

Structure–Property Relationships of Solution-Processable Diarylethene-Based Main-Chain Photochromic Polymers

Sandile Gwebu, David Marshall, Prashant Sonar, Bronson Philippa, and George Vamvounis*

A series of alternating copolymers of a dithienylethene with di-*n*-alkyl-fluorene (P1–P3), di-*n*-hexylphenylene (P4), 9-heptadecanycarbazole (P5), and 4,8-bis(3,5-dioctyl-2-thienyl)-1,5-dithia-*s*-indacene (P6) are designed, synthesized, and characterized. All of the polymers are soluble in common organic solvents such as chloroform, dichloromethane, toluene, and tetrahydrofuran. The side-chain length affected the solubility of the polymer, molecular weight, and the glass transition temperature. Solutions of P1–P6 show photochromism with high quantum yields of 6- π electrocyclization (41–87%) and cycloreversion (0.4–1.1%). These polymers also formed uniform thin films and the rates of solid state photoisomerization are measured relative to P4, which has the highest cyclization and cycloreversion rates. The color of the photochromic polymer is tuned according to the comonomer and the maximum absorption wavelength ranged from 569 to 675 nm in the closed isomeric form. All the polymers are thermally stable and show no signs of photodegradation after being exposed to UV-light for 120 min in air. Based on these promising results, these polymers may be useful for multifunctional organic electronic devices.

flexible, efficient, and long-lasting devices. Solution processable conjugated polymers have been used as the active semiconductor layer in these devices because simple and inexpensive processing can readily form uniform thin-films. To broaden the foot-print of these devices, multifunctional conjugated materials are in demand to allow for instance smart solar cell windows^[6] and nondestructive memory devices.^[7] Organic photochromic materials are ideal in this regard because they are conjugated and their optoelectronic properties can be tuned using light. However, organic photochromic materials developed so far have been primarily limited to crystalline small molecule materials which are not solution processable or side-chain photochromic polymers which have poor charge transport properties.^[8] This study explores synthetic strategies to produce solution-processable main-chain photochromic polymers. The quality of

the films and their photoswitchable properties are investigated as a function of alkyl chain length and conjugation length.

Photochromic materials can be broadly classed as thermally-reversible or light-reversible materials.^[9] For organic optoelectronic and photonic devices, light-reversible materials are ideal because of the thermal stability of both colorless and colored states.^[10,11] One class of light-reversible materials is based on the dithienylethene (DTE) motif which undergoes an efficient 6- π electrocyclization and cycloreversion process in the presence of UV–vis light to switch from their colorless open-isomeric form to their colored closed-isomeric form.^[11,12] Furthermore, DTEs have been shown to be fatigue resistant over 14 000 cycles in solution and 30 000 cycles in the single crystalline phase, showing great promise for robust organic electronic devices.^[9,13] However, studies to date have primarily focused on the solution or single crystal photonic properties, which have limited applications in organic electronic devices, since these devices typically require uniform thin films.^[14–16]

Solution-processable thin-film forming photochromic materials have been achieved by dispersing photochromic molecules into an insulating or semiconducting polymer matrix. These photochrome dispersed films have successfully controlled the emission,^[17] charge transport,^[18–20] and energy conversion^[6] properties of the resultant films. For instance, the charge transport in a field effect transistor was controlled by switching a

1. Introduction

Organic electronics, such as organic field effect transistors (OFETs),^[1–3] organic light emitting diodes (OLEDs),^[4] actuators,^[5] and organic photovoltaics (OPVs)^[6] have the potential to revolutionize the semiconductor industry with ultrathin,

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photochrome containing dielectric layer.^[18–20] Furthermore, blended films have been used as photoactive layers in solar cell devices to control their absorption properties with a given light source.^[6] Although solid matrices can be used to modify the bulk film properties, these films are limited to the photochrome loading, where Li et al.^[21] has shown that phase segregation of a photochrome in P3HT occurred above 10 wt%. Clustering due to phase separation has also been shown in OLEDs at low concentrations (6 wt%).^[22] To limit this phase segregation, polymers have been developed that contain photochromic moieties. To that end, side-chain photochromic polymers have been developed by Kobatake^[23] and Branda.^[24] These side-chain polymers are excellent materials for photonic applications; however charge conduction, which is required for organic electronic devices, may be limited due to the lack of intrachain charge transport.^[8]

Polymers which contain the DTE photochrome along the main-chain are ideal for organic electronic devices because they can enable inter- and intrachain transport in the closed form. However, DTEs lack alkyl chains that are required for solubilization, which therefore inhibits their solution processability.^[25,26] To overcome insolubility, aromatic co-monomers containing solubilizing alkyl-chains based on fluorene,^[27] phenylene,^[8,28,29] and quinolone^[30] can be used, however, most of the resultant polymers either have poor solubility,^[8] low molecular weights,^[27,31] poor photoswitching quantum yields in solid state^[27] or are photochemically unstable.^[29] For instance, Kawai et al.^[27] reported a main chain photochromic copolymer comprised of a hexafluorocyclopentene-benzothiophene switching unit and dioctylfluorene derivatives that were found to be photochemically unstable. In addition, Zerbi and coworkers^[8] prepared photo-switchable main-chain conjugated polymers incorporating hexafluorocyclopentene-based switching units and dialkoxyphenylene derivatives (dihexyloxyphenylenevinylene or didodecyloxy-phenylenevinylene), of which the dihexyloxyphenylenevinylene-based polymer showed lower solubility in chloroform. Solubility and polymer molecular weights are inter-related due to the presence of the solubilizing group, and the switching ability can be attributed to the steric encumbrance.^[32,33] Therefore, the design of main-chain photochromic polymers with improved thin-film photochromic properties requires a fundamental understanding of the structural requirements for optimal solubility, thin film formation and photoswitching quantum yields. This study, therefore, explores the effect of the alkyl side-chain length and comonomer conjugation to understand the design requirements for efficient main-chain photoswitchable polymers.

2. Experimental Section

2.1. Chemicals and Reagents

2-Methylthiophene, *N*-bromosuccinimide (NBS), trimethylsilyl chloride (TMSCl), *n*-butyllithium (*n*-BuLi), fluorene, bromine, tetrabutylammonium bromide, 1-bromopropane, bromobenzene and phenylboronic acid, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2]dioxaborolane were pur-

chased from Sigma Aldrich. 9,9-di-*n*-hexylfluorene-2,7-diboric acid bis(pinacol) ester and 9,9-di-*n*-octylfluorene-2,7-diboric acid bis(pinacol) ester were purchased from Boron Molecular. Octafluorocyclopentene was supplied by TCI chemicals. Sodium hydroxide (NaOH) pellets, anhydrous sodium sulphate (Na₂SO₄), sodium chloride (NaCl) and potassium carbonate (K₂CO₃) were purchased from Univar. Tetrahydrofuran (THF) was dried over sodium/benzophenone and then distilled under argon atmosphere immediately before use. Dichloromethane (DCM) and petroleum ether (PE) were distilled prior to use.

