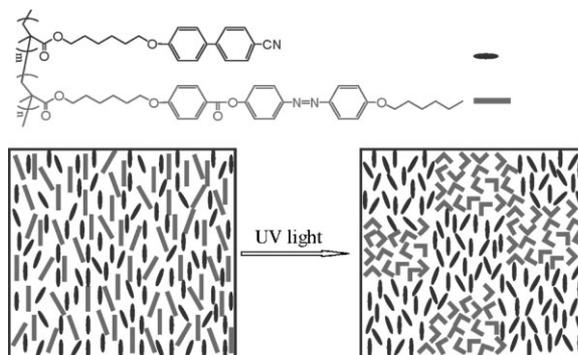# Photoinduced Microphase Separation in Block Copolymers: Exploring Shape Incompatibility of Mesogenic Side Groups[a]

Yi Zhao, Xia Tong, Yue Zhao*

Photoinduced microphase separation in block copolymers (BCP) was achieved for the first time, using a rationally designed diblock copolymer composed of two side-chain liquid crystalline polymers (SCLCP). The miscibility of the two blocks was promoted by the miscibility between the two types of mesognic side groups, while upon UV exposure inducing the *trans–cis* isomerization of azobenzene mesogens on one SCLCP, the shape incompatibility of bent *cis* isomers with an ordered liquid crystalline phase drove the separation of the two blocks resulting in a microphase separated morphology. This result shows the perspective of using light to process and organize BCP morphology and related nanostructures in a lithography-free manner.

Introduction

The ability to control the microphase separation-induced morphology and the related nanostructures of block copolymers (BCPs) in the solid state is a key to enable their applications.[1] The perspective of using light as a flexible means to process and spatially organize the morphology without lithography-based procedures is appealing. Some possibilities have been shown with the use of azobenzene-containing BCPs (referred to as azo BCPs hereafter). Ikeda and Seki's groups[2–4] reported the photocontrolled alignment of nanocylinders using the photoinduced orientation of azo mesogens. Kadota et al.[5] showed that the photoisomerization could change the morphology of a Langmuir–Blodgett monolayer film. Okano et al.[6] synthesized a liquid crystalline polymer with an azo block mesogenic side group and showed that the photoisomerization could erase the lamellar morphology formed due to microphase-separated block side groups. In all these studies, BCPs were microphase-separated before illumination and light was used either to change the morphology, or to induce ordering or pattern different alignments of nanocylinders.[2–6] To the best of our knowledge, no photoinduced microphase separation in a BCP has been achieved thus far. Herein we report the first example.

The used azo BCP has the chemical structure shown in Figure 1. The design rationale to achieve photoinduced microphase separation is as follows: For a diblock copolymer with a given composition and molecular weight, the phase behavior is determined by the product χN (N is the index of polymerization and χ the interaction parameter).[7] To induce the microphase separation by light, the two blocks should be miscible before illumination, while upon

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[a] Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at http://www.mrc-journal.de, or from the author.
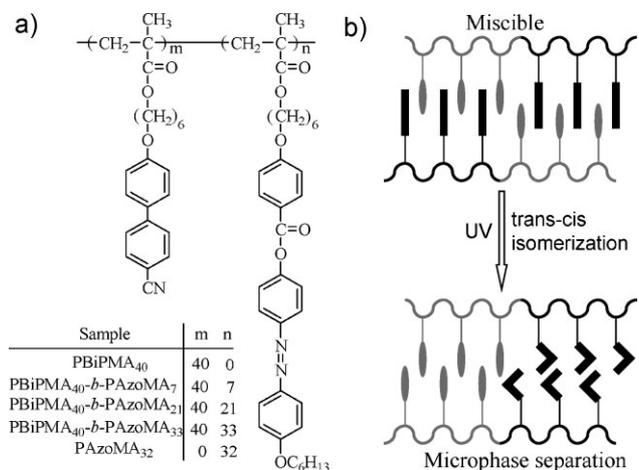
Figure 1. (a) Chemical structure of the double side-chain liquid crystalline block copolymer. (b) Schematic illustration of the photoinduced microphase separation driven by the shape incompatibility of mesogenic side groups.

