Building Nanowires from Micelles: Hierarchical Self-assembly of Al-ternating Amphiphilic Glycopolyamide Brushes with Pendants of High-Mannose Glycodendron and Oligophenylalanine

Yijiang Liu, Yufei Zhang, Zheyu Wang, Jue Wang, Kongchang Wei, Guosong Chen, and Ming Jiang

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.6b05044 • Publication Date (Web): 22 Jul 2016

Downloaded from http://pubs.acs.org on July 23, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Building Nanowires from Micelles: Hierarchical Self-assembly of Alternating Amphiphilic Glycopolymer Brushes with Pendants of High-Mannose Glycodendron and Oligophenylalanine

Yijiang Liu, Yufei Zhang, Zheyu Wang, Jue Wang, Kongchang Wei, Guosong Chen*, Ming Jiang

The State Key Laboratory of Molecular Engineering of Polymers and Department of Macromolecular Science, Fudan University, Shanghai 200433, China

ABSTRACT: Mimicking the diverse glyco-conjugate structures in nature is always the dream of scientists. Right now, hierarchical self-assembled structures of natural conjugates of peptides and sugars could not easily be achieved via linear glycopolyptide with monosaccharides as attachments. In this work, by using a series of well-designed alternating amphiphilic glycopolyptide brushes (AAGBs) with pendants of glycodendrons and short peptides, various self-assembled morphologies were achieved, including nanowires, nanoribbon and compound micelles mainly depending on the number ratio of the sugar units to the amino acids species (S/F). Among these morphologies, nanowire attracted our great attention. TEM studies demonstrated that it is formed via a hierarchical self-assembly i.e. a series of successive processes, including micellization, micelles alignment forming nano-filament, branching of the nano-filaments by micelles, and finally nanowire formation. As far as we know, such hierarchical self-assembly process with high complexity has not been observed in literature for glycopolyptides even polypeptides, which will deepen our understanding on self-assembly mechanism of natural glyco-conjugates and expand the library of biomimetic materials.

Introduction

In nature, saccharides and peptides are often covalently connected to each other forming various biomacromolecular conjugates, such as glycoproteins, mucins and proteoglycans, which can form a variety of assembled structures especially hierarchical ones, including micelles, vesicles, worm-like micelles, nanowires, nanoribbons etc. These self-assembled structures play key roles in a broad range of biological processes including modulating intercellular communication, cell adhesion, and immunological recognition. In the last decade, significant progresses on bioinspired synthetic glyco-peptides have been achieved via different approaches aiming at mimicking the functions of the native ones and developing new biocompatible materials. Among these mimics, glycopolyptide prepared by ring-opening polymerization is a promising one, featured by facile preparation and easy scale-up. In this field, artificial glycopolypeptides with a polypeptide backbone and monosaccharides as pendant groups were prepared by controlled polymerization, and in some cases, followed by post-polymerization modification. In these artificial glyco-polypeptide systems, the carbohydrates not only contribute to the bioavailability, but also modulate the folding and the self-assembly of the conjugates. However, among these elegant works in the past, very differing from the architectural varieties of their native counterparts, the artificial glycopolyptides studied were mainly focusing on linear or linear-branched block copolymers, which usually led to zero dimensional structures, e.g. micelles and vesicles exclusively. Thus these limitations hamper our understanding on the self-assembly mechanism of native glyco-conjugates, as well as the development of functional biomaterials based on glyco-poly-peptides for drug delivery, bio-imaging, tissue engineering etc.

Aiming at creating more abundant morphologies, especially the hierarchical self-assembled ones from artificial glycopolyptides approaching to those in nature, in this work we tried a new type of glycopolyptide, prepared by post-polymerization modification of a polypeptide backbone with oligosaccharide and oligopeptide as pendant brushes. The obtained new polymer is featured by the alternating amphiphilic brushes of dendronized oligosaccharides and oligopeptides along the polymeric peptide backbone. It is well known that polymer brushes, particularly amphiphilic polymer brushes, being a family of new architectures of copolymers have drawn great attention in the last two decades as their relatively well defined structures provide broad opportunities to control hydrophobic-hydrophilic balance and then the final assemblies. However, in most cases their assemblies possess lamellar structure as the result of phase separation of the side chains to opposite sides of the polymer backbone. Some recent works introduce crystallizable chains, liquid crystal or bulky POSS as brushes but did not bring out new findings in self-assembly. It is also well known that short peptides are excellent building blocks to create a wide variety of nanostructures, some of which, such as nanowire, nanoribbon resembles those in nature. However, such strong assembly ability of peptide leading to morphologies found in nature has rarely occurred in brush polymers with peptide as side chains, and even less in glycopolyptides.