2.2. Characterization

¹H NMR spectra were recorded using a Bruker Ascend 400 MHz spectrometer for samples in CDCl₃. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent peak (chloroform, ¹H = 7.28 ppm). Peak multiplicities are designated in the following manner: singlet (s), doublet (d), triplet (t), doublet and multiplet (m). The polymer molecular weights were determined using gel permeation chromatography (GPC) (Agilent Technologies 1260 Infinity Series) using THF as eluent and polystyrene narrow standards. The PLgel 5 μm Mixed-C columns (300×7.5 mm)×2 were calibrated using polystyrene narrow standards in THF. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with an attenuated total reflection (ATR) crystal. Absorption spectra were recorded using a Shimadzu UV2600 spectrophotometer. Positive ion mass spectra were acquired with an Orbitrap Elite (Thermo Fisher Scientific), equipped with an atmospheric pressure chemical ionization or atmospheric pressure photoionization source.

Molar absorption coefficients of closed-form isomers were determined by exposing the five polymer solutions to UV light until the maximum absorption was obtained in the visible region and applying a linear fit to the concentration versus absorption data. It was assumed that the photoisomerization to the open form was minimal. Solution quantum yields of cyclisation ($\Phi_{o \rightarrow c}$) and cycloreversion ($\Phi_{c \rightarrow o}$) were measured by a relative method in THF using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene as the reference standard/actinometer, which has quantum yields of cyclization of 0.59 and 0.574 at 280 and 365 nm, respectively and quantum yield of cycloreversion of 0.013 at $\lambda > 492$ nm.^[34,35] The quantum yield was calculated using the equation^[36]

$$\Phi_{o \rightarrow c} = \frac{\Delta A \times V}{I_0 \times (1 - 10^{-A\lambda}) \times \epsilon \times \Delta t} \quad (1)$$

where ΔA is the increase of absorbance at λ_{\max} of the closed-form isomer; Δt is the irradiation time required to reach the photostationary state; V is the volume (L) of irradiated solution; ϵ is the molar absorption coefficient of the closed-form isomer obtained using a linear fit between concentration and absorption (reported in Table 3), A is the absorbance of the solution at the irradiation wavelength (mean value during the irradiation period) and I_0 is the photon flux determined using the actinometer (reference molecule) 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene. The photon flux was measured

as previously reported.^[36] The expression for the ring-opening quantum yield $\Phi_{c \rightarrow o}$ is the same as Equation 1 but in this case ΔA is the decrease in absorbance at λ_{\max} of the closed-form isomer.

The rates of solid state photoswitching were measured relative to P4, and calculated using the equation

$$\frac{\chi_i}{\chi_4} = \frac{S_i}{S_4} \frac{\epsilon_i}{\epsilon_4} \quad (2)$$

where χ_i is the rate of photoswitching of polymer *i* (representing P1, P2, P3, P5, and P6), χ_4 is the rate for P4, $S_i = \frac{dA}{dt}$ is the slope of the absorbance-versus-time plot for polymer *i* as shown in Figure S4 (Supporting Information), S_4 is the slope for P4, ϵ_i is the molar absorption coefficient of polymer *i* and ϵ_4 is the same for P4. The reference values for P4 were taken to be $\chi_{o \rightarrow c} = 1$ and $\chi_{c \rightarrow o} = 0.1$.

Thin films for measuring UV-vis absorption spectroscopy and atomic force microscopy were prepared on glass (Sail Brand) by spin coating 10 mg mL⁻¹ (for UV-vis) and 20 mg mL⁻¹ (for AFM) in toluene at 1500 rotations per minute for 45 s using a Chemat KW-4A spincoater. Glass substrates were cleaned prior to use in an ultrasound bath for 10 min using soapy water, acetone and ethanol, respectively, and dried under nitrogen. The surface morphology and thickness of the films was measured using an NTEGRA TS-150 atomic force microscope (AFM) in semi contact mode. Molar absorption coefficients in solid state were evaluated by UV-vis spectroscopy from linear fits of absorbance of films of different thicknesses. In a typical procedure, four films of the same polymer were prepared by spin coating solutions with different concentrations. The absorbance of each film was recorded before and after switching the polymers. The absorbance values were plotted against film thickness (cm) to estimate the absorption coefficients and reported in Table 3. Thermal properties were investigated using an SDT 650 (TA instruments) and DSC 250 (TA instruments). The DSC was equipped with a refrigeration cooling system (RCS) and the heating and cooling rates were equal at 10 °C min⁻¹. TGA ramp rate was maintained at 10 °C min⁻¹. Degradation temperatures were estimated at 5% wt. loss. Photochemical stability measurements were performed by switching repeatedly between the colored and colorless isomeric forms of the polymers using a handheld UVGL-58 lamp at 365 nm (6 W) and visible light Cole-Parmer Fiber Optic Illuminator (150 W) and measuring the absorption spectra. A cut-off filter was used for cycloreversion experiments to eliminate UV light. Polymer films (≈ 20 nm) were irradiated with alternate UV and visible light for 600s in air and absorbance was measured and recorded after each switching cycle. The switching cycles were repeated twelve times.

2.3. Polymer Synthesis

Poly(3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-3-thienyl)-1-cyclopenten-1-yl]-2-methylthiophene)-*alt*-(9,9-di-*n*-propyl-9H-fluorene) (P1)

A 50 mL Schlenk tube was charged with 5-bromo-3-[2-(5-bromo-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl]-2-methylthiophene (0.1050 g, 0.194 mmol),

9,9'-*n*-propylfluorene-2,7-diboronic acid bis(pinacol) ester (0.09 g, 0.194 mmol), THF (3.5 mL), and aqueous potassium carbonate (2 mL, 2 M). This mixture was purged with nitrogen for 10 min and Pd(PPh₃)₄ (0.0022 g, 0.0019 mmol) was added. The mixture was then degassed three times using freeze-pump thaw cycles then covered under a blanket of argon. The mixture was stirred at 60 °C for 120 h. To remove the reactive end-groups, the resultant polymer was treated with bromobenzene and phenylboronic acid after 72 and 84 h, respectively. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with water (2×50 mL) and brine (20 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent was removed under reduced pressure to afford a teal green colored oil. The oil was dissolved in 5 mL of chloroform and precipitated into 25 mL methanol to afford a teal green solid (0.08 g, 76%). λ_{\max} (open isomer) (THF)/nm 365 [log(ϵ /dm³ mol⁻¹ cm⁻¹) (4.64)], λ_{\max} (closed isomer) (THF)/nm 625 [log(ϵ /dm³ mol⁻¹ cm⁻¹) (4.38)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.22–7.44 (m, 8H), 1.84–1.93 (m, 10H), 0.52–0.81 (m, 10H); ν_{\max} /cm⁻¹ 853, 990, 1008, 1053, 1113, 1135, 1198, 1216, 1228, 1270, 1365, 1455, 1738, 2968; $T_d = 344$ °C; GPC: $M_w = 10.73$ kg mol⁻¹, PDI = 3.53.