illumination, a photoreaction increases χ so significantly that χN brings the BCP into a two-phase region (disorder-to-order transition). Though conceptually sound, it is hard to envision how a photoreaction alone could change the intermolecular interactions between the two blocks dramatically to fulfill the condition. In a previous work on small-molecule LC doped by a large amount of an LC azo dye, we found that the *trans–cis* photoisomerization could result in not only a nematic–isotropic phase transition,[8] but also a phase separation[9] because bent-shaped *cis* isomers are incompatible with an ordered LC phase. Our diblock copolymer was designed to make use of the photochemical phase separation observed for a mixture of two LCs. The two blocks are side-chain liquid crystalline polymers (SCLCPs); for the azo block, the azo side group linked to the polymethacrylate backbone is the LC azo dye used in the previous work,[9] while for the other SCLCP block, the biphenyl side moiety is a typical mesogen in LCs. Therefore, as sketched in Figure 1, the miscibility between the two mesogens would promote the miscibility of the two blocks, while upon UV-induced *trans–cis* isomerization, the incompatibility of the *cis* azo groups in the ordered LC phase would drive the two blocks to separate. In other words, the shape incompatibility of *cis* isomers in an LC phase could enhance the increase in χ leading to the photoinduced

microphase separation. We synthesized this azo double-SCLC BCP and the results confirmed the design principle. We note here that photoinduced phase separation in a blend of anthracene-labeled polystyrene and poly(vinyl methyl ether), driven by photodimerization of the chromophore, was reported,[10] which of course differs from the photo-induced microphase separation in BCPs.

Experimental Part

The azo double-SCLC BCP was synthesized by using the reversible addition-fragmentation chain transfer polymerization method (RAFT)[11] Details on the synthesis and characterizations of the polymers are given in the Supporting Information.

Results and Discussion

The samples of the azo double-SCLC BCP are listed in Figure 1. The same macrochain-transfer agent of poly{6-[4-(4-cyanophenyl)phenoxy]hexyl methacrylate}, PBiPMA$_{40}$, was used to grow the second block of poly{4-[4-(6-methacryloyoxyhexyloxy)benzoate]-4'-hexyloxyazobenzene} (PAzoMA) of various lengths. The example of results in Figure 2 show the first feature required for photoinduced microphase separation. That is the initial miscibility
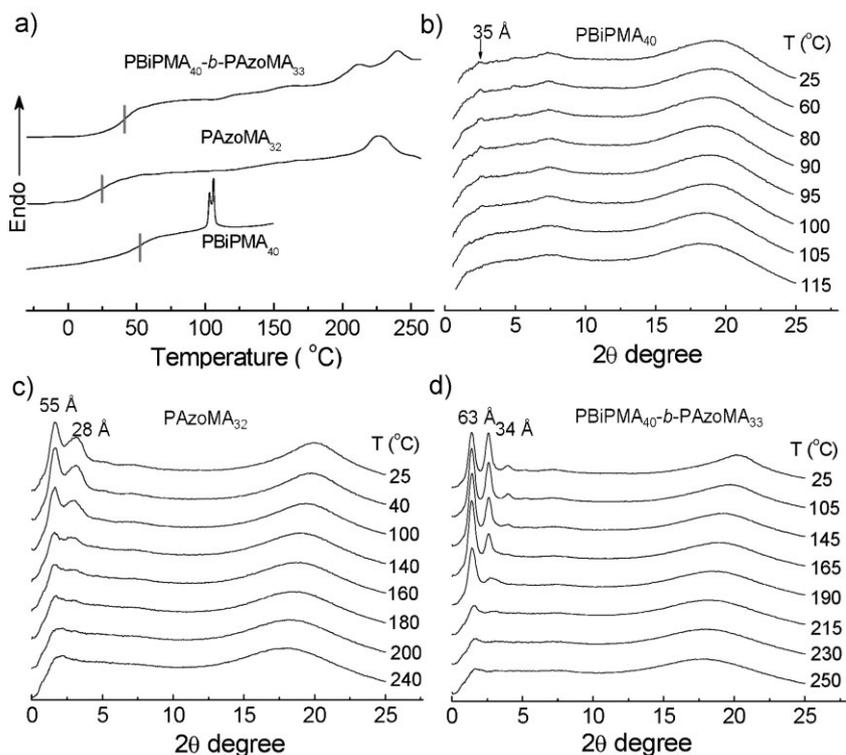
Figure 2. (a) DSC heating curves of the diblock copolymer PBiPMA$_{40}$-*b*-PAzoMA$_{33}$ and the two constituting homopolymers PBiPMA$_{40}$ and PAzoMA$_{32}$. (b–d) Variable-temperature X-ray diffractograms of PBiPMA$_{40}$, PAzoMA$_{32}$, and PBiPMA$_{40}$-*b*-PAzoMA$_{33}$, respectively.

