CHAPTER 2

Diblock Copolymer/Homopolymer Blends
2.1. Diblock copolymer/homopolymer blends with repulsive interactions

Experimental overview

Diblock copolymer/homopolymer blends became attractive subjects for experimental and theoretical investigations due to possible practical applications based on improved properties of different materials. Many publications are devoted to diblock-copolymer-homopolymer blends where the homopolymer is chemically identical to one of the diblock copolymer blocks. Depending on the concentration of the block copolymer, different morphologies, including spherical, cylindrical and lamellar are observed experimentally. It has been shown that the addition of a certain amount of homopolymer can either stabilize or destabilize already formed microdomains depending on the amount of homopolymer. Hence, adding some homopolymer, even though it is chemically identical to one of the copolymer components, can noticeably affect the resulting equilibrium structures. Depending on the homopolymer molar mass, a diblock copolymer/homopolymer mixtures can exhibit both microphase and macrophase separation.

Recently Hashimoto and co-workers [1-3] used a combination of small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) to investigate the ordered microdomain structures of a mixture of poly(styrene)-b-polyisoprene (PS-b-PI) diblock copolymer with polystyrene homopolymer (hS) as a function of the homopolymer molecular weight. They found that blends containing up to 20% of hPS maintain a well-ordered lamellar structure. In these blends, the thickness of the polystyrene microdomain increases with increasing hPS volume fraction, whereas the thickness of the PI microdomains decreases. The latter effect became less pronounced for higher molecular weight homopolymers. In the situation where the molecular weights of the PS block and the hS homopolymer were comparable, the thickness of the PI microdomain was not affected by increasing the amount of homopolymer. When the amount of homopolymer reached 35%, the lamellar morphology changed to hexagonally packed cylindrical microdomains. For the situation where the molecular weight of the hPS is smaller than the molecular weight of the PS block, it was concluded that the homopolymer chains dissolved in the PS domains. Longer homopolymer chains, but still with a molecular weight smaller than that of the corresponding PS block, preferred to be localized in the centre of the PS domains.

Winey et. al [4,5] studied the morphologies of AB/A and AB/B blends. The diblock copolymer used was again poly(styrene)-b-polyisoprene with a total molecular weight of 48700 g/mol and a polystyrene block molecular weight of 26600 g/mol. The polystyrene homopolymer molecular weights were in the range between 2600 g/mol to 36700 g/mol. As the homopolymer concentration increased (at fixed homopolymer molecular weight) the thickness of PS domains increased and the thickness of the PI domains decreased, just as observed by Hashimoto and co-workers. Increasing the homopolymer molecular weight at fixed concentration of homopolymer led to an increase in layer thickness of both PS and PI domains.
Russell and co-workers [6] used neutron reflectivity to obtain detailed information about the homopolymer distribution in ordered symmetric diblock copolymers. They used mixtures of polystyrene or poly(methyl methacrylate) (PMMA) homopolymers with symmetric PS-b-PMMA diblock copolymers. By adding perdeuterated homopolymer to unlabeled copolymer, the authors quantitatively characterized the spatial distribution of the homopolymer. They observed an almost uniform distribution of the low molecular weight homopolymer inside the corresponding domains. For molecular weights of the homopolymer that are comparable with the molecular weight of the corresponding copolymer block, the homopolymer was confined to the respective copolymer domain, with a homopolymer distribution peaked at the center of the domain.

Experiments on blends of poly(styrene)-b-poly(2-vinylpyridine) (PS-b-P2VP) block copolymer and homopolymer polystyrene, hPS, with a molecular weight that is lower than the molecular weight of the corresponding block of the block copolymer, have been reported by Matsushita and co-workers [7-9]. They used SAXS to investigate the lamellar domain spacing in this PS-b-P2VP/hPS blend. Small-angle neutron scattering (SANS) was further used to investigate the conformations of the block chains in the lamellar microdomains. The authors also concluded that homopolymers with higher molecular weight are localized in the center of the corresponding lamellae while the lower molecular weight homopolymers are distributed throughout these domains. Furthermore, the authors also investigated and compared binary PS-b-P2VP/hPS and ternary PS-b-P2VP/hPS/hP2VP blends. This comparison showed that for the same molecular weight the homopolymers in binary blends are more localized than in the ternary ones.

