ATRP Synthesis of Oligofluorene-Based Liquid Crystalline Conjugated Block Copolymers

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ABSTRACT: A series of well-defined conjugated-liquid crystalline (LC) block copolymers containing oligofluorene and side-chain liquid crystalline polymers with cyanobiphenyl moieties were successfully synthesized by atom transfer radical polymerization. The block copolymers were prepared with number-averaged molecular weights (M_n) ranging from 8000 to 16 000 and narrow molecular weight distribution less than 1.20. The chemical structures of these block copolymers were confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR studies. All of the block copolymers exhibited the smectic mesophase as illustrated by differential scanning calorimetry, polarized optical microscopy, and wide-angle X-ray diffraction. A bilayer structure of mesogens was formed in the smectic layer of block copolymers with a thickness of 3.5 nm. The isotropization of the smectic phase increased with the molecular weight and leveled off at $M_n = 14\,000$. The optical properties of these block copolymers in solution and solid-films were investigated comparatively by UV spectroscopy, photoluminescence, and photoluminescent excitation characterization. The results suggest that energy transfer from the LC mesogens to the conjugated oligomer occurs both in dilute solution and in the solid state, which was more efficient in solid state due to higher local chromophore density.

Introduction

Block copolymers with functional groups have been extensively investigated in the past decades due to their potential applications in industry.[1] On account of the microphase separation of block copolymers, the domain-selective functionalities could be achieved in these functional block copolymers.[2] For example, pendant mesogenic groups have been attached to block copolymers to obtain side chain liquid crystalline (LC) block copolymers for applications in the optical data storage, nonlinear optics and display.[3] A variety of side chain LC block copolymers have been proposed and much research effort has been devoted to elucidating the relationship between the block copolymer structures and their physical properties.[4] However, most of the LC block copolymers are based on flexible segments, i.e., LC−coil block copolymers, while conjugated-LC block copolymers, which can also be viewed as a subclass of rod−coil block copolymers,[5] have rarely been studied.

Conjugated-LC block copolymers also provide a novel class of optoelectronic block copolymers opening a new route to design optoelectronic materials with liquid crystalline properties. Liquid crystalline conjugated polymers are likely to stimulate technological innovations in the development of novel electronic and photonic devices such as light-emitting diodes, field effect transistors, photovoltaic cells, and plastic lasers.[6,7] Compared to direct incorporation of mesogenic molecules onto a conjugated polymer backbone as pendant groups, which has been reported previously,[8,9] the block copolymer approach is expected to achieve the control of self-assembly of optoelectronic materials by the anisotropic aggregation of mesogenic groups for each block within nanoscales, which is critical to optimal device performance.[10]

Recently, we have designed and synthesized a series of polyfluorene-based conjugated-coil multifunctional block copolymers.[11] Polyfluorenes and their derivatives are the most promising blue-light emitting polymers due to their excellent chemical, thermal, processing and emission properties.[12] However, to systematically investigate the structure−property relationship of a rod−coil block copolymer, oligofluorenes would be superior to their polymeric counterparts due to the well-defined conjugation length and absence of chain defects.[13] In addition, poly(6-((4-cyano-4′-biphenyl)oxy)hexyl methacrylate) (PCBHMA) is well-known as a LC polymer that has been used as a building block in many block copolymer systems.[14] The combination of oligofluorene and PCBHMA serves as a model system to investigate such an unexplored class of optoelectronic block copolymers.

In this paper, we reports on the first use of a conjugated segment with luminescent properties to replace the coiled block thus forming conjugated-LC multifunctional block copolymers. The chemical structure of the target block copolymer is shown in Scheme 2. It was synthesized by atom transfer radical polymerization (ATRP) initiated by oligofluorene macroinitiator. We also investigated the liquid crystalline and light-emitting properties of the block copolymers and studied the energy transfer between oligofluorene and biphenyl chromophores.

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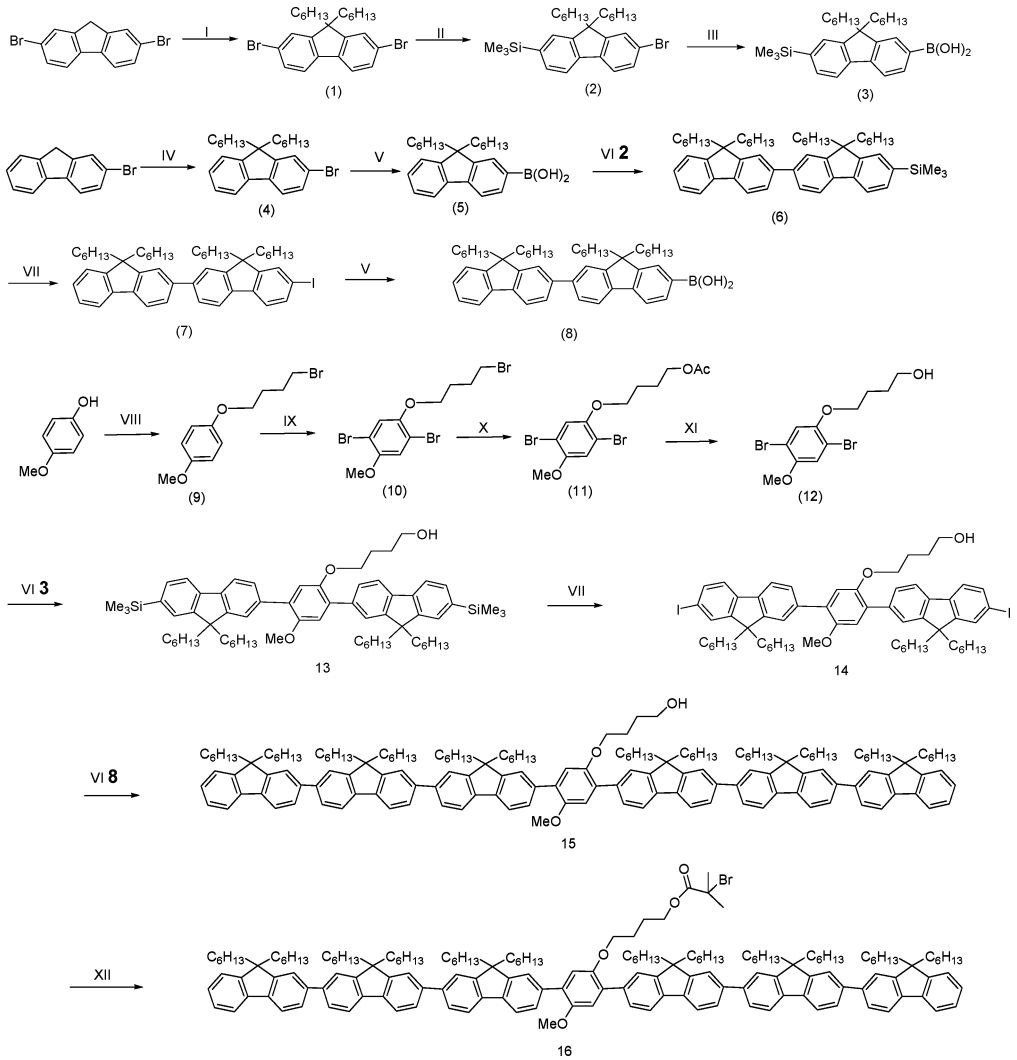
Scheme 1. Synthesis of the OFB Macroinitiator[a]



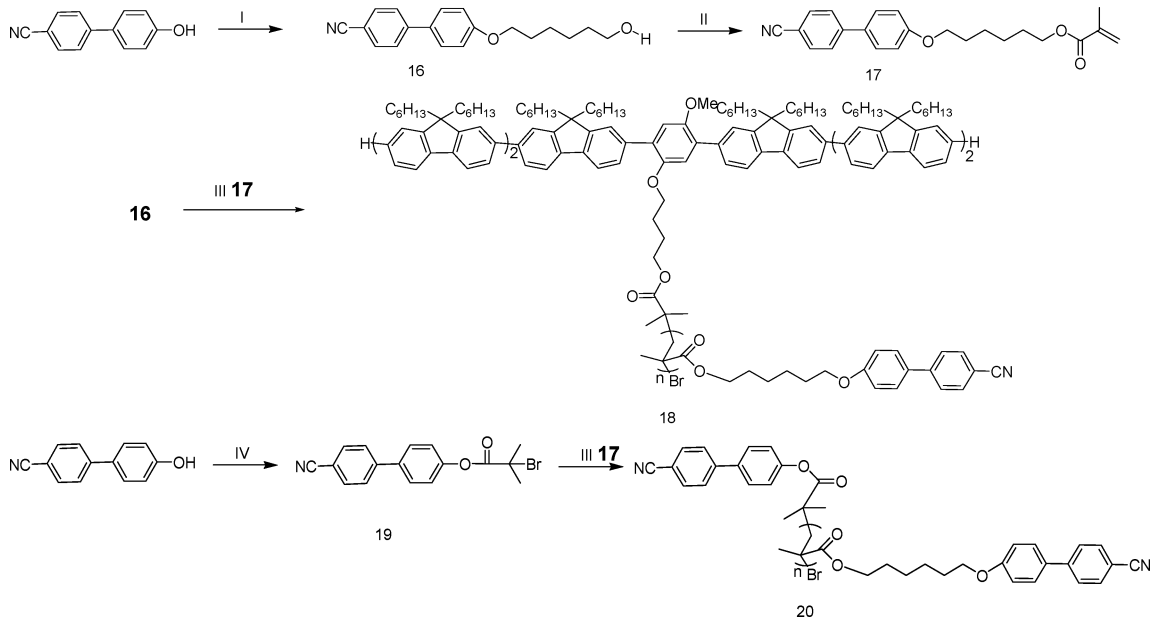
[a] Key: (I) DMSO, NaOH (w/w, 50%), 1-bromohexane, room temperature; (II) (1) *n*-BuLi, −78 °C (2) $ClSiMe_3$, −78 °C to room temperature; (3) H_2O; (III) (1) *n*-BuLi, −78 °C; (2) $(i\text{-}PrO)_3B$, −78 °C to room temperature; (IV) DMSO, NaOH (w/w, 50%), 1-bromohexane, 70 °C; (V) (1) *n*-BuLi, −78 °C; $(MeO)_3B$, −78 °C to room temperature; (3) H_3O^+; (VI) $Pd(PPh_3)_4$, Na_2CO_3(2 M aqueous), 90 °C. (VII) ICl, 0 °C; (VIII) 1.4-dibromobutane, KOH, 90 °C; (IX) Br_2 (3 M in chloroform), room temperature; (X) KAc, 70 °C; (XI) $Pd(PPh_3)_4$, Na_2CO_3 (2 M aqueous), 90 °C; (2) KOH, room temperature; (XII) 2-bromoisobutyryl bromide, $N(CH_2CH_3)_3$, 0 °C.

Results and Discussion

Synthesis of Functionalized Macroinitiator and its Block Copolymers. The general synthetic routes toward the oligofluorene macroinitiator and the block copolymers are outlined in Schemes 1 and 2, respectively. The ATRP initiator, modified phenylene group, was built into the oligofluorene structure through a convergent way to obtain the OFB (oligofluorene with benzene) macroinitiator. The resulted "T"-shaped block copolymers is a new type of rod−coil block copolymers, which may show unique morphologies. Suzuki coupling reaction was employed to prepare the OFB, which is a very efficient and convenient way to synthesize fluorene-based conjugated molecules.[15] The trimethylsilyl groups were used as dormant iodides to make Suzuki coupling reactions unitary as well as the easiness of purification.[16] To obtain the final oligomer, the coupling reaction of **8** and **14** was performed as the last step to circumvent the synthesis of fluorene trimer intermediates, which is more troublesome to purify.[17] At last, 2-bromoisobutyrate, which is versatile for ATRP of many vinyl monomers,[18] was successfully coupled to the oligomer to obtain the OFB macroinitiator. The OFB macroinitiator was verified by its matrix-assisted laser desorption ionization−time-of-flight mass spectrum (MALDI−TOF MS), and the mass of the major peak (m/z = 2341) matched the expected value of the OFB structure (see Supporting Information).

