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## Synthesis and self-assembly of phthalocyaninetethered block copolymers†

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A series of novel phthalocyanine (Pc)-tethered block copolymers, Pc-poly(methyl methacrylate)-*block*-polystyrene (Pc-PMMA-*b*-PS), with various molecular weights (number average molecular weight mass = 41, 66, 86 kg mol<sup>-1</sup>), were prepared by atom transfer radical polymerization and click chemistry. The structurally related Pc-tethered homopolymer, Pc-PMMA was also synthesized for comparison. Pc-PMMA forms homogeneous polymer films containing  $\pi$ -assemblies of the terminal Pc groups, whereas Pc-PMMA-*b*-PS self-assembles into a cylindrical morphology in which the Pc units show  $\pi$ - $\pi$  interactions inside the confined PMMA cylinders. Such polymer designs have potential applications in optoelectronic devices.

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### Introduction

Phthalocyanines are planar aromatic macrocycles with attractive electronic and optical properties; these properties have led to the incorporation of phthalocyanines as active components in semiconductors, electrochromic devices, informationstorage systems, and liquid-crystal color displays.1 Pc molecules tend to form one-dimensional (1D) columnar structures through  $\pi$ - $\pi$  interactions, exhibiting anisotropic semiconducting properties.<sup>2</sup> Discotic liquid-crystalline (LC) Pcs, which can self-assemble into two dimensional (2D) patterned columnar structures, have also been studied extensively in recent decades and can be used in many of the applications described above.3 Pc-containing polymers are also attracting attention owing to their high stability and their processability.4 Polymers in which Pc groups are present in the main chains, networks, side chains, or cores, or as terminal groups have been prepared.<sup>1c</sup> Among these, stable 1D columnar structures of Pc can be obtained reasonably directly from main-chain-type Pc polymers.<sup>5</sup> However, the synthesis of such functional polymers remains challenging, mainly because of their low solubilities, and it is even more difficult to prepare highly ordered

assemblies of Pc molecules in polymer films in a predictable manner.<sup>6</sup> Therefore, the development of versatile and robust methodologies for preparing polymer materials with Pc assemblies has been the area of research focus.

There have been several recent reports on various designs of  $\pi$ -molecule-containing block copolymers that form well-defined nanostructures of  $\pi$ -assemblies in their polymer films.<sup>7</sup> Block copolymers show phase-separated morphologies such as lamellae, gyroids, hexagonal cylinders, cubes, or spheres, depending on the components and the relative molecular weights of each block.8 Incorporation of molecular semiconductors into such block copolymer morphologies is of particular interest because of the potential optoelectronic applications of the resulting materials.9 For instance, cylindrical and/or lamellar morphologies can serve as active layers in organic photovoltaic (OPV) devices or organic field-effect transistors (OFETs) in which the directional  $\pi$ -conjugated pathways in the polymer films are expected to permit efficient transport of charge and excitons.9 Thelakkat and co-workers reported that perylene bisimide-containing block polymers form  $\pi$ -assemblies in block copolymer nanostructures that are useful in optoelectronic devices.10 Fullerene-containing block copolymers have also been synthesized and show unique phase behaviors.11

Here we report our attempts to construct Pc-containing nanostructures in polymer films by microphase separation of block copolymers. Because of the difficulties in predicting the morphology of newly synthesized functional block copolymers, we decided to modify the well-studied versatile block copolymer, poly(methyl methacrylate)-*block*-polystyrene (PMMA-*b*-PS), with a Pc molecule to minimize the effects of  $\pi$ -assemblies on the morphology. There are few reports of polymer designs in which  $\pi$ -molecules are attached to the termini of block

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copolymers rather than onto their side chains or main chains.<sup>11a</sup> The Pc-tethered block copolymer Pc-poly(methyl methacrylate)block-poly(styrene) (Pc-PMMA-b-PS), in which the Pc unit is attached at the terminus of the PMMA-b-PS, therefore represents a novel type of polymer. PMMA-b-PS was targeted to have cylindrical morphology, while the Pc unit is attached at the end of the cylinder-forming PMMA block. We surmised that if this block copolymer was capable of self-assembly to form a cylindrical morphology in a thin film, the Pc end-groups might be concentrated inside the confined PMMA columns and that anisotropic alignment might be achievable by manipulating the orientation of the cylindrical structure of the PMMA-b-PS. Such control of the alignment of the cylindrical morphology of PMMA-b-PS has been widely studied in the field of block copolymer lithography, where perpendicularly oriented cylinders of PMMA-b-PS are used as etch masks to transfer patterns onto underlying silicon substrates.12 The preparation of Pctethered block copolymers and the characterization of their film morphologies are discussed in this paper.

