Published in final edited form as:

Nano Lett. 2008 October ; 8(10): 3434–3440. doi:10.1021/nl802298m.

Controlling the Morphology of Side Chain Liquid Crystalline Block Copolymer Thin Films through Variations in Liquid Crystalline Content

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Abstract

In this paper we describe methods for manipulating the morphology of side-chain liquid crystalline block copolymers through variations in the liquid crystalline content. By systematically controlling the covalent attachment of side chain liquid crystals to a block copolymer (BCP) backbone, the morphology of both the liquid crystalline (LC) mesophase and the phase segregated BCP microstructures can be precisely manipulated. Increases in LC functionalization lead to stronger preferences for the anchoring of the LC mesophase relative to the substrate and the inter-material dividing surface (IMDS). By manipulating the strength of these interactions the arrangement and ordering of the ultrathin film block copolymer nanostructures can be controlled, yielding a range of morphologies that includes perpendicular and parallel cylinders, as well as both perpendicular and parallel lamellae. Additionally, we demonstrate the utilization of selective etching to create a nanoporous liquid crystalline polymer thin film. The unique control over the orientation and order of the self-assembled morphologies with respect to the substrate will allow for the custom design of thin films for specific nano-patterning applications without manipulation of the surface chemistry or the application of external fields.

Keywords

liquid crystal; block copolymer; thin films; selective etching

Recently there has been a great deal of research directed at controlling the self-assembly of block copolymer thin films, with specific interest in obtaining the desired orientation of nanoscale features relative to the substrate, such as perpendicular or parallel cylinders^{1, 2}. Progress has been made in controlling the morphologies of block copolymer thin films through techniques such as solvent annealing^{3, 4}, zone casting⁵, electric field alignment⁶, optical alignment⁷, topographical patterning^{8, 9}, and chemical substrate patterning^{10–12}. Due to the large interfacial area of thin films, the orientation of the domains depends greatly upon the relative surface energies of the blocks^{13–16}. We will show that the incorporation of a liquid crystalline (LC) component into such systems offers a powerful tool for manipulating the

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orientation of the self-assembled structures. When an LC component is introduced, several factors such as conformational asymmetry, structural asymmetry, and the anchoring of the LC mesophase to the inter-material dividing surface (IMDS) can alter the self-assembly behavior^{17–24}. The two possible scenarios for smectic LC anchoring relative to an interface – such as a substrate or the IMDS – are homeotropic or homogeneous, where the smectic layer normal is perpendicular or parallel to the interface, respectively. It has been shown that the LC mesophase will preferentially orient with respect to the IMDS due to surface stabilization effects^{25–27}. In this way a well oriented block copolymer mesophase can be used to template order in the LC mesophase. Additionally, liquid crystalline polymers (LCP) are of particular interest as they can allow for the introduction of responsive elements into the system, e.g. thermo-, chemo-, electro-, or photo-responsive²⁸.

In this paper we will describe the effects of varying the LC content upon the self-assembled morphologies of side chain liquid crystalline block copolymers synthesized via attachment of LC moieties to a poly(styrene)-poly(vinylmethylsiloxane) (PS-PVMS) block copolymer backbone. The strong preference for homogeneous LC anchoring relative to the IMDS couples the orientations of the LC mesophase and the block copolymer nanostructures. Using the LC content as a tool to tune the interfacial interactions of the LC mesophase allows for the orientation and ordering of the morphologies to be manipulated. The synthetic techniques previously described²⁹ allow for systematic control over the covalent attachment of LC moieties to the functional siloxane based block copolymer backbone. The linear increase in the LC attachment as a function of time enables precise control over the LC content. By removing and quenching portions of the reaction mixture during the functionalization reaction, numerous samples with systematically increasing LC functionalization can be achieved from a single synthesis batch. This synthetic control enables a unique tunability over the structure of these materials, allowing for the self-assembled thin film morphologies to be tailored for specific applications. The surface morphologies of these films are revealed with atomic force microscopy (AFM) and grazing incidence small-angle X-ray scattering (GISAXS) is utilized to probe the order and interior structure.

