2020

Gradient Photonic Materials Based on One-Dimensional Polymer Photonic Crystals

Andreas E. Schedl

Irene Howell

James J. Watkins

Hans-Werner Schmidt

Macromolecular Rapid Communications
www.mrc-journal.de

Gradient Photonic Materials Based on One-Dimensional Polymer Photonic Crystals

Andreas E. Schedl, Irene Howell, James J. Watkins, and Hans-Werner Schmidt**

In nature, animals such as chameleons are well-known for the complex color patterns of their skin and the ability to adapt and change the color by manipulating sophisticated photonic crystal systems. Artificial gradient photonic materials are inspired by these color patterns. A concept for the preparation of such materials and their function as tunable mechanochromic materials is presented in this work. The system consists of a 1D polymer photonic crystal on a centimeter scale on top of an elastic poly(dimethylsiloxane) substrate with a gradient in stiffness. In the unstrained state, this system reveals a uniform red reflectance over the entire sample. Upon deformation, a gradient in local strain of the substrate is formed and transferred to the photonic crystal. Depending on the magnitude of this local strain, the thickness of the photonic crystal decreases continuously, resulting in a position-dependent blue shift of the reflectance peak and hence the color in a rainbow-like fashion. Using more sophisticated hard-soft-hard-soft-hard gradient elastomers enables the realization of stripe-like reflectance patterns. Thus, this approach allows for the tunable formation of reflectance gradients and complex reflectance patterns. Envisioned applications are in the field of mechanochromic sensors, telemedicine, smart materials, and metamaterials.

Living organisms with an amazing variety of colors are found in nature. The various coloration effects may arise due to pigments, bioluminescence, or periodic structure.[1] The colors arising due to periodic structure, structural color, exhibit a large variety of color tones and can change color if subjected to external stimuli.[2] In nature, the reflecting colors of butterfly[3] or beetle wings,[4] peacock feathers,[5] tropical fish scales,[6] and the chameleon skin demonstrate nonresponsive and responsive optical phenomena based on structural color.[7] Motivations for such color changes include camouflage, warning, exhibition, and communication.[8]

Fulfilling certain requirements, photonic crystals will give rise to structural color.[9] The principle of photonic crystals was explained by John and Yablonovitch in the late 1980s.[10] It is based on the periodic arrangement (1D, 2D, or 3D) of regularly shaped, mostly transparent materials with different dielectric constants.[11] One of the major characteristics of a photonic crystal is the photonic band gap, which forbids light within a certain wavelength range from propagating within the periodic arrangement.[12] If the photonic band gap is in the visible region, structural color due to Bragg diffraction of the decoupled light is observed. Applications for photonic crystals are found in the fields of sensors,[13] light-emitting diodes,[14] photovoltaics,[15] and lasers.[16]

Responsive photonic crystals can undergo a color change if subjected to external stimuli.[17] A well-known example from nature is the remarkable color shift of chameleon skin that is based on a lattice of guanine nanocrystals embedded in dermal iridophores.[7] Deformation of the skin rapidly alters the spacing of the nanocrystals within the lattice that in turn causes a reversible color change.

A 1D photonic crystal (1DPC)—often also called a Bragg mirror—is the simplest geometry of a photonic crystal and possesses a periodicity in one direction.[11] It consists of alternating layers of high and low refractive index layers, resulting in an enhanced reflection due to constructive interference. Optical properties of 1DPCs depend on the refractive index contrast, the number and thickness of layers, and the angle of incident light. The thickness, and therefore the reflectance of certain wavelengths, can be tuned via the strain.[18] Most publications on responsive photonic crystals are limited to systems that reveal only a discrete color change in response to an external stimulus.[19]

In this work, we demonstrate the preparation and function of a gradient photonic material that reveals a gradient color change upon application of an external stimulus. The composite material consists of a polymer-based 1DPC that is attached on top of an elastomer with a longitudinal stiffness gradient (**Figure 1**). The 1DPC has been designed to reveal a uniform reflectance in the red region of the visible spectrum in the unstrained state. Application of a strain leads to a gradient

A. E. Schedl, Prof. H.-W. Schmidt
Department of Macromolecular Chemistry I
and Bavarian Polymer Institute
University of Bayreuth
Bayreuth 95440, Germany
E-mail: hans-werner.schmidt@uni-bayreuth.de

Dr. I. Howell, Prof. J. J. Watkins
Center for Hierarchical Manufacturing
Department of Polymer Science and Engineering
University of Massachusetts Amherst
120 Governors Drive, Amherst, MA 01003, USA
E-mail: watkins@polysci.umass.edu

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/marc.202000069.

