



Shear-induced slippage of the self-assembly of crown ether-centered two-armed copolymers

Jun Fu^a, Yang Cong^a, Xiang Yu^b, Jian Li^a,
Caiyuan Pan^b, Binyao Li^a, Yanchun Han^{a,*}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China

^b Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China

Received 2 December 2004; received in revised form 23 January 2005; accepted 2 February 2005

Available online 12 March 2005

Abstract

Crown ether-centered two-armed polymers, i.e., polystyrene-dibenzo-18-crown-6-polystyrene (PSCS) and poly(methyl methacrylate)-dibenzo-18-crown-6-poly(methyl methacrylate) (PMCM), were designed to self-assemble in a proposed manner directed by the specific affinity between the polar crown ether rings. When spin coated onto a silicon wafer surface, macroporous films were obtained. In contrast, the proposed assemblies were strongly adsorbed on a highly polar mica surface, looking like porous islands near the spin center. At areas far from the spin center, these islands slipped to form terrace islands under the huge shear by the centrifugal force. The formation of the porous islands and terrace islands provide further evidence to the proposed assembling of the two-armed polymers.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Crown ether-centered two-armed polymers; Self-assembly; Slippage; Spin coating

1. Introduction

Self-assembly is a powerful “bottom-up” strategy for fabrication of regular structures from micro- to meso- and macro-scales [1–3]. Hence, it is of increasing importance because of the potential application in

a number of fields of, for example, fabrication of microelectronics, surface patterning, three-dimensionally ordered nanostructures and even hierarchically organized assemblies [1].

For the purpose of creating molecules with assembling property, it is essential to introduce some functional groups [4–10], which can offer additional non-covalent interactions such as hydrogen bonding [5–7], electrostatic attraction [8], π – π stacking [9], nematic interaction [10], and amphiphilicity [11], etc.

* Corresponding author. Tel.: +86 431 5262175;
fax: +86 431 5262126.

E-mail address: yhan@ciac.jl.cn (Y. Han).

At properly controlled conditions, supramolecules with regular short-range and/or long-range structures may be obtained. For example, Jiang and co-workers achieved molecular complexes (micelles [5] and vesicles [6]) by simply introducing selected pairs of functional groups that can form hydrogen bonds to unlike homopolymers. Polymers with discoid moieties at side chain, main chain and chain end, starlike polymers with discoid core [12] and rigid rodlike polymers with crown ether substituents [13] are able to self-assemble into fibers [9], rods [12,13], and ribbons [13], etc. due to nematic and/or π - π stacking.

Compounds containing crown ether moieties have been proved to self-organize into well-defined regular structures since the special stereo configuration and synergetic polar C–O bonds provide strong affinity between crown ethers [14,15]. Besides, the complexation of crown ethers and cations can be favorable [13] or unfavorable [9] to the self-assembling of crown ethers, mainly depending on the specific molecular architectures. In our previous reports [16,17], new crown ether-centered two-armed polymers were demonstrated able to form macroporous films. The integrated crown ether core was expected to drive self-assembling. Accordingly, a possible assembling mechanism was suggested.

In this work, we will show that the expected assemblies can be tightly adsorbed to the highly polar mica substrates. During spin coating, the internal slippage of the assemblies due to the strong shearing can be observed by atomic force microscopy. The formation of these patterns are discussed in the context of self-assembling and the spin coating process.

2. Experiments

2.1. Synthesis and sample preparation

The crown ether-centered two-armed polymers, polystyrene-dibenzo-18-crown-6-polystyrene (PSCS) and poly(methyl methacrylate)-dibenzo-18-crown-6-poly(methyl methacrylate) (PMCM), were synthesized by atom transfer radical polymerization (ATRP), using a two functional crown ether initiator (bis [4'-(2-bromobutyl)] dibenzo-18-crown-6 [BBDC]) to initiate polymerization of styrene and methyl methacrylate monomers. The synthesis details have been

described in reference [18]. The number average molecular weights of PSCS and PMCM are, respectively, 5700 (polydisperse index, PDI \approx 1.25) and 7200 (PDI \approx 1.18) according to ^1H NMR and gel permeation chromatography (GPC) measurements.