A prime example of a block copolymer thin film application is the demonstrated utility of block copolymer domains as lithographic masks^{2, 30–33}. Ordered and oriented layers of microphase domains, deposited onto a suitable substrate, can be selectively etched via a reactive ion etch to remove one of the block components³². In block copolymer lithography, arrays of holes or dots may be defined using a cylindrical-morphology block copolymer with the cylinders oriented perpendicular to the substrate^{34–37}. In contrast, patterns consisting of parallel lines may be defined using a cylindrical-morphology block copolymer with the cylinders parallel to the surface^{38–41} or a lamellar block copolymer with a perpendicular orientation^{10, 12, 42, 43}.

We will describe efforts to selectively etch the PS domains, leaving behind a nanoporous liquid crystalline polymer matrix. For the system described here, the removal of the high glass transition temperature (T_g) amorphous block results in a nanoporous liquid crystalline polymer film. The incorporation of responsive liquid crystalline moieties, in combination with the low T_g siloxane based backbone, could allow for actuation of the resulting nanoporous film. These materials show promise for creating tunable porosity membranes for chemical and biological protection.

Effect of liquid crystal content upon the orientation of cylindrical morphologies

A series of well-defined smectic side chain liquid crystalline (LC) block copolymer thin films have been prepared. The materials discussed in this section were synthesized by attaching the

LC moieties to a poly(styrene)-poly(vinylmethylsiloxane) (PS-PVMS) diblock copolymer that has PS and PVMS blocks with number-average molecular weights of 26,900 g/mol and 14,200 g/mol, respectively. Scheme 1 shows the chemical structure of the side chain liquid crystalline block copolymer used, where the ratio $y / (y + z)$ is the LC attachment percent. A detailed characterization of the structure, morphology, thermal, and mechanical properties of these side-chain liquid crystalline block copolymers has been previously reported²⁹. Spin casting was used to produce films between 100 nm and 250 nm in thickness; the self-assembly behavior was not variant with the film thickness over this range. Details regarding the sample preparation are provided in the Supporting Information. The d-spacings of these hexagonally packed cylinder materials are ~40 nm; therefore, the film thicknesses are at least twice as large as the period d-spacing of the features. In all cases, the block copolymer feature spacings determined via GISAXS and AFM are in agreement (see Supporting Information for details). Increasing the LC content leads to both an increase in the volume fraction of the liquid crystalline polymer block and an increase in the preference for anchoring of the LC mesophase.

The block copolymers with the lowest LC content (PS27-LCP_{4BPP446} and PS27-LCP_{4BPP457}) display a poorly oriented cylindrical morphology in which there is random orientation of cylinders with respect to the substrate. Annealed block copolymers with an intermediate LC content exhibit an ordered parallel cylinder morphology (PS27-LCP_{4BPP479} and PS27-LCP_{4BPP490}). Further increase of the LC content, to 100% functionalization, results in the perpendicular cylinder morphology (PS27-LCP_{4BPP4115}). These results are summarized in Table 1. It is important to note that homogenous anchoring of the LC mesophase to the IMDS was observed for all of the morphologies, such that the smectic layer normal is parallel to the cylinder axis. In this section we will detail the effects of variations in the degree of LC functionalization upon the orientation and order of these self-assembled morphologies.

For materials with low LC content (PS27-LCP_{4BPP446} and PS27-LCP_{4BPP457}), the poorly defined LC mesophase does not provide sufficient driving force for domain orientation, resulting in randomly oriented morphologies for both the as-cast and annealed films. Grazing incidence small-angle X-ray scattering (GISAXS) and grazing incidence wide-angle X-ray scattering (GIWAXS) images of PS27-LCP_{4BPP446} are provided in Supporting Information, Figure S2. This poorly ordered morphology does not show significant long-range order or any preferred orientation of either the polystyrene cylinders or the smectic LC mesophase relative to the substrate. Increasing the LC content increases the interactions of the LC mesophase and the IMDS, resulting in hexagonally ordered cylinder morphologies with significant ordering and preferential orientation relative to the substrate.

