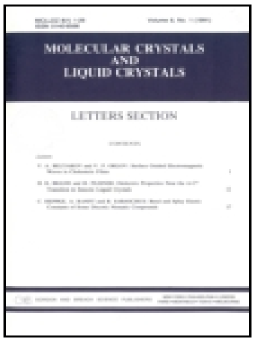

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Masahiro Kaneko, Nana Takayanagi, Toru Ube, Masa-Aki Haga & Tomiki Ikeda (2015) Nano Structures of Thin Films of Block Copolymers with Oligothiophene Side Chains, Molecular Crystals and Liquid Crystals, 617:1, 58-66, DOI: 10.1080/15421406.2015.1075823

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1075823

Mol. Cryst. Liq. Cryst., Vol. 617: pp. 58–66, 2015
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2015.1075823

Nano Structures of Thin Films of Block Copolymers with Oligothiophene Side Chains

MASAHIRO KANEKO,[1] NANA TAKAYANAGI,[1] TORU UBE,[2]
MASA-AKI HAGA,[1] AND TOMIKI IKEDA[2,*]

[1]Graduate School of Science and Engineering, Chuo University, Bunkyo-ku, Tokyo, Japan
[2]Research & Development Initiative, Chuo University, Bunkyo-ku, Tokyo, Japan

We synthesized polymers containing a liquid-crystalline (LC) oligothiophene moiety in the side chain. This oligothiophene shows LC behavior between 101°C and 194°C in its original form, while when incorporated into the side chains of a polymer, the resultant polymer showed a nematic phase in a much wider temperature range. Thin films of these polymers showed nano-phase-separated structures with domain sizes of 15–40 nm upon annealing.

Keywords Liquid-crystalline polymer; Oligothiophene; Photoalignment; Photovoltaic

Introduction

Organic photovoltaic (OPV) cells have attracted much attention due to their potential in low-cost solar energy harvesting, as well as applications in flexible, light-weight, colorful and large-area devices [1, 2]. Optimizing performance for the OPV cells necessitates precise control of thin film structures, and the use of molecular design to control polymer thin film morphology continues to be an active area of research [3–6]. To achieve high power conversion efficiency, the scale of the active layer microstructure should lie in the order of tens of nanometers [7], which provides the spatially distributed interfaces necessary for efficient charge separation of photogenerated excitons and direct pathways for collecting electron and holes [8]. Therefore precise control of the active layer structure and morphology is one of the most critical issues to obtain high-performance OPV cells [9].

A large number of research groups have investigated the self-assembly of organic molecules and polymers through various synthetic methodologies and one of the most common techniques employs block copolymers that can undergo self-assembly and offer control over nanoscale morphologies [10]. A block copolymer composed of poly(ethylene oxide) (PEO) and azobenzene methacrylate forms a cylindrical nano-phase-separated structure similar to an interpenetrating structure (Figure 1a) [11, 12]. In this paper, we aimed at improvement of the efficiency of organic solar cells by building interpenetrating structures utilizing a block copolymer containing a LC oligothiophene moiety in the side chain

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[*] Address correspondence to Tomiki Ikeda, Research & Development Initiative, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan. E-mail: tikeda@tamacc.chuo-u.ac.jp

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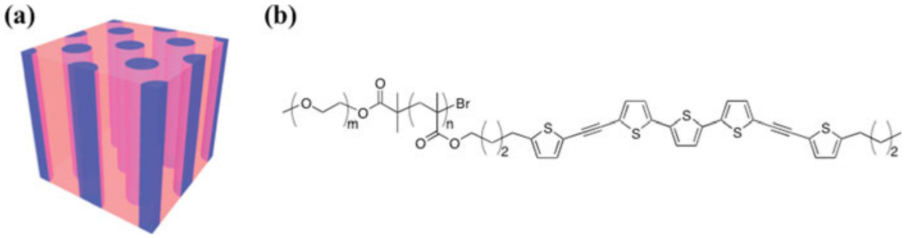


Figure 1. Schematic illustration of (a) a cylindrical nano-phase-separated structure and (**b**) chemical structure of PEO-*b*-PTR5MA.

