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Supporting Information

Tacticity Effect in Side-Chain Photoluminescent Polymers

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Abstract: Stereoregular side-chain photoluminescent (PL) polymers were synthesized via the stereospecific polymerization of 9,9-dibutyl-2-(4-vinylphenyl)-9*H*-fluorene. The resulting isotactic, syndiotactic and atactic poly(9,9-dibutyl-2-(4-vinylphenyl)-9*H*-fluorene) were used as stereoregular polymer samples for examining the configurational tacticity effect on their PL properties. Our results revealed a unique tacticity-dependant effect as observed by an obvious red-shifting of the PL emission by increasing the degree of isotacticity of these stereoregular polymers; despite the ultraviolet spectra of these polymers exhibited similar absorption patterns. This study provides a new structural design for the syntheses of PL polymers.

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Experimental Section

General Procedure

All reactions and manipulations were conducted under a N_2 atmosphere using standard Schlenk line or dry box techniques. Solvents and common reagents were obtained commercially and used either as received or purified through distillation over sodium/benzophenone. Dimethyl sulfoxide (DMSO, >99%), sodium hydroxide (NaOH, >98%), bromobenzene (>99.5%), 4-bromostyrene (>97%), 1-bromobutane (C_4H_9Br, >99%), 2-bromofluorene (>95%), triisopropyl borate [$(i\text{-PrO})_3B$, >98%], tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$, >99%], potassium carbonate (K_2CO_3, >99%), magnesium sulfate ($MgSO_4$, >99.5%), *n*-butyllithium (*n*-BuLi, 2.5 M in hexane), and triethylaluminum (TEA, 1 M in hexane) were purchased from Aldrich. 9,9-Dibutylfluorenyl-2-boronic acid was prepared according to a procedure described in the literatures.[1,2] Nickel(II) acetylacetonate [$Ni(acac)_2$, >95%] and trimethoxy(pentamethylcyclopentadienyl)titanium(IV) [$Cp^*Ti(OMe)_3$] were purchased from Strem Chemicals and used as received. Methylaluminoxane (MAO, 14% in toluene), purchased from Albemarle, was dried under vacuum to remove residual trimethylaluminum (TMA); the resulting TMA-free MAO was diluted in toluene to the desired concentration prior to use.

Synthesis of 9,9-dibutyl-2-phenyl-9*H*-fluorene (DBPF)

A mixture of 9,9-dibutylfluorenyl-2-boronic acid (3.87 g, 12.0 mmol), K_2CO_3 (2.4 M aqueous solution, 5.0 mL), bromobenzene (1.05 mL, 10.0 mmol), and $Pd(PPh_3)_4$ (0.116 g, 0.100 mmol) in THF (50 mL) was heated at 80 °C with stirring for 2 days. After cooling to room temperature, the mixture was poured into water and extracted with chloroform. The organic phase was dried (anhydrous $MgSO_4$), filtered, and concentrated to dryness. The residue was purified through column chromatography (aluminum oxide, hexane) to afford a white solid (2.5 g, 70% yield), i.e., 9,9-dibutyl-2-phenyl-9*H*-fluorene (DBPF).

Synthesis of 9,9-dibutyl-2-(4-vinylphenyl)-9*H*-fluorene (DBVPF)

A mixture of 9,9-dibutylfluorenyl-2-boronic acid (7.74 g, 24.0 mmol), K_2CO_3 (2.4 M aqueous solution, 5.0 mL), 4-bromostyrene (2.7 mL, 20.0 mmol), and $Pd(PPh_3)_4$ (0.116 g, 0.100 mmol) in THF (50 mL) was heated at 80 °C with stirring for 2 days. After cooling to room temperature, the mixture was poured into water and extracted with chloroform. The organic phase was dried (anhydrous $MgSO_4$), filtered, and concentrated to dryness. The residue was purified through column chromatography (aluminum oxide, hexane) to afford a white solid (6.1 g, 80% yield), i.e., 9,9-dibutyl-2-(4-vinylphenyl)-9*H*-fluorene (DBVPF).

Synthesis of syndiotactic poly(9,9-dibutyl-2-(4-vinylphenyl)-9*H*-fluorene) (syndiotactic PDBVPF)

A 100-mL Schlenk tube, equipped with a magnetic stirrer, was dried at 120 °C under vacuum. After cooling and refilling with N_2, the Schlenk tube was charged with toluene (15 mL), DBVPF (1.90 g, 5.00 mmol), TEA (1.0 M in toluene, 0.5 mL), and MAO (1.0 M in toluene, 10.0 mL). After stirring the solution at 50 °C for 5 min, the Schlenk tube was charged with $Cp^*Ti(OMe)_3$ (0.02 M in toluene, 5 mL) to initiate polymerization. After 3 h at 50 °C, the reaction was quenched through the addition of excess acidic methanol, which led to the deposition of a white precipitate. Filtration and drying under vacuum provided 1.5 g of syndiotactic PDBVPF, i.e., PDBVPF92 [M_n = 10,700 g/mol; M_w/M_n = 1.50, by gel permeation chromatography (GPC) in THF at 35 °C].