Annealed films with an intermediate LC content (PS27-LCP_{4BPP479} and PS27-LCP_{4BPP490}) display a parallel cylinder morphology. GISAXS (Figure 1a) and GIWAXS (Figure 1c) images of annealed PS27-LCP_{4BPP479} thin films indicate polystyrene cylinders oriented parallel to the substrate and smectic layers oriented perpendicular to the substrate, respectively. A schematic of this parallel cylinder morphology is shown in Figure 1g. In a recent communication, we described the observation of a metastable perpendicular cylinder morphology in the as-cast film of PS27-LCP_{4BPP479} and a rearrangement to the parallel cylinder morphology upon thermal annealing²⁶. The as-cast metastable perpendicular cylinder morphology is stabilized by the interactions – i.e. homeotropic anchoring – of the LC mesophase with the substrate. With the LC normal oriented perpendicular to the substrate, and the requirement of homogeneous anchoring of the LC mesophase to the IMDS, the PS cylinders are forced to orient perpendicular to the substrate. When these films are annealed above the polystyrene glass transition temperature and above the smectic to isotropic transition temperature, the anchoring of the LC mesophase no longer dominates the self-assembly. A reorientation to the parallel cylinder morphology occurs in order to minimize the interfacial energies and avoid unfavorable PS-air interactions⁴⁴. Upon cooling below the polystyrene

glass transition temperature and above the smectic to isotropic transition temperature, the PS is vitrified and no further reorientation can occur when cooled below the smectic to isotropic transition temperature, locking in the parallel cylinder morphology. Figure 1e shows an atomic force microscopy (AFM) phase image of the annealed PS27-LCP_{4BPP479} film. In these phase images the more rigid PS domains appear lighter and the LCP domains appear darker; the line patterns are indicative of cylinders parallel to the interface, as evidenced by the observation of bright lines. The contrast of this image is reduced, due to the presence of a layer of LCP on the surface that is present in order to minimize the interfacial energy.

When the LC functionalization is increased to 100% (PS27-LCP_{4BPP4115}), a perpendicular cylinder morphology is observed for both the as-cast and annealed films. GISAXS (Figure 1b) and GIWAXS (Figure 1d) images of annealed PS27-LCP_{4BPP4115} thin films indicate polystyrene cylinders oriented perpendicular to the substrate and smectic layers oriented parallel to the substrate, respectively. A schematic of this perpendicular cylinder morphology is shown in Figure 1h. The increased preference for homeotropic anchoring of the LC mesophase to the substrate and homogeneous anchoring to the IMDS prevents reorientation, even while the material is heated above the smectic to isotropic transition temperature. Similar phenomena in which the anchoring of the LC mesophase affects the self-assembly behavior of this system – even at temperatures above the smectic to isotropic transition temperature – have been previously demonstrated, namely increases in the order-disorder transition temperature²⁹ and the orientation of the morphology in response to oscillatory shear²⁷. An AFM phase image of the annealed PS27-LCP_{4BPP4115} film with 100% LC functionalization is shown in Figure 1f. In order to minimize the interfacial energy of the system the polymer-air interface is wet by a layer of liquid crystalline polymer to avoid unfavorable PS-air interactions. The AFM tip of the annealed film probes the PS cylinders through a thin LCP layer at the air interface, resulting in the lower contrast of the features in the annealed film. Additionally, in all of the samples, water contact angles of ~95° and ~100° were observed for the as-cast and annealed samples, respectively. Upon annealing, the lower energy LCP migrates to the surface and results in a ~5° increase in the water contact angle, corroborating the AFM observations of a LCP wetting layer. It is also expected that a similar effect occurs at the substrate interface, where the LCP wets the substrate interface, lowering the interfacial energy of the system; however, we have no experimental evidence supporting the latter. Additionally, heating above the PS glass transition temperature (T_g) allows the system to further equilibrate, resulting in increased long range order of the cylinders for the annealed film. This morphology is similar to the schematic shown in Figure 1h, with a LCP wetting layer at the substrate and air interfaces.