DOI: 10.1002/marc.202000069

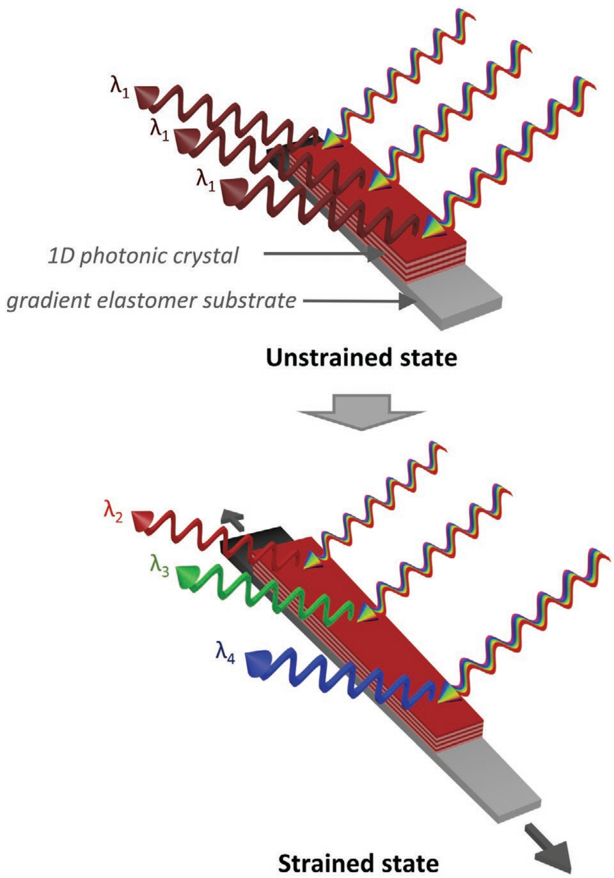

Figure 1. Gradient photonic material with a 1DPC on top of a longitudinal gradient elastomer substrate. The unstrained sample (top) reveals a uniform reflectance at one wavelength over the entire sample surface during illumination with visible light. Application of a strain (bottom) leads to a position-dependent gradient in reflectance along the sample.

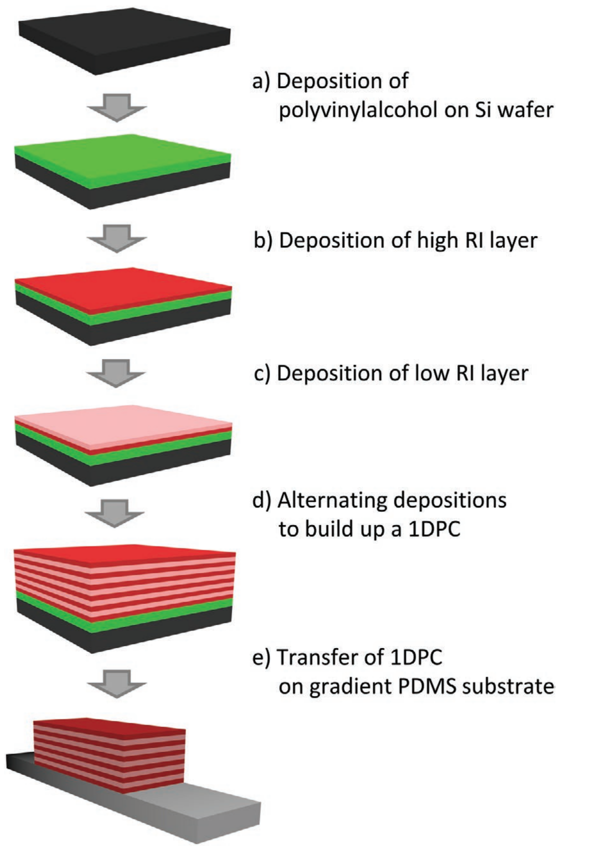

Figure 2. Preparation steps to a gradient photonic material: A) Polyvinyl alcohol is spin coated on top of a silicon wafer. B) A high refractive index layer is spin coated and UV-cured. C) Subsequently, a low refractive index layer is deposited on top and UV-cured. D) The 1DPC is built up by repeating these two steps multiple times. e) Finally, the 1DPC is floated and placed on top of a plasma-activated PDMS substrate with a gradient in stiffness to yield a gradient photonic material.

color shift in the reflectance along the sample. This effect is caused by the stiffness gradient of the substrate that transfers a gradient in local strain to the 1DPC upon deformation. The magnitude of this local strain influences the local thickness of the refractive index layers and hence the magnitude of the local color shift. In this manner, a position-dependent gradient in reflectance with a strain-tunable wavelength range is formed. A strain of 25% yields a rainbow-like gradient in reflectance from red to blue.

