Novel Photochromic Homopolymers Based on 1,2-Bis(3-thienyl)cyclopentenes

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ABSTRACT: Incorporation of photochromic molecules into polymer matrices is necessary for materials applications such as optical information processing. Several novel homopolymers were prepared from 1,2-bis(3-thienyl)cyclopentene derivatives using ring-opening metathesis polymerization techniques. Analysis by UV−vis absorption spectroscopy revealed that, in solution, they retained the appealing photochromic behavior exhibited by their respective monomers. The polymers were cast as thin films and spin-coated onto quartz substrates where the solid-state photochromic properties of the polymers were similar to those in solution.

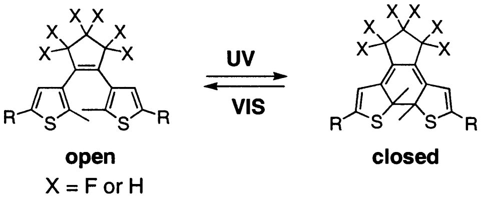
Introduction

Photochromic compounds based on 1,2-bis(3-thienyl)cyclopentene derivatives undergo reversible photocyclization between their colorless ring-open and colored ring-closed forms when irradiated with appropriate wavelengths of light (Scheme 1).[1] The appeal of this particular photochromic process lies in its impressive fatigue resistance and thermal irreversibility. Switching between the two forms of 1,2-dithienylalkene derivatives can also be accompanied by changes in physical properties other than the variations in absorbance.[1] Useful properties that may be varied include luminescence,[2] refractive index,[3] electronic conductance,[4] acidity,[5] viscosity,[6] and optical rotation.[7] Applications using this photochromic skeleton hinge on exploiting these accompanying changes and offer promise in actinometry, read/write/erase optical data storage, holography, and molecular electronics.

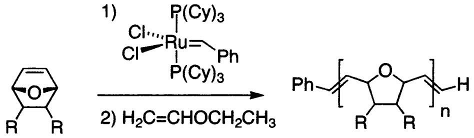
Despite the breadth of the potential applications of photochromic 1,2-dithienylethenes as functional materials, the published studies, with a few exceptions,[3,4] have focused on evaluating the utility of monomeric photochromic systems in solution. Practical application of photochromic technology requires the photochromic compounds to be immobilized in the form of films, sheets, or beads, which dictates the use of polymers rather than monomers.[8] Photochromic polymers also have the advantage over their monomeric counterparts in that, if designed appropriately, they may contain a high effective concentration of the photochromic component without being plagued by crystallization, phase separation, or the formation of concentration gradients.[3c]

Several examples of photochromic polymers have been reported, using 1,2-dithienylalkene[3,4b,9] or other photochromic derivatives.[10] Polymer matrices doped or side-chain-modified with 1,2-dithienylalkene have been reported to display photochromic behavior;[9a−e] however, the low concentration of photochromic component in the bulk polymer makes them less than ideal for realistic materials application. An increase in the concentration of the photochromic component in the polymer would result in amplification of the desired function; thus, homopolymers are more desirable, especially in applications such as optical information processing because they will offer a significant increase in the density of the photochromic compound per unit area or volume. Other problems commonly hindering the widespread use of photochromic polymers are poor solubility, making it difficult to process the polymers as thin films, and poor photochromic activity of the polymer relative to the monomers.

Scheme 1



Scheme 2



1,2-Bis(3-thienyl)cyclopentene derivatives not only exhibit excellent photochromic properties; the colors expressed by the ring-closed forms can be fine-tuned by tailoring the electronic distribution within the conjugated pathway created upon photocyclization. This is most conveniently achieved by modifying the functional groups located on the thiophene heterocycles (the “R” groups in Scheme 1). It is, therefore, critical to search out a mild polymerization method so the pool of potential photochromic derivatives is not limited by the compatibility of the polymerization process with the pendant functional groups. Ring-opening metathesis polymerization (ROMP) of strained bicyclic olefins (Scheme 2)[11] has risen in popularity because it is carried out under very mild reaction conditions, which are tolerant to a wide range of functional groups, and provides polymers with low polydispersities. In this report, we exploit ROMP techniques to prepare a series of photochromic homopolymers **P1−P4**.