Synthesis of atactic poly(9,9-dibutyl-2-(4-vinylphenyl)-9*H*-fluorene) (atactic PDBVPF)

A 100-mL Schlenk tube, equipped with a magnetic stirrer, was dried at 120 °C under vacuum. After cooling and refilling with N_2, the Schlenk tube was charged with DBVPF (1.90 g, 5.00 mmol) and THF (20 mL). This solution was cooled to –78 °C and then charged with *n*-BuLi (0.1 mL) to initiate polymerization. After 3h at –78 °C, the reaction was quenched through the addition of excess methanol, which led to deposition of a white precipitate. Filtration and drying under vacuum provided 1.7 g of atactic PDBVPF, i.e., PDBVPF71 (M_n = 10,000 g/mol; M_w/M_n = 1.16, by GPC in THF at 35 °C).

Synthesis of isotactic poly(9,9-dibutyl-2-(4-vinylphenyl)-9*H*-fluorene) (isotactic PDBVPF)

A 100-mL Schlenk tube, equipped with a magnetic stirrer, was dried at 120 °C under vacuum. After cooling and refilling with N_2, the Schlenk tube was charged with DBVPF (1.90 g, 5.00 mmol), toluene (20 mL), TEA (1.00 mL, 1.00 mmol), and MAO (10.0 mL, 10.0 mmol). After stirring the solution at 50 °C for 5 min, the Schlenk tube was charged with $Ni(acac)_2$ (1.0 M in toluene, 1.0 mL) to initiate polymerization. After 3 h at 50 °C, the reaction was quenched through the addition of excess acidic methanol, which led to the deposition of a white precipitate. Filtration and drying under vacuum provided 1.1 g of isotactic PDBVPF, i.e., PDBVPF33 (M_n = 14,000 g/mol; M_w/M_n = 1.38, by GPC in THF at 35 °C).

Polymer analyses

The molecular weights (M_w, M_n) and molecular weight distributions (MWDs, M_w/M_n) were determined through gel permeation chromatography (GPC) using a Waters 150-CALAC apparatus, a refractive index (RI) detector, and a set of U-Styragel columns (10^6, 10^5, 10^4, and 10^3 pore sizes, in series). The chromatograms were recorded at 35 °C using THF as the solvent. PS samples of narrow MWD (absolute molecular weights ranging from 980 to 2,110,000) were used as standards for calibration; the values of R^2 of the ideal calibrated lines were limited to 0.999. ^1H and ^{13}C NMR spectra were recorded using a VARIAN VNMRS 700 MHz NMR spectrometer. The polymer samples were dissolved in chloroform-*d*; the spectra were recorded at a temperature of 50 °C.

The stereoregularity (tacticity) of styryl polymers can be typically determined by ^{13}C NMR spectroscopy through analyzing the aromatic quaternary carbon (with the typical chemical shift between 143 and 146 ppm; see references 3 and 4 of supporting information) bonding on to the polymer main chain or by analyzing the methylene carbon (with the typical chemical shift between 42.5 to 46.5 ppm; see reference 5 of supporting information) within the polymer main chain. Efforts to evaluate the tacticity of PDBVPFs through analyzing ^{13}C resonance of the methylene carbon were unsuccessful because of the presence of other ^{13}C resonances in the 42.5 to 46.5 ppm region. Accordingly, measurement of the tacticity of PDBVPF samples prepared in this study can only depend on the analyses of the aromatic quaternary carbon resonances. Figure S3 shows the comparison of ^{13}C resonances between isotactic, atactic and syndiotactic PDBVPFs. As revealed by Figure S3, ^{13}C NMR spectra clearly reveal the presence of the sharp syndiotactic (at δ = 144.2 ppm) and the sharp isotactic (at δ = 145.3 ppm) aromatic quaternary ^{13}C resonances. By comparison of these ^{13}C NMR resonances with the reported data (references 3 and 4 of supporting information), these ^{13}C NMR resonances can be denoted as the syndiotatic *rr* triads and isotactic *mm* triads, respectively. Unfortunately, these ^{13}C NMR spectra are not sufficient to provide the full scale analyses of the stereoregularity (tacticity) of PDBVPF samples because of the lack of the *mr* resonance peaks in these ^{13}C NMR spectra. From Figure S3, the syndiotactic and isotactic PDBVPFs show the respective sharp resonances at 144.2 and 145.3 ppm; however, due to the absence of the *mr* resonance peaks, we are unable to locate the boundary between *mm* and *mr* triads and the boundary between *mr* and *rr* triads. This analytical problem can be resolved by ^{13}C resonance comparison of PDBVPFs with the stereoregular poly(9,9-dimethyl-2-(4-vinylphenyl)-9*H*-fluorene) (PDMVPF). Of note, stereoregular PDMVPFs have been prepared as the targeting materials for investigation of their side-chain photoluminesence properties in our previous studies. Although these materials failed to meet the experimental requirement (the isotactic and syndiotactic PDMVPFs were found to have poor solubility in organic sovlent), these samples offer excellent structural comparison for determining the tacticity of PDBVPF samples. As shown in Figure S4, atactic PDBVPF and atactic PDMVPF show similar aromatic quaternary ^{13}C resonances in the *mm* and *rr* regions. The major differences between the ^{13}C NMR spectra of the atactic PDBVPF and the PDMVPF samples are that the ^{13}C NMR spectrum of the atactic PDMVPF contains apparent resonance peaks between 144.2 and 145.3 ppm. These new aromatic quaternary ^{13}C resonances can be denoted as the resonances of *mr* triads by comparing with data reported by Li and Deffieux (references 3 and 4 in the supporting information). Thus, boundaries between *mm* and *mr* and between *mr* and *rr* can be determined and located based on these spectroscopy analyses. As a result, the tacticity (*mm*, *mr* and *rr*) of the prepared PDBVPF samples cane be determined thereof. In summary, our analyses of the tacticity of PDBVPF samples are based on the ^{13}C NMR analyses of the aromatic quaternary ^{13}C resonances. The *mm*, *mr* and *rr* ratios can be calculated by the resonance integral between 145.0 and 145.8 ppm, between 144.4 and 145.0 ppm and between 143.6 and 144.4 ppm, respectively.

