

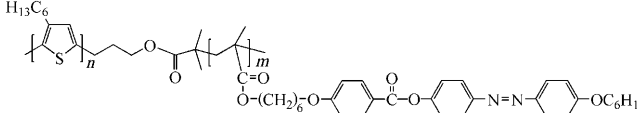
Block Copolymers Comprising π -Conjugated and Liquid Crystalline Subunits: Induction of Macroscopic Nanodomain Orientation**

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The tuning of microphase separation and self-organization in block copolymers (BCPs) with π -conjugated subunits (rod-coil or rod-rod) is a promising means to control the microstructure or morphology that may be crucial for the electronic and optoelectronic applications of such BCPs.^[1] In the case of BCPs based on poly(3-hexylthiophene) (P3HT),^[2–7] which is one of the most important conducting polymers, as regioregular P3HT has a very high melting temperature T_m , a long-range ordered morphology is difficult to obtain, because of the dominant crystallization process that competes with self-assembly.^[3] As a consequence, it is even more challenging to obtain nanodomains of P3HT that are preferentially oriented in one direction at a macroscopic scale. The development of a technique for the manipulation of a phase-separated morphology and ordered nanodomains in P3HT-based BCPs is thus of general interest. We report herein a study designed to address this important issue.

We synthesized a P3HT-based copolymer, which, to the best of our knowledge, is the first diblock copolymer composed of regioregular P3HT and a side-chain liquid crystalline polymer (SCLCP) that bears azobenzene mesogens (Table 1). Previously, Yu et al.^[8,9] and Morikawa et al.^[10,11] showed that the macroscopic orientation of cylindrical nanodomains of PEO or PS could be obtained by orienting azobenzene mesogens either optically^[9–11] or along the rubbing direction of a rubbed surface^[8] by using BCPs of an azobenzene-containing SCLCP with either poly(ethylene oxide) (PEO) or polystyrene (PS). The fact that crystalline PEO has a low T_m value and PS is amorphous accounts for the ease of orientation of their nanodomains. However, it is challenging to achieve the same effect for P3HT for the reasons mentioned above. The design principle of our BCP is as follows: to induce orientation of azobenzene mesogens by either surface effects or by linearly polarized light,^[12] the BCP

Table 1: Chemical structure of the block copolymers and characteristics of the synthesized samples.



Sample	$M_n^{[a]}$ [g mol ⁻¹]	$M_n^{[b]}$ [g mol ⁻¹]	PDI ^[b]	P3HT [wt %]
P3HT ₂₆ -Br	4510	6400	1.12	100
P3HT ₂₆ - <i>b</i> -PAzoMA ₂₃	17990	22650	1.15	25
P3HT ₂₆ - <i>b</i> -PAzoMA ₃₆	25610	27350	1.18	17
P3HT ₄₃ -Br	7330	10150	1.13	100
P3HT ₄₃ - <i>b</i> -PAzoMA ₃₈	29600	32200	1.26	25
P3HT ₄₃ - <i>b</i> -PAzoMA ₁₂₀	75540	76500	1.32	10

[a] Determined by ¹H NMR spectroscopy in CDCl₃. [b] Determined by size exclusion chromatography, using polystyrene standards and THF as eluent.

needs to be thermally annealed in a liquid-crystalline (LC) phase of the SCLCP block, while P3HT should be in the isotropic state ($T > T_m$) to facilitate the microphase separation and allow fluid nanodomains of P3HT to be oriented by an anisotropic environment of oriented mesogens. This prerequisite means that the SCLCP should have a high LC \rightarrow isotropic phase transition (clearing) temperature. The SCLCP used to construct the BCP with P3HT, namely, poly[4-[4-(6-methacryloyloxyhexyloxy)benzoate]-4'-hexyloxyazobenzene] (PAzoMA), meets the criterion. With an extended mesogenic core that contains three phenyl rings, PAzoMA has a clearing temperature of approximately 240 °C,^[13] which is higher than the T_m value of P3HT. With this BCP, we found that surface-induced orientation of mesogens could align striplike nanodomains of P3HT in the same direction. Likewise, photoinduced orientation of mesogens could also result in a certain degree of macroscopic orientation of the nanodomains. This proof-of-principle study thus demonstrates that the use of LC field-induced alignment is a pathway to achieving and manipulating macroscopic orientation of nanodomains of conducting polymers.