Poly(3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-3-thienyl)-1-cyclopenten-1-yl]-2-methylthiophene)-*alt*-(9,9-di-*n*-hexyl-9H-fluorene) (P2)

A 50 mL Schlenk tube was charged with 5-bromo-3-[2-(5-bromo-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl]-2-methylthiophene (0.1020 g, 0.194 mmol, 1.0 eq.), 9,9-di-*n*-hexylfluorene-2,7-diboronic acid bis(pinacol) ester (0.114 g, 0.194 mmol, 1.0 eq.), toluene (3.5 mL), and aqueous potassium carbonate (2 mL, 2 M). This mixture was purged with nitrogen for 10 min and Pd(PPh₃)₄ (0.0021 g, 0.0019 mmol) was added. The mixture was then degassed three times using freeze-pump thaw cycles then covered under a blanket of argon. The mixture was stirred at 100 °C for 120 h. To remove the reactive end-groups, the resultant polymer was treated with bromobenzene and phenylboronic acid after 72 and 84 h, respectively. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with water (2×50 mL) and brine (20 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent was removed under reduced pressure to afford a teal green colored oil. The oil was dissolved in 5 mL of chloroform and precipitated into 25 mL methanol to afford a teal green solid (0.09 g, 68%). λ_{\max} (open isomer) (THF)/nm 365 [log(ϵ /dm³ mol⁻¹ cm⁻¹) (4.56)], λ_{\max} (closed isomer) (THF)/nm 625 [log(ϵ /dm³ mol⁻¹ cm⁻¹) (4.38)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.71 ppm (d, 2H), 7.58 ppm (d, 2H), 7.49 ppm (s, 2H), 7.38 ppm (s, 2H), 2.06 ppm (m, 9H), 1.10 ppm (m, 13H), 0.77 ppm (m, 10H); ν_{\max} /cm⁻¹ 812, 856, 898, 990, 1031, 1054, 1116, 1133, 1202, 1216, 1228, 1272, 1351, 1364, 1454, 1737, 2855, 2055, 2968; $T_d = 389$ °C; GPC: $M_w = 13.27$ kg mol⁻¹, PDI = 2.28.

Poly(3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-3-thienyl)-1-cyclopenten-1-yl]-2-methylthiophene)-*alt*-(9,9-di-*n*-propyl-9H-fluorene) (P3)

A 50 mL Schlenk tube was charged with 5-bromo-3-[2-(5-bromo-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-

cyclopenten-1-yl]–2-methylthiophene (0.1010 g, 0.194 mmol, 1.0 eq.), 9,9-di-*n*-octylfluorene-2,7-diboronic acid bis(pinacol) ester (0.123 g, 0.194 mmol, 1.0 eq.), toluene (3.5 mL), and aqueous potassium carbonate (2 mL, 2 M). This mixture was purged with nitrogen for 10 min and Pd(PPh₃)₄ (0.0022 g, 0.0019 mmol) was added. The mixture was then degassed three times using freeze-pump thaw cycles then covered under a blanket of argon. The mixture was stirred at 100 °C for 120 h. To remove the reactive end-groups, the resultant polymer was treated with bromobenzene and phenylboronic acid after 72 and 84 h, respectively. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with water (2×50 mL) and brine (20 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent was removed under reduced pressure to afford a teal green colored oil. The oil was dissolved in 5 mL of chloroform and precipitated into 25 mL methanol to afford a teal green solid (0.110 g, 76%). λ_{max} (open isomer) (THF)/nm 365 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.70)], λ_{max} (closed isomer) (THF)/nm 625 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.45)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.12–7.44 (m, 8H), 1.90–2.01 (m, 10H), 0.78–0.87 (m, 20H), 0.61–0.70 (m, 10H); $\nu_{\text{max}}/\text{cm}^{-1}$ 813, 898, 989, 1053, 1116, 1204, 1216, 1228, 1271, 1364, 1454, 2852, 2925, 2968, 3014; T_{d} = 404 °C; GPC: M_{w} = 20.21 kg mol⁻¹, PDI = 2.18.

Poly(3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-3-thienyl)–1-cyclopenten-1-yl]–2-methylthiophene)-*alt*-(di-*n*-hexylphenylene) (P4)

A 50 mL Schlenk tube was charged with 5-bromo-3-[2-(5-bromo-2-methyl-3-thienyl)–3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl]–2-methylthiophene (0.113 g, 0.215 mmol, 1.0 eq.), 2,5-di-*n*-hexyl-1,4-phenylene-bis(pinacolato boronate) (0.107 g, 0.215 mmol, 1.0 eq.), THF (4 mL) and aqueous potassium carbonate (2 mL, 2 M). This mixture was purged with nitrogen for 10 min, Pd(PPh₃)₄ (0.0023 g, 0.00215 mmol, 0.01 eq.) and Aliquat 336 (0.00096 g, 0.00215 mmol, 0.01 eq.) were added. The reaction was degassed with three freeze-pump thaw cycles and covered by a blanket of argon. The reaction was stirred at 60 °C for 120 h. To remove the reactive end-groups, the resultant polymer was treated with bromobenzene and phenylboronic acid after 84 and 96 h, respectively. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with water (2×50 mL) and brine (20 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent was removed under reduced pressure to afford a violet-colored oil. The crude product was purified by column chromatography (chloroform and silica gel; column diameter 3 cm, column height, 10 cm) to afford a violet solid (0.06 g, 52%). λ_{max} (open isomer) (THF)/nm 282 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.31)], λ_{max} (closed isomer) (THF)/nm 569 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.20)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.24–7.08 (m, 4H), 2.69 (m, 4H), 2.04–1.91 (m, 6H), 1.38–1.28 (m, 16H), 0.90–0.86 (m, 6H); $\nu_{\text{max}}/\text{cm}^{-1}$ 823, 849, 896, 988, 1052, 1114, 1134, 1192, 1216, 1228, 1270, 1340, 1364, 1439, 1737, 2855, 2925, 2968; T_{d} = 188 °C; GPC: M_{w} = 6.69 kg mol⁻¹, PDI = 5.58.

