Multiple-Scale Self-Organization

From Angstroms to Micrometers: Self-Organized Hierarchical Structure within a Polymer Film**

Teruaki Hayakawa and Shin Horiuchi*

Structural order over varying length scales is a commonly encountered phenomenon in nature, but achieving this in the synthetic world is a challenge.[1,2] Progress in synthesis and characterization of self-organizing synthetic materials has been astounding, and block copolymers have played a significant role in this process. They offer intriguing possibilities for preparation of materials with tunable structures and tailored properties.[3–10] However, the length scales attainable by self-assembly of block copolymers have been smaller than about 100 nm.[5b,6–10] In contrast, there have been recent reports on a self-assembly templating process for the creation of microsized structures.[11–13] In this templating process using water droplets, polymers with π-conjugated rod–coil-type architectures[12] or amphiphilic molecules[13] in the primary structure form hexagonally packed arrays of holes in the micrometer range in a thin polymer film. However, little attention has been paid to the formation of ordered structures on the nanometer-size scale by these approaches. For a wide range of advanced technological devices incorporating organic materials, it is desirable, advantageous, and often necessary that the hierarchical structures of these materials can be precisely controlled from the nano- to the micrometer regime.[5b] Here we report the creation of hierarchical structures from the molecular to the micrometer scale by using specifically designed block copolymers that self-organize at length scales from nanometers or angstroms to micrometers over areas in the square centimeter range.

Block copolymers with side chains can form regular nanoscale hierarchical structures through phase separation and intermolecular interactions,[5b,14] while the aromatic rigid-rod segments incorporated in rod–coil-type block copolymers form microsized structures, in contrast to the usual coil–coil-type block copolymers.[12] The incorporation of π-conjugated rigid-rod molecules in the side chain can thus play a role in forming both nano- and microsized structures and create the desired hierarchical structures over multiple length scales. For this purpose, we synthesized a semi-rod–coil block copolymer of styrene (ST) and an isoprene with oligothiophene-modified side chains (POTI), namely, PS_{400}-*b*-$POTI_{25}$ (**4**; the subscripts indicate the number of repeat monomer units; Figure 1), by esterifying a poly(styrene-*b*-substituted isoprene) block copolymer with an oligothiophene derivative.[15] The PS and POTI blocks in **4** represent coil and semi-rod segments, respectively. A poly(styrene-*b*-isoprene) block copolymer **1** was prepared by anionic polymerization of styrene monomers with 400 repeat units and isoprene monomers with 25 repeat units. Block copolymer **1** was modified by hydroboration of the polyisoprene block to yield poly(styrene-*b*-hydroxylated isoprene) block copolymer **2** with hydroxy groups in the polyisoprene block.[14] Oligothiophene with an acid terminus was synthesized by Stille coupling reactions.[16] Oligothiophene acid chloride **3** was esterified with **2** to obtain the target block copolymer **4**. Infrared and ^1H and ^{13}C NMR spectroscopy showed that the desired block copolymer **4** was obtained in quantitative yield without a side product. Gel permeation chromatography (GPC) indicated a narrow

