Photoresponsive Polymers

DOI: 10.1002/anie.201300560

Liquid-Crystalline Polymer and Block Copolymer Domain Alignment Controlled by Free-Surface Segregation**

Kei Fukuhara, Yasuyoshi Fujii, Yuki Nagashima, Mitsuo Hara, Shusaku Nagano, and Takahiro Seki**

The surface effects and anchoring of liquid crystals (LCs) have long been significant concerns for material chemists and physicists.[1] The surface alignment of LCs by mechanical rubbing[2] is a widely recognized phenomenon and of particular significance in technological applications for display device fabrication.[3] Surface molecular orientations[4] and topographical grooves and undulations[5] of the substrate provide LC alignment effects. Furthermore, in the past two decades, the photoalignment of LCs on photoreactive polymer film surfaces by anisotropic irradiation[6] has become a significant method and an alternative to mechanical rubbing processes. The aligning substrates are not limited to polymer surfaces; various types of surfaces, such as hard inorganic materials[7] and soft bio-related interfaces,[8] can be used for the alignment induction. In addition to low-molecular-mass LCs, polymer LC materials are also aligned by the surface effect.[9] Despite the tremendous amount of accumulated knowledge and the number of potential applications, the surface alignment processes developed to date mostly involve manipulations on the surfaces of solid or condensed phases.

Herein, we report on LC alignment alternation, which is attained by a modification of the free surface (air–film interface). The homeotropic surface anchoring effect and layer structuring at the free surface of calamitic LC molecules have been shown experimentally[10] and have been further verified by theoretical simulations.[11] To modify the free surface, the present approach adopts the surface segregation[12,13] of a small amount of a free-surface-active polymer. We demonstrate here that the coverage of the surface with the free-surface-active polymer leads to a homeotropic-to-parallel orientation change of LC mesogens, which further leads to an efficient in-plane photoalignment of microphase separation (MPS) domains of a relevant LC block copolymer by linearly polarized light (LPL).[14] With regard to the MPS alignment control, the important role of a top coat layer has recently been demonstrated by Bates et al.[15] In this case, a polar-to-nonpolar chemical conversion of the top layer is achieved to fulfill the requirement of spin-casting from an aqueous solvent and to provide a neutral (non-preferential) layer for the hydrophobic block copolymer during the annealing. In the present approach, in contrast, no additional coating procedure is required, providing a simple, versatile method for the desired alignment control of MPS domains.

First, the alignment behavior of an LC azobenzene (Az) homopolymer (PAz in Figure 1a; $M_n = 8.0 \times 10^4$, $M_w/M_n = 1.13$, and g-43°C-SmC-100°C-SmA-120°C-iso) was examined. A spincast film of PAz was prepared (thickness: 100–200 nm) from a chloroform solution. After annealing at 130°C (above the isotropization temperature) for 10 min followed by gradual cooling via a smectic LC phase to room temperature, this film spontaneously formed the out-of-plane (perpendicular) orientation of Az side mesogens, as judged by

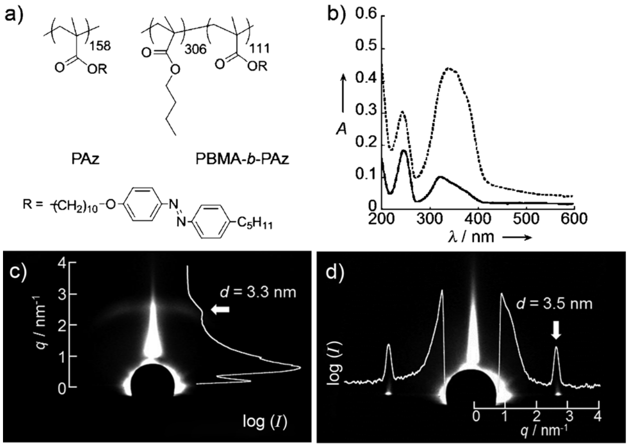


Figure 1. a) Molecular formula of PAz and PBMA-*b*-PAz. b) UV/Vis absorption spectra of the PAz thin film (——) and the PBMA-*b*-PAz (10%)/PAz blend thin film (-----) after annealing at 130°C. c) and d) The 2D GI-XRD patterns of a pure PAz film and PBMA-*b*-PAz (10%)/PAz blend thin films after annealing at 130°C, respectively. In the XRD patterns, 1D intensity profiles are indicated as white lines.