between the two blocks. In (Figure 2a) the DSC heating curves (second scan) of PBiPMA$_{40}$-b-PAzoMA$_{33}$ and the two constituting homopolymers (with virtually the same molecular weights) are compared. As marked, PBiPMA$_{40}$ displays a glass transition temperature (T_g) at $\approx 52\,^\circ$C and two endothermic peaks at 103 and 106 $^\circ$C (smectic A-to-nematic and nematic-to-isotropic phase transition, respectively).[12] As for PAzoMA$_{32}$, it shows a lower T_g at $\approx 26\,^\circ$C and a broad endotherm peaked at 230 $^\circ$C (assigned to an overlapping smectic-to-nematic and nematic-to-isotropic phase transition too). The diblock PBiPMA$_{40}$-b-PAzoMA$_{33}$, having basically the two SCLCPs linked together; shows a single T_g of $\approx 40\,^\circ$C that is intermediate between the T_gs of the two blocks, and three endothermic peaks at about 159, 210, and 240 $^\circ$C that are also very different from the two blocks. This result clearly indicates that the two blocks of PBiPMA$_{40}$-b-PAzoMA$_{33}$ are miscible. Similar DSC results were obtained for other azo BCP samples, all displaying a single T_g. Moreover, Figure 2b–d compare the X-ray diffraction patterns of the copolymer and the two homopolymers recorded at different temperatures upon cooling from the isotropic phase to room temperature. Though PBiPMA is known to have a narrow nematic phase followed by a smectic A phase,[12] only a very weak diffraction peak related to the smectic layer could be observed corresponding to a layer spacing of $\approx 35\,\text{\AA}$ that suggests a partial interdigitation of the biphenyl side groups (the length of biphenyl mesogen + spacer is about 23 Å). In contrast, the smectic order in PAzoMA$_{32}$ is easy to notice. The diffraction peaks, at Bragg spacing of 55 and 28 Å, are close to first- and second-order peaks and suggest a limited interdigitation of the side groups since the full length of the side group (azobenzene moiety + spacer) is about 34 Å. For the diblock copolymer, the diffraction peaks arising from smectic ordering become sharper than the homopolymers. The positions of the two main diffractions are rather similar to those of PAzoMA suggesting that with the mixing of the two mesogenic side groups the smectic layer spacing be controlled by the longer azobenzene side group. On cooling, the transition from a smectic A to a more ordered smectic phase is noticeable (below about 170 $^\circ$C) resulting in an increase in the intensity of the apparent second-order peak and the appearance of additional higher-order diffraction peaks at larger angles. We note also that as compared to PBiPMA, the increasingly ordered phase upon cooling in PAzoMA and the diblock copolymer is also reflected by the significant narrowing and shift of maximum of the halo at wide angles from $2\theta \approx 18$ to $21\,^\circ$.

