

## Synthesis and Nanostructure of Phase-segregated Block Copolymer with Photo- and Electrochemically Active Perylenediimide Dyes toward Photovoltaics.

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**Abstract:** By applying phase segregated nano structures to the *p-n* molecular heterojunction system, novel amphiphilic block copolymers containing donor and acceptor moieties are designed to fabricate the large area contact effective for the photo-induced electron transfer and the independent carrier pathways for generated holes and electrons. In order to establish the synthetic method for donor-acceptor type diblock copolymers, the atom transfer radical polymerization (ATRP) of monomers possessing electron acceptor group was investigated. A diblock copolymer was synthesized by ATRP of methacrylate monomers tethered by Boc-protected alkylamine to afford a block copolymer with polydispersity of 1.38. After deprotection of Boc group, it was treated with perylenemonoimide to give an amphiphilic diblock copolymer possessing perylenediimide dyes in its side chains. The photochemical properties in chloroform solution as well as the surface morphology on a spin-coated film of the copolymer were explored.

**Keyword:** Amphiphilic diblock copolymer, Microphase separation, Atom transfer radical polymerization, *p-n* molecular heterojunction, perylenediimide dye

### Introduction

Various types of organic thin-layer photovoltaic cells have been extensively studied so far by the promise of low cost, tunable optical properties, flexibility, and large area coverage. Since the concept of photovoltaic devices based on interpenetrating blends of donors and acceptors by Heeger et al.,<sup>1</sup> considerable number of research have been devoted in this area, and Sariciftci et al. reported that the energy efficiency of 3.5% was attained by using poly(3-hexylthiophene) and C<sub>60</sub> blend system recently.<sup>2</sup>

There has been an increasing interest in the morphology of organic semiconductors<sup>3-5</sup> in film because of its strong influence on the performance of devices using these materials. Especially for electro optical applications like solar cells, an increase in the interface area between the electron and the hole transport material could enhance the performance since the interface is the active area for charge recombination or separation. In photovoltaic devices the light is absorbed by the dye, and the generated exciton (electron-hole pair) has to diffuse to the interface where they are separated. The exciton diffusion length is only in the order of a few nanometers, which is at least 10 times

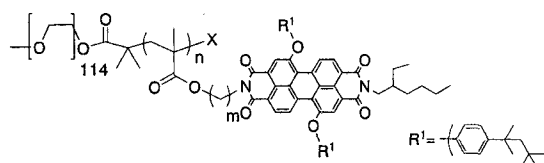
smaller than the optical absorption depth. This limits the efficiency for simple two-layer devices.<sup>6</sup> To overcome this problem, the active organic layer has to be structured on a nanometer scale.

The microphase separation can be realized using block copolymers. Synthetic attempts for obtaining functionalized block copolymers have been successfully tried out by Hadziioannou et al.<sup>7</sup> using *p*-phenylenevinylene and a partially fullerene functionalized block copolymer. However, the designed nanostructures with significant donor-acceptor interface and channels have never been confirmed in these polymer blend systems, so that the relationship between the nanostructures and photovoltaic efficiency are still unclear.

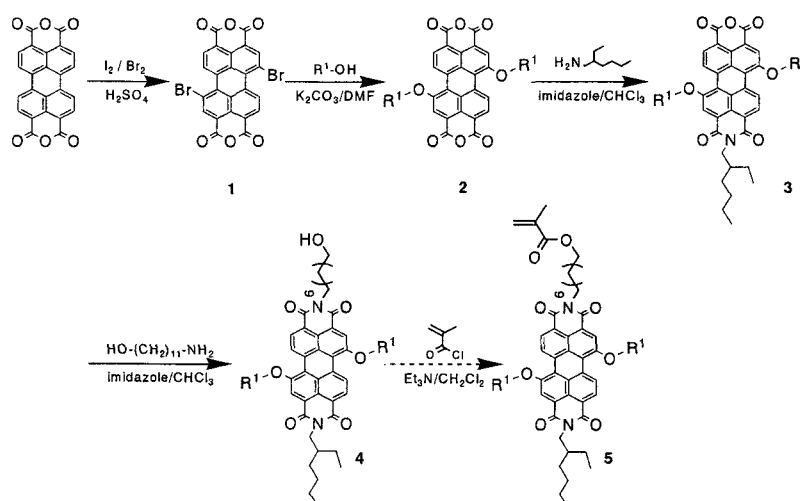
In order to investigate the relationship between the nanostructures and photovoltaic efficiency, it should be important to establish the synthetic method for donor-acceptor type diblock copolymers. In this work, we wish to report the synthesis of a functionalized block copolymer consist of photo- and electro active segment, perylenediimide as electron acceptor units.

