Tailor-Made Polymer Multilayers

*Kerstin Schuh, Oswald Prucker, and Jürgen Rühe**

The fabrication of multilayer assemblies from polymeric compounds is an important tool for precise control of film architecture on the nanoscale. In this report, a general, novel approach for the preparation of well-defined polymeric multilayers is described. To achieve this, sulfonyl-azide group containing polymers are first generated and deposited as thin films onto solid (organic) substrates. Upon thermal activation, the system crosslinks and binds to the substrate via C–H bond insertion. Through step-and-repeat procedures, multilayer assemblies are then generated where all the individual layers are linked to each other. As the assembly process does not require any specific molecular interactions, the described process represents a general strategy to generate tailor-made multilayer surface coatings with wide range of film thickness and composition.

1. Introduction

One means of controlling the interaction of a material with the environment is to deposit thin organic coatings onto its surface. Thin surface-attached coatings are not only interesting from a scientific point of view, but are also crucial for many applications ranging from biological and medical technologies to technologies involved in the generation of optical and electronic devices.[1–6] In the last two decades, the design and construction of polymeric multilayers has emerged as a key means for the preparation of functional materials with tailored architectures and thus represents an important tool to control interfacial properties of a material. The possibility of hosting functional molecules, e.g., inorganic nanoparticles, dyes or biological molecules, without significant alteration of the properties of the coatings represent only one of the prospects of such systems.[3,7–11]

A variety of approaches to preparing polymer multilayers, such as the generation of self-assembled monolayers (SAM),[12,13] the Langmuir–Blodgett-technique,[14,15] and the so-called layer-by-layer (LbL) assembly method,[3,11] has been developed. Thousands of publications concerning generation of polymer multilayers have appeared—with still increasing tendency. Although they have been widely investigated and used for the fabrication of well-defined organic multilayers, the described methods have some inherent limitations. For example, Langmuir–Blodgett deposition requires complex equipment, very stringent deposition conditions, has restrictions concerning substrate size and topology and may only be used for molecules with a rather limited spectrum of compositions[3,6] The generation of self-assembled monolayers usually has even stricter limitations concerning the spectrum of molecules and substrates which can be employed. It is mostly restricted to inorganic substrates and highly reactive groups such as chlorosilyl moieties are required for efficient surface attachment. On the other side many functional groups such as amine groups or alcohols do not tolerate the presence of such groups.[4,6]

The LbL method has generated considerable scientific interest in recent years, as it has become a convenient and versatile method for the fabrication of polymer multi-layers. In this approach, film assembly depends on specific interactions of the molecules involved, mostly ionic interactions between polyelectrolytes[3] though, in fewer cases, hydrogen-bonding or other interactions[16] are also used for multilayer build-up. In the layer-by-layer process, the substrate is exposed alternately to solutions containing positively or negatively charged polyelectrolytes. It is usually assumed that, upon immersion polyelectrolyte molecules from the solution adsorb to the oppositely charged substrate in such a way that some overcompensation occurs, even after washing of the substrate, so that the surface of the substrate remains constantly charged. When this process is repeated many times multilayer stacks can be obtained.

Although the process is very simple and versatile, the deposition mechanism of the layers reduces the spectrum of polymers which might be used to the class of polyelectrolytes. Some inherent problems of this method are that the adjacent layers typically intermix quite strongly, which limits the possibility for superlattice build-up, and that the layers are typically not strongly swollen, which reduces the accessibility of groups residing in the interior of the films.[3] Under harsh solvent conditions, such as high or low pH or high salt concentration, disassembly might occur since the assembly process is charge-driven.[17–19]

To overcome these drawbacks extensive research efforts have been undertaken on the stabilization of such films, mostly through the establishment of covalent bonds between the layers. These include, for example, subsequent photo- or thermal crosslinking as well as chemical reactions.[20–23] Alternatively, polymer multilayers fabricated by direct covalent assembly of functional polymers or small compounds with typical chemical reactions such as esterifications, amine-isocyanate and "click"-chemistry[16,24–26] have been demonstrated.