The example of UV–Vis spectra in Figure 3 is used to explain the second condition that needs to be fulfilled for the photoinduced microphase separation. That is, under UV irradiation the *cis* isomers of azo mesogens must be stable at an elevated temperature for polymer chain mobility. Indeed, upon UV induced *trans–cis* isomerization, the
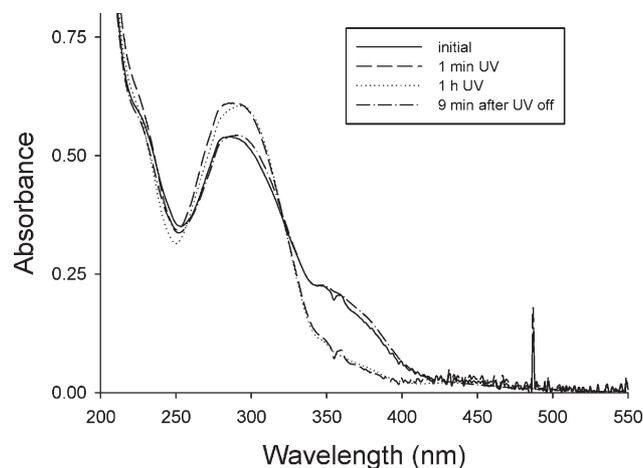

Figure 3. UV–Vis spectra recorded at 80 $^\circ$C for a thin film of PBiPMA$_{40}$-b-PAzoMA$_{21}$.

microphase separation of the two blocks necessitates the chain mobility and is more likely to develop at an elevated temperature above T_g. For this, the *cis* isomer of the azo mesogen should be very stable so that the thermally activated *cis–trans* back-isomerization at the elevated temperature is slow. This is the case with the used azo mesogen. Figure 3 shows the UV–Vis spectra of a thin film of PBiPMA$_{40}$-b-PAzoMA$_{21}$ recorded at 80 $^\circ$C. The *trans–cis* isomerization was completed after 1 min UV exposure as revealed by the drop of the absorption of *trans* azo groups at 360 nm and the noticeable appearance of absorption of *cis* isomers at 450 nm. The amount of *cis* azo groups appeared unchanged during 1 h continuous UV exposure, which may allow the separation of PAzoMA bearing *cis* azo groups from PBiPMA to develop over time. But shortly after turning off the UV light, *cis* azo groups were converted back to the *trans* form due to a fast thermal relaxation at this temperature.
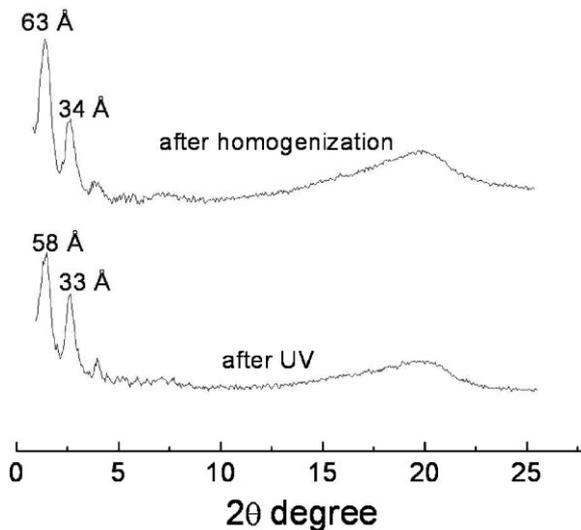
With the above two conditions fulfilled, photoinduced microphase separation was observed in thin films of this azo double-SCLC BCP. Figure 4 shows room-temperature AFM phase images of PBiPMA$_{40}$-b-PAzoMA$_{21}$ before UV exposure (film cooled from the isotropic phase) and after UV exposure at 70 $^\circ$C for 1 h (film cooled under UV). The appearance of a second microphase is visible, with a domain size around 15 nm. The surface roughness of the film remained the same after UV exposure (about 4 nm). Similar microphase-separated morphologies were observed with other BCP samples. For comparison, the images of a thin film of PAzoMA$_{32}$ subjected to exactly the same thermal and UV irradiation treatment (with azo mesogens undergoing the photoisomerization) display no meaningful change in morphology (the same result was obtained with PBiPMA$_{40}$). Here it is important to emphasize that the polymer film was exposed to ''flood'' UV irradiation; the two-phase morphology could not be related to the mass
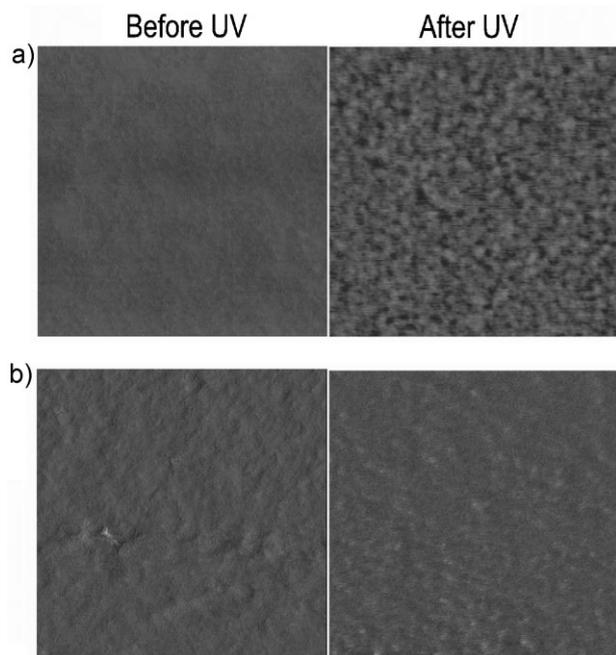
Figure 4. AFM phase images of (a) a thin film of PBiPMA$_{40}$-*b*-PAzoMA$_{21}$ and (b) a thin film of PAzoMA$_{32}$ before and after UV exposure at 70 °C for 1 h (365 nm, 29 mW · cm^{-2}).