The unique feature of this system is that the orientation of the morphology is determined by the interactions of the LC mesophase with the IMDS and the substrate. Increases in LC functionalization lead to stronger preferences for the anchoring of the LC mesophase relative to the substrate and the IMDS. By essentially manipulating the strength of these interactions the morphology of the thin film can be controlled, allowing poorly oriented cylinder, parallel cylinder, and perpendicular cylinder morphologies to be achieved.

Effect of liquid crystal content upon the orientation of lamellar morphologies

A higher molecular weight series, PS61-, of side chain liquid crystalline block copolymers was also investigated; these polymers have a significantly larger PS block than the PS27- series, resulting in larger PS volume fractions for comparable LC functionalization. The materials discussed in this section were synthesized by attaching the LC moieties to a PS-PVMS diblock copolymer that has PS and PVMS blocks with number-average molecular weights of 60,800 g/mol and 18,300 g/mol, respectively. As the molecular weight increases, so does the d-spacing of the self-assembled morphologies. These larger features could not be observed with GISAXS,

as the scattering features of interest were obscured by the beamstop and specular reflectance. For these materials increasing the LC functionalization leads to a dramatic change in the PS volume fraction, allowing for a range of morphologies to be obtained from a single polymer backbone. These films range in thickness from 150 nm to 300 nm, and the self-assembly behavior was not dependant upon the film thickness over this range.

AFM phase images are shown in Figure 2 for PS61-LCP_{4BPP483}, PS61-LCP_{4BPP4101}, and PS61-LCP_{4BPP4123} with LC functionalizations of 62, 79, and 100%, respectively. This increase in LC content reduces the PS volume fraction allowing lamellar, transitional, and cylindrical morphologies to be obtained for PS61-LCP_{4BPP483}, PS61-LCP_{4BPP4101}, and PS61-LCP_{4BPP4123}, respectively; these results are summarized in Table 1. These are the same morphologies that were observed for these materials in the bulk²⁹. The as-cast films all display these morphologies oriented perpendicular to the substrate (see Figures 2a, 2c, and 2e). Upon annealing sample PS61-LCP_{4BPP4123}, the cylinders remain perpendicular (see Figure 2f), exhibiting the same behavior as PS27-LCP_{4BPP4115} from the lower molecular weight series. Interestingly, annealing of PS61-LCP_{4BPP4101}, which displays a lamellar/cylindrical transitional morphology in the as-cast film and in bulk, results in a perpendicular cylinder morphology with the typical liquid crystalline polymer wetting layer at the air interface (see Figure 2d). This result indicates that the cylindrical morphology is stabilized, in favor of the lamellar morphology. This stabilization to the cylinder morphology was not observed in bulk samples of this material that were annealed. It is believed that the relatively small sample thickness of the thin film allows for the rearrangement to the equilibrium morphology to occur more quickly than in bulk.

The perpendicular lamellar morphology observed for PS61-LCP_{4BPP483} in the as-cast film reorients to the parallel lamellar morphology after annealing (see Figure 2b). This behavior is very similar to that of PS27-LCP_{4BPP479} and PS27-LCP_{4BPP490} from the lower molecular weight series, which have similar attachment percents to PS61-LCP_{4BPP483}. In a perfect lamellar morphology there is no curvature of the IMDS, so presumably either the homeotropic or homogeneous orientations are possible^{1, 17, 45–47}. When considering the conformational space of the siloxane backbone, it is believed that the homogeneous orientation of the LC moieties relative to the IMDS is more entropically favorable as the siloxane backbone has more conformational freedom than in the homeotropic orientation. Once again the as-cast perpendicular morphology is stabilized by the LC anchoring, and upon annealing, the morphology reorients in order to minimize the interfacial energy with the air and substrate interfaces. For each of these films, the orientation of the LC mesophase was confirmed with GIWAXS; in all cases the LC mesophase was oriented consistent with homogeneous anchoring with respect to the morphologies determined via AFM (see Figure S3 in the Supporting Information for details). Presumably, a perpendicular lamellar morphology could be stabilized during annealing by synthesizing a side chain liquid crystalline block copolymer with a polystyrene block large enough to yield a lamellar morphology with 100 percent LC attachment. For such a material it would be expected that the interactions of the smectic LC mesophase with the substrate and the IMDS would stabilize the perpendicular lamellae in the same manner as is observed for the cylindrical morphologies with 100 percent LC attachment.