Dr. K. Schuh, Dr. O. Prucker, Prof. J. Rühe
Department of Microsystems Engineering (IMTEK)
University of Freiburg
Georges-Köhler-Allee 103, 79110 Freiburg, Germany
E-mail: ruehe@imtek.de

DOI: 10.1002/adfm.201300846

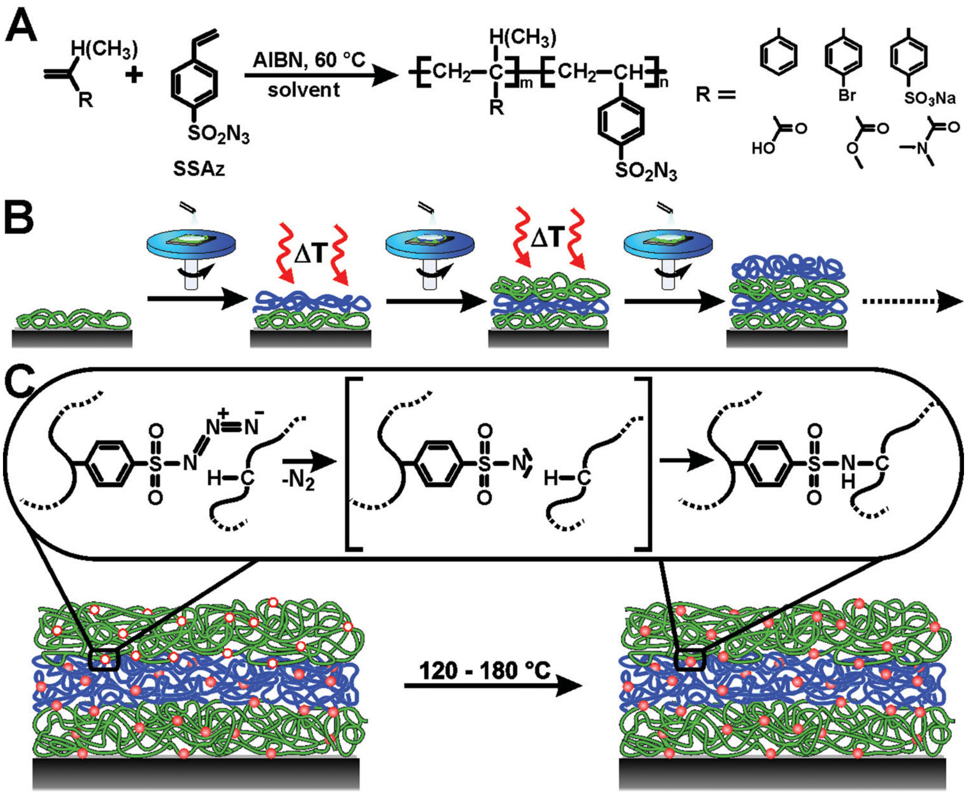

Figure 1. Schematic description of the major steps for multilayer preparation by alternating (spin)coating and thermal cross-linking. A) Synthesis of polymers with sulfonylazide groups (AIBN = Azobisisobutyronitrile. B) Multilayer formation process. C) Internal crosslinking and interconnection of the polymer layers. After heating and the loss of nitrogen from sulfonyl azide groups, a nitrene is formed, which inserts into adjacent C–H– bonds so that the individual layers become crosslinked and attached to the layer below.

Most of these approaches are effective and improve the stability of the layers quite strongly. However, they are often restricted to certain classes of molecules, which use specific interactions to link the multilayers together.

Finally, the film thickness of the individual layers is restricted to typically about 0.5 nm per layer. Some control of the thickness is possible through influence of the environment, such as the pH-value or salt concentration of the system.[11,27] Generation of systems with film thicknesses approaching the micrometer regime thus typically requires several hundred deposition cycles. Therefore, the development of simple and variable strategies for the fabrication of polymer multilayers still posses significant technological challenges.

The approach for the generation of covalently bound polymer multilayers presented here is based on surface-attached polymer networks generated through thermal crosslinking of sulfonyl azide group containing polymers via C–H bond insertion,[28] **Figure 1**A). Similar strategies are available for photochemical crosslinking and surface-attachment.[29–31] The general method is shown in Figure 1B. Once the first surface-attached polymer network layer is generated, a second polymer is spin-coated from solution. During the heating process, crosslinking of the polymer occurs, together with a simultaneous attachment of the polymer layer to the underlying layer. The layer thickness of every layer depends only on the deposition conditions, such as the concentration of the polymer solution and the details of the coating process (here spin or dip casting), although other methods are also possible. After completion of the process, an arbitrary number of further layers, can be attached in the same manner. The number of layers and the thickness of each layer can be arbitrarily chosen and tailored for specific applications.