To fabricate a gradient photonic material, a strain-tunable 1DPC was prepared in a first step from a photo-curable slide-ring elastomer resin in a manner similar to that of Howell et al. (cf. S1, Supporting Information, for experimental details).[18] The crosslinks in such an elastomer consist of functionalized, figure-of-eight shaped cyclodextrin rings that are freely movable along polyethylene glycol chains.[20] This allows a very homogeneous stress distribution within the elastomer upon loading, since the cross-links can act like pulleys. Additionally, this elastomer system has the potential to be highly filled with nanoparticles, by that different refractive indices can be realized. The 1DPC film was prepared via sequential spincoating and UV-curing of alternating high and low refractive index layers on top of a polyvinylalcohol-coated silicon wafer (**Figure 2**). Polyvinylalcohol was used as a sacrificial layer for the later film transfer. The low refractive index layer consists exclusively of the UV-cured slide-ring elastomer. The high refractive index layer is composed of the slide-ring elastomer that is additionally highly filled with functionalized and well-dispersed zirconium oxide nanocrystals with an average diameter of 6 nm. ZrO_2 is well-known to increase the refractive index of composite materials[21] and was dispersed very well in this resin at a percentage of 70 wt%.

Utilizing this procedure, reversible strain-tunable 1DPCs with defined layer structures can be prepared. An analysis of the cross section of that 1DPC system as well as a cycling analysis at a strain of 10% was reported previously.[18] Ellipsometric measurements revealed thicknesses of 110 nm for the high refractive index layer and 125 nm for the low refractive index layer. Refractive indices at 750 nm were determined as r_{low} = 1.50 and r_{high} = 1.66 that gives a difference in refractive index of 0.16.

The substrate for the gradient photonic material was prepared utilizing a high-precision syringe pump setup (cf. S2, Supporting Information, for a detailed description of the elastomer preparation and characterization). This setup allows the preparation of longitudinal polymer gradient materials.[22] In this study, a poly(dimethylsiloxane) (PDMS) substrate with a gradient in stiffness was prepared from a "hard" and a "soft" silicone resin that differ in the concentration of curing agent. The siloxane/curing agent ratio was 10:1 for the "hard" resin and 25:1 for the "soft" resin. The two silicone resins were mixed with the syringe pump setup and extruded with a flow profile into a moving mold. After cross-linking via thermal curing, substrates with a longitudinal hard-soft gradient in Young's modulus from 0.6 to 1.3 MPa were obtained. The surface of the PDMS elastomer substrate was then activated via O_2 plasma. This step is necessary to ensure an optimal adhesion of the 1DPC on the substrate.

The 1DPC was then transferred to the gradient PDMS substrate (cf. S3, Supporting Information, for a detailed experimental description). For that, both components were immersed in water. After dissolving the sacrificial PVOH layer, the 1DPC floated on the water surface and was transferred to the gradient PDMS substrate. After draining the water and drying, a gradient photonic material was obtained.

In an unstrained state, the entire surface of the 1DPC appears red (**Figure 3**). Reflectance was measured at five different positions (cf. S4, Supporting Information, for experimental description) with distances of 1 cm in the unstrained state. The maximum reflectance peak occurs at 616 ± 5 nm and does not vary significantly over the entire sample surface. Upon stretching to 25%, the intrinsic stiffness gradient causes a gradient in local strain (cf. S2, Supporting Information). This local strain is transferred to the 1DPC, resulting in a rainbow-like gradient color shift of the reflected wavelength. The maximum reflectance peak here is shifted down to 524 ± 5 nm that indicates a color shift of 92 nm compared to the initial reflectance in the unstrained state.

