Multifunctional Block Copolymers Based on Styrene Derivatives

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Summary: Several functionalized block copolymers based on polystyrene with considerably different block polarities have been prepared using controlled radical polymerization techniques (NMRP, RAFT). The target polymers, having hydroxy, alkyne or amine functionalities in at least one block were characterized by techniques like NMR, GPC and DSC to verify structure, molar masses, molecular weight distributions and thermal properties. With the example of partly protected hydroxystyrene based block copolymers, regular structured film surfaces could be created and were shown to be converted into homogeneous polymer surfaces by applying heat as external trigger. With alkyne functionalized block copolymers, modifications with objects of varying sizes were carried out, employing the 1,3-dipolar cycloaddition of alkynes with azides. Once again, the "click approach" proved its high efficiency as the reactions proceeded completely even with objects of high steric demand. Studying the influence on the macromolecular architecture, we found a strong alteration of glass transition temperatures for the compared polymer materials, indicating a bracing of the chains due to steric hindrance between the bulky side objects.

Keywords: block copolymers; controlled radical polymerization; 1,3-dipolar cycloaddition; NMRP; RAFT

Introduction

The application of a polymeric material in micro and nanotechnology is determined by its functionality as well as the molecular architecture. Thus, control over both enables the tailoring of a macromolecule with respect to its utilization as a functional material.

For that, powerful and precise synthetic tools are required. In this context, controlled radical polymerization techniques like NMRP[1], ATRP[2] and RAFT[3] have been established, particularly for the synthesis of functionalized polymers.

These methods offer a high control over molecular architecture as the molar masses are adjustable and products of low polydispersity are obtained. Furthermore, the synthesis of block copolymers is possible by sequential monomer addition as the active end groups of the polymer chains are retained. As block copolymers are capable to self assemble into regular structures of mesoscopic dimensions, the materials have found attention in nanoscience and nanotechnology,[4–6] i.e. for utilization as nanotemplates in block copolymer lithography.[7,8]

By applying different methods, control over alignment and orientation of self assembled domains in block copolymer films can be achieved.[9–11]

In order to fulfil the demands on polymer materials with respect to functionality, the incorporation of specific functional groups into the polymer structure is

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needed. Thus, area selective provision of functionalities for specific interactions in nanoscopic dimensions by combining self assembly with functionality is a major challenge but will open up further perspectives for applications in nanotechnology.[12,13] For that, the development of functionalized block copolymers which allow microphase segregation into regular nanostructures in thin films is required. In this concern, the combination of controlled radical polymerization with the 1,3-dipolar cycloaddition of alkynes with azides constitutes a powerful tool for the efficient modification of a macromolecule.[14] Thus, it facilitates both the decoration with functional groups and control over size and shape of the polymer chains.

Herein, we report on the synthesis of styrene based block copolymers having varying functionalities and consisting of different polar blocks. The possibility to modulate the macromolecular architecture and the morphology of self assembled block copolymer films is studied.

Results and Discussion

One synthetic strategy towards functionalized block copolymers showing a strong tendency to microphase segregation is based on the use of polyhydroxystyrene derivates. The synthesis of hydroxystyrene based block copolymers with orthogonally protected blocks enables the preparation of structures with substantially different block polarities by selective deprotection of one block.[15]

For the preparation of the precursor block copolymers, the nitroxide mediated radical polymerization (NMRP) was used, resulting in well defined materials of narrow molecular weight distributions. Figure 1 displays the synthesis of the orthogonally protected precursor block copolymer **1** and the selective cleavage of the *tert.*-butyl-dimethylsilyl (TBDMS) protecting groups with tetrabutyl ammoniumfluoride (TBAF), resulting in the partly *tert.*-butyl (TBU) protected block copolymer **2**.

