Supramolecular Polymer Brushes

International Edition: DOI: 10.1002/anie.201601048
German Edition: DOI: 10.1002/ange.201601048

# Kinetically Controlled Sequential Growth of Surface-Grafted Chiral Supramolecular Copolymers

*Hendrik Frisch[+], Eva-Corinna Fritz[+], Friedrich Stricker, Lars Schmüser, Daniel Spitzer, Tobias Weidner, Bart Jan Ravoo,* and Pol Besenius**

***Abstract:*** *We report a facile strategy to grow supramolecular copolymers on Au surfaces by successively exposing a surface-anchored monomer to solutions of oppositely charged peptide comonomers. Charge regulation on the active chain end of the polymer sufficiently slows down the kinetics of the self-assembly process to produce kinetically trapped copolymers at near-neutral pH. We thereby achieve architectural control at three levels: The β-sheet sequences direct the polymerization away from the surface, the height of the supramolecular copolymer brushes is well-controlled by the stepwise nature of the alternating copolymer growth, and 2D spatial resolution is realized by using micropatterned initiating monomers. The programmable nature of the resulting architectures renders this concept attractive for the development of customized biomaterials or chiral interfaces for optoelectronics and sensor applications.*

Interfacial oligopeptides have sparked tremendous efforts in the areas of biomimetic materials and polymer chemistry, enabling one to tailor various surface properties, such as its wettability, biocompatibility, cell-adhesion, or antifouling properties.[1] To date, however, the large majority of surface-bound covalent polymers that emulate biological functionality are based on purely covalent architectures.[1a,d] In pioneering studies, Gazit and co-workers prepared vertically aligned supramolecular nanotubes on surfaces by crystallization or vapor deposition techniques using hydrophobic diphenylalanine.[2] More recently, the Matile group developed sophisticated synthetic methods, referred to as self-organizing surface-initiated polymerization,[3] that rely on the ring opening of cyclic disulfide monomers to produce synthetic photosystems.[4] Ternary supramolecular cucurbituril complexes were used by Kim and co-workers[5] to grow poly(pseudorotaxanes) on a Au surface and by Scherman and co-workers[6] to reversibly link polyethylene glycol polymers on gold. To date, ordered supramolecular polymer brushes have not been obtained as the kinetically controlled self-assembly of supramolecular polymers remains challenging[7] and prevents the dynamic polymerization from being confined to surfaces. To overcome this limitation, we report a facile concept that combines charge-regulated self-assembly and supramolecular copolymerization techniques. This combined approach passivates the growing chain end of the surface-anchored polymers, slowing down the self-assembly kinetics sufficiently to graft copolymers in a stepwise fashion perpendicular to the solid substrate. Using surface plasmon resonance (SPR), we show that the polymerization at near-neutral pH is additive and can only be reversed under acidic and basic conditions. Sum frequency generation (SFG) and IR vibrational spectroscopy studies also confirm that the peptidic hydrogen-bonding sequences direct the polymerization away from the surface. AFM in water was used to resolve the length of the surface-bound copolymers as well as the microstructured 2D patterns of controlled height.

We synthesized a set of complementary supramolecular comonomers, **1**, **2**, and **3**, based on dendritic $C_3$-symmetric peptide motifs[8] (Figure 1). The incorporation of basic (K) and acidic (E) amino acids into alternating hydrophilic–hydrophobic oligophenylalanine sequences results in oppositely charged complementary comonomers **1** and **2**. We have previously reported on similar dendritic amphiphiles that

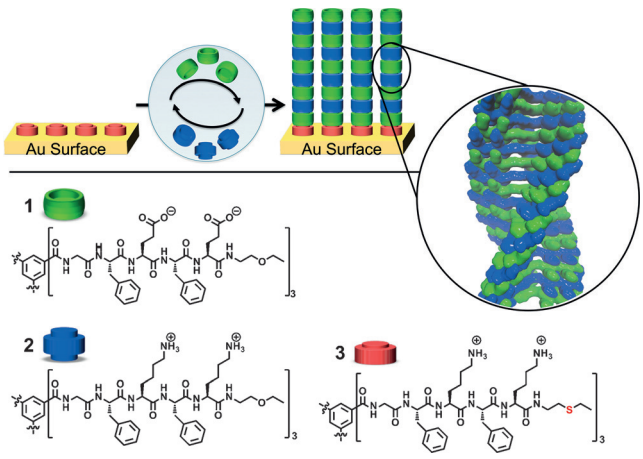


***Figure 1.*** Surface-grafted supramolecular copolymerization and the molecular structures of the complementary comonomers **1** and **2** and the initiator **3**.

