PS-b-P4VP(PDP) comb-shaped supramolecules
Zoelen, Wendy van

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A polymer is a long and usually flexible chain molecule composed of small monomeric units. Some well-known polymers are polystyrene (coffee cups), polyethylene (plastic bags), and poly(vinyl chloride) (PVC tubing), but of course there are many others, as nowadays, polymers can be tailor-made to have almost any desirable property, such as high strength, biodegradability, electrical conductivity, fluorescence, etc., and new types of polymers are synthesized on a regular basis. However, all these different polymers have one property in common: they do not mix. It is this specific property that has made research on block copolymers immensely popular among polymer scientists.

Block copolymers are created by joining together two different polymer chains, or “blocks”, by a chemical bond, sometimes vividly compared with tying the tail of a cat to that of a dog. Both animals want to get as far away from each other as possible, but can’t get any further than their body lengths. A polymer chain on the other hand is not longer than several nanometers, which is why block copolymers separate from each other in structures with nanometer length scales. Depending on the relative lengths of both blocks, different structures can be formed. If both blocks have a comparable size, then a collection of identical block copolymers will spontaneously form well ordered alternating lamellae if the block copolymer is heated above its glass transition temperature $T_g$. If one of the blocks is shorter than the other, these blocks will form hexagonally ordered cylinders or even cubically packed spheres in a matrix consisting of the other blocks. These microphase separated structures are very interesting from a nanotechnological point of view, as selectively removing the minority blocks may result in e.g. nanoporous membranes. Removing the matrix blocks may lead to nano-objects such as nanospheres and nanocylinders, which can also further be used as templates to create nano-objects of other materials. This is not only interesting for nanotechnology, but also from a fundamental point of view, as nanoscale materials may have different, unknown, properties compared to their bulk counterparts.
Furthermore, especially thin films of such well-ordered block copolymers are interesting candidates for nanotechnological applications. For example, a highly ordered hexagonal dot pattern, obtained from a thin film of ordered polymer spheres or short perpendicular cylinders may be used as a template to create an array of well-ordered dots of a ferroelectric material. The dipole moment of such a material can be switched in two directions by applying an electric field, and hence the dots can serve as bits in computer memory applications. Removing one of the blocks of a block copolymer is however not as straightforward as it may sound, as harsh reaction conditions or radiation often have to be employed to break the chemical bonds and selectively remove one of the blocks.

This thesis is devoted to block copolymers of polystyrene (PS) and poly(4-vinyl pyridine) (P4VP), abbreviated PS-\textit{b}-P4VP. Together with pentadecylphenol (PDP) they form so called comb-shaped supramolecules. As an amphiphilic chain-like molecule PDP is by far not as long as a polymer, but it displays some polymer-like behavior in terms of mixing. When combined with PS-\textit{b}-P4VP, it will be connected with the 4VP monomer units in P4VP through hydrogen bonds, resulting in a comb like structure. The total P4VP(PDP) comb will microphase separate from PS, and within the comb itself, PDP will microphase separate from P4VP in even smaller lamellar structures, resulting in structures-\textit{within}-structures.

The advantage of such systems is that after self-assembly, the only weakly hydrogen bonded PDP molecules may easily be washed away with ethanol, simplifying the formation of nano-objects and nanoporous membranes. If the PS block is relatively large compared to the P4VP(PDP) comb, nanorods can be obtained from the cylinders-\textit{within}-lamellae morphology. For a relatively large P4VP(PDP) comb, washing away PDP from the resulting lamellae-\textit{within}-cylinders morphology may result in a nanoporous membrane. Furthermore, the amount of PDP can easily be adjusted, thereby changing the relative weight fractions of the PS and P4VP(PDP) blocks, which makes it easy to tune the microphase separated morphology from spheres to cylinders and lamellae, without having to synthesize different PS-\textit{b}-P4VP block copolymers.

After a short introduction to block copolymer microphase separation in bulk, the first chapter of this thesis starts with a review on block copolymer thin films. Especially the behavior and advantages of thin films of complexed block copolymer systems such as PS-\textit{b}-P4VP(PDP) are emphasized. The first two experimental chapters, chapters 2 and 3, report on nanorods obtained from comb-shaped supramolecules in bulk. These nanorods, which have a PS core and a P4VP corona, were found to have very poor mechanical properties, due to the absence of entanglements in the PS core. The molecular weight between entanglements (\(M_e\)) of PS is
19100 g mol\(^{-1}\), and the molecular weight of the used PS block was 21400 g mol\(^{-1}\), only slightly higher, which means that the polymer chains are not entangled with each other and will easily be pulled apart when force is exerted on them. However, using such individual rods as templates for other materials would require sufficient strength to allow handling and manipulation. The problem was solved by adding poly(2,6-dimethyl-1,4-diphenylene oxide) (PPE) to the PS core. PPE is one of the few polymers that mixes very well with PS, and furthermore, it also has excellent mechanical properties. Its \(M_e\) is 4300, and the PPE that was used had a molecular weight of 25700 g mol\(^{-1}\), meaning that if enough PPE is mixed with PS, a sufficient amount of entanglements is created to improve the mechanical properties. This was the case when the weight fraction of PPE in PS was 0.27. After reinforcement the \(\sim20\) nm thick nanorods were strong enough to cross the \(\sim200\) nm wide pores of an alumina ultrafiltration membrane, something that was not possible before reinforcement.

