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Orientational Switching of Mesogens and Microdomains in Hydrogen-Bonded Side-Chain Liquid-Crystalline Block Copolymers Using AC Electric Fields**

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In this report, we show that the microstructures of hydrogen-bonded side-chain liquid-crystalline block copolymers can be rapidly aligned in an alternating current (AC) electric field at temperatures below the order–disorder transition but above the glass transition. The structures and their orientation were measured in real time with synchrotron X-ray scattering. Incorporation of mesogenic groups with marked dipolar properties is a key element in this process. A mechanism related to the dissociation of hydrogen bonds is proposed to account for the fast orientation switching of the hydrogen-bonded blends.

1. Introduction

Block copolymers (BCPs) can self-assemble into highly regular, microphase-separated structures at length scales of several tens of nanometers.[1] Desirable microstructures can be selected by varying the number of blocks, the relative volume ratio between different blocks, and their chemical composition. Specific potential applications, including template formation for nanolithographic patterning[2] or high-density arrays of nanowires en route to thin films for optoelectronic devices,[3] require not only well-ordered microdomains, but also macroscopic alignment of the microstructure. Though a single BCP grain may have a highly anisotropic structure, a bulk sample usually exhibits isotropic properties due to its “polygrain” nature. The orientation of microstructures of thin films, which is necessary for most potential electro-optical applications, depends on a variety of processing conditions and on such features as interfacial properties among polymers, substrates and air unless some ordering field is applied.

One successful approach to alignment of BCPs is by means of applied mechanical fields. BCP melts can be oriented by oscillatory shear[4] or extrusion;[5] while BCP solutions can be aligned via roll-casting.[6] It is difficult, however, to use mechanical fields when creating a small, integrated device. Thus, in addition to mechanical fields, the use of electric fields has drawn increasing attention. Melts of polystyrene-*block*-poly(methyl methacrylate), PS-*b*-PMAA, have been readily aligned by the application of a direct current (DC) field due to the difference in the static dielectric constants between the two blocks.[7,8] Most prior electric-field alignment experiments have required application of electric fields for at least several hours at elevated temperatures close to the polymer decomposition temperature. However, fast DC field-induced alignment within minutes has been recently achieved in a solvent-swollen microphase-separated block copolymer.[9,10] The resulting orientation of the intermaterial dividing surface (IMDS) is always parallel to the applied DC electric field in block copolymers oriented from the melt or solution for both lamellar and cylindrical[11] microstructures.

Orientational control of low-molecular-weight (LMW) liquid-crystalline materials and side-chain liquid-crystalline polymers with an applied alternating current (AC) electric field is well known.[12] The orientation of liquid crystals is determined by their dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) between the longitudinal permittivity ($\varepsilon_{\parallel}$, the permittivity parallel to the molecular axis) and the lateral permittivity ($\varepsilon_{<\mathrm{MPQ}>}$, the permittivity perpendicular to the molecular axis). Mesogens having positive $\Delta\varepsilon$ align parallel to an AC field or perpendicular to the field if $\Delta\varepsilon$ is negative. Since the permittivity of a liquid-crystal molecule is a function of frequency and temperature, $\Delta\varepsilon$ is also frequency-dependent. Thus, varying the frequency of the AC field can often selectively change the orientation of liquid crystals.[13] Orientational switching can take place in milliseconds in LMW liquid crystals and in tens of seconds on polymeric liquid-crystalline materials whose molecular weights are typically less than 10 000 g mol^{-1} with AC electric fields of approximately 1 V µm^{-1}.[14] Such frequency-dependent orientation characteristics were successfully used to control the macroscopic alignment of liquid-crystal thermosets during concurrent network formation.[15] By combining the unique field-alignment properties of liquid-crystalline materials with those of BCPs,[16,17] control of the orientation of microstructure should be possible by

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[**] Initial research was carried out with the partial funding of the Air Force Office of Scientific Research (Liquid Crystal MURI). The NSF-supported NIRT (ECS-0103297) is acknowledged for major support of this work. This material is also based upon work supported by the National Science Foundation under Grant No. 0208825. The Cornell Center of Materials Research (CCMR) and Cornell High Energy Synchrotron Source (CHESS) are gratefully acknowledged for partial support and for use of their facilities. The authors would like to thank Dr. Hilmar Körner and Dr. Tim Bunning for useful discussions.

DOI: 10.1002/adfm.200305159

AC field alignment as a result of a strong anchoring condition of mesogens with respect to the IMDS.