Poly(3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-3-thienyl)–1-cyclopenten-1-yl]–2-methylthiophene)-*alt*-(9-(1-octylonyl)carbazole) (P5)

A 50 mL Schlenk tube was charged with 5-bromo-3-[2-(5-bromo-2-methyl-3-thienyl)–3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl]–2-methylthiophene (0.1010 g, 0.192 mmol, 1.0 eq.), 9-(heptadecan-9-yl)–2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)–9*H*-carbazole (0.1262 g, 0.192 mmol, 1.0 eq.), toluene (3.5 mL), and aqueous potassium carbonate (2 mL, 2 M). This mixture was purged with nitrogen for 10 min and Pd(PPh₃)₄ (0.0022 g, 0.0019 mmol) was added. The mixture was then degassed three times using freeze-pump thaw cycles then covered under a blanket of argon. The mixture was stirred at 100 °C for 120 h. To remove the reactive end-groups, the resultant polymer was treated with bromobenzene and phenylboronic acid after 72 and 84 h, respectively. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with water (2×50 mL) and brine (20 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent was removed under reduced pressure to afford a teal green colored oil. The oil was dissolved in 5 mL of chloroform and precipitated into 25 mL methanol to afford a teal green solid (0.110 g, 76%). λ_{max} (open isomer) (THF)/nm 365 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.46)], λ_{max} (closed isomer) (THF)/nm 622 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.32)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.17–8.08 (m, 8H), 4.65 (m, 1H), 1.92–2.34 (m, 10H), 1.15–1.28 (m, 24H), 0.80–0.88 (t, 6H); $\nu_{\text{max}}/\text{cm}^{-1}$ 844, 904, 985, 1052, 1114, 1135, 1203, 1216, 1228, 1271, 1364, 1434, 1454, 1599, 1737, 2853, 2924, 2968; T_{d} = 359 °C; GPC: M_{w} = 12.90 kg mol⁻¹, PDI = 2.43.

Poly(3-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-3-thienyl)–1-cyclopenten-1-yl]–2-methylthiophene)-*alt*-(4,8-bis(3,5-dioctyl-2-thienyl)–1,5-dithia-s-indacene) (P6)

A 50 mL Schlenk tube was charged with 5-bromo-3-[2-(5-bromo-2-methyl-3-thienyl)–3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl]–2-methylthiophene (0.051 g, 0.097 mmol, 1.0 eq.), 4,8-bis(3,5-dioctyl-2-thienyl)–2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (0.1023 g, 0.097 mmol, 1.0 eq.), toluene (3.5 mL), and aqueous potassium carbonate (2 mL, 2 M). This mixture was purged with nitrogen for 10 min and Pd(PPh₃)₄ (0.0022 g, 0.0019 mmol) was added. The mixture was then degassed three times using freeze-pump thaw cycles then covered under a blanket of argon. The mixture was stirred at 100 °C for 96 h. To remove the reactive end-groups, the resultant polymer was treated with bromobenzene and phenylboronic acid after 72 and 84 h, respectively. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with water (2×50 mL) and brine (20 mL). The organic layer was dried over anhydrous sodium sulphate, filtered, and the solvent was removed under reduced pressure to afford a lime green colored oil. The oil was dissolved in 5 mL of chloroform and precipitated into 25 mL methanol to afford a teal green solid (0.08 g, 71%). λ_{max} (open isomer) (THF)/nm 381 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.72)], λ_{max} (closed isomer) (THF)/nm 675 [log($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (4.49)]; ¹H NMR (400 MHz, CDCl₃) δ : 7.18–7.24 (m, 4H), 6.83 (s, 2H), 2.90 (m, 4H), 2.40 (m, 4H), 1.98–1.76 (m, 10H), 1.32 (m, 20H), 1.09 (m, 22H), 0.76–0.90 (m, 14 H); $\nu_{\text{max}}/\text{cm}^{-1}$ 828, 899, 985, 1049, 1090, 1194, 1216, 1271, 1364, 1454, 1737, 2851, 2922, 2968; T_{d} = 425 °C; GPC: M_{w} = 12.41 kg mol⁻¹, PDI = 2.52.

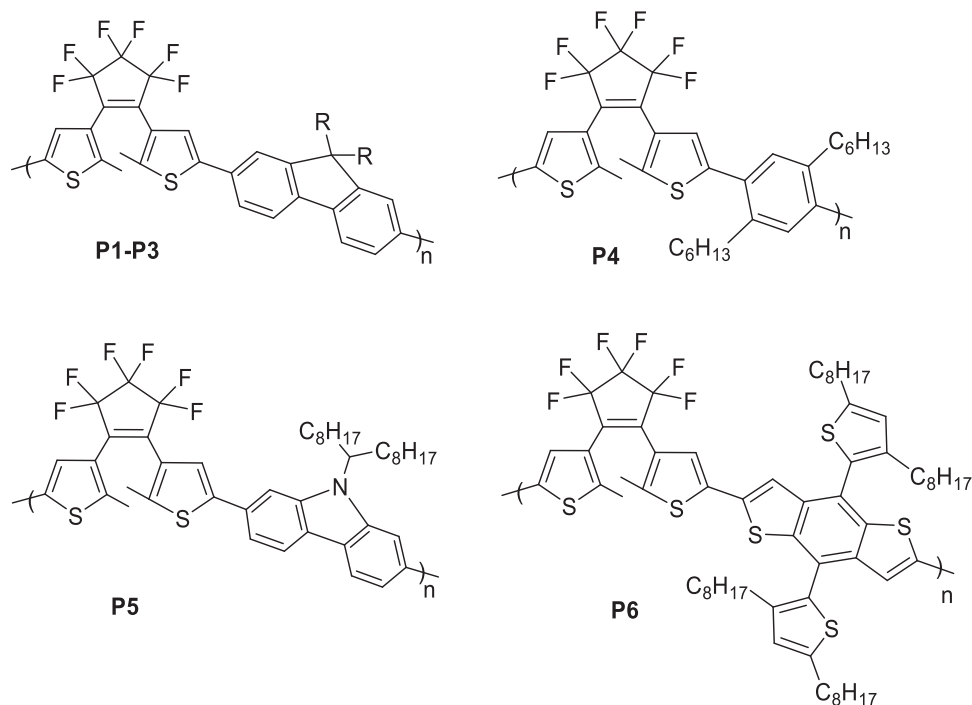


Figure 1. Chemical structures of P1–P6. P1:R = C₃H₇; P2: R = C₆H₁₃; P3: R = C₈H₁₇.