---

[*] K. Fukuhara, Y. Nagashima, Dr. M. Hara, Prof. T. Seki
Department of Molecular Design and
Engineering Graduate School of Engineering, Nagoya University
Furo-cho, Chikusa, Nagoya, 464-8603 (Japan)
E-mail: tseki@apchem.nagoya-u.ac.jp
Y. Fujii
Optical Materials Group Yokkaichi Research Laboratory
Tosoh Corporation
Kasumi, Yokkaichi 510-8540 (Japan)
Prof. S. Nagano
Nagoya University Venture Business Laboratory, Precursory
Research for Embryonic Science and Technology (PRESTO)
E-mail: snagano@apchem.nagoya-u.ac.jp

[**] This work was supported by a Grant-in-Aid for Basic Scientific Research S (23225003), the Global COE program, the Program for Leading Graduate Schools from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and the JST-PRESTO program (Japan). The synchrotron X-ray scattering experiments were performed at the BL-15A in the KEK-Photon Factory, Tsukuba (proposal No. 2012G629).

Supporting information for this article, including experimental details, is available on the WWW under http://dx.doi.org/10.1002/anie.201300560.

a significant reduction in π–π* light absorption around 320 nm (b, solid line). By adding 10 weight% (%) PBMA-*b*-PAz (Figure 1 a; $M_n = 8.3\times10^4$, $M_w/M_n = 1.22$, g-57 °C-SmC-90 °C-SmA-118 °C-iso, glass transition temperature (T_g) (PBMA) = ca. 20 °C), the same procedure led to a drastic spectral change (b, dotted line), showing that the Az mesogenic group of the total PAz film tends to orient randomly or nearly parallel to the substrate. In the grazing-angle incidence X-ray diffraction (GI-XRD) measurement (c and d), the diffraction spots ascribed to the smectic layer structure of pure PAz and PBMA-*b*-PAz (10 %)/PAz blend films of the Az mesogens ($d = 3.5$ nm) were observed in the out-of-plane (vertical, $d = 3.3$ nm) (c) and in-plane (horizontal, $d = 3.5$ nm) (d) directions, respectively. Thus, marked orientational alternations in the molecular and layer orientations were observed by the adding PBMA-*b*-PAz. Addition of the same amount of PBMA homopolymer did not lead to this effect, indicating that sufficient compatibility of the block copolymer of PBMA-*b*-PAz containing the PAz block is required for the alignment alternation.

The contact angles of water droplets (θ_w) on the surfaces of the polymer films under study are summarized in Table 1. For all of the polymer films, annealing led to slightly larger θ_w values, indicating that more hydrophobic moieties, such as the hydrocarbon part and the chain ends,[16] became exposed to the air side. θ_w of the PAz homopolymer (107 ± 0.9°) was significantly lowered by adding 10 % PBMA-*b*-PAz to 95.5 ± 0.2°. The lowered value virtually agrees with that of a pure PBMA-*b*-PAz film ($\theta_w = 97.0 \pm 0.6°$), indicating that the minor amount of PBMA-*b*-PAz migrated and was enriched at the free surface. This enrichment of PBMA-*b*-PAz should occur because of the lower surface free energy of PBMA[17] and also because of the entropic requirement,[18] that is, PBMA possessing a flexible side chain ($T_g = 20$ °C) should migrate to the free surface. The direct visual evidence of the PBMA-*b*-PAz segregation at the surface will be discussed later for the block copolymer system. Thus, PBMA-*b*-PAz works as a free-surface-active polymer.

Table 1: Contact angles of water droplets (θ_w) on polymer surfaces of as-cast films and after annealing at 130 °C.