Network formation is induced by thermal decomposition of the sulfonyl azide moieties contained in the polymers, followed by an insertion reaction in adjacent C–H bonds (Figure 1C). If the groups are located on the interface of the polymer layers, attachment to the layer beneath occurs; otherwise, an internal crosslinking takes place. The mechanism of such a C–H bond insertion has been well described.[28,32] Loss of nitrogen upon heating leads to formation of a nitrene, and the insertion reaction leads to sulfonyl amide groups as crosslinks.[28,32] In contrast to other crosslinking methods, where two functional groups react with each other,[33] such a strategy does not require any functional group nearby to form a crosslink. Thus, already a very small concentration of functional groups is sufficient yield to a stable network and the physical properties of the bulk material are not strongly affected. The covalent attachment of the first layer to the substrate below, was accomplished by formation of a self-assembled monolayer of an appropriate silane, which provides many C–H groups as potential binding partners for C–H bond insertion.[28] We are aware of the fact that such a crosslinking of sulfonyl azide groups also occurs by UV-illumination, but report here exclusively on the thermal process.

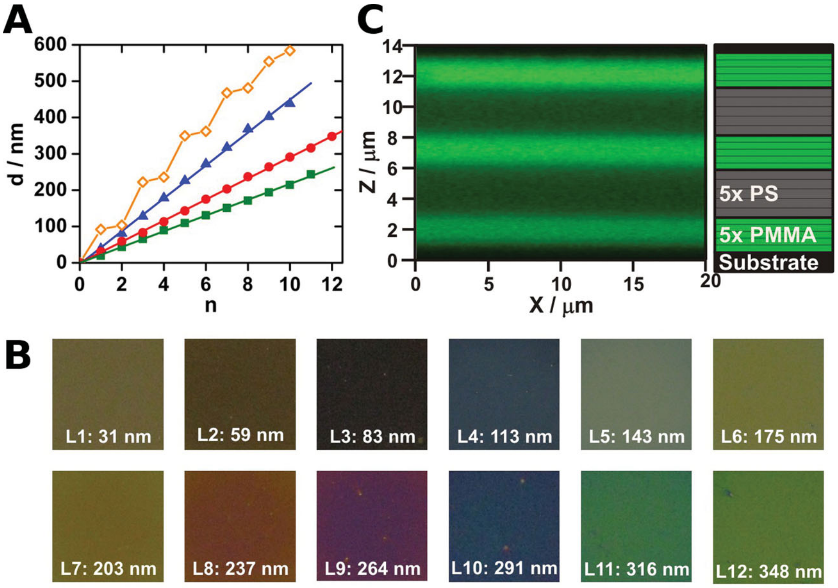

Figure 2. AB-Multilayer stacks from alternating PMMA and PS layers. A) Total film thickness d as a function of the number of layers n; Film thicknesses of the individual layers d_{av}: □: PMMA: d_{av} = 101 nm, PS: d_{av} = 16 nm, ▲: d_{av} = 45 nm ●: d_{av} = 29 nm, ■ d_{av} = 21 nm; the concentrations during film preparation are given in the Supporting Information Table S2. B) Photographs of PMMA-PS Multilayers (from Graph ● in Figure 2A). Homogeneous and smooth surfaces are obtained, although all polymers are spin-coated from the same solvent. C) Micrographs obtained by confocal microscopy of alternating layers consisting of PMMA (modified with Rhodamine as a fluorescence label) and non-fluorescent PS. The interface of the single layers in Z-direction can clearly be observed. Each visible layer consists of five individual PMMA (c = 40 mg/mL dioxane) and five PS (c = 100 mg/mL toluene) layers. Azide contents of the polymers and experimental details of the layer assembly are listed in the Supporting Information Table S2.

The sulfonyl azide groups are incorporated into the polymer during standard free radical copolymerization of standard monomers with styrene sulfonyl azide (SSAz), which allows to modify a variety of different polymers with sulfonyl azide groups and to tune the density of the crosslinker only by the copolymerization composition (Figure 1A). The thus obtained copolymers used for multilayer preparation are very versatile concerning their chemical and physical properties. The thermally labile groups can be incorporated into hydrophobic copolymers such as poly(styrene) (PS), poly(methyl methacrylate) (PMMA) or halogenated poly(4-bromostyrene) as well as into hydrophilic poly(*N*,*N*-dimethyl acrylamide) (PDMAA), poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA) and poly(styrene sulfonate) (PSS).