[*] H. Frisch,[+] F. Stricker, D. Spitzer, Prof. Dr. P. Besenius
Institute of Organic Chemistry
Johannes Gutenberg-Universität Mainz
Duesbergweg 10–14, 55128 Mainz (Germany)
E-mail: besenius@uni-mainz.de
H. Frisch,[+] E.-C. Fritz,[+] Prof. Dr. B. J. Ravoo
Organic Chemistry Institute
Westfälische Wilhelms-Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
E-mail: b.j.ravoo@uni-muenster.de
L. Schmüser, Dr. T. Weidner
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz (Germany)
[+] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201601048.

  

polymerize in solution to produce one-dimensional alternating supramolecular copolymers with a nanorod-like morphology by a combination of attractive Coulomb interactions, hydrogen bonding, and hydrophobic shielding.[9] Furthermore, we prepared a tripodal thioether derivative of the cationic comonomer **3** that served as a surface-anchored supramolecular initiator for Au surface substrates.

To determine the isoelectric point of the ampholytic supramolecular copolymer based on the comonomer pair **1** and **2**, we performed pH-dependent polymerization studies in solution. In pure monomer solutions, self-assembly into homo-aggregates at acidic and basic pH is observed when the charges are screened (Supporting Information, Figure S1). The pH titration curves intersect at pH 5.2 (Figure S2). Mixing the two monomer solutions at this pH leads to an instant change in the circular dichroism (CD) spectrum, which deviates strongly from the linear combination of the spectra of **1** and **2** (Figure S3). A negative CD band appears at 215 nm, indicative of the formation of parallel β-sheets.[9,10] Negative-stain transmission electron microscopy (TEM) images further confirm the presence of nanorod-like structures (Figure S4).

We postulated that the β-sheet-directed[11] and charge-regulated self-assembly[12] of cationic and anionic comonomers in solution could be translated onto solid substrates, allowing us to graft supramolecular polymers off surfaces. The multivalent tripodal cationic monomer **3** binds strongly to Au surfaces via multiple gold–sulfur interactions, and therefore functions as an initiator for the copolymerization on the solid support. SPR analysis allowed us to monitor the supramolecular polymerization in real time and to resolve the comonomer selectivity as well as the polymerization kinetics. To avoid non-specific binding to the bare Au surface, all SPR experiments were performed on a triethylene glycol thioether (**4**) functionalized self-assembled monolayer (SAM). Control experiments showed that **1** and **2** have no affinity for surfaces functionalized with SAMs of **4** (Figure S5). In the first step, initiator **3** was immobilized by displacing weakly binding **4** (Figure 2A), causing an increase in the refractive index of 1.4 mRIU. Partial displacement of **4** ensures SPR conditions under which each monomer addition occurs in a non-mass-limited process, which is necessary to investigate the sequential addition and polymer growth mechanisms (Figure 2B). After immobilization of **3**, solutions of monomers **1** or **2** were successively flushed over the surface at identical time intervals. Each binding event resulted in an instantaneous stepwise signal increase of $1.2 \pm 0.3$ mRIU, and the plateau observed within 6 min is indicative of the saturation of the active chain ends of the surface-bound copolymers. Importantly, the observed plateau does not decrease when the functionalized surface is washed with buffer, even when the washing time is extended to one hour. Summarizing these findings, a stepwise elongation process has been observed by SPR, and the amount of available binding sites on the growing supramolecular copolymer chain end remains constant for up to 15 iterative additions of each monomer (Figure 2B, blue and green arrows).