Hydrogen bonding, the modest "glue" that nature uses to build three-dimensional protein structures, is another way to bind the small liquid crystal side moieties with polymeric backbones to form supramolecular assemblies. Side-chain block copolymers (SCBCPs) with hydrogen bonds linking aliphatic side groups to the host polymeric backbone also permit fine-tuning desirable morphologies by simply varying the quantities of incorporated side groups as well as the relative molecular-weight ratio of the constituent polymeric blocks.[18,19] The use of hydrogen bonds to attach mesogenic moieties to host homopolymers is well documented.[20–23] Our hydrogen-bonded side-chain liquid-crystalline block copolymers (H-bonded SCLCBCPs) integrate the superior features of liquid crystallinity, hydrogen bonding of mesogens to host polymeric backbones, as well as self-assembly to create the opportunity for field-tunable nanostructures.

In this work, polystyrene-*block*-poly(acrylic acid), PS-*b*-PAA, diblock copolymers and imidazole-terminated hydrogen-bonding mesogenic groups (I1) were synthesized. The feasibility of microstructural orientation switching of hydrogen-bonded complexes using AC electric fields was examined. Hydrogen-bonded complexes containing non-mesogenic side groups and covalently-bonded SCLCBCPs were prepared for reference experiments to investigate the driving force of this orientational change.

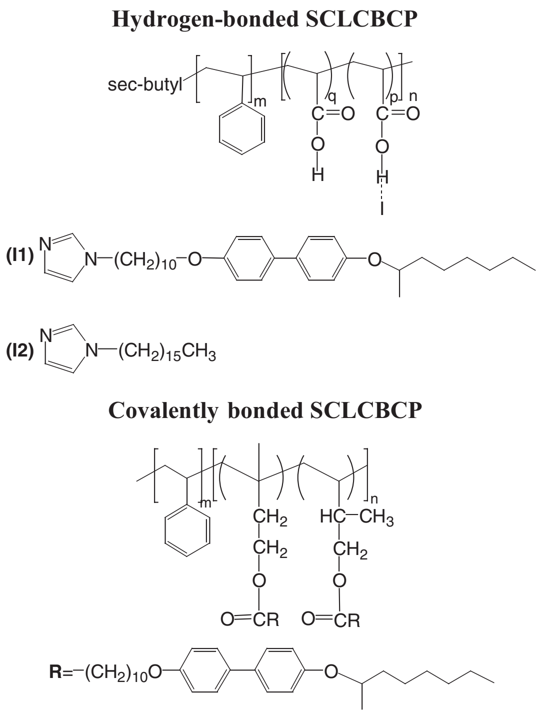


Figure 1. Chemical structures of hydrogen-bonded and covalently bonded SCLCBCPs. The H-bonded complex consists of the host polymer, PS-*b*-PAA, and the guest imidazole-terminated side moieties, I1 or I2 where PAA is a proton donor in hydrogen-bonding pairs and the imidazole group is a proton acceptor.

2. Results and Discussions

2.1. Molecular Design and Synthesis

PS-*b*-PAA consisting of a 25 000 g mol^{-1} polystyrene block and a 5300 g mol^{-1} poly(acrylic acid) block (denoted as PSPAA) was anionically polymerized via sequential monomer addition under nitrogen followed by hydrolysis of the precursor polystyrene-*block*-poly(*tert*-butylacrylate). The molecular weight was chosen to assure a microphase-separated structure with reasonable chain mobility to enable well-ordered self-assembly. Imidazole-terminated mesogens were selectively inserted into the PAA block via hydrogen bonding with the carboxylic acid group during simple solvent casting. By incorporating the imidazole-terminated side moieties, the molecular weight of the PAA/LC block was augmented along with the introduction of liquid crystallinity (LC refers to the liquid-crystal component) and a different microdomain morphology from that of the neat PSPAA. The chemical structures and the quantity of side groups added determine the final molecular weight, morphology and liquid-crystal phase of the PS-*b*-PAA/LC) materials (see Fig. 1).

Imidazole-terminated mesogenic group I1 consisting of a biphenyl mesogenic core and a branched alkoxy tail, whose molecular structure is illustrated in Figure 1, has a strong dipole moment (~3.9 Debye from molecular simulation) lying in a direction nearly parallel to the molecular axis due to the imidazole group. The hydrogen-bonding mesogenic group has almost no effective lateral dipole moment since in the racemic mixture the two optically active chiral mesogens tend to cancel each other. When hydrogen-bonded, the dipole moment attributed to the imidazole is eliminated so that the attached mesogen can be considered as nearly dielectrically isotropic. I2, consisting of an imidazole-terminated group and a long alkyl chain, was designed to eliminate liquid crystallinity for reference experiments.

2.2. Liquid-Crystalline Phase Behavior of Hydrogen-Bonded Complexes

Hydrogen-bonded blends composed of PSPAA and I1 with two different blend ratios, denoted as PSPAA/0.8I1 and PSPAA/0.5I1 (0.8 and 0.5 are the molar ratio of I1 to acrylic acid repeated units), were prepared. The molecular weights of PSPAA/0.8I1 are 25 000 g mol^{-1} for the PS block and 35 000 g mol^{-1} for the PAA/LC block, while those of PSPAA/0.5I1 are 25 000 g mol^{-1} and 24 000 g mol^{-1}, respectively. Transmission electron microscopy (TEM) and polarized optical microscopy (POM) showed no evidence for macroscopic phase separation between I1 and PSPAA.