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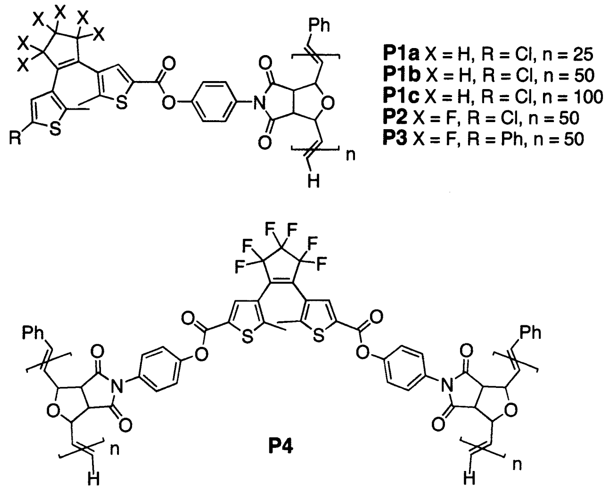
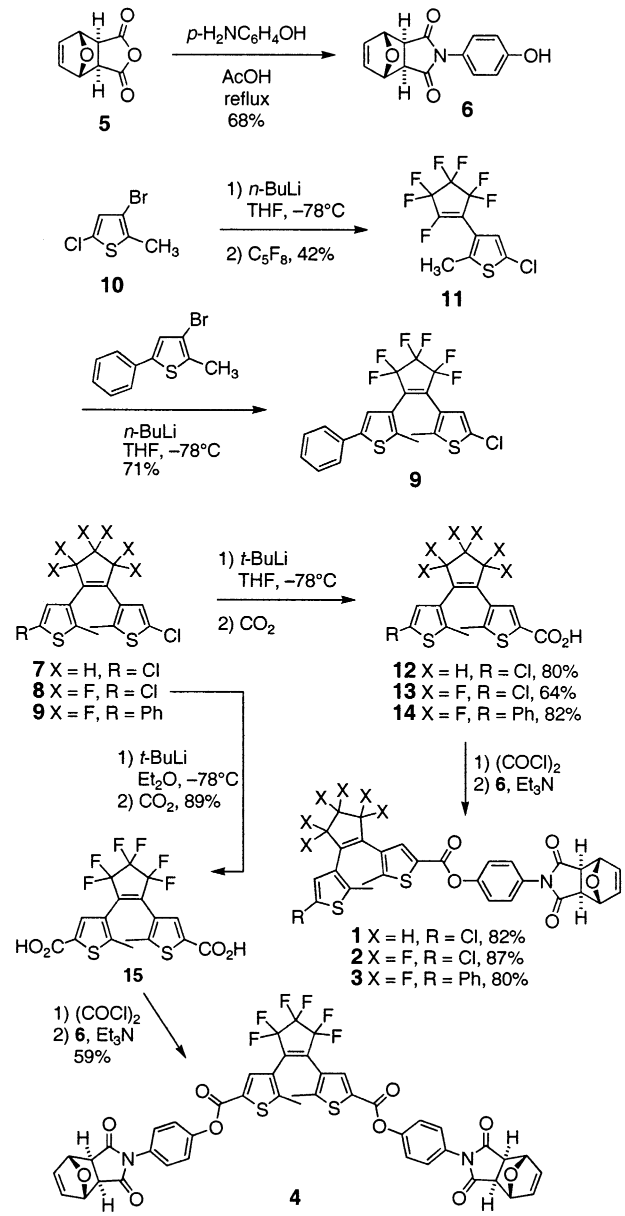
Chart 1



Scheme 3



We have previously reported the synthesis and characterization of monomer **1** and polymers **P1a−c** (Chart 1) and have proven that the photochromism exhibited by the monomer is retained after polymerization.[12] The resulting polymers could be cast as amorphous thin films that reversibly changed color upon irradiation with appropriate wavelengths of light. These successful and interesting results prompted us to explore the versatility of this class of photochromic polymers. We report here the preparation and characterization of three additional novel polymers (**P2−P4**) in both solution and the solid state.

Polymer **P2** is identical to **P1b** except that it contains a perfluorinated cyclopentene ring. Perfluorinated 1,2-bis(3-thienyl)cyclopentene derivatives are found more often in the literature, and there is precedent for their being substantially more robust than their nonfluorinated counterparts.[13] The addition of fluorine atoms on the cyclopentene fragment should also result in a red shift of the light absorbed by the photochromic compounds, and we report that polymer **P2** is purple as compared to polymer **P1b**, which is red in color.[12] We also show that, as expected, the replacement of the chlorine atoms on the thiophene heterocycles in monomer **2** and polymer **P2** by phenyl substituents (**3** and **P3**) results in a red shift of the absorbed light due to the extended π-conjugation created upon ring closure. Polymer **P4**, which results from the polymerization of the symmetric bis(norbornene) **4**, is cross-linked and shows a greatly increased robustness.

Results and Discussion

Synthesis of Monomers. Polymerization of all monomers (**1−4**) relies on the presence of the 7-oxanorbornene moiety **6** in order to facilitate the ROMP process and generate the polymers **P1−P4** (Scheme 3). Oxanorbornene **6** can be readily prepared in good yield by condensing the known 7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**5**)[14] with *p*-aminophenol. The direct precursors to monomers **1−3** are the photochromic carboxylic acids **12−14** which can be prepared from dichlorides **7**[15] and **8**[16] and monochloride **9**. This monochloride is prepared by treating 3-bromo-5-chloro-2-methylthiophene (**10**)[17] with *n*-butyllithium followed by quenching with commercially available octafluorocyclopentene. The synthesis of the photochromic backbone in **9** is completed by reacting the lithium salt of 3-bromo-5-phenyl-2-methylthiophene[18] with compound **11** as also shown in Scheme 3. When dichloride **8** is treated with an excess of *tert*-butyllithium and quenched with carbon dioxide, the diacid **15** is the product. All four photochromic carboxylic acids **12−15** can be coupled to oxanorbornene **6** through their respective acid chlorides. All new compounds were characterized by NMR spectroscopy, UV−vis spectroscopy, and mass spectrometry.

