Comb-shaped supramolecules

de Moel, C

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Chapter Seven

Polymeric nanofibers prepared from self-organized supramolecules

This chapter is submitted to Chemical Materials as: “Polymeric nanofibers prepared from self-organized supramolecules” by K. de Moel, G.O.R. Alberda van Ekenstein, H. Nijland, E. Polushkin, and G. ten Brinke, R. Mäki-Ontto and O. Ikkala

Abstract
Polymeric nanofibers, consisting of a polystyrene (PS) core and a thin corona of poly(4-vinylpyridine) (P4VP) chains, are prepared from P4VP(PDP)-block-PS comb-coil supramolecules. P4VP-PS diblock copolymers 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. Selecting appropriate relative block lengths, 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 polymeric nanofibers with a core of PS and a thin corona of P4VP.
7.1 Introduction

There is an extensive literature describing patterning of matter based on soft lithography, which allows engineering of complex shapes on micro- and nanoscale.\textsuperscript{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,\textsuperscript{2} which can be realized in many ways, such as using block copolymers\textsuperscript{3,4} or self-organizing supramolecules,\textsuperscript{5,6} which can render responsive and functional materials. On the other hand, individual nano-objects, e.g. carbon nanotubes,\textsuperscript{7} can have fascinating properties, which have encouraged developing ways to prepare nano-objects of different compositions, see e.g. ref\textsuperscript{8-19}.

Self-organization of block copolymers has been used to prepare individual polymeric “nano-objects”, each concept having their specific merits and disadvantages. A general method is based on crew-cut aggregates,\textsuperscript{8,9,11,12} where amphiphilic diblock copolymers\textsuperscript{20} can be used, such as polystyrene-\textit{block}-polyacrylic 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.\textsuperscript{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.\textsuperscript{9} A particularly rich variety of polymeric nanostructures is obtainable, including nanoscale rods. However, the design principles to predict the nanostructures seem not very straightforward, because the phase behavior of strongly asymmetric block copolymer in solvents and solvent mixtures may be complicated.\textsuperscript{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 photocrosslinkable moieties.\textsuperscript{13,15,16} In this case, a diblock or triblock copolymer is selected properly to allow the desired morphology in bulk, for example the hexagonal self-organization of cylinders if nanofibers are to be prepared. The concept requires a photocrosslinkable block, which allows fixing the structure by photocrosslinking. Ultimately, the fibers and tubes can be “sculptured”
based on selective dissolution and/or degradation. Individual fibers of diameter of ca. 40nm are resolved and can even be redissolved in other solvents to allow liquid crystalline solutions. The advantage of this concept is that the design is based on the straightforward bulk phases of block copolymers, instead of the more complicated solvent phases. However, there is a limitation that specific photocrosslinkable moieties are required.

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. The block copolymer allows to template aluminosilicate into various bulk self-organized phases and to prepare 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.

In this work, we introduce a novel and general concept to prepare crew-cut aggregates with the following properties: 1) The conditions to fabricate the desired elementary shapes of the nano-objects can easily be predicted based on the straightforward block copolymer principles. 2) It does not need photocrosslinkable 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 using one particular shape, by preparing nanoscale rods or fibers.

### 7.2 Experimental Section

#### 7.2.1 Materials

The supramolecular comb-coil diblock copolymers used are obtained by 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 P4VP-block-PS used was obtained
from Polymer Source Inc. with $M_w = 20.700$ g/mol and 21.400 g/mol for the P4VP and PS blocks and $M_w/M_n = 1.13$ for the complete polymer. PDP was purchased from Aldrich and originally 98% pure. It was twice recrystallized with petroleum ether and dried at 40°C in a vacuum for 4 days.

7.2.2 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 hrs. Next, 0.5g of the material was placed in a dialysis tube (Servapor, cut $M=12000$, Serva, Heidelberg, Germany) filled with ethanol and dialyzed against ethanol for two weeks. After one week, the solvent was replaced. The residue contained predominantly PDP, as demonstrated by infra-red (FTIR) spectroscopy. Furthermore, after one week almost all of the PDP 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 petridish 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.

7.2.3 Scanning Transmission Electron Microscopy

STEM was performed with a JEOL 6320 Field Electron Scanning Electron microscope, equipped with a transmission detector allowing 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.

7.2.4 Small Angle X-ray Scattering

SAXS was performed with a Bruker NanoSTAR, consisting of a Kristalloflex K760-8 3.0 kW X-ray generator and a camera with cross-coupled Göbel mirrors.
Fig. 7.1. Schematics to form the supramolecular comb-coil diblock copolymer: a) the initial hexagonally self-organized structure before removing the PDP amphiphiles, as demonstrated by SAXS; b) Scheme of a fibrillar nano-object.

for CuKα-radiation (\(\lambda = 1.54 \text{ Å}\)) resulting in a parallel beam of about 0.05mm\(^2\) at the sample position. A Siemens multiwire type area detector was used. The sample-detector distance was 1.08 m.