Thermogravimetric Analysis (TGA)

The thermal stabilities of the polymers were examined under N_2 at temperatures from 30 to 800 °C using a TA Instruments TGA Q50 apparatus operated at a heating rate of 10 °C/min. The sample weight was fixed at 5 mg.

Differential Scanning Calorimetry (DSC)

The powder samples were first heated to 300 °C for 2 min, using a PerkinElmer Pyris1 apparatus equipped with a compressor of Intracooler 2P, to eliminate the thermal history from synthesis. The samples were then slowly cooled to 25 °C at a rate of 10 °C/min to examine the non-isothermal crystallization. Glass transition temperatures (T_g) were probed during heating at a scan rate of 10 °C/min, with calibration using cyclohexane and indium as standard materials.

Ultraviolet–Visible (UV–Vis) Absorption Spectrometry

Stock solutions of stereoregular polymers were prepared in THF at a concentration of 10^{-4} or 10^{-6} M. UV–Vis absorption spectra were recorded using a JASCO V-770 spectrophotometer.

PL Spectrometry

PL spectra were recorded using a LabGuide X350 fluorescence spectrophotometer equipped with a 450W Xe lamp as the continuous light source. Thin films of the various tactic polymers were prepared using the spin-coating method. The powder samples of the stereoregular polymers were first dissolved in THF at a concentration of 3 wt%. When completely dissolved, the solutions were spread onto glass substrates by spin-coating at 1000 rpm for 90s. Finally, the thin films were dried in a vacuum oven at 25 °C for 1 h to remove the residual solvent. PL spectra were recorded immediately thereafter.

Photoinduced oxidation

The photo-irradiation of stereoregular PDBVPF thin films on glass substrates was accomplished using UV light source with 254 nm [3 mW $(cm^2\ s)^{-1}$] for different time periods.

Computer simulation

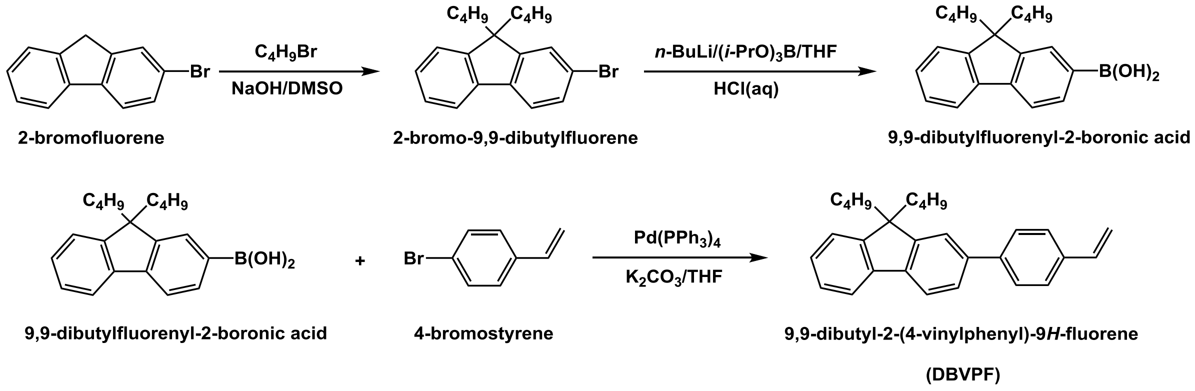
To estimate the averaged correlation length and the corresponding chain conformation, the computer simulation was performed using Materials Studio software package. The stereoregular PDBVPF with 28 or 36 pendent fluorophore units adopting syndiotactic or isotactic configuration, respectively, (corresponding to molecular weights of 10700 and 14000 g/mol for PDBVPF92 and PDBVPF33, respectively) was constructed. The geometric energy was minimized using the Smart Minimizer incorporated in the Discover Molecular Simulation program.

