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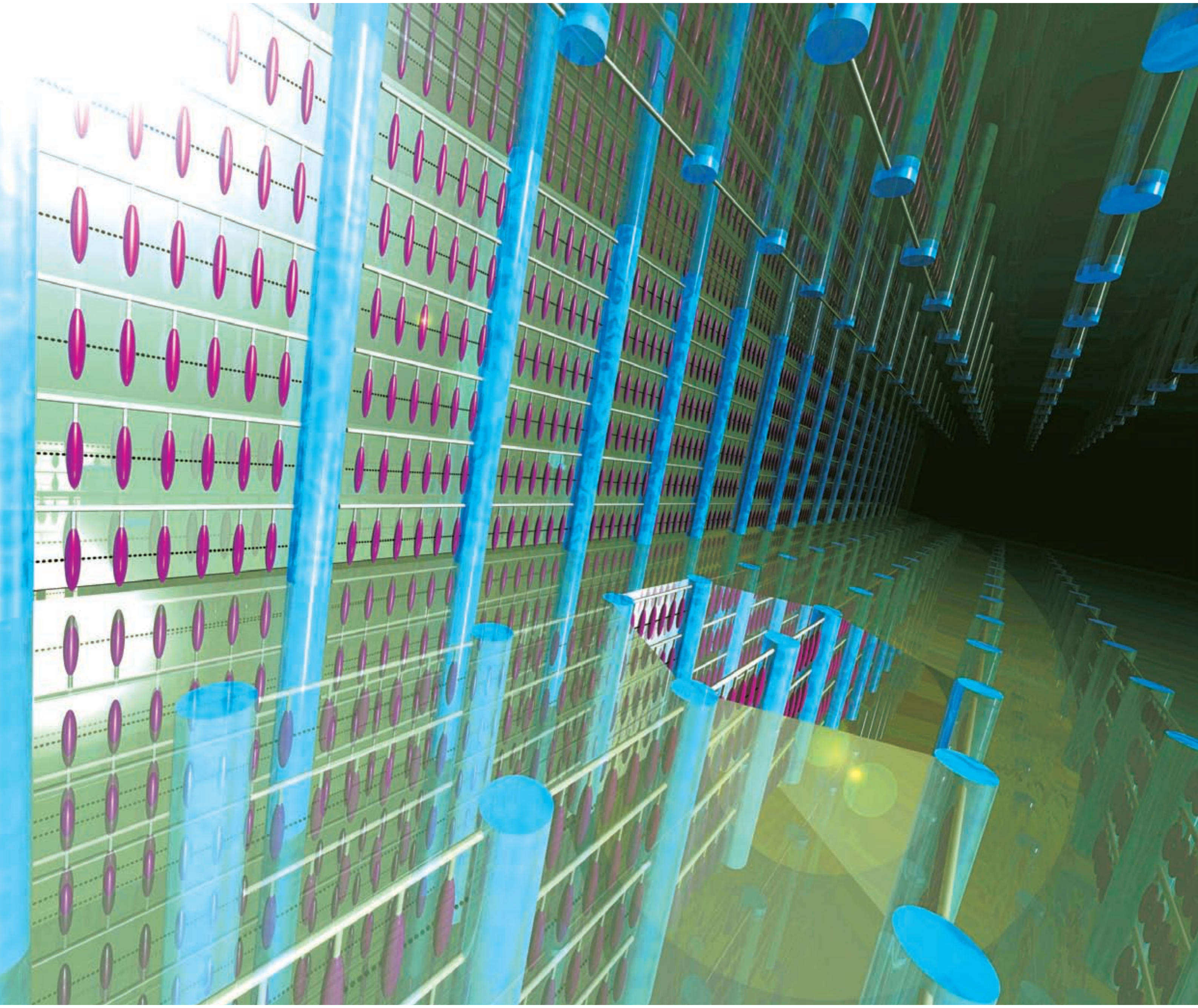

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Stable macroscopic nanocylinder arrays in an amphiphilic diblock liquid-crystalline copolymer with successive hydrogen bonds†

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In bulk films of a novel well-defined amphiphilic diblock liquid-crystalline copolymer with aramid moieties, a stable perpendicularly orientated hydrophilic nanocylinder array with hexagonal packing was formed in a large area by supramolecular self-assembly.