To study the dependence of the physical properties of block copolymers on different molecular weight of the PCBHMA block, five block copolymers, **P1**−**P5** (See Table 1), were synthesized by ATRP by using OFB macroinitiator and by following the procedures described in our previous work.[11] To achieve desired polymerization degree, the initial monomer/initiator molar ratio ($[M]_0/[I]_0$) was increased from 10 to 50 with a stepwise increment of 10 (illustrated as **P1**−**P5**). On the other hand, the initiator concentration was lowered from 0.09 mol/L for **P1** to 0.036 mol/L for **P5**, maintaining a comparable polymerization rate. The reactions were quenched using liquid nitrogen at about 90% monomer conversion monitored by ^1H NMR. The monomer conversion was calculated by comparing the relative integrations of the peaks at 7.0 and 6.9 ppm ascribed to the monomer and polymer, respectively. The relative molecular weights and polydispersity of the block copolymers were determined by gel permeation chromatography (GPC). Figure 1 shows the GPC profiles of the block copolymers and OFB macroinitiator. It can be seen that the GPC curves steadily shift

Scheme 2. Synthesis of the OFB−PCBHMA Block Copolymers and PCBHMA Homopolymer[a]



[a] Key: (I) 6-bromo-1-hexanol, K_2CO_3, 60 °C; (II) DCC, DMAP, room temperature; (III) HMTETA, CuBr, 60 °C; (IV) 2-bromoisobutyryl bromide, $N(CH_2CH_3)_3$, 0 °C.

Table 1. ATRP Results of OFB−PCBHMA Block Copolymers and PCBHMA Homopolymer[a]

polymer	time (min)	I/solvent (mol/L)	M/solvent (mol/L)	$[M]_0/[I]_0$	conv (%)[b]	M_n(theor)[c]	M_n(NMR)[d]	M_n(GPC)	M_w/M_n
P1	30	0.090	0.9	10	85	5500	7800	10 100	1.12
P2	60	0.070	1.4	20	85	8600	9200	12 300	1.18
P3	100	0.047	1.4	30	90	12 200	11 400	14 600	1.16
P4	120	0.045	1.8	40	90	15 600	13 600	17 100	1.20
P5	150	0.036	1.8	50	95	19 400	15 800	21 200	1.16
homo	180	0.027	2.7	100	70	25 400		21 000	1.32

[a] [HMTETA]:[CuBr]:[I] = 1:1:1. All the reactions were conducted at 60 °C. [b]The conversion was determined by comparing the relative integration areas of the peaks at 7.0 and 6.9 ppm in the ^{1}H NMR spectra, for the biphenyl protons of monomers and polymers, respectively. [c] The theoretical molecular weight was calculated by the conversion rate of the monomer. [d] The molecular weight was determined by the relative integrations of the phenyl protons of the biphenyl moieties at 6.9 ppm ($I_{6.9}$) ("m" in Figure 3B) to that of the OFB initiator at 7.2 ppm ($I_{7.2}$) ("a" and "b" in Figure 3B).

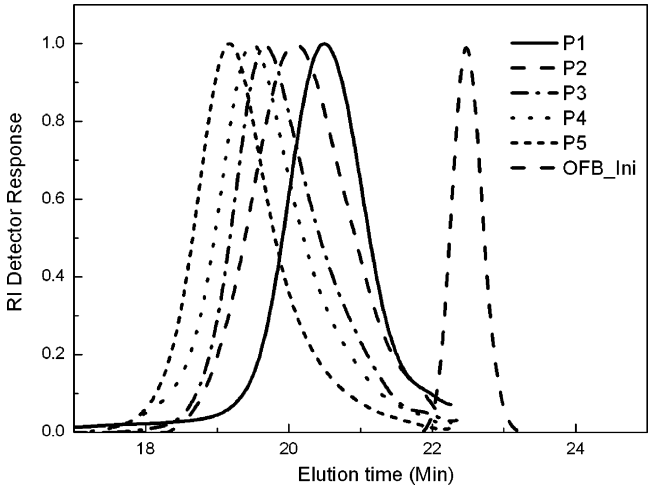


Figure 1. GPC traces of the OFB macroinitiator and the OFB−PCBHMA block copolymers.

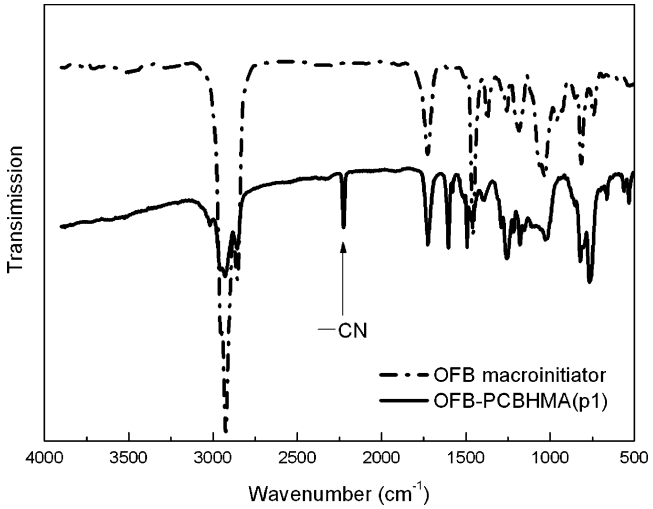


Figure 2. FTIR spectra of the OFB−PCBHMA block copolymer (sample: **P1**) (solid line) and the OFB macroinitiator (dashed line).

to high molecular weights from **P1** to **P5** with the typical polydispersity being below 1.2. The detector responses corresponding to the OFB macroinitiator residues are negligibly weak. Therefore, the macroinitiator has been successfully incorporated into the block structure, and a well-controlled polymerization has been achieved.

Structural Characterization. The chemical structure of the OFB macroinitiator and the block copolymers were confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopy. In Figure 2, the FTIR spectra of the OFB−PCBHMA block copolymer (sample: **P1**) shows characteristic bands of biphenyl mesogens at 1607 cm^{-1} and cyano groups at 2230 cm^{-1} in comparison with the OFB macroinitiator. The ^{1}H NMR and ^{13}C NMR spectra of the OFB macroinitiator and the OFB−PCBHMA block copolymer (sample: **P1**) are presented in Figures 3 and 4, respectively. The resonances of those protons and carbons from the OFB segments of the block copolymers are almost

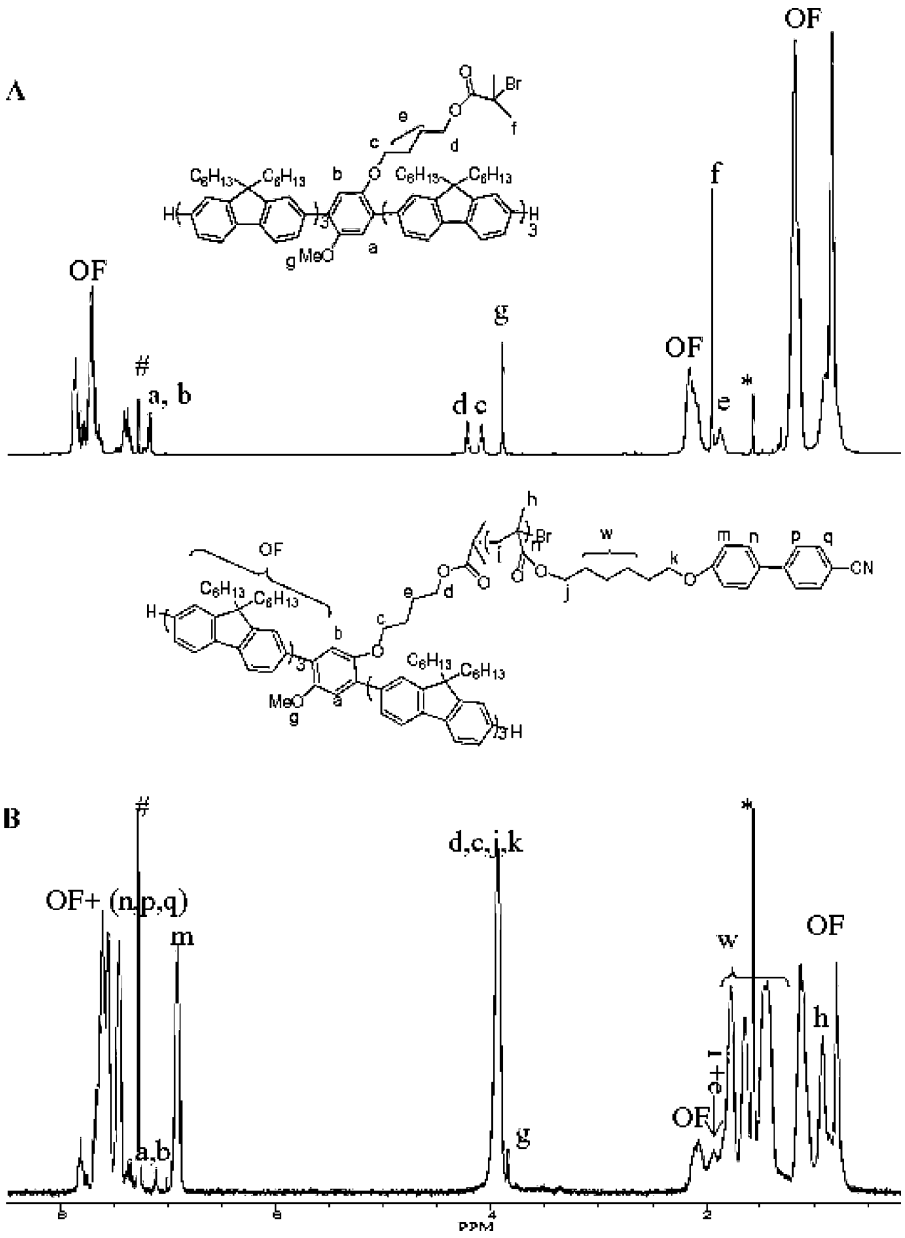


Figure 3. ^{1}H NMR spectra of the OFB macroinitiator (A) and the OFB−PCBHMA block copolymer (sample: **P1**) (B) in $CDCl_3$. ((∗) H_2O; (#) $CHCl_3$; (OF) oligofluorene (fluorene trimer)).

identical to those from the OFB macroinitiator, which indicates the successful integration of the OFB structure into the block copolymers. The disappearance of the resonance at $\delta = 1.91$ ppm (proton f in Figure 3A), which has been assigned to the $-C(C\boldsymbol{H}_3)_2Br$, further demonstrates that the OFB is a good initiator for the ATRP of CBHMA. This observation is also verified by ^{13}C NMR characterization. The peaks at 30.8 and 55.8 ppm (carbons f and y in Figure 4A), which are assigned to the $-C(=O)C(\boldsymbol{C}H_3)_2Br$ and $-C(=O)\boldsymbol{C}(CH_3)_2Br$ respectively, also disappear as shown in Figure 4B due to the local changes of the chemical environment after the polymerization. The results strongly demonstrate the successful polymerization of the 6-((4-cyano-4′-biphenyl)oxy)hexyl methacrylate with the OFB macroinitiator. In addition, the relative compositions of PCBHMA to OFB block in the block copolymers were estimated from the integration of the phenyl protons of the biphenyl moieties at 6.9 ppm ($I_{6.9}$) (proton m in Figure 3B) to that of the phenyl protons of the OFB macroinitiator at 7.2 ppm ($I_{7.2}$) (proton a and b in Figure 3B). The molecular weight can thus be calculated based on ^{1}H NMR spectra (M_n(NMR)) using eq 1 which has been summarized in Table 1.

$$M_n(\text{NMR}) = 2340 + (I_{6.9}/I_{7.2}) \times 363 \qquad (1)$$

in which 2340 and 363 are the molecular weights of the OFB macroinitiator and the ATRP monomer, respectively.