Photopatterning of stereoregular polymer thin films

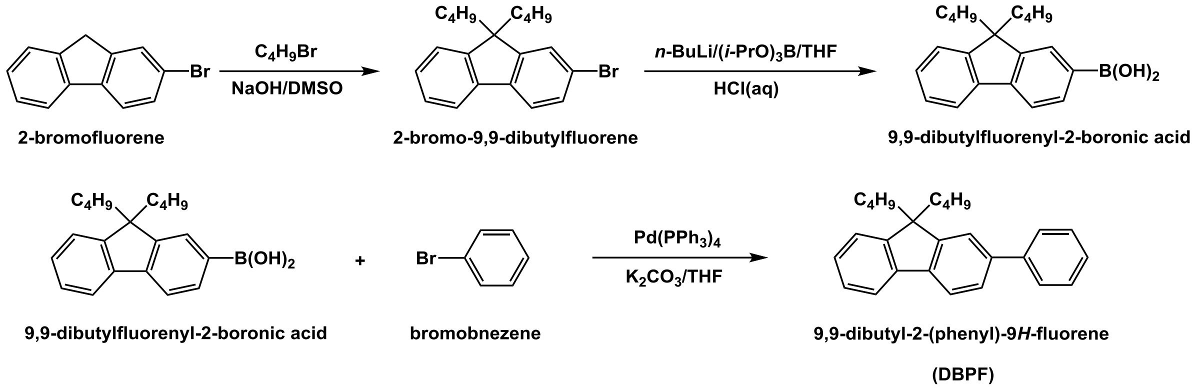
First, a fish-shaped mask was placed on the stereoregular polymer thin film. With UV irradiation (at $\lambda = 254$ nm) for 6h, PL emission of the exposed film without mask was examined by photoexcitation (at $\lambda = 365$ nm), in which blue and green emissive colours were observed in the screened and exposed regions, respectively. This shows a blue fish swimming in green water. After immersion in THF solvent for 1 min to remove the unexposed fish-shaped polymer, only green emission could be observed upon photoexcitation (at $\lambda = 365$ nm).

Supplementary Schemes

Scheme S1. Synthesis of styrene monomer substituted in the para position with a fluorene unit.



Scheme S2. Synthesis of benzene substituted with a fluorene unit.



Supplementary Figures

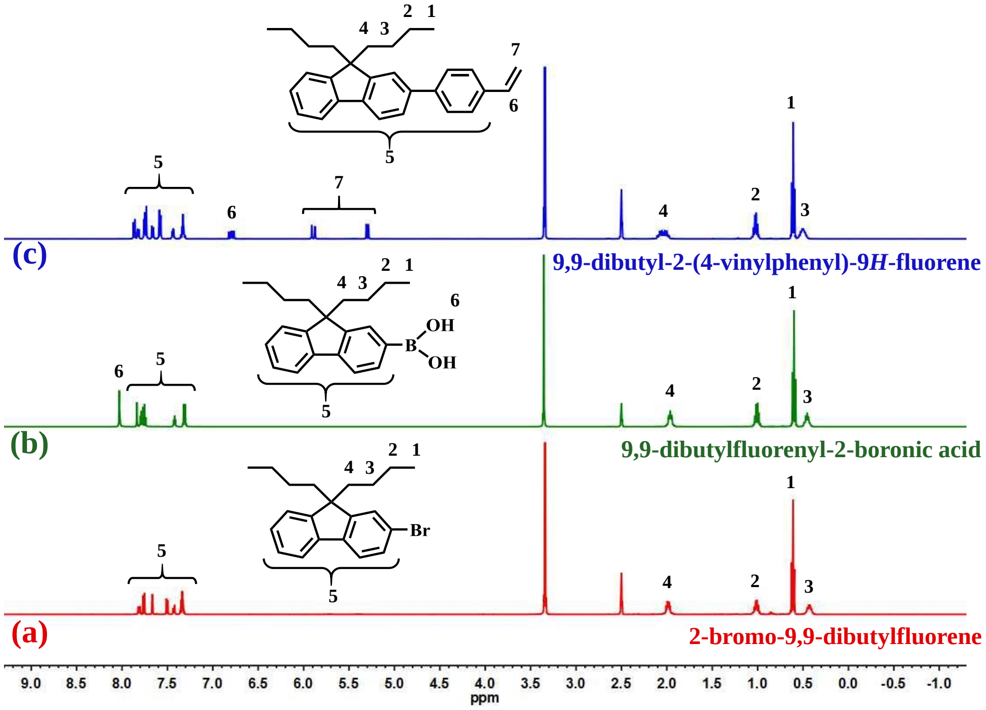


Figure S1. ^{1}H NMR spectra of monomers (a) 2-bromo-9,9-dibutylfluorene, (b) 9,9-dibutylfluorenyl-2-boronic acid, and (c) 9,9-dibutyl-2-(4-vinylphenyl)-*9H*-fluorene (DBVPF).

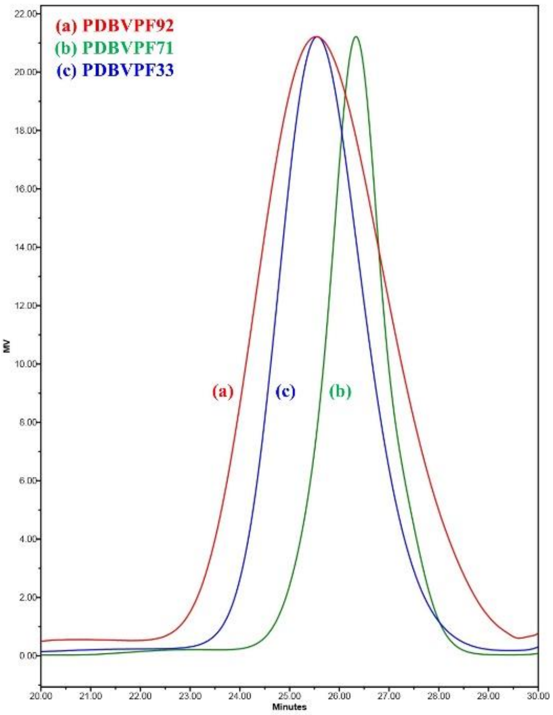


Figure S2. Gel permeation chromatography curves of (a) PDBVPF92 (M_n = 10,700 g/mol; M_w/M_n = 1.50), (b) PDBVPF71 (M_n = 10,000 g/mol; M_w/M_n = 1.16), and (c) PDBVPF33 (M_n = 14,000 g/mol; M_w/M_n = 1.38) measured in THF at 35 °C.