As shown in Figure 2, the protected block copolymers (**1**) could be obtained with narrow molar mass distributions. The DSC curve of the partly protected polymer **2** (lower curve) shows two separate glass transitions denoting microphase segregation in the bulk material. The comparison with the DSC trace of a poly-TBU-oxystyrene homopolymer (**P(TBU-OSt)**, upper curve) points out that the glass

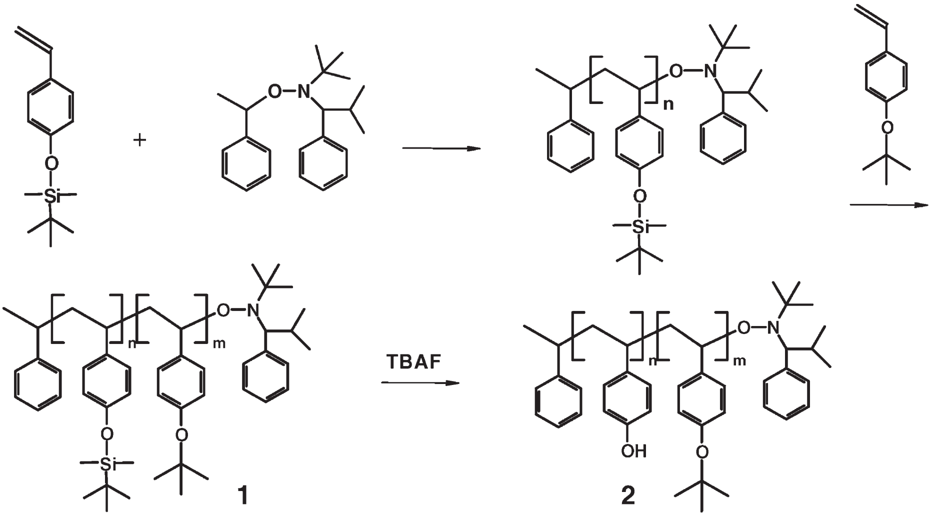


Figure 1.
Synthetic pathway for the synthesis of a partly TBU protected block copolymer.

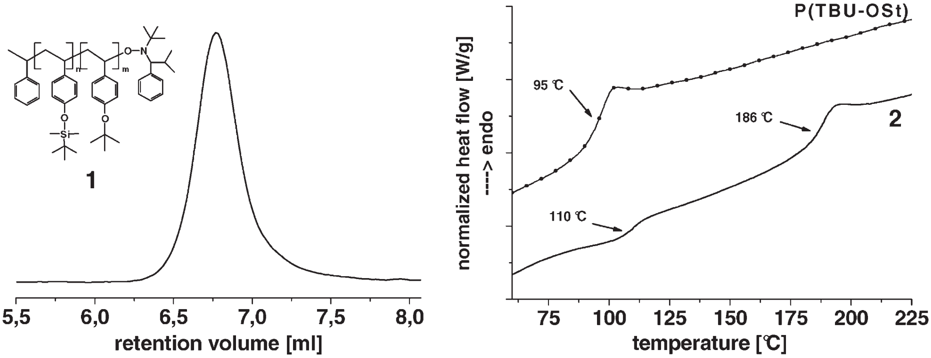


Figure 2.
GPC trace of a sample of polymer **1** (M_n: 40500 g/mol, PDI: 1.21), DSC curves of poly-TBU-oxystyrene (**P(TBU-OSt)**) and of polymer **2**.[15]

transition at 186 °C is attributed to the polyhydroxystyrene block.

Moreover, the design of partly BOC protected polyhydroxystyrene block copolymers was intended. For that purpose a sequence of quantitative and orthogonal polymer analogous reactions was applied to yield the target polymers consisting of an unprotected 4-hydroxystyrene block and a *tert*-butoxycarbonyl (BOC) or a *tert*-butyl (TBU) protected block, Figure 3. Starting from block copolymer **3**, the acetoxy groups in one block were selectively removed by hydrazine, followed by the protection of the