All the above mentioned studies focused on diblock copolymers having a lamellar morphology and considered in particular the distribution of the homopolymer species and the change in lamellar spacing as a function of the amount of homopolymer added. The experimental observations on the lamellar self-assembled state showed that the spatial distribution of the homopolymer depends strongly on its relative molar mass. Generally, for low molar masses the homopolymer will be distributed uniformly throughout the layers of the corresponding block. For a molar mass of the homopolymer that is comparable to that of the corresponding block, the homopolymer will be confined to the center of the layers, i.e. segregated in the mid-plane. A significantly higher molar mass of the homopolymer, finally, results in macrophase separation.

In Ref.10, Thomas and co-workers investigated the micellar structure of a blend of poly(styrene)-b-polybutadiene diblock copolymer and polystyrene homopolymer using SAXS and TEM. They observed a homogeneous mixture of block copolymer and homopolymer at low diblock copolymer concentrations. When the block copolymer concentration became larger than the critical micelle concentration the formation of spherical micelles with a polybutadiene core and a polystyrene corona occurred. The micelles’ coronae consist of the polystyrene block chains swollen with the homopolystyrene. Upon further increasing the block copolymer concentration, the coronae from neighboring micelles started to overlap. The authors also observed an increase in the critical micelle concentration when the molecular weight of the homopolymer decreased.

Russell and co-workers [11] investigated mixtures of PMMA homopolymers and asymmetric PMMA-b-PS diblock copolymers forming periodic, close-packed cylindrical PMMA microdomains with approximately 22nm in diameter. The authors observed
changes in both the diameter and the spacing of the cylindrical microdomains with the addition of PMMA homopolymer. From the AFM images they observed the decrease of the areal number density of cylinders from $7.3 \times 10^{10}$ cylinders/cm$^2$ for pure PMMA-$b$-PS diblock copolymers to $6.6 \times 10^{10}$ cylinders/cm$^2$ with the addition of 10% of PMMA homopolymer. The cylinder diameter of the latter mixture was about 24 nm. The authors also observed the formation of about 6 nm pores after the removal of the PMMA homopolymer from the mixture of PMMA-$b$-PS diblock with 10% PMMA. The pores were formed in the centre of the PMMA cylinders.

Finally we mention the study by Russell and co-workers [12] on mixtures of PMMA-$b$-PS diblocks and PMMA or PEO (poly(ethylene oxide)) homopolymers in thin film and bulk to compare the copolymer/homopolymer miscibility. They found that the PMMA homopolymer miscibility in thin films was enhanced compared with that in the bulk. PMMA homopolymer in thin films was more localized at the centre of the PMMA microdomains compared to the bulk. The same tendencies were observed in PMMA-$b$-PS/PEO blends, where PMMA interacts weakly favorable with PEO.

**Theoretical overview**

One of the first theoretical mean-field calculations on diblock copolymer/homopolymer blends were done by Shull and Winey [13] who used the hyperbolic tangent function given by Eq. 2.1 to model the distribution $\phi_a(x)$ of the homopolymer segments. Their results were in good agreement with the experimentally observed distribution of homopolymer in the lamellar microdomains. The profile which Shull and Winey used to describe homopolymer distribution has the form

$$\phi_a(x) = \frac{1}{2} \left[ \tanh \frac{\phi_a d_A + 2x}{w} + \tanh \frac{\phi_a d_A - 2x}{w} \right]$$  (2.1)