The obtained BCP samples of P3HT-*b*-PAzoMA, that is, two regioregular P3HT macroinitiators and four BCPs of varying compositions, are listed in Table 1. The P3HT macroinitiator was first obtained by using a previously reported method,^[14] and was then used to grow the second block of PAzoMA through atom transfer radical polymerization (ATRP). Figure 1 shows examples of characterization results for P3HT₄₃-Br and P3HT₄₃-*b*-PAzoMA₁₂₀. The size exclusion chromatography (SEC) curves show that the as-obtained BCP contained a small fraction of nonreacted P3HT (Figure 1a), but it could readily be removed by a fractionated

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Supporting information for this article (details of block copolymer synthesis and characterization) is available on the WWW under <http://dx.doi.org/10.1002/anie.201004445>.

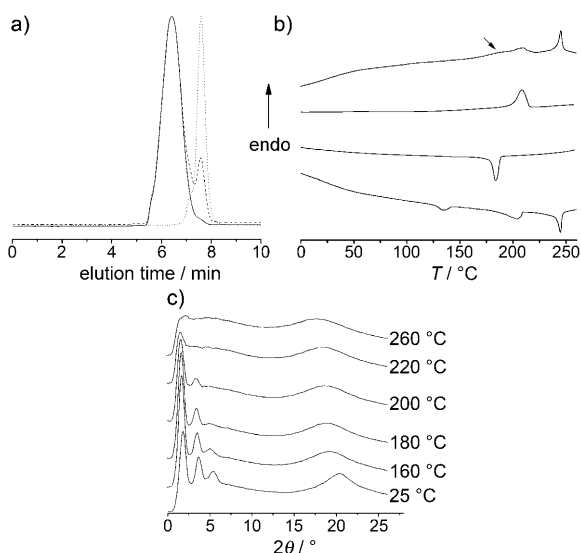


Figure 1. a) Size-exclusion chromatograms of a P3HT macroinitiator (.....) and P3HT₄₃-*b*-PAzoMA₁₂₀ block copolymer before (-----) and after (—) fractionation; b) Differential scanning calorimetry (DSC) curves (heating and cooling scans) of the P3HT macroinitiator (two curves in the center) and the block copolymer (two outer curves); the arrow indicates P3HT crystal melting at ca. 180°C; c) Variable-temperature X-ray diffractograms of the block copolymer.

precipitation, thus giving rise to a BCP sample with a low polydispersity index (PDI) for P3HT-based BCPs. DSC heating and cooling curves confirmed that the PAzoMA block has a clearing temperature higher than the T_m of the P3HT block (Figure 1b). While P3HT₄₃-Br exhibits an exothermic peak that indicates a crystallization temperature $T_c \approx 182^\circ\text{C}$ on cooling from the isotropic state and a melting endothermic peak at approximately 206°C on heating, the BCP shows two additional mesophase transitions from the SCLCP block at higher temperatures. On cooling, the first two exothermic peaks at 242°C and 208°C correspond to the isotropic \rightarrow LC1 and LC1 \rightarrow LC2 phase transition respectively, and the peak at approximately 135°C arises from the crystallization of the P3HT block. On heating, the crystal melting of P3HT occurs at approximately 180°C (indicated by an arrow in Figure 1b), and is partially overlapped with the endothermic peak of the LC2 \rightarrow LC1 transition, while the clearing (LC1 \rightarrow isotropic) temperature is about 240°C . These phase transition assignments were confirmed by variable-temperature X-ray diffractograms of P3HT₄₃-*b*-PAzoMA₁₂₀ (Figure 1c). The diffraction peak at $2\theta \approx 5.4^\circ$ (d spacing: 16.5 \AA) at 25°C arises from crystallized P3HT chains, while the other two peaks at $2\theta \approx 1.8^\circ$ (d spacing: 49 \AA) and 3.7° (d spacing: 24 \AA) arise from a smectic phase (LC2) of PAzoMA. Crystalline P3HT melted upon heating to 180°C , the LC2 \rightarrow LC1 phase transition was completed at 220°C with PAzoMA in a less ordered nematic phase with smectic ordering (polarized optical microscopy (POM) images in the Supporting Information), while the PAzoMA block was in the isotropic phase at 260°C . These results confirm that the main feature of our BCP design was successful, that is, the P3HT block crystallizes in the BCP, but has a T_m value lower than

the clearing temperature of the SCLCP. It is interesting to note that from Figure 1b, the supercooling of P3HT, defined as $T_m - T_c$, is larger for the BCP (approximately 45°C) than for P3HT₄₃-Br (approximately 24°C). This result reflects the increased difficulty of crystallization under the effect of nanodomain confinement and interfacial interactions with PAzoMA. Similar characterization results were obtained with other BCPs (Table 1).