Due to the insolubility of the crosslinked single layers, there is almost no restriction in the type of solvents used in the assembling process for the approach presented here. Therefore, a wide spectrum of different compositions can be realized. An assembly of an AB-multilayer generated from alternating PS and PMMA layers is depicted in **Figure 2**A. Both polymers were spin-coated from toluene and crosslinked at 160 °C for 30 min. Lower temperatures can be used, albeit at the expense of increased crosslinking time.[28] Depending on the polymer concentration, multilayers with different thicknesses of the individual layers (Supporting Information Table S2) were obtained. By stacking layers with identical layer thickness on top of each other, a linear increase of the total thickness is obtained (Figure 2A) However, a gradual increase of the thickness of the AB-multilayer system can also be achieved by gradually changing the concentration of the polymers (Figure 2A). Although both polymers were coated from the same solvent, we obtained homogenous and smooth multilayer stacks as is seen in the photographs of a PS-PMMA-multilayer-assembly with an average film thickness of 29 nm in Figure 2B. Note, that any deviations in the film thickness would be directly visible in the micrographs as the interference colors are quite sensitive to such variations. The assembly of PS-PMMA-multilayers was also examined by confocal microscopy. For this, we synthesized PMMA-SSAz polymers incorporating a fluorescent Rhodamine-group and subsequently assembled them with non-fluorescing PS-SSAz into a multilayer stack. To obtain an adequate resolution, film thicknesses of each polymer was chosen to be >1 µm. To this, five PMMA-layers were deposited through spin-coating and thermally induced crosslinking onto each other (40 mg/mL dioxane,) followed by the deposition of five PS-layers (100 mg/mL toluene). The resulting confocal micrograph of these layers clearly shows the existence of the superlattice. The layer thicknesses determined with the microscope agree with the values obtained by profilometry (Supporting Information Table S3).

We have extended the preparation of AB-polymer multilayers to other polymer systems (**Figure 3**). Multilayers consisting of one hydrophilic and one hydrophobic polymer (PMMA and PMAA, Figure 3A), two hydrophilic polymers (PDMMA and PMAA, Figure 3B) and two negatively charged polymers (PMAA and PSS, Figure 3C) were assembled. As for the hydrophobic PMMA-PS multilayers, a linear increase of the film thickness is obtained for all three cases, when appropriate concentrations were chosen, but other superlattices can also be realized by adjusting the polymer concentration (Figure 3C). It should be noted that PMAA-PSS multilayers (10 layers, d_{av} = 44 nm) are stable, even under rather harsh conditions, such as when the assemblies are exposed to aqueous solutions with high or low pH-value, or solutions having a high salt concentration (Supporting Information Figure S1).

The described approach for multilayer preparation is not restricted to AB-multilayer systems since no special interactions between the polymers are necessary to connect the layers. Thus, a broad range of possible multilayer arrangements is conceivable. To demonstrate this, we prepared a sample with eight different polymers assembled onto each other. The stacks were prepared via sequential dip coating and crosslinking of the respective azide containing polymers. A photograph of a sample prepared in this manner is shown in **Figure 4**. Here the depth of immersion is gradually decreased from layer to layer, so that terrace-like structures with step-wise varying film