## **Results and discussion**

### Synthesis and characterization

The synthetic route to the Pc-tethered block copolymers is shown in Scheme 1. To functionalize the Pc unit and attach it to the polymer, we used an azide–alkyne Huisgen cycloaddition, termed a "click reaction", in combination with atom transfer radical polymerization (ATRP).<sup>13</sup> The click reaction is widely used as a polymer-modification technique owing to its high fidelity, quantitative yields, tolerance to a variety of functional groups, mild reaction conditions, and minimal work-up

requirements.14 A zinc complex of Pc with a terminal hydroxyl group Pc-OH was synthesized by means of a mixed tetracyclization of 4,5-bis(dodecyloxy)phthalonitrile with 4-benzyloxyphthalonitrile in a 3:1 molar ratio in the presence of  $ZnCl_2$ , followed by deprotection of the benzyl group with Pd/C. The hydroxyl group of Pc-OH was reacted with 6-chloro-1-hexyne to give the functionalized phthalocyanine 1, which was unambiguously characterized by means of <sup>1</sup>H NMR and absorption spectroscopy along with MALDI-TOF mass spectrometry (see ESI<sup>†</sup>). Meanwhile, the azide-terminated poly(methyl methacrylate) N<sub>3</sub>-PMMA was prepared via ATRP using an azide-bearing ATRP initiator and CuBr/CuBr<sub>2</sub>/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) as the catalyst system. The resulting N<sub>3</sub>-PMMA macroinitiator was subsequently block-extended with styrene by ATRP, to give the azide-terminated block copolymer N<sub>3</sub>-PMMA-b-PS (N<sub>3</sub>-BCP) after reprecipitation in methanol. Samples of  $N_3$ -BCP with various molecular weights were prepared to permit investigations on the effects of the size of the polymer on the morphology of its thin films. The reaction conditions, compositions, number-average molecular weights and polydispersities of the homopolymer and block copolymers are summarized in Table S1.† The volume fractions of PMMA in the  $N_3$ -BCP ( $f_{MMA}$ ) were estimated by manipulating the integral ratios from the <sup>1</sup>H NMR spectra recorded in CD<sub>2</sub>Cl<sub>2</sub> and mass densities of two components (1.05 and 1.184 g cm<sup>-3</sup> for PS and PMMA, respectively), the values of which were controlled to obtain a cylindrical morphology.

The Pc-tethered (co)polymers were synthesized by treating  $N_3$ -PMMA or  $N_3$ -BCP with an excess of Pc derivative 1 in the presence of copper(1) iodide and diisopropylethylamine (DIPEA) in tetrahydrofuran (THF) as a solvent (Scheme 1). The course of



Scheme 1 Synthesis of Pc-PMMA and Pc-PMMA-b-PS (PcBCP), where Pc moiety is complexed with a zinc ion.



**Fig. 1** GPC profiles during the synthesis of **Pc-PMMA** by click chemistry monitored at 0 h (black solid lines) and after 48 hour (black dashed lines) with RI detector (a) and UV-vis detector at 400 nm (b). **Pc-PMMA** was obtained by reprecipitation in diethyl ether (red solid line).

the reaction was monitored by gel permeation chromatography (GPC) with a refractive index (RI) detector, along with UV-vis absorption detector at 400 nm, corresponding to the phthalocyanine Soret absorption band. The product was precipitated in diethyl ether to remove any catalyst or unreacted 1, giving the Pc-tethered polymers with unmodified polymers as green powders (Fig. 1 and S3<sup>†</sup>). The conversion of the reaction, or the rate of functionalization of the polymers by Pc estimated from the absorbance of the Q-band for the molecular absorption coefficient of Pc derivative 1 ( $\varepsilon = 41\ 000\ M^{-1}\ cm^{-1}$ ,  $\lambda = 608\ nm$ ), was 83% for Pc-PMMA, and 20-43% for Pc-PMMA-b-PS (PcBCP1-PcBCP3). The data of the Pc-tethered (co)polymers are summarized in Table 1. The relatively low degree of conversions of Pc functionalization of block copolymers with high molecular weights were probably due to the loss of terminal azide groups during the block extension with styrene.14b

