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Bridging Properties of Multiblock Copolymers

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ABSTRACT

Using self-consistent field theory, we attempt to elucidate the links between microscopically determined properties, such as the bridging fraction of chains, and mechanical properties of multiblock copolymer materials. We determine morphological aspects such as period and interfacial width and calculate the bridging fractions, and compare with experimental data.

INTRODUCTION

Block copolymers exhibit a fascinating variety of structured mesoscale phases when the different blocks are sufficiently incompatible. Most work [1] has focused on diblock copolymers A_nB_m. The chemical dissimilarity between the A and B species (quantified through the segment-segment Flory-Huggins interaction parameter, χ) produces periodic mesoscale morphologies [2-4] with symmetries determined by the overall volume fraction, f, of the A block and by the degree of immiscibility, χN, (where N=n+m is the total number of segments). The lowest degree of immiscibility ($\chi N \approx 10.5$) leading to mesoscale morphologies occurs for symmetric systems ($f \approx 0.5$ or $n \approx m$) where a lamellar structure emerges. Other equilibrium structures [2] established to date include spheres of A (B) arranged on a body-centered cubic lattice in a B (A) matrix, cylinders of A (B) arranged on a hexagonal lattice in a B (A) matrix, and bicontinuous gyroid channels.

Multiblock copolymers [$(A_nB_m)_p$ or $(A_nB_m)_pA_n$], on the other hand, have received considerably less attention, although many commercial applications requiring mechanical strength rely on these systems [5]. It has been established that the mesoscopic phases of the multiblock systems are indistinguishable from those formed by diblocks. The onset of microsegregation, i.e. the disorder-order transition, however, occurs at increasingly higher χN as the diblock unit is repeated (larger p) [6, 7, 8]. The period of the segregated structures has similarly been found to decrease with p.

The most comprehensive theoretical study of linear multiblock copolymers has been published by Matsen and Schick [9] in the many-block (p >> 1) limit using the self-consistent mean-field theory (SCFT) initially developed by Helfand [10]. Matsen and Schick theoretically established the morphological phase diagram and found that the periodicity $D \sim \chi^{1/6}N^{2/3}$ and the interfacial width $w \sim \chi^{-1/2}$ scale with the same exponents as for diblock systems. The principal feature that makes the multiblock copolymers more attractive for commercial applications is the double tethered central portion of the molecule. In contrast to diblock copolymers, this tethering allows blocks in the central portions of a multiblock copolymer to bridge their respective domains. Bridging blocks are thought to provide multiblock copolymers with superior mechanical properties, relative to their diblock analogs, as they provide a physically cross-linked network. Several theoretical studies have been directed towards predicting the bridging fraction in multiblock copolymer systems. These studies have focused on the limiting cases of the either triblock (ABA) or the many-block (p >>1) systems. In contrast we will study theoretically the intermediate systems (1 < p <10).

Although there have been quite extensive attempts to calculate morphologies and bridging fractions in triblock and many-block systems, there is still no real understanding of how morphology and bridging characteristics relate to mechanical properties of the systems. However, recently Spontak and Smith [11] published experimental results from a careful study of poly(styrene—*b*—isoprene)$_p$ (SI)$_p$ ($1 \leq p \leq 4$) multiblock copolymers. Two series were considered: (1) a constant chain mass (CCM) series, and (2) a constant block mass (CBM) series. Here, we concentrate on the CCM series where the molecular weight was kept at 120kg/mol resulting in the block weight—the weight of a SI segment—varying as M_b=120/(2p) kg/mol. Since the system is almost symmetric, a lamellar structure emerges as a result of the microphase segregation. The period of the lamellar structures was found to be in the 5 nm-18 nm regime, with the following dependence on p: $D \sim p^{-0.8}$. Further, the authors performed rheological measurements on the phase segregated system and extracted the dependence of the tensile modulus, E, and the tensile yield stress σ_y on the block repeat number, p. Unfortunately, no simple (power-law, exponential) functional relationship could be established in either of these cases, but both quantities increase dramatically as a function of p and this increase is intuitively ascribed to the increased bridging ability of the copolymer. This experimental study provides a unique opportunity for us to begin to elucidate the quite poorly understood morphology-property relationship and also to qualitatively understand how bridging of the central parts of multiblock copolymers affects elastic properties.