3. Results and Discussion

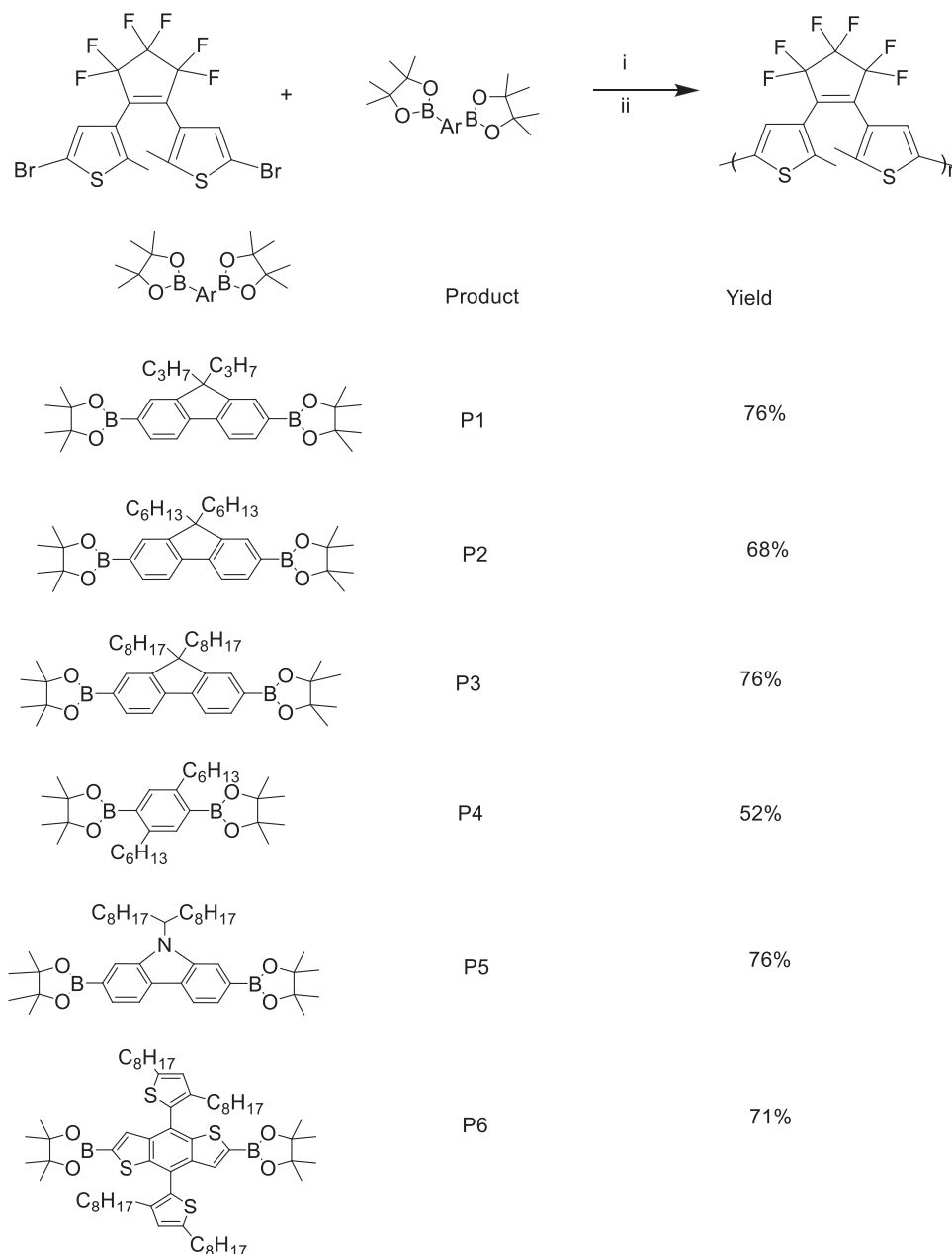
3.1. Polymer Synthesis

The syntheses of P1–P6 (**Figure 1**) were attempted using direct arylation^[37] Stille coupling^[38] and Suzuki-Miyaura cross-coupling reactions.^[39] It was found that Suzuki-Miyaura polycondensation reactions between 5-bromo-3-[2-(5-bromo-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl]-2-methylthiophene and the corresponding diboronic acid bis(pinacol) esters resulted in the highest molecular weight polymers, as shown in **Scheme 1**. The dibromide monomer was prepared according to a modified procedure as described by Liu et al.^[40] and details of this synthesis is outlined in the Supporting Information. This monomer was chosen as a building block to prepare the corresponding polymers as there are many diboronic acid bis(pinacol) esters (or other dimetal cross-coupling reagents) available to co-polymerize with this comonomer. The reactive end-groups of the polymers were replaced with phenylene units using phenyl boronic acid and bromobenzene to avoid unwanted post-polymerization reactions/degradation^[41,42] of the polymers during photoswitching. The polymer structure was confirmed using ¹H-NMR and FT-IR and their spectra are given in the Supporting Information. The polymer's average molecular numbers (M_n) ranged from 1312 to 9308 Daltons and are summarized in **Table 1**. The M_n of P1 to P3 increased and may be attributed to enhanced solubility in the polymerization solvent.^[43] The (M_n) of P3 is one of the highest reported so far for diarylethene-based main-chain photochromic polymers^[8,30] and twice the size of the analogous polymer synthesized by Kawai et al.^[27] P4 had the lowest M_w despite optimizing the reaction parameters such as solvent (toluene or THF), catalyst (Pd(PPh₃)₄

or Pd (II) acetate) and base type (K₂CO₃ or Cs₂CO₃). This could be attributed to the use of sterically hindered 2,5-di-*n*-hexyl-1,4-phenylene-bis(pinacolato boronate) monomer. The highest degree of polymerization of P4 was achieved by using 1 mole% of a phase transfer catalyst (Aliquat 336) to the reaction mixture. All the polymers were thermally stable ≥ 188 °C (**Figure S6**, Supporting Information).

3.2. Solution Physicochemical Properties

The solution properties of the photochromic polymers are depicted in **Figure 2** and summarized in **Table 2**. The photostationary state (PSS) of all the polymers under ambient conditions were dominated by the open isomer of the photochromic polymer (**Figure S1**, Supporting Information). The polymer's photostationary properties are similar to isolated DTE photochromic molecules and indicates that the long-range conjugation of the polymer backbone does not affect the PSS of these polymers.^[44] The open isomer of the polymers containing the fluorene comonomer (P1–P3) showed a strong peak centered at 365 nm in THF due to a π - π^* transition and not related to the alkyl side-chain length.^[45,46] The maximum absorption of P1 was red-shifted compared to a model compound reported by Woodland et. al. indicating an extension of the conjugation in both the open (336 vs 365 nm) and closed (618 vs 625 nm) isomeric forms of the polymers (**Figure S2**, Supporting Information).^[47] P5 displayed a maximum absorption at 365 nm, which is similar to P1–P3, and is expected since polyfluorenes and polycarbazoles have a similar absorption maximum.^[48] The emergence of a higher energy peak at 272 nm is also typical to carbazole based polymers and related to π - π^* electronic transition of the conjugation.^[49]



Scheme 1. Synthetic protocol for preparation of photochromic polymers. Reagents and conditions: (i) tetrahydrofuran or toluene, 2 M K_2CO_3 , $Pd(PPh_3)_4$, 60 °C or 90 °C, 96–120 h, (ii) phenylboronic acid, and bromobenzene.