The study of the liquid-crystalline phase behaviors of PSPAA/0.8I1 and PSPAA/0.5I1 was carried out through differential scanning calorimetry (DSC), POM, and temperature-dependent small-angle X-ray scattering (SAXS) with a heating rate of 10 °C min^{-1}. DSC traces in Figure 2 showed that during

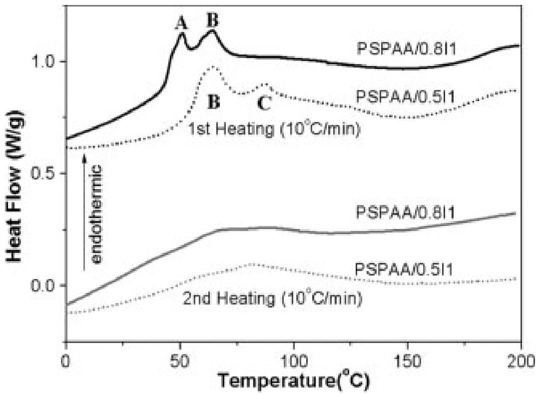


Figure 2. DSC traces from the bulk sample of PSPAA/0.8I1 (solid line) and the bulk sample of PSPAA/0.5I1 (dashed line). All traces are normalized to the sample weight. The heating rate was 10 °C min^{-1}.

the first heating, a transition B from a highly ordered phase to a mobile smectic phase occurs at 55–75 °C for both blends. For the PSPAA/0.8I1 samples a transition A at 50 °C suggests the existence of free I1 (i.e., non-hydrogen-bonded I1) sequestered in PAA/LC domains since this transition is close to the crystalline–isotropic-transition temperature of the pure mesogen I1 (46 °C). The glass-transition temperature (T_g) of the PS block of PSPAA/0.8I1 could not be observed, while that of PSPAA/0.5I1 is located at approximately 85 °C (transition C). The absence of a distinct PS T_g is believed to result from the overlap of transition B and the PS T_g, which was suppressed due to the plasticizing effect from the presence of some non-bonded I1 in the PS microdomains. The onset of heat flow above 160 °C indicates the formation of acid anhydride between acrylic acid repeated units. The DSC traces during the second heating, which only showed the glass transition of PS, reflect the irreversible nature of the liquid-crystalline phase transitions of the PAA/LC blocks. The T_g of PS for PSPAA/0.8I1 is around 70 °C, which is 10 °C lower than that of PSPAA/0.5I1, suggesting that for the high-mesogen-content blends more mesogens could partition into the PS domains as a plasticizer.

Both PSPAA/I1 samples showed smectic layers of 60 Å thickness from SAXS, while the layer period of pure I1 is 54 Å. Since the fully elongated molecular length of mesogen I1 is 30 Å, a partially interdigitated and/or tilted bilayer smectic arrangement of the mesogens in the hydrogen-bonded blends is suggested. The SAXS signature of the smectic mesophase disappeared above 110 °C for both blends although this transition cannot be observed in the DSC traces. POM on both blends showed birefringence above 110 °C when a stress was applied. The intensity of the birefringence decreases as temperature increases and the sample reached an optically isotropic phase above 135 °C. Thus a highly mobile liquid-crystalline phase is present between 110 °C and 135 °C in accordance with the existence of birefringence. The scattering peaks corresponding to the microstructures from SAXS disappeared at approximately 170 °C for PSPAA/0.8I1 and at about 180 °C for PSPAA/0.5I1. The temperatures regarding the absence of microstructural scattering are defined as the order–disorder transition (ODT) temperatures using the experimental setups with a heating rate of 10 °C min^{-1}.

2.3. Orientation Switching of Hydrogen-Bonded Complexes

Two-dimensional SAXS was carried out at the Cornell High Energy Synchrotron Source (CHESS) facility and was used to monitor real-time electric-field-induced realignment on the seconds-to-minutes time scale. The experiment setup was illustrated in Figure 3. At room temperature the bulk PSPAA/0.8I1 showed a lamellar microstructure with a 270 Å period corresponding to a bilayer stacking of PS and PAA/LC as judged from the TEM image and the SAXS pattern (Fig. 4). The lamellar normals were initially aligned perpendicular to the electrode surface (hereby denoted “parallel orientation”) due to shear along the x-direction during the sample preparation (see Fig. 5a). The SAXS diffraction pattern also showed a second scattering corresponding to a 60 Å spacing oriented along the x-direction perpendicular to the plane of the electrodes, which indicated the smectic bilayers of the mesogens were aligned perpendicular to the lamellae as well as to the electrodes. This

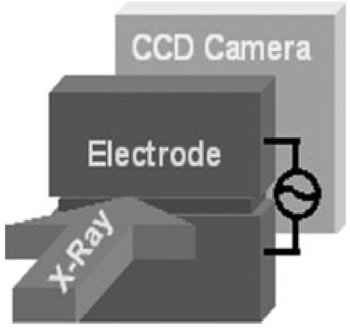


Figure 3. Schematic illustration of the SAXS experimental arrangement. The sample was held in the gap between two stainless steel electrodes. The gap thickness was 150–250 µm.