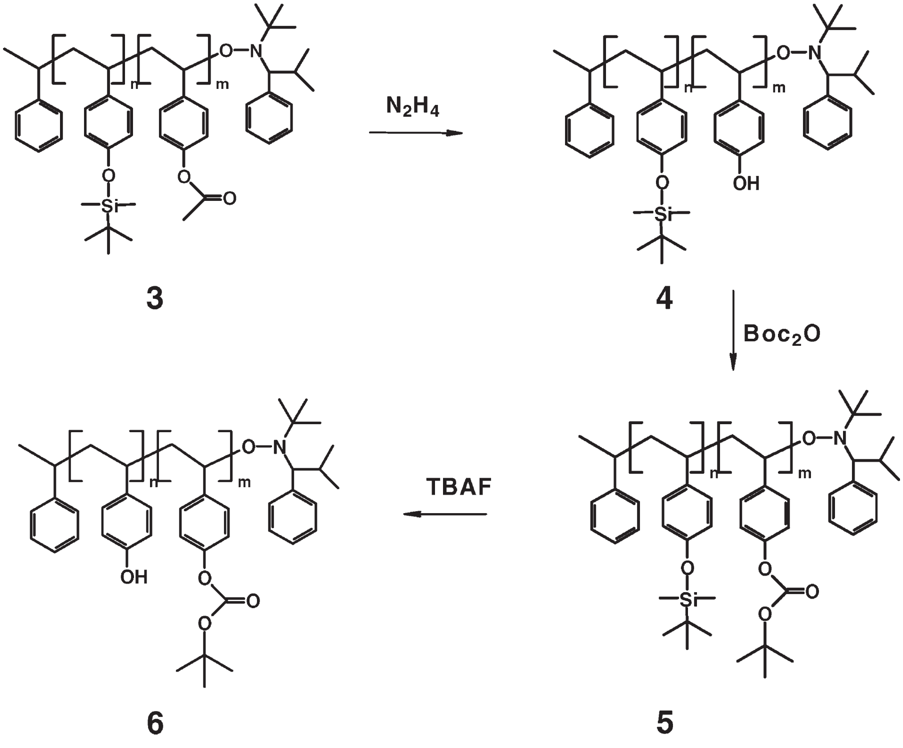
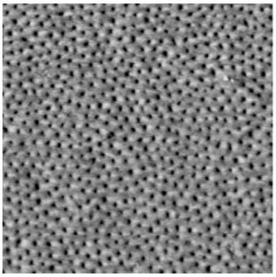
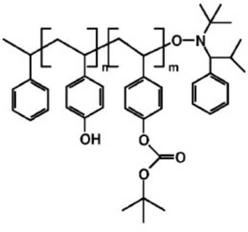


Figure 3.
Synthetic strategy for the preparation of the partly BOC protected block copolymer **6**.[15]





6

Block ratio 1 : 9

M_n = 60700 g/mol
PD (precursor) = 1.2

Figure 4.
AFM phase image of a block copolymer film prepared of **6** by dip coating, film thickness: 20 nm, distance of domains: 30 nm.[16]

phenol by BOC-anhydride. The subsequent cleavage of the TBDMS – protecting groups led to the aimed partly BOC protected polymer structures.[15]

To verify the absence of uncontrolled side reactions, GPC measurements of the protected products (**5**) were conducted. It could be found, that the modification steps did not affect the molar mass distribution adversely, thus, we can presume that no appreciable side reactions took place during the polymer analogous conversions.

The partly protected polymer systems were demonstrated to exhibit pronounced phase segregation in thin films, pictured in Figure 4.[16]

The block copolymer films, produced by dip coating, self assemble into regular structures of nanometer dimensions.[16] In the example shown in Figure 4, the formed structures can be interpreted as polyhydroxystyrene spheres within a poly-BOC-oxystyrene matrix.

By heating the structured films to 190 degrees for about 1 hour, the BOC protecting groups of the second polymer block were completely cleaved off according to the equation displayed in Figure 5.