The polymer powders were dissolved in purified tetrahydrofuran (THF). For comparison, other good solvents including toluene and chloroform were used, in which the two-armed polymer acted as homopolymers, indicating that the very strong solvent-polymer interaction could prohibit the self-assembling [17]. After at least 24 h storage at room temperature, the solutions were spin coated onto clean silicon wafers and freshly cleaved mica sheets. The films were then annealed at 40 °C in vacuum for more than 72 h in order to remove the residual solvent. All the containers were thoroughly cleaned with deionized water before use.

2.2. Tapping mode atomic force microscopy (AFM)

The surface morphologies of the spin-coated films were obtained by scanning the samples with a commercial atomic force microscope (SPA 300HV/SPI 3800 N probe station, Seiko Instruments Inc., Japan) in tapping mode. A silicon microcantilever (spring constant \sim 2 N/m and resonant frequency \sim 70 kHz, Olympus, Japan) integrated with a conical tip (radius of curvature \sim 40 nm as characterized by scanning over a grating of very sharp needles with radius curvature less than 10 nm from NT-MDT, Russia) at the free end was used as force sensor. The scanning rate was varied within 1–2 Hz for acquisition of images with the best quality. All the analysis of the AFM images was conducted with the software provided by the manufacturer.

3. Results and discussion

As stated in Section 1, the crown ether-centered two-armed polymers are designed to take advantage of the specific affinity between the crown ether rings, which is expected to direct self-assembly of the crown-ether-based polymers. In the literature [14,15], crown ether-containing compounds could self-assemble to form regular structures and the overlapping crown ether rings formed ion channels. This may

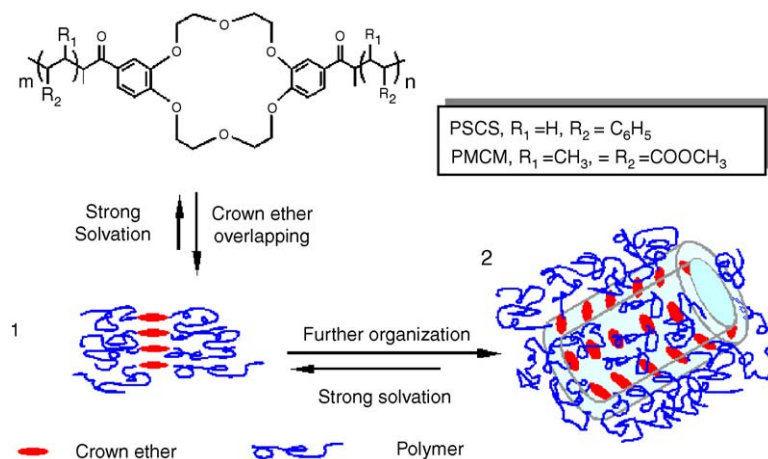


Fig. 1. Schematic representation of a possible assembling process of the crown ether-centered two-armed polymers in THF solution.

illuminate a possibility that the crown ether rings in the two-armed polymers may overlap each other to yield some regular structure (e.g., aggregate **1** in Fig. 1) in solutions. The overlapping of the rings will undoubtedly drive the overlapping of the polymer arms. Apparently, in good solvents that strongly dissolve the polymer side arms, the affinity between the crown ether rings will be overcome by the strong solvation effect so that the proposed assembly **1** cannot form. This has been demonstrated in our previous work [16,17].

Furthermore, an important property of such suprastructures, as conceptually set forth in general by Ikkala and ten Brinke [1], is that they are likely to organize into larger (secondary) aggregates due to the very weak van der Waals interaction between the polymer side arms. Accordingly, many assemblies **1** may organize to form larger aggregates by entangling the surrounding polymer side arms, as well as by the van der Waals interaction. On the other hand, the solvent will swell the entangling polymer chains. Thus, the interplay of the crown ether affinity and the swelling effect may yield, for example, some hollow supra-structure (as arbitrarily schemed by **2** in Fig. 1).