Critically, upon washing the surface-bound copolymers with buffer, we did not observe any depolymerization, which indicates that the copolymers are indeed kinetically trapped and simultaneously highlights the stability of the surface-bound copolymers. To further confirm that the assemblies are stabilized by reversible electrostatic interactions, aqueous solutions of pH 2 and pH 12 were added to the surface. Switching off the attractive Coulomb interactions leads to disassembly of the copolymers, and loss of material is observed after the alternating addition of acid and base (Figure 2B, orange and brown arrows). These observations demonstrate that we can achieve kinetically trapped polymeric states at near-neutral pH values, but that the structures remain stimuli-responsive and can be disassembled by changing the pH.

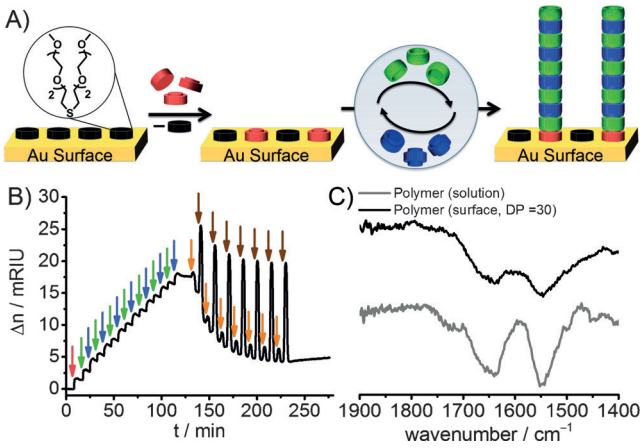


***Figure 2.*** A) Experimental setup of the SPR measurements, including the exchange reaction of **3** (red discs) and the copolymerization of **1** and **2** (green and blue discs). B) SPR sensorgram of the copolymerization (addition of the initiator **3** and the complementary comonomers **1** and **2**) with subsequent polymer removal by the addition of acid (pH 2, orange arrow) and base (pH 12, brown arrow). C) IR spectra of surface-grafted copolymers and the copolymers formed in solution.

To investigate the molecular order and secondary structure of the supramolecular copolymers grafted from the Au surface, FT-IR spectroscopy experiments were carried out. We focused on the amide I and II absorption bands, which are characteristic for hydrogen-bonded secondary structures.[13] The surface-grafted copolymers show two bands at $\tilde{\nu} = 1638$ cm$^{-1}$ (amide I; C=O stretching) and $\tilde{\nu} = 1550$ cm$^{-1}$ (amide II; CN stretching, NH bending) that increase in intensity with increasing degrees of polymerization (DP = 10, 20, and 30). These bands compare very well with those observed for copolymers consisting of **1** and **2** that were self-assembled in solution and then deposited on a Au surface ($\tilde{\nu} = 1641$ and 1548 cm$^{-1}$, Figures 2C, S6). This result indicates that the secondary structure achieved by our grafting from approach is identical to the one achieved by conventional solution self-assembly of **1** and **2**, and has a very high β-sheet content. The FT-IR investigations thereby support the conclusions drawn from the CD spectra, and, in combination with the SPR experiments, provide strong evidence that the rather bulky and rigid phenylalanine-based anionic and cationic monomers form ordered copolymers that grow perpendicular to the Au surface.

  

To demonstrate that our stepwise copolymerization approach can be used to graft tailor-made materials on Au, we grew brushes of supramolecular polymers on microstructured surfaces. Microcontact printing[14] was first applied to obtain patterned surfaces of tetraethylene glycol thiol (**5**) SAMs (Figure 3A). In the next step, the obtained microstructured gaps on the Au surface were functionalized with **3**