In our design, the glycodendron attachment makes the conjugates unique in very high density of sugar units, of which carbohydrate-carbohydrate interaction may promote assembly of the conjugates; meanwhile, the pendent β-sheet forming oligopeptide is expected to provide driving force for the assembly resemble to that occurring in nature. Thus, new glycopolyptide architecture, i.e. Alternating Amphiphilic Glycopeptide Brushes (AAGBs) was prepared by modification of Manα1-2Man oligomannosides and oligophenylalanines to the Lysine/Glutamate based dendritic backbone. Manα1-2Man was selected because this structure was highly expressed on the surface of virus and bacteria, e.g., gp120, a major envelope protein of HIV, which could be recognized by human monoclonal antibody (mAbs) 2G12.
Meanwhile, the oligophenylalanine (L-Phe$_{3n}$, FF or FFFF) extracted from the Alzheimer’s β-amyloid polypeptide, was found to have an excellent capacity in forming a wide range of nanostructures. To prepare AAGBs, these two representative components were linked alternatively as pendent groups onto a polypeptide backbone prepared by condensation polymerization via our previous strategy. In order to explore the basic role of the complex amphiphilic structure in controlling its assembly morphologies, a small library of AAGBs has been constructed where the polymeric structure was tuned by three parameters, i.e. generations of the backbone dendrons, structure of the conjugated oligosaccharides and number of the oligophenylalanine. We found that the resulting AAGBs self-assembled into various morphologies, including compound micelle, nanowire, nanoribbon etc., mainly depending on the ratio of mannoside number in glycodendron and number of phenylalanine in oligophenylalanine component. Strong evidence showed that nanowires were formed from hierarchical self-assembly processes, i.e. the AAGBs first formed micelles, the micelles then further aligned into filaments, the filaments grew with branches via micelles, and finally the filaments fused into nanowires. This hierarchical self-assembly mechanism has not been reported previously in any research on brush copolymers. Furthermore, the protein binding ability of different assembled morphologies was evaluated.

### Result and Discussion

**Design and Synthetic Strategies of Alternating Amphiphilic Glycopeptide Brushes (AAGBs).** Very recently, we used metal-free step-growth copolymerization to prepare hybrid copolymers from oligopeptide blocks linked by small molecules. In this paper, the same strategy has been employed. Briefly, the step-growth polymerization between pentafluorophenol (PFp) active ester and primary amine functionalized monomer was used due to their high reactive efficiency under mild conditions (Scheme 1). PFp active ester functionalized monomer M$_0$, M$_1$, M$_2$ and amine-functionalized monomer M-a based on Lysine and Glutamate were first prepared separately via liquid phase peptide synthesis (synthetic details in supporting information, Scheme S1-5). Different generations of dendron scaffolds were attached to PFp active ester monomer as pendent groups. Then step-growth polymerization was performed by simply adding 1.2 equiv. N,N-Diisopropyl ethylamine (DIPEA) to the equal molar mixture of M-a with M$_0$, M$_1$ or M$_2$ in DMSO at room temperature. The resulted viscous
mixtures were allowed to precipitate in diethyl ether, giving alkyne-functionalized precursors. These precursors were deprotected in TFA and then modified with aminooxy monomer M-b, giving scaffolds P0, P1 and P2 (Scheme 1). The aminooxy nucleophiles are introduced for their high reactivity with reducing saccharides under mild reaction condition. Molar mass of P0, P1 and P2 was measured by gel permeation chromatography with multi-angle light scattering detector (GPC-MALS) in DMF. P0 and P1 gave the molar mass of 18.9 kDa and 16.6 kDa, respectively, while the molar mass of P2 can hardly be measured due to its poor solubility in DMF (molar mass of corresponding precursors were listed in Table S1). The nanowires inclined to entangle into large cluster at thickness of 10 nm (Figure 1e).