Recently, much attention has been paid to well-defined block copolymers or polymer alloys because they can self-assemble into ordered periodic nanostructures,[1] which have been widely used as templates or scaffolds for bottom-up nanotechnology.[1,2] Unfortunately, good domain order over a large area cannot be achieved by molecular self-assembly alone, and external forces or modified substrates have been explored to obtain long-range order.[1–4] Based on the pioneering work of Iyoda *et al.*,[3a] we have combined liquid-crystalline polymers (LCPs) with microphase separation of block copolymers to obtain macroscopic regular nanostructures in the designed materials by supramolecular self-assembly.[3,4] In the process of microphase separation, inherent LC properties such as self-organising nature, fluidity of long-range order and cooperative motion are involved,[5] which enables the microphase-separated periodic structures to be controlled.[4] For instance, azobenzene moieties can play roles both as a mesogen and as a photosensitive chromophore in LC block copolymers,[3–6] whose microphase-separated nanostructures have been manipulated by either the rubbing technique or polarized laser beams.[4] Obviously, the obtained nanostructures have a poor optical durability, which limits their wide application. To improve the stability of the obtained nanostructures, in this study, non-photosensitive aramid moieties were introduced as mesogens to form successive hydrogen bonds (H-bonds) in the matrix.

Owing to their molecular rigidity, aramid groups have been utilized as mesogens to build LCPs,[7,8] and their strong H-bonds enable polyaramid fibers such as Kevlar and Nomex (Dupont) to be among the toughest organic materials.[8] Since H-bonds have been extensively explored to tailor self-organized nanostructures,[9] introduction of the aramid groups into LC block copolymers might bring about more stable nanostructures by supramolecular self-assembly. Here, we design a novel amphiphilic diblock LC copolymer (ADLC) consisting of flexible poly(ethylene oxide) (PEO) as a hydrophilic segment and poly(methacrylate) containing an aramid moiety in the side chain as a hydrophobic LC segment. To prepare the ADLC, a bromo-terminated PEO with 114 repeat units ($PEO_{114}Br$) was used as a macroinitiator to undergo a typical atom transfer radical polymerization (ATRP).[3,4] Fig. 1 shows the molecular structures of the block copolymer, in which about 70 repeat units of the aramid block were estimated by the integration of the phenyl proton NMR peak at 6.72 ppm of the aramid to that of the oxyethylene protons of the PEO at 3.64 ppm. The GPC curve gives a number-average molecular weight (M_n) of 42 400 and a narrow polydispersity index of 1.15. The obtained ADLC is only soluble in polar solvents such as chloroform, dichloromethane, and *N*,*N*-dimethylformamide because of the existence of strong H-bonds among the aramid groups. Such strong interactions are responsible for broadening an absorption peak at 3340 cm^{-1} in the FTIR spectrum (stretch vibration of N–H in aramid, Fig. 2a). When the copolymer was heated, three phase-transition peaks appeared at 32.2, 124.7 and 134.3 °C in its thermogram by differential scanning calorimetry (DSC, Fig. 1), corresponding to the PEO melting point, the aramid block melting point, and smectic phase to isotropic phase transition, respectively. On cooling, a wider LC range was observed, and the PEO melting point appeared at −32.6 °C because of the super-cooling effect. No obvious glass-transition temperature (T_g) was obtained in the DSC curve.

Copolymer films with a thickness of about 140 nm were prepared by spin-coating from a chloroform solution onto clean glass substrates. After the solvent was removed at room