### Experimental Section

**General.** <sup>1</sup>H NMR spectra were measured by using a JEOL EX270 spectrometer. Molecular weights of polymers were determined by gel permeation chromatography eluted by CHCl<sub>3</sub> on KF 801 and KF802 column (Shodex) according to polystyrene standards using a JASCO liquid



**Chart 1** Chemical structure of synthesized amphiphilic diblock copolymer tethered by perylenediimide **P3**



**Scheme 1** Synthesis of methacrylate monomer tethered by perylene-3,4,9,10-tetracarboxydiimide dye.

chromatography system equipped with 870-UV and RI-2031 Plus detectors. UV-vis absorption spectrum and fluorescence spectrum were measured with a Shimadzu UV-200 and a Jasco V-550 spectrometer, respectively. AFM observation was conducted by using Veeco nanoscope IV under tapping mode.

**Materials.** *t*-Butylacetate as the solvent for polymerization was purified by distillation from calcium hydride. All materials purchased commercially (Tokyo Kasei, Kanto Chemical Co. and Aldrich Co) without further purification. ATRP macroinitiator  $\alpha$ -methoxy-poly(ethylene oxide  $\omega$ -(2-bromo-2-methylpropionate) (PEO-BMP) was synthesized by determination of poly(ethylene oxide) monomethyl ether ( $M_n = 5000$ , Aldrich) according to the procedure reported previously. The ligand 1,1,4,7,10,10-hexamethyldiethylenetriamine (HMTETA, Aldrich) was used as received without further purification.

**2.2. 1,7-dibromoperylene-3,4,9,10-tetracarboxydiimide (1).** 3,4,9,10-perylene tetracarboxic acid anhydride (10.7 g, 27 mmol) was dissolved in 160 mL of concentrated sulfuric acid and stirred at 55 °C for 18 hours under  $N_2$  atmosphere. Iodine ( $2.3 \times 10^{-1}$  g, 10 mmol) was quickly added to reaction mixture and stirred for an additional 15 hours at 55 °C. Bromine (10 g, 63 mmol) was added dropwise to the reaction flask over 1 hour and stirred for 24 hours at 85 °C. Excess bromine was then displaced with  $N_2$  gas. Water (50 ml) was added dropwise to the cooled mixture and the precipitate filtered off and washed thoroughly with water (two times) to afford crude product (14.5 g, 96% yield). This product was used without further purification.

**1,7-bis(4-(*tert*-octyl)phenoxy)perylene-3,4,9,10-tetracarboxydiimide (2).** Compound 1 (3.7 g, 6.6 mmol), *tert*-octylphenol (5.5 g, 26 mmol), and potassium carbonate (1.85 g, 13.2 mmol) were dissolved in 250 ml of *N,N*-dimethylformamide and stirred for 4 hours at 80 °C

under nitrogen. Then the reaction mixture was added to 25 ml of acetic acid and cooled. The mixture was filtered, washed with cold methanol, and dried to give the product (4.2 g, 83% yield).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  9.64 (d,  $J = 8.4$  Hz, 1H), 8.62 (d,  $J = 8.4$  Hz, 1H), 8.29 (d,  $J = 8.4$  Hz, 1H), 7.49 (d,  $J = 6.8$ , 2H), 6.72 (d,  $J = 6.8$ , 2H), 1.33 (s, 12H), 0.75 (s, 18H).