Figure 1. The TEM and AFM images of the nanowires formed by P1tM-F4 in water, (a) chemical structure, and 2D schematic illustration of P1tM-F4, (b, c) low/high-magnification TEM images, (d) cryo-TEM image and (e) AFM image of the P1tM-F4 nanowires.
Table 1. Sample codes, 2D illustrations, S/F ratios and the assembled morphologies of AAGBs library

<table>
<thead>
<tr>
<th>Sample codes</th>
<th>Morphology</th>
<th>S/F</th>
<th>2D illustrations</th>
<th>Sample codes</th>
<th>Morphology</th>
<th>S/F</th>
<th>2D illustrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0M-F₂</td>
<td>Precipitate</td>
<td>0.5</td>
<td><img src="image1" alt="2D Illustration" /></td>
<td>P0M-F₄</td>
<td>Precipitate</td>
<td>0.25</td>
<td><img src="image2" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P1M-F₂</td>
<td>Precipitate</td>
<td>1.0</td>
<td><img src="image3" alt="2D Illustration" /></td>
<td>P1M-F₄</td>
<td>Precipitate</td>
<td>0.5</td>
<td><img src="image4" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P2M-F₂</td>
<td>Nanowire</td>
<td>2.0</td>
<td><img src="image5" alt="2D Illustration" /></td>
<td>P2M-F₄</td>
<td>Precipitate</td>
<td>1.0</td>
<td><img src="image6" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P0dM-F₂</td>
<td>Precipitate</td>
<td>1.0</td>
<td><img src="image7" alt="2D Illustration" /></td>
<td>P0dM-F₄</td>
<td>Precipitate</td>
<td>0.5</td>
<td><img src="image8" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P1dM-F₂</td>
<td>Nanowire</td>
<td>2.0</td>
<td><img src="image9" alt="2D Illustration" /></td>
<td>P1dM-F₄</td>
<td>Nanoribbon</td>
<td>1.0</td>
<td><img src="image10" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P2dM-F₂</td>
<td>Compound Micelle</td>
<td>4.0</td>
<td><img src="image11" alt="2D Illustration" /></td>
<td>P2dM-F₄</td>
<td>Nanowire</td>
<td>2.0</td>
<td><img src="image12" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P0tM-F₂</td>
<td>Nanowire</td>
<td>1.5</td>
<td><img src="image13" alt="2D Illustration" /></td>
<td>P0tM-F₄</td>
<td>Precipitate</td>
<td>0.75</td>
<td><img src="image14" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P1tM-F₂</td>
<td>Compound Micelle</td>
<td>3.0</td>
<td><img src="image15" alt="2D Illustration" /></td>
<td>P1tM-F₄</td>
<td>Nanowire</td>
<td>1.5</td>
<td><img src="image16" alt="2D Illustration" /></td>
</tr>
<tr>
<td>P2tM-F₂</td>
<td>Compound Micelle</td>
<td>6.0</td>
<td><img src="image17" alt="2D Illustration" /></td>
<td>P2tM-F₄</td>
<td>Nanowire</td>
<td>3.0</td>
<td><img src="image18" alt="2D Illustration" /></td>
</tr>
</tbody>
</table>

Figure 2. TEM images of (a) P₂dM-F₂ (compound micelle), (b) P₁dM-F₂ (nanowire), (c) P₂tM-F₂ (nanowire) and (d) P₁dM-F₄ (nanoribbon).

high concentration ([P₁tM-F₄] > 1 mg/mL) in less than 7 days (Figure S9a), but they are quite stable for more than 30 days at a low concentration ([P₁tM-F₄] < 0.2 mg/mL) at room temperature. We noticed that such long and uniform nanowires are rarely observed for the assemblies of amphiphilic block copolymers and polymeric brushes, which deserved further investigation in detail.