(Figure 1b) [13], which is expected to form cylindrical nano-phase-separated structures if its structure is carefully optimized.

Experimental

Materials

All chemicals were purchased from Wako, TCI, Kanto Chemical, Nacalai Tesque and Aldrich, and used without further purification unless stated otherwise.

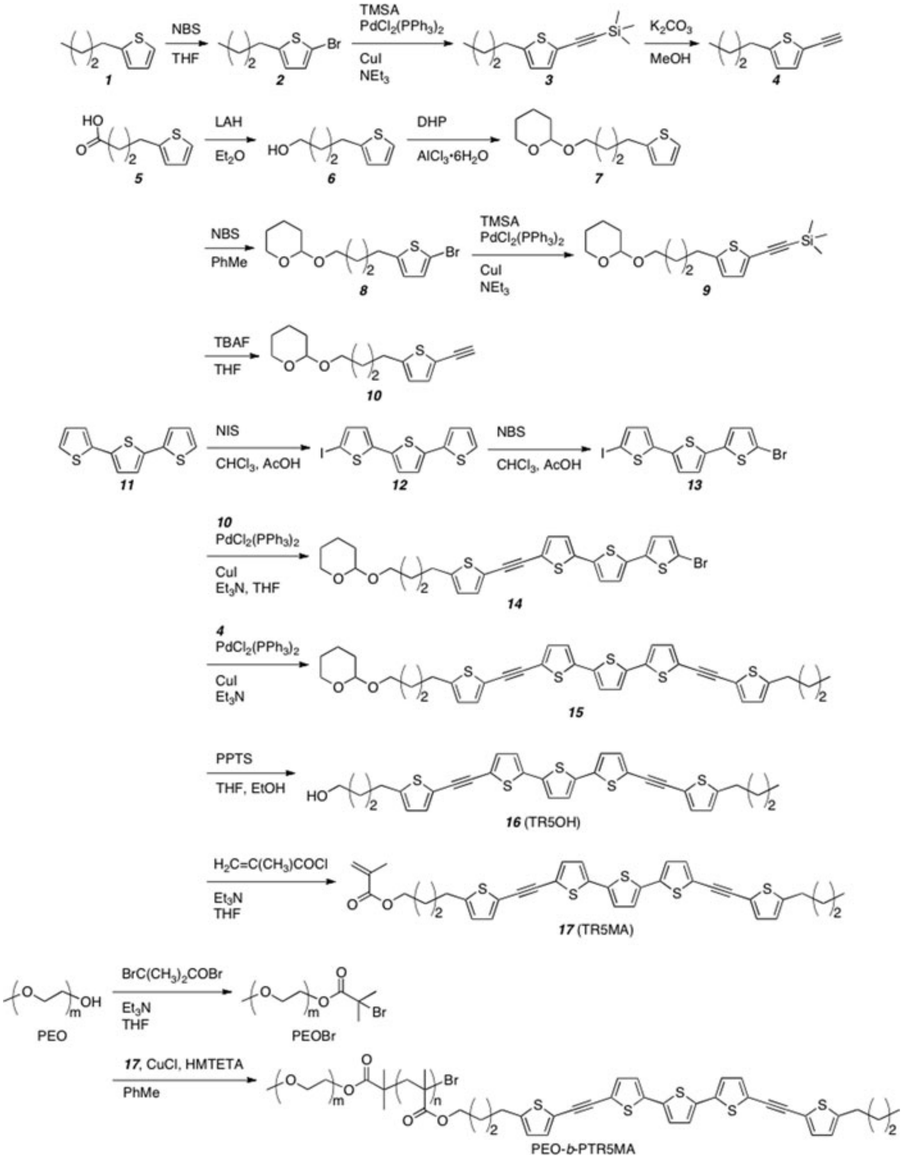
Scheme 1 shows the synthetic routes for monomer ***17*** (TR5MA) and a block copolymer (PEO-*b*-PTR5MA). 2-Butyl-5-ethynyl-thiophene (***4***), 2-thiophenebutanol (***6***) and PEO macroinitiator (PEOBr) were synthesized according to the previously reported methods [11, 13, 14]. The copolymer was synthesized by atom-transfer radical polymerization (ATRP) using an α-bromo ester of PEO composed of 150 monomer units as a macroinitiator.