***N*-(2-ethylhexyl)-1,7-bis(4-(*tert*-octyl)phenoxy)perylene-3,4-dicarboxyimide-9,10-dicarboxyanhydride (3)**

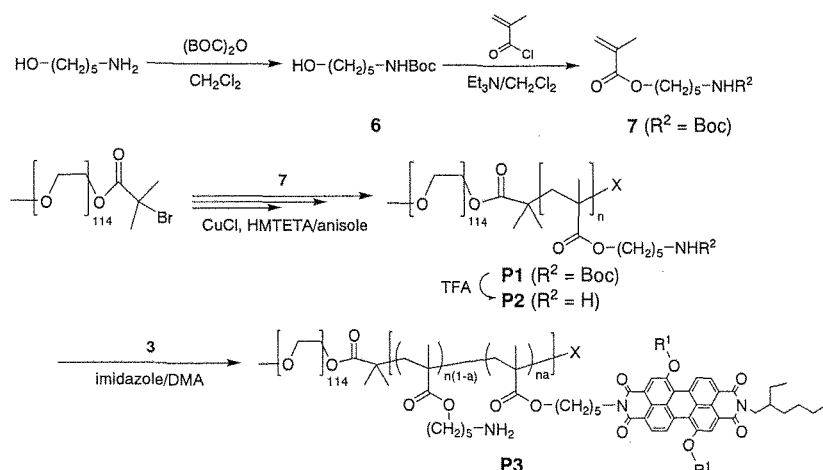
Compound 2 (2.5 g, 3 mmol) and imidazole (2.5 g, 36.5 mmol) were added to 250 ml of chloroform and

refluxed. 2-ethylhexylamine (0.4 g, 3.3 mmol) in 10 ml of  $CHCl_3$  was added to the solution, followed by 5 drops of trifluoroacetic acid. The reaction mixture was refluxed for 3 days. Then the reaction mixture was added to 80 ml of acetic acid and cooled. The solution was extracted three times with water, and dried over anhydrous  $K_2CO_3$ . The solvent was evaporated, and the residual solid was purified on silica gel chromatography using  $CHCl_3$  as the eluent to yield product (820 mg, 29% yield).  $^1H$  NMR:  $\delta$  ( $CDCl_3$ ): 9.61 (d,  $J = 8.4$  Hz, 1H), 8.60 (d,  $J = 8.4$  Hz, 1H), 8.34 (s, 1H), 7.49 (d,  $J = 6.8$  Hz, 2H), 7.09 (d,  $J = 6.8$  Hz, 2H), d : 5.26 (q,  $J = 7.2$  Hz, 2H), 2.19 (m, 2H), 1.92 (m, 2H), 1.80 (m, 2H), 1.59 (s, 18H), 0.84 (m, 6H); MS (FAB)  $m/z$  1063.

***N*-(2-ethylhexyl)-*N'*-(11-hydroxyundecyl)-1,7-bis(4-(*tert*-octyl)phenoxy)perylene-3,4,9,10-tetracarboxydiimide (4)**

Compound 3 (300 mg, 0.4 mmol) and imidazole (29 mg, 0.4 mmol) were added to 30 ml of *N,N*-dimethylacetamide (DMA) and refluxed. 11-amino-1-undecanol (673 mg, 4 mmol) in 10 ml of chloroform was added, followed by 5 drops of trifluoroacetic acid. The reaction mixture was refluxed for 20 h under Ar atmosphere. Chloroform was added and washed three times with water, and dried over anhydrous  $K_2CO_3$ . The solvent was evaporated and residue was purified on silica gel chromatography using  $CHCl_3$  as the eluent ( $R_f = 0.26$ ) to give product (290 mg, 75% yield).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  9.61 (d,  $J = 8.4$  Hz, 1H), 8.60 (d,  $J = 8.4$  Hz, 1H), 8.34 (s, 1H), 7.49 (d,  $J = 6.8$  Hz, 2H), 7.09 (d,  $J = 6.8$  Hz, 2H), 5.26 (q,  $J = 7.2$  Hz, 2H), 4.13 (q,  $J = 8.9$  Hz, 2H), 2.19 (m, 2H), 1.92 (m, 2H), 1.80 (m, 2H), 1.59 (s, 18H), 1.26 (m, 18H), 0.84 (m, 6H).

**5-(*N*-BOC amino)pentan-1-ol (6).** 5-Aminopentan-1-ol was dissolved in 50 ml of  $CH_2Cl_2$  di-*t*-butyl carbonate ((BOC) $_2$ O) was added dropwise to the flask over a hour with cooling at 0 °C. The reaction mixture was stirred at



**Scheme 2** Synthesis of amphiphilic diblock copolymer having perylenediimides dye as side chains.

room temperature for 18 hours. The solvent was removed under reduced pressure and dissolved in  $\text{CHCl}_3$ . Washed three times with  $\text{NaHCO}_3$ , water, Brine, then dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated to afford colorless liquid with quantitative yield.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.57 (s, 1H), 3.63 (q,  $J = 4.0$  Hz, 2H), 3.12 (q,  $J = 4.0$  Hz, 2H), 1.60 (m, 2H), 1.51 (m, 2H), 1.41 (m, 2H).