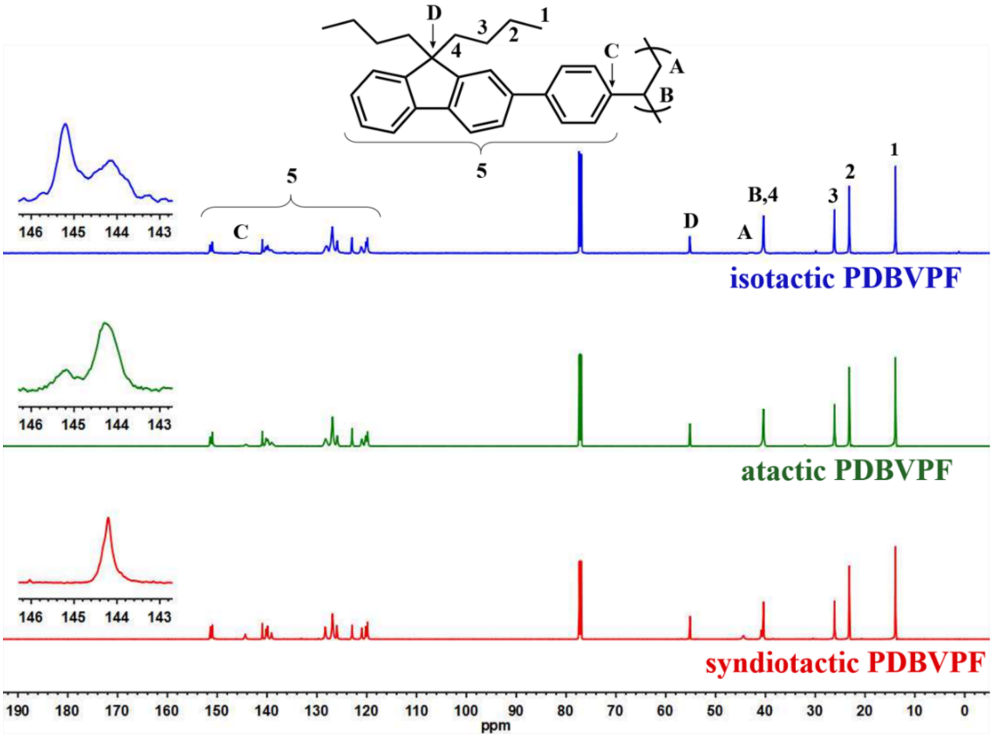


Figure S3. ^{13}C NMR spectra of the PDBVPF samples.

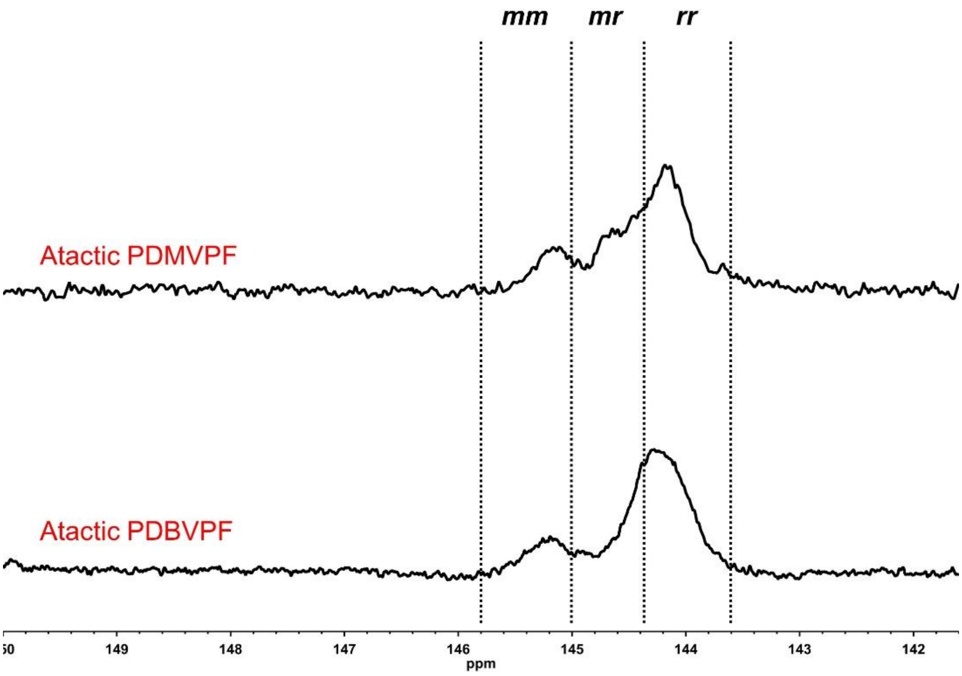


Figure S4. ^{13}C NMR spectra of atactic PDBVPF and PDMVPF samples.