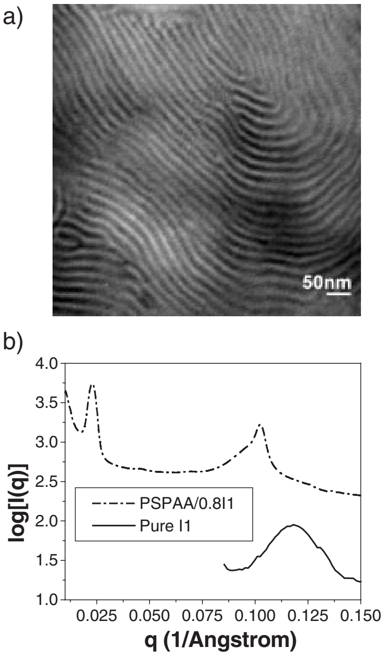


Figure 4. TEM image (A) and q-plot retrieved from the SAXS pattern (B) of PSPAA/0.8I1.

arrangement leaded to a homogeneous boundary condition of the mesogens with respect to the IMDS. This observation agreed with our previously reported microdomain lamellar–smectic model for covalently bonded SCLCBCPs.[15,16]

A reference experiment was carried out to demonstrate the influence of electric fields on orientation. In the absence of electric fields, the diffraction signal from the smectic layers of the mesogens disappeared above 110 °C and the lamellar morphology retained their initial orientation during the heating period until the ODT (~ 170 °C) was reached. An improvement in microstructural organization was observed during heating as a result of annealing (Fig. 5B). Heating above the ODT resulted in a complete loss of orientation upon cooling, as indicated by an azimuthally isotropic SAXS pattern (see Fig. 5C).

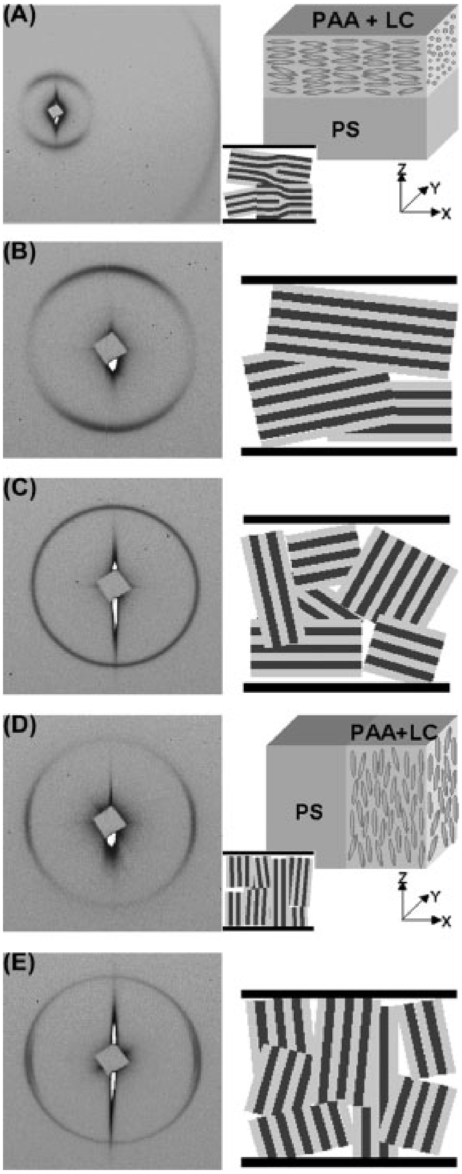


Figure 5. SAXS patterns from PSPAA/0.8I1) at room temperature without an electric field, B) at 110 °C without and electric field, C) at room temperature after cooling from a temperature above the order–disorder transition at a rate of 10 °C min^{-1} without applied electric fields, D) at room temperature after cooling from above the order–disorder transition in an AC field of 1 V µm^{-1} and 10 Hz (the same pattern also occurred when the frequency of the AC field was 20 kHz), and E) at 110 °C during heating with an AC field at 1 V µm^{-1} and 10 Hz.

