] \tag{17}$$

with

$$P_{\text{half,rod}}(q) = \frac{2}{u\sqrt{3}}\int_0^{u\sqrt{3}} \frac{\sin x}{x}\,\mathrm{d}x - \frac{\sin^2(u\sqrt{3}/2)}{(u\sqrt{3}/2)^2} \tag{18}$$

where $u = qR_{\text{gt}} = qL/\sqrt{12}$.

**(iv) Linear Rod–Coil Diblock.** In the rod–coil copolymer case, the form factors for the blocks are different, and therefore the scattering intensity in the ZAC is calculated using relations 1–3 according to

$$I_{\text{ZAC}}(q) = S_{\text{rod,rod}}(q) + S_{\text{coil,coil}}(q) - 2S_{\text{rod,coil}}(q) \tag{19}$$

For a symmetrical diblock rod–coil ($R_{ga} = R_{gb}$), the scattering intensity reduces to

$$\frac{I_{\text{ZAC}}(q)}{\Phi N} = \left(\frac{a_0 - b_0}{2}\right)^2 \times \left\{[P_{\text{half,rod}}(q) + P_{\text{half,coil}}(q)]/2 - P_{\text{t,rod-coil}}(q) + \left(\frac{\Phi N}{4}\right)\left(\nu + \frac{\chi}{2}\right)\Delta P_{\text{rod-coil}}(q)\right\} \Big/ \left\{1 + \nu \Phi N P_{\text{t,rod-coil}}(q) - \left(\frac{\chi \Phi N}{2}\right)\left[P_{\text{rod-coil}}(q) + \left(\frac{\Phi N}{4}\right)\left(\nu + \frac{\chi}{2}\right)\Delta P_{\text{rod-coil}}(q)\right]\right\} \tag{20}$$

In eq 20,

$$P_{\text{t,rod-coil}}(q) = \frac{1}{4}[P_{\text{half,rod}}(q) + P_{\text{half,coil}}(q) + 2P_{\text{rod-coil}}(q)] \tag{21}$$

and

$$\Delta P_{\text{rod-coil}}(q) = P_{\text{rod}}(q)\,P_{\text{coil}}(q) - P^2_{\text{rod-coil}}(q) \tag{22}$$

We note that when both blocks have the same form factor, eq 20 reduces to eq 12.

The different form factors for both the half-rod and the half-coil are given by the standard formulas

$$P_{\mathrm{half,rod}_a}(q) = \frac{2}{u\sqrt{3}}\int_0^{u\sqrt{3}} \frac{\sin x}{x}\,\mathrm{d}x - \frac{\sin^2\left(\frac{u\sqrt{3}}{2}\right)}{(u\sqrt{3}/2)^2};\quad u = \frac{qL}{\sqrt{12}} \qquad (23)$$

$$P_{\mathrm{half,coil}_b}(q) = \frac{8}{u^4}\left(\mathrm{e}^{-u^2/2} + \frac{u^2}{2} - 1\right) \qquad (24)$$

After straightforward calculation, we find that the intramolecular form factor between the rod and coil blocks is given by

$$P_{\mathrm{rod-coil}}(q) = \left[\frac{1}{u'\sqrt{3}}\int_0^{u'\sqrt{3}} \frac{\sin x}{x}\,\mathrm{d}x\right]\left[\frac{1 - \mathrm{e}^{-u^2/2}}{u^2/2}\right] \qquad (25)$$

where $u' = qL/\sqrt{12}$ and $u = qR_{\mathrm{gt}}$. We note that relations 12 and 20 are also valid for the melt state with $v \to \infty$ and $\Phi = 1$.

To illustrate the static properties of diblock copolymer chains having different architectures, we have plotted in Figure 2 the normalized scattering intensity in zero average contrast conditions $I_{\mathrm{ZAC}}(q)/[\Phi N(a_0 + b_0)^2/4]$ as a function of $qR_{\mathrm{gt}}$. Curves a, b, c, and d represent respectively ring, linear, rod–coil, and once-broken rod copolymers made of noninteracting monomers of different structure (interaction parameter $\chi = 0$).

The behavior of flexible coil–coil linear and ring coil–coil copolymers has already been examined,[2] and we here simply recall the fact that the peak positions are different in the two systems. Again referring to Figure 2, we see they are at $q_{\mathrm{m}}R_{\mathrm{gt}} = 2$ for linear and at $q_{\mathrm{m}}R_{\mathrm{gt}} = 2.9$ for rings, indicating a smaller scale microphase separation in the case of the ring diblock copolymer system. Furthermore, the height of the scattering intensity is higher in the linear case than in the ring case, indicating the ring diblock is more homogeneous.