Selective etching of side-chain liquid crystalline block copolymer thin films

A two step etch process was used⁴⁰ in order to selectively remove the PS domains and obtain porous liquid crystalline polymer thin films. The first step is a very short CF₄ reactive ion etch (RIE) that removes the top siloxane wetting layer, followed by an O₂ reactive ion etch step that selectively removes the PS domains. The removal of the top siloxane liquid crystalline polymer (LCP) layer allows the second O₂ RIE to have more direct access to the PS domains, thus enhancing the final etch quality. Poly(styrene) and poly(dimethylsiloxane) (PDMS)

provide an extremely high etch contrast⁴⁰, and the siloxane based liquid crystalline polymers in this study are expected to have similar properties in response to the O₂ reactive ion etch. Figure 3a displays an AFM phase image of an annealed PS27-LCP_{4BPP4}115 thin film before etching and Figure 3b shows SEM images of the same film after the two-step etch. The porous features observed with SEM in the etched film correspond to the PS domains observed in the AFM images of the film before etching. Additionally, as-cast films with perpendicular cylinder morphologies were etched using a single O₂ RIE; details are provided in Supporting Information. These as-cast films do not have a liquid crystalline polymer layer at the air interface, thus the initial CF₄ RIE is not necessary. However, these unannealed films are not well ordered and thus do not result in well defined pores.

A unique feature of this system is that after the removal of the amorphous polystyrene domains a porous liquid crystalline polymer matrix is left behind. This liquid crystalline matrix possesses both a low T_g siloxane backbone and responsive liquid crystalline moieties, allowing for the design of a responsive elastomer that can operate at room temperature. By utilizing responsive liquid crystalline moieties a change in the pore size in response to an external stimulus might be achieved. These materials show promise for creating tunable porosity membranes for chemical and biological protection.

In summary, we have demonstrated a means of utilizing the covalent attachment of LC moieties to a siloxane based block copolymer backbone as a tool for controlling the thin film morphologies. Increases in LC functionalization lead to stronger preferences for the anchoring of the LC mesophase relative to the substrate and the IMDS. The morphology of the thin film can be controlled by essentially manipulating the strength of these interactions through variations in the LC content, allowing poorly oriented cylinder, parallel cylinder, and perpendicular cylinder morphologies to be achieved. A second series of side chain liquid crystalline polymers was studied, which contained a larger PS block. These materials resulted in lamellar, transitional, and cylindrical morphologies with larger feature spacings, with similar control over the orientations of the morphologies as the lower molecular weight series. Initial results demonstrate the ability to selectively remove the PS domains through a series of reactive ion etches. One potential application for these materials is as a tunable porosity membrane for use in chemical and biological protection applications. By utilizing the low T_g siloxane backbone and responsive liquid crystalline moieties present in this system a responsive room temperature elastomer can be designed, allowing for a change in the pore size in response to external stimuli. Perhaps more significantly, these systems represent the use of LC anchoring as a means of manipulating thin film block copolymer domain ordering, and could provide a tool for generating technologically advantageous perpendicular orientations without prior surface modification or the use of electromagnetic or shear fields.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgement

We gratefully acknowledge the support of the U.S. Army Research Office through the Institute for Soldier Nanotechnologies at MIT under contract #: DAAD-19-02-D0002 and funding from the Semiconductor Research Corporation. This work is based upon research conducted at the Cornell High Energy Synchrotron Source (CHESS) which is supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under award DMR-0225180. The authors would like to give special thanks to Arthur Woll at the G1 beamline at CHESS for his support and Darren Verploegen for his assistance with profilometry and collection of GISAXS data.

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Figure 1.