Thermotropic Phase Behavior and Structure of Mesophase. The thermotropic phase behavior of the block copolymers was investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). DSC thermographs of the block copolymers for the (first) cooling and (second) heating scans are shown in Figure 5. In the heating curves (Figure 5B), all of the block copolymers show an endothermic peak, which is assigned to the smectic A (SmA) → isotropic (I) phase transition. The well-defined SmA → I phase transition is relatively narrow, probably due to the low polydisperisity. The transition temperatures of these block copolymers are determined by the peak temperatures of the

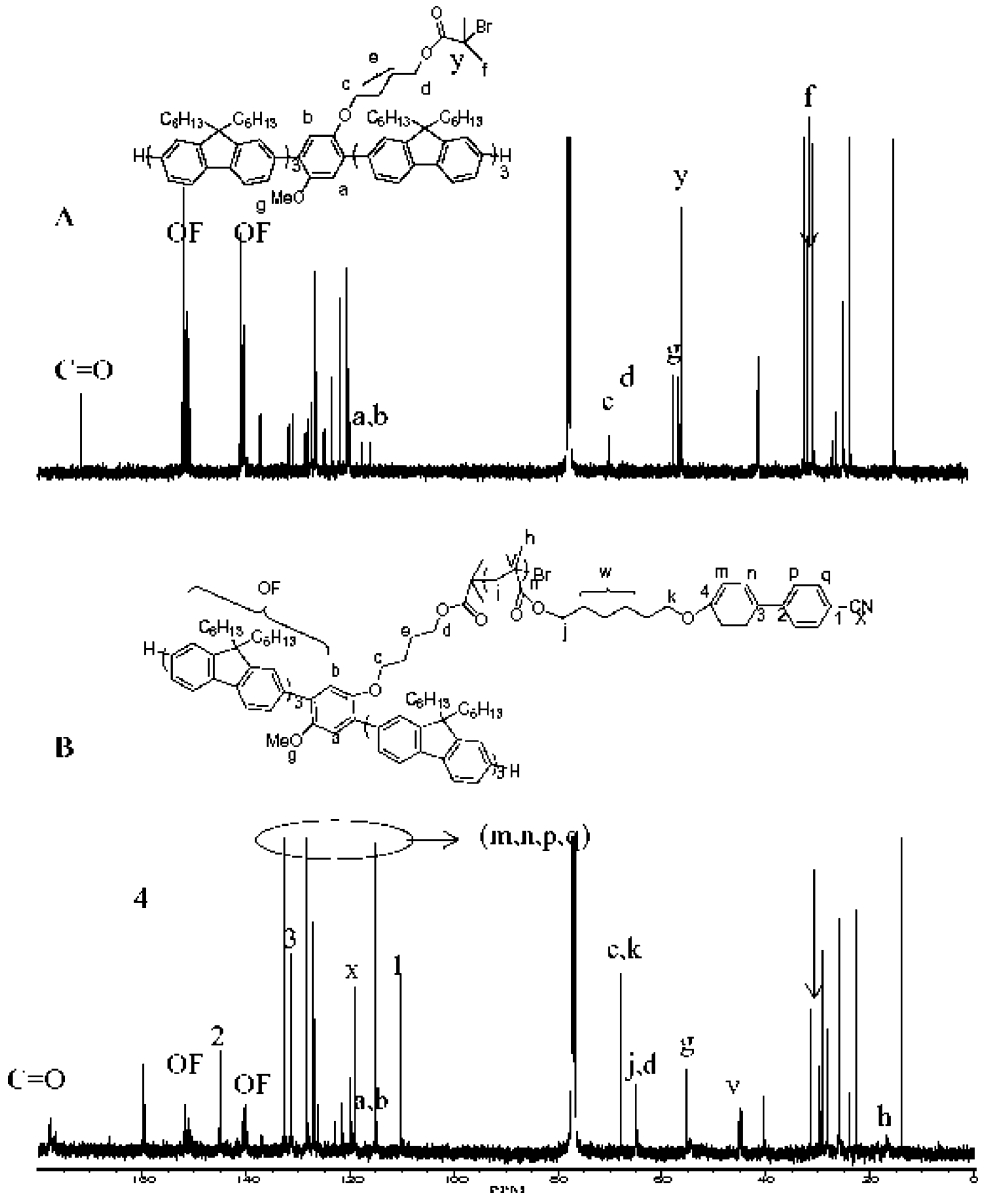


Figure 4. ^{13}C NMR spectra of the OFB macroinitiator (A) and the OFB−PCBPHMA block copolymer (sample: **P1**) (B) in $CDCl_3$. ((OF) oligofluorene (fluorene trimer)).

endothermic maxima, which have been summarized in Table 2. In both heating and cooling scans the transition temperatures, $T_{SmA\rightarrow I}$ and $T_{I\rightarrow SmA}$, steadily shift toward higher temperature with higher molar composition of the PCBHMA block as shown in Figure 5. Figure 6 depicts the relationship between SmA → I transition temperatures and M_n (NMR) also between I → SmA and M_n (NMR). The transition temperatures of respective block copolymers change from 90 to 110 °C when the molecular weight increases from 8000 to 16 000. This is consistent to the transition temperature of side-chain liquid crystalline polymers, which usually increases with molecular weight until a maximum value is achieved.

In Figure 5, the glass transition temperatures (T_gs), which are estimated from the middle of the glass transition region, can also be observed in both cooling and heating scans. The data are listed in Table 2 with the T_gs of OFB macroinitiator and homo-PCBHMA as comparison. It can be seen that the T_gs of the block copolymers are located between that of OFB macroinitiator and homo-PCBHMA. From **P1** to **P5**, the T_g of the respective block copolymer slightly increases with the molecular weight of the PCBHMA block. However, the T_g of **P1** with the lowest molecular weight is significantly below those of other four samples, probably due to higher chain end population.

POM was used to identify the mesophase. Unfortunately, no typical texture was observed during the cooling process from isotropic melt even after the samples had been annealed at 80 °C in liquid crystalline state for 12 h (see Supporting Information). Wide-angle X-ray diffraction (WAXD) was further employed to confirm the smectic phases. The samples were cooled from the isotropic melt and annealed at 85 °C in the liquid crystalline state for 8 h. In Figure 7, the first, second, and third reflections of the smectic layer at high angle of 2θ = 2.56, 5.12, and 7.40° can be observed in the WAXD pattern, corresponding to *d* spacing of 3.5, 1.7, and 1.2 nm, respectively. The broader peak at 2θ = 7.40° may be associated with the ordering of biphenyl cores.[8] The layer spacing (3.5 nm) is consistent with that of the LC homopolymer and LC−coil copolymers observed by Watanabe et al.[14] The smectic layers are apparently constructed with a bilayer character in which two mesogenic layers are included within a repeating length.[14]

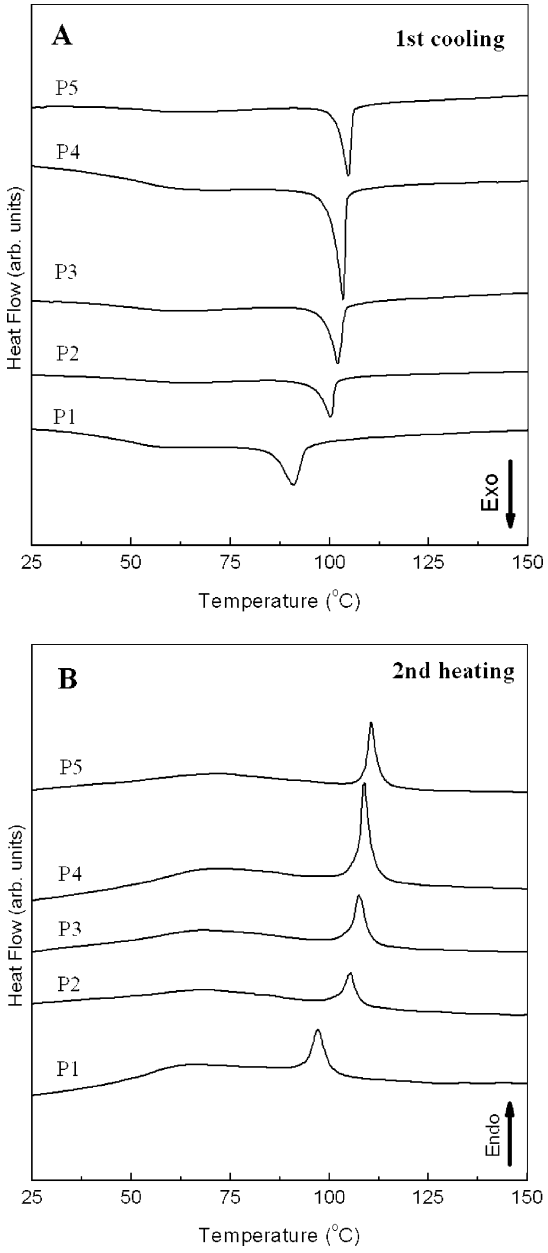


Figure 5. (A)First cooling scans of the OFB−PCBHMA block copolymers measured at a cooling rate of 10 °C/min. (B) Second heating scans of the OFB−PCBHMA block copolymers measured at a heating rate of 10 °C/min. The peaks are attributed to the smectic−isotropic phase transitions of copolymers.