We observe that the replacement of a coil block by a rigid block changes the peak position and the height of the maximum in the scattering intensity (see curves b, c, and d). Although in the rod–coil system the expression depends on $v\Phi N$ (see eq 20), its contribution to the shape of the scattering intensity is very small (few percent). Curve c has been plotted at $v\Phi N = 10$.

On the other hand, the position of the maximum is insensitive to changes in $\chi$ or $\Phi$, but its height increases substantially with increasing $\chi$ or $\Phi$. Thus, when the quantity $\chi\Phi N$ reaches the critical value listed in Table 1, the scattering intensity diverges and the system undergoes a MST. Figure 3 shows the variation of the intensity in the zero average contrast conditions $I_{\mathrm{ZAC}}(q)/[\Phi N(a_0 + b_0)^2/4]$ as a function of $qR_{\mathrm{gt}}$ for cyclic (curve a), linear (curve b), rod–coil (curve c), and rod–rod (curve d) copolymers for $(\chi\Phi N)_{\mathrm{c}} = 8.2$, which corresponds to the conditions of MST for rod–rod copolymers. The critical values corresponding to the divergence of $I(q)(\chi\Phi N)_{\mathrm{c}}$ obtained for the linear, cyclic, and rod–coil copolymers are respectively 10.5 (known result), 17.7 (known result), and 9.5. These results confirm the enhancement of compatibility in mixtures involving cyclic polymers[19] and reveal the tendency of rod–rod and rod–coil copolymers to phase separate for smaller $(\chi\Phi N)_{\mathrm{c}}$ values than the linear coil–coil ones.

**II.1. Dynamic Structure Factors.** The dynamic properties of diblock copolymers can be studied by techniques such as dynamic light scattering (DLS) and neutron spin echo (NSE). These techniques measure the dynamic structure factor (also called the "intermediate scattering function") $S(q,t)$ of the system. For diblock copolymers this function exhibits two relaxation modes:[9,15]

$$S(q,t) = A_1(q)\mathrm{e}^{-\Gamma_1(q)t} + A_2(q)\mathrm{e}^{-\Gamma_2(q)t} \qquad (26)$$

where $A_1(q)$, $A_2(q)$ and $\Gamma_1(q)$, $\Gamma_2(q)$ are respectively the amplitudes and the frequencies of the two normal modes characterizing the dynamics of the system. The physical meaning of these modes has been determined from DLS and NSE experiments. For a symmetrical system, one of the modes is the "cooperative mode" that depends on the excluded volume parameter. The other and, from our point of view, more interesting mode is called the "internal relaxation mode". The frequency of this mode

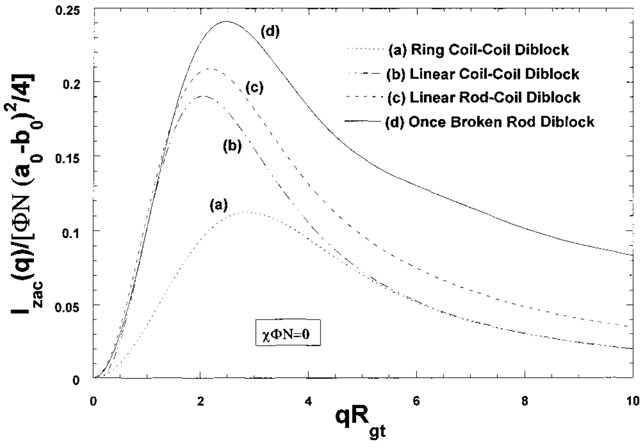

**Figure 2.** Variation of the scattered intensity as a function of $qR_{\mathrm{gt}}$ for diblock copolymers made of compatible monomers (i.e., $\chi = 0$). Curve a: ring symmetric coil–coil. Curve b: linear symmetric coil–coil. Curve c: symmetric rod–coil. Curve d: symmetric rod–rod.

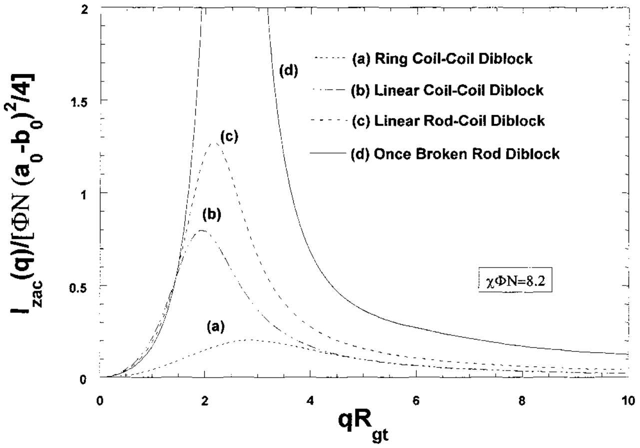

**Figure 3.** Variation of the scattered intensity as a function of $qR_{\mathrm{g}}$ for diblock copolymers made of interacting monomers at a value of the interaction parameter corresponding to the MST for rod–rod copolymers (i.e., $\chi\Phi N = 8.2$). Curve a: ring symmetric coil–coil. Curve b: linear symmetric coil–coil. Curve c: linear symmetric rod–coil. Curve d: symmetric rod–rod.