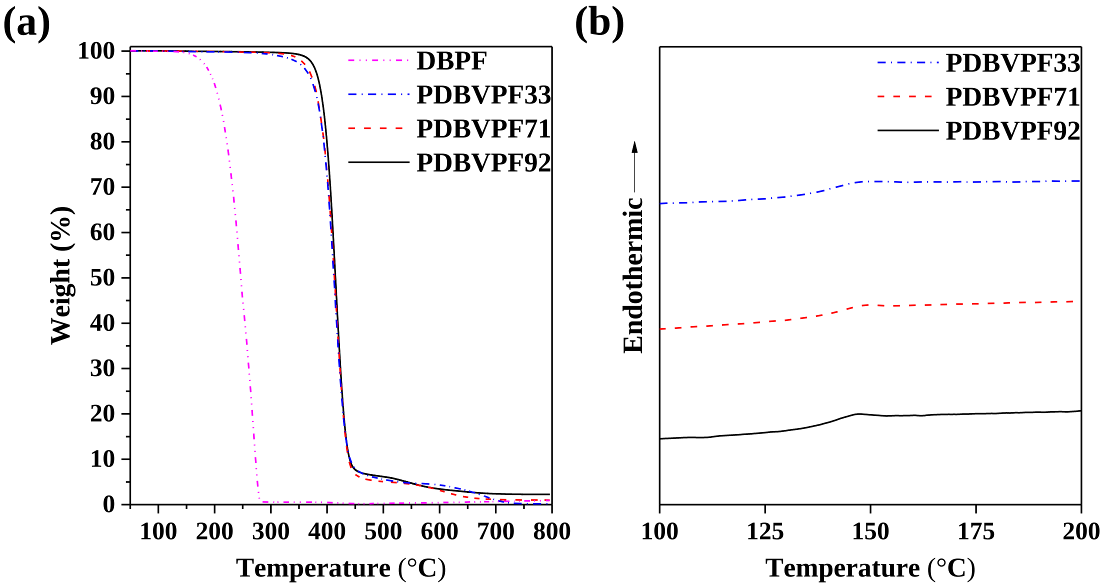


Figure S5. (a) Thermogravimetric analysis and (b) differential scanning calorimetry profiles of DBPF monomer and PDBVPF polymers with various stereoregularities. Heating rate: 10 °C/min.

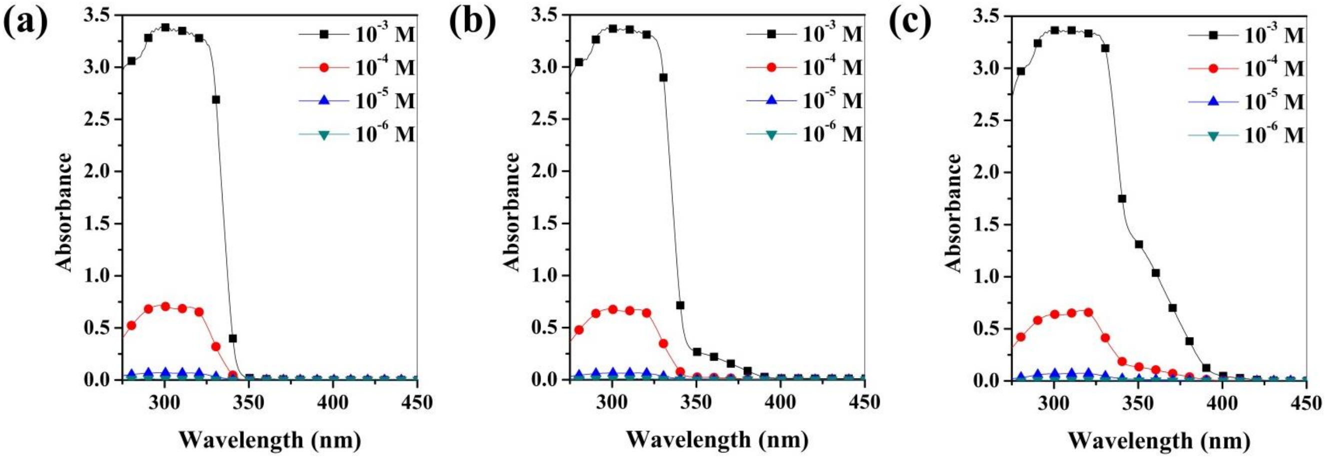


Figure S6. UV-Vis spectra of stereoregular PDBVPF polymers in THF at concentrations from 10^{-3} to 10^{-6} M. (a) PDBVPF92, (b) PDBVPF71, and (c) PDBVPF33.