Table 2. Thermal Properties of the OFB Macroinitiator, OFB−PCBHMA Block Copolymers and PCBHMA Homopolymers Determined by DSC

		transition temp (°C)	
sample	T_g (°C)	heating (T_{s-i})	cooling (T_{i-s})
OFB initiator	50		
P1	52	97.3	90.2
P2	56	105.8	99.6
P3	56	107.6	101.5
P4	57	108.9	102.7
P5	57	110.4	104.0
PCBHMA	64	112.6	108.2

Optical Properties

Figure 8 presents the representative absorption spectra of the OFB macroinitiator and the OFB−PCBHMA block copolymers in chloroform. The absorption of these block copolymers at 297 and 370 nm is attributed to the cyanobiphenyl and OFB chromophores, respectively. The absorption of OFB block in these copolymers does not have any changes comparing that OFB macroinitiator, indicating that there is no observable interaction between the two chromophores in the ground states in dilute solution. This may be an advantage of the conjugated block copolymers vs side-chain LC conjugated polymers, since the conjugation structures of many side-chain LC conjugated polymers are unlikely affected by the mesogens.[8−9] It can also be observed that the absorption of cyanobiphenyl chromophores increases with the molecular weight of the PCBHMA block in the copolymers, which agrees well with the desired copolymer composition. Comparison of the absorption and emission spectra of the OFB macroinitiator and the PCBHMA homopolymer in Figure 9A demonstrates that the absorption of the OFB macroinitiator and the emission of the PCBHMA homopolymer overlap significantly, from which the donor−acceptor energy transfer can be expected. In fact, the energy transfer between the two chromophores was probed by photoluminescent excitation (PLE) spectra. The PLE spectra measured at 413 nm as a function of the excitation wavelength in chloroform solution were normalized in the range of 370−400 nm where only the OFB macroinitiator absorbs, as illustrated in Figure 9B. The

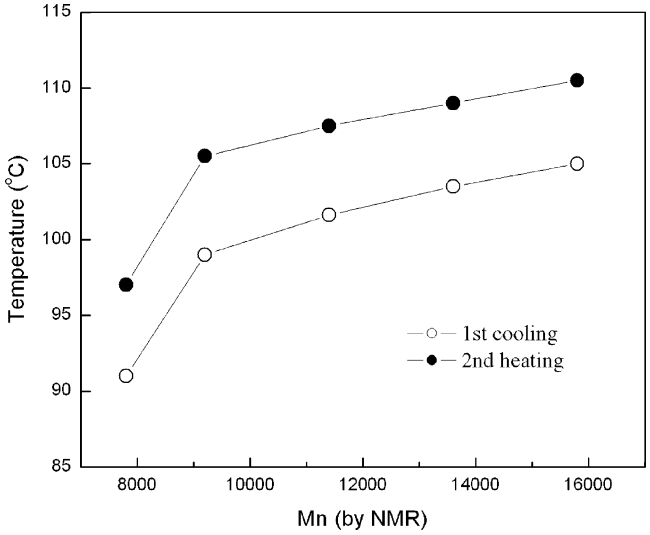


Figure 6. Dependence of the phase transition temperatures on the molecular weight. The transition temperatures (determined by the peak temperatures of the endothermic maxima) are calculated from the first cooling and the second heating.

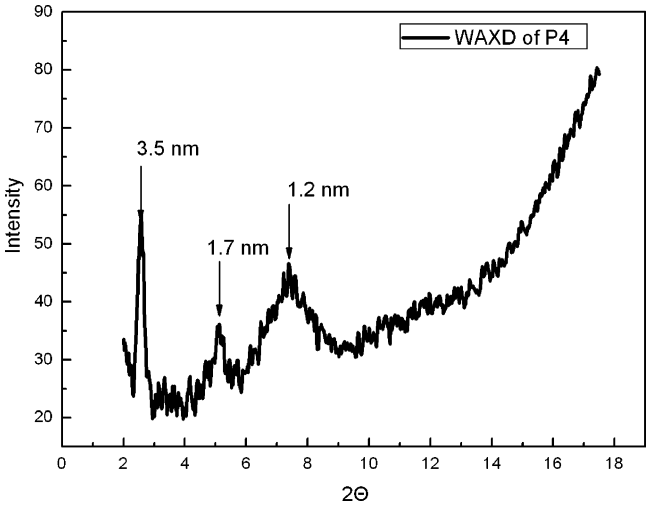


Figure 7. Wide-angle X-ray diffraction of **P4** at room temperature (the scan scale is from 2° to 17.5°). The samples were cooled from isotropic melt and annealed at 85 °C in liquid crystalline state for 8 h.

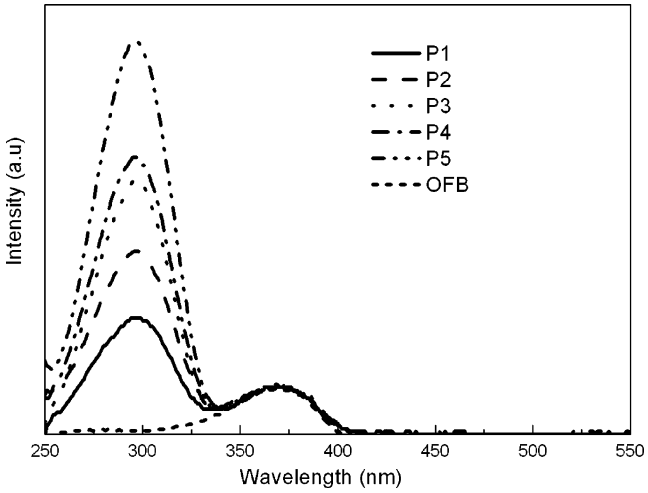


Figure 8. UV−vis spectra of the OFB−PCBHMA block copolymers in chloroform at 1×10^{-6} M (normalized at 413 nm).

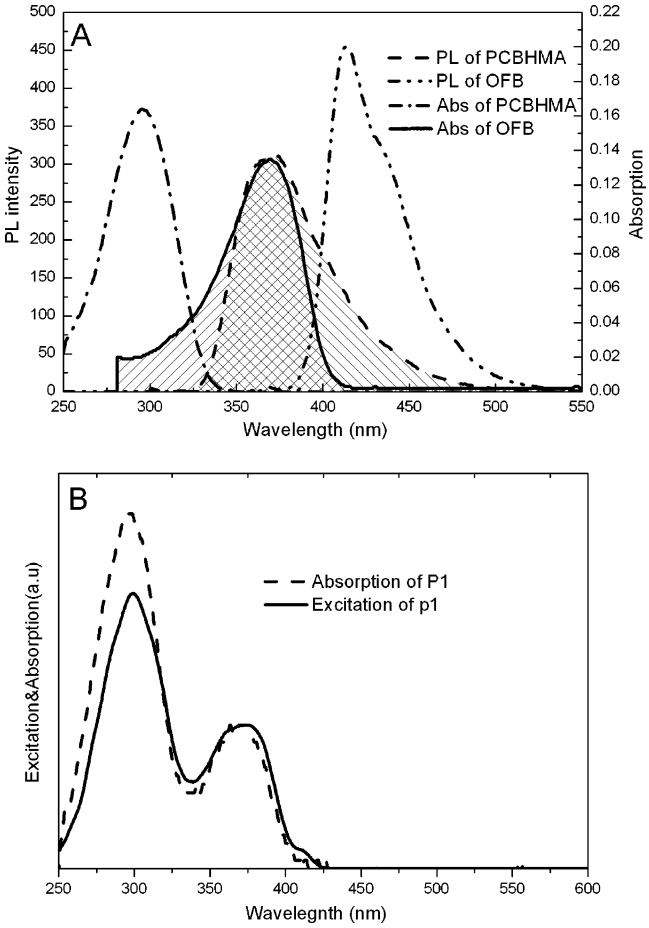


Figure 9. (A) UV−vis absorption and photoluminescence of the OFB macroinitiator and the PCBHMA homopolymer in chloroform. (B) UV−vis absorption and photoluminescent excitation (at 413 nm) of the OFB−PCBHMA block copolymer (**P1**) in chloroform.

PLE spectrum shows similar spectral features to the corresponding absorption, indicating that energy transfer from OFB block to PCBHMA block dose occur. However, the normalized excitation band at about 300 nm corresponding to the donor is lower than the corresponding absorption, demonstrating that the donor−acceptor energy transfer is incomplete.[19] The energy tranfer was further confirmed by the photoluminescence of the block copolymers, as shown in Figure 10A. The excitation wavelength was adjusted to 297 nm, where the emission of the PCBHMA block is much stronger than that of OFB (see Figure 9A). The photoluminescence of the copolymers was normalized by the corresponding absorption bands at 297 nm and the direct emission of OFB chromophore has been extracted from the emission spectra of the block copolymers. The weak residual fluorescence was observed at 340−390 nm which is attributed to the emission of the cyanobiphenyl chromophores. The efficiency of energy transfer decreases significantly when the percentage of the PCBHMA block in the polymeric chain increases. This result indicates that an intrachain energy transfer is involved in the emission of the block copolymers in dilute solution. To confirm this, a mixture of PCBHMA homopolymer and OFB macroinitiator in chloroform solution with the weight ratio of 2.5:1 was used as a control sample. The blend and the block copolymer showed similar absorption spectra as shown in the inset in Figure 10B. However, the PLE spectrum of the mixture is identical to that of OFB macroinitiator and does not exhibit any signal from PCBHMA homopolymer, in contrast to the block copolymer with the same composition, as shown in Figure 10B. Therefore, the singlet excited states in the mixture are generated only by the direct photoexcitation of the OFB segment. The phenomenon of energy transfer from the cyanobiphenyl chromophores to fluorene-based chromophores was also reported in the fluorene-*alt*-biphenyl copolymers.[20]

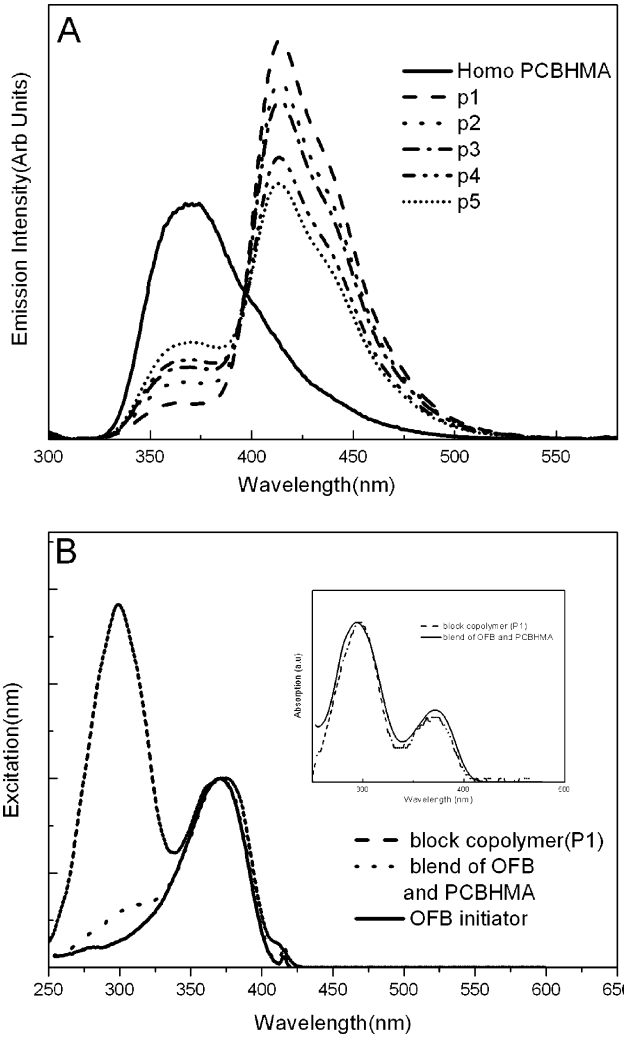


Figure 10. (A) Photoluminescence spectra of the PCBHMA homopolymer and the OFB−PCBHMA block copolymers in chloroform solution. An excitation wavelength of 297 nm was used for all samples. (B) Photoluminescent excitation (PLE) spectra of the block copolymer (**P1**), OFB macroinitiator and the mixture of OFB macroinitiator and homo-PCBHMA. Inset: absorption spectra of the block copolymer (**P1**) and the mixture of OFB macroinitiator and homo-PCBHMA solutions.

