Polymeric Nanofibers Prepared from Self-Organized Supramolecules

K. de Moel, G. O. R. Alberda van Ekenstein, H. Nijland, E. Polushkin, and
G. ten Brinke*

*Department of Polymer Chemistry, Materials Science Center, Dutch Polymer Institute,
University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*

R. Mäki-Ontto and O. Ikkala*

*Department of Engineering Physics and Mathematics, Helsinki University of Technology,
P.O. Box 2200, FIN-02015 HUT, Espoo Finland*

A facile concept to prepare nano-objects based on self-organizing polymeric supramolecules (also called supramolecular block copolymers) is demonstrated using one particular shape, i.e., nanorods or nanofibers. Cylindrical aggregates consisting of a polystyrene (PS) core and a thin corona of poly(4-vinylpyridine) (P4VP) chains are prepared from P4VP-(pentadecylphenol)-block-PS comb-coil supramolecules. Diblock copolymers P4VP-block-PS are stoichiometrically (with respect to the number of pyridine groups) hydrogen-bonded with pentadecylphenol (PDP) amphiphiles to yield P4VP(PDP)-block-PS comb-coil supramolecules. By the selection of appropriate relative block lengths for P4VP(PDP) and PS, a micro-phase-separated cylindrical morphology of PS cylinders inside a P4VP(PDP) matrix is obtained. Subsequent removal of the amphiphiles, accounting for ca. 75% of the matrix material, results in cylinders with a core of PS and a corona of easily adjustable thickness of P4VP. The advantages of the present concept compared to the existing procedures are discussed.

Introduction

There is extensive literature that describes patterning of matter based on soft lithography, which allows the engineering of complex shapes on micro- and nanoscale levels.[1] When the dimensions approach the molecular scale, concepts based on spontaneous ordering into simple "elementary" morphologies within bulk or film materials have been pursued, e.g., lamellae, cylinders, spheres, etc. In polymers, this is allowed by self-organization,[2] which can be realized in many ways such as by the use of block copolymers[3,4] or self-organizing supramolecules,[5,6] which can render responsive and functional materials. On the other hand, individual nano-objects, e.g., carbon nanotubes,[7] can have fascinating properties which have encouraged the development of ways to prepare nano-objects of different compositions, see example.[8-19]

Self-organization of block copolymers has been used to prepare individual polymeric "nano-objects", with each concept having its specific merits and disadvantages. A general method is based on crew-cut aggregates,[8,9,11,12] where amphiphilic diblock copolymers[20] can be used, such as polystyrene-block-poly(acrylic acid) with a short hydrophilic block. The crew-cut aggregates are typically constructed by first dissolving the chains in a solvent, which dissolves both blocks, and subsequently adding water to cause controlled aggregation of the hydrophobic blocks.[8,11,12] Another option is to use a single solvent in which both blocks are soluble at high temperatures, and the aggregation of the hydrophobic block results on decreasing the temperature.[9] A particularly rich variety of polymeric nanostructures is obtainable, including nanoscale rods. However, the design principles to predict the nanostructures don't seem very straightforward because the phase behavior of strongly asymmetric block copolymer in solvents and solvent mixtures may be complicated.[11,20,21] In addition, the structures may be relatively sensitive to the details of the dissolution procedures.

Another method describes the preparation of polymeric nanofibers and nanotubes, as well as the corresponding spherical objects, based on block copolymers, which consist of photo-cross-linkable moieties.[13,15,16] In this case, a diblock or triblock copolymer is properly

* To whom correspondence should be addressed.
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selected to allow the desired morphology in bulk, for example, the hexagonal self-organization of cylinders is selected if nanofibers are to be prepared. The concept requires a photo-cross-linkable block, which allows the fixing of the structure by photo-cross-linking. Ultimately, the fibers and tubes can be "sculptured" based on selective dissolution and/or degradation. Individual fibers of diameter of ca. 40 nm are resolved and can even be redissolved in other solvents to allow liquid crystalline solutions.[15] The advantage of this concept is that the design is based on the straightforward bulk phases of block copolymers[4] instead of the more complicated solvent phases.[11,20,21] However, the requirement of specific photo-cross-linkable moieties is a limitation.