Tetrahydro-2-[4-(2-thienyl)butoxy]-*2H*-pyran (*7*). A mixture of 2-thiophenebutanol (***6***, 2.00 g, 12.8 mmol), 3,4-dihydro-*2H*-pyran (DHP, 1.21 g, 14.3 mmol, 1.1 eq.) and $AlCl_3$•$6H_2O$ (33.1 mg, 0.137 mmol, 1 mol%) was placed in an eggplant flask. The mixture was stirred at 30°C for 3 h and then heated at 60°C for 5 h. The crude product was then purified by flash chromatography (silica gel, $CHCl_3$) to give ***7*** (pale yellow liquid; 2.88 g, 12.0 mmol, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.10 (d, 1H), 6.91 (t, 1H), 6.79 (d, 1H), 4.58 (t, 1H), 3.88–3.84 (m, 1H), 3.79–3.75 (m, 1H), 3.52–3.48 (m, 1H), 3.44–3.39 (m, 1H), 2.86 (t, 2H), 1.87–1.50 (m, 10H).

Tetrahydro-2-[4-(5-bromo-2-thienyl)butoxy]-*2H*-pyran (*8*). *N*-Bromosuccinimide (NBS, 2.14 g, 12.0 mmol, 1 eq.) was added to a solution of ***7*** (2.88 g, 12.0 mmol) in toluene (12 mL). The mixture was stirred under Ar at room temperature for 4 h. The reaction was quenched by the addition of water and washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$) to obtain ***8*** (reddish brown liquid; 3.33 g, 10.4 mmol, 87 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 6.84 (d, 1H), 6.54 (d, 1H), 4.57 (t, 1H), 3.88–3.83 (m, 1H), 3.78–3.74 (m, 1H), 3.52–3.48 (m, 1H), 3.42–3.38 (m, 1H), 2.79 (t, 2H), 1.85–1.51 (m, 10H).

Tetrahydro-2-[4-(5-[2-(trimethylsilyl)ethynyl]-2-thienyl)butoxy]-*2H*-pyran (*9*). ***8*** (3.33 g, 10.4 mmol), trimethylsilylacetylene (TMSA, 1.46 g, 14.8 mmol, 1.4 eq.) and trimethylamine (10 ml) were mixed together in an eggplant flask. Then Ar was bubbled for 15 min. The solution was added to a mixture of $PdCl_2(PPh_3)_2$ (221 mg, 0.316 mmol, 3 mol%) and CuI (70.7 mg, 0.371 mmol, 3.6 mol%) in a reaction flask and stirred under Ar at room temperature for 22 h. Then the reaction mixture was poured into distilled water and extracted with $CHCl_3$. The solution was dried using anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$) to obtain ***9*** (brown solid; 3.29 g, 9.79 mmol, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.04 (d, 1H), 6.62 (d, 1H), 4.57 (t, 1H), 3.87–3.83 (m, 1H), 3.78–3.73 (m, 1H), 3.52–3.48 (m, 1H), 3.42–3.37 (m, 1H), 2.80 (t, 2H), 1.85–1.51 (m, 10H) 0.23 (s, 9H).