**(5-(BOC)aminopentyl)methacrylate (7)** To Compound **6** (0.4 g, 2 mmol) in THF, added methacryloyl chloride (0.25 g, 2.4 mmol) and triethylamine (0.3 g, 3 mmol) dropwise over a hour with cooling at  $0^\circ\text{C}$ . The reaction mixture was stirred for 18 hours at room temperature. The solvent was evaporated and the residue was dissolved in  $\text{CHCl}_3$ , washed three times with  $\text{NaHCO}_3$ , water, Brine, and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure to yield yellow liquid. (0.23 g, 67% yield)  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.01 (s, 1H), 5.48 (s, 1H), 4.43 (s, 1H), 4.06 (t,  $J = 6.5$  Hz, 2H), 3.04 (m,  $J = 6.6$  Hz, 2H), 1.62 (m,  $J = 7.1$  Hz, 2H), 1.51 (m,  $J = 6.6$  Hz, 2H), 1.37 (s, 9H), 1.35 (m,  $J = 3.7$  Hz, 2H).

**Polymerization of 7 (preparation of P1).** The polyethylene oxide initiator (PEO-BMP, 144 mg,  $28\ \mu\text{mol}$ ), compound **8** (500 mg, 2 mmol),  $\text{CuCl}$  (8.3 mg,  $84\ \mu\text{mol}$ ), HMTETA (19 mg,  $84\ \mu\text{mol}$ ) was dissolved in 2 ml of *t*-butyl acetate. The solution was degassed by three freeze-pump-thaw cycles and then sealed off. The mixture was stirred and heated at  $80^\circ\text{C}$  for 20 h. The copper complex was removed through silica gel column chromatography using chloroform as eluent. The obtained polymer was purified by reprecipitation from dichloromethane into hexane three times and dried under vacuum for 24 hours. (230 mg, 35% yield)

**Deprotection of P1 (preparation of P2).** To diblock copolymer (**P1**) (5 g, 24.5 mmol) in  $\text{CH}_2\text{Cl}_2$ , trifluoroacetic acid (TFA, 3.72 g, 36.7 mmol) was added and the reaction

mixture was stirred for 12 hours at room temperature. The solvent was removed under reduced pressure, and the residual product was used without further purification.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  4.17 (t,  $J = 7.2$  Hz, 2H), 3.11 (q,  $J = 7.2$  Hz, 2H), 1.93 (s, 6H), 1.60 (m, 2H), 1.51 (m, 2H), 1.41 (m, 2H).

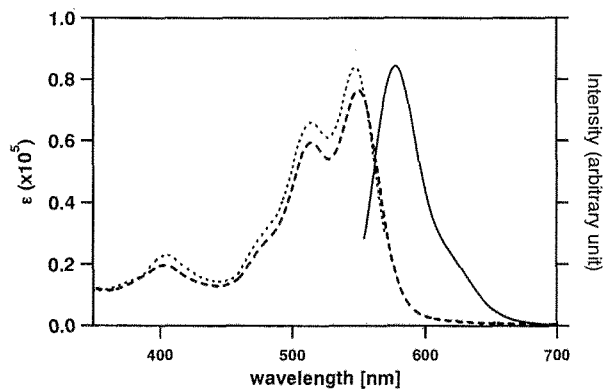
**Polymer reaction of P2 (preparation of P3).** Compound **3** (79 mg,  $86\ \mu\text{mol}$ ) and diblock copolymer (**P2**) (55 mg,  $6.7\ \mu\text{mol}$ ), imidazole (29 mg,  $0.4\ \text{mmol}$ ) were added to 30 ml of DMA.

The reaction mixture was refluxed for 20 h under Ar atmosphere. The solution was added to 1N HCl, and the organic layer was washed three times with water, and dried over anhydrous  $\text{K}_2\text{CO}_3$ . The solvent was evaporated to give the product.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  9.61 (d,  $J = 8.4$  Hz, 1H), 8.60 (d,  $J = 8.4$  Hz, 1H), 8.34 (s, 1H), 7.49 (d,  $J = 6.8$  Hz, 2H), 7.09 (d,  $J = 6.8$  Hz, 2H), 5.26 (q,  $J = 7.2$  Hz, 2H), 4.13 (q,  $J = 8.9$  Hz, 2H), 2.19 (m, 2H), 1.92 (m, 2H), 1.80 (m, 2H), 1.59 (s, 18H), 1.26 (m, 18H), 0.84 (m, 6H).