Compound	Contact angle θ_w [°]	
	As-cast	After annealing
PS	95.0 ± 0.9	98.0 ± 0.7
PBMA	95.0 ± 1.0	99.7 ± 1.0
PAz	103.7 ± 0.3	107.2 ± 0.9
PS-*b*-PAz	103.4 ± 0.7	109.8 ± 0.9
PBMA-*b*-PAz	95.2 ± 0.7	97.0 ± 0.6
PBMA-*b*-PAz/PAz	94.3 ± 0.8	95.5 ± 0.2
PBMA-*b*-PAz/PS-b-PAz	95.3 ± 0.8	99.5 ± 0.5

Next, the same procedures were conducted for a polystyrene (PS)-based block copolymer film (PS-*b*-PAz in Figure 2 a, $M_n = 1.2\times10^5$, $M_w/M_n = 1.29$, and g-59 °C-SmC-90 °C-SmA-118 °C-iso, T_g (PS) = ca. 104 °C) that forms cylindrical MPS domains of coiled PS. UV/Vis absorption spectra of pure PS-*b*-PAz and blended PBMA-*b*-PAz (10 %)/PS-b-PAz films after annealing at 130 °C for 10 min followed by a gradual cooling are shown in Figure 2 b. These marked changes show that, also for the block copolymer system, the homeotropic-to-parallel orientational change of Az mesogens occurs upon addition of the PBMA-*b*-PAz and subsequent annealing. GI-XRD measurements similarly revealed that the addition of PBMA-*b*-PAz and annealing drastically changes the orientation of the smectic layer ($d = 3.6$ nm), as shown in Figure 2 c and d. The MPS cylindrical pattern within the PBMA-*b*-PAz (10 %)/PS-*b*-PAz film are oriented parallel to the substrate following the Az mesogen alignment.[14b,c]

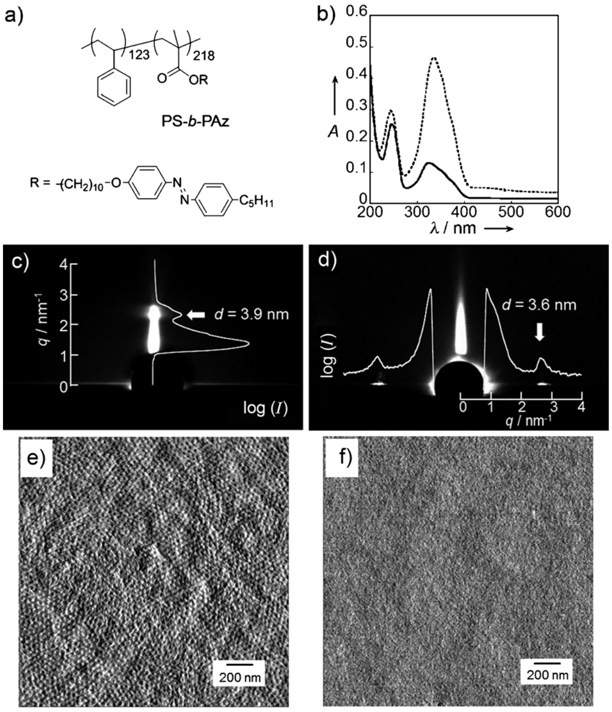


Figure 2. a) Molecular formulas of PS-*b*-PAz. b) UV/Vis absorption spectra of a PS-*b*-PAz thin film (——), and the PBMA-*b*-PAz (10%)/PS-*b*-PAz blend thin film (-----) after annealing at 130 °C. c) and d) The 2D GI-XRD patterns of a pure PAz film and PBMA-*b*-PAz (10%)/PS-*b*-PAz blend thin films after annealing at 130 °C, respectively. In the XRD patterns, 1D intensity profiles are indicated as white lines. e) and f) 2.0 × 2.0 μm AFM images (phase mode) of annealed PS-*b*-PAz and PBMA-*b*-PAz (10%)/PAz blend films, respectively.