Self-Assembly of AAGB Library. To further explore the general rule of AAGB assembly with emphasis on the effects of glycodendron and oligophenylalanine brushes, a library of AAGBs was designed varying in dendritic polypeptide scaffold (P₀, P₁ and P₂), hydrophobic peptide domain (F₂/F₄) and oligomannoside domain (M, dM and tM, Table 1). The same procedures as the mentioned for P₁tM-F₄ were used for the sample preparation and their assembly.

Generally, during the process of dialysis where the medium turned from hydrophobic to hydrophilic, the 18 samples showed very different responses: a great part of them, i.e. seven samples precipitated without any assembled structures. Three samples showed compound micelles, P₂dM-F₂, P₁tM-F₂ and P₂tM-F₂ (Figure 2a, S9b-c). The nanowires, which were seldom found in synthetic copolymers and interested us most, became the common features of the samples including P₁dM-F₂, P₂tM-F₂, P₂M-F₂, P₀tM-F₂ and P₂dM-F₂ (Figure 2b-c, S9d-f). Nanoribbon is a special case, obtained only from P₁dM-F₄ (Figure 2d). Different from the long and homogeneous nanowire, the nanoribbon was heterogeneous with its width distributed in the range of 50–100 nm. The ribbons were not stable and easy to precipitate in water. At first glance, such diversity of the morphologies observed seems not easy to be explained by relating the results to the structural parameters directly.
Figure 3. The phase diagram of AAGP assemblies depends on S/F ratio and different polypeptide scaffolds (P0, P1 and P2).

Although the architectures of our AAGB are complicated, we inclined to think that the hydrophobicity-hydrophilicity balance is still the main factor governing their behavior in self-assembly. Therefore, we simply introduced a parameter S/F, i.e. number ratio of saccharide units to phenylalanine monomer units in evaluating the assembly (Table 1). Thus a "phase diagram" was constructed (Figure 3), in which S/F ratio and the scaffolds character (P0, P1 and P2) serve the abscissa and ordinate axes respectively. Fortunately, in the diagram, a clear relationship between the assembly behavior and the structural parameters of the library members displayed as follows. At low S/F ratios (≤ 1.0), precipitates or irregular aggregates appeared, probably because their relatively small hydrophilic domains failed to stabilize the aggregates in water. When the S/F ratio was increased to a much larger value (≥ 3.0), compound micelle became the major morphology, because of the large hydrophilic and small hydrophobic domains of the polymers in this area. When S/F exists in the small window of 1.5 ≤ S/F ≤ 3.0, nanowire was the only morphology observed. It was noticed that at the upper boundary value 3.0 of S/F ratio, stable nanowires were formed by P2tM-F4 with FFFF domain, while compound micelles were formed by P1tM-F2 with FF domain, so the longer phenylalanine had stronger regular packing tendency leading to nanowires. In short, the self-assembled morphologies were generally controlled by S/F ratio, i.e. precipitates, nanoribbon, nanowires and compound micelles were sequentially observed, when the S/F ratio was increased.

Self-Assembly Mechanism of the AAGB Nanowires. The nanowire, which was found in the small S/F "window", deserves deep research because in previous self-assembly studies on glycopolypeptide, either peptide as main chain or pendant groups, nanowire was rarely observed. However, in this work, nanowires could be formed for all kinds of the main chain peptide, i.e. P0, P1 and P2 provided S/F exists in the window. Therefore, we tried to use electronic microscopy to trace the formation of the nanowires for understanding the mechanism. Nevertheless, formation of P1tM-F4 nanowires, as mentioned above was quite fast (within a couple of hours), it was almost not possible to capture stable intermediate states under TEM. Considering that S/F of P2tM-F4 (3.0) was much higher than that of P1tM-F4 (1.0), showing lower packing strength and slower assembly process and therefore, it was selected for this mechanical study. In addition, to further retard the process, a highly diluted solution (2 mg/mL) of P2tM-F4 was used for dialysis. Thus the assembly process finished in about 2 days, which made the TEM sample preparation at different stages possible. Typically, at each time intervals of 3 h, 12 h, 24 h and 48 h, a small aliquot of the solution was taken out and quenched by a large amount of water to "freeze" the intermediate morphology.