In chapter 3, the exact distribution of the PPE chains within the PS core was further investigated. If homopolymer PS of a comparable molecular weight as the used PPE would have been mixed with the PS blocks, then these chains would be segregated in the middle of the nanorods, not very much mixed with PS, due to the fact that it is difficult to homogeneously mix a long homopolymer chain with the shorter blocks of a microphase separated block copolymer. Namely, for a homogeneous distribution, the block copolymer chains would have to stretch very much in order to accommodate the homopolymer chains, something which is energetically not favorable. However, due to the fact that the interaction between PPE and PS is even more favorable than the interaction between two PS chains, PPE was found to be distributed throughout the PS core, even though its molecular weight was higher than that of the used PS block.

The remaining chapters focus on thin films of PS-\(b\)-P4VP(PDP). In chapter 4, the behavior of thin films with a relatively high molecular weight and large PS block on silicon substrates was examined. Instead of heating to temperatures above the \(T_g\), the samples were swollen in vapors of chloroform to induce enough mobility in the samples for creating well ordered microphase separated structures. However, because chloroform is a selective solvent towards PS, swelling in chloroform effectively increased the volume of the PS blocks compared to the P4VP(PDP) combs, which could change the microphase separated structure of a lamellar thin film to cylindrical. Because of the affinity of PDP for the air interface, and of P4VP for silicon, the P4VP(PDP) comb was present on the very top of the film as well as at the silicon interface, while in between, layers of parallel
P4VP(PDP) cylinders in a PS matrix were formed. Furthermore, incommensurability of the distance between layers of cylinders and the film thickness caused quantization of the film thickness to fit an integral number of parallelly oriented cylindrical layers, resulting in terrace formation. Also, some non-common terrace formation behavior was observed in a sample that was on the boundary between a lamellar and a cylindrical morphology. In this sample, perpendicularly oriented lamellae were observed, even though PS-\(b\)-P4VP(PDP) samples normally form parallelly oriented structures. However, in all of the thin films, the morphology of the small P4VP(PDP) structures was never observed due to the relatively low P4VP(PDP) comb fraction.

In chapter 5, mainly thin films of samples with a relatively high fraction of the P4VP(PDP) comb and low molecular weight, comparable with the polymers used in chapters 2 and 3, were studied. The most remarkable result presented in this chapter was the formation of terraces-within-terraces. Terraces of the parallel PS cylinders inside a P4VP(PDP) matrix were formed during annealing in chloroform, while the smaller terraces of layered P4VP and PDP were created after drying. This means that in thin films, both the cylinders as well as the lamellae of the cylinders-within-lamellae morphology orient parallel to the surface, while in bulk samples, both structures spontaneously orient perpendicular with respect to each other. This unusual behavior is caused by the influence of the substrate and air interfaces, which is stronger than that of the PS domains. Furthermore, washing away PDP from these structures resulted in identical individual nanorods as prepared in chapter 2, however, the nanorods which were formed at the silicon surface simply remained there due to the strong interaction of P4VP with silicon. In this way, an array of a single layer of ordered nanorods could be obtained at the silicon surface.

Chapter 6 reports about the use of these ordered nanorods as well as single lamellar thin film layers as templates for the polymerization of polypyrrole, an electrically conducting polymer. Cu\(^{2+}\) ions were complexed to P4VP after which it was tried to synthesize polypyrrole using chemical oxidative polymerization of pyrrole. However, the reactant concentration turned out to be so low that reaction did not take place. Addition of a catalytical amount of bipyrrole to the solution resulted in templated polypyrrole polymerization on top of the P4VP layers.

In the final chapter, ordered nanorods were used as a template to create nanopatterned lead titanate, PbTiO\(_3\), a ferroelectric material. A layer of PbTiO\(_3\) was deposited on the nanorods at room temperature, after which the samples were heated to \(\sim 565^\circ\)C to crystallize PbTiO\(_3\). During heating, the nanorods are degraded at a temperature of \(\sim 450^\circ\)C, however, the
shape of the nanorods remarkably remained visible in the remaining PbTiO$_3$.

In conclusion, besides serving as an investigation on the behavior of PS-$b$-P4VP(PDP) comb-shaped supramolecules under several bulk and thin film conditions, the results presented in this thesis have shown how nano-objects obtained from these supramolecules can be made suitable for template applications, by either reinforcing individual nanorods or arranging them in thin films.