#### Self-assembly behavior in solution

The Pc derivative **1** was readily soluble in THF, chloroform  $(CHCl_3)$ , dichloromethane  $(CH_2Cl_2)$ , or toluene. These solutions showed a typical spectrum for a zinc complex of a phthalocyanine with sharp peaks appeared in the visible region at 674 nm

(Q-band) and in UV region at 350 nm (Soret band), originating from a  $\pi$ - $\pi$ \* transition (Fig. 2a). In THF solution, **Pc-PMMA** showed a similar spectrum to that of 1 (Fig. 2b, black line). However, Pc-PMMA in CH<sub>2</sub>Cl<sub>2</sub> solution showed split absorption bands at 677 and 693 nm in the Q-band region (Fig. 2b, blue line). Such split bands are known to result from edge-to-edge interaction of Pc units.<sup>15</sup> On addition of pyridine to the CH<sub>2</sub>Cl<sub>2</sub> solution, the longer-wavelength band disappeared and a similar spectrum to that in THF was observed (Fig. 2b, red dashed line). The <sup>1</sup>H NMR spectrum of **Pc-PMMA** in CD<sub>2</sub>Cl<sub>2</sub> showed multiple signals at  $\delta = 6-10$  ppm and  $\delta = -3$  to 0 ppm in addition to large signals from PMMA. Upon the addition of a drop of THF- $d_8$  to the CD<sub>2</sub>Cl<sub>2</sub> solution, the signals in the downfield region were simplified and could be assigned to the Pc core protons, whereas signals in the upfield region were diminished (Fig. S4<sup>†</sup>). Considering that the non-equivalent signals were



Fig. 2 (a) Absorption spectra of phthalocyanine derivative 1 in THF (black line) and  $CH_2Cl_2$  (blue line). (b) Absorption spectra of Pc-PMMA in THF (black line),  $CH_2Cl_2$  (blue line) and  $CH_2Cl_2$ -pyridine (95 : 5 v/v) (dashed red line).

| Table 1         Pc-tethered polymers |  |  |                         |                  |                           |  |  |  |
|--------------------------------------|--|--|-------------------------|------------------|---------------------------|--|--|--|
| Entry                                | Polymer  | $M_{\mathrm{n}}^{a} (\mathrm{g}  \mathrm{mol}^{-1})$ | $M_{ m w}/M_{ m n}{}^a$ | $f_{ m MMA}{}^b$ | Pc yield <sup>c</sup> (%) |  |  |  |
| Pc-PMMA                              | Pc-PMMA  | 22 200   | 1.07                    | _                | 83                        |  |  |  |
| PcBCP1                               | Pc-PMMA <sub>220</sub> - <i>b</i> -PS <sub>553</sub> | 86 400   | 1.18                    | 0.27             | 20                        |  |  |  |
| PcBCP2                               | Pc-PMMA <sub>160</sub> - <i>b</i> -PS <sub>456</sub> | 65 500   | 1.12                    | 0.24             | 30                        |  |  |  |
| PcBCP3                               | Pc-PMMA <sub>107</sub> - <i>b</i> -PS <sub>200</sub> | 41 400   | 1.18                    | 0.33             | 43                        |  |  |  |

<sup>*a*</sup> Number-average molecular weight and polydispersity determined by GPC analysis with polystyrene standards. <sup>*b*</sup> Volume fraction of PMMA determined from <sup>1</sup>H NMR spectroscopy. <sup>*c*</sup> The conversion of click reaction estimated by absorption spectra.

diminished upon addition of a drop of coordinating solvent (THF-d<sub>8</sub>), axial coordination of the triazole ligand is most likely.<sup>16</sup> As shown in Fig. S5,<sup>†</sup> the triazole group formed in the click reaction can coordinate to a Zn center of a second Pc-PMMA macromolecule to form a dimeric structure, that exhibits split Q-bands in its absorption spectrum and multiple signals in its <sup>1</sup>H NMR spectrum as a result of ring-current effect from the neighboring Pc ring. In polar solvents, such as methanol, Pc-PMMA forms aggregates to show a blue shifted absorption spectrum (Fig. S6;† vide infra).