Synthesis and Characterization of Polymers. Monomers **1−4** were subjected to the ROMP conditions shown in Scheme 2. In a typical polymerization procedure, a CH_2Cl_2 solution of commercially available bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (Grubbs' catalyst) is cannulated into a vigorously stirred CH_2Cl_2 solution of appropriate monomer under anhydrous conditions. The resulting homogeneous solution is stirred for 16 h at room temperature, at which time it is treated with excess ethyl vinyl ether to terminate the living polymerization reaction. All polymers can be conveniently isolated in high purity by precipitating them out of their CH_2Cl_2 solutions by adding excess diethyl ether and collecting them by

Table 1. Polymerization Yields and Polymer Characterization

monomer (equivalents)[a]	% yield	M_w	M_n	PDI (M_w/M_n)	T_g (°C)
1 (25)	76	11 917	7920	1.50	−51
1 (50)	78	24 577	16 771	1.47	−36
1 (100)	75	43 820	28 007	1.56	−42
2 (50)	53	26 150	22 869	1.14	−55
3 (50)	69	25 382	21 447	1.18	−43
4 (50)	86				−50

[a] Relative to the molar equivalents of catalyst.

filtration. Because the fluorinated polymers **P2** and **P3** are partially soluble in ether, the isolated yields were slightly lower using this particular isolation procedure.

The chain length of the polymers can be tailored, and in the present case, three different nonfluorinated polymers **1a**−**c** made from the same monomer are described. This is achieved by simply varying the relative molar amounts of monomer **1** and the ROMP catalyst. By using catalyst stoichiometries of 1, 2, and 4 mol %, the 100-mer (**P1c**), the 50-mer (**P1b**), and the 25-mer (**P1a**) can all be isolated, respectively. Analysis by gel permeation chromatography (GPC) reveals that the relative ratio of the number-average molecular weights for **P1c**:**P1b**:**P1a** was approximately 4:2:1, as expected (Table 1). The only polymers made from the fluorinated monomers **2** and **3** are the 50-mers, which are prepared using 2 mol % catalyst stoichiometry. The chain lengths of these two polymers (**P2**) and (**P3**) also correspond well with the GPC data. When the symmetrical monomer **4** is polymerized using 2 mol % catalyst stoichiometry per oxanorbornene unit, the highly cross-linked polymer is produced. Because of the cross-linked nature of this particular polymer, GPC data were uninformative.

The ^{1}H NMR spectra of all polymers **P1**−**P4** show broadened peaks compared to those of the monomers and the absence of the peak for the vinylic proton of the strained olefin. The results from the GPC analysis on the polymers are reported in Table 1 and show low polydispersity indices (M_w/M_n) in all cases. The glass transition temperatures (T_g) for all polymers measured using differential scanning calorimetry (DSC) are also included in the table. Low values of T_g are desirable for photochromic polymers as it corresponds to more inner space to allow conformation freedom needed for cyclization.[9c] The results from thermogravimetric analysis (TGA) on all of the polymer (not shown) indicate that they are stable at high temperature (340 °C).

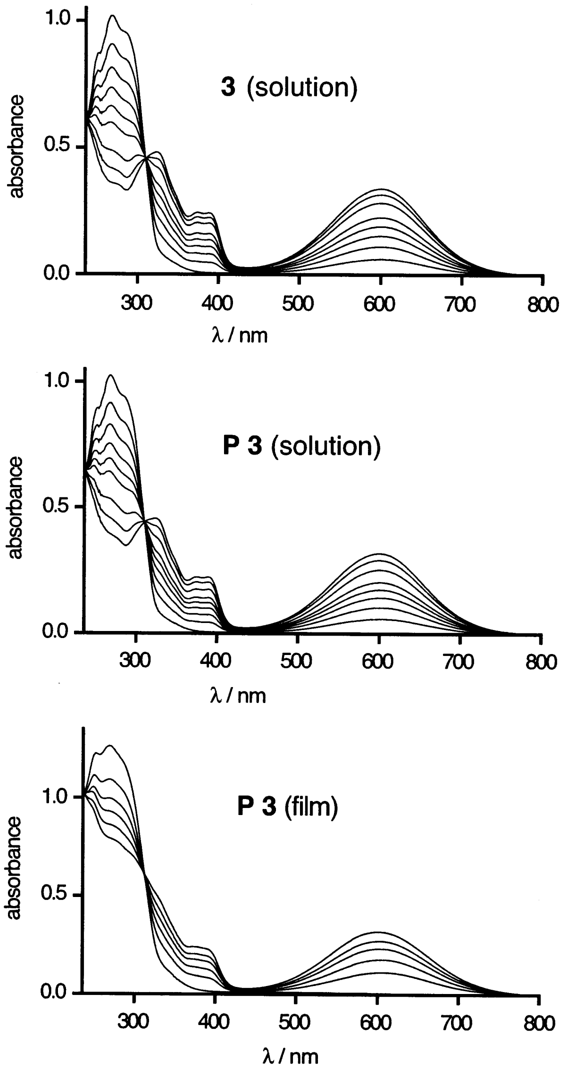


Figure 1. Changes in the UV−vis absorption spectra of monomer **3** and polymer **P3** in solution (THF at 3 × 10^{-5} M) and as a film when irradiated with 254 nm light. Irradiation periods for the solution studies are 0, 2, 4, 6, 8, 10,15, 20, and 30 s. Irradiation periods for the studies on the polymer film are 0, 10, 30, 60, 100, and 180 s.