In this way, a polyhydroxystyrene homopolymer is formed and as a result the surface structure disappears.[16] Thus, by this approach we were able to create switchable surfaces with respect to the surface morphology by applying heat as external trigger. As the BOC group is also cleavable by UV light (using a photo acid generator), a laterally selective removal can be realized by irradiation resulting in defined areas with and without a self assembled structure. This issue is actually studied in our group.

In order to improve the versatility of such polymer systems, hydroxystyrene based block copolymers containing alkyne units in one block, available for the subsequent connection of different objects were prepared.[17] Figure 6 shows an example for the synthesis of an alkyne functionalized block copolymer consisting of two blocks of considerably different polarities, starting with NMRP macroinitiator **7**.

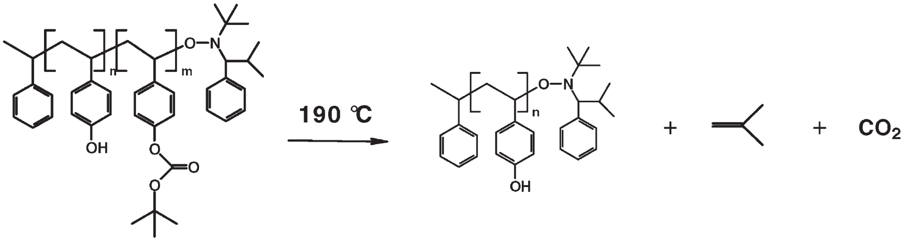


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Figure 5.
Formation of polyhydroxystyrene starting from block copolymer **6**.

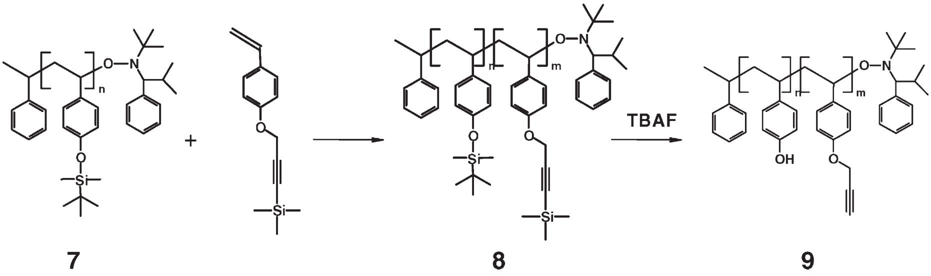


Figure 6.
Reaction scheme for the synthesis of block copolymer **9**.

GPC measurements of the protected polymers showed again symmetrical and narrowly distributed curves. Figure 7 displays the GPC trace of a sample of polymer structure **8**. The appearance of two separate glass transition temperatures (Tg) in the DSC curve of **9** indicates a micro phase segregation within the bulk material, which is attributed to the incompatibility between the two polymer blocks of different polarity.

Employing the Cu(I) catalyzed 1,3 dipolar cycloaddition of alkynes with azides, substances of varying sizes have been attached at the alkyne functionalized polymer block.[17] Hereby, even with molecules of high steric demand, the reactions proceeded with very high conversions, enabling highly efficient modifications of the polymer backbone. Figure 8 displays the scheme for the polymer analogous connection of 1-adamantane azide at the alkyne block of the depicted block copolymer **10**. The reaction was conducted at 50 °C for 48 hours to give complete conversion.

For the evaluation to which extent the decoration of a respective polymer chain with the bulky adamantane units influences the glass transition temperature of the material, model experiments were conducted, in which a polypropargyl oxystyrene homopolymer of a low molecular weight (4400 g/mol) was converted with the adamantane azide units. The comparison of the DSC curves (see Figure 9) reveals dramatically changed thermal properties of the adamantane modified product, as the Tg increased from 54 to 168 degrees. We attribute this fact to a bracing of the adressed polymer block, induced by the sterically demanding adamantane units which push off themselves. The steric hindrance between the bulky molecules