By applying an external AC electric field of 1 ~ 2 V µm^{-1} with a frequency of either 10 Hz (denoted "low frequency") or 20 kHz (denoted "high frequency") throughout the experiment, above the ODT for 10 min and then cooling down at a rate of 10 °C min^{-1}, the hydrogen-bonded blend showed alignment of the lamellar normal parallel to the electrodes;, i.e., along to the *x*-direction. (denoted "perpendicular orientation", see Fig. 5D) However, by using DC electric fields with similar field strengths throughout the above experiment settings, no orientation of the microstructure could be detected.

Interestingly, by using either a 10 Hz or 20 000 Hz AC electric field at temperatures above the glass-transition temperatures of both blocks but below the ODT, the microdomain orientation of the PSPAA/0.8I1 blend could be switched over a few minutes from the initial parallel orientation to the perpendicular orientation. For example, starting with a parallel lamellar morphology, a structural orientation change could be detected at 110 °C with an AC electric field at 1 ~ 2 V µm^{-1} and a frequency of 10 Hz during heating (Fig. 5E). By holding the sample at 130 °C for 5 min under the AC field, the orientation was completely changed to the perpendicular orientation. A similar structural reorientation was also observed when an AC electric field with a frequency of 20 kHz was applied. The reorientation first started at a higher temperature (130 °C) and was essentially complete after 10 min at 140 °C. Previous work on PS-*b*-PMMA melts required a DC electric field of 3 V µm^{-1} at 250 °C for 24 h to achieve such domain orientation.

The PSPAA/0.5I1 blend, containing a molar ratio of mesogens to acrylic acid repeat units of 0.5, also exhibited a lamellar morphology in bulk. The same set of experiments that were done on PSPAA/0.8I1 was repeated. Similar to PSPAA/0.8I1, the microstructure of PSPAA/0.5I1 could be aligned in the perpendicular orientation when the sample was cooled down from a temperature above the ODT in an applied AC field. The orientation, however, could not be changed from the starting parallel orientation induced by shear during the sample preparation to the perpendicular orientation at temperatures below the ODT during heating with an AC electric field of 1 ~ 2 V µm^{-1} with either a high or low frequency.

2.4. Mechanism of Orientation Switching

In order to understand the mechanism and the driving forces of the AC-field-induced re-orientation, several reference systems were studied. A covalently bonded SCLCBCP (denoted as PS-*b*-PILC) whose molecular structure is illustrated in Fig. 1) whose molecular weight and morphology approximated those of the PSPAA/0.8I1 blend was built by modifying a polystyrene-*block*-poly(hydroxylated isoprene), PS-*b*-PIOH, diblock copolymer with mesogens similar to I1 via the esterification reactions between the hydroxyl groups of hydroxylated isoprene and the carboxylic acid terminated groups of mesogens. The orientation of PS-*b*-PILC with an ODT above 250 °C, could not be changed with an AC electric field at either high or low frequency at temperatures up to 250 °C over experiments lasting tens of minutes. Another PS-*b*-PAA block copolymer, having a molecular weight of 30 k (PS) and 30k (PAA) and an ODT above 250 °C, designed to match both the total molecular weight and the lamellar morphology of the PSPAA/0.8I1 blend showed no orientation after the same treatment. A PSPAA/0.8I2 hydrogen-bonded complex with the non-mesogenic side groups I2 as the proton acceptor also exhibited no orientational ordering when cooled from the disordered state in AC fields. The orientational switching was also not achievable at temperatures below ODT using AC fields.

Due to the inability to induce orientation for the pure PS-*b*-PAA block copolymer and for the PSPAA/0.8I2, the presence of liquid crystallinity is obviously integral to the orientational alignment in the applied AC field. PSPAA/0.8I1 exhibits microdomain re-orientation in the highly mobile LC phase and in the isotropic phase below the ODT. On the other hand, PSPAA/0.5I1 and the covalently bonded PS-*b*-PILC having similar LC and isotropic phases could not be oriented by the applied fields; these results suggest that the orientational change of the microdomains requires a mobility higher than that provided by the restrained mesogens (either hydrogen-bonded or covalently bonded) in the liquid-crystalline and isotropic phases. The "higher mobility" in sample PSPAA/0.8I1 might arise from excess non-hydrogen-bonded mesogenic molecules sequestering in the PAA/LC domains as well as some mesogenic molecules present in the PS domains.

The existence of unconstrained I1 could be confirmed using Fourier-transform infrared (FTIR) spectroscopy by study of the intensity of characteristic stretching bands of hydrogen bonding. Figure 6A shows the normalized integrated area of characteristic hydrogen-bonding stretching band at 2530 cm^{-1} (Fig. 6B) versus temperature for both blends. The decrease of hydrogen-bond intensity with increasing temperature indicates that fewer mesogens bind to the host polymer backbones as the sample is heated. The hydrogen-bonding intensity of PSPAA/0.8I1 at room temperature is very similar to that of PSPAA/0.5I1, which implies that the amount of PAA/I1 hydrogen bonds does not scale linearly with mesogens added. This suggests that only a limited quantity of I1 could be hydrogen bonded with the PAA block due to equilibrium between the hydrogen bonding of imidazole–acid, intramolecular acid–acid and intermolecular acid–acid interactions. Therefore, there are some unconstrained mesogens (denoted "free mesogens") in the PSPAA/0.8I1 blend. Though these free mesogens are not hydrogen-bonded, they still sequester homogeneously in the PAA/LC domain and partially locate in the PS domain as judged by the absence of macroscopic phase separation of the I1 mesogens based on TEM and POM observation.