Table 2. Solution UV−vis Absorption Data for Monomers 1−4 and Their Corresponding Polymers P1−P4 (in THF at 3 × 10^{-5} M)

compd	λ_{max}/nm ($\epsilon \times 10^{-4}$ L mol^{-1} cm^{-1}) ring-open form	ring-closed form[a]	color of the ring-closed form
1	246 (2.70)	512 (0.703)	red
P1b	247 (2.79)	512 (0.587)	red
2	247 (3.69)	558 (0.760)	purple
P2	247 (3.58)	557 (0.727)	purple
3	267 (3.40)	600 (1.13)	blue
P3	267 (3.42)	599 (1.06)	blue
4	256 (3.80)	596 (0.660)	blue
P4	244 (3.41)	587 (0.164)	blue

[a] Obtained by irradiating (254 nm) THF solutions of the ring-open forms for 30 s for polymers **P1b**−**P3** and 60 s for cross-linked polymer **P4**.

UV−vis Absorption Spectroscopy. The comparison of the absorption spectra of THF solutions of polymers **P1**−**P3** to their corresponding monomers **1**−**3**, at identical concentrations with respect to the photochromic component, shows that, in each case, the photochromism is the same in both the polymeric and monomeric forms (Figure 1 and Table 2). The changes in the UV−vis absorption spectra that accompany the photoinduced isomerization of all photochromic compounds upon irradiation with a hand-held (254 nm) lamp[19] are similar to those for monomer **3** and polymer **P3** shown in Figure 1. Within the first 10 s of irradiation, absorption bands centered between 500 and 600 nm appear as the photochromic compounds are converted from their colorless ring-open to their linearly π-conjugated colored ring-closed forms. The presence of isosbestic points in all cases indicates clean photochemical transformations occur. After 30 s of exposure at this concentration, the increases in the absorbance bands stop. The fact that the optical densities of polymers **P1**−**P3** in the visible region of the spectra are the same as those for their corresponding monomers attests to the conservation of photochromism. When these ring-closed samples are irradiated with broad-band visible light using a cutoff filter to eliminate light of wavelengths less than 434 nm, the original absorption spectra are obtained, confirming the reversibility of the electrocyclic reactions.

The only case where the photochromic properties of the polymer in solution differed from those of its monomer involves the cross-linked polymer **P4**. Here, the growth of the absorbance of the ring-closed form of **P4** levels off after 60 s at only 25% the intensity of the absorbance of monomer **4**. We attribute this lowering of the extent of photoisomerization to the decrease in rotational freedom about the C−C bonds between the thiophene and cyclopentene rings due to the rigidification of each end of the photochromic skeleton joining the cross-linked polymer backbones. Free rotation about these bonds is essential to orient the orbitals for the electrocyclic ring closing reaction, and a reduced amount of ring-closing is not unexpected.

Spin-coating $CHCl_3$ solutions of the polymers (0.5 mM) onto quartz substrates results in thin films that are approximately 250 nm in thickness. Photocoloration of the films by irradiating them with 254 nm light substantiates the solid-state photochromism. In all cases, clean photochemical transformations are confirmed by the presence of the isosbestic points at 303, 311, 312, and 310 nm for polymers **P1b**, **P2**, **P3**, and **P4**, respectively (see Figure 1 for an example). The resulting UV−vis spectra of each of the films show almost identical absorbances to those for the analogous polymers in solution corresponding to the ring-closed forms of the photochromic compounds (see Table 2). The photostationary states of the films made from polymers **P1b**−**P3** are attained after 3 min of irradiation at 254 nm, whereas that of the film made from polymer **P4** is reached after 4 min.

As alluded to in the Introduction, varying the pendant functional groups on the 5-ring position of the thiophene heterocycle provides a convenient means to tailor the absorbance properties of the photochromic compounds and thus the color expressed by the polymers. Changing the chloro substituent in monomer **2** to a phenyl ring results in the red-shifting of the absorbance bands of the corresponding ring-closed forms of both the monomer **3** and the polymer **P3** due to the extended π-conjugation created upon photocyclization. Monomer **3** and polymer **P3** are blue both in solution and as films. This structure/property control is effectively exploited in these polymers, allowing for the development of polymers whose color can be predetermined by choosing the appropriate pendant functionality.

Upon broad-band irradiation with light above 434 nm, each of the polymer films can be decolorized, resulting in the regeneration of the original UV−vis spectra, thus confirming the reversibility of the photocyclization process in the solid state much as it exists in solution. Akin to its photochromic behavior in solution, polymer **P4** as a film shows a smaller change in its absorption spectrum when irradiated with 254 nm light than its non-cross-linked counterparts **P1b**−**P3**. Again, we attribute this reduced photochromism to a decrease in the rotational freedom of the ring-open form of the 1,2-dithienylcyclopentene skeleton due to its confinement within the cross-linked polymer.