The effect of surface-induced LC orientation on the phase-separated morphology of P3HT₄₃-*b*-PAzoMA₁₂₀ was first investigated. A thin BCP film was spin-coated on a glass slide with a rubbed polyimide layer on the surface (LC cell, E.H.C., Japan); after drying, the film was cooled from 260°C (isotropic phase) to 220°C within 10 minutes for orientation of the mesogens (with P3HT in the isotropic state and PAzoMA in the LC phase), and was then slowly cooled to room temperature. For comparison, another film was cast on a nonrubbed quartz surface and was subjected to the same thermal treatment (the film thickness was about 30 nm). Figure 2a,b show the AFM phase images of the films over an area of $1 \mu\text{m} \times 1 \mu\text{m}$, the fast Fourier transform (FFT) of the images (lower left), as well as their polarized UV/Vis spectra (lower right), respectively. In both films, P3HT was well phase-separated from PAzoMA and formed striplike nanodomains (lighter color) as in other P3HT-based BCPs.^[4–5] On the nonrubbed surface (Figure 2a), P3HT nanodomains are randomly oriented on the macroscopic scale, as are the mesogens in PAzoMA, the random orientation of which is indicated by the absence of dichroism of the azobenzene absorption band around 360 nm . By contrast, on the rubbed surface (Figure 2b), the orientation of mesogens along the rubbing direction can be seen from the large dichroic ratio of their absorption band, and P3HT striplike nanodomains are uniformly aligned in the same direction as the LC orientation. In this case, the enhanced periodicity in the direction perpendicular to the aligned P3HT stripes is also reflected by the FFT pattern. These results show that an oriented SCLCP could align phase-separated, striplike nanodomains of P3HT in the isotropic phase, and this macroscopic orientation of P3HT nanodomains remains intact upon crystallization of P3HT when cooling to room temperature. The crystalline packing of P3HT chains in the nanodomains is indicated by the absorption band of the thiophene rings around 520 nm . However, in the oriented film, the small dichroism of the thiophene band implies that P3HT chains inside the aligned stripe-like nanodomains are not preferentially oriented along the rubbing direction. This result is in contrast to the chain orientation observed for a conducting polymer soluble in a small-molecule nematic LC.^[15] Without annealing the BCP with P3HT in the isotropic state, a uniform orientation of the striplike P3HT nanodomains could not be obtained.

Photoinduced orientation of the azobenzene mesogens in a SCLCP like PAzoMA could be accomplished by first exposing a thin film to nonpolarized UV light (360 nm) in order to convert *trans* isomers into *cis* isomers, and by then irradiating the film with linearly polarized visible light (440 nm) to convert the *cis* isomers back into the *trans* form while inducing a molecular orientation of the chromophore