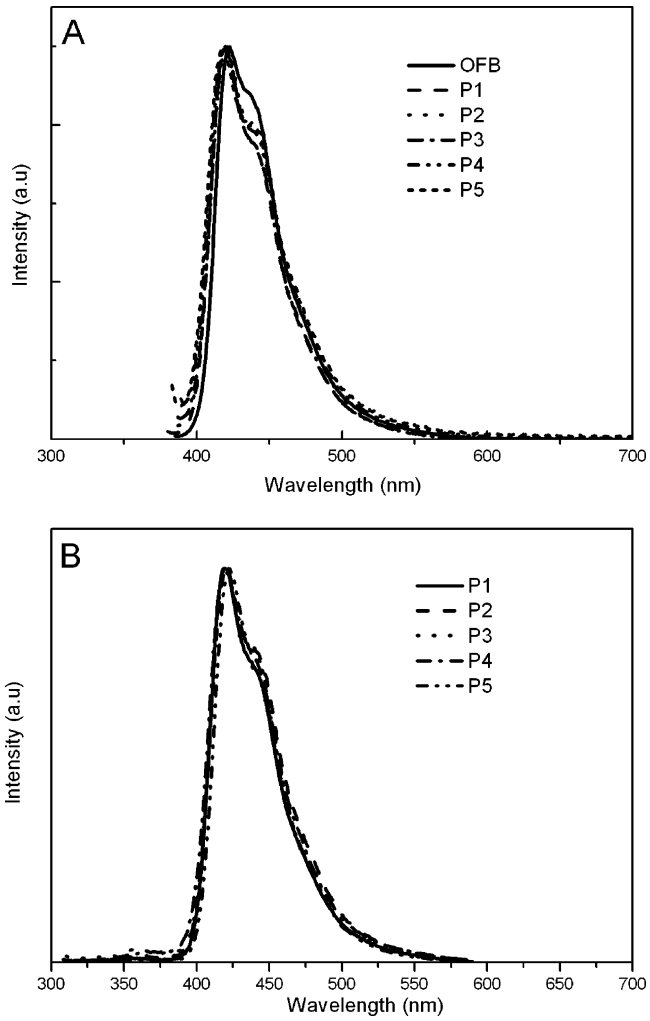


Figure 11. Photoluminescence spectra of the OFB macroinitiator and the OFB−PCBHMA block copolymers freshly spin-coated on quartz substrate from chloroform solution (5 mg/mL). The excitation wavelengths are 370 nm (A) and 300 nm (B), respectively.

Parts A and B of Figure 11 show the photoluminescence spectra (excited at 300 and 370 nm, respectively) of the OFB macroinitiator and the block copolymers in solid films freshly spin-coated on quartz substrate from chloroform solution (5 mg/mL), respectively. The emission peak of the OFB macroinitiator has a red-shift at about 10 nm in the solid state (Figure 11A) compared to the PL spectrum of in the solution (Figure 9A). However, the PL spectra of the block copolymers have slight blue shifts and their vibronic structures at 440 nm have been weakened compared to the OFB macroinitiator in the solid state, indicating that the LC blocks may affect the intermolecular packing of the OFB segment and thus influence the luminescent properties of the OFB chromophores.[21] It is important to note that the fluorescence from the PCBHMA block (excited at 300 nm) is almost completely quenched. The high efficiency of energy transfer from the PCBHMA block to the OFB segment indicates that the interchain fashion dominates the energy transfer in solid state.[22] The interchain energy transfer has recently been suggested to be more significant than the down chain fashion if both are present.[23]

Conclusions

We have synthesized a series of liquid crystalline conjugated block copolymers containing oligofluorene as the rigid segment and side-chain liquid crystalline polymer with cyanobiphenyl moieties as LC block by ATRP with narrow molecular weight distribution less than 1.20. The OFB macroinitiator was verified with the MALDI−TOFMS technique and the incorporation of the macroinitiator into the copolymer backbone was confirmed by GPC, ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopy. DSC investigations indicated that the isotropization of the smectic phase increased with molecular weight and leveled off at around $M_n = 14\,000$. WAXD studies verified the smectic mesophase and clarified the bilayer structure of mesogens in the smectic layer. In addition, energy transfer from the cyanobiphenyl chromophore to the OFB chromophore was observed in dilute solution and in solid films. An intrachain mechanism of energy transfer was demonstrated in dilute solution and an interchain mechanism was suggested in the solid films. The in-depth understanding on the relationship between the morphology/phase structure and photoluminescence are under investigation in our group and the application of these multifunctional block copolymers in light emitting devices will also be explored.

Experimental Section

Measurements. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectroscopy were performed on a Varian Mercury Plus 400 with tetramethylsilane as the internal standard. UV−vis spectra were collected on a Shimadzu UV-3150 spectrophotometer. Fluorescence measurement was carried out on a Shimadzu RF-5300PC spectrophotometer. FTIR spectra were collected on a Shimadzu IR Prestige-21 spectrophotometer. Relative molecular weights were determined by Agilent 1100 GPC at 35 °C, using an Agilent 1362A differential refractometer, three 5 μm Styragel columns (pore size: 10^3, 10^4, and 10^5 Å) in series, polystyrene as the standard, and THF as the eluent at a flow rate of 1.00 mL/min. The thermal behavior of the polymers synthesized was studied using a differential scanning calorimeter (DSC)-2920 from TA Instruments coupled with a TA-2000 control system. The temperature was accurately calibrated with tin, gallium, and indium using standard procedures. The weights of all the samples were in the range 4−6 mg. All the powdery samples were heated and cooled with a scanning rate of 10 °C/min under a nitrogen atmosphere in order to diminish oxidation. Wide-angle X-ray diffraction (WAXD) measurements were carried out using a Bruker D8 Discover diffractometer with GADDS as a 2D detector. Calibration was conducted using silicon powder and silver behenate. The samples were prepared by cooling from the isotropic melt and annealing at 85 °C in the liquid crystalline state for 8 h.

Materials. 2,7-Dibromofluorene (97%), 1-bromohexane (98%), 2-bromofluorene (95%), 4′-hydroxy-4-biphenylcarbonitrile (98%), 6-bromo-1-hexanol (97%), 4-methoxyphenol (99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%), 2-bromoisobutyryl bromide (98%), 1,4-dibromobutane (99%), butyllithium (1.6 M solution in hexanes), tetrakis(triphenylphosphine)palladium(0) (99%), 4-(dimethylamino)pyridine (DMAP) (99%), and *N*,*N*′-dicyclohexylcarbodiimide (DCC) (99%) were purchased from Aldrich Chemical Co. and were used as received. THF (99%, Sinopharm) was distilled from sodium/benzophenone and *o*-dichlorobenzene (99%, Across) was distilled from calcium hydride and stored under argon. Copper(I) bromide (CuBr, 98%, Adirich) was purified by stirring in acetic acid, then washing with methanol, and finally drying.[24]

Described below are the synthesis and purification procedures for the OFB macroinitiator and the OFB−PCBHMA block copolymers.

2,7-Dibromo-9,9-dihexyl-9*H*-fluorene (1). 1-Bromohexane (11.0 mL, 77.2 mmol) was added to a mixture of 2,7-dibromofluorene (10.0 g, 30.9 mmol) and tetrabutylammonium bromide (1.0 g, 3.1 mmol) in DMSO (50 mL) and 50% (w/w) aqueous NaOH (12 mL). The reaction mixture was cooled to room temperature and stirred for 5 h. An excess of ethyl acetate (200 mL) was added to the reaction mixture, and the NaOH precipitate was filtered off. The organic extract was washed with dilute HCl (200 mL) and brine (2

× 150 mL). Then the organic layer was dried, concentrated, and purified by column chromatography on silica gel with petroleum ether as eluent. The product was recrystallized from ethanol and dried to afford **1** (13.9 g, 90%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.51, 7.44 (2 d, fluorenyl H, 6H), 1.91 (m, $-CH_2C_5H_{11}$, 4H), 1.07 (m, $-CH_2(CH_2)_3CH_3$, 12H), 0.777 (t, $-CH_3$, 6H), 0.583 (m, $-CH_2(CH_2)_3CH_3$, 4H). ^{13}C NMR ($CDCl_3$, ppm) δ 153.44 (fluorenyl q-C), 139.93 (fluorenyl q-C), 131.01 (fluorenyl H−*C*), 127.05 (fluorenyl H−*C*), 122.31 (fluorenyl H−*C*), 121.89 (fluorenyl q-C), 56.61 ($C(Ph)_2(C_6H_{13})_2$), 41.08 (CH_2), 32.33 (CH_2), 30.47 (CH_2), 24.53 (CH_2), 23.44 (CH_2), 14.84 (CH_3).

(2-Bromo-9,9-dihexyl-9*H*-fluoren-7-yl)trimethylsilane (2). A hexane solution of *n*-BuLi (1.6 M, 12.8 mL, 20.4 mmol) was added to **1** (10.0 g, 20.4 mmol) in THF (140 mL) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C before adding chlorotrimethylsilane (3.08 mL, 24.5 mmol). The mixture was then warmed to room temperature, stirred for 30 min, and poured into a large amount of water (500 mL) for extraction with petroleum ether. The organic extracts were washed with brine (2 × 150 mL) and dried over sodium sulfate. The residue was purified by column chromatography on silica gel with petroleum ether as eluent to yield colorless **2** (8.64 g, 87.8%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.64, 7.56 (2 d, fluorenyl H, 2H), 7.48 (m, fluorenyl H, 6H), 1.94 (m, $-CH_2C_5H_{11}$, 4H), 1.10 (m, $-CH_2(CH_2)_3CH_3$, 12H), 0.779 (m, $-CH_3$, 6H), 0.63 (m, $-CH_2(CH_2)_3CH_3$, 4H), 0.315 (d, $-Si(CH_3)_3$, 9H). ^{13}C NMR ($CDCl_3$, ppm): δ 154.08 (fluorene q-C), 150.38 (fluorenyl q-C), 141.53 (fluorenyl q-C), 141.02 (fluorenyl q-C), 140.56 (fluorenyl q-C), 132.85 (fluorenyl H−*C*), 131.06 (fluorenyl H−*C*), 130.76 (fluorenyl H−*C*), 128.46 (fluorenyl H−*C*), 127.13 (fluorenyl H−*C*), 122.00 (fluorenyl H−*C*), 119.90 (fluorenyl q-C), 56.24 ($C(Ph)_2(C_6H_{13})_2$), 40.95 (CH_2), 32.24 (CH_2), 30.42 (CH_2), 24.51 (CH_2), 23.38 (CH_2), 14.88 (CH_3), −0.648 ($-Si(CH_3)_3$).

9,9-Dihexyl-7-(trimethylsilyl)-9*H*-fluoren-2-yl-2-boronic acid (3). A hexane solution of *n*-BuLi (1.6 M, 12.6 mL, 20.2 mmol) was added to **2** (8.0 g, 16.5 mmol) in THF (50 mL) at −78 °C. The reaction mixture was stirred for 1 h before adding triisopropyl borate (8.0 mL, 32.0 mmol) at −78 °C. The mixture was then warmed to room temperature, stirred overnight, and poured into a large amount of water (500 mL) for extraction with ethyl ether. The organic extracts were washed with brine (2 × 150 mL) and dried over with sodium sulfate. After the solvent was evaoporated off, the residue was purified by chromatography on silica gel with petroleum ether: ethyl acetate (4:1) as the eluent to yield **3** (5.23 g, 71%) as white powder. ^{1}H NMR ($CDCl_3$, ppm): δ 8.30−8.22 (m, $-B(OH)_2$, 2H), 7.89, 7.79 (2 d, fluorenyl H, 2H), 7.74−7.47 (m, fluorenyl H, 4H), 2.09−1.98 (m, $-CH_2C_5H_{11}$, 4H), 1.09−0.60 (m, $-CH_2C_5H_{11}$, 22H), 0.32 (d, $-Si(CH_3)_3$, 9H). ^{13}C NMR ($CDCl_3$, ppm): δ 155.38 (fluorenyl q-C), 153.33 (fluorenyl q-C), 149.36 (fluorenyl q-C), 141.66 (fluorenyl q-C), 137.58 (fluorenyl q-C), 134.29 (fluorenyl q-C), 131.80 (fluorenyl H−*C*), 127.39 (fluorenyl H−*C*), 120.67 (fluorenyl H−*C*), 118.13 (fluorenyl H−*C*), 113.92 (fluorenyl H−*C*), 110.20 (fluorenyl H−*C*), 54.96 ($C(Ph)_2(C_6H_{13})_2$), 40.32 (CH_2), 31.40 (CH_2), 29.62 (CH_2), 23.62 (CH_2), 22.53 (CH_2), 14.02 (CH_3), −0.82 ($-Si(CH_3)_3$).

