

Novel Synthesis of Photochromic Polymers via ROMP

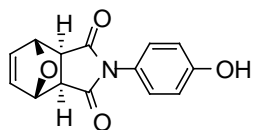
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Supporting Information

Experimental

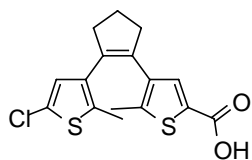
General. THF (Caledon) was distilled over sodium/benzophenone ketyl radical under argon. CH₂Cl₂ (Caledon) was distilled over calcium hydride under argon. All other solvents were used as received. Solvents for NMR analysis (Cambridge Isotope Laboratories) were used as received. Bis(tricyclohexylphosphine)benzylidene ruthenium(IV)dichloride (Grubbs's catalyst) was purchased from Strem and was stored and weighed in a glove box under a nitrogen atmosphere. All other reagents and starting materials were purchased from Aldrich. Dichloride **3**¹ and 7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride² were prepared as described in the literature.

All polymerization reactions were carried out on a Schlenk line. GPC analyses (calibrated by polystyrene) were performed on THF solutions of the polymers using a Waters 515 HPLC pump and 2410 Refractive Index Detector at a flow rate of 1.0 mL/minute through a 7.8 x 300 mm column at 30°C. ¹H NMR characterizations were performed on a Varian Inova-300 instrument, working at 299.96 MHz. 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. UV-Vis measurements were performed using a Pharmacia Biotech Ultraspec 3000 spectrophotometer.

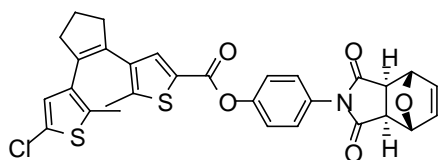


Synthesis of *exo*-N-(*p*-hydroxyphenyl)-3,6-epoxy-4-cyclohexene-1,2-dicarboximide

(2). A mixture of 7-oxa-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (2.0 g, 12 mmol) and *p*-aminophenol (1.31 g, 12 mmol) were heated at reflux for 10 minutes in glacial acetic acid (3 mL), after which time a precipitate formed. The reaction mixture was cooled to room temperature and the product was collected by filtration, washed with water and dried *in vacuo* to afford 2.10 g (68%) of **2** as a white solid: ^1H NMR (DMSO- d_6) δ 9.71 (s, 1H), 6.95 (d, $J = 8.75$ Hz, 2H), 6.83 (d, $J = 8.75$ Hz, 2H), 6.58 (s, 2H), 5.21 (s, 2H), 3.02 (s, 2H); ^{13}C NMR (DMSO- d_6) δ 175.95, 157.27, 136.53, 127.98, 123.19, 115.38, 80.66, 47.20; EIMS (m/z): 257 (M^+), 189 ($\text{M}^+ - \text{C}_4\text{H}_4\text{O}$); FTIR $\bar{\nu}$ 3334 (s, broad), 3143, 3102, 3076, 3049, 3029, 2973, 1697, 1612, 1594.



Synthesis of carboxylic acid 4. A solution of dichloride **3** (385 mg, 1.17 mmol) in dry THF (50 mL) at -78°C under argon was treated with *tert*-butyllithium (0.7 mL of 1.7 M solution in hexane, 1.17 mmol). After stirring for 15 minutes, excess dry CO_2 was bubbled through the solution. The reaction mixture was warmed to room temperature, quenched with dilute HCl, extracted with Et_2O (3 x 50 mL), dried over Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography through silica (5% $\text{CH}_3\text{OH} - \text{CH}_2\text{Cl}_2$) afforded 318 mg (80%) of the product as a pale yellow solid: ^1H NMR (CDCl_3) δ 7.55 (s, 1H), 6.52 (s, 1H), 2.72 (m, 4H), 1.99 (m, 5H), 1.80 (s, 3H).



Synthesis of monomer 5. A vigorously stirred solution of carboxylic acid **4** (136 mg, 0.4 mmol) and 5 drops of DMF in CH₂Cl₂ (4 mL) at 0°C was treated with a solution of oxalyl chloride (254 mg, 2.0 mmol) in CH₂Cl₂ (6 mL) dropwise over 10 minutes. After stirring at room temperature under argon for 2 hours, the reaction mixture was concentrated to dryness *in vacuo*. The residue was dissolved in CH₂Cl₂ (10 mL) and added dropwise over 10 minutes to a solution of olefin **2** (154 mg, 0.6 mmol) and triethylamine (0.5 mL) in acetone cooled to 0°C. The mixture was stirred overnight under argon and the solvent was removed *in vacuo*. Purification by column chromatography through silica (2% CH₃OH-CHCl₃) afforded 188 mg (82%) of the product as a pale yellow solid: ¹H NMR (CDCl₃) δ 7.67 (s, 1H), 7.31 (m, 4H), 6.56 (s, 3H), 5.38 (m, 2H), 3.00 (s, 2H), 2.76 (m, 4H), 2.05 (m, 5H), 1.87 (s, 3H); ¹³C NMR (CDCl₃) 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; ESMS(+ive): 600.0 (M+Na⁺), 532 (M-Cl); IR (KBr-cast): 3050 (w), 2951 (w), 2843 (w), 1713 (s), 1202 (s).

Polymerization of bicyclic olefin 5. In a typical procedure a solution of monomer **5** in dry deoxygenated CH₂Cl₂ was cannulated into a CH₂Cl₂ solution of bis(tricyclohexylphosphine)benzylidene ruthenium(IV)dichloride (0.04 equivalents for **1a**, 0.02 equivalents for **1b**, and 0.01 equivalents for **1c**). The final monomer concentrations were 0.1 M. After stirring at room temperature for 14 hours, excess ethylvinyl ether was added and the solutions were stirred exposed to the atmosphere for 30 minutes. The polymers were precipitated in pure form by pouring the reaction solutions into cold ether and collecting the precipitates by vacuum filtration (yields: 75% for **1a**, 78% for **1b**, and 75% for **1c**). The success of the polymerization reactions was assessed by using ¹H NMR spectroscopy. In the ¹H NMR spectrum of monomer **5**, the peak corresponding to the methine proton of the bicyclic olefin overlaps with the peak corresponding to the hydrogen on the chlorothiophene heterocycle at 6.56 ppm resulting in the area under the peak integrating to 3 protons. After the polymerization reactions, the peak at 6.56 ppm integrated to only 1 proton with respect to the other thiophene proton at 7.67 ppm. A new peak for the olefin protons appeared at 6.10 ppm. A typical ¹H NMR

(CDCl₃) is as follows: δ 7.6 (br s), 7.3 (br s), 6.6 (br s), 6.1 (br s), 5.8 (m), 5.2 (m), 4.6 (m), 3.4 (br s), 2.7 (br s), 2.0 (m), 1.8 (br s).

References.

- 1 Lucas, L. N.; van Esch, J.; Kellog, R. M.; Feringa, B. L. *Chem. Commun.* **1998**, 2313.
- 2 Bolm, C; Dinter, C. L.; Seger, A.; Höcker, H.; Brozio, J. *J. Org. Chem.* **1999**, *64*, 5730.