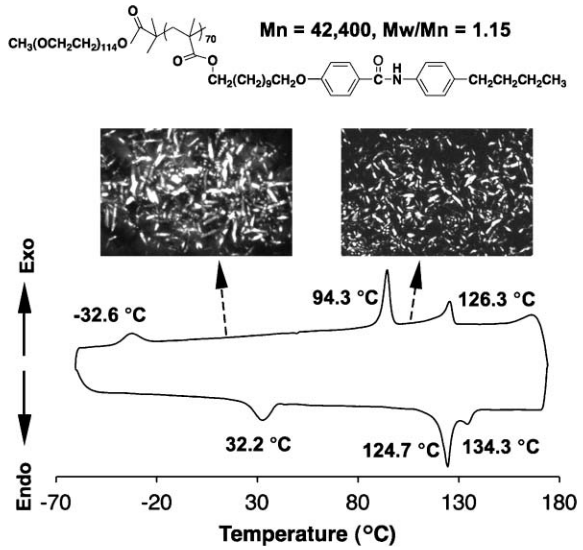

Fig. 1 Molecular structure and thermal properties of the block copolymer. The polarizing optical microscopic pictures (500) were obtained at 30 °C and 120 °C, respectively.

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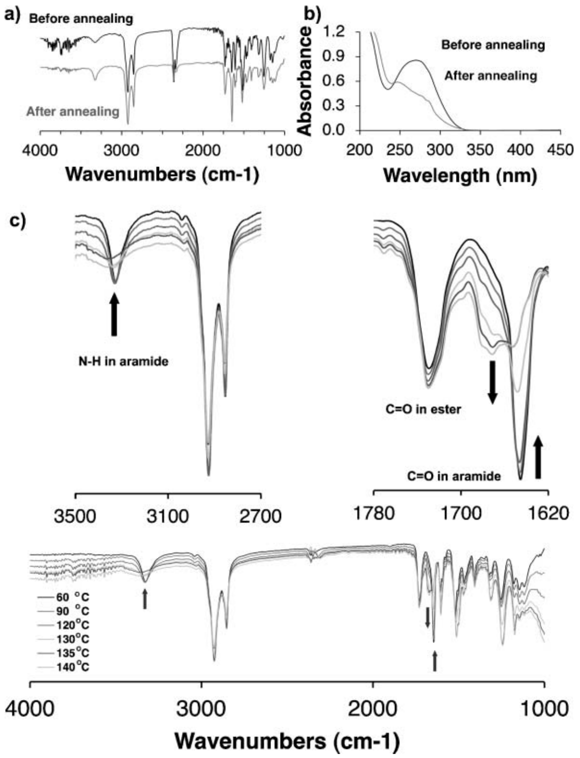

Fig. 2 Absorption spectra of the block copolymer films. (a,b) FTIR and UV-Vis spectra of the block copolymer films before and after annealing, respectively. (c) *In-situ* FTIR spectra of the annealed films.

temperature, the films were annealed at 140 °C for 24 h by controlling both the heating and cooling rates at 1 °C min^{-1}. Upon annealing, the UV-Vis maximum absorbance at 271 nm shown in Fig. 2b decreased greatly, probably attributed to the out-of-plane alignment of the aramid mesogens. Such perpendicular orientation of the mesogens also gives rise to the in-plane orientation of the carboxyl groups inside the aramid mesogens, which is indicated by an obvious increase in the intensity of the FTIR absorption peak at 1646 cm^{-1} (stretch vibration of C=O in aramid, Fig. 2a). Furthermore, a blue shift of 24 nm occurred in the UV-Vis maximum absorption owing to the formation of H-aggregates of the mesogens.

Generally, the covalently-connected immiscible block copolymers thermodynamically show microphase-segregated nanostructures including spheres, cylinders, gyroid and lamellae, driven by the positive free energy of mixing of the polymeric composites.[10] In the present ADLC films, both the H-bonds and the LC ordering affect the microphase-separation process, enabling them to form hierarchical structures by supramolecular self-assembly. As shown in Fig. 3, unambiguous regular nanostructures were clearly observed in the atomic force microscopic (AFM) images. Considering the composition of the block copolymer, although the repeat units of PEO are much more than those of the aramid block, the PEO block still constitutes the minority component in the microphase separation of the ADLC bulk films. The PEO block is well known for its crystallization and strong inter- or intra-molecular interaction (H-bonds), while the block of aramid mesogens has the inherent LC properties of self-organization and long-range ordering,[6] as well as H-bonds.[8,9] As a result, strong molecular interactions exist in both of the polymeric constituent segments of the ADLC, which makes its microphase separation different from other block copolymers with relatively weak molecular interactions.