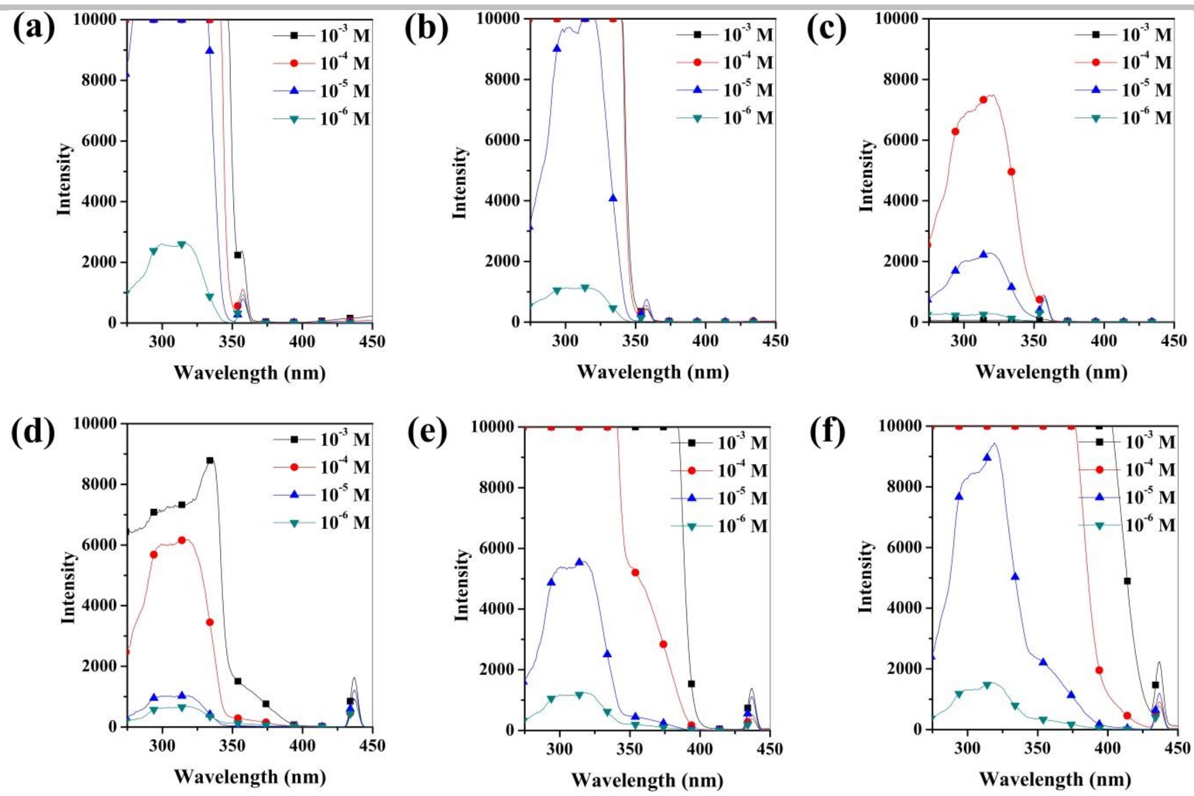


Figure S7. PL excitation (PLE) spectra of stereoregular PDBVPF polymers in THF at concentrations from 10^{-3} to 10^{-6} M for (a)(d) PDBVPF92, (b)(e) PDBVPF71, and (c)(f) PDBVPF33. The PLE spectra of (a), (b), (c) as well as (d), (e), (f) were monitored at 357 nm and 436 nm, respectively.

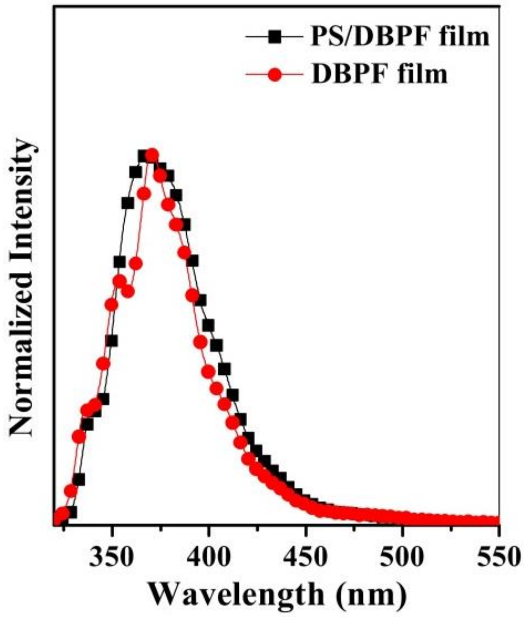


Figure S8. PL spectra of the neat DBPF film and the DBPF/PS blended film (DBPF doped in PS by a 1:1 weight ratio). Excitation wavelength: 300 nm. Similar profiles indicate that PS chains could not strongly interact with the DBPF due to their dissimilar chemical structures and incompatible miscibility.

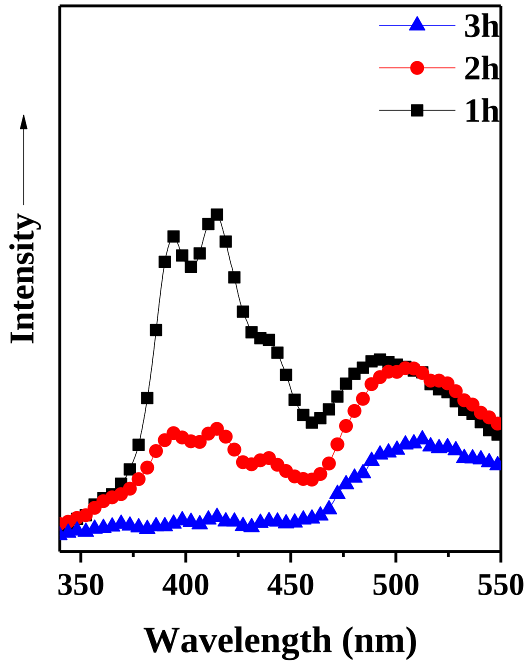


Figure S9. PL spectra of PDBVPF71 thin films after UV irradiation for various time periods. Excitation wavelength is 300 nm. With increasing exposure time, the short-wavelength emission peaks gradually become weaker and eventually disappear (at an exposure time of above 3 h). A new emission peak appears at about 520 nm.