$\phi_a$ is the total volume fraction of homopolymer in the A-layer, $d_A$ is the A-layer thickness and $w$ characterizes the interpenetration between copolymer and homopolymer chains localized to the domain center. The analysis of Shull and Winey assumed that the homopolymer chains are fully located within the corresponding copolymer layer and that the boundaries between adjacent domains are sharp (so-called strong segregation limit). According to their analysis, the homopolymer molecular weight dependence of the copolymer profile is small for $\frac{N_b}{N_c} >> 1$ which fully agrees with previously described experimental observations. $N_b$ and $N_c$ being respectively the degree of polymerization for homopolymer and corresponding copolymer. Note, that in fact, the concepts of “wet brush” and “dry brush” were developed from these observations: in the strong segregation limit A and B blocks of lamellar AB diblock copolymers are stretched and oriented perpendicular to narrow AB-interface. At this level of segregation one can model a diblock copolymer as a brush of polymer chains, adsorbed to a non-penetrable surface. The term “wet brush” in this analogy corresponds to the situation when A(B)
homopolymer penetrates into the A(B) block domain. Likewise, the term “dry brush” reflects the situation where the homopolymer does not penetrate into the block copolymer layers but is located between the lamellar domains – the brush remains “dry”.

Shull, Mayes and Russell [14] used numerical SCFT calculations to compare experimentally and numerically obtained results for homopolymer distribution profile in PS-\textit{b}-PMMA diblock copolymer/PMMA homopolymer blends. The authors performed calculations for homopolymer molecular weights of 12 000 g/mol and 57 000 g/mol. In both cases the overall homopolymer weight fraction in the blend was about 10%. They observed that the homopolymer distribution for low molecular weight homopolymers is much broader than for high molecular weight homopolymers, which is in agreement with the theoretical predictions of Shull and Winey.

Using numerical self-consistent field theory (SCFT), Matsen [15] and Vavasour and Whitmore [16] reproduced many results of Winey et al [13]. In particular, Matsen calculated the homopolymer distribution for lamellar and hexagonal phases. He also found that while the pure diblock copolymer exhibited the spherical, cylindrical, gyroid and lamellar ordered phases, the addition of homopolymer stabilized the close-packed spherical, double-diamond and hexagonally perforated lamellar phases. It was also demonstrated than in general the minority-component microdomain can only absorb a limited amount of homopolymer before macrophase separation occurs. The phase coexistence between a diblock-rich microstructure and a homopolymer-rich disordered phase was also studied by Matsen using self-consistent field calculations. This study focused on a single slightly asymmetric diblock copolymer ($f = 0.45$) and was restricted to the consideration of the lamellar microstructure. It was found that the addition of high-weight homopolymer leads to macrophase separation between a diblock-rich lamellar microstructure and a homopolymer-rich disordered phase. This separation was ascribed to the attractive interactions between lamellar bilayers. In contrast, low molecular weight homopolymer can be added without resulting in macrophase separation; its addition gives rise to a repulsive interaction between the bilayers which leads to fully different behavior.

Likhtman and Semenov [17] theoretically investigated phase equilibria in block copolymer/homopolymer mixtures. They derived a general expression for the free energy and calculated it numerically for different microstructures: classical lamellar, hexagonal, body-centered cubic and also for bicontinuous double diamond and gyroid structures. Their calculations resulted in a phase diagram in the ($\phi$, $f$)-plane, where $f$ is the diblock copolymer composition and $\phi$ is the volume fraction of the homopolymer in the blend. The authors found that for all compositions and for all morphologies the free energy per block copolymer chain shows a minimum as a function of the homopolymer volume fraction at some $\phi = \phi_{\text{max}}$. Thus the addition of some amount of homopolymer $\phi < \phi_{\text{max}}$ always results in a free energy decrease. For $\phi > \phi_{\text{max}}$ it is energetically favorable for the system to separate into two macrophases: a block copolymer phase with $\phi = \phi_{\text{max}}$ and a pure homopolymer phase. Furthermore, Likhtman and Semenov predicted a region of stability for the double diamond and the gyroid phase in the composition range $f = 0.62 - 0.66$ for a homopolymer volume fraction $\phi \approx 0.3 - 0.4$. For $\phi < 0.3$ they found coexistence between lamellar and bicontinuous structures. In particularl they found that when the homopolymer volume fraction changed from 0 to 0.4, the structures changed as
hex $\rightarrow$ hex+BCC $\rightarrow$ BCC$\rightarrow$ BCC+homopolymer for $f = 0.8-0.9$ and hex+lam $\rightarrow$ hex $\rightarrow$ hex+homopolymer for $f = 0.66-0.73$.