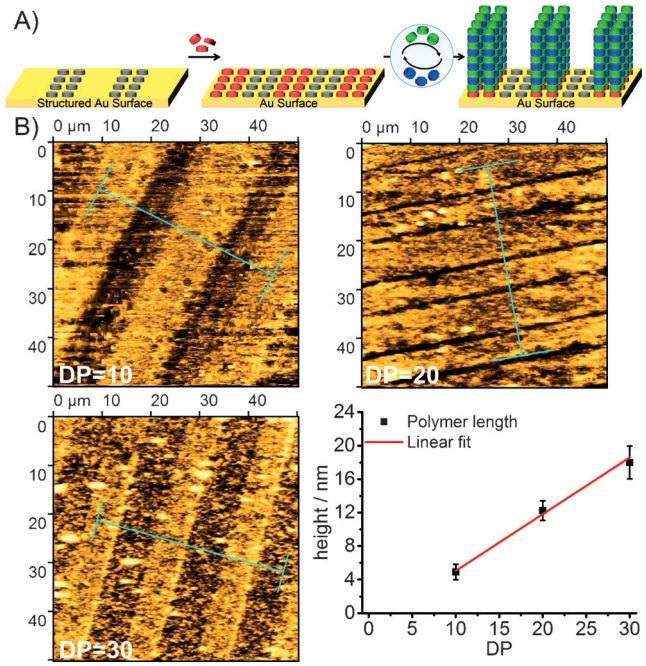


***Figure 3.*** A) Structured polymerization for AFM analysis. B) AFM topographic images of different degrees of polymerization (DP = 10, 20, 30) and the corresponding height profiles as a function of the polymer length.

to obtain line-shaped patterns of the surface-anchored supramolecular initiator. Note that **3** was anchored directly onto the Au surface as a free base to ensure dense packing, which is crucial to obtain brush-like polymer structures.[15] The grafting of copolymers by the successive addition of anionic **1** and cationic **2** was investigated by AFM. We performed these experiments in phosphate buffer (20 mM, pH 5.2) to image the material in its hydrated and native state.[16] As the monomers have no affinity towards the ethylene glycol SAM, the height of the grafted brush and the length of the copolymer could be determined relative to the SAM. Topographic images of different degrees of polymerization (DP = 10, 20, and 30) as well as different line patterns were recorded (Figure 3B, S7). A direct correlation between the degree of polymerization and the grafted copolymer height was observed, and a linear regression revealed an increase in the polymer length of $0.68 \pm 0.05$ nm per monomer. This value agrees with our previous molecular dynamics simulations of copolymers based on alanine derivatives of **1** and **2** in water, which suggested comonomer distances of 0.47 nm.[9a] The high fidelity and selectivity of our stepwise grafting strategy allows us to adjust the height of the ordered supramolecular copolymer brush and demonstrates the power of this approach.

We used SFG to glean information about the order within the assemblies. SFG is a surface-specific vibrational spectroscopy method where the intensity of the signal is proportional to the order and density of the interfacial species. The selection rules of SFG dictate that only ordered species at interfaces are visible. Disordered ligands or molecules in solution near the surface are not detected.[17] This allowed us to record SFG spectra in situ at gold surfaces coated with initiator **3** while they were successively exposed to solutions of comonomer **1** and **2**. We focused on the C=O glutamic acid side chain modes to determine the order within the assemblies because the β-sheet amide resonances observed by IR (Figure 2C) are SFG inactive.[18] The SFG spectra showed a pronounced feature near $\tilde{\nu} = 1725$ cm$^{-1}$, which was assigned to ordered C=O moieties of the glutamic acid side chain within **1** (Figure 4A).[19] The polarity of the peak indicates the

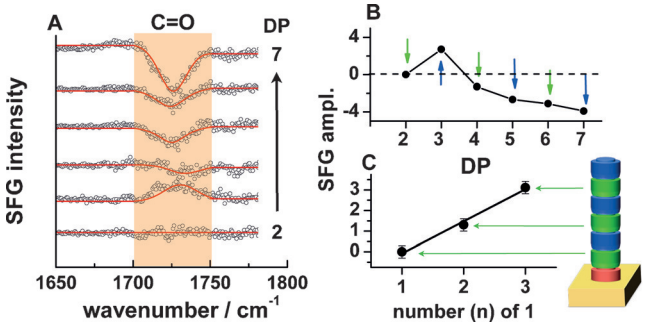


***Figure 4.*** A) SFG spectra showing the C=O side-chain bands for different degrees of polymerization (DP). B) Amplitudes of the C=O modes. C) Absolute SFG amplitudes as a function of the number of **1**.

net orientation of all C=O groups within the stack. The peaks started out as positive peaks for the trimeric species (DP = 3) and then became negative. Figure 4B summarizes the SFG amplitudes as a function of the DP. The reason for the positive polarity for DP = 3 is likely the bipolar charge distribution within the trimer. Figure 4C summarizes the absolute amplitudes of the SFG signal for the number $n$ of **1** within the stacks. A linear fit of the SFG amplitude yields a slope of $1.5/n$. As the SFG signal depends on both the number and order of the glutamic acid C=O groups, a slope of $> 1/n$ indicates that the overall order within the assemblies is increasing.[17,20] It is also interesting to note that the overall C=O signal increases after each addition of the lysine-containing comonomer **2**. This result demonstrates that the order within the surface-confined supramolecular stacks is promoted by interactions between **1** and **2**.