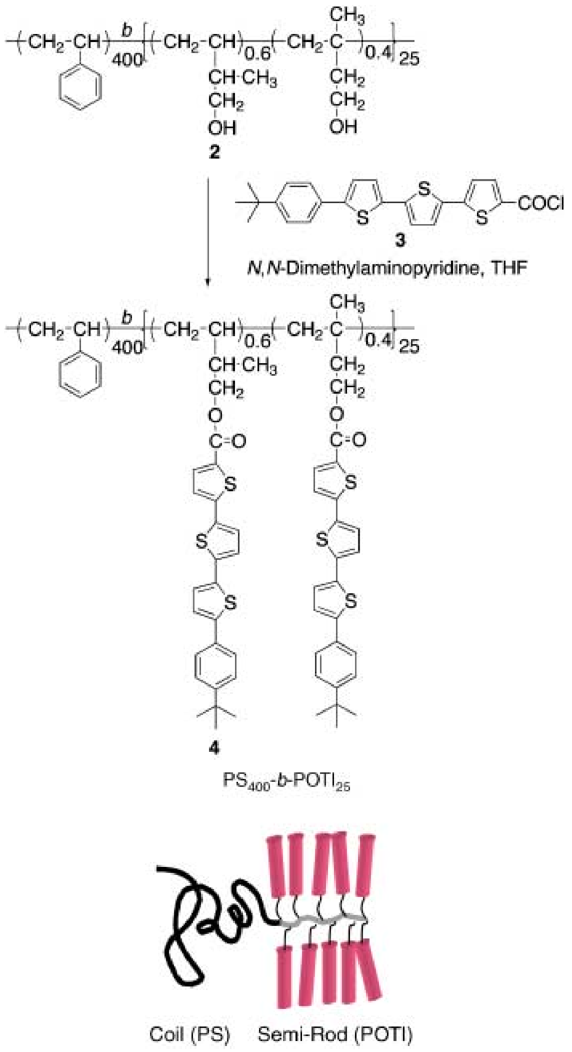

Figure 1. Synthesis and schematic representation of self-organizing semi-rod–coil block copolymer **4**.

---

[*] Dr. T. Hayakawa, Dr. S. Horiuchi
Research Center of Macromolecular Technology
National Institute of Advanced Industrial Science and Technology
1-1-1 Higashi, Tsukuba, Ibaraki 305-8565 (Japan)
Fax: (+81) 298-61-6327
E-mail: teru.hayakawa@aist.go.jp

[**] This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) for the nanostructure polymer project. We thank Prof. T. Kajiyianma and Prof. A. Takahara for their useful suggestions, Dr N. Sundararajan for his valuable discussions, and the referees for their constructive comments.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200219877

polydispersity index of 1.08 and a number-average molecular weight M_n of 55000 (versus polystyrene standard in tetrahydrofuran).

Films were prepared from 0.2 mL of a 0.25 wt% polymer solution in CS_2 on a variety of substrates such as glass slides, silicon wafers, cured epoxy plates, polyimide films, and water surfaces by casting at room temperature (22 °C) under a moist air flow. The humidity and the flow rate were kept at 85% and 3.0 L min^{-1}, respectively. The solvent completely evaporated within 10–20 s, and a periodic microporous structure was instantly obtained over an area of 3 cm^2 (Figure 2). Observations under a polarized optical microscope (POM) and a scanning electron microscope (SEM) confirmed the formation of hexagonally packed micropores with a narrow size distribution (Figure 2 a and b). The diameter of the open pores on the surface is approximately 1.3 μm (Figure 2 d). A cross-sectional view (Figure 2 c) shows a single layer with empty spheres, in which spheres with a diameter of 2.3 μm are separated from each other by thin walls of less than 100 nm.

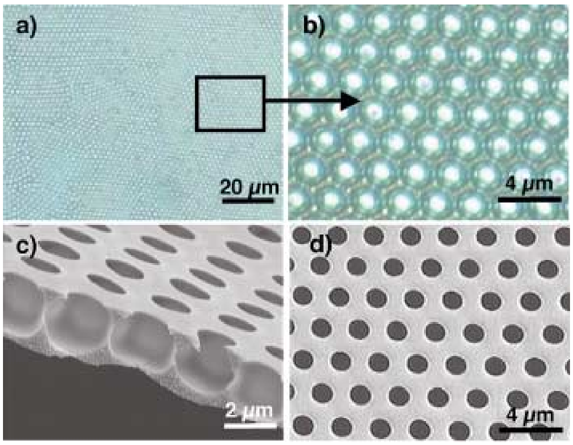

Figure 2. Self-organized microporous structure. The film of **4** was prepared from a 0.25 wt% solution under a moist air flow. a) Medium- and b) high-magnification optical micrographs of a hexagonally packed microporous structure on a glass slide. c) Side view and d) top view of SEM images of a).

This microporous film was sectioned perpendicular and horizontal to the substrate to give thin specimens which, after embedding in epoxy resin, were observed under a transmission electron microscope (TEM; Figure 3). Although the entire structure, especially that of the horizontally cross-sectioned film, is somewhat deformed during sectioning (Figure 3 c and e), the film contains a nanoscale phase-separated structure characterized by layers perpendicular to the substrate with a periodicity of approximately 25 nm (Figure 3 d, f, g, and h). A sulfur-distribution image created by electron spectroscopic imaging on an energy-filtering TEM (EFTEM) indicated that the phase-separated PS and POTI blocks aligned layer by layer due to the self-assembly characteristic of the diblock copolymer (Figure 3 h). The phase-separated nanostructure of a nonmicroporous cast film prepared from the same solution was also investigated under the TEM. The TEM images (Figure 3 a) revealed formation of a cylindrical nanostructure parallel to the substrate and a domain spacing of approximately 27 nm, in good agreement with that of the microporous film.