2-Bromo-9,9-dihexyl-9*H*-fluorene (4). 1-Bromohexane (20.14 mL, 142.8 mmol) was added to a mixture of 2-bromofluorene (10.0 g, 40.8 mmol) and tetrabutylammonium bromide (1.32 g, 4.1 mmol) in DMSO (50 mL) and 50% (w/w) aqueous NaOH (12 mL). The reaction mixture was stirred for 6 h at 70 °C. An excess of methylene dichloride (100 mL) was added to the reaction mixture, and the NaOH precipitate was filtered off. The organic layer was washed with dilute HCl (2 M, 200 mL) then with brine (3 × 150 mL), and dried with sodium sulfate. After the solvent was evaporated off, the residue was purified by chromatography on silica gel with petroleum ether as eluent to yield **4** (15.6 g, 92.3%) as white yellow liquid. ^{1}H NMR ($CDCl_3$, ppm): δ 7.67 (m, fluorenyl H, 1H), 7.56 (d, fluorenyl H, 1H), 7.47 (m, fluorenyl H, 2H), 7.33 (d, fluorenyl H, 3H), 1.96 (m, $-CH_2C_5H_{11}$, 4H), 1.11 (m, $-CH_2(CH_2)_3CH_3$, 12H), 0.788 (m, $-CH_3$, 6H), 0.63 (m, $-CH_2(CH_2)_3CH_3$, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 153.83 (fluorenyl q-C), 151.17 (fluorenyl q-C), 141.01 (fluorenyl q-C), 140.89 (fluorenyl q-C), 131.02 (fluorenyl H−*C*), 130.74 (fluorenyl H−*C*), 128.30 (fluorenyl H−*C*), 127.77 (fluorenyl H−*C*), 127.00 (fluorenyl H−*C*), 123.73 (fluorenyl H−*C*), 121.85 (fluorenyl H−*C*), 120.54 (fluorenyl q-C), 56.24 ($C(Ph)_2(C_6H_{13})_2$), 41.16 (CH_2), 32.33 (CH_2), 30.51 (CH_2), 24.54 (CH_2), 23.42 (CH_2), 14.84 (CH_3).

9,9-Dihexyl-9*H*-fluoren-2-yl-2-boronic acid (5). A hexane solution of *n*-BuLi (1.6 M, 18.8 mL, 30.1 mmol) was added to **4** (10.0 g, 24.2 mmol) in THF (100 mL) at −78 °C. The reaction mixture was stirred for 1 h before trimethyl borate (11.8 mL) was added at −78 °C. The mixture was then warmed to room temperature and stirred overnight. The mixture was washed with dilute HCl (2 M) until the liquid was neutral. The mixture was extracted with ethyl ether; then the organic layer was washed with brine (2 × 150 mL) and dried with sodium sulfate. Upon evaporating the solvent, the residue was purified by chromatography on silica gel with petroleum ether: ethyl acetate (4:1) as eluent to yield **5** (6.15 g, 67%) as white powder. ^{1}H NMR ($CDCl_3$, ppm): δ 8.31−8.22 (m, $-B(OH)_2$), 2H), 7.89−7.39 (m, fluorenyl H, 7H), 2.10 (m, $-CH_2C_5H_{11}$, 4H), 1.08−0.59 (m, $-CH_2C_5H_{11}$, 22H). ^{13}C NMR ($CDCl_3$, ppm): δ 151.89 (fluorenyl q-C), 150.36 (fluorenyl q-C), 145.80 (fluorenyl q-C), 140.96 (fluorenyl q-C), 134.84 (fluorenyl H−*C*), 129.92 (fluorenyl H−*C*), 128.14 (fluorenyl H−*C*), 127.06 (fluorenyl H−*C*), 123.28 (fluorenyl q-C), 120.62 (fluorenyl H−*C*), 119.49 (fluorenyl H−C), 55.29 ($C(Ph)_2(C_6H_{13})_2$), 40.63 (CH_2), 31.69 (CH_2), 29.98 (CH_2), 23.85(CH_2), 22.79 (CH_2), 14.28 (CH_3).

(9,9-Dihexyl-2-(9,9-dihexyl-9*H*-fluoren-2-yl)-9*H*-fluoren-7-yl-trimethylsilane (6). The mixture of **5** (5.0 g, 13.2 mmol), **2** (5.0 g, 10.3 mmol), $Pd(pph_3)_4$ (0.40 g, 0.34 mmol) and tetrabutylammonium bromide (1.0 g, 3.1 mmol) in the toluene (50 mL) and potassium carbonate solution (2 M, 50 mL) was stirred for 2 days at 90 °C in dark. Then the mixture was cooled to room temperature and extracted with petroleum ether. The organic layer was separated, washed with brine (2 × 150 mL), and dried with sodium sulfate. After the solvent was evaporated off, the residue was purified by chromatography on silica gel with petroleum ether as the eluent to yield **6** (5.94 g, 78%) as the colorless liquid. ^{1}H NMR ($CDCl_3$, ppm): δ 7.79−7.29 (m, fluorenyl H, 13H), 2.02 (t, $-CH_2C_5H_{11}$, 8H), 1.09−0.70 (m, $-CH_2C_5H_{11}$, 44H), 0.37 (s, $-Si(CH_3)_3$, 9H). ^{13}C NMR ($CDCl_3$, ppm): δ 152.53 (fluorenyl q-C), 152.29 (fluorenyl q-C), 151.86 (fluorenyl q-C), 151.03 (fluorenyl q-C), 142.28 (fluorenyl q-C), 141.67 (fluorenyl q-C), 141.52 (fluorenyl q-C), 141.40(fluorenyl q-C), 141.14(fluorenyl q-C), 141.11 (fluorenyl q-C), 139.80 (fluorenyl q-C), 132.67 (fluorenyl H−C), 128.49 (fluorenyl H−*C*), 127.80 (fluorenyl H−*C*), 127.62 (fluorenyl H−*C*), 126.87 (fluorenyl H−*C*), 123.76 (fluorenyl H−*C*), 122.33 (fluorenyl H−*C*), 122.29 (fluorenyl H−*C*), 120.82 (fluorenyl H−*C*), 120.69 (fluorenyl H−*C*), 120.54 (fluorenyl H−*C*), 119.83 (fluorenyl H−*C*), 56.02 ($C(Ph)_2(C_6H_{13})_2$), 55.95 ($C(Ph)_2(C_6H_{13})_2$), 41.23 (CH_2), 40.91 (CH_2), 32.79 (CH_2), 32.32 (CH_2), 32.20 (CH_2), 30.55 (CH_2), 30.42 (CH_2), 24.63 (CH_2), 24.58 (CH_2), 23.55 (CH_2), 23.40 (CH_2), 23.32 (CH_2), 14.83 (CH_3), −0.648 ($-Si(CH_3)_3$).

9,9-Dihexyl-2-(9,9-dihexyl-2-iodo-9*H*-fluoren-7-yl)-9*H*-fluorene (7). Iodine monochloride (7.59 mL, 7.59 mmol) in methylene chloride solution (1.0 M) was added to **6** (5.60 g, 7.59 mmol) in carbon tetrachloride solution (40 mL) at 0 °C. After stirring for 4 h, the reaction mixture was poured into a sodium thiosulfate aqueous (5 wt %, 100 mL) with vigorous stirring until discoloration. The mixture was extracted with methylene chloride and the organic layer was washed with brine (2 × 150 mL) before being dried with sodium sulfate. Upon evaporating off the solvent, the residue was washed with methanol and purified by recrystallization from acetone to yield **7** (4.60 g, 76.5%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.78−7.33 (m, fluorenyl H, 13H), 2.00 (m, $-CH_2C_5H_{11}$, 8H), 1.07−0.69 (m, $-CH_2C_5H_{11}$, 44H). ^{13}C NMR ($CDCl_3$, ppm): δ 153.66 (fluorenyl q-C), 151.71 (fluorenyl q-C), 151.21 (fluorenyl q-C), 151.1 (fluorenyl q-C), 141.46 (fluorenyl q-C), 141.21 (fluorenyl q-C), 140.94 (fluorenyl q-C), 140.70 (fluorenyl q-C), 140.62 (fluorenyl q-C), 140.50 (fluorenyl q-C), 139.62 (fluorenyl H−*C*), 139.43 (fluorenyl H−*C*), 136.12 (fluorenyl H−*C*), 132.34 (fluorenyl H−*C*), 127.24 (fluorenyl H−*C*), 127.00 (fluorenyl H−*C*), 126.46 (fluorenyl H−*C*),

126.25 (fluorenyl H−*C*), 123.14 (fluorenyl H−*C*), 121.64 (fluorenyl H−*C*), 120.26 (fluorenyl H−*C*), 120.22 (fluorenyl H−*C*), 120.09 (fluorenyl H−*C*), 119.94 (fluorenyl H−*C*), 92.68, 92.58 (fluorenyl q-*C*−I), 55.67 ($C(Ph)_2(C_6H_{13})_2$), 55.38 ($C(Ph)_2(C_6H_{13})_2$), 40.56 (CH_2), 40.43 (CH_2), 31.64 (CH_2), 29.88 (CH_2), 29.81 (CH_2), 23.98 (CH_2), 23.94 (CH_2), 22.75 (CH_2), 14.19 (CH_3).

9,9-Dihexyl-7-(9,9-dihexyl-9*H*-fluoren-2-yl)-9*H*-fluoren-2-yl-2-boronic acid (8). A hexane solution of *n*-BuLi (1.6 M, 4.64 mL, 7.45 mmol) was added to **7** (4.60 g, 5.72 mmol) in anhydrous THF (50 mL) in nitrogen at −78 °C. The reaction mixture was stirred for 1 h before triisopropyl borate (2.60 mL, 11.33 mmol) was added at −78 °C. The mixture was warmed to room temperature, stirred overnight and then quenched with HCl (2.0 M, 40 mL) before adding a large amount of water (300 mL) for extraction with ethyl ether. The organic extracts were washed with brine (2 × 150 mL) and dried over sodium sulfate. After solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether: ethyl acetate (4:1) as the eluent to yield **8** (2.06 g, 50%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.36−8.27 (m, $-B(OH)_2$, 2H), 7.96−7.35 (m, fluorenyl H, 13H), 2.05 (m, $-CH_2C_5H_{11}$, 8H), 1.11−0.77 (m, $-CH_2C_5H_{11}$, 44H). ^{13}C NMR ($CDCl_3$, ppm): δ 153.86 (fluorenyl q-C), 149.80 (fluorenyl q-C), 144.52 (fluorenyl q-C), 140.68 (fluorenyl q-C), 130.14 (fluorenyl q-C), 129.69 (fluorenyl q-C), 126.39 (fluorenyl q-C), 123.07 (fluorenyl H−*C*), 121.78 (fluorenyl H−*C*), 120.43 (fluorenyl H−*C*), 119.40 (fluorenyl H−*C*), 55.45 ($C(Ph)_2(C_6H_{13})_2$), 40.33 (CH_2), 31.52 (CH_2), 29.69 (CH_2), 23.79 (CH_2), 22.58 (CH_2), 14.01 (CH_3).