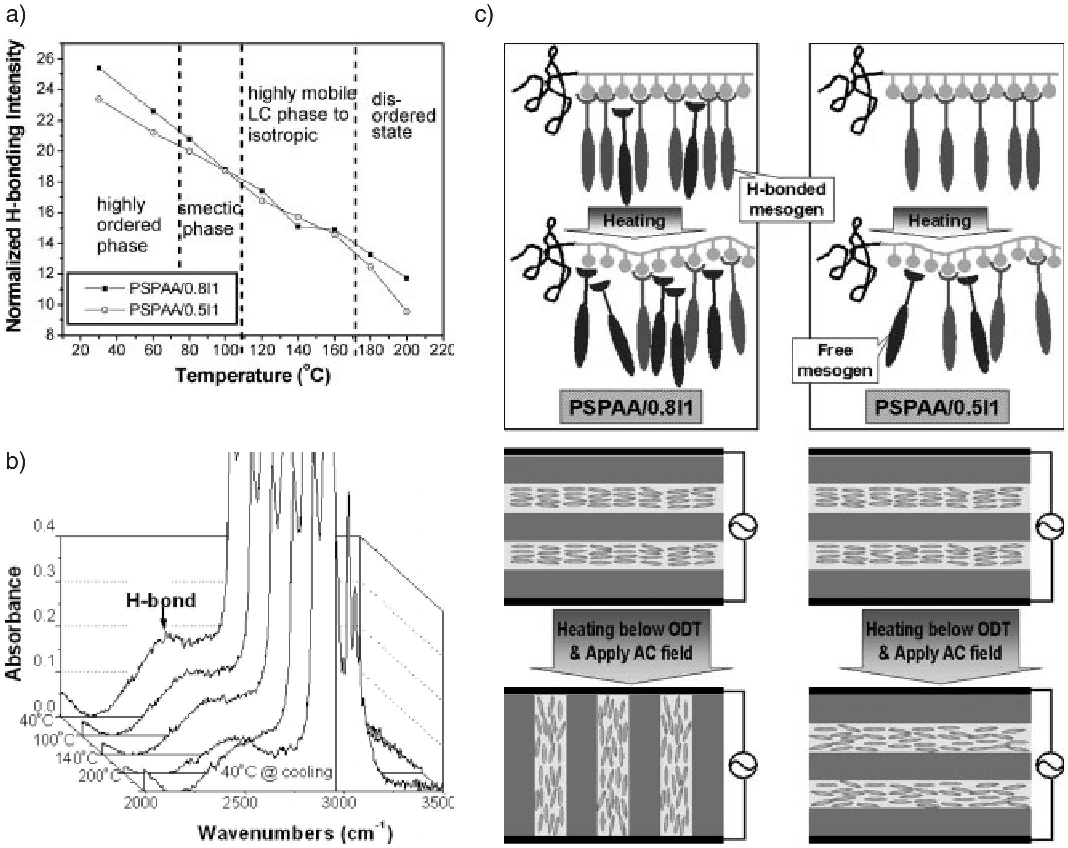


Figure 6. A) Plot of normalized hydrogen bonding intensity (integrated area of the stretching band centered at 2530 cm^{-1}) versus temperature for PSPAA/0.8I1 and PSPAA/0.5I1. B) Temperature-dependent FTIR spectra of PSPAA/0.5I1 (normalized with the stretching of polystyrene). C) Schematic illustration of the proposed model for "free" mesogen formation and re-orientation of blends heated below ODT in an applied AC field.