Conclusion

We have successfully demonstrated that ROMP provides a mild, versatile, and well-controlled method to generate photochromic homopolymers based on 1,2-bis(3-thienyl)cyclopentene derivatives. The novel homopolymers are soluble in common organic solvents, have low polydisperties, are readily cast as thin films, and, most importantly, retain their photochromic properties both in solution and in the solid state. The application of these novel polymers to optic and electronic devices is currently underway and will be reported in due time.

Experimental Section

All solvents for synthesis were purchases from Caledon Laboratories Limited. THF and diethyl ether were distilled over sodium/benzophenone, hexane was distilled over potassium/benzophenone, and CH_2Cl_2 was distilled over calcium hydride before use. All other solvents were used as received. Solvents for NMR analysis were purchased from Cambridge Isotope Laboratories and used as received. Column chromatography was performed using silica gel 60 (230−400 mesh) from Silicycle Inc. Bis(tricyclohexylphosphine)benzylidine-ruthenium(IV) dichloride was purchased from Strem Chemical Co. and was stored and weighed in a glovebox under a nitrogen atmosphere. All other reagents and starting materials were purchased from Aldrich. 7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**5**),[14] 3-bromo-5-chloro-2-methylthiophene (**10**),[17] 3-bromo-2-methyl-5-phenylthiophene,[18] and the photochromic dichlorides **7**[15] and **8**[16] were prepared as described in the literature. Octafluorocyclopentene was obtained from Nippon Zeon Corp.

GPC analyses (calibrated by polystyrene) were performed on THF solutions of the polymers using a Waters 515 HPLC pump and 2410 refractive index or a 486 tunable absorbance dectector at a flow rate of 1.0 mL/min through a 7.8 × 300 mm column running at 30 °C. ^{1}H NMR characterizations were performed on a Varian Inova-300 or Bruker AMX 400 instrument. ^{13}C NMR characterizations were performed on a Bruker 300 or Bruker AMX 400 instrument. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane using the residual solvent peak as a reference standard. Coupling constants (J) are reported in hertz. FT-IR measurements were performed using a Nicolet Magna-IR 750 or a Nexus 670 instrument. UV−vis measurements were performed using a Pharmacia Biotech Ultraspec 3000 or a Varian Cary 300 Bio spectrophotometer. UV irradiation was performed using a hand-held UV lamp operating at 420 μW/cm^2 for 254 nm. Differential scanning calorimetry (DSC) was performed using a Seiko Instruments Inc. EXSTAR 6000 and DSC 6200 instrument. Thermogravimetric analysis was performed using a Shimadzu TGA-50 thermogravimetric analyzer. Solid-state UV−vis spectra were obtained from polymer films spin-coated onto quartz plates from $CHCl_3$ solutions (3 mg of polymer in 0.2 mL of $CHCl_3$). The polymer films were between 160 and 270 nm thick as measured using a Tencor Instruments Alpha Step 100 profilimeter.

Synthesis of *exo*-*N*-(*p*-Hydroxyphenyl)-3,6-epoxy-4-cyclohexene-1,2-dicarboximide (6). A mixture of 7-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (**5**) (2.0 g, 12 mmol), *p*-aminophenol (1.31 g, 12 mmol), and glacial acetic acid (3 mL) was heated at reflux for 10 min, after which time a precipitate formed. The heating source was removed, and the reaction mixture was allowed to cool to room temperature. The precipitate was collected by vacuum filtration, washed with water, and dried in vacuo to afford 2.10 g (68%) of **6** as a white solid; mp = 188−189 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.71 (s, 1H), 6.95 (d, J = 9 Hz, 2H), 6.83 (d, J = 9 Hz, 2H), 6.58 (s, 2H), 5.21 (s, 2H), 3.02 (s, 2H). ^{13}C NMR (75.49 MHz, DMSO-d_6): δ 175.95, 157.27, 136.53, 127.98, 123.19, 115.38, 80.66, 47.20. FTIR: 3334, 3143, 3102, 3076, 3049, 3029, 2973, 1775, 1697, 1612, 1594,1516, 1448, 1402, 1273, 1223, 1191, 1162, 1149, 1015, 915, 875, 855, 846, 809. MS (EI): m/z = 257 [M]$^+$, 189 [M−C_4H_4O]$^+$.

Synthesis of Cyclopentene 11. A vigorously stirred solution of 3-bromo-5-chloro-2-methylthiophene (**10**)[17] (1.0 g, 4.7 mmol) in Et_2O (20 mL) cooled to −78 °C was treated with *n*-butyllithium (1.88 mL of 2.5 M solution in hexanes, 4.7

mmol) dropwise under argon. This solution was added through a cannula to a solution of octafluorocyclopentene (1.2 mL, 9.5 mmol) in 1:1 THF:Et_2O (10 mL) also cooled to −78 °C. The reaction mixture was stirred at this temperature for 1 h, the cooling bath was removed, and the mixture was allowed to warm to room temperature where it was stirred for a total of 16 h. The solvent was removed in vacuo, and the residue mixture was partitioned between CH_2Cl_2 and H_2O. The organic layer was separated, washed with water and then brine, dried over Na_2SO_4, filtered, and evaporated in vacuo. Purification by column chromatography through silica (hexanes) afforded 0.63 g (42%) of the product as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (s, 1H), 2.39 (d, $J = 3$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (7 of 10 signals were observed) 152.78, 149.81, 142.36, 128.24, 125.48, 118.99, 14.47 (d, $J = 6$ Hz). FTIR (KBr-cast): 3110, 2972, 2931, 2869, 1703, 1469, 1390, 1358, 1331, 1282, 1205, 1157, 1121, 1040, 996, 973. MS (EI): $m/z = 324$ $[M]^+$, 305 $[M-F]^+$, 289 $[M - Cl]^+$.