Tetrahydro-2-[4-(5-ethynyl-2-thienyl)butoxy]-*2H*-pyran (*10*). Tetrabutylammonium fluoride (TBAF, 11.0 mL, 11.0 mmol, 1.1 eq.) was added dropwise to a solution



Scheme 1. Synthetic routes of PEO-b-PTR5MA.

of ***9*** (3.29 g, 9.79 mmol) in THF (60 mL) under Ar. The mixture was stirred at room temperature for 1 h. The solvent was evaporated under reduced pressure and washed with distilled water, and extracted with $CHCl_3$. The solution was dried using anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$) to give ***10*** (reddish brown liquid; 2.21 g, 8.34 mmol, 85 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.09 (d, 1H), 6.65 (d, 1H), 4.57 (t, 1H), 3.88–3.83 (m, 1H), 3.79–3.74 (m, 1H), 3.52–3.48 (m, 1H), 3.43–3.38 (m, 1H), 3.29 (s, 1H), 2.82 (t, 2H), 1.85–1.51 (m, 10H).

5-Iodo-2,2′:5′,2″-terthiophene (*12*). *N*-Iodosuccinimide (NIS, 1.08 g, 4.81 mmol, 1.2 eq.) was added to a solution of 2,2′:5′,2″-terthiophene (***11***, 1.00 g, 4.03 mmol) in $CHCl_3$/AcOH (1:1, 16 mL). The mixture was stirred under Ar at room temperature for 19 h. The reaction was quenched by the addition of water and washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The product obtained was recrystallized from $CHCl_3$/hexane to obtain ***12*** (yellow solid; 1.44 g, 3.86 mmol, 96 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.23 (dd, 1H), 7.17 (dd, 1H), 7.16 (d, 1H), 7.06 (d, 1H), 7.03 (d, 1H), 7.02 (d, 1H), 6.84 (d, 1H).

5-Bromo-5″-iodo-2,2′:5′,2″-terthiophene (*13*). Prepared similarly to ***12*** from ***12*** (2.62 g, 7.00 mmol) and NBS (1.25 g, 7.02 mmol, 1 eq.) in $CHCl_3$/AcOH (1:1, 28 mL). The product obtained was recrystallized from $CHCl_3$/hexane to obtain ***13*** (yellow needle crystal; 2.41 g, 5.33 mmol, 76 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.16 (d, 1H), 7.01–6.99 (m, 2H), 6.97 (d, 1H), 6.91 (d, 1H), 6.83 (d, 1H).

Tetrahydro-2-(4-{5-[2-(5″-bromo-2,2′:5′,2″-terthiophene)-5-ethynyl]-2-thienyl} butoxy)-*2H*-pyran (*14*). Prepared similarly to ***9*** from ***13*** (1.36 g, 3.01 mmol), $PdCl_2(PPh_3)_2$ (65.3 mg, 93.0 μmol, 3.1 mol%), CuI (21.6 mg, 0.113 mmol, 3.8 mol%), ***10*** (0.795 g, 3.01 mmol, 1 eq.) trimethylamine (90 ml) and THF (60 mL). The product obtained was purified by column chromatography (silica gel, CH_2Cl_2) to give ***14*** (orange solid; 0.929 g, 1.58 mmol, 52 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.14 (d, 1H), 7.10 (d, 1H), 7.07 (d, 1H), 7.05 (d, 1H), 7.01 (d, 1H), 6.98 (d, 1H), 6.92 (d, 1H), 6.70 (d, 1H), 4.58 (t, 1H), 3.88–3.84 (m, 1H), 3.80–3.75 (m, 1H), 3.53–3.49 (m, 1H), 3.44–3.40 (m, 1H), 2.85 (t, 2H), 1.85–1.51 (m, 10H).