A third related concept to prepare individual nano-objects is based on poly(ethylene oxide)-block-poly-(isoprene) to render self-organization in a sol–gel process.[14] The block copolymer allows aluminosilicate to be templated into various bulk self-organized phases[22] and the preparation of the corresponding mineralization into controlled inorganic–organic bulk nanoscale structures. In the next step, the structures can be separated to render "hairy objects". In this concept, the objects are interlocked by mineralization. This concept is related to the much studied "inverse" process where inorganic–organic mesoporous materials are constructed.[23]

In this work, we introduce a novel and general concept to prepare crew-cut aggregates, with the following properties: (1) The conditions needed to fabricate the desired elementary shapes of the nano-objects can be easily predicted on the basis of straightforward bulk-phase block copolymer principles. (2) It does not need photo-cross-linkable units. However, the structures can be selected such that they can be cross-linked at the final stage, if required. (3) The thickness of the corona can be selected almost at will. (4) It does not depend on the specificities of sol–gel processes. In this paper, we illustrate the concept by the use of one particular shape, by preparing nanoscale rods or fibers.

Experimental Section

Materials. The supramolecular comb-coil diblock copolymers used are obtained by the hydrogen-bonding poly(4-vinylpyridine-block-polystyrene) (P4VP-block-PS) diblock copolymers to a stoichiometric (with respect to the number of pyridine groups) amount of 3-*n*-pentadecylphenol (PDP). The scheme for the complexation is presented in Figure 1). The P4VP-block-PS used was obtained from Polymer Source Inc. with M_w = 20 700 and 21 400 g mol⁻¹ for the P4VP and PS
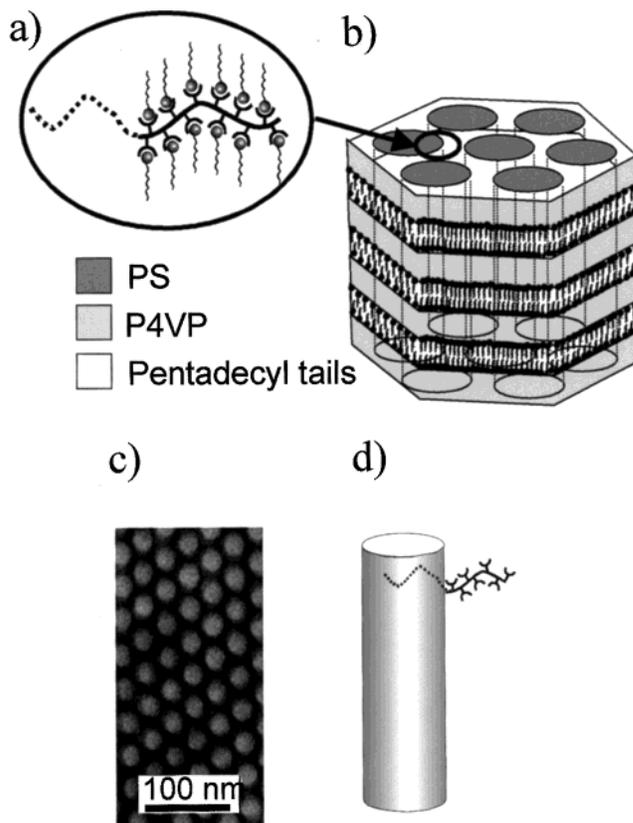

Figure 1. (a) Schematics to form the supramolecular comb-coil diblock copolymer; (b) the initial hexagonally self-organized structure before the removal of the PDP amphiphiles, as demonstrated by SAXS; (c) a transmission electron microscopy picture of the cylindrical structure of a similar supramolecular P4VP(NDP)-b-PS comb-coil diblock copolymer based on a slightly longer amphiphile nonadecylphenol (NDP);[6] (d) Scheme of a fibrillar nano-object.

blocks, respectively, and M_w/M_n = 1.13 for the complete polymer. PDP was purchased from Aldrich and was originally 98% pure. It was recrystallized twice with petroleum ether and dried at 40 °C in a vacuum for 4 days.