Synthesis of Photochromic Chloride 9. A vigorously stirred solution of 3-bromo-2-methyl-5-phenylthiophene[18] (837 mg, 3.3 mmol) in a mixture of hexanes (20 mL) and THF (5 mL) cooled to −78 °C was treated with *n*-butyllithium (1.32 mL of a 2.5 M solution in hexanes, 3.3 mmol) dropwise under argon. After stirring at this temperature for 10 min, a solution of cyclopentene **11** (1.06 g, 3.3 mmol) in hexanes (10 mL) was added through a cannula. The reaction mixture was stirred at −78 °C for 1 h, the cooling bath was removed, and the mixture was allowed to warm to room temperature where it was stirred for 16 h. The solvent was removed in vacuo, and the residue was partitioned between CH_2Cl_2 and H_2O. The organic layer was separated, washed with water (2 × 30 mL) and then brine (30 mL), dried over Na_2SO_4, filtered, and evaporated in vacuo. Purification by column chromatography through silica (hexanes) afforded 1.11 g (71%) of the product as a viscous yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, $J = 7$ Hz, 2H), 7.39 (t, $J = 8$ Hz, 2H), 7.31 (t, $J = 8$ Hz, 1H), 7.24 (s, 1H), 6.93 (s, 1H), 1.97 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (14 of 19 signals were observed) 142.46, 141.25, 140.47, 133.19, 129.01, 127.99, 127.75, 125.59, 125.51, 125.46, 123.35, 122.18, 14.52, 14.35. FTIR (KBr-cast): 3060, 3026, 2957, 2922, 2853, 1462, 1441, 1335, 1275, 1194, 1136, 1118, 1060, 1004, 982, 898, 888, 755, 742, 690. MS (CI): $m/z = 479$ $[M + H]^+$.

Synthesis of Carboxylic Acids 12−14. A solution of the appropriate dichloride **7**−**9** in dry THF or Et_2O cooled to −78 °C was treated with *tert*-butyllithium (1.7 M solution in hexane) dropwise under argon. After stirring for 10−15 min, excess dry CO_2 was bubbled through the solution. The reaction mixture was removed from the cooling bath, allowed to warm to room temperature, quenched with 5% HCl, and extracted three times with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated in vacuo. The products were purified by column chromatography through silica (2−5% CH_3OH/CH_2Cl_2).

(12) Dichloride **7** (385 mg, 1.17 mmol) and *tert*-butyllithium (0.7 mL, 1.17 mmol) in THF (50 mL) afforded 318 mg (80%) of acid **12** as a pale yellow solid after purification; mp = 175−176 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 6.56 (s, 1H), 2.79−2.73 (m, 4H), 2.05 (p, $J = 8$ Hz, 2H), 1.99 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.15, 144.78, 137.12, 136.00, 135.17, 134.63, 134.05, 134.00, 133.26, 126.55, 125.48, 38.49, 38.42, 22.80, 14.94, 14.14. FTIR (KBr-cast): 3428, 2959, 2924, 2841, 1669, 1552, 1448, 1310, 1269, 1159, 1000, 993, 731. MS (CI): $m/z = 339$ $[M + H]^+$.

(13) Dichloride **8** (1.01 g, 2.3 mmol) and *tert*-butyllithium (1.36 mL, 2.3 mmol) in Et_2O (100 mL) afforded 660 mg (64%) of acid **13** as a white solid after purification. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 6.85 (s, 1H), 2.02 (s, 3H), 1.83 (s, 3H).

(14) Chloride **9** (1.11 g, 2.34 mmol) and *tert*-butyllithium (1.38 mL, 2.34 mmol) in Et_2O (50 mL) afforded 900 mg (82%) of acid **14** as a white solid after purification; mp = 189−191 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.53 (d, $J = 7$ Hz, 2H), 7.39 (t, $J = 8$ Hz, 2H), 7.31 (t, $J = 8$ Hz, 1H), 7.24 (s, 1H), 2.02 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (15 of 20 signals were observed) 166.03, 150.40, 142.79, 141.27, 134.88, 133.08, 130.51, 129.04, 128.08, 126.28, 125.62, 125.29, 122.03, 15.04, 14.52. FTIR (KBr-cast): 3414, 3028, 2924, 2855, 1678, 1545, 1462, 1274. MS (CI): $m/z = 489.5$ $[M + H]^+$.