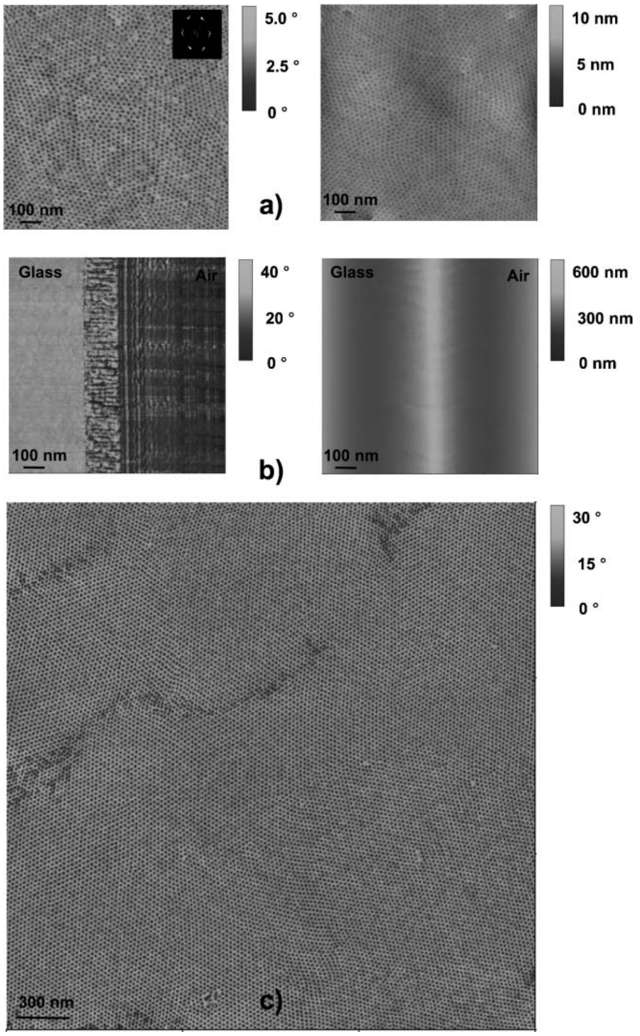

Fig. 3 AFM images of the annealed block copolymer films. (a,b) AFM image of surface and cross section, respectively. Phase images are on the left, whereas topological ones are on the right. Inset into the phase picture is the fast Fourier transform image. (c) AFM phase image of the block copolymer film with a large area of 3 mm × 3 mm.

By supramolecular self-assembly, the PEO blocks segregated into hydrophilic nanocylinders of 9 nm diameter and a 21 nm periodicity dispersed in a matrix of aramid mesogens, and the hexagonal packing of the PEO nanocylinders was indicated by the fast Fourier transform shown in Fig. 3a. Although no external driving forces were exerted on the sample films, such regularly periodic arrangements of the nanocylinders were not limited to the film surface alone; three-dimensional (3-D) arrays were confirmed by a cross-sectional image (Fig. 3b). The PEO nanocylinders of 140 nm in length are normal to the glass substrate, just the same as the film thickness, showing a perpendicularly orientated nanocylinder array (PONA) with hexagonal packing in the bulk films. Such well-ordered arrays of nanoscale phase domains can be regarded as analogous to "a polymeric single crystal", which may extend to a macroscopic scale. Owing to the AFM resolution, an image of PONA in an area of 3 μm × 3 μm is provided in Fig. 3c.

In fact, such dotted patterning of PEO nanocylinders can be perfectly achieved over several centimeters, which have been confirmed by acquiring AFM images spaced by 100 μm over the whole substrate.

To obtain good microphase-separated structures, the annealing temperature was chosen as 140 °C, slightly higher than the phase-transition temperature (Fig. 1),[4] which acts by destroying the H-bonds, lowering the viscosity of the block copolymer films and enabling the microphase separation to proceed completely in an isotropic state. Furthermore, a wider range of LC temperature was obtained on cooling than the heating process, permitting the LC ordering to influence the microphase separation and achieve regularly ordered nanostructures. In the cooling process, the PEO domains are confined to the continuous phase of the aramid mesogens, and mass transport of the PEO domains is prevented. Contraction of the confined PEO domains might occur on cooling,[11] leading to a dent of several nanometers in the 3-D AFM image (Fig. 4b). Compared with our previous work,[3,4] the stability of the microphase-separated structures has been improved by replacing the azobenzene mesogens with the aramid groups, which have strong H-bonds. No obvious change in the PONA structures was detected by AFM after the ADLC films were exposed to room light for six months (Fig. S3 and S4†).