To demonstrate the versatility of our approach, even more complex gradient structures can be realized beside the hard-soft gradient. **Figure 4** depicts a 1DPC attached to a hard-soft-hard-soft-hard gradient PDMS elastomer. The stiffness is also controlled via the siloxane/curing agent ratio of the resins and is 50:1 in the soft parts and 5:1 in the hard parts. The Young's modulus ranges from 0.038 ± 0.004 MPa in the soft part and 2.3 ± 0.1 MPa in the hard part. Reflectance was measured at nine different positions with distances of 0.5 cm in the unstrained state. The maximum of the reflectance peak in the unstrained state occurs at 612 ± 6 nm and is comparable to the hard-soft gradient sample. Straining to 25% leads to a stripe-like appearance. The initial red appearance is shifted towards smaller wavelengths whereby the softer regions reveal a larger color shift than the harder regions.

We have demonstrated a facile preparation of gradient photonic materials consisting of a 1D polymer photonic crystal on a centimeter scale on top of an elastic PDMS substrate with a gradient in stiffness. In the unstrained state, this system reveals a uniform red reflectance over the entire sample. Upon deformation, a gradient in local strain of the substrate is formed and transferred to the photonic crystal. Depending on the magnitude of this local strain, the thickness of the photonic crystal decreases continuously, resulting in a position-dependent blue shift of the reflectance peak and hence the color in a rainbow-like fashion. Using more sophisticated hard-soft-hard-soft-hard gradient elastomers enables the realization of stripe-like reflectance patterns. We envision applications in the field of mechanochromic sensors, telemedicine, smart materials, and metamaterials.

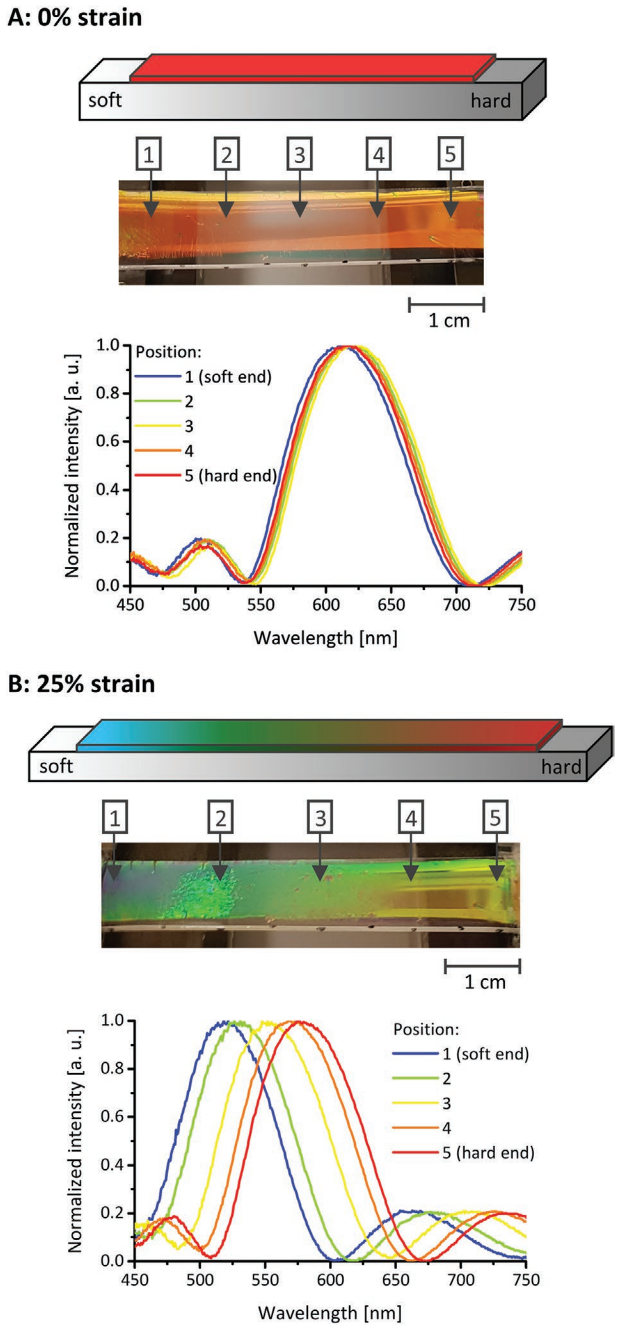

Figure 3. Influence of strain on the reflectance of a 1DPC on PDMS with a hard-soft gradient. A) The unstrained sample (0% strain) reveals a uniform reflectance over the entire surface. B) Upon application of a strain (25%), a gradient in reflectance with smaller wavelengths is obtained. Reflectance spectra were normalized to the maximum peak height for better visualization of the color shift effect.