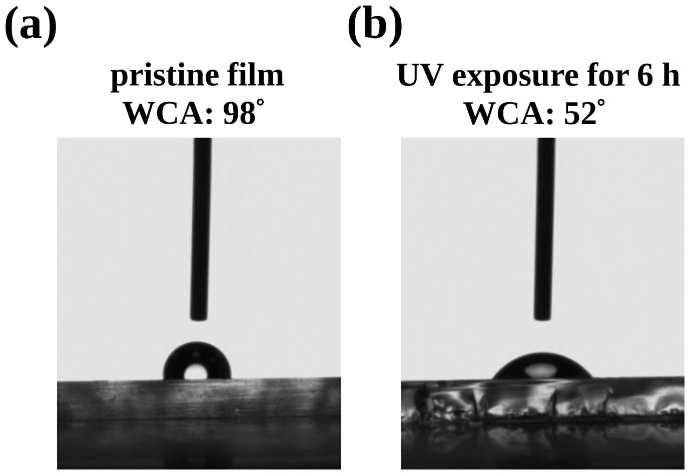


Figure S10. Water contact angle (WCA) measurements of PDBVPF71 thin film (a) before (98°) and (b) after (52°) UV irradiation under atmosphere for 6 h. The PDBVPF71 thin film changes from hydrophobic to hydrophilic after UV irradiation.

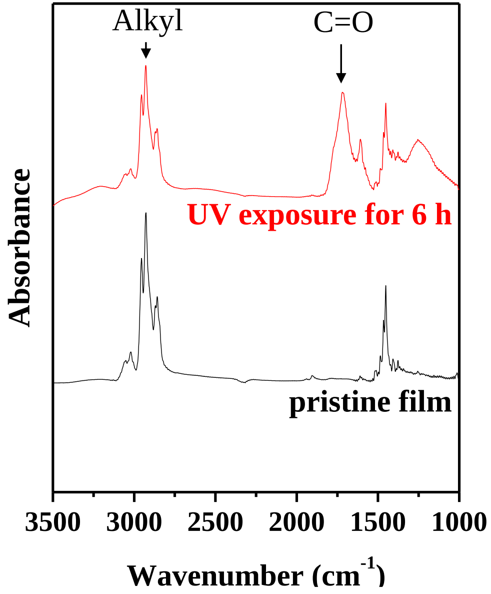


Figure S11. Fourier transform infrared spectroscopy spectra of PDBVPF71 thin film (a) before and (b) after UV irradiation under atmosphere for 6 h. The peaks at 2956, 2922, and 2852 cm^{-1} are assigned to the stretching modes of the alkyl side chains. The peaks at 3040 and 1450 cm^{-1} are attributed to aromatic C-H stretching; these peaks are almost unchanged after UV irradiation. A new absorption band at 1715 cm^{-1} appears after UV irradiation, corresponding to the C=O stretching mode of an aromatic ketone (fluorenone) due to photo-oxidation. The enhanced hydrophilicity of the UV-exposed PDBVPF71 film was thus due to photoirradiation-triggered oxidation of the pendent fluorenes.

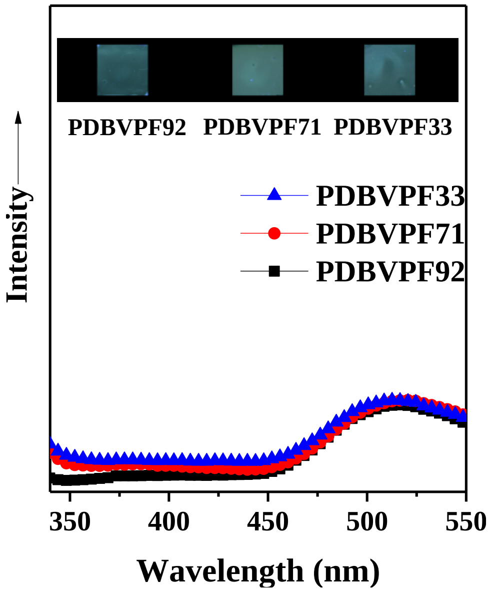


Figure S12. PL spectra of PDBVPF thin films after UV irradiation under atmosphere for 6 h. Excitation wavelength is 300 nm. The inset shows a PL photograph taken under UV illumination of PDBVPF thin films after UV irradiation under atmosphere for 6 h. After UV irradiation for 6 h, all of the stereoregular PDBVPF thin films exhibited green emission at 520 nm.

Supplementary Table

Table S1. Quantum efficiency of the stereoregular PDBVPF polymers

Quantum Yield (Φ_F)	Dilute solution (10^{-5}M)	Film state
PDBVPF92 (*rr*=92%, *mm*=0%)	30	69
PDBVPF71 (*rr*=71%, *mm*=20%)	42	68
PDBVPF33 (*rr*=33%, *mm*=58%)	43	64

References

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