Tetrahydro-2-(4-{5-[2-(5-{5″-[2-(5-butyl-2-thienyl)ethynyl]-2,2′:5′,2″-terthiophene}-yl)ethynyl]-2-thienyl}butoxy)-*2H*-pyran (*15*). Prepared similarly to ***9*** from ***14*** (0.901 g, 1.53 mmol), $PdCl_2(PPh_3)_2$ (37.4 mg, 53.3 μmol, 3.5 mol%), CuI (11.3 mg, 59.3 μmol, 3.9 mol%), ***4*** (0.374 g, 2.28 mmol, 1.5 eq.) and trimethylamine (90 ml). The product obtained was purified by column chromatography (silica gel, CH_2Cl_2) to obtain ***15*** (orange solid; 0.938 g, 1.39 mmol, 91 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.14 (dd, 2H), 7.11 (d, 2H), 7.01 (s, 2H), 7.06 (d, 2H), 6.70 (d, 1H), 6.68 (d, 1H), 4.58 (t, 1H), 3.89–3.84 (m, 1H), 3.80–3.75 (m, 1H), 3.53–3.49 (m, 1H), 3.44–3.40 (m, 1H), 2.85 (t, 2H), 2.81 (t, 2H), 1.86–1.50 (m, 12H), 0.94 (t, 3H).

5-[2-(5-{5″-[2-(5-Butyl-2-thienyl)ethynyl]-2,2′:5′,2″-terthiophene}-yl)ethynyl]-2-thiophenebutanol (*16*). Pyridinium *p*-toluenesulfonate (PPTS, 21.6 g, 86.0 μmol, 30 mol%) was added to a solution of ***15*** (0.211 g, 0.313 mmol) in THF/EtOH (1:1, 20 mL). The solvent was evaporated under reduced pressure and purified by column chromatography (silica gel, $CHCl_3$) to give ***16*** (orange solid; 180 mg, 0.306 mmol, 98 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.14 (dd, 2H), 7.11 (d, 2H), 7.10 (s, 2H), 7.06 (d, 2H), 6.70 (d, 1H), 6.68 (d, 1H), 3.68 (q, 2H), 2.85 (t, 2H), 2.81 (t, 2H), 1.81–1.75 (quint, 2H), 1.69–1.62 (m, 4H), 1.43–1.36 (sext, 2H), 0.94 (t, 3H).

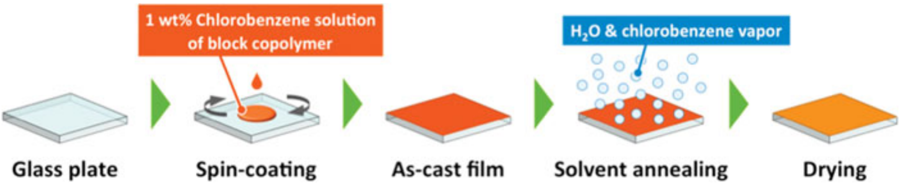


Figure 2. Schematic illustration of the preparation method.

4-{5-[2-(5-{5′′-[2-(5-Butyl-2-thienyl)ethynyl]-2,2′:5′,2′′-terthiophene}-yl) ethynyl]-2-thienyl}butyl Methacrylate (*17*). A THF (0.670 mL) solution of methacryloyl chloride (0.330 mL, 3.47 mmol, 20 eq.) was added dropwise to a solution of ***16*** (0.103 g, 0.174 mmol), hydroquinone (trace) and trimethylamine (0.480 mL, 3.45 mmol, 20 eq.) in THF (20 mL) at 0°C. The mixture was stirred at room temperature for 4 h and quenched by the addition of $NaHCO_3$aq. The solvent was evaporated under reduced pressure and washed with distilled water, extracted with $CHCl_3$. The solution was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$) to obtain ***17*** (orange solid; 97.2 mg, 0.148 mmol, 85 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 7.14 (dd, 2H), 7.11 (dd, 2H), 7.09 (s, 2H), 7.06 (d, 2H), 6.70 (d, 1H), 6.68 (d, 1H), 6.11 (s, 1H), 5.56 (s, 1H), 4.18 (t, 2H), 2.86 (t, 2H), 2.81 (t, 2H), 1.95 (s, 3H), 1.81–1.77 (m, 4H), 1.69–1.63 (quint, 2H), 1.44–1.36 (sext, 2H), 0.94 (t, 3H). FT-IR (ATR): ν/cm^{-1} = 3059, 2916, 2177, 1705, 1630, 1537, 1159, 931, 852, 779. MS (MALDI-TOF): *m*/z = 656 (M^+).