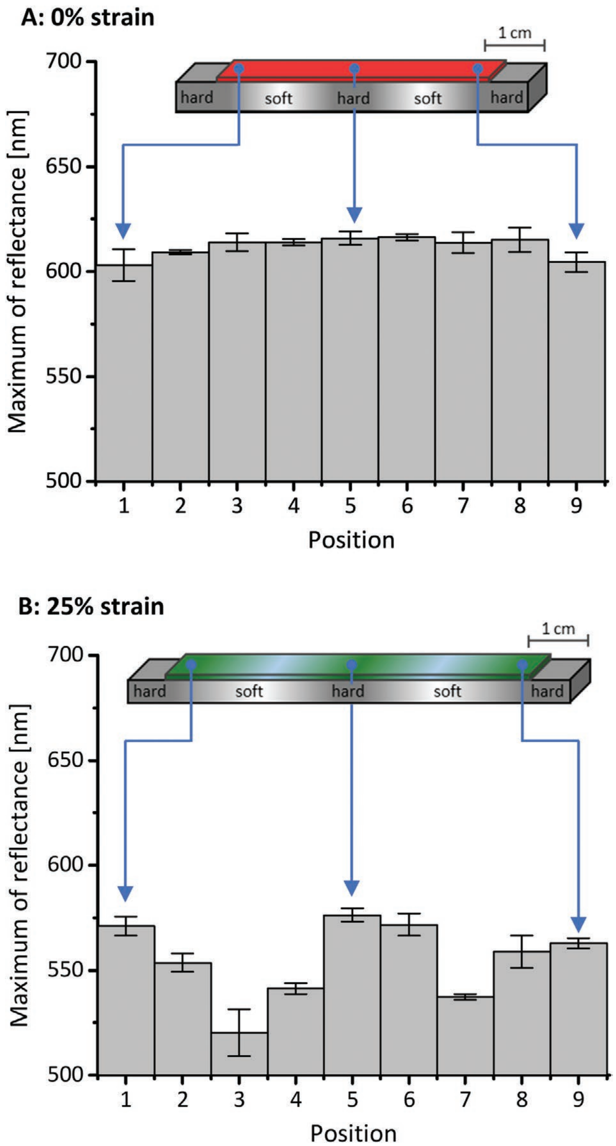

Figure 4. Influence of strain on the reflectance of a 1DPC on PDMS with a hard-soft-hard-soft-hard gradient. A) The unstrained sample reveals a uniform red reflectance over the entire surface with only slight deviations to the edges. B) Upon application of a strain (25%), the 1DPC reveals a gradient reflectance pattern with smaller wavelengths.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Funding of this work was provided by the University of Bayreuth, and the Elite Network of Bavaria (ENB), Macromolecular Science, is gratefully acknowledged. This work was further supported by the NSF Center for Hierarchical Manufacturing at the University of Massachusetts, Amherst (CMMI-1025020) and the Army Research Lab (W911NF-15-2-0026).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

gradient photonic materials, longitudinal gradients, one-dimensional photonic crystals