## Results and discussions

**Syntheses of amphiphilic diblock copolymer possessing perylenediimide as side chains.** Two types of synthetic routes were studied; One is the atom transfer radical polymerization (ATRP) of monomers which contain perylenediimide in their side chain (Scheme 1), and another is utilization of post-functionalization of a pre-polymer possessing aminoalkane with perylenemonoimide via polymer reaction (Scheme 2). The former procedure is considered to ensure the quantitative introduction of perylenediimide dyes to each methacrylate unit. But unfortunately, the synthesis of methacrylate monomer **5** was not succeeded because of the low solubility of compound **4** to such conventional solvents as THF, DMF,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . In this context, we adopted the latter synthetic route.

Since the free amino group should have unfavorable influences upon ATRP condition, the monomer having protected amino group with *t*-butoxycarbonyl (BOC) group was synthesized. This monomer could be polymerized by ATRP method with slightly large polydispersity ( $M_w/M_n$ ) of 1.38. The number averaged molecular weight ( $M_n$ ) was 13800 determined by NMR and/or GPC according to polystyrenes as standards. The  $M_n$  was also calculated as 8000 based on peak area ratio on  $^1\text{H NMR}$  spectrum.



**Figure 1** UV-vis spectrum in chloroform (dotted), fluorescence (full, excited at 548 nm) and excitation (dashed, emission at 576 nm) in chloroform solution of **P3**.

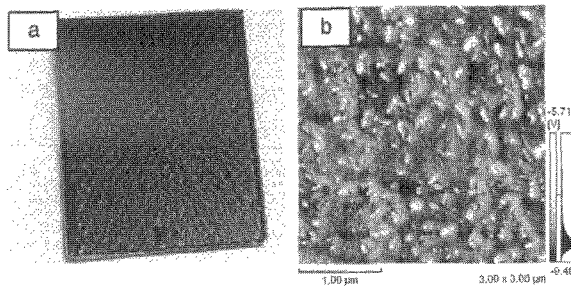
The BOC groups on obtained block copolymer were deprotected by treatment with TFA, and then perylenemonoimides **3** were introduced via polymer reaction to give randomly dye-introduced copolymer **P3**. The  $M_n$  was of 17100 determined by GPC analysis with polydispersity ( $M_w/M_n$ ) of 1.57. The number of perylenediimide introduced in the copolymer was calculated from  $^1\text{H}$  NMR spectrum to be 4.9 which 44% of amino group was exchanged for perylenediimide.

#### UV-vis and fluorescence spectra in solution.

Perylenediimide is known as one of the most efficient fluorescent molecules. In order to elucidate the photochemical properties, UV-vis and fluorescence spectra were measured in solution, as shown in Figure 1. The absorption spectra of the copolymer in chloroform ( $2 \times 10^{-6}$  M) showed a set of strong absorption band at 550 nm ( $\epsilon = 3.7 \times 10^5$ ) and 514 nm ( $\epsilon = 3.0 \times 10^5$ ), together with a weak band 402 nm ( $\epsilon = 9.9 \times 10^4$ ), which were assignable as typical absorption of perylenediimide moieties.

Upon excitation at 548 nm, the copolymer gave a strong orange fluorescence with the maximum of 576 nm in chloroform solution ( $10^{-6}$  M). The fact that excitation spectrum was almost completely overlapped on the absorption spectrum implies that the fluorescence emitted from a single component of excited perylenediimide.

The block copolymer **P3** was dissolved in chloroform as 2 wt% solution and spin-casted on Si wafer substrate. Unfortunately, no smooth polymer film was formed because of repelling on Si surface, as shown in Figure 2a. The observation of surface morphology on the film by AFM revealed the existence of randomly formed large crystall-like (hard) domains, as shown in Figure 2b. No ordered nanostructure could be formed as the result of the extremely hydrophobic nature, which is never miscible with hydrophilic PEO, and strong crystallinity (or aggregation nature through the stacking interaction) of perylenediimide segments.



**Figure 2** Picture of spin-coated film from chloroform solution of **P3** (a), and phase image of surface morphology observed by AFM (b).

#### Conclusion

A novel amphiphilic block copolymer possessing electron-acceptor perylenediimide in the side chain was synthesized by post-functionalization of block copolymer prepared via ATRP. This copolymer emitted strong orange fluorescence with a maximum of 576 nm upon excitation at 548 nm. But unfortunately, the formation of smooth surfaced film was failed because of the extreme hydrophobic and aggregation nature of perylenediimide groups. By reducing the number of perylenediimide unit, the miscibility with PEO domain is considered to be improved. Such a molecular design is under investigation.

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