In previous work [16,17], such supra-structure has been reported to produce macroporous films by spin coating or casting the solutions onto silicon wafers. The pore diameter monotonically increased with decreasing concentration of the solutions. Provided that the pore size of the films corresponds to the size of the proposed assembly **2**, the concentration depen-

dence of pore size may root from the polymer–solvent interaction, which monotonically increases with decreasing concentration.

Fig. 2 extends this viewpoint by considering the dependence of the assembly size on both the chemical structure of the polymer arms and the solution concentration. Macroporous films of PSCS (Fig. 2a–d) and PMCM (Fig. 2e–h) were spin coated from their THF solutions with concentrations from 0.5% (by weight, as throughout the paper), 0.25, 0.1, and 0.08% (from left to right). Similar to previous results, the pore size increases from ~80 to ~300 nm, 450 nm and larger (Fig. 2d–h) with decreasing concentration before the films break at some critical concentration, c_c . For concentration lower than c_c , network or islands formed (Fig. 2 c–d), accompanied with pores.

Comparing the morphologies of PSCS and PMCM films, one finds that the average diameter for the former is always larger than that of the latter at a given concentration. Moreover, the likely c_c of PSCS films is much higher than that of PMCM films. These experimental results can be understood in two aspects.

First, since THF (solubility parameter $\delta = 9.52$ ($\text{cal cm}^{-3})^{1/2}$) is a better solvent for PS ($\delta = 9.81$ ($\text{cal cm}^{-3})^{1/2}$) than for PMMA ($\delta = 11.27$ ($\text{cal cm}^{-3})^{1/2}$) [19], the PS–THF interaction is larger than that of PMMA–THF pairs. The aggregate **2** of PSCS should be more severely swollen than that of PMCM, leading to larger pore diameter.

Second, the interaction between the PS side arms is weaker than that between the PMMA arms because