Figure 5. X-ray diffractograms at room temperature of PBiPMA$_{40}$-*b*-PAzoMA$_{21}$ subjected to UV irradiation at 70 °C for 2 h (labeled after UV) and after subsequent re-equilibrium in the isotropic phase (250 °C) (labeled after homogenization).

transport responsible for the surface relief grating (SRG) of azo polymers generally obtained with an interference pattern of the irradiation light.[13] The microdomains should result from the photoinduced microphase separation between the two blocks driven by the incompatibility of *cis* azo mesogens with the biphenyl mesogens. It can be noticed that the microdomains are not well defined, which is likely to be caused by the low polymer chain mobility since the microphase separation occurs in an ordered smectic phase. The experiment could not be carried out at higher temperatures because azo mesogens in the *cis* form could not be retained even under continuous UV irradiation due to a dominant thermal relaxation of *cis* isomers.

We also attempted to observe the photoinduced microphase separation by the X-ray diffraction measurements. For this experiment, a film of PBiPMA$_{40}$-*b*-PAzoMA$_{21}$ on a Teflon plate was subjected to UV irradiation at 70 °C for 2 h before cooling to room temperature; the sample was then collected and the measurement was conducted at room temperature the next day (all azo mesogenic groups were back to the *trans* form then through thermal relaxation). As shown in Figure 5, as compared to the sample without UV treatment (Supporting Information), the X-ray diffractogram displayed a shift of the 1st-order diffraction peak corresponding to a change of the smectic spacing from ≈63 to 58 Å, which is closer to the 55 Å layer spacing of the azo homopolymer. Subsequently, the sample was heated to the isotropic phase (250 °C) for remixing (homogenization) of the two polymers; after being cooled back to room temperature, the 63 Å spacing was recovered according to the diffraction pattern. This result thus supports the AFM observation as to the occurrence of the photoinduced microphase separation.

Conclusion

In summary, we presented the first observation of photoinduced microphase separation in a BCP. This was achieved by using a rationally designed azo double-SCLC BCP. We showed that the photochemical phase separation in a mixture of two LCs due to the shape incompatibility of *cis* isomers of azo moieties with an ordered LC phase could be used to amplify the effect on χ between the two blocks. Despite the ill-defined microdomains due to the lack of polymer chain mobility in the smectic phase, this study is a significant step forward toward lithography-free, light-processable BCP morphology. To allow a better-defined morphology or nanostructure to develop and to be controlled by light, it might be necessary to have the photoinduced microphase separation occur in a fluid nematic phase. New azo double-SCLC BCPs need to be designed following the principle. Studies are underway and the results will be reported at due time.

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