RESULTS AND DISCUSSION

The self-consistent field theory applied to multiblock copolymers and the technique used to calculate the bridging fractions, i.e. the number of molecules bridging a given domain has been detailed elsewhere [12] and will not be repeated. Here, it will suffice to discuss the main results.

As the experiments use equal overall mass fractions of the two polymer species, we can determine the volume fractions required by the theory using the homopolymer densities 1.00 and 0.84 g/cm^3 (from Ref. [13]) for polystyrene and polyisoprene, respectively to get f_S=0.54/p and f_I=0.46/p. These almost equal amounts of styrene and isoprene lead to a lamellar morphology throughout the study. Reliable information on the Flory-Huggins parameter χ is not available, so we elect to examine at the range χN=105, 100, 95, 90.

First, we have determined the period, D, of the equilibrium lamellar structures. We find that this quantity is virtually independent of χN. We therefore show in Fig. 1 only the results (circles) for χN_t =100. In Fig. 1, the solid line represents the functional relationship D/R_g=5.9 p$^{-0.81}$ which has been obtained as the least squares fit to the six data points. It is important to note that the radius of gyration is constant for all data points since the polymerization N_t is kept constant. This relation is exactly what was found experimentally, however here it is based on six data points rather than four as in Ref. [11]. The diblock (p=1) value D=5.8R_g is consistent with the value previously obtained by other authors [14]. In Fig. 1 we also show (diamond) the period for ABA triblock system which is intermediate to the diblock and the tetrablock. This data point is seen to fall below the curve for multiblock systems. Based on the results of Ref. [7] this is expected as that work predicts a strong dependence on the type of terminal block. This effect is expected to diminish as the number of blocks increases [15]. We finally note that taking R_g= 8.5 nm makes the agreement between theory
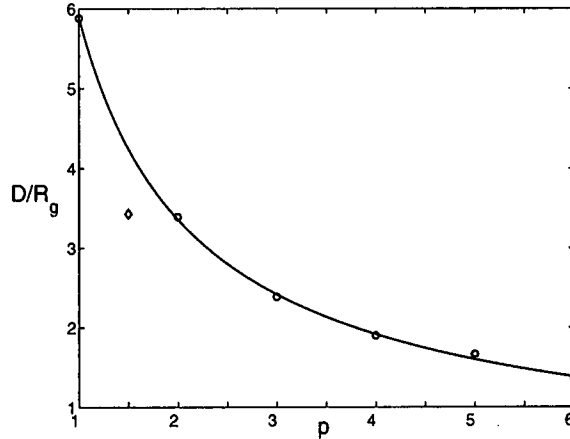
Figure 1. Lamellar period versus p for χN=100 (circles). Solid line represents the fit to $D/R_g = 5.9 p^{-0.81}$. The diamond shows the period of an N segment ABA triblock (taken from Ref. [15]).

and experiment qualitative as far as the lamellar period is concerned, and this value of the radius of gyration is consistent with independent experiments [13, 16].