**Table 1. Values of $(X\Phi N)_{\mathrm{c}}$ and $q_{\mathrm{m}}R_{\mathrm{gt}}$ at Which the Different Block Copolymers Microphase Separate**

| | linear coil–coil | ring coil–coil | rod–coil | rod–rod |
|---|---|---|---|---|
| $(\chi\Phi N)_{\mathrm{c}}$ | 10.5 | 17.7 | 8.5 | 8.2 |
| $q_{\mathrm{m}}R_{\mathrm{gt}}$ | 2.0 | 2.9 | 2.2 | 2.5 |

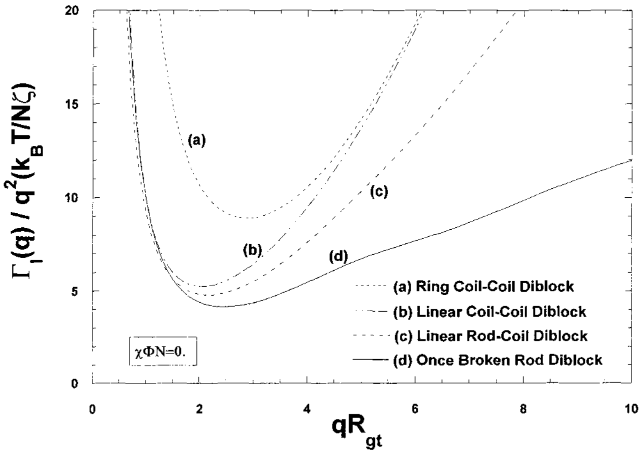

**Figure 4.** Variation of $\Gamma_I(q)/q^2(k_BT/N\xi)$ as a function of $qR_g$ at $\chi = 0$ in the Rouse model. Curve a: ring symmetric coil–coil. Curve b: linear symmetric coil–coil. Curve c: linear symmetric rod–coil. Curve d: symmetric rod–rod.

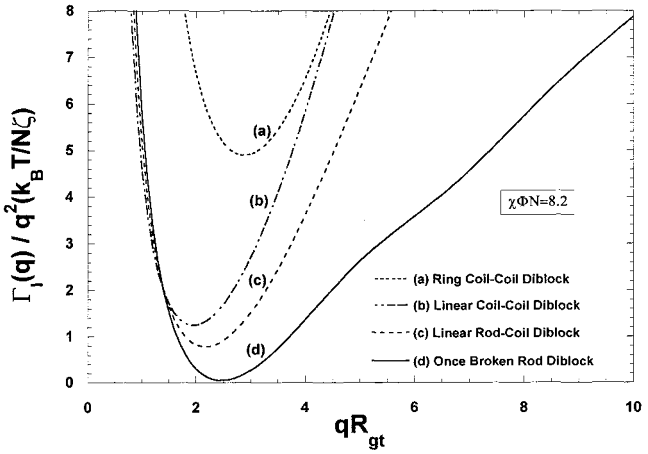

**Figure 5.** Variation of $\Gamma_I(q)/q^2(k_BT/N\xi)$ as a function of $qR_g$ at $\chi\Phi N = 8.2$ in the Rouse model. Curve a: ring symmetric coil–coil. Curve b: linear symmetric coil–coil. Curve c: linear symmetric rod–coil. Curve d: symmetric rod–rod.

depends (mainly) on the Flory $\chi$-parameter. The internal relaxation mode, often called the copolymer mode, is directly related to the microphase separation because of its dependence on the $\chi$-parameter. We denote the frequency of this mode below as $\Gamma_I(q)$. The system undergoes a phase transition from disordered to ordered when the scattering intensity diverges. At the same time the internal relaxation mode frequency goes to zero at the critical value $(\chi\Phi N)_c$ and $qR_{gt}$. In the Rouse model, where the hydrodynamic interactions are screened out, the interdiffusion frequency is given by

$$\Gamma_I(q) = q^2\left(\frac{k_B T}{N\zeta}\right)\left[\frac{1}{P_{\text{half}}(q) - P_t(q)} - \frac{\chi\Phi N P_t(q)}{2}\right] \qquad (27)$$

$k_BT$ is the Boltzmann energy, and $\zeta$ is the friction coefficient.

The same expression holds for linear, cyclic, and rod–rod diblock systems with the appropriate form factors $P(q)$ and $P_{\text{half}}(q)$ cited above.