Similarly to the PAz homopolymer case, θ_w of the PS-*b*-PAz film surface significantly decreased from 109.8 ± 0.9° to 99.5 ± 0.5° (Table 1) by adding 10 % PBMA-*b*-PAz and annealing, which is indicative of the surface segregation and enrichment of PBMA-*b*-PAz. The surface morphology evaluated by atomic force microscopy (AFM) revealed that the vertically oriented cylindrical domains of PS are exposed to the surface in the pure PS-*b*-PAz film (Figure 2 e). The AFM image in the phase mode showed a dot array structure (average dot-to-dot distance; 46 ± 0.7 nm), which coincides well with the $2/\sqrt{3}$ times the (1 0) cylindrical plane spacing of the bulk structure (40 nm) assuming hexagonal packing. In contrast, the surface of the blend film of PBMA-*b*-PAz (10 %)/PS-*b*-PAz exhibited a highly uniform surface. This fact directly shows that the MPS domains of PS-*b*-PAz are buried beneath the surface-segregated PBMA-*b*-PAz layer (Figure 2 f).

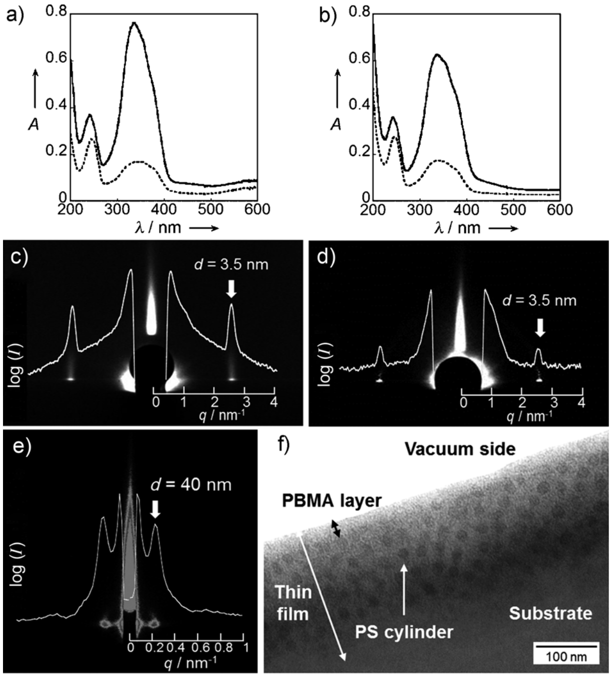
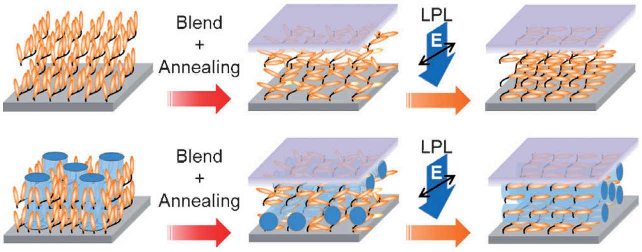


Figure 3. a) and b) UV/Vis absorption spectra of PBMA-*b*-PAz (10%)/PAz (a) and PBMA-*b*-PAz (10%)/PS-*b*-PAz blend (b) films after irradiation with 436 nm LPL at 1000 mJ cm^{-2}. The spectra were taken with the probing beam parallel (-----) and orthogonal (——) to the actuating light. c) and d) 2D GI-XRD patterns of LPL-irradiated PBMA-*b*-PAz (10%)/PAz (homopolymer) and PBMA-*b*-PAz (10%)/PS-*b*-PAz (block copolymer) blend films, respectively (X-ray incidence: orthogonal to the actinic LPL). e) GI-SAXS patterns for the MPS cylindrical domain detection (X-ray incidence: parallel to the actinic LPL). In the GI-XRD and GI-SAXS patterns, 1D intensity profiles are indicated as white lines. f) TEM image of a cross-section of the PBMA-*b*-PAz (10%)/PS-*b*-PAz film. The sample was sliced in the direction parallel to the actinic LPL.