A morphological feature of some importance for the mechanical properties that the experiments have not been able to extract is the interfacial width of the lamellar structures. However, in the context of the SCFT this particular feature is easy to extract. In the equilibrium configuration, the interface between an S-rich region and an I-rich region (see Fig. 2, left panel) is fitted with a functional form [14] from which the interfacial width w is found.
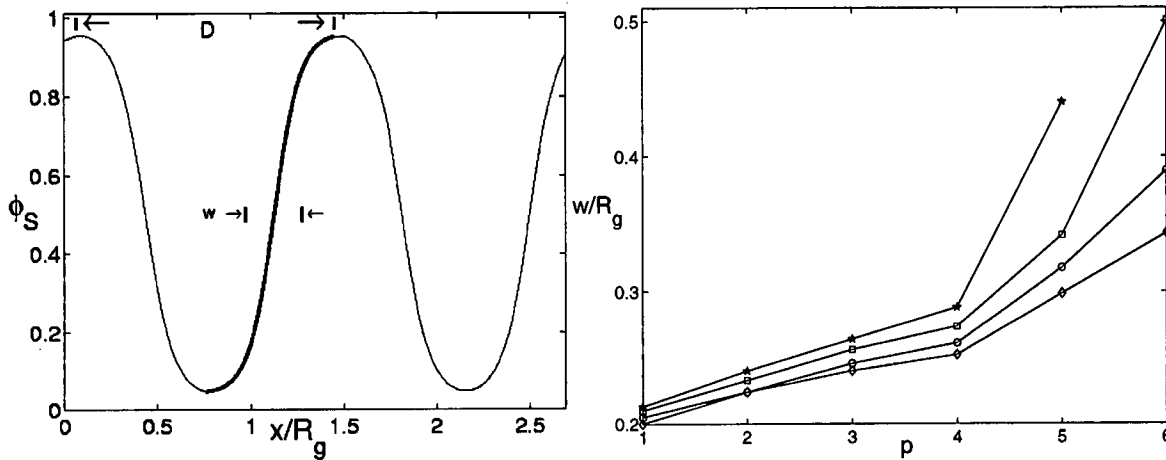
Figure 2. Left: Profile of S-monomers in the lamellar phase for χN =100 and p=4, the period of the lamellar structure D and the interfacial width w are indicated. Thick solid line shows the least squares fit to the functional form used to extract the interfacial width (for details see Ref. [12]). Right: Interfacial width w versus p for several χN's: χN =105 (diamonds), χN =100 (circles), χN =95 (squares), and χN =90 (stars). For χN =90 the p=6 point is missing as the segregation is very weak at this point.

In contrast to the period D, the interfacial width has noticeable dependence on χN . Therefore we plot, in the right panel of Fig.2, w versus p for all four different values of χN .The interfacial width is seen to depend rather strongly on p, particularly as p becomes larger than p=4. This is

mainly due to the fact that the system approaches the weak segregation limit. In this system, the disorder-order transition occurs [8] at $\chi N \approx 15$.
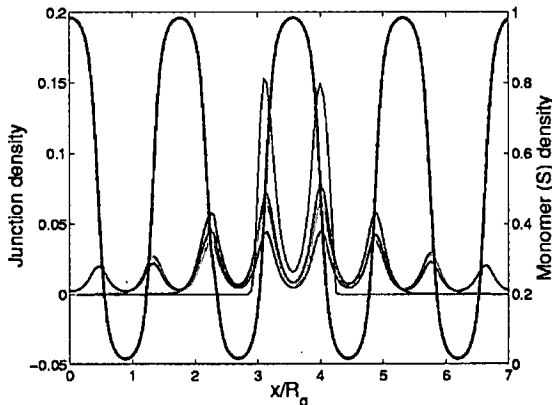
Figure 3. (Color) Illustration of the junction distribution leading to the bridging fraction determination. Thick solid line shows the S monomer density profile (right axis) in a system that has segregated into four lamellae. Thin solid line shows the distribution of the first S-I junction point related to the central lamella and blue line shows the distribution of the second junction point under the constraint that the first junction was within the central lamella. Similarly, red and green lines show the distribution of the third and fourth junctions, respectively.

Having determined that SCFT can reproduce the experimentally observed morphological features we now investigate the looping and bridging behavior of the chains in the system. First, we illustrate in Fig. 3 how the junctions between polymer species S and I are distributed within a given lamellar (the density of S monomers is shown with a thick solid line referring to the right axis). Not surprisingly the junctions tend to reside in the interfacial regions as this clearly helps minimize the free energy of the system. Figure 3 also illustrates how the bridging and looping occurs: the blue curve shows the spatial distribution of the S-I junction in the polymer chain under the constraint that the first S-I junction belongs to the central lamella. Clearly, in this particular case a little less than 50% of the chains bridge to reach the adjacent lamellae. As it has been argued before [14], based on the symmetry and the assumed diffusive character of the chains, the maximum bridging fraction for a lamellar configuration will be 50% at least in the context of SCFT. Further, the red line shows the distribution of the junctions connecting the first I-block with the second S-block. From this distribution we can extract the fraction of polymer chains that bridge an S *and* an I domain. Similarly, the green curve shows the distribution of the junction between the second I-block and the second S-block from which we can calculate the fraction of polymer chains bridging three consecutive lamellar domains.