Similarly, Pc-PMMA-b-PS (PcBCP1-PcBCP3) showed split Qbands in non-coordinating solvents such as CH<sub>2</sub>Cl<sub>2</sub> or toluene, whereas the intensity of a shoulder peak at a longer wavelength decreased in coordinating solvents such as THF (Fig. S7<sup>†</sup>). These phenomena confirm that we had successfully synthesized Pc-tethered (co)polymers through formation of triazole rings via click chemistry.

#### Self-assembly behaviors in the solid states

When examined by differential scanning calorimetry (DSC), Pc derivative 1 exhibits an endothermic transition with a maximum at 103 °C in a second heating run at a scanning rate of 10 °C min<sup>-1</sup>. This corresponds to a transition from a crystalline phase into an LC mesophase (Fig. S8a<sup>†</sup>). During the second cooling run, the DSC profile also gives an exothermic transition at 54 °C originating from crystallization. This is a typical feature of *n*-alkoxyphthalocyanines with flexible alkyl chains, which form a major class of LC materials.17 The sample decomposed above 320 °C before forming an isotropic liquid; we could not therefore characterize the mesophase structure by temperature-controlled polarizing optical microscopy (POM). LC mesophase was investigated by means of small and wide angle X-ray scattering (SWAXS) at elevated temperatures using a SAXSess mc<sup>2</sup> instrument (Anton Paar GmbH, Graz, Austria). Above the transition temperature, a powder sample of 1 sealed in a glass capillary showed a set of scattering peaks with peak positions in the ratio  $1: \sqrt{3}: \sqrt{4}: \sqrt{7}$ ; this is characteristic of a hexagonal columnar mesophase (Col<sub>h</sub>) (Fig. 3a). The lattice parameter a was calculated to be 3.21 nm, a slightly smaller value than that of symmetric octakis(dodecyloxy)phthalocyanito

b)

80 °C

20°C

0.1

20

5 10 *q* (nm<sup>-1</sup>) 5

Pc-PMMA

PcBCP<sup>-</sup>

PcBCP3

1

 $q (nm^{-1})$ 



zinc (ArPc) (a = 3.42 nm) (Fig. S9<sup>†</sup>). In the wide angle region, a diffused halo was observed at about 4.3 Å, due to the molten alkyl chains (Fig. 3a, black arrow), whereas another peak corresponding to a face-to-face distance in the columnar mesophase appeared at around 3.4 Å (Fig. 3a, red arrow). The SWAXS profile at 20 °C showed diffuse peaks assignable to (001) through (004), suggesting the presence of a lamellar structure in the Pc crystal (Fig. 3a, black dots).

In its DSC profile, Pc-PMMA showed an endothermic transition at 115 °C characterized as the glass transition (devitrification) temperature  $(T_g)$  of PMMA (Fig. S8b<sup>+</sup>). Because of no transition characteristic of the LC-Pc was observed in Pc-PMMA, no large domain of LC-Pc phase is expected to exist inside the PMMA matrix. POM analysis and tapping-mode atomic force microscopy (AFM) measurements also provided no evidence of macroscopic phase segregation between LC-Pc domains and PMMA in the transparent green polymer film. On the other hand, SWAXS profiles of Pc-PMMA showed a diffuse scattering at q values of about 0.46 and 2.3  $\text{nm}^{-1}$ , corresponding to domain sizes of around 13.6 and 2.7 nm, respectively, which might indicate that the Pc end-groups form nano-size aggregates that are dispersed in the PMMA matrix (Fig. 3b). In the wide angle region, a large broad PMMA amorphous halo around 6.2 Å was dominant even at 120 °C; therefore, no LC mesophase was present in the bulk Pc-PMMA (Fig. S10<sup>†</sup>).