Janert and Schick [18] used mean-field theory to study binary blends of homopolymer A and symmetric diblock copolymer AB. They examined the development of lamellar, hexagonal and body-centered cubic phases starting from the weak and moving towards the intermediate segregation limit as a function of the volume fraction homopolymer in the blend.

De Pablo and co-workers [19] performed a Monte Carlo simulations study to explore the behavior of a single nanoparticle and a single homopolymer chain in the cylinders of asymmetric diblock copolymers. The authors found that homopolymers that prefer the shorter blocks of the diblock are strongly localized inside the cylinders. This result is consistent with experiments of Russell and co-workers [11] who used PMMA homopolymers added to asymmetric PS-$b$-PMMA diblock copolymers with the PMMA blocks forming cylinders. They discovered that, while short neutral homopolymers segregate at the diblock interface, longer neutral homopolymers prefer the cylinders rather than the matrix.

2.2. Diblock copolymer/homopolymer blends with attractive and repulsive interactions

Diblock copolymer/homopolymer blends with homopolymers that have a specific exothermic interaction with one of the blocks of the block copolymer form a separate topic. Such blends have already been addressed in the literature, but not nearly so extensively as diblock copolymer/homopolymer blends with exclusively repulsive interactions. Experimentally copolymer/homopolymer blends with both attractive and repulsive interactions have been investigated by a small number of groups, usually involving polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) as two of the three chemically different species.

In several studies polystyrene-based block copolymers were combined with homopolymer PPO. Paul and co-workers [20,21] used styrene-butadiene-styrene triblock copolymers in combination with PPO homopolymer to investigate the degree of solubilization of PPO by differential scanning calorimetry. They varied the molecular weight of the polystyrene block from 5300g/mol to 87000g/mol and the PPO molecular weight was varied from about 24000g/mol to 39000g/mol. A dramatic increase in the degree of homopolymer solubilization was observed compared to the situation when the homopolymer was polystyrene. This was ascribed to the additional driving force provided by the exotermic mixing of PPO and PS (the corresponding Flory-Huggins parameter $\chi_{PPO-PS} \approx -0.043$). The authors observed, that mainly the molecular weight of the polystyrene block determines to which extent PPO and PS mix, whereas the molecular weight of PPO has a very small or no influence at all on PPO-PS. No macrophase separation between PPO and the block copolymer was observed, PPO was always completely dissolved in the PS microdomains [20,21].

In Ref.22 Hashimoto and co-workers reported self-assembled pattern formation in PPO/PS-$b$-PI binary mixtures with low molecular weight of PPO compared to molecular
weight of the PS block. The authors discussed several possible states of the PPO/PS-b-PI mixture. Macrophase and microphase transitions which occur in the system were found as the most important factor for the final pattern formation.

In a recent study Ten Brinke and co-workers [23,24] used PPO in combination with PS to introduce entanglements in the core of nanorods made from polystyrene-block-poly(4-vinylpyridine) (PS-b-P4VP) diblock copolymers and consisting of a PS core and a P4VP corona. Due to the perfect mixing properties of PPO and PS, PPO is distributed throughout the PS cylinders even if its molecular weight is larger than the molecular weight of the PS block. The authors showed that the addition of 17% PPO with a molar mass of 25700g/mol is enough to introduce sufficient entanglements in the PS cylinders thereby considerably improving the nanorods mechanical properties.