The TEM image of P2tM-F4 taken at 3 h (Figure 4a) was featured by the coexistence of micelles with a diameter around 3-5 nm and nano-filaments with the same width. It could be clearly seen that some of the small micelles were aligned and linked to strings, which obviously was the primary form of nano-filament (nano-filament I). When the dialysis time was increased to 12 h (Figure 4b), the nano-filaments could still be observed, but more micelles were found attaching to the surface of the nano-filaments, forming "branches" (nano-filament II). In the same stage (Figure 4c), thin nanowires (nano-wire I) with rough surface and a wider diameter (ca. 10 nm) compared to the primary nano-filaments were observed. These results indicated that the nano-filaments were partially transformed into nanowires via the growth of micelle "branch" on the filament surface. Meanwhile, at this stage, single micelles or micelle strings disappeared. Then from the sample taken at 24 h (Figure 4d), wide and compact nanowires with a diameter around 20-30 nm became the dominate morphology (nano-wire II). "Branched" structure was also found on the surface of these nanowires, but here the "branch" turned to nano-filaments with a diameter around 10 nm. These attached filaments were found twisted on the stem of the nanowire. Finally, after 48 h (Figure 4e; Figure S10-11), these twisted nano-filament "branches" became regularly circling the wire with a period of 10 nm as shown in the inset of Figure 4e. Similar regular structure was also observed in the assemblies of P1tM-F4 under TEM (Figure S12) and of P2tM-F4 by cryo-fixation sample preparation method (Figure S13). At the same time interval, thick and wide nanowires were also observed (Figure 4f; nano-wire III, diameter ca. 50 nm). Such thick nanowires became more uniformity without inner structures as probably a result of fusion of the surrounding nano-filaments (Figure 4f; Figure S11).

Although the TEM studies could not trace the details of the whole hierarchical self-assembly process of AAGBs, the evolution outline of the morphologies has been clearly sketched. It becomes clear that the formation of the nanowires of AAGBs stems from the basic assemblies i.e. the ordinary micelles of AAGBs formed due to their amphiphilicity. The following steps include the micelles alignment, formation of the nano-filaments, attachment of micelles to the filaments, formation of the nanowires due to the fusion of the attached micelles and finally, formation of the thick nanowire etc. It is not difficult to realize that the key factor driving all the steps is the association between the sugar ‘shell’ of the primary micelles, as well as the subsequent assemblies including the nano-filaments, branches and nanowires. Such hierarchical assembly has not been reported for other glycopolypeptides in literature, probably because in our AAGBs, the coating hydrophilic layers of all of the assemblies at different levels consist of much high sugar density due to the dendron structure of the sugar pendants. The dense sugar shell might favor the
alignment of micelles forming string or nano-filament, which became the second primary building block of the final nanowire. In our previous study, we proposed that when two micelles of block copolymers fused to each other, the chain density of the shell on the two ends was lighter than that of the lateral sides, which would direct the next coming micelle to approach and attach to the two ends of the fused micelle. With the heavy glyco-dendron shell in the current case, the alignment of micelles could be explained by the same rationale. On the other hand, typical signal of β-sheet structure was observed among the nanowire samples including P1tM-F4, P2tM-F4 and P2dM-F4 by Circular dichroism (CD) spectroscopy (Figure S14), so β-sheet packing is another driving force leading to nanowires. In contrast, CD spectra indicated that all compound micelles exhibit typical random coil secondary structure rather than β-sheet, and the nanowires formed by AAGBs with the short peptide FF brushes show the same results (Figure S15-16). The result indicates that β-sheet forming tendency of oligophenylalanine is determined by the length of oligophenylalanine species and is affected by the dense sugar shell.