1-(4-Bromobutoxy)-4-methoxybenzene (9). 1.4-Dibromobutane (51.7 g, 28.6 mL) was added to a mixture of 4-methoxyphenol (10.00 g, 0.08 mol) and potassium hydrate (4.6 g, 0.8 mol) in ethanol (200 mL). The reaction mixture was stirred at 90 °C for 4 h. The organic layer was separated, washed with brine (2 × 150 mL) and dried with sodium sulfate.After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether: ethyl acetate (4:1) as the eluent to yield **9** (14.0 g, 70%). ^{1}H NMR ($CDCl_3$, ppm): δ 6.83 (s, phenyl H, 4 H), 3.94 (t, $-OCH_{2-}$, 2H), 3.77 (s, $-OCH_3$, 3H), 3.485 (t, $-CH_2$-Br, 2H), 2.06−1.91 (m, $-OCH_2(CH_2)_2CH_2Br$, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 154.11 (phenyl q-C), 153.26 (phenyl q-C), 115.68 (phenyl H−*C*), 114.91 (phenyl H−*C*), 67.74 ($-OCH_2-$), 55.96 ($-OCH_3$), 33.67 (CH_2Br), 29.74 (CH_2), 28.24 (CH_2).

1-(4-Bromobutoxy)-2,5-dibromo-4-methoxybenzene (10). Bromine (6.20 mL, 0.12 mol) in chloroform (40 mL) was added dropwise to 1-(4-bromobutoxy)-4-methoxybenzene (13.00 g, 0.05 mol) in chloroform (200 mL). The mixture was stirred for 12 h, and the produced HBr gas was collected in saturated aqueous sodium hydrate. The organic layer was separated, washed with brine (2 × 150 mL) and dried over sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether: ethyl acetate (4:1) as the eluent to afford **10** (17.6 g, 85%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.07 (s, phenyl H, 2H), 3.99 (t, $-OCH_2-$, 2H), 3.84 (s, $-OCH_3$, 3H), 3.52 (t, $-CH_2Br$, 2H), 2.11−1.97 (m, $-OCH_2(CH_2)_2CH_2Br$, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 150.90 (phenyl *C*−OCH_3), 150.04 (phenyl *C*−OCH_2−), 118.83 (phenyl *C*−H), 117.19 (phenyl *C*−H), 111.48 (phenyl *C*−Br), 110.65 (phenyl *C*−Br), 69.46 ($-OCH_2-$), 57.22 ($-OCH_3$), 33.73 (CH_2Br), 29.66 (CH_2), 27.98 (CH_2).

4-(2,5-Dibromo-4-methoxyphenoxy)butyl Acetate (11). A mixture of potassium acetate (2.5 g, 50.8 mmol), **10** (10.0 g, 25.4 mmol) and acetic anhydride (5.0 mL) in acetic acid (100 mL) was stirred and refluxed for 1 day. The precipitate KBr was filtered off, and the excess acetic acid was evaporated off. Then the residue was washed with a large amount of water (500 mL). The mixture was extracted with chloroform, and the organic layer was washed with brine (2 × 150 mL) and dried over sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether:ethyl acetate (4:1) as the eluent to afford **11** (8.32 g, 87.4%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.10 (s, phenyl H, 2H), 4.16 (t, $-CH_2OAc$), 2H), 4.14 (t, $-OCH_2-$, 2H), 3.98 (s, $-OCH_3$, 3H), 1.88 (m, $OCH_2(CH_2)_2CH_2$-OAc, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 171.99 (*C* = O), 151.47 (phenyl *C*−OCH_3), 150.72 (phenyl *C*−OCH_2−), 119.49 (phenyl *C*−H), 117.82 (phenyl *C*−H), 112.12 (phenyl *C*−Br), 111.22 (phenyl *C*−Br), 70.47 ($-OCH_{2-}$), 64.85 ($-CH_2OAc$), 57.81 ($-OCH_3$), 26.62 (CH_2), 26.15 (CH_2), 21.80(−(C═O)CH_3).

4-(2,5-Bis(9,9-dihexyl-2-(trimethylsilyl)-9*H*-fluoren-7-yl)-4-methoxyphenoxy)butan-1-ol (12). A mixture of **11** (2.00 g, 5.05 mmol), **3** (5.00 g, 11.11 mmol), toluene (50 mL), potassium carbonate (2 M, 50 mL), $Pd(pph_3)_4$ (0.20 g, 0.17 mmol), and tetrabutylammonium bromide (0.3 g, 1.0 mmol) was stirred for 2 days at 90 °C in dark. The mixture was poured into a large amount of water and then extracted with petroleum ether. The organic layer was washed with brine and dried over sodium sulfate. After the solvent was evaporated off, the residue was solved in methanol (200 mL), in which the sodium hydrate (1.0 g, 25.0 mmol) was solved. The mixture was stirred for 3 h at room temperature. The excess methanol was evaporated and the residue was poured into a large amount of water (200 mL) then extracted by the petroleum ether. The organic layer was washed with brine (2 × 50 mL) and dried over sodium sulfate. After solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether: ethyl acetate (4:1) as the eluent to afford **12** (4.1 g, 81%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.76−7.33 (m, fluorenyl H, 12H), 7.10 (d, phenyl H, 2H), 3.99 (t, $-OCH_2-$, 2H), 3.81 (s, $-OCH_3$, 3H), 3.59 (q, $-CH_2OH$ 2H), 2.00 (m, $-CH_2C_5H_{11}$, 8H), 1.79−1.63 (m, $OCH_2(CH_2)_2CH_2OH$, 4H), 1.16−0.8 (m, $-CH_2C_5H_{11}$, 44H), 0.33 (s, $-Si(CH_3)_3$, 18H). ^{13}C NMR ($CDCl_3$, ppm): δ 151.43 (phenyl *C*−OCH_3), 151.25 (phenyl *C*−OCH_2−), 142.41 (fluorenyl q-C), 140.95 (fluorenyl q-C), 139.79 (fluorenyl q-C), 138.06 (fluorenyl q-C), 132.66 (fluorenyl q-C), 128.81 (fluorenyl *C*-H), 128.46 (fluorenyl *C*-H), 125.40 (fluorenyl *C*-H), 125.16 (fluorenyl *C*-H), 120.28 (phenyl q-*C*), 119.83 (phenyl q-C), 117.96 (phenyl *C*−H), 116.59 (phenyl *C*−H), 70.73 ($-OCH_2-$), 63.22 ($-CH_2$-OH), 57.57 ($-OCH_3$), 55.84 ($C(Ph)_2(C_6H_{13})_2$), 55.78 ($C(Ph)_2$-$(C_6H_{13})_2$), 41.04 (CH_2), 40.91 (CH_2), 32.28(CH_2), 30.52(CH_2), 30.36(CH_2), 26.78(CH_2), 24.61(CH_2), 23.38(CH_2), 14.85 (CH_3).

4-(2,5-Bis(9,9-dihexyl-2-iodo-9H-fluoren-7-yl)-4-methoxyphenoxy)butan-1-ol (13). Iodine monochloride (5.7 mL, 5.7 mmol) in methylene chloride solution (1.0 M) was added to **12** (2.90 g, 2.89 mmol) in carbon tetrachloride solution (35 mL) at 0 °C. After stirring for 4 h, the reaction mixture was poured into a sodium thiosulfate aqueous (5 wt %, 100 mL) with vigorous stirring until discoloration. The organic extracts were washed with brine (2 × 100 mL) before being dried with sodium sulfate. After the solvent was evaporated off, the residue was washed with methanol and purified by recrystallization from acetone to yield **13** (2.48 g, 77.5%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.72−7.54 (m, fluorenyl H, 12H), 7.06 (d, phenyl H, 2 H), 3.98 (t, $-OCH_2-$, 2H), 3.80 (s, $-OCH_3$, 3H), 3.59 (q, $-CH_2OH$ 2H), 1.97 (m, $-CH_2C_5H_{11}$, 8H), 1.79−1.62 (m, $OCH_2(CH_2)_2CH_2OH$, 4H), 1.29 (m, $-OH$, 1H), 1.15−0.78 (m, m, $-CH_2C_5H_{11}$, 44H). ^{1}H NMR ($CDCl_3$, ppm): δ 153.67 (phenyl *C*−OCH_3), 152.01(phenyl *C*−OCH_2−), 150.05 (fluorenyl q-C), 149.80 (fluorenyl q-C), 140.53 (fluorenyl q-C), 139.08 (fluorenyl q-C), 137.44 (fluorenyl q-C), 135.85 (fluorenyl q-C), 132.11 (fluorenyl q-C), 131.11 (fluorenyl *C*-H), 130.65 (fluorenyl *C*-H), 128.07 (fluorenyl *C*-H), 124.43 (fluorenyl *C*-H), 121.46 (phenyl q-C), 119.46 (phenyl q-C), 116.91 (phenyl *C*−H), 115.36 (phenyl *C*−H), 92.44 (fluorenyl *C*−I), 69.81 ($-OCH_2-$), 62.32 ($-CH_2OH$), 56.71 ($-OCH_3$), 55.30 ($C(Ph)_2(C_6H_{13})_2$), 40.32 (CH_2), 31.51 (CH_2), 29.72 (CH_2), 29.50 (CH_2), 25.92 (CH_2), 23.85 (CH_2), 22.62 (CH_2), 14.03 (CH_3).

4-(2,5-Di(oligofluorenyl)-4-methoxyphenoxy)butan-1-ol (14) (OFBOH). The mixture of **13** (1.20 g, 1.08 mmol), **8** (1.92 g, 2.7 mmol), toluene (20 mL), potassium carbonate aqueous solution (2 M, 20 mL), $Pd(pph_3)_4$ (0.050.0 g, 0.043 mmol) and tetrabutylammonium bromide(0.3 g, 1.0 mmol) was stirred for 2 days at 90 °C in dark. The mixture was washed with water (200 mL) and then extracted by petroleum ether. The organic layer was washed with brine (2 × 100 mL) and dried with sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether:ethyl acetate (4:1) as the eluent. The products were precipitated to methanol to yield **14**

(1.5 g, 50.6%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.84−7.30 (m, fluorenyl H, 38H), 7.13 (d, phenyl H, 2H), 4.03 (t, $-OCH_2-$, 2H), 3.85 (s, $-OCH_3$, 3H), 3.63 (q, $-CH_2OH$, 2H), 2.16−2.00 (br, $-CH_2C_5H_{11}$, 24H), 1.83−1.67 (m, $OCH_2(CH_2)_2CH_2OH$, 4H), 1.31 (m, $-OH$, 1H), 1.12−0.8 (m, $-CH_2C_5H_{11}$, 132H). ^{13}C NMR ($CDCl_3$, ppm): δ 152.01 (phenyl $C-OCH_3$), 152.0 (fluorenyl q-C), 151.68 (fluorenyl q-C), 151.46 (fluorenyl q-C), 151.22 (fluorenyl q-C), 150.93 (fluorenyl q-C), 150.52 (phenyl $C-OCH_2-$), 141.01 (fluorenyl q-C), 140.74 (fluorenyl q-C), 140.53 (fluorenyl q-C), 140.34 (fluorenyl q-C), 140.30 (fluorenyl q-C), 140.22 (fluorenyl q-C), 140.01 (fluorenyl q-C), 127.20 (fluorenyl *C*-H), 127.00 (fluorenyl *C*-H), 126.35 (fluorenyl *C*-H), 126.24 (fluorenyl *C*-H), 123.14 (fluorenyl *C*-H), 121.73 (fluorenyl *C*-H), 121.65 (phenyl q-C), 120.16 (phenyl q-C), 120.09 (fluorenyl *C*-H), 119.92 (fluorenyl *C*-H), 119.80 (fluorenyl *C*-H), 119.65 (fluorenyl *C*-H), 119.57 (phenyl *C*-H), 117.34 (phenyl *C*-H), 70.12 ($-OCH_2-$), 62.60 ($-CH_2OH$), 56.98($-OCH_3$), 55.54 ($C(Ph)_2(C_6H_{13})_2$), 55.39 ($C(Ph)_2(C_6H_{13})_2$), 40.58 (CH_2), 40.58 (CH_2), 31.76 (CH_2), 31.67 (CH_2), 30.01 (CH_2), 29.88 (CH_2), 29.76 (CH_2), 26.18 (CH_2), 24.19 (CH_2), 24.14 (CH_2), 24.06 (CH_2), 24.00 (CH_2), 22.83 (CH_2), 22.77 (CH_2), 14.23 (CH_3).