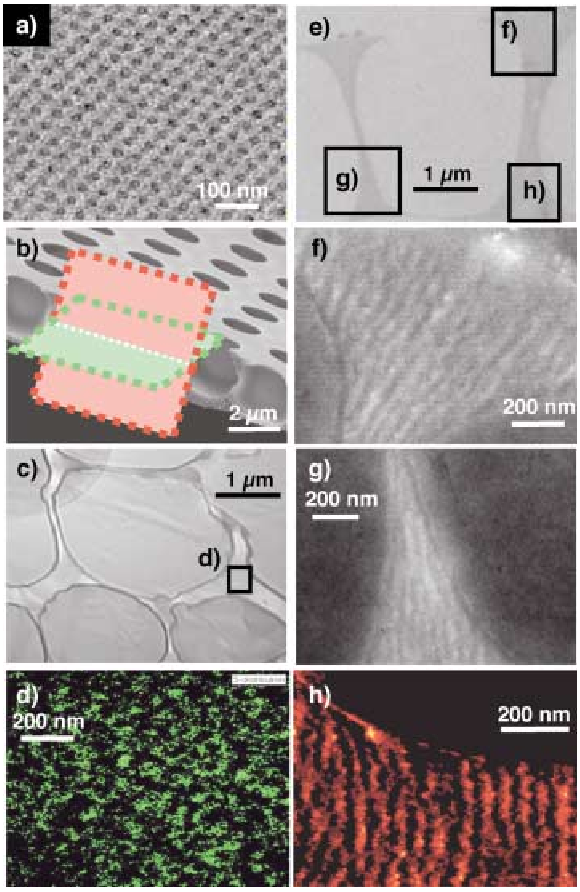

Figure 3. Self-organized phase-separated nanostructures, TEM images of cross sections of the microporous film (ca. 50 nm thick). Although the entire structure is somewhat deformed during sectioning, alignment layer-by-layer perpendicular to the substrate with a spacing of about 25 nm is apparent. a) Nonmicroporous film. b) Directions of cross-sectioned film. c) Horizontally cross-sectioned film. d) Sulfur-distribution image to detect POTI domains (green) in an unstained specimen by EFTEM. e) Perpendicularly cross-sectioned film. f, g) High-magnification micrographs of e) (red: POTI).

The mesophase structure of the block-copolymer thin film was investigated by differential scanning calorimetry (DSC), polarized optical microscopy, and X-ray diffraction (XRD). The DSC trace on the second heating showed three distinct thermal transitions (Figure 4 a). The baseline shifts observed at 104 and 168 °C correspond to the glass transitions (T_g) of the PS and POTI blocks, respectively. Above the T_g temperature, an endothermic peak was observed at 238 °C, and a phase transition to an isotropic phase was found to occur around this temperature by means of POM observations. These transition temperatures showed very good agreement with those of the homopolymers. On the DSC traces of the homopolymers, the T_g of PS and POTI were 103 and 166 °C, respectively, and the phase transition of POTI from the smectic A mesophase to the isotropic phase was observed at