Based on these observations, the photoalignment behavior by irradiation with linearly polarized light (LPL) was examined for the surface-segregated films (Figure 3) because the planar orientation of Az mesogenic groups is favorable for photoalignment in the in-plane directions.[19] The PAz homopolymer and PS-*b*-PAz blended with 10% PBMA-*b*-PAz and annealing at 130 °C for 10 min first, and then irradiated with 436 nm LPL at 1 mW cm^{-2} for 1000 s at 90 °C and 110 °C was performed, for PAz and PS-b-PAz, respectively. The resultant polarized UV/Vis absorption spectra are shown in Figure 3 a and b. In both cases, highly aligned Az mesogens in the in-plane direction were obtained. The order parameter S [$=(A_{\perp}-A_{\parallel})/(A_{\perp}+2A_{\parallel})$], where $A_{\perp}$ and $A_{\parallel}$ denote absorbance at the λ_{max} of the π–π^* absorption band of the Az unit (ca. 350 nm) obtained by measurements using polarized light with E perpendicular and parallel to that of actinic polarized light respectively, reached 0.67 and 0.48, respectively. The GI-XRD results indicate the existence of more ordered, vertically aligned smectic layers in the film when the direction of the X-ray beam incidence was set orthogonal to the actinic LPL direction (Figure 3 c and d).[14b,19]

For the photoaligned block copolymer film of PBMA-*b*-PAz (10%)/PS-*b*-PAz, the structure of the MPS cylinders of the PS-*b*-PAz film was evaluated by GI-small angle X-ray scattering (GI-SAXS) measurements (Figure 3 e) and transmission electron microscopy (TEM, Figure 3 f). The scattering spots in the GI-SAXS were observed at ($q=0.22$ nm^{-1} ($d=40$ nm, white arrows), which corresponds to the in-plane aligned MPS cylindrical domains. In the TEM image of a RuO$_4$-stained sample, a cross-section sliced in the parallel direction to the actinic LPL provided regularly arranged dark dot parts of the PS domains within the film with a total thickness of about 200 nm. The averaged center-to-center domain distance between the PS cylinders was 46 nm, in good agreement with the above X-ray and AFM (Figure 2 e) data. It should be noted that the light dose required for MPS alignment is 1000 mW cm^{-2}, which is much less than that required for the relevant PS-*b*-PAz film without the segregated layer (6000 mJ cm^{-2}),[14a] indicating that more efficient in-plane MPS domain alignment is attained owing to the preorientation in the in-plane direction by the surface layer. More importantly, the TEM image revealed the existence of a thin skin layer of about 20 nm thickness at the topmost surface, observed as a brighter region. This surface skin layer should correspond to the surface-segregated PBMA-*b*-PAz. In this case, 10% PBMA-*b*-PAz was blended, and therefore the thickness of the top layer was almost 10% of the total thickness. In the skin layer, no MPS was recognized, which can be understood from the fact that the skin thickness is below the level of MPS domain formation of this PBMA-*b*-PAz (lamella-forming polymer with a 49 nm period).

The orientation and alignment behaviors proposed in this work are illustrated in Scheme 1. In the pure PAz film (upper process), the homeotropic anchoring to the free surface of Az mesogens (rodlike orange units) induces the normal orientation. For the PS-*b*-PAz block copolymer film (lower process), the MPS cylindrical domains (blue cylinders) are accordingly oriented perpendicularly to the substrate (top left). Blending the surface-active PBMA-*b*-PAz and subsequent annealing lead to a skin layer formation on the surface, which blocks the homeotropic anchoring of Az mesogens, and provides planar orientation of Az mesogens and MPS cylindrical domains with the substrate surface (schemes in the middle for both processes). Owing to the preformed parallel orientation, LPL irradiation efficiently leads to homogeneous in-plane alignment orthogonal to the electric field of the LPL (top right schemes for both processes).



Scheme 1. Illustrations of the orientation and alignment process for the PAz homopolymer (upper) and PS-*b*-PAz block copolymer (lower) described in this study.