Synthesis of the Rigid OFB Macroinitiator (15). 2-Bromoisobutyryl bromide (1.4 mL, 11.0 mmol) was added dropwise to a mixture of **OFBOH** (1.236 g, 0.565 mmol) and triethylamine (0.16 mL, 1.10 mmol) in THF (30 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solution was washed with a large amount of water (200 mL) to remove the salt and the excess of 2-bromoisobutyryl bromide before extraction with chloroform. The organic layer was dried over anhydrous sodium sulfate and evaporated off the excess solvent. The residue was purified by column chromatography on silica gel with petroleum ether:ethyl acetate (8:1) as the eluent. The products were precipitated to methanol to yield **15** (1.2 g, 91%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.84−7.3 (m, fluorenyl H, 38H), 7.13 (d, phenyl H, 2H), 4.17 (t, $-CH_2O(C=O)$, 2H), 4.04 (t, $-OCH_2-$, 2H), 3.85 (s, $-OCH_3$, 3H), 2.15−2.00 (br, $-CH_2C_5H_{11}$, 24 H), 1.91 (d, $C(CH_3)_2$, 6H), 1.82 (m, $OCH_2(CH_2)_2CH_2O$, 4H), 1.12−0.78 (br, $-CH_2C_5H_{11}$, 132H). ^{13}C NMR ($CDCl_3$, ppm): δ 172.2 ($C=O$), 152.1 (phenyl $C-OCH_3$), 151.8 (fluorenyl q-C), 151.5 (fluorenyl q-C), 151.3 (fluorenyl q-C), 151.0 (fluorenyl q-C), 150.8 (fluorenyl q-C), 150.3 (phenyl $C-OCH_2-$), 140.82 (fluorenyl q-C), 140.58 (fluorenyl q-C), 140.38 (fluorenyl q-C), 140.18 (fluorenyl q-C), 140.02 (fluorenyl q-C), 139.82 (fluorenyl q-C), 137.18 (fluorenyl q-C), 136.82 (fluorenyl q-C), 131.8 (fluorenyl q-C), 131.4 (fluorenyl q-C), 130.6 (fluorenyl q-C), 128.4 (fluorenyl *C*-H), 128.1 (fluorenyl *C*-H), 127.1 (fluorenyl *C*-H), 126.8 (fluorenyl *C*-H), 126.3 (fluorenyl *C*-H), 126.1 (fluorenyl *C*-H), 124.7 (fluorenyl *C*-H), 124.4 (fluorenyl *C*-H), 122.9 (phenyl q-C), 121.6 (phenyl q-C), 120.1 (fluorenyl *C*-H), 119.9 (fluorenyl *C*-H), 119.7 (fluorenyl *C*-H), 119.5 (fluorenyl *C*-H), 119.4 (fluorenyl *C*-H), 117.2 (phenyl *C*-H), 115.6 (phenyl *C*-H), 69.3 ($-OCH_2-$), 66.5 ($-CH_2O(C=O)$), 56.78 ($-OCH_3$), 55.80 ($-C(CH_3)_2Br$), 55.36 ($C(Ph)_2(C_6H_{13})_2$), 55.28 ($C(Ph)_2(C_6H_{13})_2$), 55.19 ($C(Ph)_2(C_6H_{13})_2$), 40.1 (CH_2), 31.82 (CH_2), 31.78 (CH_2), 30.8 ($-C(CH_3)_2Br$), 29.7 (CH_2), 29.6 (CH_2), 26.1 (CH_2), 25.2 (CH_2), 24.1 (CH_2), 23.8 (CH_2), 22.52 (CH_2), 14.82 (CH_3).

4-Cyano-4′-(6-hydroxyhexan-1-yloxy)-biphenyl (16). 6-Bromo-1-hexanol (4.60 g, 25.64 mmol) was added to a mixture of 4′-hydroxy-4-biphenylcarbonitile (5.00 g, 25.64 mmol) and potassium carbonate (6.0 g) in DMF (60 mL). The reaction mixture was stirred for 1 day at 60 °C. After the precipitate was filtered off, the mixture was washed by water and extracted with ether. The organic layer was washed with brine (2 × 150 mL) and dried over sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether: ethyl acetate (2:1) as the eluent to yield **16** (6.39 g, 84.4%) as white powder. ^{1}H NMR ($CDCl_3$, ppm): δ 7.69 (d, phenyl H, 2H), 7.63 (d, phenyl H, 2H), 7.51 (d, phenyl H, 2H), 6.97 (d, phenyl H, 2H), 4.01 (t, $PhOCH_2-$, 2H), 3.66 (q, $-CH_2OH$, 2H), 3.41 (m, $-OH$, 1H), 1.82−1.23 (m, $-CH_2(CH_2)_4CH_2OH$, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 159.76 (phenyl $C-O$), 145.27 (phenyl q-C), 132.56 (phenyl $C-H$), 131.28 (phenyl q-C), 128.32 (phenyl $C-H$), 127.07 (phenyl $C-H$), 119.12 ($-CN$), 115.09 (phenyl $C-H$), 110.00 (phenyl $C-CN$), 68.02 ($PhOCH_2-$), 62.80 ($-CH_2OH$), 32.66 (CH_2), 29.19 (CH_2), 25.55 (CH_2), 24.88 (CH_2).

6-(4′-Cyanobiphenoxy)hexyl methacrylate (17). A mixture of **16** (6.32 g, 21.3 mmol), *N*,*N*′-dicyclohexylcarbodiimide (4.5 g), 4-(dimethylamino)pyridine (DMAP) (0.70 g), and the methacrylic acid (3.5 mL) in dichloromethane (63.2 mL) was stirred at room temperature for 1 day. The mixture was poured into a lot of water (300 mL) and extracted by dichloromethane. The organic layer was washed with brine (2 × 150 mL) and dried over sodium sulfate. After the solvent was evaporated off, the residue was purified by column chromatography on silica gel with petroleum ether: ethyl acetate (2:1) as the eluent. The products were then purified by recrystallization from a mixture solution of dichloromethane:ethanol (1:5) to yield **17** (5.83 g, 75%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.69 (d, phenyl H, 2H), 7.64 (d, phenyl H, 2H), 7.53 (d, phenyl H, 2H), 7.0 (d, phenyl H, 2H), 6.10, 6.55 (2 s, $C=CH_2$, 2H), 4.17 (t, $-CH_2O(C=O)$, 2H), 4.01 (t, $PhOCH_2-$, 2H), 1.94 (s, $-CH_3$, 3H), 1.83−1.51 (m, $-CH_2(CH_2)_4CH_2O(C=O)$, 8H). ^{13}C NMR ($CDCl_3$, ppm): δ 167.48 ($C=O$), 159.75 (phenyl $C-O$), 145.21 (phenyl q-C), 136.50 ($-(CH_3)C=CH_2$), 132.54 (phenyl $C-H$), 131.26 (phenyl q-C), 128.32 (phenyl $C-H$), 127.04 (phenyl $C-H$), 126.23 ($-(CH_3)C=CH_2$), 119.09 ($-CN$), 115.09 (phenyl $C-H$), 110.03 (phenyl $C-CN$), 67.94 ($PhOCH_2-$), 64.60 ($-CH_2O-$), 29.11 (CH_2), 28.56 (CH_2), 26.02 (CH_2), 25.97 (CH_2), 18.33 (CH_3).

4-Cyano-4′-biphenyl 2-bromo-2-methyl propanoate (19). 2-bromoisobutyryl bromide (1.9 mL, 15.4 mmol) was added dropwise to a mixture of 4′-hydroxy-4-biphenylcarbonitile (2.00 g, 10.26 mmol), triethylamine (2.86 mL, 20.5 mmol) in THF (30 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solution was washed with a large amount of water (200 mL) to remove the salt and the excess of 2-bromoisobutyryl bromide before extraction with chloroform. The organic layer was dried over anhydrous sodium sulfate, and the excess solvent was evaporated off. The residue was purified by column chromatography on silica gel with petroleum ether:ethyl acetate (5:1) as the eluent. The products were purified by recrystallization from the mixture solution of dichloromethane: ethanol (1:5) to yield **19** (2.32 g, 70%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.73 (d, phenyl H, 2H), 7.66 (d, phenyl H, 2H), 7.62 (d, phenyl H, 2H), 7.26 (d, phenyl H, 2H), 2.09 (s, $-C(CH_3)_2$, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 170.4 ($C=O$), 151.44 (phenyl $C-O$), 144.8 (phenyl q-C), 137.6 (phenyl q-C), 132.9 (phenyl $C-H$), 128.6 (phenyl $C-H$), 127.8 (phenyl $C-H$), 122.01 (phenyl $C-H$), 118.9 ($-CN$), 111.43 (phenyl $C-CN$), 55.41 ($-C(CH_3)_2$), 30.82 (CH_3).

Synthesis of OFB—PCBHMA Block Copolymers by ATRP: In a typical run, a glass tube was loaded with CuBr (3.15 mg, 0.022 mmol), OFB macroinitiator (0.052 g, 0.022 mmol), 6-(4′-cyanobiphenoxy)hexyl methacrylate (0.4 g, 1.1 mmol) and 0.5 mL of *o*-dichlobenzene. The glass tube was degassed with three freeze−pump−thaw cycles to remove air and moisture. The mixture was stirred for 10 min, and then 6 μL of HMTETA was introduced with a syringe. The glass tube was then immersed in an oil bath at 60 °C. After the reaction was stirred for 3 h, a solution was taken for ^{1}H NMR measurement. Conversion was 85%, derived from the integration of the phenyl protons of the monomer at 7.0 ppm ($I_{7.0}$) and that of the polymer at 6.9 ppm ($I_{6.9}$). The conversion is calculated by eq 2.

$$\text{Conv}\ (\%) = (I_{6.9}/(I_{7.0} + I_{6.9})) \times 100\% \qquad (2)$$

The solution was diluted in THF and then passed through neutral alumina to remove the catalysts. The polymers were precipitated into excess hexane and dried in a vacuum oven at 40 °C to yield white powdery samples. Yield: 250 mg (56%); M_n (GPC) = 10 100; M_w/M_n = 1.12.

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Supporting Information Available: Text detailing the MALDI and POM experiments, figures showing the MALDI-TOF spctrum of the OFB initiator and the POM image of **P1**, amd a table summarizing the UV-vis and photoluminescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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