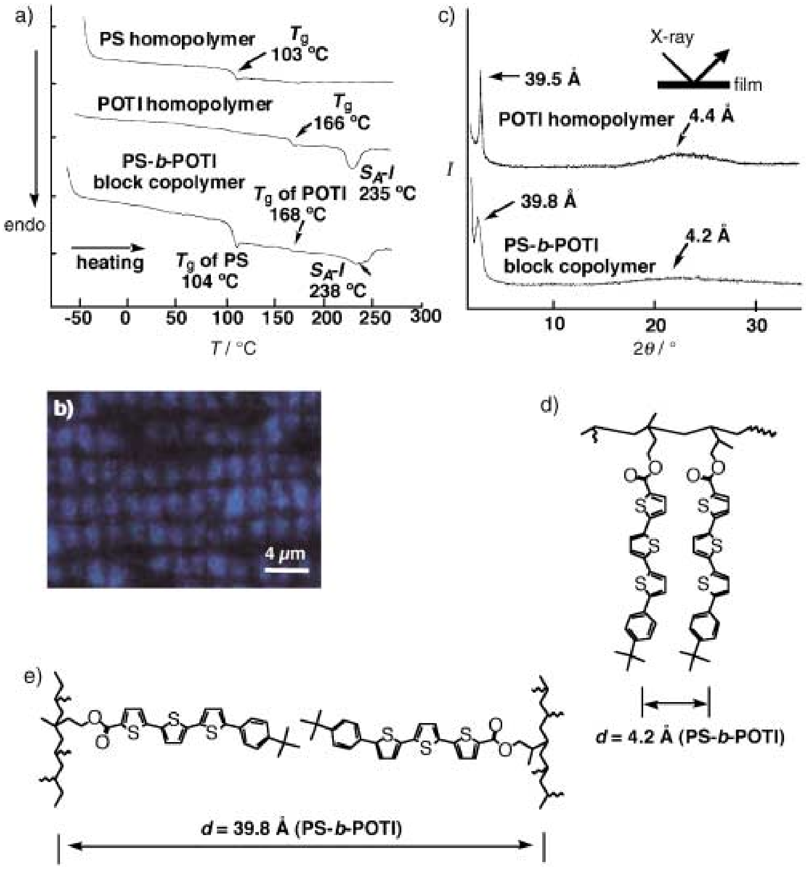

Figure 4. a) DSC traces of PS and POTI homopolymers and PS-*b*-POTI block copolymer. b) Polarized optical micrograph of microporous film in Figure 2 after thermal annealing at 170 °C for 1 min. c) X-ray diffraction pattern of film b). d, e) Schematic representation of proposed molecular arrangement of POTI polymer within the smectic A mesophase.

235 °C. Below T_g, the POTI homopolymer is in the glassy liquid-crystalline state with a smectic mesophase. Under the POM with crossed polarizers, a faint optical texture that maintains the hexagonal pore arrangement appears in a microporous film, prepared from 0.25 wt % solution, after heating from room temperature at 10 K min^{-1}, annealing for 1 min at 170 °C, that is, slightly above the T_g of POTI, and subsequent quenching to room temperature (Figure 4b). The XRD pattern after annealing at 170 °C showed a sharp inner reflection corresponding to the phase-separated layer structure, and a very broad outer reflection corresponding to the intermolecular spacing of oligothiophene molecules (Figure 4c). The layer spacing of 39.8 Å and the intermolecular spacing within the POTI layer of 4.2 Å are in good agreement with those of the POTI homopolymer film, and this suggests that the oligothiophene moieties in the POTI block are packed regularly to form a liquid crystalline smectic A mesophase within the phase-separated POTI nanodomains (Figure 4d and e). Thus, the semi-rod–coil block copolymer can form organized structures on three different length scales, ranging from angstroms to micrometers, by simple solvent casting and annealing (Figure 5). The combination of a liquid-crystal phase and phase-separated nanodomain structures formed by block copolymers has been reported before,[5b] and ordered microporous materials have been previously created by using rod–coil-type block copolymers.[12] This is the first report, however, that demonstrates three tiers of hierarchically organized structure created by molecular design and a simple process. Our synthetic approach for constructing such a highly organized structure is attachment of a rigid-rod molecule such as oligothiophene