Sample Preparation. The P4VP(PDP)-b-PS samples were prepared by dissolving P4VP-b-PS in analysis grade chloroform. A nominally stoichiometric amount of PDP with respect to the number of pyridine groups in P4VP was added to the solution. The concentration was kept low to ensure homogeneous complex formation. Then the solvent was evaporated very slowly, and the material was vacuum-dried at 50 °C for at least 12 h. Next, 0.5 g of the material was placed in a dialysis tube (Servapor, cut M = 12 000, Serva, Heidelberg, Germany) filled with ethanol and dialyzed against ethanol for 2 weeks. After 1 week, the solvent was replaced. The residue predominantly contained PDP as demonstrated by IR (FTIR) spectroscopy. Furthermore, after 1 week, almost all of the PDP that was originally present had been washed out from the material based on FTIR. The solvent was replaced, and finally, the content of the dialysis tube was emptied on a Petri dish to allow for evaporation of ethanol. Subsequently, the washed material was dried overnight in a vacuum oven at 50 °C. FTIR spectroscopy of the washed material showed no trace of PDP remaining in the material.

Scanning Transmission Electron Microscopy. Scanning transmission electron microscopy (STEM) was performed with a JEOL 6320 field electron scanning electron microscope, equipped with a transmission detector that allowed increased contrast. For STEM, a drop of the dilute suspension was placed onto a gold grid with a carbon layer. Samples were investigated with and without staining with iodine.

Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) was performed with a Bruker NanoSTAR,

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consisting of a Kristalloflex K760-8 3.0 kW X-ray generator and a camera with cross-coupled Göbel mirrors for Cu Kα radiation ($\lambda = 1.54$ Å) resulting in a parallel beam of about 0.05 mm^2 at the sample position. A Siemens multiwire type area detector was used. The sample–detector distance was 1.08 m.

Results and Discussion

The concept of the preparation of nano-objects is illustrated in Figure 1 in the case of nanorods. The starting material is P4VP-b-PS. Different self-organized phases will be formed in bulk, depending on the relative volume fraction f of PS.[3] If a hexagonal assembly of PS cylinders within a P4VP matrix is needed, the required volume fraction of PS should be in the range of $f = 0.16$–0.32. To achieve separate nano-objects, however, in practice, it turns out to be rather difficult to separate the polystyrene "rods" using P4VP-selective solvents as such, probably because rather long P4VP-chains are required to obtain self-organizing rods with a PS core. Equally important is that there is only a very limited control over the length of the P4VP blocks, which have to be 3–5 times larger than the PS blocks.