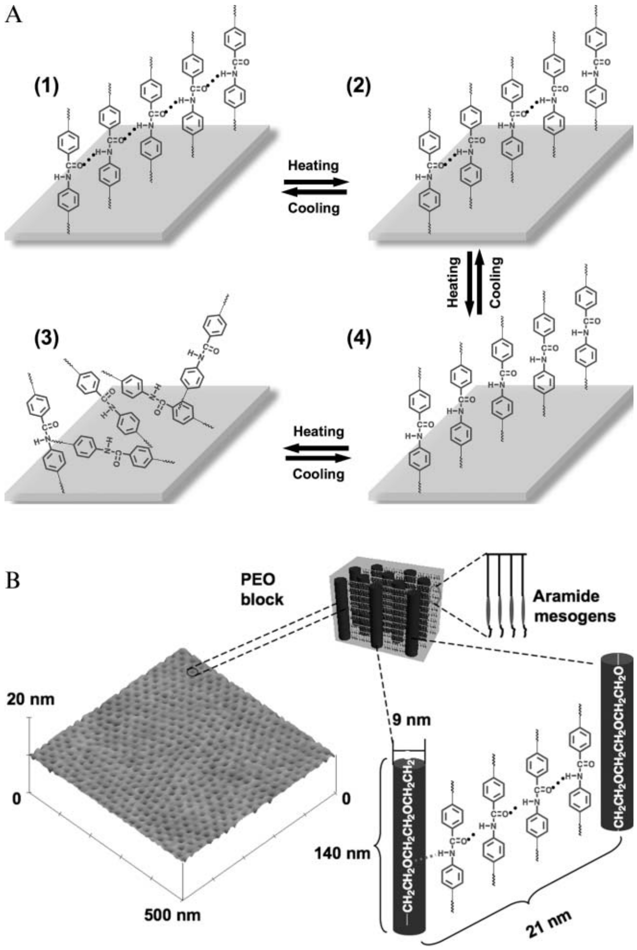

Fig. 4 Schematic illustration of the microphase-separated structures and the hydrogen bonds in the block copolymer films. (A) Possible scheme of hydrogen bonds and orientation of the aramid mesogens upon heating. (B) Three-dimensional AFM image of the block copolymer film and plausible structures of the microphase separation by supramolecular self-assembly.

To check the H-bonds in the annealed block copolymer films with regular stable PONA structures, *in situ* FTIR spectra were measured at different temperatures, which are given in Fig. 2c. According to the analysis, four possible stages are summarized in Fig. 4a. Stage (1) shows that strong H-bonds exist among the out-of-plane aligned aramid mesogens in the annealed copolymer film at room temperature, which may play an important role in the stabilization of the microphase-separated nanostructures. Upon heating, the H-bonds are partly destroyed, leading to a slight decrease in both absorption peaks at 3340 cm^{-1} and 1646 cm^{-1} (Fig. 2c) prior to the melting, and the alignment of the mesogens remains in stage (2). When the film temperature is higher than the melting point but lower than the LC phase-transition temperature, all of the H-bonds might be destroyed completely, resulting in an obvious decrease in both of the peaks shown in Fig. 3c. A new shoulder peak at 1672 cm^{-1} appeared, which is attributed to the vibration of carbonyl bond in aramid without H-bonds. Due to the smectic LC ordering, the alignment of the aramid groups was maintained in stage (3). Evidently, random alignment of the aramid mesogens was induced because of the loss of LC properties in an isotropic phase in stage (4), leading to a further decrease in the peak at 1646 cm^{-1} and a corresponding increase in its shoulder peak at 1672 cm^{-1}. Both the out-of-plane alignment of aramid mesogens and the formation of H-bonds are reversible upon cooling the sample films, as shown in Fig. 4a. It is worth mentioning here that H-bonds might also be formed between the EO units and the aramid mesogens, and a plausible microphase-separated structure by supramolecular self-assembly is depicted in Fig. 4b. Obviously, the introduction of aramid mesogens with H-bonds in the ADLC not only enables one to obtain macroscopic regular arrays of PONA without external forces, but also improves the stability of the self-assembled nanostructures.