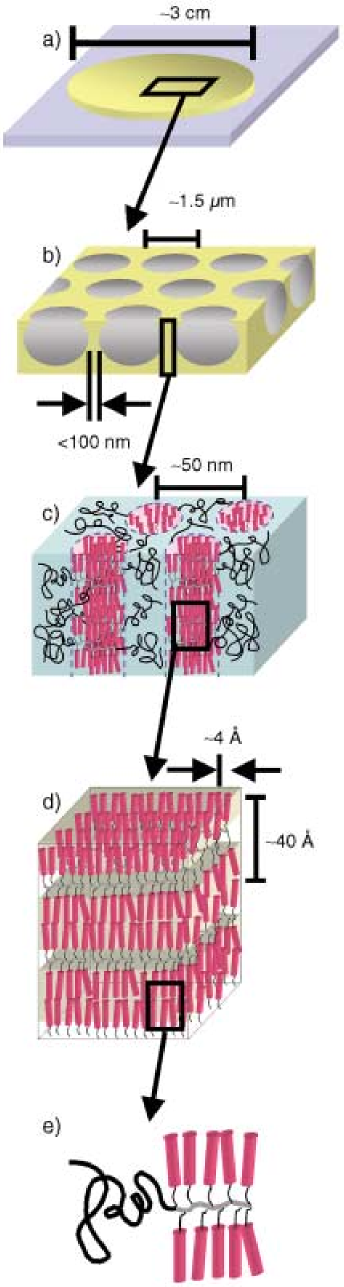

Figure 5. Schematic representation of self-organized hierarchical structure of **4**. a) Centimeter-sized film. b) Microsized porous structure. c) Nanosized phase-separated structure of PS and POTI blocks. d) Oligothiophene with molecularly orientated smectic A liquid-crystalline structure in POTI nanophase-separated domains. e) Molecular structure of **4**.

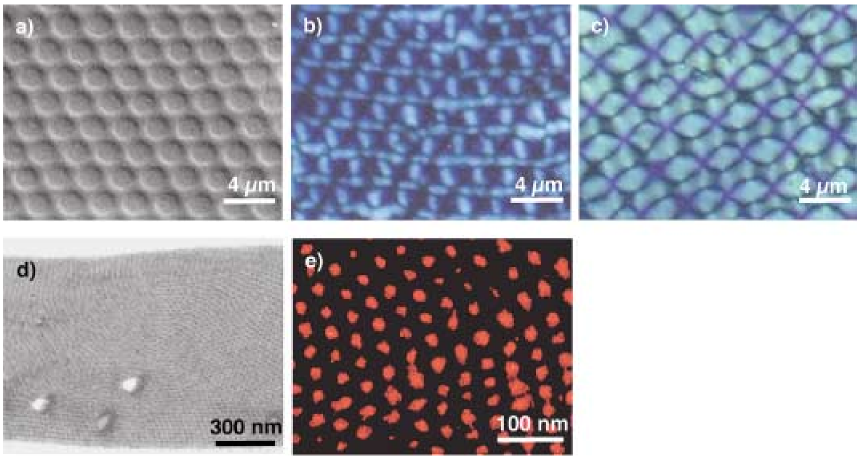

Figure 6. Micrographs of a thermally fabricated film. a) SEM micrograph of "embossed" pattern of the film in Figure 2, formed after annealing at 240 °C for 1 min. b) The "ladder"-pattern optical texture corresponds to the surface and c) to the bottom of the "embossed" pattern. d) TEM image of the cross section of completely filled film (ca. 50 nm thick) prepared by annealing at 260 °C for 1 min. The direction of the cylinder changes from perpendicular to parallel to the substrate. e) Sulfur-distribution image under the EFTEM.

onto the side chain of one block of the diblock copolymer. This has the advantage that functions such as electrical conductivity, optical storage, and photoluminescence can be added to the films.

The other advantage of the semi-rod–coil block copolymer over rod–coil block copolymers is that the ordered structure at the molecular level within the rod blocks can be fabricated by thermal treatment, because the side chain rod moieties can rearrange before complete isotropization of the block copolymer. Under the POM, film melting and micropores filling were gradually observed around 185 °C on heating at 10 K min^{-1} from room temperature. Annealing at 240 °C, that is, slightly above the phase-transition temperature from the smectic A to the isotropic phase, for 1 min and quenching to room temperature yields a "microembossed" pattern (Figure 6a) in which the pores are incompletely filled, and the height thus undulates in a regular fashion. The XRD pattern of the film indicated the same smectic A mesophase as shown in Figure 4c. This texture of the smectic A mesophase under the POM has a unique "ladder" pattern, for which the "ladder" corresponds to the top surface of the "embossed" pattern (Figure 6b). By focusing on the bottom surface of the "embossed" pattern, another texture with periodic microscale patterns was observed (Figure 6c). These optical textures indicate the creation of a micropatterned liquid crystalline film. Annealing at 260 °C for 1 min completely fills the pores to give a nonmicroporous film. A cross-sectional TEM image of this film shows the cylindrical phase-separated structure (Figure 6d and e), that is, annealing changes the direction of the cylinders from perpendicular to parallel to the bottom of the film, while the upper side just below the surface remains the same as it was just after casting. We also changed the depth of the pores by changing the annealing conditions. The possibility of such thermal fabrication is likely to extend the range of applications of these materials. For example, thermal treatment of the block-copolymer thin film leads to a surface that appears to have a microembossed pattern over areas of several square centimeters. These surfaces could be envisioned as being used as tunable diffraction gratings or holograms. Other examples include ordered microporous materials as templates for the patterning of functional materials in two or three dimensions. The experimental results presented above on the microporous structures also indicate the possibility of fixation or encapsulation of functional materials after patterning of the block copolymer film.

