

## Directing self-assembly in macromolecular systems: Hydrogen bonding in ordered polymers\*

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*Abstract:* Hydrogen-bonded side-chain liquid-crystalline block copolymers (SCLCBCPs) containing block segments with proton donors were combined with functionalized mesogenic pendent groups. Studies of a wide range of mesogen and polymer combinations were carried out to study the relationship between morphology and mesophase behavior. The thermal behaviors of the resulting self-assembled microstructures were also examined. A model of the assembly process leading to mesogenic group organization corresponding to different compositions was proposed.

### INTRODUCTION

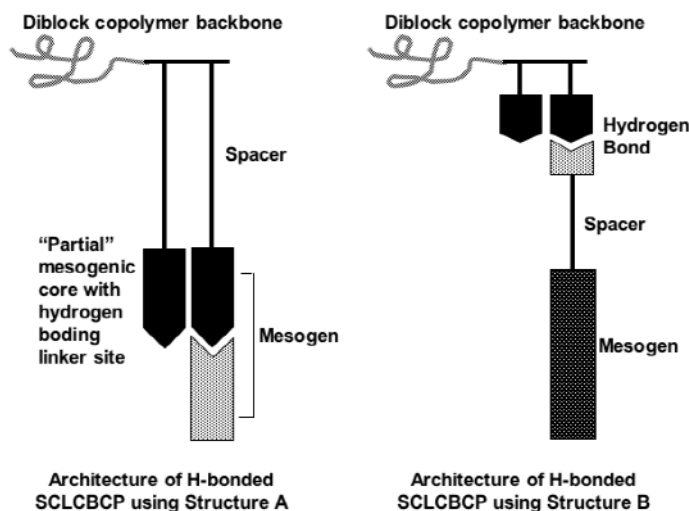
Many polymeric liquid-crystalline structures have been produced using covalent bond chemistry [1–4]. In particular, side-chain liquid crystalline polymers (SCLCPs) have attracted much interest in recent years for their potential application in electrooptical technologies. More recently, however, molecular recognition processes between different molecular species using noncovalent bonded interactions have been reported for their versatility in constructing dynamically functional LC molecules. These self-assembly strategies including hydrogen bonds [5–29], ionic interactions [30,31], and charge-transfer complexes [32,33] have been used to construct liquid-crystalline polymers as “supramolecular” materials. Hydrogen bonding is particularly attractive since there are many natural models for it. The formation and dissociation of the hydrogen bonds play an important role in many biological processes. The use of hydrogen bonds has been demonstrated in building low-molecular-weight liquid crystals as well as liquid-crystalline polymers of side-chain supramolecular assemblies [5–22], main-chain complexes [23–26], and networks [27–29].

By integrating the concepts of hydrogen-bonded SCLCPs with block copolymer structures, a novel architecture of side-chain liquid-crystalline block copolymers (SCLCBCPs) using hydrogen bonds, has been developed. Two approaches may be applied to build a hydrogen-bonded LC block using structures for hydrogen-bonded SCLCPs. The synthetic methods of preparing a block copolymer backbone for H-bonded SCLCBCPs are similar to those for covalently bonded SCLCBCPs. When forming structure A (Fig. 1), either living polymerization of vinyl monomers with spacer and hydrogen bonding “partial” mesogenic core is needed or polymer-analog chemistry is used to incorporate the molecules with spacer and “partial” mesogenic core with hydrogen-bonding linker site. However, the degree of polymerization is expected to be relatively small for the former, while the grafting density is difficult to control for the latter. When forming structure B (Fig. 1), the hydrogen-bonding linker site is directly attached to the polymer backbone. The polymer backbone of the LC block, such as poly(vinyl pyridine),

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**Fig. 1** Schematic illustration of the architecture of hydrogen-bonded side-chain liquid-crystalline block copolymers constructed using “Structure A” and “Structure B” approaches.

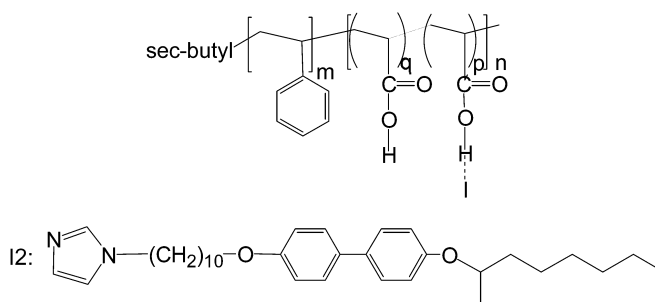
poly(vinyl phenol), or poly(acrylic acid), is easily prepared with a wide range of molecular weights and narrow molecular weight distribution by living polymerization techniques. In addition to the variety of chain lengths and the well-controlled molecular weight distribution, the approach using structure B may offer the feasibility of accurate compositional control by varying the molar ratio between the repeated units with hydrogen-bonding link site and the mesogenic side groups.