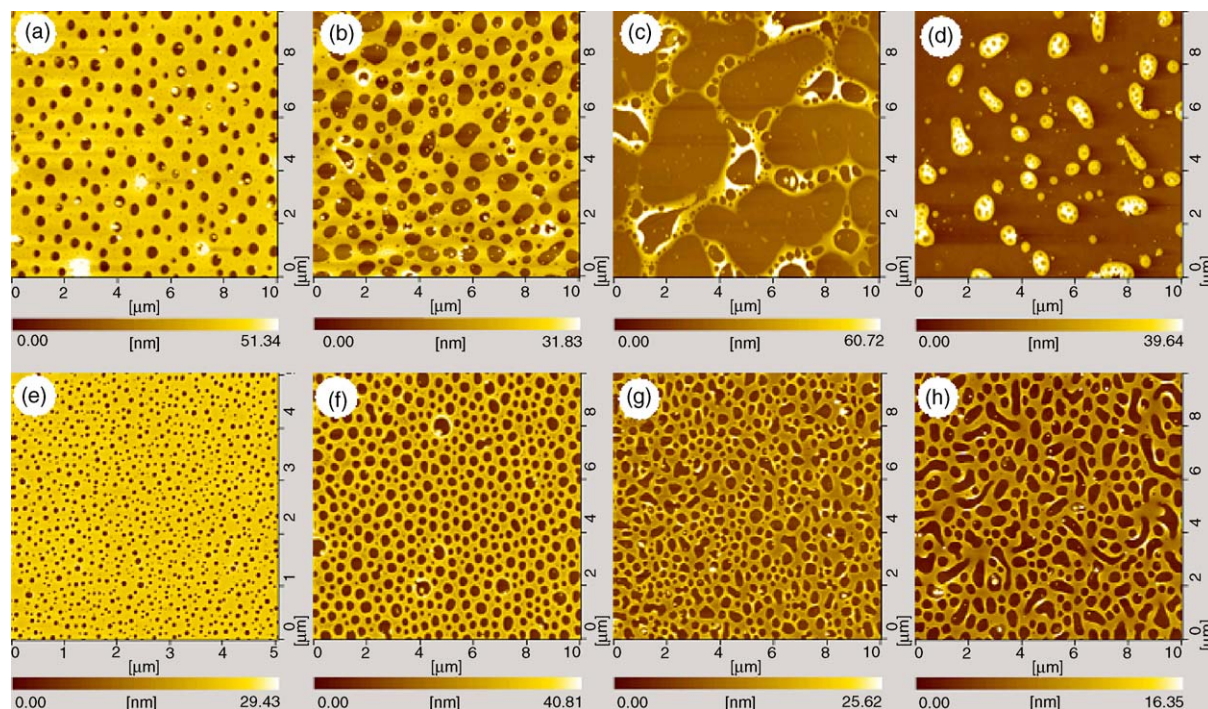


Fig. 2. Spin coated films on silicon substrates of the two-armed polymers from THF solutions with different concentrations. (a)–(d) PSCS and (e)–(h) PMCM. The corresponding solution concentrations (from left to right) are 0.5, 0.25, 0.1 and 0.08%.

the cohesion energy density (CED) of PS (305 J cm^{-3}) is smaller than that of PMMA (347 J cm^{-3}) [19]. This may account for the fact that PSCS films are more likely to break than PMCM films are.

In order to achieve direct visualization of the proposed aggregates, the 0.5% PMCM/THF solution was spin coated onto a freshly cleaved mica surface. The mica substrate was chosen because of its high polarity that can attract the polar PMMA chains. Once the solution was cast onto the mica surface, the proposed aggregates (if present) may be adsorbed on the mica surface.

At the place close to the spin center on the mica sheet (Fig. 3a), isolated islands, instead of the continuous thin macroporous films, are found with a height of $\sim 250 \text{ nm}$ and lateral dimension of a few micrometers. These islands contain holes with $\sim 100\text{--}300 \text{ nm}$ in diameter and $\sim 70 \text{ nm}$ in depth (Fig. 3d–f). (In fact, through SEM micrographs (not shown), the holes look like they extend through the island down to the substrate. That is, the actual depth of the holes is much larger than the AFM value, which

is limited by the size of the tip.) The dilation in the lateral dimension of the holes with respect to Fig. 2d may be caused by the strong adsorption of the aggregates once the solution was cast on the mica surface. At first, the adsorption of *free* aggregates from solution to flat surface may force some configuration alteration of the porous aggregates. Second, when spin coated, the individual aggregate (island) will suffer strong vertical airflow, which may deform the porous structure by jetting and dilating the swollen pores. For the continuous flat film, this ideal airflow is homogeneous within a small enough local area so that the dilating effect can be counteracted. For the porous islands, there is no counteracting around the islands. Since, as proposed in Fig. 1, the two-armed polymers are non-covalently and loosely organized, the strong airflow may compel expansion of the holes and the islands.

On the other hand, at areas far from the spin center, terrace structures were observed. Fig. 4 represents a typical morphology of such terrace islands. These islands are $\sim 200 \text{ nm}$ in height and a few micrometers