Received: February 14, 2020
Published online: March 13, 2020

[1] C. L. Booth, *Biol. J. Linn. Soc.* **1990**, *40*, 125.
[2] G. Isapour, M. Lattuada, *Adv. Mater.* **2018**, *30*, 1707069.
[3] L. P. Biro, Z. Balint, K. Kertesz, Z. Vertesy, G. I. Mark, Z. E. Horvath, J. Balazs, D. Mehn, I. Kiricsi, V. Lousse, J.-P. Vigneron, *Phys. Rev. E* **2003**, *67*, 21907.
[4] J. W. Galusha, L. R. Richey, J. S. Gardner, J. N. Cha, M. H. Bartl, *Phys. Rev. E* **2008**, *77*, 50904.
[5] J. Zi, X. Yu, Y. Li, X. Hu, C. Xu, X. Wang, X. Liu, R. Fu, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 12576.
[6] Y. Yue, T. Kurokawa, M. A. Haque, T. Nakajima, T. Nonoyama, X. Li, I. Kajiwara, J. P. Gong, *Nat. Commun.* **2014**, *5*, 4659.
[7] J. Teyssier, S. V. Saenko, D. van der Marel, M. C. Milinkovitch, *Nat. Commun.* **2015**, *6*, 6368.
[8] H. Fudouzi, *Sci. Technol. Adv. Mater.* **2011**, *12*, 064704.
[9] J. Sun, B. Bhushan, J. Tong, *RSC Adv.* **2013**, *3*, 14862.
[10] a) E. Yablonovitch, *Phys. Rev. Lett.* **1987**, *58*, 2059; b) S. John, *Phys. Rev. Lett.* **1987**, *58*, 2486.
[11] C. Fenzl, T. Hirsch, O. S. Wolfbeis, *Angew. Chem., Int. Ed.* **2014**, *53*, 3318.
[12] Z. Lin, Y. Yang, A. Zhang, *Polymer-Engineered Nanostructures for Advanced Energy Applications*, Springer, Cham **2017**.
[13] a) S. A. Asher, V. L. Alexeev, A. V. Goponenko, A. C. Sharma, I. K. Lednev, C. S. Wilcox, D. N. Finegold, *J. Am. Chem. Soc.* **2003**, *125*, 3322; b) D. K. C. Wu, B. T. Kuhlmey, B. J. Eggleton, *Opt. Lett.* **2009**, *34*, 322; c) K. Lee, S. A. Asher, *J. Am. Chem. Soc.* **2000**, *122*, 9534; d) E. Chow, A. Grot, L. W. Mirkarimi, M. Sigalas, G. Girolami, *Opt. Lett.* **2004**, *29*, 1093.
[14] a) T. N. Oder, K. H. Kim, J. Y. Lin, H. X. Jiang, *Appl. Phys. Lett.* **2004**, *84*, 466; b) K. McGroddy, A. David, E. Matioli, M. Iza, S. Nakamura, S. DenBaars, J. S. Speck, C. Weisbuch, E. L. Hu, *Appl. Phys. Lett.* **2008**, *93*, 103502; c) J. J. Wierer, A. David, M. M. Megens, *Nat. Photonics* **2009**, *3*, 163.
[15] A. Chutinan, N. P. Kherani, S. Zukotynski, *Opt. Express* **2009**, *17*, 8871.
[16] H.-G. Park, S.-H. Kim, S.-H. Kwon, Y.-G. Ju, J.-K. Yang, J.-H. Baek, S.-B. Kim, Y.-H. Lee, *Science* **2004**, *305*, 1444.
[17] J. Ge, Y. Yin, *Angew. Chem., Int. Ed.* **2011**, *50*, 1492.
[18] I. R. Howell, C. Li, N. S. Colella, K. Ito, J. J. Watkins, *ACS Appl. Mater. Interfaces* **2015**, *7*, 3641.
[19] a) L. M. Fortes, M. C. Gonçalves, R. M. Almeida, *Opt. Mater.* **2011**, *33*, 408; b) G. H. Lee, T. M. Choi, B. Kim, S. H. Han, J. M. Lee, S.-H. Kim, *ACS Nano* **2017**, *11*, 11350.
[20] K. Ito, *Curr. Opin. Solid State Mater. Sci.* **2010**, *14*, 28.
[21] a) P. Kim, C. Li, R. E. Riman, J. Watkins, *ACS Appl. Mater. Interfaces* **2018**, *10*, 9038; b) D.-P. Song, C. Li, W. Li, J. J. Watkins, *ACS Nano* **2016**, *10*, 1216.
[22] a) K. U. Claussen, T. Scheibel, H.-W. Schmidt, R. Giesa, *Macromol. Mater. Eng.* **2012**, *297*, 938; b) K. U. Claussen, M. Tebbe, R. Giesa, A. Schweikart, A. Fery, H.-W. Schmidt, *RSC Adv.* **2012**, *2*, 10185; c) K. U. Claussen, E. S. Lintz, R. Giesa, H.-W. Schmidt, T. Scheibel, *Macromol. Biosci.* **2013**, *13*, 1396; d) K. U. Claussen, R. Giesa, T. Scheibel, H.-W. Schmidt, *Macromol. Rapid Commun.* **2012**, *33*, 206; e) K. U. Claussen, R. Giesa, H.-W. Schmidt, *Polymer* **2014**, *55*, 29.