A related system involving the interaction of amphiphilic molecules with functionalized block copolymers was reported by Ikkala et al. [31–35]. Similar to the covalently bonded SCLCBCPs, the polymeric complexes composed of poly(styrene-*b*-4-vinylpyridine) and an alkylphenol also formed microphase-separated structures with a layered mesophase inside the domains consisting of poly(4-vinylphenol) and alkylphenol. However, the alkylphenol group does not possess any electro-optical anisotropy as do the liquid-crystal groups used in this study.

In our present study, several poly(styrene-*block*-acrylic acid) polymers with a wide range of molecular weights were combined with imidazole-terminated mesogenic side groups to form H-bonded complexes. A variety of compositions were prepared in order to systematically study these model systems. The creation of H-bonded SCLCBCPs is a complex process involving a series of competing interactions between kinetic and thermodynamic processes. Factors including hydrogen bonding, steric effects, and liquid crystallinity all affect the morphology and mesophase formation of the H-bonded complexes. In this study, these complex problems are investigated.

## RESULTS AND DISCUSSION

The chemical structures of diblock copolymers and imidazole terminated mesogenic side groups employed in the study are illustrated in Fig. 2. Five P(S-*b*-AA) diblock copolymers with different molecular weights were synthesized and are listed in Table 1. Side group I2 was chosen for its ability to form homogeneous hydrogen-bonded blends as described in ref. [30]. Mixing the designed block copolymers and I2 with different blend ratios (the blend ratio,  $f$ , is the molar ratio of the imidazolyl side groups to acrylic acid repeat units) formed hydrogen-bonded complexes with the theoretical weight percentage of PAA/LC block [the domains containing poly(acrylic acid) and I2] ranging from 11 to 93 %. The theoretical weight percentage of the PAA/LC block equals the projected molecular weight of PAA/LC over the total projected molecular weight of the H-bonded complexes, which is based on the assumption that



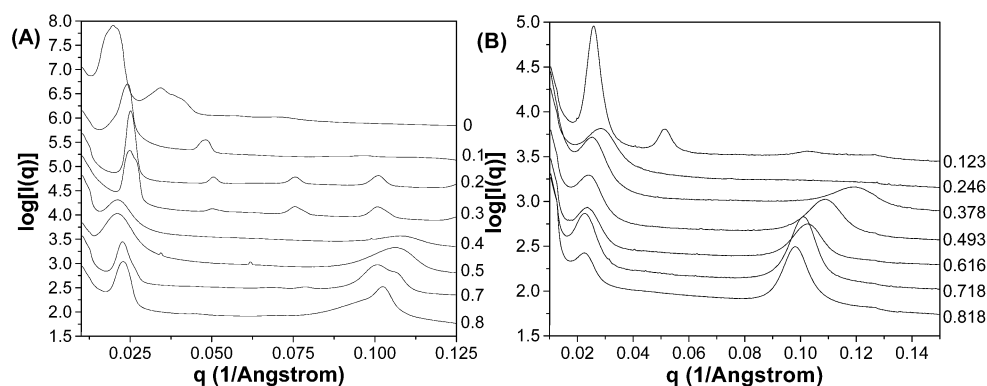
**Fig. 2** Chemical structures of poly(styrene-*b*-acrylic acid) and 4-[10-(Imidazolyl)-decyloxy]-4'-[1-(methyl)heptyloxy] biphenyl (I2).

every I2 is hydrogen-bonded with one acrylic acid repeat unit. The morphologies and structural periodicities of the blends were studied by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

**Table 1** Morphology and theoretical weight percentage of PAA/LC block of H-bonded complexes composed of different blend ratios and polymeric backbones. For SA87/I2 blends, the numbers inside the brackets were the precise blend ratio. Complexes with \* indicated the observation of a *mesophase scattering peak* from SAXS. (C and C' are cylinder morphologies, S and S' are spherical morphologies, L is lamellar, and X is a crystalline phase).

Polymer blend ratio	SA84 25.7–3.2 k	SA82 25–5.3 k	SA87 22–7.1 k	SA85 14.6–16.7 k	SA86 10.3–19.6 k
0	S' 11.1 %	C' 17.5 %	C' 24.5 %	L 53.1 %	L 65.5 %
0.05	C' 14.5 %	L 22.3 %		L 60.4 %	L 72.0 %
0.1	C' 17.6 %	L 26.5 %	L 37.7 % (0.123)	L 65.7 %	C 76.4 %
0.15	C' 20.5 %	L 30.3 %			
0.2	L 23.2 %	L 33.7 %		C 73.1 %	*C 82.0 %
0.25			L 47.0 % (0.246)		
0.3		L 39.7 %		*C 78.0 %	*C 85.5 %
0.4	L 32.4 %	*L 44.6 %	*L 53.8 % (0.378)	*C 81.1 %	*C 87.8 %
0.5	*L 36.1 %	*L 48.8 %	*L 59.1 % (0.493)	*C 83.6 %	*X 89.6 %
0.6			*L 63.3 % (0.616)	*C 85.5 %	
0.7		*L 55.6 %	*L 66.7 % (0.718)		
0.8		*L 58.3 %	*L 69.6 % (0.822)	*X 88.3 %	*X 92.6 %