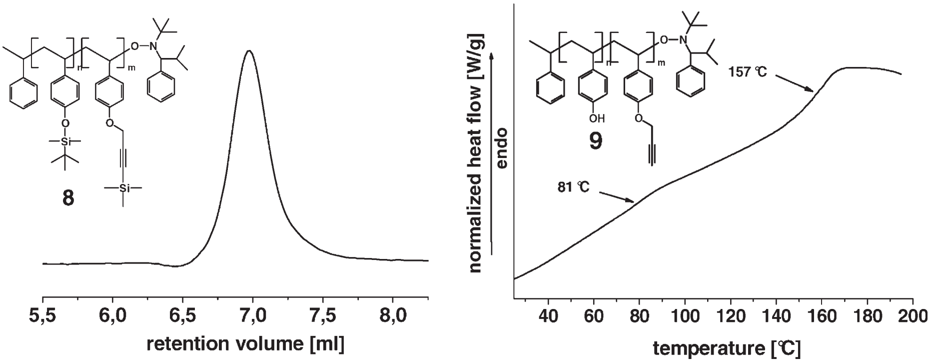
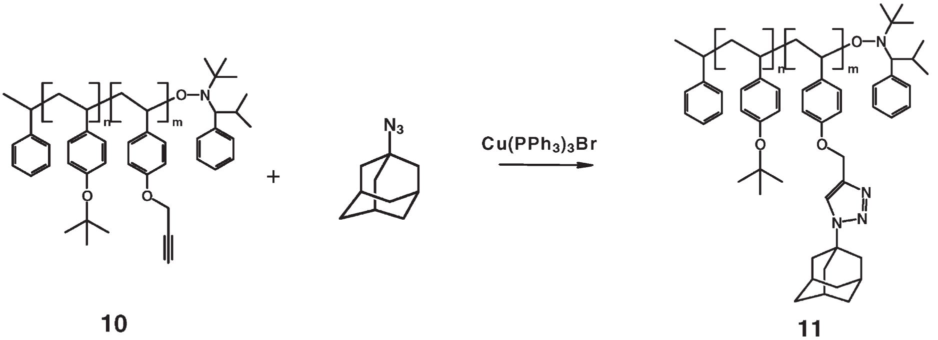


Figure 7.
GPC trace of a sample of the silyl protected polymer **8** (M_n: 20500 g/mol, PDI: 1.20) and the DSC curve of the deprotected product **9**.[17]



10

11

Figure 8.
Attachment of 1-adamantane azide at the alkyne block of block copolymer **10**.

forces the polymer chains to stretch themselves. Thus, the modified block becomes less flexible resulting in a higher Tg.

A similar behavior was observed for the adamantane modified block copolymer **11** (Figure 8).[17] Currently we are studying the attachment of dendritic units of different generations at the alkyne precursor block copolymers. By examining the resulting polymer systems as thin films, we are verifying how the incorporation of these objects influences the shape of the addressed polymer block and in consequence the film morphology.

By introducing additional epoxy anchor groups into the described alkyne containing polymers, thin films of the samples can be covalently attached to silicon wafer surfaces allowing subsequent film functionalization in liquid media. We could prove that click chemistry can then be successfully carried out for postmodification of the immobilized films.[18]

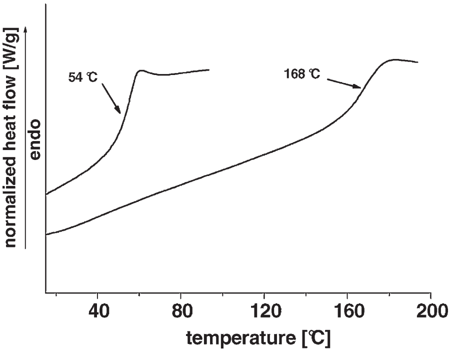


Figure 9.
DSC curves of a polypropargyl oxystyrene homopolymer (upper curve) and of the product after conversion with adamantane azide (lower curve).[17]

In a further approach, amino functionalized block copolymers have been prepared via NMRP and RAFT. Figure 10 displays the polymerization sequences that were carried out to obtain the BOC protected versions (**12** and **13**) of the target block copolymers, employing NMRP for **12** and RAFT polymerization for **13**. Products of adjustable molar masses and narrow molecular weight distributions were obtained.