In an analogous approach to solid-phase synthesis,[21] we have herein reported the supramolecular alternating copolymerization of oppositely charged peptide-based monomers to graft chiral polymers off Au surfaces. Superficially, this strategy is not dissimilar to the layer-by-layer (LBL) deposition of oppositely charged polyelectrolytes into multilayered films.[7c,22] Our strategy confines the dynamic polymerization to the Au surface as charge regulation on the active

  

chain end of the supramolecular polymer slows down the kinetics during the self-assembly process and thus leads to kinetically trapped assemblies at near-neutral pH. These assemblies can only be disrupted by screening the charges at either high or low pH. Our approach allows us to gain architectural control at three levels:

1) The order encoded by the chiral β-sheets on the molecular level directs the polymerization perpendicular to the Au surface.
2) The number of monomer addition cycles determines the height of the copolymer brush.
3) Two-dimensional spatial resolution is achieved with micropatterned initiating monomers.

This facile strategy and the programmable nature of the produced surface-anchored morphologies open up opportunities for a range of applications, such as the development of adaptive biomaterials or chiral interfaces for optoelectronics and sensor applications.

## Acknowledgements

We thank Rebecca Niebuhr (WWU Münster) for the synthesis of molecule **3** and the Fonds der Chemischen Industrie for a Liebig (P.B.) and a doctoral (H.F.) fellowship. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 858, E.-C.F. and B.J.R.). L.S. and T.W. thank the Max Planck Graduate Center for support.

**Keywords:** charge regulation · kinetic control · microstructures · self-assembly · supramolecular chemistry

**How to cite:** *Angew. Chem. Int. Ed.* **2016**, *55*, 7242–7246
*Angew. Chem.* **2016**, *128*, 7358–7362

[1] a) M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, *9*, 101–113; b) S. T. Milner, *Science* **1991**, *251*, 905–914; c) M. Husseman, E. E. Malmström, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russell, C. J. Hawker, *Macromolecules* **1999**, *32*, 1424–1431; d) S. Edmondson, V. L. Osborne, W. T. S. Huck, *Chem. Soc. Rev.* **2004**, *33*, 14–22; e) W. Senaratne, L. Andruzzi, C. K. Ober, *Biomacromolecules* **2005**, *6*, 2427–2448; f) X. Liu, Y. Liang, F. Zhou, W. Liu, *Soft Matter* **2012**, *8*, 2070–2086; g) Q. Wei, T. Becherer, S. Angioletti-Uberti, J. Dzubiella, C. Wischke, A. T. Neffe, A. Lendlein, M. Ballauff, R. Haag, *Angew. Chem. Int. Ed.* **2014**, *53*, 8004–8031; *Angew. Chem.* **2014**, *126*, 8138–8169; h) B. B. Hsu, K. S. Jamieson, S. R. Hagerman, E. Holler, J. Y. Ljubimova, P. T. Hammond, *Angew. Chem. Int. Ed.* **2014**, *53*, 8093–8098; *Angew. Chem.* **2014**, *126*, 8231–8236.

[2] a) M. Reches, E. Gazit, *Nat. Nanotechnol.* **2006**, *1*, 195–200; b) L. Adler-Abramovich, D. Aronov, P. Beker, M. Yevnin, S. Stempler, L. Buzhansky, G. Rosenman, E. Gazit, *Nat. Nanotechnol.* **2009**, *4*, 849–854.

[3] N. Sakai, M. Lista, O. Kel, S.-i. Sakurai, D. Emery, J. Mareda, E. Vauthey, S. Matile, *J. Am. Chem. Soc.* **2011**, *133*, 15224–15227.