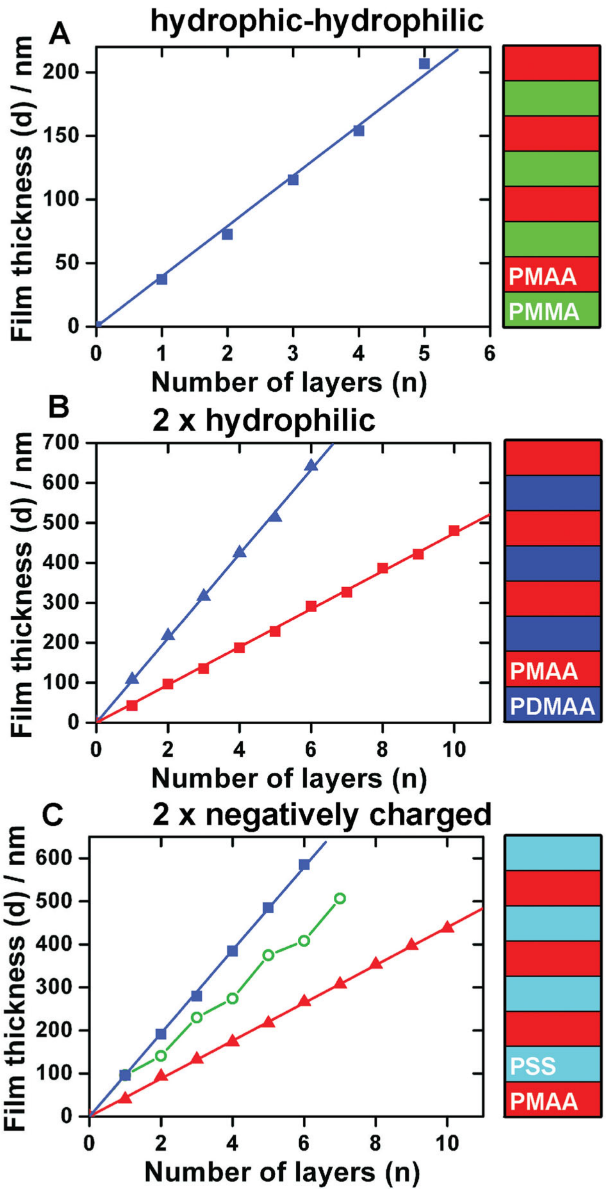

Figure 3. Film thickness as a function of the number of layers from different alternating AB-multilayers. A) AB-multilayer-assembly of one hydrophobic (PMMA) and one hydrophilic polymer (PMAA). The average film thickness obtained from the slope is $d_{av} = 40$ nm. B) AB-multilayers of two hydrophilic polymers. (PDMAA and PMAA) (▲) d_{av} = 106 nm, (■)d_{av} = 47 nm. C) Alternating AB-multilayer assembly of two negatively charged polymers (PMAA and PSS). (■) d_{av} = 97 nm, (○) d_{av}(PMAA) = 94 nm and d_{av}(PSS) = 44 nm, (▲) d_{av} = 44 nm. Azide contents and experimental details are listed in the Supporting Information Table S4.

thickness are obtained, which can be easily identified by the corresponding interference colors. The different polymers are also shown in the picture. In this system, interfaces between two hydrophobic (PS-PSBr), between a hydrophobic and a hydrophilic polymer (PSBr-PDMAA; PDMAA-PMMA, PMMA-PMAA) and between a hydrophilic neutral and a charged polymer are generated on one single sample, demonstrating the versatility of the system.

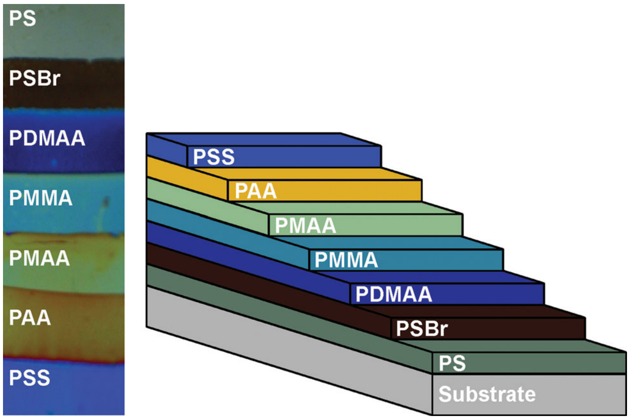

Figure 4. Photograph and schematic depiction of a silicon wafer prepared with a stepped multilayer of seven different polymers, with PS as the lowest layer and PSS as the upper layer. The layers were prepared by sequential dip-coating and thermal crosslinking, where the immersion depth of the wafer was reduced from layer to layer. Azide contents of the polymers and further experimental details are given in Supporting Information Table S5.

In summary, layer deposition followed by thermally-induced C–H insertion reactions represents a simple method for the preparation of polymer multilayers through consecutive deposition of surface-attached polymer networks. This technique does not require specific molecular interactions or chemical reactions for multilayer fabrication and a wide spectrum of polymers can be stacked onto each other. As film thickness and composition are easily controlled by the coating process, tailor-made polymer multilayers can be obtained. The multilayer assemblies are very stable, since the substrate and polymer network layers, as well as all subsequent layers are covalently connected to each other, and the obtained multilayer stacks are robust and survive even harsh conditions, such as extended solvent exposure or high ionic strength solutions.