The DSC trace of PcBCP1 showed two endothermic transitions at 105 and 120 °C, corresponding to the  $T_{\rm g}$  values of PS and PMMA, respectively (Fig. S8b<sup>†</sup>). PcBCP3 also shows two endothermic transitions at slightly lower temperatures than PcBCP1 owing to its lower molecular weight. These results indicate that the polymer domains of Pc-PMMA and PS in Pc-PMMA-b-PS exhibit phase separation. Powdered PS-b-PMMA block copolymers (N<sub>3</sub>-BCP1-N<sub>3</sub>-BCP3) with various molecular weights did not show significant scattering peaks in SAXS measurements, probably because of the small difference in the electron densities of PS and PMMA (Fig. S11<sup>†</sup>). On the other hand, the Pc-tethered block copolymers PcBCP1-PcBCP3 showed significant peaks in the small angle region with q values of 0.18  $nm^{-1}$  for **PcBCP1**, 0.22  $nm^{-1}$  for **PcBCP2**, and 0.26  $nm^{-1}$ for PcBCP3 (Fig. 3b). PcBCP2 also shows a broad shoulder peak at a *q* value of 0.59, corresponding to  $\sqrt{7q}$ , tentatively suggesting that PcBCP2 forms a cylindrical morphology through microphase separation. On tethering of the Pc unit to the N<sub>3</sub>-BCP by click chemistry, the contrast in the electron density in the SAXS profile increased to show a significant primary scattering peak from microphase separation, although a lack of long-range order in the polymer powders was implied. In the wide angle region, large amorphous halos for PS and PMMA appeared at around 4–10 Å, which overlapped the expected peaks from assembled Pc end-group (Fig. S12<sup>†</sup>). We therefore investigated the Pc assembly by means of electronic absorption spectroscopy measurements.

#### Self-assembling behaviors in film states

The absorption spectrum of Pc derivative 1 drop cast on a quartz plate from toluene solution showed broad Q-bands at 630 nm

a)

Intensity (AU)

1

#### Paper

and 683 nm, along with a shoulder peak at 770 nm. The intensity of the shoulder peak decreased on heating the film to 110 °C, and a blue-shifted peak was observed at 625 nm (Fig. S13†). According to the molecular exciton theory, the shape of the spectrum in the Q-band region is the result of the interactions of two neighboring Pc units in a dimer; these interactions can be generalized into four types of dipole transitions in cofacial, in-line, coplanar or herringbone arrangements, respectively.<sup>15a,18</sup> At 20 °C, **1** showed a split Q-band, indicating a herringbone arrangement of the Pc molecules, typical of many crystalline Pcs. Upon heating at 110 °C, **1** formed Col<sub>h</sub> mesophase as mentioned above, resulting in a blue-shifted spectrum assigned to cofacial (or coplanar) aggregates (Fig. S13†).

To investigate the assembled structure of the Pc in polymer films, toluene solutions of the Pc-tethered (co)polymers were drop-cast on quartz plates and then annealed at above 150 °C for three hours. The UV-vis spectra of the transparent green film of Pc-PMMA shows similar characteristics to that of aggregated 1 at 110 °C, with a blue-shifted broad absorption band in the Qband region (Fig. S14<sup>†</sup>), which is also comparable to that of aggregated Pc-PMMA in MeOH solution mentioned above (Fig. S6<sup>†</sup>). Similarly, the film of PcBCP showed a broad blueshifted Q-band, revealing the presence of Pc stacking (Fig. 4a and S14<sup>†</sup>). The blue-shifted band at 630 nm was more apparent after sample annealing, suggesting that the Pc end-group in Pc-PMMA-*b*-PS also aggregates through  $\pi$ - $\pi$  interactions in the polymer film and that the formation of aggregates proceeds by softening of polymer matrix on annealing above  $T_{g}$  of PMMA and PS. It is noteworthy that  $\pi$ - $\pi$  interactions of Pcs are formed despite the low concentration of Pc molecules in a large volume of polymer matrix compared with Pc-PMMA.

To further discuss that Pc forms aggregates in the thin polymer films, we investigated the absorption spectra of films obtained from mixtures of 1 and  $N_3$ -BCP2 containing various concentrations of Pc. As shown in Fig. 4b, the  $N_3$ -BCP2 film containing 10 wt% of 1 showed a similar spectrum of that of 1 at room temperature, indicating that 1 forms a crystalline structure in the polymer blend. POM observations showed textures of Pc crystals at the edge of the film, showing that 1 is not fully miscible with the polymer at high concentrations (Fig. S15†). At the lowest concentration of 1 (0.01 wt%), the film showed a



Fig. 4 (a) Absorption spectra of PcBCP2 immediately after dropcasting on quartz plate from a toluene solution (dashed line) and after annealing at 150 °C for 3 h (solid line). (b) Absorption spectra of films of mixtures of 1 and N<sub>3</sub>-BCP2 containing various concentrations of 1.

sharp Q-band corresponding to the monomer structure of **1**. On the other hand, the transparent green polymer film containing 1.0 wt% of **1** showed a blue-shifted Q-band. This spectrum was quite similar to that of the Pc-tethered (co)polymers. Therefore, it is obvious that Pc end-groups in Pc-tethered (co)polymers aggregate through  $\pi$ - $\pi$  interactions inside the polymer films to form cofacial or coplanar aggregates.