Comparison of the parallel cylinder morphology (55% LC attachment) and the perpendicular cylinder morphology (100% LC attachment). Both samples were annealed under vacuum at 170°C for 36 hours. GISAXS images of a) PS27-LCP_{4BPP479} (55% LC attachment) and b) PS27-LCP_{4BPP4115} (100% LC attachment) indicate parallel and perpendicular cylinders, respectively. GIWAXS images of c) PS27-LCP_{4BPP479} and d) PS27-LCP_{4BPP4115} indicate smectic layers oriented perpendicular and parallel to the substrate, respectively. Atomic force microscopy (AFM) phase images of e) PS27-LCP_{4BPP479} and f) PS27-LCP_{4BPP4115}. In the AFM phase images the rigid polystyrene domains appear light. Schematics of the observed morphologies with the cylinder axis and the smectic layer normal parallel (g) and perpendicular

(h) to the substrate. For annealed perpendicular cylinder morphologies a wetting layer would be present at the substrate and air interfaces. Both morphologies display homogeneous anchoring of the LC mesophase, relative to the IMDS.

Figure 2.

Atomic force microscopy phase images of: a) as-cast PS61-LCP_{4BPP483} (62% LC attachment) displaying a perpendicular lamellar morphology, b) annealed PS61-LCP_{4BPP483} (62% LC attachment) displaying a parallel lamellar morphology, c) as-cast PS61-LCP_{4BPP4101} (79% LC attachment) displaying a perpendicular lamellar/cylindrical morphology, d) annealed LCP_{4BPP4101} (79% LC attachment) displaying a perpendicular cylinder morphology, e) as-cast PS61-LCP_{4BPP4123} (100% LC attachment) displaying a perpendicular cylinder morphology, f) annealed PS61-LCP_{4BPP4123} (100% LC attachment) displaying a perpendicular cylinder morphology. In the AFM phase images the rigid polystyrene domains appear light. For image b), an image was chosen with a high number of terrace defects to show

the parallel lamellar morphology. Most of the AFM images of these films only show a flat film that is wet by the LCP layer at the air interface.

Figure 3.

a) AFM phase image of PS27-LCP_{4BPP4115} (100% LC attachment) annealed for 36 hours at 170°C. b) SEM image of the same PS27-LCP_{4BPP4115} film annealed for 36 hours at 170°C followed by a CF₄ reactive ion etch (RIE) then an O₂ RIE.

Scheme 1.

Schematic of side chain liquid crystalline block copolymer.

The number of styrene repeat units is n , the ratio $y / (y + z)$ is the LC attachment percent, and $x \ll (y + z)$, with y and z random.

Table 1

Summary of thin film morphologies.

Sample name *	PS wt %	Attach %	T _{iso}	As-cast orientation	Annealed orientation
PS27-LCP _{4BPP4} 46	37	31	42	Disordered Cylinder	Disordered Cylinder
PS27-LCP _{4BPP4} 57	32	41	55	Disordered Cylinder	Disordered Cylinder
PS27-LCP _{4BPP4} 79	26	55	67	Perpendicular Cylinder	Parallel Cylinder
PS27-LCP _{4BPP4} 90	23	76	83	Perpendicular Cylinder	Parallel Cylinder
PS27-LCP _{4BPP4} 115	19	100	90	Perpendicular Cylinder	Perpendicular Cylinder
PS61-LCP _{4BPP4} 83	42	62	77	Perpendicular Lamellar	Parallel Lamellar
PS61-LCP _{4BPP4} 101	38	79	81	Perpendicular Transitional	Perpendicular Cylinder
PS61-LCP _{4BPP4} 123	33	100	89	Perpendicular Cylinder	Perpendicular Cylinder

* PS27-LCP_{4BPP4}46 indicates a side chain liquid crystalline block copolymer that has a polystyrene block with a number-average molecular weight of 27,000 g/mol and a liquid crystalline polymer block with a number-average molecular weight of 46,000 g/mol. 4BPP4 denotes the structure of the LC moiety²⁹. The smectic to isotropic transition temperature (T_{iso}) was determined via differential scanning calorimetry (DSC). All annealing was performed at 170°C for 36 hours under vacuum and cooled to room temperature at 0.5°C/min.