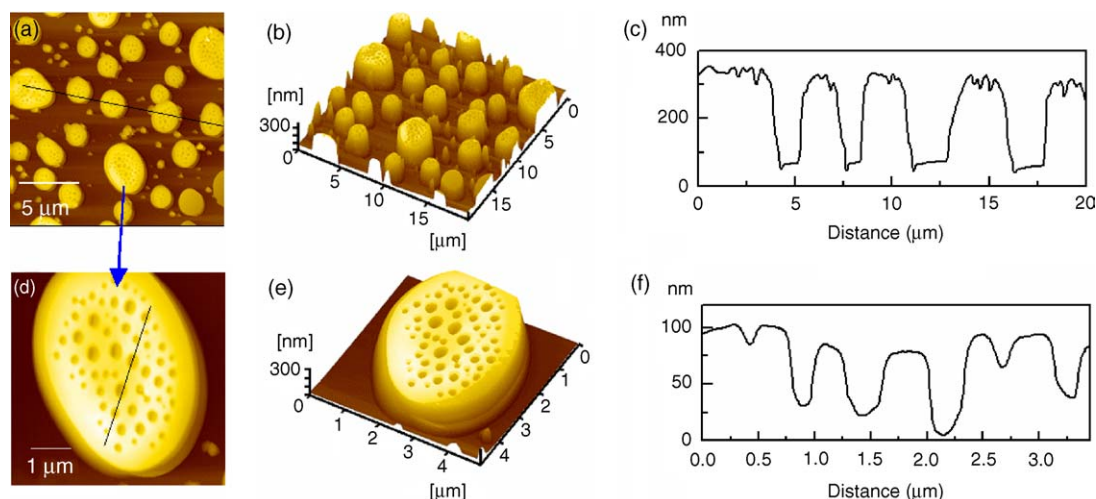


Fig. 3. Tapping mode AFM images of the self-assemblies of PMCM spin coated onto the mica surface from 0.5% THF solution: (a and d) and (b and e) are the surface topography and the corresponding three-dimensional view, with (c) and (f) as the cross section profiles along the black solid lines in (a) and (d), respectively.

in diameter. The island height is slightly lower than that of the islands at the spin center (Fig. 3a). In each island, holes with diameters ~ 80 – 150 nm and depth less than 30 nm are observed. The terraces show an alignment along the direction normal to the radial direction from the spin center, as arrowed in Fig. 4b. All these facts lead to an implication that the terrace

islands are deformed assemblies of the two-armed PMCM by the huge shear during spin coating.

Normally, the spin coating process is believed composed of four consecutive stages: fluid dispensing, spin-up, stable fluids out-flow and finally evaporation-dominated drying [20]. Assuming that the latter two stages were in steady condition, the centrifugal and

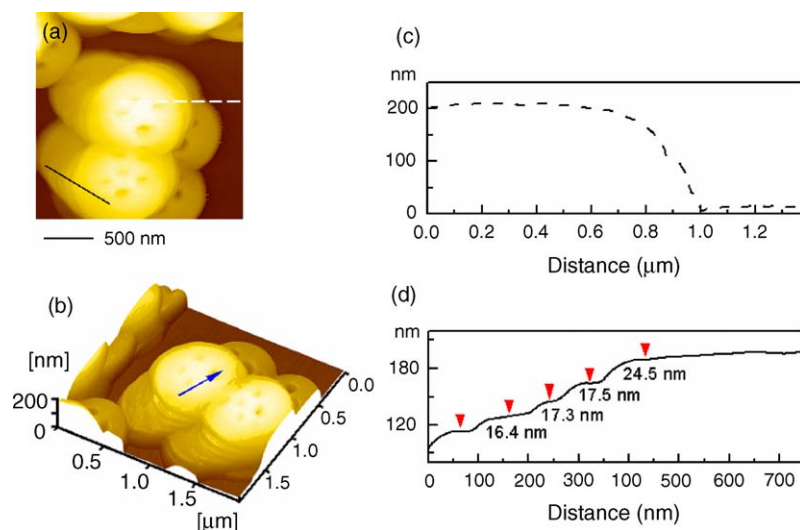


Fig. 4. Terrace structure of the PMCM self-assembly at areas far from the spin center on the mica surface. The section profile (c) along the white dashed line in (a) indicates the total height of the island, while (d) shows the terrace section profile along the black solid line in (a). The arrow in (b) indicates the shear direction.

viscous forces were hence in balance and the fluid flow velocity increased along the radial direction outwards from the center.

When THF solutions were cast on the mica surface, they spread rapidly and wetted the surface. Meanwhile, the polar PMMA side arms may be strongly adsorbed on the mica surface (Fig. 5). Thus, the assemblies of PMCM may be physically anchored to the mica surface, appearing as porous islands near the spin center (Fig. 3). The centrifugal force increases gradually from the center along the radial direction. At the point far from the center, there is strong centrifugal force. At the fluid flow and thinning stage, there is a strong inertial force that creates a shearing and stretching field in the fluid according to Meyerhofer's model [21]. For self-assembled polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene (SEBS) in dilute solutions, as reported by Li et al. [22], such huge force compelled high alignment of the copolymers along the radial direction at areas apart from the spin center. In that case, the overlapping copolymer aggregates had no specific interaction with the substrate. The pattern formation was assumed to undergo a nucleation, retraction [23] and elongation [24] process as driven by the huge shear at the areas far from the spin center.