Block copolymer (PEO-*b*-PTR5MA). Cu(I)Cl (1.2 mg, 12.1 μmol, 4.8 eq.), PEOBr (15.2 mg, 2.50 μmol) and ***17*** (131.8 mg, 0.2 mmol, 80 eq.) were mixed in an eggplant flask, degassed and filled with Ar. HMTETA (3.4 μL, 12.5 μmol, 5 eq.) in toluene (0.5 mL) was added, and the mixture was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and placed in an oil bath preheated at 60°C for 24 h. Then the mixture was cooled at 0°C and washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The filtrate was precipitated into hexane. The copolymer was collected and dried. Yield: 37 mg. $M_{\mathrm{n,PEO}}$ (NMR) = 6,600, $M_{\mathrm{n,total}}$ (GPC) = 19,000, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.21. The block of the oligothiophene-containing poly(methacrylate) had a degree of polymerization of 48, which was estimated from the ^{1}H NMR spectrum shown in Figure 3.

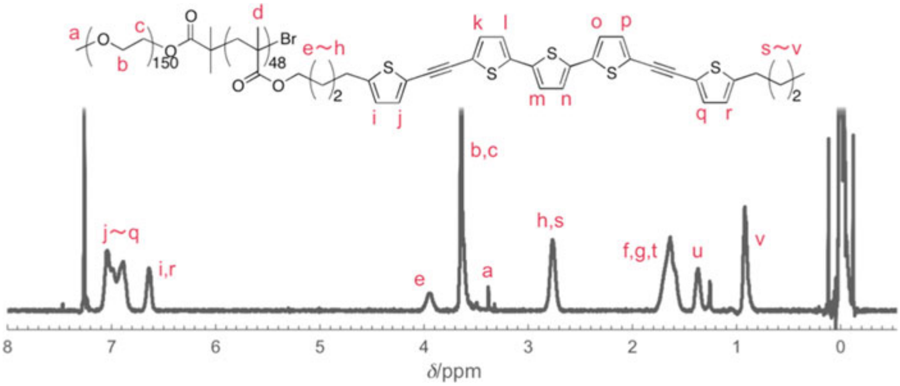


Figure 3. ^{1}H NMR spectrum of PEO-*b*-PTR5MA in $CDCl_3$.

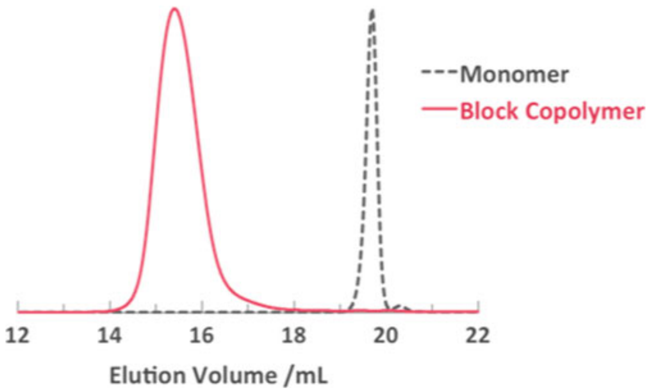


Figure 4. GPC curves of PEO-*b*-PTR5MA.