In Table I we list the bridging fractions ($\chi N = 100$) resulting from a complete study of the behavior of SI multiblock (p=1, 2,..., 6) copolymers. The empty slots in the table indicate that the particular bridging fraction is not defined for that multiblock copolymer structure.

First, we see that the single domain bridging fraction, υ_1 is relatively insensitive to the total extent of the molecule. Although there is a sharp rise form 0.30 to 0.44 in this bridging fraction when going from tetrablock copolymers to hexablock copolymers, there is a slight decrease for the higher order systems. This decrease can be ascribed to the fact that the system becomes less strongly segregated as p is increased [15]. Further, we see that this bridging fraction has no apparent correlation to the measured mechanical properties (the tensile modulus and yield stress are listed in Table I for comparison). There is only a moderate enhancement of the mechanical properties for the hexablock in comparison to tetrablock and diblock while there is an increase in

the single domain bridging fraction υ_1. On the other hand the mechanical properties are significantly enhanced for the octablock in contrast to the slight decrease in the single domain bridging fraction.

Table I. All possible bridging fractions (subscripts denote the number of consecutive domains that is bridged by a single molecule) and measured tensile modulus E and yield stress σ_y taken from Ref. [11].

P	1	2	3	4	5	6
υ_1		0.30	0.44	0.43	0.42	0.40
υ_2		0.15	0.22	0.24	0.23	0.21
υ_3			0.16	0.19	0.20	0.18
υ_4			0.14	0.15	0.17	0.15
υ_5				0.15	0.16	0.13
υ_6				0.08	0.14	0.12
υ_7					0.09	0.11
υ_8					0.05	0.09
υ_9						0.07
υ_{10}						0.05
E [MPa]	100	100	125			
σ_y [MPa]	2.3	3.0	3.6			

From Table I it is clear that for p>2 the $(SI)_p$ molecule is able to bridge multiple domains as a large increase in υ_2 and υ_3 is seen. This ability results in a material that is physically cross-linked over relatively large distances. The increase in the multi-domain bridging correlates well with the enhancement of mechanical properties for p>2. It therefore appears that the bridging fractions describing longer range bridging behavior are more appropriate descriptors of the mechanical properties than the single domain bridging fractions. The ability of the molecules to bridge multiple domains creates a strong physical cross linking of the material, in contrast to materials with a low number p=1 or 2 of blocks where the material strength to a large degree relies on entropic interactions between molecules. However, it is worth noting that although the single domain bridging fraction is not a strong function of p the actual number, n_b, of single domain bridges per unit area of interface formed is: $n_b = 2\upsilon_1(p-1)$. That is, the actual number of bridges formed is approximately a linearly increasing function of p. Nevertheless, this is still not sufficient to account for the enhancement of the mechanical properties. While these predictions of the self-consistent field theory provide useful insight into the key features determining mechanical properties of multiblock copolymer systems, it should be stressed that these are based on equilibrium considerations alone. Non-equilibrium considerations would, however, be expected to play a role in the development of nanostructures and desirable properties of copolymer materials. In our case non equilibrium effects will most strongly affect the bridging fractions near the middle of the chain.

CONCLUSION

We have theoretically investigated the morphological and property characteristics of multiblock copolymer blends in the few (p ≤ 6) blocks limit. Using self-consistent field theory we

have found that the equilibrium period of the lamellar morphology scales as $p^{-0.8}$, in accordance with experimental findings on $(SI)_p$ i.e. styrene-isoprene, systems with $p \leq 4$. Moreover, for the first time we have investigated the single and multidomain bridging behavior of multiblock copolymers and found that significant amounts (>25%) of the polymer molecules bridge multiple domains in the phase segregated morphology. Finally, we have argued that the multidomain bridging phenomenon plays a dominant role in determining the mechanical properties of multiblock copolymer materials.

ACKNOWLEDGEMENTS

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