The homeotropic anchoring of rodlike LC molecules at the free surface has been predicted by theoretical considerations,[10,20] and experimental observations of side-chain LC polymer thin films are in agreement with this.[21] When the free surface is covered with a segregated layer, the excluded volume effect from the plane solid substrate should dominate.[22] An alternative explanation can be the tendency to adopt a planar orientation of the mesogenic groups in the segregated PBMA-*b*-PAz.[14b] It is noteworthy that the LC mesogens and MPS domain orientations in pure LC polymer films were unaffected by the surface energy of the substrate surface. LC and MPS domain orientations were evaluated for both clean hydrophilic ($\theta_w < 10°$) and hydrophobized ($\theta_w =$ ca. 80°) quartz plate surfaces, and the orientation were the same, regardless of the surface energy of the solid substrate. This fact implies the predominant role of the free surface in the vertical orientation in the LC polymer film. The importance of the free surface for the Az mesogen orientation was also suggested recently by Iyoda et al.[23] Further investigation is needed to elucidate what factors significantly affect the alignment alternation. The blend ratio, molecular weight, block ratio of the added polymer, chemical structure, thermophysical property of the coil block of the added polymer, total film thickness, and annealing procedures should greatly influence the orientation behavior. For example, reduction of the mixing ratio to 5 wt% of PBMA-*b*-PAz resulted in an incomplete planar orientation. We are now making efforts to gain a better understanding of this phenomenon.

In conclusion, this work first demonstrates the clear orientational alternations of LC mesogens and the MPS domains by modifying the free surface, which is accomplished by simply blending a surface-active polymer and performing the appropriate annealing step. This strategy is very simple and is therefore expected to open up new possibilities for orientation controls of various types of LC materials. Selective surface segregation of a surface-active polymer component has promising applications for imposing surface functions such as adhesive and frictional properties[24] and for improving biocompatibility.[25] In addition to such functions accessing the exterior phase, the present work indicates that free surface segregation is also valuable for the control of the interior structure of the polymer film.

Received: January 22, 2013
Revised: March 8, 2013

Keywords: azobenzene · diblock copolymers · liquid crystals · microphase separation · orientational control

---

[1] B. Jerome, *Rep. Prog. Phys.* **1991**, *54*, 391–451.

[2] a) P. Chatelain, *Bull. Soc. Fr. Mineral.* **1943**, *66*, 105; b) J. Cognard, *Mol. Cryst. Liq. Cryst. Suppl. Ser.* **1982**, *1*(suppl1), 1–77.

[3] M. Schadt, *Liq. Cryst.* **1993**, *14*, 73–104.

[4] a) M. Toney, T. Russell, J. Logan, H. Kikuchi, J. Sands, S. Kumar, *Nature* **1995**, *374*, 709–711; b) K. Weiss, C. Woll, E. Bohm, B. Fiebranz, G. Forstmann, B. Peng, V. Scheumann, D. Johannsmann, *Macromolecules* **1998**, *31*, 1930–1936.

[5] a) D. Berreman, *Phys. Rev. Lett.* **1972**, *28*, 1683–1686; b) T. Ohzono, J. Fukuda, *Nat. Commun.* **2012**, *3*, 701.

[6] a) K. Ichimura, *Chem. Rev.* **2000**, *100*, 1847–1873; b) T. Seki, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 2084–2109; c) K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, K. Aoki, *Langmuir* **1988**, *4*, 1214–1216; d) W. Gibbons, P. Shannon, S. Sun, B. Swetlin, *Nature* **1991**, *351*, 49–50; e) M. Schadt, K. Schmitt, V. Kozinkov, V. Chigrinov, *Jpn. J. Appl. Phys.* **1992**, *31*, 2155–2164; f) O. Yaroshchuk, Y. Reznikov, *J. Mater. Chem.* **2012**, *22*, 286–300.

[7] S. Chae, B. Hwang, W. Jang, J. Oh, J. Park, S. Lee, K. Song, H. Baik, *Soft Matter* **2012**, *8*, 1437–1442.

[8] a) J. Brake, M. Daschner, Y. Luk, N. Abbott, *Science* **2003**, *302*, 2094–2097; b) J. Brake, N. Abbott, *Langmuir* **2007**, *23*, 8497–8507.