The proposed mechanism for the re-orientation (see Fig. 6C) of the PSPAA/0.8I1 microstructures involves the following features: a strong homogeneous anchoring condition between the mesogens and the IMDS, an increase in the numbers of the dielectrically anisotropic free mesogens with increasing temperature; and a higher mobility of the block copolymer due to the plasticization of both blocks by the non-hydrogen-bonded mesogens. According to Figure 6A, the hydrogen-bonding intensity of the PSPAA/0.5I1 blend was similar to that of the PSPAA/0.8I1 blend over a wide temperature range, which suggests that the number of free mesogens in the former was about half the number of those in the latter at a given temperature. Fewer free mesogens in the PSPAA/0.5I1 blend causes a lower system mobility preventing microstructural re-orientation below the ODT. The perpendicular orientation of the lamellar structure is the consequence of the interaction of the homogeneous mesogen-IMDS boundary condition and the alignment of the mesogens in the applied AC field. By applying either a 10 Hz or 20 000 Hz AC field, free mesogen I1 is aligned parallel to the field since its dipole moment is nearly parallel to the molecular axis of I1 in this frequency range. As the free mesogens readily align parallel to the applied AC field, they influence the hydrogen-bonded mesogens in the PAA/LC block to adopt the same orientation. In order to retain the preferential homogeneous IMDS so as to minimize the interfacial free energy between two contiguous blocks, the PS domains need to be aligned in the direction parallel to the mesogens. The free mesogens in the PS domains enable and accelerate the alignment of PS due to both the plasticizing effect on PS and their capability to respond the AC field.

3. Conclusion

In summary, our studies of hydrogen-bonded side-chain liquid-crystalline block copolymers have demonstrated that block copolymers can be aligned in AC electric fields in minutes. This process occurs while cooling from the melt above the order-disorder tranistion using a very modest AC electric field of $1 \sim 2\ \mathrm{V\,\mu m^{-1}}$. Moreover, the orientation of the block copolymer can be changed within minutes in a direction parallel to the electrodes at temperatures above the glass-transition temperature of both blocks but below the order–disorder transition using an applied AC electric field. A model involving free mesogens was proposed to explain the driving forces for the orientational change at relatively low temperatures. By selecting a suitable mesogen with a strong lateral dipole moment, it may be possible to selectively and rapidly align a block copolymer either parallel or perpendicular to the electrodes by selecting the appropriate AC frequencies. These studies are underway.

4. Experimental

Preparation of Hydrogen-Bonded Complexes: Synthesis of block copolymers: polystyrene-*block*-(*tert*-butylacrylate), PS-*b*-P*t*BA, BCPs with designed molecular weight were synthesized by sequential anionic polymerization in tetrahydrofuran (THF) at –78 °C under nitrogen atmosphere using *sec*-butyllithium as the initiator, lithium chloride as the counter ion and anhydrous methanol for reaction termination. Poly(acrylic acid), PAA, was produced by hydrolysis of the P*t*BA block which was carried out by reaction with hydrochloric acid in 1,4-dioxane solution.[24,25] The excess hydrochloric acid was neutralized by titration with a potassium hydroxide solution and the precipitated polymer was washed with copious amounts of distilled water to avoid ionic contamination. The molecular weight of PS-*b*-*t*BA was characterized by gel-permeation chromatography using a Waters instrument. NMR and FTIR were employed to assure the completion of hydrolysis.

4-(10-(Imidazolyl)-decyloxy)-4′-(1-(methyl)heptyloxy))biphenyl (denoted as I1) was synthesized from imidazole and 4-(10-(bromo)-decyloxy)-4′-(1-(methyl)heptyloxy))biphenyl according to a method described elsewhere.[23,25]

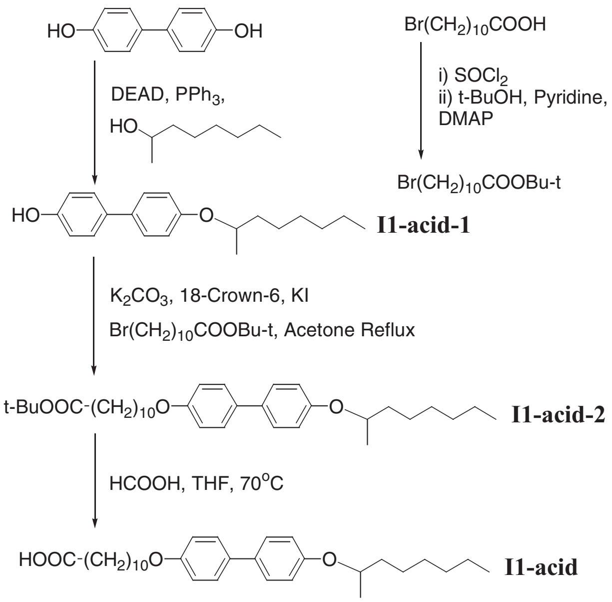
1-(Imidazolyl)-hexadecane (denoted as I2) was synthesized from 1-bromohexadecane and imidazole as follows: 1-bromohexadecane was heated with imidazole (0.9 molar equivalents with respect to 1-bromohexadecane) in a concentrated THF solution at 80 °C for 5 h and the mixture was partitioned between dichloromethane and distilled water. Evaporation the organic layer afforded the crude product and it was then further purified by chromatography with a chloroform/methanol (v/v = 20:1) mixed solvent as eluent. The final product was collected after recrystallization from hexane.