Figure 3A shows representative SAXS patterns of blends of polymer SA82 and mesogen I2 with blend ratios ranging from 0 to 0.8. For neat SA82 composed of a 25 000 g/mole PS block and a 5300 g/mole PAA block, the SAXS pattern showed the characteristic pattern of a cylindrical morphology. Since the PAA/LC phase was the minor component, a C' morphology with PAA/LC cylinders embedded in a PS matrix is proposed. For SA82/0.2I2 (blends containing SA82 and I2 with a 0.2 blend ratio) with a theoretical 33.7 %wt of PAA/LC, the SAXS patterns clearly showed a characteristic pattern of a lamellar morphology (denoted as L). For a high mesogen content blend SA82/0.8I2 with a theoretical 58.3 %wt of PAA/LC phase, the SAXS patterns showed only first-order scattering corresponding to the microphase-separated microstructure. In addition, a scattering peak corresponding to the layered arrangement of hydrogen-bonded I2 (denoted as "mesophase scattering") was also observed. It was noted that for blends with  $f < 0.3$ , sharper first-order as well as higher-order *microstructure scattering* peaks were observed while no *mesophase scattering* could be detected. However,



**Fig. 3** Small-angle X-ray scattering (SAXS) patterns of H-bonded blends with various blend ratios for (A) mixtures consisting of SA82 and I2 and (B) mixtures consisting of SA87 and I2.

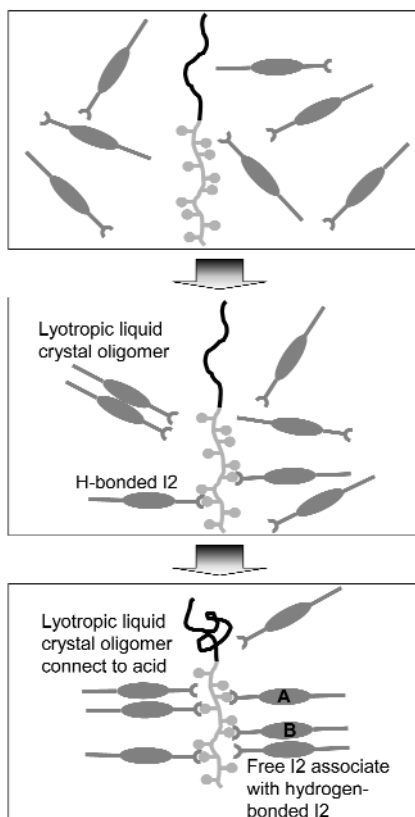
only a broader first-order *microstructure scattering peak* along with a *mesophase scattering peak* could be observed for blends with  $f > 0.4$ . Therefore, the IMDS (intermaterial dividing surface) between PS and PAA/LC of the H-bonded complexes with  $f < 0.3$  is inferred to be sharper than those of the blends with  $f > 0.4$  as suggested by the sharper scattering peak for the former [36]. Moreover, the layered stacking of I2 could be detected only when the blend ratio was higher than a certain critical value between 0.3 and 0.4. These results are consistent with X-ray diffraction of other blend compositions.

Figure 3B shows SAXS patterns of blends consisting of polymer SA87 (composed of a 22 000 g/mole PS block and a 7100 g/mole PAA block) and mesogen I2 with blend ratios ranging from 0.123 to 0.818. For SA87/0.123I2, a lamellar morphology was suggested based on the *microstructure scattering* with a 1:2:4 ratio of  $d^0:d^1:d^2$  from its SAXS pattern. For complexes with  $f > 0.246$ , their lamellar morphologies were confirmed through TEM due to the absence of higher-order *microstructure scattering*. Similar to SA82/I2 blends, *mesophase scattering* could be detected only when the blend ratio was larger than a critical value between 0.246 and 0.378. Sharp interfaces could also be surmised for the blends with low I2 content while thicker interfaces were suggested for the blends with medium to high I2 content.

The morphology table (Table 1) was constructed by integrating the SAXS patterns with a TEM analysis of all blends studied. It is inappropriate to establish a morphology diagram with morphology as a function of the weight percentage of PAA/LC block since the complexes with low blend ratios would be different in nature from those with high blend ratios. However, the morphology table still provides a general view of the relationship between the morphology and the weight ratio. The absence of microstructures for blends with a theoretical weight percentage of PAA/LC larger than 88 % is thought to result from the severe plasticization of PS domains by I2 since the P(S-*b*-AA) block copolymer serves as a solute dissolved in the I2 solid solvent.