In summary, a novel PEO-based diblock LC copolymer with aramid mesogens was prepared by ATRP. The bulk films of the well-defined block copolymer showed macroscopic PONA structures of PEO phase domains dispersed in the continuous phase of aramid mesogens, owing to supramolecular self-assembly. Such periodic nanostructures showed a high stability under room light because of the existence of successive H-bonds in the matrix. The obtained block copolymer may function as a reliable nano-template for restricted chemical or electrochemical reactions to prepare desirable arrays of nanowires, tube, rods, dots, *etc*.

Acknowledgements

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Notes and references

1 S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. Pablo and P. F. Nealey, *Nature*, 2003, **424**, 411.

2 (*a*) W. A. Lopes and H. M. Jaeger, *Nature*, 2001, **414**, 735; (*b*) C. A. Breen, T. Deng, T. Breiner, E. L. Thomas and T. M. Swager, *J. Am. Chem. Soc.*, 2003, **125**, 9942; (*c*) T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen and T. P. Russell, *Science*, 2000, **290**, 2126; (*d*) J. Y. Cheng, C. A. Ross, H. T. Smith and E. L. Thomas, *Adv. Mater.*, 2006, **18**, 2505.

3 (*a*) Y. Tian, K. Watanabe, X. Kong, J. Abe and T. Iyoda, *Macromolecules*, 2002, **35**, 3739; (*b*) H. F. Yu, K. Okano, A. Shishido, T. Ikeda, K. Kamata, M. Komura and T. Iyoda, *Adv. Mater.*, 2007, **17**, 2184; (*c*) H. F. Yu, A. Shishido, T. Ikeda and T. Iyoda, *Macromol. Rapid Commun.*, 2005, **26**, 1594; (*d*) H. F. Yu, A. Shishido, T. Iyoda and T. Ikeda, *Macromol. Rapid Commun.*, 2007, **28**, 927.

4 (*a*) H. F. Yu, J. Z. Li, T. Ikeda and T. Iyoda, *Adv. Mater.*, 2006, **18**, 2213; (*b*) Y. Morikawa, S. Nagano, T. Watanabe, K. Kamata, T. Iyoda and T. Seki, *Adv. Mater.*, 2006, **18**, 883; (*c*) H. F. Yu, T. Iyoda and T. Ikeda, *J. Am. Chem. Soc.*, 2006, **128**, 11010; (*d*) H. F. Yu, S. Asaoka, A. Shishido, T. Iyoda and T. Ikeda, *Small*, 2007, **3**, 768.

5 M. Walther and H. Finkelmann, *Prog. Polym. Sci.*, 1996, **21**, 951.

6 (*a*) D. Deus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, *Handbook of Liquid Crystals*, Wiley-VCH, Weinheim, Germany, 1998, vol. 3, pp. 66; (*b*) T. Ikeda, *J. Mater. Chem.*, 2003, **13**, 2037.

7 R. Ruhmann, J. Rübner, G. Rodekirch, V. Zschuppe, R. Gnauck, M. Netopilik and D. Wolff, *Acta Polym.*, 1990, **41**, 492.

8 T. Yokozawa, M. Ogawa, A. Sekino, R. Sugi and A. Yokoyama, *J. Am. Chem. Soc.*, 2002, **124**, 15158.

9 T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38.

10 (*a*) M. Fasolka and A. Mayes, *Annu. Rev. Mater. Res.*, 2001, **31**, 323; (*b*) F. Bates and G. Fredrickson, *Phys. Today*, 1999, **52**, 32.

11 G. Reiter, G. Castelein, P. Hoerner, G. Riess, A. Blumen and J. U. Sommer, *Phys. Rev. Lett.*, 1999, **83**, 38.