[4] a) G. Sforazzini, R. Turdean, N. Sakai, S. Matile, *Chem. Sci.* **2013**, *4*, 1847–1851; b) H. Hayashi, A. Sobczuk, A. Bolag, N. Sakai, S. Matile, *Chem. Sci.* **2014**, *5*, 4610–4614; c) K.-D. Zhang, S. Matile, *Angew. Chem. Int. Ed.* **2015**, *54*, 8980–8983; *Angew. Chem.* **2015**, *127*, 9108–9111.

[5] K. Kim, D. Kim, J. W. Lee, Y. H. Ko, K. Kim, *Chem. Commun.* **2004**, 848–849.

[6] C. Hu, F. Tian, Y. Zheng, C. S. Y. Tan, K. R. West, O. A. Scherman, *Chem. Sci.* **2015**, *6*, 5303–5310.

[7] a) J. M. Lehn, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4763–4768; b) X. Wang, G. Guerin, H. Wang, Y. Wang, I. Manners, M. A. Winnik, *Science* **2007**, *317*, 644–647; c) N. Sakai, R. Bhosale, D. Emery, J. Mareda, S. Matile, *J. Am. Chem. Soc.* **2010**, *132*, 6923–6925; d) Y. Tidhar, H. Weissman, S. G. Wolf, A. Gulino, B. Rybtchinski, *Chem. Eur. J.* **2011**, *17*, 6068–6075; e) P. A. Korevaar, S. J. George, A. J. Markvoort, M. M. J. Smulders, P. A. J. Hilbers, A. P. H. J. Schenning, T. F. A. De Greef, E. W. Meijer, *Nature* **2012**, *481*, 492–496; f) P. A. Korevaar, C. Grenier, A. J. Markvoort, A. P. H. J. Schenning, T. F. A. de Greef, E. W. Meijer, *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 17205–17210; g) P. A. Korevaar, C. J. Newcomb, E. W. Meijer, S. I. Stupp, *J. Am. Chem. Soc.* **2014**, *136*, 8540–8543; h) S. Ogi, K. Sugiyasu, S. Manna, S. Samitsu, M. Takeuchi, *Nat. Chem.* **2014**, *6*, 188–195; i) A. G. L. Olive, N. H. Abdullah, I. Ziemecka, E. Mendes, R. Eelkema, J. H. van Esch, *Angew. Chem. Int. Ed.* **2014**, *53*, 4132–4136; *Angew. Chem.* **2014**, *126*, 4216–4220; j) S. Ogi, V. Stepanenko, K. Sugiyasu, M. Takeuchi, F. Würthner, *J. Am. Chem. Soc.* **2015**, *137*, 3300–3307; k) J. Kang, D. Miyajima, T. Mori, Y. Inoue, Y. Itoh, T. Aida, *Science* **2015**, *347*, 646–651; l) A. Pal, M. Malakoutikhah, G. Leonetti, M. Tezcan, M. Colomb-Delsuc, V. D. Nguyen, J. van der Gucht, S. Otto, *Angew. Chem. Int. Ed.* **2015**, *54*, 7852–7856; *Angew. Chem.* **2015**, *127*, 7963–7967; m) A. Aliprandi, M. Mauro, L. De Cola, *Nat. Chem.* **2016**, *8*, 10–15.

[8] a) K. Matsuura, K. Murasato, N. Kimizuka, *J. Am. Chem. Soc.* **2005**, *127*, 10148–10149; b) B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.* **2009**, *109*, 6275–6540.

[9] a) H. Frisch, J. P. Unsleber, D. Lüdeker, M. Peterlechner, G. Brunklaus, M. Waller, P. Besenius, *Angew. Chem. Int. Ed.* **2013**, *52*, 10097–10101; *Angew. Chem.* **2013**, *125*, 10282–10287; b) H. Frisch, Y. Nie, S. Raunser, P. Besenius, *Chem. Eur. J.* **2015**, *21*, 3304–3309; c) P. Ahlers, H. Frisch, P. Besenius, *Polym. Chem.* **2015**, *6*, 7245–7250.

[10] S. Brahms, J. Brahms, G. Spach, A. Brack, *Proc. Natl. Acad. Sci. USA* **1977**, *74*, 3208–3212.