Measurements

NMR spectra were collected on a JNM-ECX500 spectrometer (JEOL) using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) (JASCO LC-2000Plus; elution solvent, THF; temperature, 40°C; flow rate, 1.0 mL/min). Polystyrenes were used as calibrating standards. LC behavior of the polymers was evaluated by polarizing optical microscopy (POM).

The block copolymer films with a thickness of about 100 nm were prepared by spin-coating (800 rpm for 100 s) its 1wt% chlorobenzene solution on glass substrates (Figure 2). Solvent annealing was performed by placing the samples in a petri dish containing water and chlorobenzene vapor with various exposure times. Finally, the samples were dried in a desiccator. The microphase separation in the block copolymer films was explored at room temperature with an atomic force microscope (5500 AFM, Agilent Technologies) in a tapping mode.

Results and Discussion

The structure of the PEO-*b*-PTR5MA block copolymer was examined by ^{1}H NMR. As shown in Figure 3, a signal assignable to PEO was observed at 3.7 ppm, which indicates that the oligothiophene monomer is successfully polymerized by the PEO macroinitiator. In addition, the number-average molecular weight of the polymer was M_n = 19,000 (48 oligothiophene monomer units) with the polydispersity index (M_w/M_n, PDI) of 1.21 as measured by GPC (Figure 4). Asaoka et al. reported that amphiphilic block copolymers consisting PEO and poly(methacrylate) with azobenzene derivatives in the side chain (PEO-*b*-PAzMAs) afford highly ordered nano-phase-separated structures, in which their PDIs were 1.07–1.36 [15]. PEO-*b*-PAzMAs exhibit hexagonally arranged dot patterns with a diameter of 3 nm over the whole surface as observed by AFM. Furthermore, SAXS revealed hexagonally arranged structures, assignable to PEO cylinders and PMA matrix domains. The nano-phase-separated structures depend on the molecular weight, the volume fraction of each segment and temperature. The M_ns of the PEO-*b*-PAzMAs were around 24,000, and the degree of polymerization (DP) of the PMA segment was around 54.

The oligothiophene shows LC behavior between 101°C and 194°C in its original form [13]. However, when it is incorporated into the side chains of a polymer, the resultant

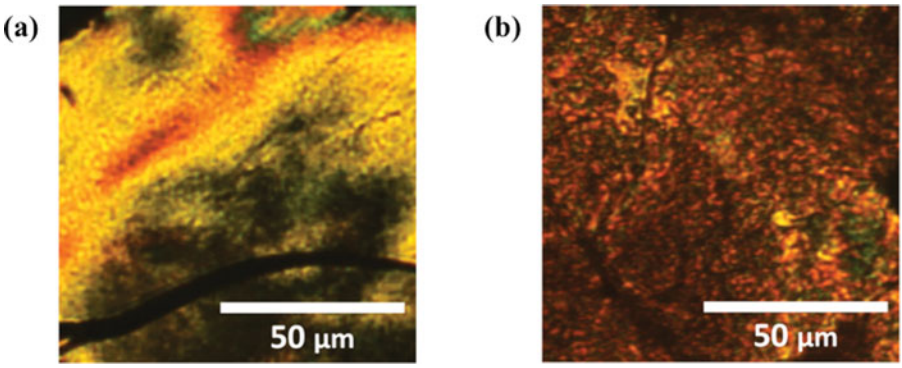


Figure 5. POM images of the block copolymer at (a) 25°C and (b) 200°C.

polymer showed a nematic phase between 25°C and 200°C (Figure 5). Yu et al. also examined if LC phases are stabilized by polymerization [14]. They found that a monomer, 11-(4-cyanobiphenyloxy)undecyl methacrylate (M11CB), showed a smectic LC phase only in a narrow temperature range of 70–79°C, while its block copolymer with PEO, PEO-*b*-PM11CB exhibited a smectic phase in a wide temperature range of 37–117°C .