Table 1. Molecular weight, glass transition, and degradation temperatures of P1–P6.

Polymer	M_n	PDI	T_g [°C]	T_d [°C]
P1	2889	3.53	165	344
P2	5789	2.28	135	389
P3	9308	2.17	96	404
P4	1213	5.52	49	188
P5	5098	2.53	94	359
P6	4920	2.52	58	425

Interestingly, the variation of the HOMO and LUMO levels of a carbazole based polymer^[50] does not affect the main absorption maximum in the photostationary state when compared to P1–P3. In contrast, P4 displays a hypsochromic shift and P6 displays a bathochromic shift related to P1–P3 related to the degree of π -orbital overlap in the polymer backbone.^[51,52] Upon photoexcitation using 365 nm light for up to 600 s, a peak appears in the visible range and is related to the π - π^* transition of the closed isomer of the photochromic polymers. The trend in the closed isomers is the same as the open isomers with P4 having the shortest conjugation length (569 nm) and P6 having the longest conjugation length (662 nm), which were not affected by

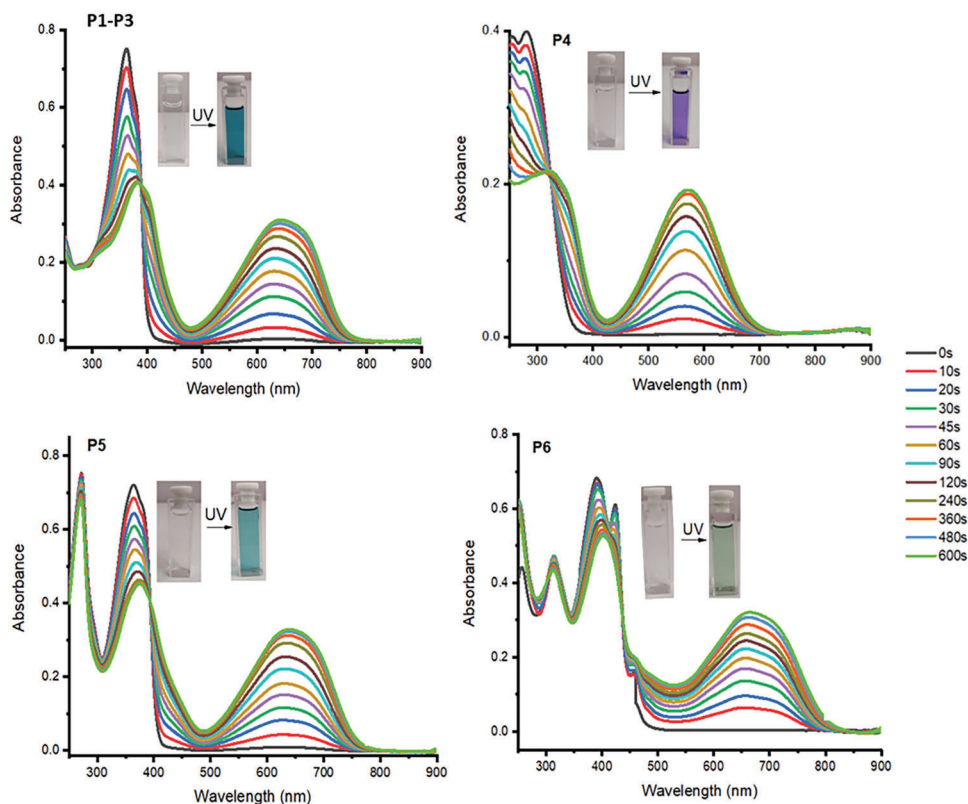


Figure 2. UV-vis absorption spectra of 1×10^{-5} M solutions of P1–P6 in THF upon irradiation with 365 nm monochromatic light.

the alkyl chain length, molecular weight distribution and energy levels.

The quantum yield of the $6-\pi$ electrocyclicization of the polymers was measured as described by Santos et al.,^[36] where the rates of photoisomerization was compared to 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene having values of 0.59 and 0.574 at 280 and 365 nm, respectively (Figure 3). The ring closing quantum yield ranged from 0.41 to 0.87 depending on the comonomer and summarized in Table 2. Polymers based on fluorene, phenylene and carbazole comonomer showed cyclization quantum yields over 0.5 suggesting a primarily antiparallel conformation of the dithienylethene moieties.^[30,47] The photoswitching properties were not molecular weight dependent, where lower molecular weight analogues of P1, P3, and P4 (Table S1, Supporting Information) had similar quantum yields of cycliza-

tion. Cycloreversion quantum yields varied between 0.004 and 0.011 and are typical for DTE based materials. It was found that the higher degree of conjugation resulted in lower cycloreversion quantum yields, which has been observed in bbaomolecular based systems.^[53,54]

3.3. Thin Film Physicochemical Properties

Solutions of P1–P6 in toluene (20 mg mL^{-1}) were cast onto glass substrates to form 20 nm polymer films. These films were characterized using atomic force microscopy (AFM) and differential scanning calorimetry (DSC) to determine the quality of the film and the thermal properties of the resultant films, respectively. Figure S5 in the Supporting Information depicts the AFM of

Table 2. Summary of solution properties of P1–P6.

	$\lambda_{\text{max}}; \epsilon$ [$\text{M}^{-1} \text{cm}^{-1}$] (open-form)	$\lambda_{\text{max}}; \epsilon$ [$\text{M}^{-1} \text{cm}^{-1}$] (closed-form)	$\Phi_{o \rightarrow c}$	$\Phi_{c \rightarrow o}$
P1	365; 43606	625; 24054	$0.594 \pm 0.002^{\text{a}}$	$0.009 \pm 0.001^{\text{c}}$
P2	365; 36141	625; 24087	$0.591 \pm 0.001^{\text{a}}$	$0.008 \pm 0.001^{\text{c}}$
P3	365; 50264	625; 28506	$0.524 \pm 0.002^{\text{a}}$	$0.007 \pm 0.001^{\text{c}}$
P4	282; 20336	569; 15712	$0.795 \pm 0.001^{\text{b}}$	$0.011 \pm 0.001^{\text{c}}$
P5	272; 29 074	622; 21 120	$0.851 \pm 0.002^{\text{b}}$	$0.011 \pm 0.001^{\text{c}}$
	365; 27678	–	$0.866 \pm 0.002^{\text{a}}$	–
P6	381; 53 105	675; 30868	$0.412 \pm 0.003^{\text{a}}$	$0.004 \pm 0.001^{\text{c}}$

^{a)} Upon irradiation with 365 nm UV light; ^{b)} Upon irradiation with 280 nm UV light; ^{c)} Upon irradiation with visible light $> 550 \text{ nm}$.