Developments in recent years convincingly demonstrate that chainlike molecular entities, resembling in many ways normal covalently connected polymer molecules, can be also constructed using physical interactions. They are identified as polymeric supramolecules, for general references for supramolecules, see refs 24 and 25.[24,25] For example, the connection of identical repeat units by combinations of hydrogen bonds allows homopolymer-like supramolecules,[26] and a combination of two (or more) types of units allows copolymer-like supramolecules, as discussed for the comb-shaped architecture in references.[27,28] In the case of P4VP, the pyridine groups are hydrogen-bonding acceptors, sites for metal coordination, and proton acceptors. They allow nominally stoichiometric amounts (one physically bonded molecule vs one pyridine group) of side chains to physically bond to P4VP, such as pentadecyl or nonadecyl side chains by hydrogen-bonding pentadecylphenol or nonadecylphenol,[27,28] two dodecyl tails by coordinating zinc dodecyl benzene sulfonate,[29] or dodecyl tails by protonating dodecyl benzene sulfonic acid.[30] In this way, comb-shaped supramolecules are formed. Corresponding comb-coil supramolecules are obtained by using P4VP-b-PS diblock copolymers. Within the present work, it is essential that the effective molecular weight of the P4VP block be increased in a controlled manner by varying the amount and/or molecular weight of the complexing additive. This allows an easy way to tune the relative length of the P4VP block while maintaining the desired
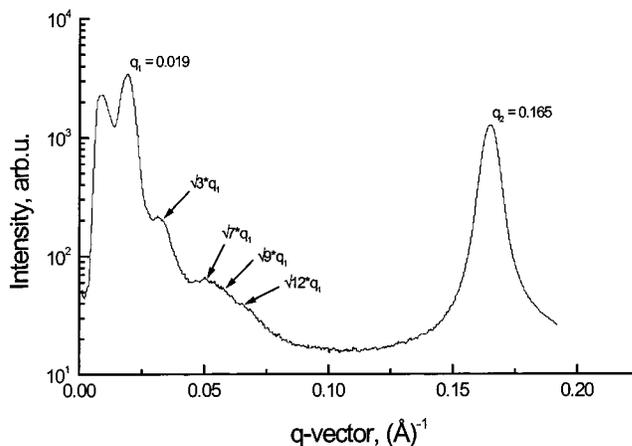
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Figure 2. SAXS pattern of P4VP(PDP)-b-PS demonstrating the cylindrical morphology. The position of the first scattering peak corresponds to $2\pi/q^* = 33$ nm. Also present is the main scattering peak of the short length scale lamellar structure of the P4VP(PDP) matrix.

morphology, e.g., PS cylinders.[31] Of no obvious importance here is the fact that the comb-shaped supramolecules, obtained by complexing P4VP with alkyl phenols, such as pentadecyl- and nonadecylphenol, also undergo self-organization,[28,29] thus leading to peculiar structure-*within*-structure hierarchies,[5,6] as shown in Figure 1. Since the side chains, such as the alkyl phenols, can be easily removed by dissolution, they play a major role in the preparation of nano-objects in the present concept.

To demonstrate the concept, PDP will be taken as complexing additive for the P4VP block of a P4VP-b-PS diblock copolymer. Furthermore, a nominally stoichiometric amount of PDP (one PDP molecule per 4-vinylpyridine group) will be used. Because we were focused on the preparation of rodlike entities, the cylindrical microdomain structure of the P4VP(PDP)-b-PS starting bulk material was first established by SAXS. Figure 2 shows the presence of the 1, $(3)^{1/2}$, $(7)^{1/2}$, and $(9)^{1/2}$ scattering peaks of the long length scale cylindrical structure (PS cylinders in a P4VP(PDP) matrix) as well as the (1, 0, 0) peak of the short length scale lamellar structure of the P4VP(PDP) matrix. The location of the (1, 0) scattering peak at $2\pi/q^* = 33$ nm corresponds to a distance of ca. 38 nm between neighboring PS cylinders. Figure 1 shows the corresponding schematic structure before the removal of the PDP molecules, showing the two levels of structures. A transmission electron micrograph demonstrating a similar hexagonal-layered structure can be found in ref 6.

Figure 3 shows a scanning transmission electron micrograph of cylinders of the P4VP-b-PS diblock copolymers with a PS core and a P4VP corona. The cylinders have diameters of 25–28 nm with lengths up to a micrometer. Besides cylindrical aggregates, spherical micelles with a similar diameter are also present. These are due to imperfections in the original cylindrical comb-coil microdomain structure and are likely to have been formed by aggregation of isolated block copolymers formed after break up of the matrix structure.

