Photoinduced Microphase Separation of Block Copolymers: Exploring Shape Incompatibility of Mesogenic Side Groups

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1. Synthesis of Diblock Copolymers

Scheme 1 shows the synthetic route to the azobenzene-containing double side-chain liquid crystalline block copolymer of poly{6-[4-(4-cyanophenyl)phenoxy]hexyl methacrylate}-b-poly{4-[4-(6-methacryloyoxyhexyloxy)benzoate]-4′-hexyloxyazobenzene} (PBiPMA-b-PAzoMA) through reversible-addition-fragmentation chain transfer polymerization (RAFT). More details are given below.

1.1. Materials

N,N’-Dicyclohexylcarbodiimide (DCC, 99%), 4-(dimethylamino)pyridine (DMAP, 99%), dichloromethane (DCM, 99%), chloroform (99%), N,N-dimethylformamide (DMF, 99%) were purchased from Sigma-Aldrich and used as received. The pyrene-containing chain transfer agent, 4-cyano-4-methyl-4-thiobenzoysulfanyl-butyric acid pyren-1-yl-methyl ester (Py-CTA), was synthesized following a literature procedure.[1, 2] The monomer of 6-[4-(4-cyanophenyl)phenoxy]hexyl methacrylate (BiPMA), was synthesized using a reported method.[3]

1.2. Synthesis of the azobenzene monomer of 4-[4-(6-methacryloyoxyhexyloxy)benzoate]-4′-hexyloxyazobenzene (AzomA) 4-(6-Methacryloyoxyhexyloxy)benzoic acid (20 mmol, 6.12 g) and 4-hydroxy-4′-hexyloxy
azobenzene (20 mmol, 5.96 g), both synthesized by using literature methods[4, 5] were added in a flask with 100 mL DCM. Under stirring were added DCC (20 mmol, 4.13 g) and DMAP (2 mmol, 0.24 g). The reaction was conducted at 0 °C for 2 h first and then at room temperature overnight. The salt formed during the reaction was removed by filtration, and the coarse product was washed with petroleum ether using a vacuum and dried for 1 day at room temperature. From GPC (PS standards, THF eluent): M\text{N}_{\text{n}}=12300 g mol\text{^{-1}}, \text{PDI}=1.15. From $^1$H NMR: M\text{N}_{\text{m}}= 15000. Monomer conversion is about 55%, which was determined by $^1$H NMR spectroscopy, comparing the integrals at the signal of CH$_3$ in monomer ($\delta=1.95$ ppm) and in polymer ($\delta=0.8-1.3$ ppm). $^1$H NMR (300 MHz, $\delta$ ppm, CDCl$_3$): 7.95-8.19 (m, 9H, ArH in Py), 7.84 (s, 2H, o-Ar H to CSS), 7.40-7.72 (t, 6H, o.m-Ar H to CN and m-Ar H to OCH$_2$), 6.90 (s, 2H, o-Ar H to OCH$_2$), 5.80 (s, 2H, OCH$_2$ to Py), 3.95 (s, 4H, OCH$_2$), 1.2-2.0 (m, 10H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O and main chain CH$_2$), 0.8-1.1 (d, 3H, main chain CH$_3$).

1.3. Synthesis of the macromolecular chain transfer agent PBiPMA-CTA
Poly(6-(4-(4-cyanophenyl)phenoxy)hexyl methacrylate) (PBiPMA) was synthesized using Py-CTA as the starting chain transfer agent (Scheme 1), yielding PBiPMA-CTA. For the reaction, BiPMA (1.0 g, 2.75 mmol), AIBN (2.3 mg, 0.014 mmol), Py-CTA (19.5 mg, 0.039 mmol) and 3 mL of anisole were added into a 10 mL one-necked flask. After 15 min nitrogen purge under stirring, the flask was sealed and put into a preheated oil bath for 3 h. The reaction solution was quenched from liquid nitrogen and diluted by 6 mL of DCM. Then 1 mL DMF was added. After 15 min N$_2$ purge, the flask was sealed and put into an 80 °C oil bath for 50 min. Then the reaction was stopped using liquid nitrogen and diluted by 6 mL of DCM. The solution was dropped into 250 mL petroleum ether/DCM mixture (9:1 by volume) to precipitate the polymer. This process was repeated three times. The collected sample was dried in a vacuum oven for 24 h before use. From GPC: M\text{N}_{\text{n}}=23000, PDI=1.22. $^1$H NMR: M\text{N}_{\text{m}}=27300. $^1$H NMR (300 MHz, $\delta$ ppm, CDCl$_3$): 8.20-8.0 (s, 2H, o-Ar H to –COO), 7.83 (s, 4H, o-Ar H to –N=N–), 7.40-7.72 (m, 6H, 0.m-Ar H to CN and m-Ar H to OCH$_2$ in biphenyl), 7.20-7.35 (s, 2H, o-Ar H to OCO, overlapped with CHCl$_3$), 6.80-6.94 (s, 6H, o-Ar H to OCH$_2$ in biphenyl and azo), 3.95 (s, 10H, OCH$_2$), 1.2-2.0 (m, 20H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O, main chain CH$_2$ and OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$O, 0.8-1.1 (d, 9H, main chain CH$_3$ and CH$_3$ in C$_6$H$_{13}$).