Synthesis of Dicarboxylic Acid 15. A solution of dichloride **8** (646 mg, 1.48 mmol) in Et_2O (70 mL) cooled to −78 °C was treated dropwise with *tert*-butyllithium (1.74 mL of 1.7 M solution in hexane, 2.96 mmol) under argon. After stirring for 15 min, excess dry CO_2 was bubbled through the solution. The cooling bath was removed, and the mixture was allowed to warm to room temperature. The precipitated dicarboxylate was dissolved in H_2O (10 mL) and acidified with concentrated HCl (2 mL). The precipitate formed upon acidification was collected by vacuum filtration, washed with H_2O, and dried in vacuo to afford 600 mg (89%) of the product as a white solid; mp = 227−229 °C. ^1H NMR (400 MHz, CD_3OD): δ 8.67 (s, 2H), 2.93 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ (6 of 9 signals were observed) 164.05, 150.46, 134.56, 133.97, 126.52, 14.91. FTIR (KBr-cast): 3073, 2983, 2918, 2857, 1676, 1547, 1465, 1336, 1262, 1193, 1120, 1038, 982, 896, 758, 667. MS (EI): $m/z = 456$ $[M]^+$, 438 $[M - H_2O]^+$.

Synthesis of Photochromic Monomers 1−4. A vigorously stirred solution of the appropriate carboxylic acid **12**−**15** and DMF (5 drops) in CH_2Cl_2 cooled to 0 °C was treated dropwise with a solution of oxalyl chloride in CH_2Cl_2 under argon over 10 min. After stirring at room temperature for 2 h (except for **15**, which was allowed to stir for 16 h), the reaction mixture was concentrated to dryness in vacuo. The residue was dissolved in CH_2Cl_2 (25 mL/mmol carboxylic acid) and added dropwise over 10 min to a solution of *exo-N*-(*p*-hydroxyphenyl)-3,6-epoxy-4-cyclohexene-1,2-dicarboximide (**6**) and triethylamine in acetone cooled to 0 °C. The reaction mixture was stirred overnight under argon, and then the solvent was removed in vacuo. The products were purified by column chromatography through silica.

(1) Carboxylic acid **12** (136 mg, 0.4 mmol), oxalyl chloride (254 mg, 2.0 mmol), dicarboximide **6** (154 mg, 0.6 mmol) and triethylamine (0.5 mL) afforded 188 mg (82%) of monomer **1** as a pale yellow solid after purification by column chromatography through silica (2% $CH_3OH/CHCl_3$); mp = 94−95 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.36−7.27 (m, 4H), 6.56 (s, 3H), 5.36−5.37 (m, 2H), 3.00 (s, 2H), 2.82−2.71 (m, 4H), 2.12−1.99 (m, 5H), 1.87 (s, 3H). ^{13}C NMR (75.49 MHz, $CDCl_3$): δ 175.22, 159.95, 150.56, 144.60, 137.19, 136.78, 136.02, 135.33, 134.75, 134.14, 133.36, 129.16, 128.03, 127.62, 126.66, 125.59, 122.38, 81.51, 47.59, 38.61, 38.52, 22.89, 14.98, 14.30. FTIR (KBr-cast): 3050, 2951, 2843, 1778, 1713, 1508, 1202. ESMS (+ive): $m/z = 600.0$ $[M + Na]^+$, 532 $[M - Cl]^+$. Anal. Calcd for $C_{30}H_{24}ClNO_5S_2$: C, 62.33; H, 4.18; N, 2.42. Found: C, 61.95; H, 4.16; N, 2.45.

(2) Carboxylic acid **13** (254 mg, 0.57 mmol), oxalyl chloride (361 mg, 2.8 mmol), dicarboximide **6** (221 mg, 0.86 mmol), and triethylamine (0.5 mL) afforded 343 mg (87%) of monomer **2** as a pale yellow solid after purification by column chromatography through silica ($CHCl_3$); mp = 141.5−142.5 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.37−7.29 (m, 4H), 6.88 (s, 1H), 6.57−6.56 (m, 2H), 5.39−5.38 (m, 2H), 3.01 (s, 2H), 2.04 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75.49 MHz, $CDCl_3$): δ (18 of 24 signals were observed) 175.20, 159.12, 150.19, 140.64, 136.79, 134.56, 130.66, 129.50, 128.40, 127.74, 126.02, 125.48, 123.91, 122.25, 81.52, 47.59, 15.08, 14.52. FTIR (KBr-cast): 3015, 1714, 1508, 1272, 1189. ESMS (+ive): $m/z = 703.1$ $[M + NH_4]^+$. Anal. Calcd for $C_{29}H_{18}ClF_6NO_5S_2$: C, 51.68; H, 2.69; N, 2.08. Found: C, 51.66; H, 2.69; N, 1.97.