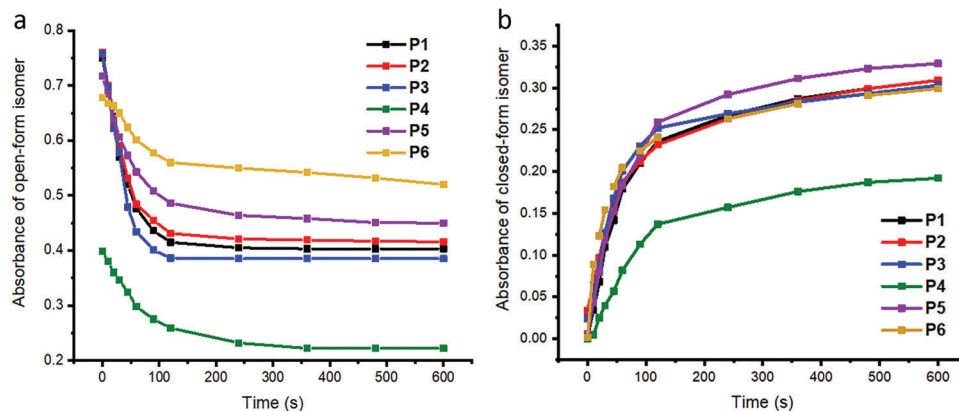


Figure 3. Switching speeds of P1-P6 in solution, showing a) the loss of the UV peak and b) the growth of the visible peak with time.

Table 3. Optical and photochromic properties of P1–P6 films.

	$\lambda_{\max}; \epsilon$ [$\text{M}^{-1} \text{cm}^{-1}$] (open-form)	$\lambda_{\max}; \epsilon$ [$\text{M}^{-1} \text{cm}^{-1}$] (closed-form)	$\chi_{o \rightarrow c}$	$\chi_{c \rightarrow o}$	RMS
P1	355; 23158	630; 10945	$0.566 \pm 0.05^a)$	$0.225 \pm 0.01^c)$	2.008 ± 0.281
P2	361; 21774	635; 10157	$0.439 \pm 0.04^a)$	$0.208 \pm 0.02^c)$	0.648 ± 0.039
P3	362; 29820	637; 13761	$0.408 \pm 0.03^a)$	$0.077 \pm 0.03^c)$	0.621 ± 0.083
P4	287; 11137	573; 6697	1.000 [*] b)	0.100 ^{c)}	0.674 ± 0.052
P5	286; 6736	621; 9322	–	$0.265 \pm 0.02^c)$	1.610 ± 0.118
	360; 19090	–	0.404 ± 0.02	–	
P6	387; 35787	662; 16628	$0.164 \pm 0.03^a)$	$0.042 \pm 0.02^c)$	0.411 ± 0.03

^{a)} Upon irradiation with 365 nm UV light; ^{b)} Upon irradiation with 280 nm UV light; ^{c)} Upon irradiation with visible light >550 nm; ^{*}used as a reference value for relative rate measurements.

the six polymer films and their corresponding root mean square (RMS) roughness are reported in Table 3. All the polymer films were smooth with low RMS roughness; however, small grains could be clearly seen from the micrograph of P1 with an RMS roughness of >2. The micrographs of P2 and P3 were smoother with RMS values <1. Our study suggests that the smaller alkyl solubilizing group in P1 may form slightly smaller crystallites due to aggregation.^[55–57] Figure 4 and Figure S7 (Supporting Information) depicts the DSC traces of P1–P6. All polymers show a weak glass transition temperature and a melting point was not observed, implying all polymers are amorphous. As the alkyl chain length increased from P1–P3, the glass transition temperature decreased from 165 to 96 °C with heat capacity ranging between 0.32 and 0.93 J g^{−1}, which has been related to an increase in internal plasticization.^[58,59] The transitions are weak and are similar to those of polyfluorenes.^[60] The T_g of P4, P5, and P6 vary from 49 to 96 °C and show little dependence on conjugation length (Figure S7, Supporting Information).

The absorption and photochromic properties of the polymer films are depicted in Figure 5 and summarized in Table 3. The maximum and onset of absorption of the open and closed isomeric form of all the polymers were similar to their solution properties, indicating that planarization of the polymer backbone does not occur in the thin film state regardless of their conjugation length and alkyl chain length. This lack of planarization is consistent with conjugated polymers composed of fluorene-*alt*-thiophene based polymers.^[61,62] To understand the differences in the photoswitching efficiency between the polymers, the rela-

tive rates of electrocyclization and cycloreversion were measured (rather than the quantum yield as an appropriate reference was not available) and shown in Figure 6. The rates of cyclization were related to P4 and set to 1 as a reference point for ring-closing and 0.1 as a reference point for ring opening. P4 has the fastest

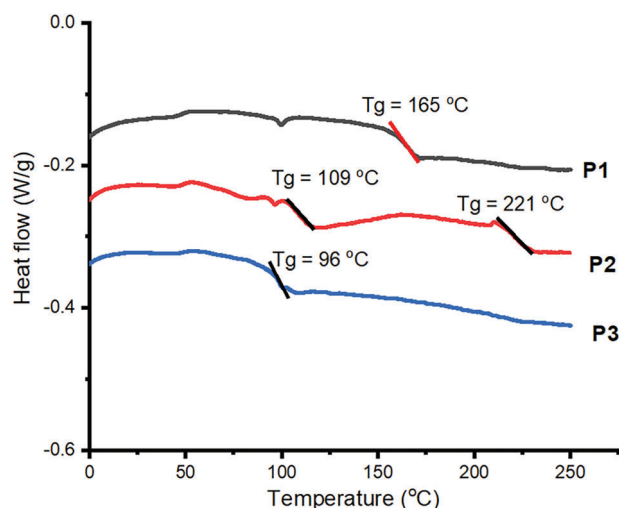


Figure 4. DSC traces of P1–P3. Heating rates were 10 °C min^{−1}. Heat capacities were 0.87, 0.93, and 0.32 J g^{−1} for P1–P3, respectively. The peak at 100 °C is an artefact.