In our case, the proposed assemblies are tightly, physically adsorbed to the substrate surface due to the very strong polar interactions. Thus, it is impossible

for the aggregates to slip as a whole on the surface along the shear direction. There would be large internal inertial force inside the adsorbed assemblies. Such strong inertial force may partly overwhelm the interaction between the crown ethers and the overlapping polymer arms to induce internal slippage along the shearing (also the radial) direction. On the other hand, the entangling polymer arms may keep the structure from breaking, terraced structures form. This process could be schematically illustrated in Fig. 5.

The lateral slippage of the porous aggregates, according to Fig. 5, should have a result that the upper layer covers the holes beneath them and thus the hole depth by AFM measurement should be much smaller than that of the original aggregates. This deduction is verified by AFM data shown in Fig. 4, where the hole depth ranges from 20 to 28 nm. From Fig. 4d, one finds that the terrace height increased with a slight gradient from 16.4, 17.3, 17.5 to 24.5 nm from the bottom to the top. Clearly, the height of the uppermost layer in Fig. 4 consists with the hole depth in that layer, indicating that the holes in the top layer extend through the layer to the beneath layer. Thus, the slippage model in Fig. 5b is reasonable.

In comparison, however, the PSCS assemblies did not form such islands or terrace islands induced by shear since the PS arms have very weak polarity. During the spin coating process, the PS chains dewetted [25] the mica surface to produce random

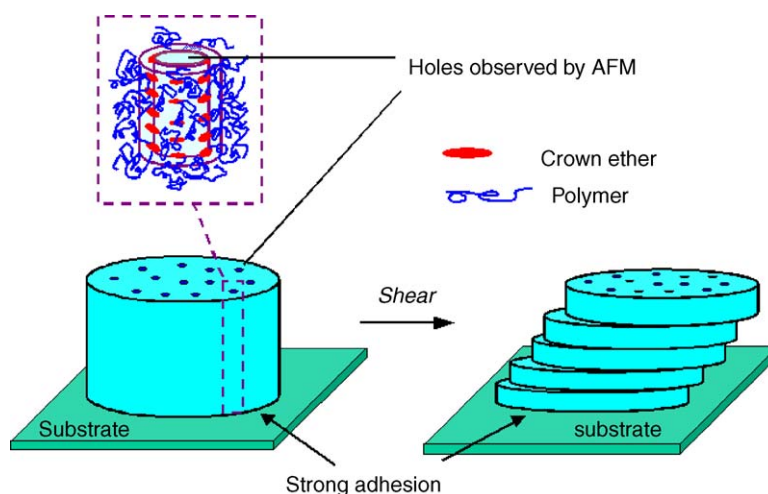


Fig. 5. Schematic drawing of the internal slippage inside the assemblies under shear. One of the holes is magnified for clarification of the proposed hierarchical assembled supra-structures.

droplets and no porous structures were found therein (not shown). This situation is very complicated since the aggregated structure, the dewetting process [25] of the aggregates and the fluid flow during spin coating [26] should be considered. It is of low correlation to the topic of this paper and will not be covered here.

4. Conclusion

The crown ether-centered two-armed polymers, i.e., polystyrene-dibenzo-18-crown-6-polystyrene and poly(methyl methacrylate)-dibenzo-18-crown-6-poly(methyl methacrylate), can self-assemble in THF solution. The assembling may be primarily driven by the affinity between the crown ether cores. The assembly dimension is determined by the interplay between the crown ether affinity, the cohesion energy of the polymer arms and the polymer–solvent interaction. For the two-armed polymers with polar PMMA arms, the assemblies will be tightly adsorbed on mica surface where the THF solution spread rapidly. This permits direct visualization of the proposed assemblies at spin center. At locations far from the center, slippage inside the adsorbed assemblies was forced by the inertial force and shearing during spin coating. These observations provide evidence for the self-assembling of the crown ether-centered two-armed polymers.