The effect of morphologies of AAGB assemblies on their binding ability to proteins. In nature, different morphologies sometimes simply indicate different functions of the assemblies. Herein, Human Immunodeficiency Virus (HIV) antibody 2G12 and plant lectin Concanavalin A (Con A) were chosen as models to evaluate the protein binding ability of the nanowires and compound micelles of AAGBs. 2G12 is a broadly neutralizing human monoclonal antibody (mAb), which can specifically recognize terminal Manα1–2Man moieties. First the binding ability of self-assembled AAGBs to 2G12 was evaluated by sandwich Enzyme Linked Immuno-sorbent Assay (ELISA). In this experiment, 2G12 was immobilized to the surface coated with gp120, a major envelope protein of HIV, which binds to 2G12 via the N-linked high mannose glycan on its surface. Then inhibition of this binding by adding free oligosaccharides and self-assembled AAGBs respectively was evaluated by ELISA. As shown in Figure 5a, both Manα1–2Man (diMan), Manα1–2Manα1–2Man (triMan) and their corresponding assemblies showed significant inhibition for 2G12–carbohydrate recognition, while mannose (Man) and its corresponding assembly P1M-F2 did not. Furthermore, generally, compound micelles e.g. P2tM-F2 showed higher inhibition ability to the binding between 2G12 and gp120 than nanowires e.g. P2tM-F4 did. These two polymer brushes shared the same generation of dendron, same trisaccharide, but different morphologies and subsequently different binding ability. The same phenomenon was also observed between P1tM-F2 compound micelle and P1tM-F4 nanowire. This may due to the less steric hindrance in com-
pound micelles than that in nanowires favoring the inhibition of the binding between 2G12 and oligosaccharides. Moreover, when plant lectin Con A was utilized, this trend was even more pronounced, as shown from the result of quantitative agglutination experiment45 (Figure 5b), i.e. the compound micelles gave a higher binding ability to Con A than nanowires did, especially between P2tM-F2/P2tM-F4 and P1tM-F2/P1tM-F4. These results might be explained by the different curvature of the nano-objects, i.e. higher curvature of micelles and lower ones of nanowires.

Figure 5. (a) ELISA analysis on 2G12-gp120 binding inhibition (%) by AAGB assemblies at mannose-residue concentration of 2 mM. (b) Qualitative agglutination of Con A with AAGB assemblies.

Conclusion

In this work, a hierarchical self-assembly process forming nanowires was observed in newly designed alternating amphiphilic glycopolymer brushes. Various self-assembled morphologies were achieved, including nanowires, nanoribbon and compound micelles mainly depending on the number ratio of the sugar units to the amino acids species (S/F). We found that the glycopolyptides first self-assembled into micelles which became the basic building block forming nanofilaments. Then the nano-filaments grew into branches and finally fused into nanowires. This very interesting phenomenon has not been reported in the previous self-assembly of glycopolyptide, polypeptide and even polymer brushes. The result indicated that by using a dense layer of oligosaccharides, new self-assembly mechanism is possible, showing a bright future of glycopolyptide in mimicking nature and developing new biocompatible materials. This newly synthesized AAGB architecture also brings us new thoughts in construction and the assembly mechanism of one dimensional nanostructure.

ASSOCIATED CONTENT

Supporting Information

Characterization of synthesized glycopolyptide and corresponding precursors, including 1H NMR and GPC results, dynamic light scattering, circular dichroism, TEM, AFM, as well as concentration dependent ELISA and UV agglutination results are all available in supporting information.

AUTHOR INFORMATION

Corresponding Author guosong@fudan.edu.cn

ACKNOWLEDGMENT

National Natural Science Foundation of China (Nos. 91527305, 21474020, 91227203 and 51322306) and the Innovation Program of the Shanghai Municipal Education Commission are acknowledged for their financial support.

REFERENCES

(3) Ladmiral, V.; Sensmaril, M.; Canton, I.; Armes, S. P., Journal of the American Chemical Society 2013, 135 (36), 13574-13581.
(7) Galan, M. C.; Durny, P.; Renaudet, O., Chemical Society reviews 2013, 42 (11), 4599-4612.
SYNOPSIS TOC (Word Style “SN_Synopsis_TOC”).
Hierarchical Self-Assembly

382x277mm (150 x 150 DPI)
Dialysis in Water

Nanowire

(b) (c)
239x230mm (150 x 150 DPI)