#### Morphology of the block copolymers

With the expectation of observing Pc stacking in the PMMA microdomains inside the microphase-separated block copolymers, we focused on the film morphology of the PcBCPs by analyzing transmission electron microscopy (TEM) images. A 2 wt% toluene solution of the block copolymer was dropped on the surface of water, and part of the resulting polymer film was scooped onto a TEM grid and subsequently annealed at 150 °C for 3 h. The film on the grid was stained by exposure to RuO<sub>4</sub> vapor for 60 s before the measurements. This treatment selectively stains PS blocks and provides contrast in terms of electron density. Dark regions in the bright-field TEM images correspond to PS domains, whereas bright regions correspond to PMMA. As can be seen in Fig. 5, the TEM images of PcBCPs show the presence of phase-separated microdomains. For instance, the image of PcBCP1 shows white dots in a partially hexagonal alignment, characteristic of a cylindrical morphology with perpendicular alignment. The average domain spacing was estimated to be 37 nm. PcBCP2 and PcBCP3 also showed wormlike microdomains, assignable to planar-aligned cylindrical morphologies with average domain spacings of 32 and 28 nm for PcBCP2 and PcBCP3, respectively. These results show that the Pc moiety on the end of the block copolymer does not disturb microphase separation of the block copolymer. Briefly, the Pc units attached to PMMA are concentrated inside the PMMA cylinders in the PS matrix. More importantly, the domain size of the microstructure can be tuned by altering the size of the block copolymer, and therefore the distance between Pc aggregates inside the PMMA cylinder can be controlled by changing the molecular weights of the block copolymers.



Fig. 5 TEM images of thin films of PcBCPs: PcBCP1 (a), PcBCP2 (b) and PcBCP3 (c).

We confirmed the phase morphologies of the thin films of block copolymers by means of glazing incidence small-angle Xray scattering (GI-SAXS) measurements. Fig. 6a shows the inplane intensity profiles of the PcBCP films. Three scattering signals with values of  $1:\sqrt{4}:\sqrt{7}$  on the q-scale appeared in PcBCP1, indicating a hexagonally arranged structure, although no peak corresponding to  $\sqrt{3}$  was observable because of the high intensity of the first-order peak. Furthermore, neither a peak nor a Debye ring originating from parallel or randomly aligned microphase-separated cylinders. This result would indicate that PcBCP1 formed a cylindrical structure normal to the surface. The domain spacing of the hexagonal cylinder was estimated to be 41.2 nm. Similarly, the second-order peak was located at  $\sqrt{3q}$  relative to the first-order reflection in the case of PcBCP2; this can be tentatively assigned to a hexagonal cylinder microdomain morphology. On the other hand, because of the lack of long-range ordering of the block copolymer throughout the film, PcBCP3 showed only one discernible higher-order peak in the in-plane scattering. The assumption of a hexagonal cylindrical structure for PcBCP leads to a domain spacing of the cylinders of 33.5 nm for PcBCP2 and 31.9 nm for PcBCP3, showing a similar tendency to the results of the TEM measurements. Tapping-mode AFM images of the surface morphologies of the PcBCP films support the results from the GI-SAXS measurements. The AFM image of PcBCP2 showed the presence of hexagonally packed cylindrical microdomains normal to the substrates, whereas that of PcBCP3 was ambiguous in terms of showing phase separation (Fig. 6b). During



Fig. 6 (a) GI-SAXS in-plane peak-intensity profiles of PcBCPs. (b) AFM phase images of PcBCP2 and PcBCP3.

these studies, we had difficulty in controlling the morphology of **PcBCP3** compared with that of PMMA<sub>107</sub>-*b*-PS<sub>200</sub> with no terminal Pc (**N**<sub>3</sub>-**PB3**), indicating a strong influence of the Pc end-group on the morphology of **N**<sub>3</sub>-**BCP3**, owing to the small molecular weight of the block copolymer and high concentration of Pc in the PMMA cylinders. In other words, the balance between the two types of self-assembly, microphase separation of the blocks copolymer and noncovalent interactions of  $\pi$ -planes, might play an important role in controlling the morphology of **PcBCP3**.