Supporting Information

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

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft through the PhD-program GR1322 ("Micro Energy Harvesting"). The authors gratefully thank Dr. Roland Nitschke from the Center for Systems Biology (ZBSA) Freiburg for taking the confocal microscopy image and Dr. Andreas Zillessen for the photograph of the sample in Figure 4. Adriana Willm is acknowledged for technical assistance.

Received: March 8, 2013
Revised: April 16, 2013
Published online: July 1, 2013

---

[1] A. Ulman, *Ultrathin Oganic Flms,* Elsevier Academic, San Diego, CA **1991**.

[2] *Biomaterial Science: An introduction to Materials in Medicine* (Eds: B. D. Ratner, A. S. Hoffman), 2nd ed., Elsevier Academic, San Diego, CA, **2004**.

[3] G. Decher, *Science* **1997**, *277*, 1232.
[4] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103.
[5] S. Onclin, B. J. Ravoo, D. N. Reinhoudt, *Angew. Chem. Int. Ed.* **2005**, *44*, 6282.
[6] J. H. Fendler, *Chem. Mater.* **1996**, *8*, 1616.
[7] P. Bertrand, A. Jonas, A. Laschewsky, R. Legras, *Macromol. Rapid Commun.* **2000**, *21*, 319.
[8] F. Caruso, *Adv. Mater.* **2001**, *13*, 11.
[9] P. T. Hammond, *Adv. Mater.* **2004**, *16*, 1271.
[10] D. M. Lynn, *Adv. Mater.* **2007**, *19*, 4118.
[11] *Multilayer Thin Films* (Eds: G. Decher, J. B. Schlenoff), Wiley, Weinheim **2003**.
[12] G. Cao, H. G. Hong, T. E. Mallouk, *Acc. Chem. Res.* **1995**, *25*, 420.
[13] W. T. S. Huck, A. Stroock, G. Whitesides, *Angew. Chem. Int. Ed.* **2000**, *39*, 1058.
[14] H. Kuhn, D. Möbius, *Angew. Chem. Int. Ed.* **1971**, *10*, 620.
[15] A. R. Esker, C. Mengel, G. Wegner, *Science* **1998**, *280*, 892.
[16] J. F. Quinn, A. P. R. Johnston, G. K. Such, A. N. Zelikin, F. Caruso, *Chem. Soc. Rev.* **2007**, *36*, 707.
[17] G. Mao, Y. Tsao, M. Tirrell, H. T. Davis, V. Hessel, H. Ringsdorf, *Langmuir* **1995**, *11*, 942.
[18] E. Kharlampieva, S. A. Sukhishvili, *Macromolecules* **2003**, *36*, 9950.
[19] J. Cho, F. Caruso, *Macromolecules* **2003**, *36*, 2845.
[20] M.-K. Park, S. Deng, R. C. Advincula, *J. Am. Chem. Soc.* **2004**, *126*, 13723.
[21] G. Wu, F. Shi, Z. Wang, Z. Liu, X. Zhang, *Langmuir* **2009**, *25*, 2979.
[22] J. J. Harris, P. M. DeRose, M. L. Bruening, *J. Am. Chem. Soc.* **1999**, *121*, 1978.
[23] S. Y. Yang, D. Lee, R. E. Cohen, M. F. Rubner, *Langmuir* **2004**, *20*, 5978.
[24] J. S. Major, G. J. Blanchard, *Langmuir* **2001**, *17*, 1163.
[25] P. Kohli, G. J. Blanchard, *Langmuir* **2000**, *16*, 4655.
[26] G. K. Such, J. F. Quinn, A. Quinn, E. Tjipto, F. Caruso, *J. Am. Chem. Soc* **2006**, *128*, 9318.
[27] S. T. Dubas, J. B. Schlenoff, *Macromolecules* **1999**, *32*, 8153.
[28] K. Schuh, O. Prucker, J. Rühe, *Macromolecules* **2008**, *41*, 9284.
[29] O. Prucker, C. A. Naumann, J. Rühe, W. Knoll, C. W. Frank, *J. Am. Chem. Soc.* **1999**, *121*, 8766.
[30] G. K. Raghumaran, K. Schuh, O. Prucker, J. Rühe, *Langmuir* **2010**, *26*, 769.
[31] R. Toomey, D. Freidank, J. Rühe, *Macromolecules* **2004**, *37*, 882.
[32] J. K. Jorgensen, E. Ommundsen, A. Stori, K. Redford, *Polymer* **2005**, *46*, 12073.
[33] D. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker, T. P. Russel, *Science* **2005**, *308*, 236.