Acknowledgements

This work is subsidized by the National Natural Science Foundation of China (50125311, 20334010, 20274050, 50390090, 50373041, 20490220, 20474065, 50403007), the Ministry of Science and Technology of China (2003CB615601), the Chinese Academy of Sciences (Distinguished Talents Program, KJCX2-SW-H07), and the Jilin Distinguished Young Scholars Program (20010101).

References

- [1] O. Ikkala, G. ten Brinke, *Science* 295 (2002) 2407.
- [2] P. Ball, *Nature* 413 (2001) 667.
- [3] I.W. Hamley, *Nanotechnology* 14 (2003) R39.
- [4] V.V. Tsukruk, *Prog. Polym. Sci.* 22 (1997) 247.
- [5] M. Wang, G. Zhang, D. Chen, M. Jiang, S. Liu, *Macromolecules* 34 (2001) 7172.
- [6] (a) H. Duan, D. Chen, M. Jiang, W. Gan, S. Li, M. Wang, J. Gong, *J. Am. Chem. Soc.* 123 (2001) 12097;
(b) M. Mu, F. Ning, M. Jiang, D. Chen, *Langmuir* 16 (2000) 10490.
- [7] L. Wang, S. Cui, Z. Wang, X. Zhang, M. Jiang, L. Chi, H. Fuchs, *Langmuir* 16 (2000) 10490.
- [8] X.-H.N. Xu, E.S. Yeung, *Science* 281 (1998) 1650.
- [9] H. Engelkamp, S. Middelbeek, R.J.M. Noltes, *Science* 284 (1999) 785.
- [10] (a) S.A. Jenekhe, X.L. Chen, *Science* 279 (1997) 1903;
(b) J. Wu, E.M. Pearce, A.A. Lefebvre, N.P. Balsara, *Macromolecules* 35 (2002) 1791.
- [11] S. Förster, M. Antonietti, *Adv. Mater.* 10 (1998) 195.
- [12] X. Yu, J. Fu, Y. Han, C. Pan, *Macromol. Rapid Commun.* 24 (2003) 742.
- [13] Y.-H. Luo, H.-W. Liu, F. Xi, L. Li, X.-G. Jin, C.C. Han, C.-M. Chan, *J. Am. Chem. Soc.* 125 (2003) 6447.
- [14] C.F. van Nostrum, S.J. Picken, A.J. Schouten, R.J.M. Nolte, *J. Am. Chem. Soc.* 117 (1995) 9957.
- [15] P. Samor, H. Engelkamp, P. de Witte, A.E. Rowan, R.J.M. Nolte, J.P. Rabe, *Angew. Chem. Int. Ed.* 40 (2001) 2348.
- [16] J. Fu, X. Feng, X. Yu, C. Pan, Y. Han, Y. Yang, B. Li, *Macromol. Rapid Commun.* 24 (2003) 487.
- [17] J. Fu, Y. Cong, X. Yu, C.Y. Pan, Y.M. Yang, B.Y. Li, Y.C. Han, *Polymer* 45 (2004) 7389.
- [18] X.S. Feng, L.F. Yan, J. Wen, C.Y. Pan, *Polymer* 43 (2002) 3131.
- [19] J. Brandrup, E.H. Immergut, E.A. Grulke, A. Abe, D.R. Bloch, *Polymer Handbook*, fourth ed. John-Wiley & Sons, New York, 1999.
- [20] D. Bornside, C.W. Macosko, L.E. Scriven, *J. Imaging Technol.* 13 (1987) 122.
- [21] D. Meyerhofer, *J. Appl. Phys.* 49 (1978) 3993.
- [22] X. Li, Y. Han, L. An, *Langmuir* 18 (2002) 5293.
- [23] H. Tanaka, *Phys. Rev. Lett.* 76 (1996) 787.
- [24] F. Qiu, H. Zhang, Y. Yang, *J. Chem. Phys.* 108 (1998) 9529.
- [25] G. Reiter, *Phys. Rev. Lett.* 68 (1992) 75.
- [26] T.G. Stange, R. Mathew, D.F. Evans, W.A. Hendrickson, *Langmuir* 8 (1992) 920.