It was also noticed that a critical composition for the manifestation of liquid crystallinity (as judged by the presence of mesophase scattering in the SAXS patterns),  $f_{cr}$ , existed for all P(S-*b*-AA) blends with different molecular weight ratios. Furthermore,  $f_{cr}$  decreased with the increment of the weight percentage of PAA block in P(S-*b*-AA) as shown in Table 1. If the ideal binary system assumption (every I2 is bonded to one acrylic acid repeat unit) is valid,  $f_{cr}$  should have been the same for all the blends consisting of different polymer backbones since the grafting density of I2 in the PAA/LC block would be the same regardless the weight ratio of PAA. Hence, it is proposed that the hydrogen-bonded blends act as three-component systems instead of an ideal binary system. That is, even though I2 preferentially binds to the PAA block, some I2 is still free to locate in either the PAA/LC or PS domains. The existence of nonbonded I2 was confirmed by FTIR studies, which can be attributed to a competition between different hydrogen-bonding groups as well as steric hindrance.

As illustrated in Fig. 4, once mesogens A and B are hydrogen-bonded, it might be difficult for the third mesogen to fill the gap between mesogen A and mesogen B due to the bulkiness and rigidity of the mesogenic groups. Therefore, the grafting density is a complex function of the stoichiometric blend ratio, the probability that the proton donor meets the proton acceptor, the thermodynamic preference of different hydrogen bonds, and steric effects. The existence of nonbonded free mesogenic groups, not observed in covalently bonded SCLCBCPs, was believed to play an important role in electric field alignment of these hydrogen-bonded complexes as published elsewhere [37].



**Fig. 4** Proposed assembly process for the formation of layered mesophase in these H-bonded blends.

## CONCLUSIONS

A series of hydrogen-bonded complexes consisting of host poly(styrene-*b*-acrylic acid) as proton donor and guest mesogenic moieties as proton acceptors were prepared via solvent casting processes. In the present study, we were able to establish a morphology table for hydrogen-bonded side-chain liquid-crystalline block copolymers. The formation of the mesophase was found to be related to both the blend ratio and the weight percentage of PAA in the polymeric backbone. A critical blend ratio for *mesophase formation* was identified, and the characteristics of the H-bonded complexes with blend ratios above and below the critical value were different as judged by the structural study as well as by their thermal behavior. In summary, the supramolecular approach using hydrogen bonds not only provides a simple alternative method to construct SCLCBCPs, but also builds a unique system that displays many properties distinct from covalently bonded systems. Hydrogen-bonded SCLCBCPs having compositionally and thermally tunable features may be useful as dynamically functional materials.

## EXPERIMENTAL

### Sample preparation

A poly(styrene-*b*-*tert*-butylacrylate), P(S-*b*-tBA), block copolymer was synthesized by sequential anionic polymerization under the atmosphere of nitrogen in THF at  $-78\text{ }^{\circ}\text{C}$  and it was then converted to a poly(styrene-block-acrylic acid) by hydrolysis following the procedures described in ref. [30].

4-[10-(Imidazolyl)-decyloxy]-4'-[1-(methyl)heptyloxy]biphenyl (denoted as **I2**) was synthesized from imidazoles and 4-[10-(bromo)-decyloxy]-4'-[1-(methyl)heptyloxy]biphenyl according to the method described in ref. [30].

Hydrogen-bonded complexes were prepared using the solvent cast procedure. Imidazolyl compound **I2** and P(S-*b*-AA) were dissolved in THF with calculated molar ratios to form a clear solution with a concentration of 10 mg/1 ml. For polymers consisting high PAA weight percentage, methanol was added dropwise until the polymer solution was clear before the addition of **I2** to prevent the formation of micelles. The solvent was removed by slow evaporation in the atmosphere saturated with THF. The blend was then dried over vacuum for 12 h at room temperature.

### Characterization

Gel permeation chromatography (GPC) using a Waters GPC apparatus was used to determine the molecular weights of polystyrene blocks and the molecular weight distributions of diblock copolymers with respect to polystyrene standards. The molecular weights of PtBA blocks were calculated from  $^1\text{H}$  NMR spectra on 200 or 400 MHz Varian NMR instruments. FTIR spectra were carried out on a Mattson 2020 Galaxy series instrument to examine the formation and dissociation of hydrogen bonds. SAXS studies were carried out in G-1 beam line in Cornell High Energy Synchrotron Source (CHESS). TEM were made using a JEOL 1200E electron microscope operated at 120 kV for the morphology and the homogeneity study.

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