2. Characterizations


$^1$H NMR spectra were recorded at room temperature on a 300 MHz Bruker spectrometer (AC300) using chloroform ($\text{CDCl}_3$) as solvent and tetramethylsilane as internal standard. UV-vis absorption spectra were taken on a Cary 50 Varian spectrophotometer. Gel permeation chromatography (GPC) measurements were conducted on a Waters system equipped with a RI410 refractive index detector, a PDA 996 photodiode array detector and one Styragel 5HE column (7.8 mm×300 mm). THF was used as the eluent containing 2% triethylamine (elution rate, 1 mL min$^{-1}$), and polystyrene standards were used for calibration. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA system under nitrogen atmosphere (scan rate: 10 °C min$^{-1}$). The phase transition behaviours were investigated by a TA Q200 differential scanning calorimeter (DSC), using indium as the calibration standard and a heating or cooling rate of 10 °C min$^{-1}$. Glass transition temperatures (T$_g$) were taken as the midpoint of the change in heat capacity. Polarizing optical microscopic (POM) observations were carried on a Leitz DMR-P microscope equipped with an Instec hot stage. X-ray diffraction (XRD) measurements were performed using a Bruker diffractometer (D8 Discover) equipped with a Bruker AXS two-dimensional wire-grid detector (Cu K$_{\alpha}$ radiation $\lambda$=1.542 Å). To record the diffraction patterns, the sample was filled into a quartz capillary tube (1.5 mm in diameter), and the sealed tube was placed in an Instec hot stage for temperature control. Tapping-mode atomic force microscopy (AFM, Nanoscope IV) was utilized to examine the morphology of thin block copolymer films spin-coated on silicon wafer from a chloroform solution. For the photoinduced microphase separation, a block copolymer film placed in the POM hot stage was heated to a predetermined temperature, exposed, through a quartz window, to UV light ($\lambda$ = 365 nm, 29 mW/cm$^2$) produced by a spot curing system (Novacure 2100) combined with interference filters (10 nm bandwidth, Oriel) for 1h, and then cooled to room temperature under UV light. After turning off the UV light at room temperature, any photoinduced morphology change was retained since the block copolymer was below the T$_g$s.

3. More Results

3.1. Characteristics of the samples

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Composition</th>
<th>Azo content</th>
<th>$M_n\times10^4$ (GPC)</th>
<th>$M_n\times10^4$ ($^1$H NMR)</th>
<th>PDI (GPC)</th>
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<td>P3</td>
<td>PBiPMA$<em>{40-b}$-PAzoMA$</em>{33}$</td>
<td>45</td>
<td>2.68</td>
<td>3.43</td>
<td>1.25</td>
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</table>

Table 1. Since the starting CTA contains a pyrene label (Scheme 1), the numbers of monomer units for the two homopolymers were determined from $^1$H-NMR spectra by comparing the integrals of resonance signals at 5.80 ppm (2H, OCH$_2$ in pyrene) with 6.8-7.1 ppm (4H, Ar-H) for PAzoMA, and at 7.95-8.20 ppm (9H, Ar-H in pyrene) with 7.35-7.7 ppm (6H, Ar-H in biphenyl) for PBiPMA. The macro-CTA (PBiPMA$_{40}$) was then used as reference to calculate the composition of diblock polymers by comparing the integrals of resonance peaks of the two blocks (7.35-7.7 ppm for PBiPMA and 7.75-7.95 ppm for PAzoMA). The NMR-determined numbers of monomer units were used to estimate the number-average molecular weights of the samples shown in Table 1.

3.2. GPC and $^1$H NMR
**Figure S1**: GPC curves of the macromolecular chain transfer agent (PBiPMA$_{40}$) and the three diblock polymers of PBiPMA-$b$-PAzoMA (P1- P3 in Table 1), showing the controlled growth of the second azo polymer block by RAFT. The polydispersity increased slightly as the PAzoMA block became longer. DMF was found to be a good solvent for the chain extension reaction and 50 min was a suitable time with the reaction conducted at 80 °C. Other solvents (such as anisole, dioxane) or longer reaction times were found to yield a larger polydispersity for the diblock polymer.
**Figure S2**: $^1$H NMR spectra of (a) PBiPMA$_{40}$ and (b) PBiPMA$_{40}$-b-PAzoMA$_{21}$. Marked resonance peaks are those used to determine the block copolymer compositions as mentioned above.

3.3. Thermal Properties (DSC and TGA)

**Figure S3**: DSC heating (a) and cooling curves (b) of the diblock polymers and homopolymers (second scan). All block copolymers display a single $T_g$ and different LC phase transitions as compared to the homopolymers, indicating the miscibility between the two blocks. Since the single $T_g$ of a diblock is determined by the $T_g$'s of the two blocks, the apparently lower $T_g$ of the sample P1 likely is caused by the shortest PAzoMA block that should have a lower $T_g$ due to its molecular weight-dependence.