The corona can also be resolved. Figure 4 shows a STEM of a sample stained with iodine for 2.5 h. The

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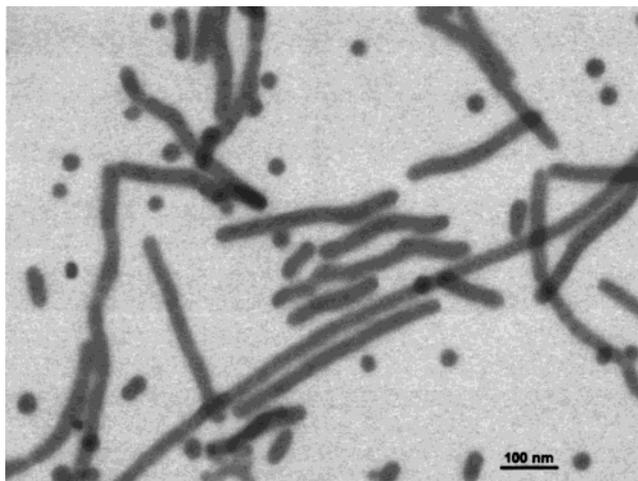**Figure 3.** STEM picture of cylindrical aggregates of P4VP-(20.7)-b-PS(21.4k) diblock copolymers.
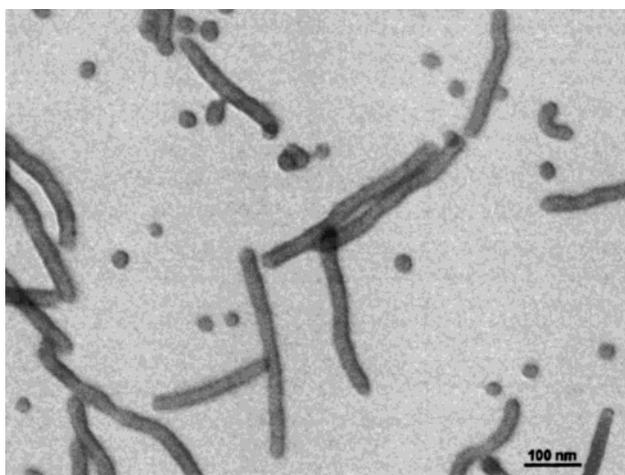

Figure 4. STEM picture of cylindrical aggregates of P4VP-(20.7)-b-PS(21.4k) diblock copolymers stained with iodine for 2.5 h.

presence of the iodine-stained P4VP is clearly visible as a contrast between the core and corona (darker), particularly in those regions where two cylinders are crossed. The thickness of the cylinders is in perfect agreement with the SAXS data (Figure 2). The position of the (1, 0) scattering peak implies a distance of ca. 38 nm between the nearest neighboring cylinders. When corrected for the presence of PDP, this amounts to a value of ca. 25 nm for the diameter of the cylinders in Figure 3. The cylinders in Figure 4 have a slightly larger diameter due to the corona being swollen by iodine.

The concept is useful not just only to extract nanofibers, as it can obviously be used also to prepare other nano-objects, such as spheres and plates when different effective values of f are selected. In addition, the only specific requirement for the templating block copolymer is that one block has to be able to form strong physical bonds to allow the formation of supramolecules. This allows to "tune" the balance f of the block copolymer by using additives that can be easily removed by solvent treatment. A practical point of view is that the additives should preferably have relatively high molecular weights to allow an efficient tuning of the effective f. Therefore, if the block copolymer contains a P4VP block, one can use many types of substituted phenols in addition to alkylphenols, and one can use, e.g., different zinc benzene sulfonates.[30] One can also replace the P4VP, e.g., by polymers containing amide groups, such as polyamides, which form strong coordination bonds with, e.g., zinc sulfonates.[32]

Concluding Remarks

We showed a concept for the preparation of individual nano-objects based on supramolecular block copolymers. This method has the considerable advantage that it combines the merits of the other two procedures used most often, i.e., the solvent processing used for crew-cut micelles and bulk processing used for photo-cross-linkable diblock copolymers. Just like ordinary block copolymer systems, the systems can be macroscopically aligned (e.g., alignment of the rods) by large amplitude oscillatory shear or electric fields (thin films!) before dissolution of the long chain amphiphiles; on dissolution of the amphiphiles, the individual nano-objects readily separate; the prediction of the shape of the nano-objects, based on well-known block copolymer principles, is straightforward; the thickness of the corona can be chosen almost at will; if required, cross-linking of either core or corona is possible at the final stage; and finally, countless many block copolymer/amphiphile pairs are possible.

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