^{1}H NMR of I2 ($CDCl_3$): δ 7.56 (1H, s, aromatic in imidazole); 7.05 (1H, s, aromatic in imidazole); 6.93 (1H, s, aromatic in imidazole); 3.94 (2H, t, next to imidazole); 1.90–1.20 (28H, m); 0.95 (3H, t, methyl group).

Hydrogen-bonded complexes were prepared by solvent casting from THF. Imidazolyl side groups and diblock copolymers were dissolved in THF with a concentration of $10\ \mathrm{mg\,mL^{-1}}$. Solvent was then removed by slow evaporation over 72 h at room temperature. The blends were subsequently dried under vacuum at room temperature for 12 h.

Preparation of Covalently Bonded SCLCBCPs: Polymer-analogous chemistry with polystyrene-*block*-poly(hydroxylated isoprene) (denoted as PS-*b*-PIOH) and carboxylic acid-terminated mesogenic side groups were applied to synthesize the covalently bonded SCLCBCPs. Polystyrene-*block*-polyisoprene, PS-*b*-PI, was synthesized by living anionic polymerization with sequential monomer addition under nitrogen atmosphere at –78 °C in anhydrous THF. The pendent C=C double bonds in the isoprene block were then converted to primary alcohol (C–C–OH) using the hydroboration procedures reported by Mao and co-workers.[15] The attachment of mesogenic side groups to polymer backbone was carried out by coupling the pendent OH groups with the corresponding acid chlorides as described in the literature.

The carboxylic acid-terminated mesogenic side groups containing the same mesogenic core and spacer (denoted as I1-acid) was synthesized following the procedure in Scheme 1. 4-Octoxy-4′-(hydroxy)biphenyls (denoted as I1-acid-1) was synthesized using the procedure described in the literature.[22] A *tert*-butyl-protected 11-bromoundecanoic acid (denoted as



Scheme 1. Synthesis of I1-acid and polymer-analogous chemistry for covalently bonded side-chain liquid-crystalline block copolymers.

$BrC_{10}COO$-*t*Bu) was synthesized by coupling the corresponding acid chloride with *tert*-butyl alchohol following the methods reported in the literature. I1-acid-1 (1 molar equivalent), $BrC_{10}COO$-tBu (1 molar equivalent), K_2CO_3 (1.3 molar equivalents), 18-crown-6 (200 mg) and KI (100 mg) were then dissolved in acetone and the reaction was carried out in the refluxed acetone solution overnight. Filtration of precipitates and evaporation of solvent afforded the crude product of I1-acid-2. Pure I1-acid-2 was then collected after the recrystallization from acetone. I1-acid could be obtained by deprotection of the *tert*-butyl group using formic acid in THF solution at 70 °C for 2 h.

^{1}H NMR for I1-acid ($CDCl_3$, D_2O): 7.48 (4H, d, aromatic in biphenyl group, meta position to OR); 6.96 (4H, d, aromatic in biphenyl group, next to OR); 4.37 (1H, m, proton in the chiral center); 3.99 (2H, t, next to ether linkage with biphenyl group); 2.35 (2H, t, next to carboxylic acid); 1.9–1.2 (29H, m, including 1.39(3H, d, methyl group next to the chiral center)), 0.92 (CH_3, 3H).

Characterization and Orientation Switching Study: Thermal properties and phase behavior of the hydrogen-bonded blends were examined using differential scanning calorimetry (DSC, TA Q1000). Polarized optical microscopy (POM) observation was performed on a Nikon optical microscope equipped with a Mettler hot stage. Fourier-transform infrared spectroscopy (FTIR, Mattson) was employed to check the formation and dissociation of hydrogen bonds. Microstructures were investigated using small-angle X-ray scattering (SAXS), and bright-field transmission electron microscopy was carried out at 120 kV (TEM, JEOL 1200E). Thin sections (50 nm in thickness) were microtomed with a Leica UCT/EM FCS Ultramicrotome machine at –50 °C using a diamond knife. The microtomed pieces were then picked up with 400 mesh copper grid from water and stained with RuO_4 vapor for 20 min in order to increase the electron density contrast between the two blocks.

Small-Angle X-Ray Scattering (SAXS): Data were obtained at the D1 and G1 beamlines (monochromatic, $\lambda = 0.154$ nm) at the Cornell High Energy Synchrotron Source (CHESS). Sample cells consisting of two 0.5 mm stainless steel electrodes separated by a gap spacing of 150–250 µm were held in a Mettler FP82HT hotstage. A sample was heated to 70 °C and pressed into a thin slice slightly thicker than the gap spacing. The slice was inserted into the cell and the parts not contiguous with electrodes were removed. Applied AC fields were controlled by passing the output from an HP3300 A function generator through a Trek (10/10) high-voltage amplifier. Scattered radiation was detected using a coupled charge device (CCD) detector. Data used for analysis were corrected after the subtraction of background.

Received: May 5, 2003
Final version: November 11, 2003

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