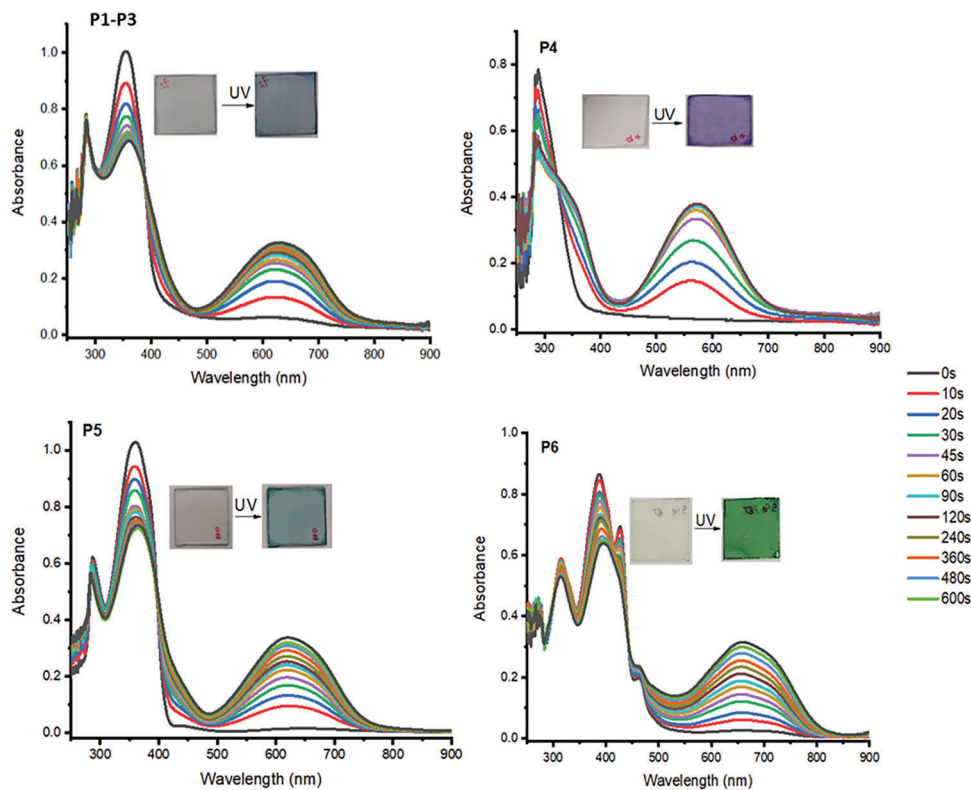


Figure 5. Absorption spectra of thin films of P1–P6 upon irradiation with UV light. Film thicknesses were ≈ 20 nm and cast from toluene.

switching rate and P6 has the slowest related to differences in conjugation. As the alkyl chain length increased for P1–P3, the relative ring-closing rate decreased indicating that morphological differences and/or steric interactions played a role in the efficiency of electrocyclization.^[63] P3 and P5 had the same relative ring-closing rates and further indicates that the energy levels (fluorene vs carbazole) do not play a role in the electrocyclization. P6 had the lowest relative electrocyclization rate and could be related to the higher absorptivity (triple that of the P4 reference), differences in the morphology and/or steric interactions. Ring-opening rates ranged between 0.04 and 0.26 relative to P4. The

cycloreversion rate trend is similar to the electrocyclization, however P3 is significantly lower than P1, P2, and P5 and the reason for this is not yet understood.

An important parameter in organic photonics and electronics is the photostability of the active layers.^[64–66] The photochemical stability of these polymers were investigated by irradiating the polymer thin films with UV light for 600 s followed by visible light for 600 s 12 times in air (Figure 6). Electrocylation and cycloreversion was observed over 12 cycles without fatigue, which represents 120 min of irradiation with UV light in air. The photochemical stability observed indicates that DTE by-products

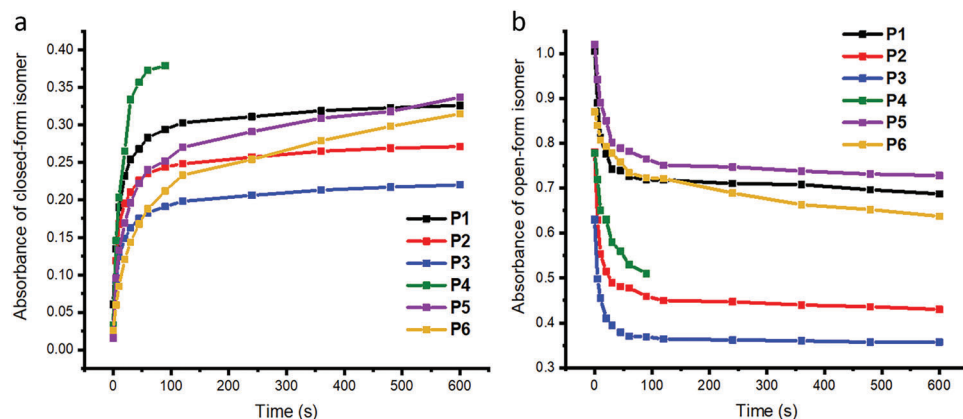


Figure 6. Switching speeds of P1–P6 in solid state: a) growth of Vis peak and b) loss of the UV peak with time.

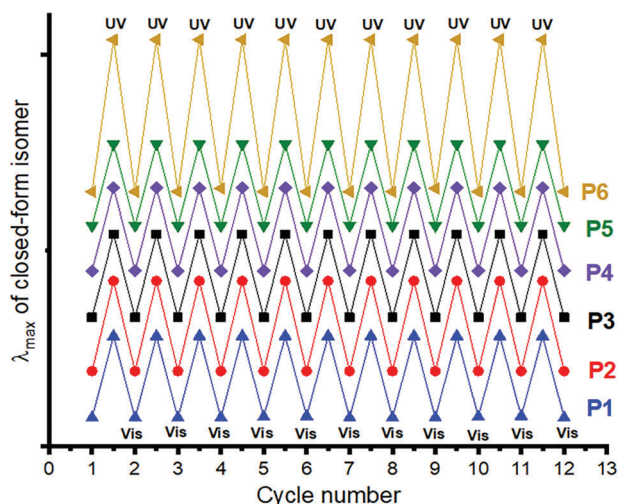


Figure 7. Reversible photoswitching of P1–P6. The film was excited with UV light for 600 s and visible light for 600 s. Points are shifted vertically for clarity.

were not formed^[67–69] and other photo-oxidation reactions did not occur,^[70–73] regardless of the side-chain length and conjugation length (Figure 7).

4. Conclusions

Solution-processable diarylethene-based main-chain photochromic polymers with various conjugation lengths were successfully synthesized by Suzuki-Miyaura polycondensation reactions. The polymers are soluble in common solvents and can be cast into high quality thin films. Photoisomerization was observed in both solution and film states with minimal photo- and thermal degradation under ambient conditions. These polymers are therefore attractive candidates for multifunctional, light-controlled optoelectronic devices such as phototransistors, optical memories, and smart solar cells. Depending on the application, photoswitchable polymers containing short alkyl solubilizing groups would be preferred when high temperature stresses are present while longer alkyl groups resulted in slightly more smooth films, which is important for charge transport characteristics. By co-polymerizing with varying conjugation length co-monomers, it was found that the conjugation length could be controlled to match the specific light source required for the application.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

diarylethenes, organic electronics, photochromes, polymers

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