The protecting groups were cleaved off by aqueous hydrochloric acid resulting in the hydrochloride structures of the amino groups. For the block copolymer **13**, the deprotection of the functional block could also be accomplished by heating the material to about 220 °C, whereby the free amino functions are released. Amino functionalized block copolymers of this architecture are utilizable for strong interactions with gold coated surfaces or gold nanoparticles but also for the stabilization of amonophilic nanoparticles like nitrides and a variety of further specific interactions and reactions. Thin films of the block copolymers have been produced and are presently studied regarding the formation of nanostructures by self assembly of the different blocks.

Furthermore our interest was focused on block copolymer structures with photosen-

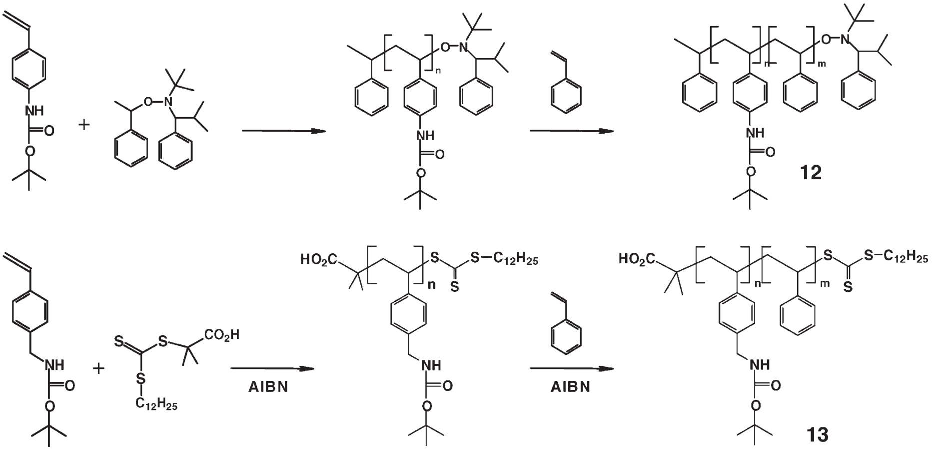
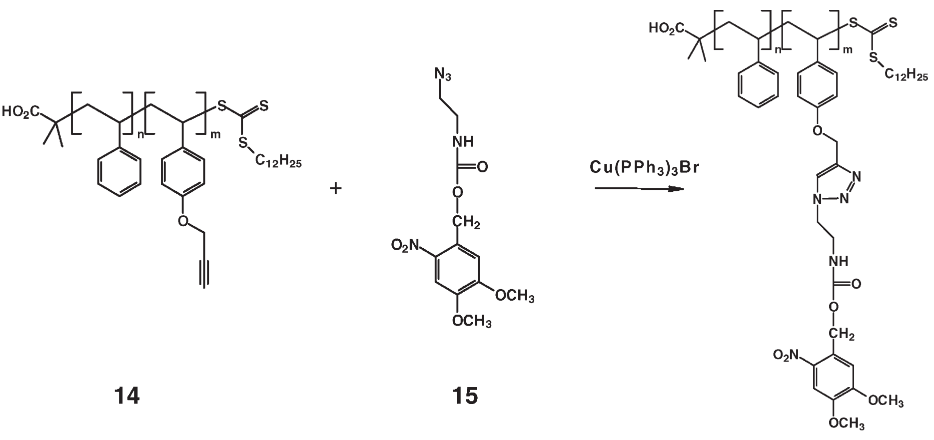


Figure 10.
Synthesis of amino functionalized block copolymers **12** and **13**.

sitive protected amino groups present in one block. As we did not succeed in the polymer analogue protection of the available amino functions by established reactions, we have applied the 1,3-dipolar cycloaddition of alkynes with azides. In a previous work we have already demonstrated the versatility of the "click approach" in modifying alkyne containing polymer backbones by functional units like photosensitive groups or different anchor units.[19]

As displayed in Figure 11, the synthetic strategy involves the modification of the polymer by attachment of a functional unit including also the introduction of an amine functionality protected by the nitroveratryloxycarbonyl (NVOC) – group. The reaction was accomplished at room temperature within 12 hours with a high conversion (96%). The NVOC group is cleavable by UV light of about 350 nm.