The structure of the microporous films can be varied by means of the concentration of the polymer in the solution. For example, a 0.1 wt% solution leads to a single layer of pores open on both sides (Figure 7a), while a 1.0 wt% solution results in multiple layers of pores ordered in three dimensions (Figure 7b and c). The pore size can also be controlled from 1.2 to 4.5 μm by changing the solution concentration.

We have developed a new strategy for constructing highly ordered hierarchical structures by combining individual self-organizing components over multiple length scales. The materials prepared by this strategy and modified by further thermal fabrication are expected to have a wide range of applications in molecular optical or electronic devices, photonic band-gap materials, and sensors.

Received: August 2, 2002
Revised: February 10, 2003 [Z19877]

Keywords: block copolymers · hierarchical structures · microporous materials · nanostructures · self-assembly

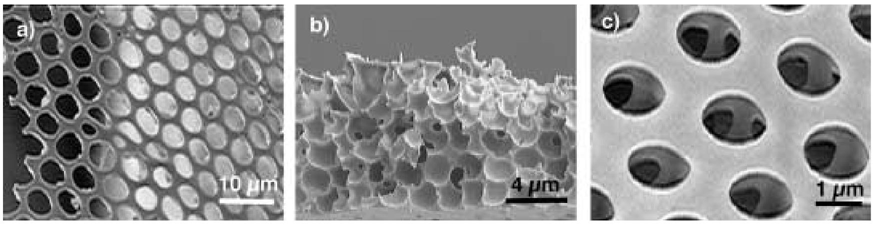

Figure 7. SEM images of a variety of microporous films. a) Film with a single layer of pores open on both sides and about 3.3 μm in diameter, prepared from 0.1 wt% casting solution. b) Side view of multilayer structure consisting of six layers, prepared from 1.0 wt% casting solution. c) Top view of micrograph b). Pores of the next layers can be seen through those of the top layer. The image shows the arrangement of pores of uniform size in multilayers.

---

[1] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319; E. Kim, G. M. Whitesides, *Chem. Mater.* **1995**, *7*, 1257–1264; G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418–2421.
[2] G. A. Ozin, *Chem. Commun.* **2000**, 419–432.
[3] F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **1990**, *41*, 525–557.
[4] Z. Li, W. Zhao, Y. Liu, M. H. Rafailovich, J. Sokolov, *J. Am. Chem. Soc.* **1996**, *118*, 10892–10893.
[5] a) C. K. Ober, G. Wegner, *Adv. Mater.* **1997**, *9*, 17–31; b) M. Muthukumar, C. K. Ober, E. L. Thomas, *Science* **1997**, *277*, 1225–1232.
[6] S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384–389.
[7] J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke, O. Ikkala, *Science* **1998**, *280*, 557–560.
[8] S. Walheim, E. Schäffer, J. Mlynek, U. Steiner, *Science* **1999**, *283*, 520–522.
[9] O. Illala, G. ten Brinke, *Science* **2002**, *295*, 2407–2409.
[10] S. Förster, T. Plantenberg, *Angew. Chem.* **2002**, *114*, 712–739; *Angew. Chem. Int. Ed.* **2002**, *41*, 688–714.
[11] M. Srinivasarao, D. Collings, A. Philips, S. Patel, *Science* **2001**, *292*, 79–83.
[12] G. Widawski, M. Rawiso, B. François, *Nature* **1994**, *369*, 387–389; S. A. Jenekhe, X. L. Chen, *Science* **1999**, *283*, 372–375.
[13] O. Karthaus, N. Maruyama, X. Cieren, M. Shimomura, H. Hasegawa, T. Hashimoto, *Langmuir* **2000**, *16*, 6071–6076.
[14] G. Mao, J. Wang, S. R. Clingman, C. K. Ober, *Macromolecules* **1997**, *30*, 2556–2567.
[15] Details of the molecular synthesis and polymerization studies are available as Supporting Information.
[16] J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524.