[9] a) T. Seki, K. Fukuda, K. Ichimura, *Langmuir* **1999**, *15*, 5098–5101; b) M. Kidowaki, T. Fujiwara, K. Ichimura, *Chem. Lett.* **1999**, 641–642; c) T. Fujiwara, J. Locklin, Z. Bao, *Appl. Phys. Lett.* **2007**, *90*, 232108.

[10] a) B. Ocko, A. Braslau, P. Pershan, J. Alsnielsen, M. Deutsch, *Phys. Rev. Lett.* **1986**, *57*, 94–97; b) P. S. Pershan, *Faraday Discuss. Chem. Soc.* **1990**, *89*, 231–245.

[11] a) N. Scaramuzza, C. Berlic, E. Barna, G. Strangi, V. Barna, A. Ionescu, *J. Phys. Chem. B* **2004**, *108*, 3207–3210; b) S.-M. Chen, T.-C. Hsieh, R.-P. Pan, *Phys. Rev. A* **1991**, *43*, 2848–2857; c) A. A. Canabarro, I. N. de Oliveira, M. L. Lyra, *Phys. Rev. E* **2008**, *77*, 011704.

[12] a) Q. Bhatia, D. Pan, J. Koberstein, *Macromolecules* **1988**, *21*, 2166–2175; b) K. Tanaka, A. Takahara, T. Kajiyama, *Macromolecules* **1998**, *31*, 863–869.

[13] E. Huang, T. Russell, C. Harrison, P. Chaikin, R. Register, C. Hawker, J. Mays, *Macromolecules* **1998**, *31*, 7641–7650.

[14] a) Y. Morikawa, T. Kondo, S. Nagano, T. Seki, *Chem. Mater.* **2007**, *19*, 1540–1542; b) S. Nagano, Y. Koizuka, T. Murase, M. Sano, Y. Shinohara, Y. Amemiya, T. Seki, *Angew. Chem.* **2012**, *124*, 5986–5990; *Angew. Chem. Int. Ed.* **2012**, *51*, 5884–5888; c) H. Yu, T. Iyoda, T. Ikeda, *J. Am. Chem. Soc.* **2006**, *128*, 11010–11011.

[15] C. Bates, T. Seshimo, M. Maher, W. Durand, J. Cushen, L. Dean, G. Blachut, C. Ellison, C. Willson, *Science* **2012**, *338*, 775–779.

[16] D. Kawaguchi, K. Tanaka, T. Kajiyama, A. Takahara, S. Tasaki, *Macromolecules* **2003**, *36*, 6824–6830.

[17] M. Khayet, M. Alvarez, K. Khulbe, T. Matsuura, *Surf. Sci.* **2007**, *601*, 885–895.

[18] S. Wu, *J. Phys. Chem.* **1970**, *74*, 632–638.

[19] a) T. Uekusa, S. Nagano, T. Seki, *Macromolecules* **2009**, *42*, 312–318; b) H. A. Haque, S. Nagano, T. Seki, *Macromolecules* **2012**, *45*, 6095–6103.

[20] H. Kimura, H. Nakano, *J. Phys. Soc. Jpn.* **1985**, *54*, 1730–1736.

[21] a) B. Sapich, A. Vix, J. Rabe, J. Stumpe, *Macromolecules* **2005**, *38*, 10480–10486; b) N. Zettsu, T. Seki, *Macromolecules* **2004**, *37*, 8692–8698; c) S. Asaoka, T. Uekusa, H. Tokimori, M. Komura, T. Iyoda, T. Yamada, H. Yoshida, *Macromolecules* **2011**, *44*, 7645–7658.

[22] K. Okano, *Jpn. J. Appl. Phys.* **1983**, *22*, L343–L344.

[23] H. Komiyama, T. Iyoda, K. Kamata, *Chem. Lett.* **2012**, *41*, 110–112.

[24] T. Schaub, G. Kellogg, A. Mayes, R. Kulasekere, J. Ankner, H. Kaiser, *Macromolecules* **1996**, *29*, 3982–3990.

[25] T. Hirata, H. Matsuno, M. Tanaka, K. Tanaka, *Phys. Chem. Chem. Phys.* **2011**, *13*, 4928–4934.