Currently we are designing similar block copolymer structures with additional



14 **15** **16**

Figure 11.
Attachment of the functional unit containing a NVOC protected amine (**15**) at the alkyne functionalized precursor polymer **14**.

anchor units for the connection of polymer films on gold surfaces. These systems are planed to be utilized for the preparation of polymer based DNA chips.

Conclusion

A family of styrene based functionalized block copolymers was synthesized and characterized. With partly BOC protected hydroxystyrene based systems, the creation of switchable surfaces with regard to the morphology has been demonstrated. Polymer analogue modifications of alkyne functionalized polymer structures with sterically demanding substances were performed giving products of considerably different caloric properties, attributed to a bracing of the addressed polymer chains. In addition, amino functionalized polymer systems as well as structures with photosensitive protected amines were synthesized which can be considered for various applications.

It has been shown that the combination of controlled radical polymerization techniques with the ‘‘click-approach’’ facilitates the designing of tailored polymer architectures with respect to the functionality and shape.

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[1] C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.* **2001**, *101*, 3661.

[2] K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921.

[3] S. Perrier, P. Takolpuckdee, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5347.

[4] M. Lazzari, M. A. Lopez-Quintela, *Adv. Mater.* **2003**, *15*, 1583.

[5] M. Lazzari, L. Guojun, S. Lecommandoux, ‘‘Block Copolymers in Nanoscience’’, Wiley, **2006**.

[6] C. Park, J. Yoon, E. L. Thomas, *Polymer* **2003**, *44*, 6725.

[7] M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* **1997**, *276*, 1401.

[8] D. Zschech, D. H. Kim, A. P. Milenin, R. Scholz, R. Hillebrand, C. J. Hawker, T. P. Russell, M. Steinhart, U. Gosele, *Nano Lett.* **2007**, *7*, 1516.

[9] J. Y. Cheng, C. A. Ross, H. I. Smith, E. L. Thomas, *Adv. Mater.* **2006**, *18*, 2505.

[10] M. P. Stoykovich, M. Müller, S. O. Kim, H. H. Solak, E. W. Edwards, J. J. Pablo, P. F. Nealey, *Science* **2005**, *308*, 1442.

[11] S. H. Kim, M. J. Misner, L. Yang, O. Gang, B. M. Ocko, T. P. Russel, *Macromolecules* **2006**, *39*, 8473.

[12] M. Aizawa, J. M. Buriak, *J. Am. Chem. Soc.* **2005**, *127*, 8932.

[13] C. Minelli, C. Hinderling, H. Heinzelmann, R. Pugin, M. Liley, *Langmuir* **2005**, *21*, 7080.

[14] W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2007**, *28*, 15.

[15] M. Messerschmidt, M. Millaruelo, H. Komber, L. Häussler, B. Voit, *Macromolecules* **2008**, *41*, 2821.

[16] M. Messerschmidt, M. Millaruelo, R. Keska, B. Voit, *Macromolecules*, submitted.

[17] S. Fleischmann, H. Komber, B. Voit, *Macromolecules* **2008**, *41*, 5255.

[18] S. Fleischmann, K. Hinrichs, U. Oertel, S. Reichelt, K.-J. Eichhorn, B. Voit, *Macromol. Rapid Commun.* **2008**, *29*, 1177.

[19] B. Sieczkowska, M. Millaruelo, M. Messerschmidt, B. Voit, *Macromolecules* **2007**, *40*, 2361.