Theoretically blends of a diblock copolymer with a homopolymer that interacts favorably with one of the blocks of the diblock copolymer have been already addressed in several studies from a stabilization point of view.

Hellmann and co-workers [25] investigated A/AB and C/AB homopolymer/diblock copolymer blends using random phase approximation (RPA) calculations and compared it with experimental work using TEM. The C/AB blend was characterized by attractive C-A interactions and repulsive C-B and A-B interactions. In the case of A/BA blend the A-B interactions were repulsive. The authors main interest concerned the question of induced microphase separation: how strong should the C-A attraction be to lead to microphase separation avoiding macrophase separation. They concluded that even if the homopolymer chain length is larger than the total diblock copolymer chain length, C/AB blends exhibit microphase separation if the C and A species attract each other sufficiently strongly, i.e there is a critical value $\chi_{AC}$ such that for $\chi_{AC} < \chi_{AC}^{*}$ microphase will be observed irrespectively of the homopolymer chain length.

Zin and co-workers examined blends of poly(styrene)-b-polyisoprene (PS-b-PI) diblock copolymers and poly(vinylmethylether) (PVME) homopolymer both theoretically, using the modified Meier’s theory, and experimentally by SAXS, TEM and light scattering techniques. Their theoretically predicted phase diagrams show that the exothermic interactions significantly increase the dissolution of homopolymer in corresponding microdomain. These predictions were in excellent agreement with the experiments on hPVME/PS-b-PI blends, where the added PVME homopolymer was completely dissolved in the polystyrene microdomains due to the specific interaction [26].

Borukhov and Leibler [27,28] discussed the enthalpic stabilization of brush-coated particles in a polymer melt and showed how favorable enthalpic interactions can change the brush from a dry to a wet brush. The favorable interactions can stabilize such a colloidal dispersion. Of course, the essential difference between homopolymer penetration inside the grafted chains of a polymer brush compared to a block copolymer layer is the possibility of the latter to adjust the interface area per block copolymer chain.

Balsara and co-workers also investigated AB/C diblock copolymer/homopolymer blends with attractive B-C interactions. The diblock copolymer they used was a poly(ethylene)-block-polypropylene (PE-b-PP) block copolymer and the homopolymer
was polyisobutylene (PIB). PE-PIB and PE-PP interactions are unfavorable, while the PIB-PP interactions are repulsive for high temperatures, but become attractive for low temperatures. Combining theoretical and experimental investigations, they observed an order-disorder transition at approximately $150^\circ C$, and macrophase separation at about $251^\circ C$. Between $150^\circ C$ and $251^\circ C$ the blend was homogeneously mixed [29,30].

Shull and Lefebvre in [31] considered blends of an AB-diblock copolymer and A- and C-homopolymer, where C interacts favorably with B. They focused on the situation where $\chi_{AB} N = 60$, $\chi_{AC} N = 60$ and $f_B = 0.2$. $N$ is the diblock copolymer chain length and $f_B$ is the diblock copolymer composition. The pure diblock copolymer system self-assembled into a BCC(body-centered cubic) structure. Swollen micelles were obtained for homopolymer C solubilized in the spherical AB copolymer micelles. For $\chi_{BC} < 0$, the copolymer chemical potential in the swollen micelle is lower than for the unswollen micelle and thus micellization is promoted by the presence of C homopolymer. The authors interest also concerned the encapsulation of nanoparticles in the centre of the swollen micelle in the case of attraction between the surface of the particles and the homopolymer.

Even though many studies have appeared already, several questions remained open. Thus we decided to study lamellar self-assembled AB-diblock copolymer/C-homopolymer blend with favorable A-C interactions in the strong segregation limit. We focused our attention on the homopolymer distribution profiles, the maximum amount of homopolymer that will dissolve in corresponding layers and the functional dependence of the lamellar period on the amount of homopolymer present. The results of this study are presented in Chapter 4 of this manuscript and have been published as Ref. 32.
REFERENCES