For the rod–coil diblock copolymer, the internal relaxation mode is

$$\Gamma_{\text{I,rod-coil}}(q) = q^2\left(\frac{k_B T}{N\zeta}\right)\left[\frac{1}{I_{\text{ZAC}}(q)}\right] \qquad (28)$$

where $I_{\text{ZAC}}(q)$ is given by eq 20.

Figure 4 represents the variation of $\Gamma_I(q)/q^2(k_BT/N\zeta)$ as a function of $qR_g$ at $\chi = 0$ (compatible system). The internal relaxation frequency exhibits a minimum at $q_mR_{gt}$, which is the signature of a diblock copolymer chain. The behavior of ring coil–coil copolymer is significantly different from those of coil–coil, rod–coil, and rod–rod systems. Figure 5 represents the variation of $\Gamma_I(q)/q^2(k_BT/N\zeta)$ as a function of $qR_g$ for $\chi\Phi N = 8.2$ where the once-broken rod frequency is zero, corresponding to the microphase separation noted earlier. The critical values of $(\chi\Phi N)_c$ and $q_mR_g$ from the dynamic scattering at which the internal relaxation frequencies are identical to those corresponding to the divergence of $I_{\text{ZAC}}(q)$ that are summarized in Table 1.

The first comment that should be made from these results is that the $q_mR_{gt}$ values are significantly shifted to higher values as we proceed from linear coil–coil to rod–coil to once-broken rod and, finally, ring coil–coil copolymers. This indicates that the characteristic size defined by $q_m^{-1}$ becomes smaller as we go from linear coil–coil to rod–coil to once-broken rod and, finally, ring coil–coil copolymer chains. This result is expected from consideration of the local densities of these diblock copolymers. A second important observation is that the $(\chi\Phi N)_c$ values do not follow the same order. In fact, $(\chi\Phi N)_c$ becomes successively smaller as we go from ring coil–coil to linear coil–coil to once-broken rod and finally to rod–coil copolymer chains (Table 1). This is essentially due to the increase of incompatibility (through the Flory $\chi$-parameter) induced by the rigid block.[5]

## III. Conclusion

In this article, we have discussed the static and dynamic scattering properties of (a–b) rod–coil and once-broken rod diblock copolymers in semidilute solutions and in the melt and compared them to older results for linear coil–coil and more recent results for ring coil–coil copolymer systems. For the sake of simplicity, we have presented the results for the symmetrical case, but the formalism can be used in the general case of arbitrary composition $x$. The microphase separation for the rod–coil and the once-broken rod copolymers are found to occur at $(\chi\Phi N)_c = 8.5$ and 8.2, respectively, while those for linear and cyclic diblock copolymer chains occur at $(\chi\Phi N)_c = 10.5$ and $(\chi\Phi N)_c = 17.7$, respectively.

These results show that the diblocks containing a stiff block are less compatible than coil–coil copolymers (either linear or cyclic) and are in accord with experimental observation using microscopy techniques[3,4] on the phase-separation occurring at low degrees of polymerization for rod–coil copolymers. This MST arises mainly from the stiffness of the block that considerably increases the effective Flory $\chi$ parameter. To demonstrate whether the present mean field theory is valid for rod–coil as well as for once-broken rod and ring coil–coil architectures, it is desirable to perform scattering experiments on them. We observe also that the position of the maximum $q_mR_{gt}$ for rod–coil ($q_mR_{gt} = 2.2$) and rod–rod ($q_mR_{gt} = 2.5$) copolymers is between the one calculated for linear ($q_mR_{gt} = 2.0$) and cyclic ($q_mR_{gt} = 2.9$) diblocks. This indicates that the microstructure appears on shorter length scale for ring coil–coil, once-broken rod, and rod–coil copolymers than for linear coil–coil diblocks. These results indicate that rod–coil copolymers, which have been extensively studied,[3] are good candidates for making ordered structures at the nanoscale level.

We have also examined the relaxation of the internal relaxation fluctuation mode. As in the case of linear and cyclic coil−coil copolymers, the internal relaxation mode frequency in rod−coil and once-broken rod systems approaches a constant when $q$ approaches zero and presents a minimum at $q = q_m$. These positions of $q_m$ are the same as those obtained from the elastic scattering model.

These theoretical results can be tested by neutron or light scattering techniques with a proper choice of mixture parameters to satisfy the ZAC. In neutron scattering, one can use diblock copolymers composed of hydrogenated and deuterated polymers in a mixture of hydrogenated and deuterated good solvents. The synthesis of such diblock copolymer systems has been completed ($PS_h$−$PS_d$ for linear and cyclic block copolymers and PS−PBLG for rod−coil block copolymers) and neutron scattering experiments on them will be reported elsewhere.[20]

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