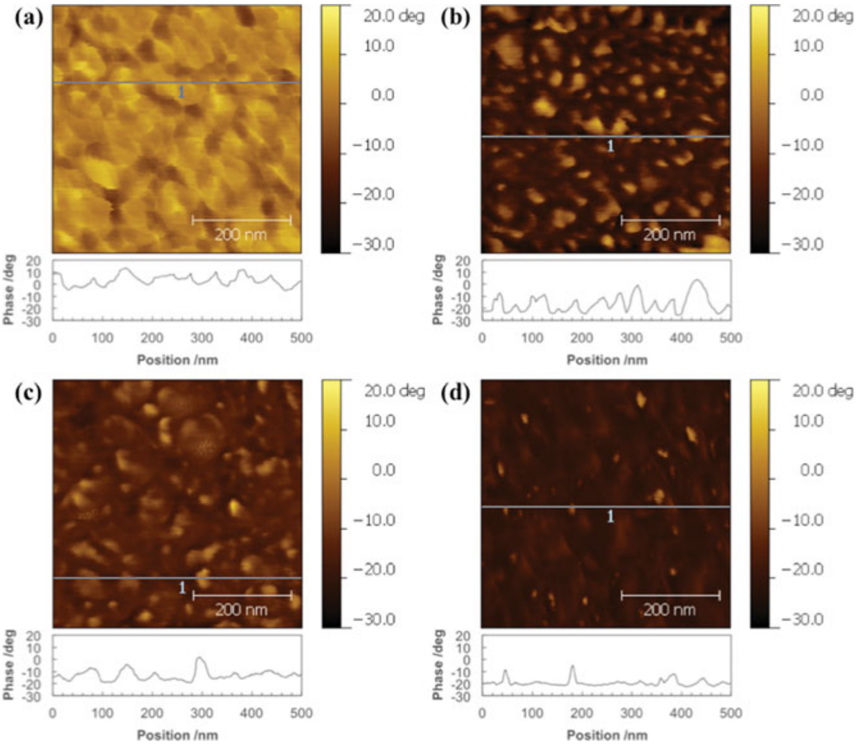


Figure 6. AFM phase images of PEO-*b*-PTR5MA thin films. (a) As-cast film; films after solvent annealing for (b) 3 days, (c) 6 days, and (d) 9 days.

Figure 6 shows the AFM phase images of the block copolymer thin film. The thin film showed bright and dark contrast more clearly after solvent annealing than the as-cast film. It is assumed that the bright and dark areas are oligothiophene moieties and PEO segments, respectively [12]. The thin film showed nano-phase-separated structures by solvent annealing, of which domain sizes are between 15 nm and 40 nm. In addition, the longer exposure time of solvent annealing, the smaller was observed the bright areas. These results suggest that the PEO component is segregated to the surface of the film after prolonged exposure to the vapor. In block copolymers containing PEO and poly(3-hexylthiophene), PEO-*b*-P3HT with $M_{\mathrm{n,PEO}}/M_{\mathrm{n,P3HT}} = 2/9\text{–}4/5$, nanofibrillar morphology has been observed by AFM, with fibril widths of 20–40 nm [16–18]. Other studies also have shown that polylactide-*b*-poly(3-alkylthiophene) (PLA-*b*-P3AT; $M_{\mathrm{n,PLA}}/M_{\mathrm{n,P3AT}} = 1/3\text{–}4/5$) exhibits a hexagonally packed structure of PLA nanocylinders [19–21]. These results suggest that the block copolymer used in this study, PEO-*b*-PTR5MA, could show well-defined nano phase separation if its structure is carefully controlled as the composition, $M_{\mathrm{n,PEO}}/M_{\mathrm{n,PTR5MA}} \sim 1/2$, is very similar to those reported previously.

Conclusion

We synthesized block copolymers containing PEO blocks and oligothiophene side chains, which showed a LC phase in a much wider temperature range than the oligothiophene. Moreover, the block copolymer thin films exhibited nano-phase-separated structures after solvent annealing.

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