(3) Carboxylic acid **14** (252 mg, 0.52 mmol), oxalyl chloride (330 mg, 2.60 mmol), dicarboximide **6** (200 mg, 0.78 mmol), and triethylamine (0.5 mL) afforded 300 mg (80%) of monomer **3** as a pale blue solid after purification by column chromatography through silica (2% $CH_3OH/CHCl_3$); mp = 149−151 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.41 (d, $J = 7$ Hz, 2H), 7.42−7.29 (m, 7H), 7.26 (s, 1H), 6.58 (s, 2H), 5.41 (s, 2H), 3.03 (s, 2H), 2.04 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (24 of 28 signals were observed) 206.93, 175.14, 159.15, 150.11, 142.80, 141.30, 136.72, 134.67, 133.10, 130.35, 129.37, 129.04, 128.08, 127.67, 126.29, 125.64, 125.31, 122.22, 122.06, 81.45, 47.53, 30.91, 15.04, 14.64. FTIR (KBr-cast): 3064, 3017, 2914, 2849, 1719, 1715, 1508, 1452, 1387, 1275, 1185. Anal. Calcd for $C_{36}H_{23}F_6NO_5S_2$: C, 59.42; H, 3.19; N, 1.92. Found: C, 59.24; H, 3.25; N, 1.90.

(4) Dicarboxylic acid **15** (100 mg, 0.22 mmol), oxalyl chloride (280 mg, 2.2 mmol), dicarboximide **6** (170 mg, 0.66 mmol), and triethylamine (0.5 mL) afforded 120 mg (59%) of monomer 4 as a pale yellow solid after purification by column chromatography through silica (5% MeOH/CHCl3) followed by recrystallization from CH_2Cl_2/hexanes; mp = 150−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 2H), 7.38 (d, J = 9 Hz, 4H), 7.33 (d, J = 9 Hz, 4H), 6.58 (s, 4H), 5.41 (s, 4H), 3.03 (s, 4H), 2.06 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (13 of 17 signals were observed) 175.15, 159.01, 150.08, 149.98, 136.72, 134.37, 130.84, 127.70, 125.72, 122.21, 81.45, 47.53, 15.15. FTIR (KBr-cast): 3097, 3007, 2924, 1724, 1717, 1710, 1510, 1400, 1276, 1179. Anal. Calcd for $C_{45}H_{28}F_6N_2O_{10}S_2$: C, 57.82; H, 3.02; N, 3.00. Found: C, 58.01; H, 2.99; N, 2.99.

Polymerization of Monomers 1−4. A solution of the appropriate monomer **1**−**4** dissolved in dry deoxygenated CH_2Cl_2 was treated with a CH_2Cl_2 solution of bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride which was added through a cannula. The final monomer concentrations were 0.1 M. After stirring at room temperature for 14 h, excess ethyl vinyl ether was added, and the resulting solutions were stirred while exposed to the atmosphere for 30 min. The polymers were precipitated in high purity by pouring the reaction solutions into cold Et_2O and collected by vacuum filtration. The success of each polymerization reaction was assessed by ^{1}H NMR spectroscopy. Typically, in the ^{1}H NMR spectrum of the monomer, the peak corresponding to the methine proton of the bicyclic olefin appears at 6.56 ppm. After the polymerization reactions, the peak at 6.56 ppm disappeared, and a new peak for the olefin protons appeared at 6.10 ppm. See text table for GPC characterization.

(P1) Monomer **1** was polymerized with 0.04, 0.02, and 0.01 mol equiv of bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride to afford polymers **P1a** (76% yield), **P1b** (78% yield), and **P1c** (75% yield), respectively. A typical ^{1}H NMR spectrum is as follows (400 MHz, $CDCl_3$): δ 7.6 (br s), 7.3 (br s), 6.6 (br s), 6.1 (br s), 5.9−5.7 (m), 5.2−5.0 (m), 4.7−4.5 (m), 3.4 (br s), 2.7 (br s), 2.1−1.9 (m), 1.8 (br s).

(P2) Monomer **2** (82.3 mg, 120 μmol) was polymerized with bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (2.0 mg, 2.4 μmol, 0.02 mol equiv). The isolation procedure was identical to that for **P1** except that the precipitation procedure was carried out twice, first with Et_2O and then with CH_3OH to afford polymer **P2** in 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.9 (br s), 7.3 (br s), 6.9 (br s), 6.1 (br s), 5.8 (br d), 5.2 (br s), 4.6 (br d), 3.4 (br s), 2.1−1.9 (m), 1.8 (br s).

(P3) Monomer **3** (72.3 mg, 100 μmol) was polymerized with bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (2.3 mg, 2.0 μmol, 0.02 mol equiv) to afford polymer **P3** in 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.9 (br s), 7.5 (br s), 7.4−7.2 (m), 6.1 (br s), 5.8 (br d), 5.2 (br s), 4.6 (br d), 3.4 (br s), 2.0−1.8 (m).

(P4) Monomer **4** (58.4 mg, 62 μmol) was polymerized with bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (2.1 mg, 2.5 μmol, 0.4 mol equiv) to afford polymer **P4** in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.1−6.8 (br m), 6.4−5.6 (br m), 5.4−4.3 (br m), 3.8−3.0 (br m), 2.8−1.7 (br m).

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(19) Standard lamps used for visualizing TLC plates (Spectroline E-series, 470 $\mu W/cm^2$) were used to carry out the ring-closing reaction of all photochromic compounds. The ring-opening reactions were carried out using the light of a 150 W tungsten source that was passed through a 434 nm cutoff filter to eliminate higher energy light.

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