[11] a) M. R. Ghadiri, J. R. Granja, R. A. Milligan, D. E. McRee, N. Khazanovich, *Nature* **1993**, *366*, 324–327; b) J. D. Hartgerink, E. Beniash, S. I. Stupp, *Science* **2001**, *294*, 1684–1688; c) J. P. Schneider, D. J. Pochan, B. Ozbas, K. Rajagopal, L. Pakstis, J. Kretsinger, *J. Am. Chem. Soc.* **2002**, *124*, 15030–15037; d) R. V. Ulijn, A. M. Smith, *Chem. Soc. Rev.* **2008**, *37*, 664–675; e) I. W. Hamley, *Soft Matter* **2011**, *7*, 4122–4138; f) J. B. Matson, R. H. Zha, S. I. Stupp, *Curr. Opin. Solid State Mater. Sci.* **2011**, *15*, 225–235.

[12] a) K. L. Niece, J. D. Hartgerink, J. J. J. M. Donners, S. I. Stupp, *J. Am. Chem. Soc.* **2003**, *125*, 7146–7147; b) H. A. Behanna, J. J. J. M. Donners, A. C. Gordon, S. I. Stupp, *J. Am. Chem. Soc.* **2005**, *127*, 1193–1200; c) R. M. Capito, H. S. Azevedo, Y. S. Velichko, A. Mata, S. I. Stupp, *Science* **2008**, *319*, 1812–1816.

[13] a) M. Jackson, H. H. Mantsch, *Crit. Rev. Biochem. Mol. Biol.* **1995**, *30*, 95–120; b) S. E. Paramonov, H.-W. Jun, J. D. Hartgerink, *J. Am. Chem. Soc.* **2006**, *128*, 7291–7298; c) H. Jiang, M. O. Guler, S. I. Stupp, *Soft Matter* **2007**, *3*, 454–462.

[14] a) A. Kumar, G. M. Whitesides, *Appl. Phys. Lett.* **1993**, *63*, 2002–2004; b) T. Kaufmann, B. J. Ravoo, *Polym. Chem.* **2010**, *1*, 371–387.

[15] T. Wu, K. Efimenko, J. Genzer, *J. Am. Chem. Soc.* **2002**, *124*, 9394–9395.

[16] W. F. Heinz, J. H. Hoh, *Biophys. J.* **1999**, *76*, 528–538.

  

[17] Y. R. Shen, *The Principles of Nonlinear Optics*, 1st ed., Wiley, New York, **1984**.
[18] T. Weidner, J. S. Apte, L. J. Gamble, D. G. Castner, *Langmuir* **2010**, *26*, 3433 – 3440.
[19] D. Schach, C. Globisch, S. J. Roeters, S. Woutersen, A. Fuchs, C. K. Weiss, E. H. G. Backus, K. Landfester, M. Bonn, C. Peter, T. Weidner, *J. Chem. Phys.* **2014**, *141*, 22D517.
[20] M. Himmelhaus, F. Eisert, M. Buck, M. Grunze, *J. Phys. Chem. B* **2000**, *104*, 576 – 584.
[21] a) R. B. Merrifield, *J. Am. Chem. Soc.* **1963**, *85*, 2149 – 2154; b) A. A. Hariri, G. D. Hamblin, Y. Gidi, H. F. Sleiman, G. Cosa, *Nat. Chem.* **2015**, *7*, 295 – 300.
[22] a) Y. Lvov, G. Decher, H. Moehwald, *Langmuir* **1993**, *9*, 481 – 486; b) Y. Lvov, K. Ariga, I. Ichinose, T. Kunitake, *J. Am. Chem. Soc.* **1995**, *117*, 6117 – 6123; c) A. Laschewsky, E. Wischerhoff, S. Denzinger, H. Ringsdorf, A. Delcorte, P. Bertrand, *Chem. Eur. J.* **1997**, *3*, 34 – 38; d) P. T. Hammond, *Adv. Mater.* **2004**, *16*, 1271 – 1293; e) N. Cini, T. Tulun, G. Decher, V. Ball, *J. Am. Chem. Soc.* **2010**, *132*, 8264 – 8265; f) J. J. Richardson, M. Björnmalm, F. Caruso, *Science* **2015**, *348*, 0.

Received: January 29, 2016
Published online: March 17, 2016

  