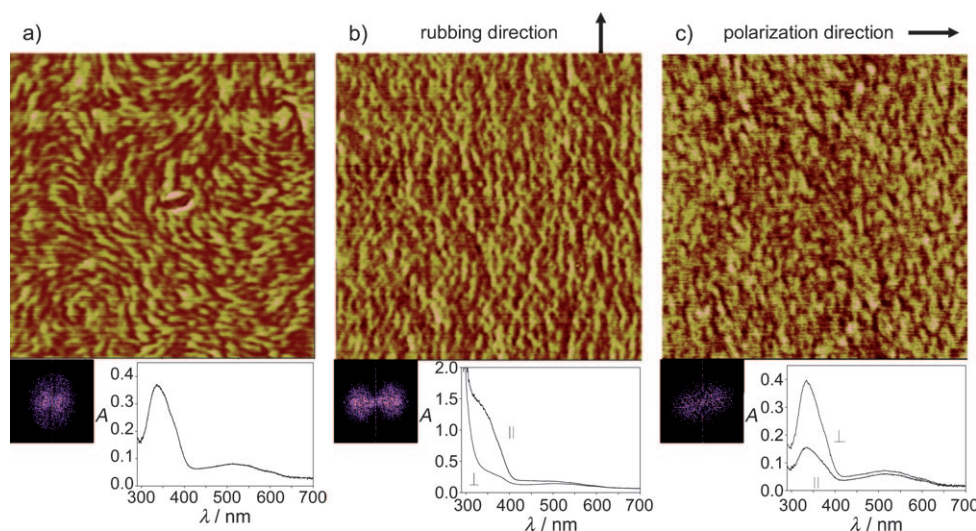


Figure 2. AFM phase images ($1\ \mu\text{m} \times 1\ \mu\text{m}$), their corresponding fast Fourier transformations, and polarized absorption spectra for thin films of P3HT₄₃-b-PAzoMA₁₂₀ cast on a) a nonrubbed quartz plate, b) a rubbed glass plate for surface-induced orientation of the mesogens, and c) a nonrubbed quartz plate subjected to irradiation for photoinduced orientation of the mesogens. Absorption spectra were recorded with the beam of the spectrophotometer polarized to be parallel and perpendicular, respectively, to either the surface-rubbing direction (b) or the polarization of the irradiating light (c).

perpendicular to the polarization of visible light.^[12] This photoinduced orientation can be enhanced by annealing the film to above the T_g value of the polymer because of a cooperative rearrangement motion of mesogens promoted by polymer chain mobility. However, we found that such a photoinduced and thermally enhanced orientation of azobenzene mesogens decreases at $T > 160^\circ\text{C}$, which is close to the melting point of crystalline P3HT. Therefore, we had to anneal the BCP film at lower temperatures to preserve the high degree of LC orientation. Given that the crystallization of P3HT may hamper the formation of a long-range ordered morphology,^[3] the possibility of using photoinduced orientation to macroscopically align the nanodomains of P3HT was investigated under the following conditions: a film of P3HT₄₃-b-PAzoMA₁₂₀ was solution-cast on a quartz plate and dried at room temperature. No well-developed microphase separation was observed in AFM in the as-cast film. The film was subjected to irradiation by UV and visible light at 45°C to induce orientation of the azobenzene mesogens and, after turning off the irradiation, the film was thermally annealed at 120°C for 1 hour before cooling to room temperature (T_g of PAzoMA in the BCP is about 45°C). Figure 2c shows the AFM phase image, FFT, and polarized UV/Vis spectra of the film recorded after the optical and thermal treatment. The strong dichroism of the azobenzene absorption band indicates orientation of mesogens in the expected direction, that is, perpendicular to the polarization of the visible light irradiation. The nanodomains of P3HT appear to be less well developed because of their lower annealing temperature. Nevertheless, the alignment of the mesogens along the LC orientation direction is obvious from the phase image and FFT (the apparent tilt of oriented nanodomains is likely caused by a misalignment of the film positioned on the AFM substrate). Under the conditions employed, LC orientation,

P3HT crystallization, and microphase separation were likely to be decoupled events. We observed that if a BCP film was first annealed at 220°C to obtain a nicely phase-separated morphology (Figure 2a), the same photo-physical and thermal treatment could not align the nanodomains of P3HT. The results show that the photo-induced orientation of azobenzene mesogens could also be used to align macroscopically the nanodomains of P3HT, but to a lesser degree because of lower annealing temperatures required to retain the orientation of azobenzene mesogens.

In summary, we synthesized the first diblock copolymer composed of regioregular P3HT and a SCLCP. By

designing a BCP that contains an SCLCP block with a clearing temperature higher than the melting temperature of the crystalline P3HT, we found that both surface- and photoinduced orientation of azobenzene mesogens in the PAzoMA major phase could be used to impose a macroscopic orientation of the stripelike nanodomains of P3HT in the same direction as the mesogens. In view of the great ease and variety of field-induced controllable LC orientation, this study has demonstrated how macroscopically ordered microstructures or morphologies of BCPs based on π -conjugated polymers can be formed and manipulated. The use of this approach to induce oriented nanodomains of both donors and acceptors in a BCP, which is a requirement for photovoltaic applications, however, remains a challenge. One possible strategy is to develop donor–acceptor diblock copolymers of which one block itself is an LCP. As an alternative, ABC triblock copolymers could be designed, where A and B are donor and acceptor blocks and C is an SCLCP. If field-induced LC orientation aligns microphase-separated domains of A and B, it will be necessary to find a way to selectively degrade the SCLCP block while retaining the continuous phases of donor and acceptor blocks. Work aimed at addressing these issues is currently underway.

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