#### Charge transporting property

The Pc assemblies formed inside the confined PMMA cylinders might provide a pathway for electronic transport. We therefore performed flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements<sup>19</sup> on PcBCP2, which has a cylindrical morphology with Pc assemblies inside PMMA cylinders (Fig. S16<sup>†</sup>). Table 2 summarizes the maximum transient photoconductivities ( $\varphi \sum \mu_{max}$ ) observed for **PcBCP2** and Pc-PMMA as well as for PcBCP2 doped with a Pc derivative (ArPc). The  $\varphi \sum \mu_{\text{max}}$  value for PcBCP2 (4 (±1) × 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) was comparatively same with that of **Pc-PMMA** (2  $(\pm 1) \times 10^{-6}$ cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) despite the much lower content of Pc in the polymer matrix. To enhance the conductivity, PcBCP2 can be used as a compatibilizer for Pc molecules and patterned block copolymers, because Pc tends to be inserted into the Pc endgroup of Pc-PMMA-*b*-PS through  $\pi$ - $\pi$  interactions, causing an increase in the Pc concentration inside the PMMA cylinders. Addition of ArPc to PcBCP2 in a 1 : 1 molar ratio gave the nearly double  $\varphi \sum \mu_{\text{max}}$  value of 1.0 (±0.5) × 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, although the increase is somewhat within the experimental error, due to the small  $\varphi \sum \mu_{\text{max}}$  value of the pristine **PcBCP2**. Meanwhile a clear four-fold improvement  $(4.1 \pm 0.8)$  was found for 10 : 1 ArPc-PcBCP2 (1.6  $(\pm 0.3) \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). In AFM measurements on polymer blends, the 10:1 blend showed ambiguous images, suggesting that microphase separation is partially disturbed by the addition of a large amount of ArPc (Fig. S17b<sup>†</sup>). On the other hand, the 1 : 1 blend showed a highly aligned hexagonal cylindrical morphology arising from microphase separation together with some kind of macrophase separation (Fig. S17a<sup>†</sup>). GISAXS profiles showed a first-order peak at a q value of 0.2 nm<sup>-1</sup> for the 1 : 1 blend film, whereas no clear scattering peak was obtained for the 10:1 blend film (Fig. S17<sup>†</sup>). These results imply that the appropriate amount of doped ArPc was introduced into the Pc-containing PMMA cylinder to increase the conductivity without disturbing the morphology of the block copolymer. The ordering of added ArPc in the cylinders is an important factor as well. A detailed

| Table 2 | Maximum transient photoconductivities ( $\varphi \sum \mu_{max}$ ) (cm | $^{2} V^{-}$ | <sup>1</sup> s <sup>-</sup> | ) of Pc-containing (co)polymers observed by FP-TRMC <sup>a</sup> |  |
|---------|--|--------------|-----------------------------|--|--|
|---------|--|--------------|-----------------------------|--|--|

| Pc-PMMA                     | PcBCP2                    | <b>ArPc</b> : <b>PcBCP2</b> = 1 : 1 | $\mathbf{ArPc}: \mathbf{PcBCP2} = 10:1$ |
|-----------------------------|---------------------------|-------------------------------------|---|
| $2 \ (\pm 1) 	imes 10^{-6}$ | $4~(\pm 1)\times 10^{-6}$ | $1.0~(\pm 0.5) 	imes 10^{-5}$       | $1.6~(\pm 0.3) 	imes 10^{-5}$           |

<sup>*a*</sup> Measured at 25 °C upon laser-pulse irradiation at 355 nm (photon density,  $9.1 \times 10^{15}$  photons per cm<sup>2</sup> per puls).

analysis of the use of **PcBCP2** and advanced engineering as a compatibilizer is currently underway toward further applications in optoelectronics.

## Conclusions

In conclusion, we prepared a series of novel Pc-tethered (co) polymers of PMMA and PMMA-*b*-PS using a combination of ATRP and click chemistry. The Pc end-groups on the polymer chains self-assembled through  $\pi$ - $\pi$  interactions inside the polymer films; nevertheless, the Pc-PMMA-*b*-PS showed microphase separation with domain spacings that depended on the molecular weights of the block copolymers. The design of a Pc-tethered block copolymer permits the concentration of semiconducting molecules inside confined columns and permits their self-assembly. These findings motivate us to utilize them in organic devices such as OFETs or OPVs.

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