7.3 Results and Discussion

The concept to prepare nano-objects is illustrated in Fig. 7.1 for the case of nano-rods. The starting material is poly(4-vinyl pyridine)-block-poly(styrene). Different self-organized phases will be formed in bulk, depending on the relative volume fraction \(f\) of PS, as demonstrated by the closely related material poly(2-vinyl pyridine)-block-poly(styrene).\(^{24}\) If a hexagonal assembly of PS cylinders within a P4VP matrix is aimed, the required volume fraction of PS should be in the range \(f = 0.16\) to 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. Moreover, 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 chain-like molecular entities, resembling in many ways normal covalently connected polymer molecules, can be constructed also using physical interactions. They are identified as polymeric supramolecules, for general references for supramolecules, see.\(^{25,26}\) For example, connection of identical repeat units by combinations of hydrogen bonds allows homopolymer-like supramolecules,\(^{27}\) and a combination of two (or
more) types of units allows copolymer-like supramolecules, as discussed for the comb-shaped architecture in references. In the case of P4VP, the pyridine groups are hydrogen bonding acceptors, sites for metal coordination, and proton acceptors. They allow to physically bond nominally stoichiometric amounts (one physically bonded molecule vs. one pyridine group) of side chains to P4VP, such as pentadecyl side chains by hydrogen bonding pentadecylphenol (PDP), two dodecyl tails by coordinating Zinc dodecyl benzene sulphonate, or dodecyl tails by protonating dodecyl benzene sulphonic acid. In this way comb-shaped supramolecules are formed. Corresponding comb-coil supramolecules are obtained using P4VP-b-PS diblock copolymers. Within the present work, it is relevant that the effective molecular weight of the P4VP-block can be increased by complexation with side chains, as discussed above. This allows an easy way to tune the volume fraction of P4VP to achieve the desired morphology, e.g. PS cylinders. Of not obvious importance here is that the comb-shaped supramolecules, obtained by complexing P4VP with alkyl phenols, such as pentadecyl- and nonadecyl-phenol, also undergo self-organization, thus leading to peculiar structure-within-structure hierarchies, as shown in Fig. 7.1. Because the side chains, such as the alkyl phenols, can be so easily removed by dissolution, they play a major role in the preparation of nano-objects in the present concept.

Because here we focus on the preparation of rod-like entities, the cylindrical micro-domain structure of the P4VP(PDP)-b-PS starting bulk material was first established by small angle X-ray scattering. Fig. 7.2 shows the presence of the 1, 1, 3, 7, and 9 scattering peaks of the large 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 $2\pi/q^* = 33\text{nm}$ corresponds to a distance of ca. 38nm between neighboring PS cylinders. Fig. 7.1 shows the corresponding schematic structure before removing the PDP molecules, showing the two levels of structures. Fig. 7.3 shows a scanning transmission electron micrograph of cylinders of the P4VP-b-PS diblock copolymers with a PS core and a P4VP corona, stained with iodine for 2.5 hrs. The cylinders have diameters of 25-28nm 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
Fig. 7.2. 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.

The comb-coil microdomain structure and are likely formed by aggregation of isolated block copolymers formed after break-up of the matrix structure. For this specific example, we selected a relatively large P4VP block in order to image the corona as well. The presence of the iodine stained P4VP is clearly visible as contrast between the core and corona (darker), in particular in those regions where two cylinders cross. The thickness of the cylinders is in perfect agreement with the small angle X-ray data (Fig. 7.2). The position of the (1,0) scattering peak implies a distance of ca. 38nm between nearest neighbor cylinders. Correcting for the presence of PDP, this amounts to a value of ca. 25nm for the diameter of the cylinders. The cylinders in Fig. 7.3 have a slightly larger diameter due to the iodine-swollen corona.

The concept is not only useful to extract nanofibers, as it can obviously be used to prepare also 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 formation of supramolecules. This allows “tuning” the balance $f$ of the block copolymer using additives that can easily be 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 sulphonates.\textsuperscript{30} One can replace also the P4VP e.g. by polymers containing amide groups, such as polyamides, polypeptides and even proteins, which form strong coordination with e.g. zinc sulphonates, as shown by the self-organized structures of comb-shaped supramolecules of polyamides, and polypeptides with Zinc dodecyl benzene sulphonic acid.\textsuperscript{32}

\section*{7.4 Concluding Remarks}

We showed a concept to prepare individual nano-objects based on supramolecular block copolymers. The 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 photocrosslinkable 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, crosslinking of either core or corona is possible at the final stage; and finally, countless many block copolymer/amphiphile pairs are possible.

### 7.5 References

25. Lehn, J.-M. *Supramolecular Chemistry*; VCH, Weinheim, **1995**.
26. Vögtle, F. *Supramolecular Chemistry*; John Wiley & Sons, Chichester, **1993**.