**Figure S4**: DSC heating and cooling curves (second scan) of two blends of different compositions obtained by dissolving the two homopolymers PBiPMA$_{40}$ and PAzoMA$_{32}$ in
THF followed by drying in vacuum. The miscibility between the two polymers is also revealed by a single $T_g$ for each blend that is intermediate between the $T_g$s of the two polymers (Fig. S3). Blend 1: 22 wt% of PAzoMA ($T_g \sim 41 \, ^\circ\text{C}$); blend 2: 45 wt% of PAzoMA ($T_g \sim 35 \, ^\circ\text{C}$). As compared to block copolymers, the LC phase transition peaks appear to be different, suggesting that the chemical links between the two blocks in block copolymers affect the LC ordering and thermal stability.

![Figure S5](image)

**Figure S5**: Thermogravimetric analysis (TGA) curves of all obtained polymers ($\text{N}_2$, 10$^\circ\text{C}$ min$^{-1}$), indicating their thermal stability below 300 $^\circ\text{C}$.

### 3.4. Polarizing Optical Microscopy

![Photomicrographs](image)

**Figure S6**: Photomicrographs under crossed polarizers for PAzoMA$_{32}$ taken upon cooling from the isotropic phase to (a) 225 $^\circ\text{C}$, (b) 215 $^\circ\text{C}$ and (c) 25 $^\circ\text{C}$ (picture area: 350 $\mu$m × 230 $\mu$m). The threaded texture at 225 $^\circ\text{C}$ indicates a nematic phase, which is quickly transformed to a more ordered smectic phase at 215 $^\circ\text{C}$, with the birefringence change and the appearance of focal conic-like domains and stripes. The smectic texture becomes more evident at lower temperatures. This is consistent with the broad exotherm on the DSC cooling curve (Fig.S3) that results from the overlapping of isotropic-to-nematic and nematic-to-smectic transition peaks (due to a narrow nematic range). This is similar to PBiPMA whose LC phases are known be nematic (very narrow temperature range) and smectic A.$^{[6]}$
Figure S7: Polarizing optical micrographs of a thin film of PBiPMA\textsubscript{40}-b-PAzoMA\textsubscript{21} recorded upon cooling from the isotropic phase to room temperature (cooling rate: 0.2 °C/min): a) 260 °C; b) 230 °C; c) 125 °C; d) 115 °C; e) 100 °C and f) 25 °C (picture area: 350 µm × 230 µm). The first LC phase appeared (b) shows the focal conic fan texture characteristic of a smectic-A phase. At a lower temperature (c) the focal conic texture remains but the birefringence is changed, indicating a change in molecular order. Upon further cooling, the focal conic texture is transformed to a broken focal conic texture, suggesting a smectic-C phase (or another more ordered smectic phase). These observations indicate that the LC phases in the block copolymers are smectic A and other more ordered smectic phases.

3.5. X-ray Diffraction

![X-ray Diffraction](image)

Figure S8: X-ray diffraction patterns of (a) PBiPMA\textsubscript{40}-b-PAzoMA\textsubscript{7} and (b) PBiPMA\textsubscript{40}-b-PAzoMA\textsubscript{21}. They display similar features to that of PBiPMA\textsubscript{40}-b-PAzoMA\textsubscript{33}. The effect of the block copolymer composition is mainly reflected by the relative intensity of the diffraction peaks in the small angle region.

3.6. UV-vis Spectra
Figure S9. UV spectra of thin films before UV irradiation, after UV (365 nm, ~25 mW/cm², 20 s) and after subsequent visible light irradiation (440 nm, ~5 mW/cm², 40 s) (photostationary state achieved under both UV and visible light irradiation) showing the reversible trans-cis photoisomerization of azobenzene groups in all samples: (a) PAzoMA₃₂, (b) PBiPMA₄₀-b-PazoMA₇, (c) PBiPMA₄₀-b-PazoMA₂₁ and (d) PBiPMA₄₀-b-PazoMA₃₃. For the homopolymer, the reverse cis-trans isomerization seems to be partial, which probably is caused by the homeotropic alignment of a number of azo molecules after the treatment. This phenomenon appears to be less important in the block copolymers, especially for P1 and P2 (b and c) in which the content of biphenyl mesogens is large.

3.7. AFM
Figure S10. Ambient-temperature AFM phase images (500 nm × 500 nm) for thin films of (a) PBiPMA\textsubscript{40}-b-PAzoMA\textsubscript{33} and (b) PBiPMA\textsubscript{40}. All films were subjected to the same treatment. The films labeled “before UV” were cooled from the isotropic phase (260 °C under N\textsubscript{2}) to room temperature, while the films labeled “after UV” were cooled from the isotropic phase to 70 °C, held at this temperature for 1 hour of UV exposure (365 nm, 29 mW/cm\textsuperscript{2}), then cooled under UV to room temperature before turning off the irradiation. In contrast with the BCP, the two homopolymers show no microdomains after the UV irradiation.

References