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Novel Synthesis of Photochromic Polymers via ROMP

Andrew J. Myles,[†] Zengrong Zhang,[‡] Guojun Liu,[‡] and Neil R. Branda*,[†]

Department of Chemistry, University of Alberta,
Edmonton, Alberta, Canada, T6G 2G2, and Department of Chemistry,
University of Calgary, Calgary, Alberta, Canada, T2N 1N4

neil.branda@ualberta.ca

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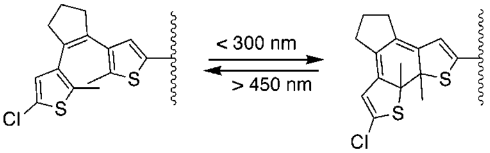
ABSTRACT



Ring-opening metathesis polymerization (ROMP) of a photochromic 1,2-bis(3-thienyl)cyclopentene monomer generated a series of novel polymers. All polymers exhibit reversible light-activated interconversion between their colorless-open and their colored-closed forms.

The photochromism of 1,2-bis(3-thienyl)cyclopentene derivatives involves the reversible photoinduced cyclization between the colorless-open and the colored-closed forms of the chromophore (Figure 1).[1] This phenomenon is interesting for its potential role in optical materials and photonic devices such as variable-transmission filters, optical information storage systems, and photoregulated molecular switches.[2] The need for practical handling of definite forms of photochromic materials such as films, sheets, fibers, or beads dictates the use of polymeric rather than monomeric photochromes.[3,4] Homopolymers are more desirable than copolymers as they will have an increased density of the photochromic unit within the material. This translates into a greater amount of information expressed or stored per unit volume or surface.

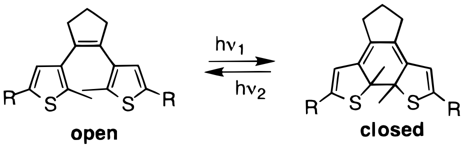


Figure 1. Photoinduced interconversion between the colorless-open and colored-closed forms of the 1,2-bis(3-thienyl)cyclopentene photochrome used in this study.

Not only do 1,2-bis(3-thienyl)cyclopentene derivatives possess optimal photochromic properties, including thermal irreversibility and fatigue resistance, but the wavelength of light expressed by the colored forms can be readily tuned by tailoring the electronic distribution in the conjugated pathway created upon cyclization.[1] This is most conveniently accomplished by modifying pendant functional groups located on the heterocycles. To fully exploit this structure−property relationship in polymers, a mild and universal polymerization technique is required so that the pool of pendant groups is not limited by functional group incompatibility.

[†] University of Alberta.

[‡] University of Calgary.

(1) (a) Irie, M. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Gugliemetti, R. J., Eds.; Plenum Press: New York, 1999; Vol. 1, Chapter 5, pp 207−222. (b) Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803. (c) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem Eur. J.* **1995**, *1*, 275.

(2) Wakashima, H.; Irie, M. *Polym. J.* **1998**, *30*, 985 and references therein.

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(4) For other examples of photochromic polymers, see: (a) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915. (b) Warshawsky, A.; Kahana, N.; Buchholtz, F.; Zelichonok, A.; Ratner, J.; Krongauz, V. *Ind. Eng. Chem. Res.* **1995**, *34*, 2825. (c) Buchholtz, F.; Zelichenok, A.; Krongauz, V. *Macromolecules* **1993**, *26*, 906. (d) Lyubimov, A. V.; Zaichenko, N. C.; Marevtsev, V. S. *J. Photochem. Photobiol. A: Chem.* **1999**, *120*, 55.

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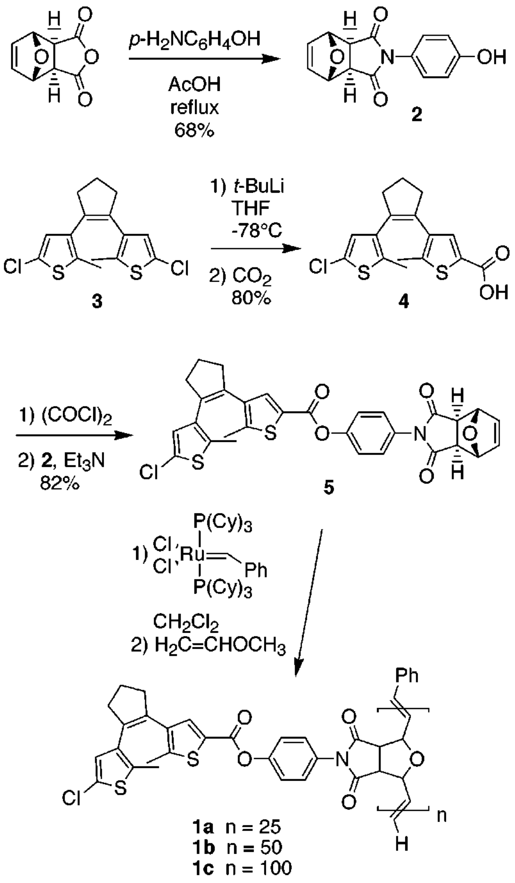
The popularity of ring-opening metathesis polymerization (ROMP) of strained bicyclic olefins is rising due to the mild reaction conditions needed, their compatibility with a wide range of functional groups, and the ease of generating well-ordered homopolymers from a wide range of strained olefin monomers.[5] These features make ROMP an attractive choice to complement the photochromic versatility of the 1,2-bis-(3-thienyl)cyclopentene photochrome. Also, by varying the catalyst-to-substrate stoichiometry, ROMP allows the polymer chain length to be readily tailored. This report represents the first example of photochromic homopolymers synthesized using ROMP technology.[6]

The monomeric precursor **5** was prepared as outlined in Scheme 1. Condensation of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride[7] with *p*-aminophenol in acetic acid generated the requisite strained olefin fragment **2**. Simultaneously, the recently reported dichloride **3**[8] was treated with *tert*-butyllithium to convert it into its monoanion, which was quenched with carbon dioxide to afford the photochromic carboxylic acid **4**. It is interesting to note that the yield of the monoanion in the lithiation step is greater than would be expected from a statistically governed product distribution. We attribute this to the unfavorable charge buildup that would exist if both chlorine atoms underwent metal−halogen exchange reactions. This charge buildup is still significant despite the fact that the two thiophene rings are cross-conjugated instead of directly conjugated, suggesting the charge−charge repulsion between two thiophene heterocycles would be felt through space.

Scheme 1



Coupling the acid chloride of **4** with the strained olefin **2** completed the preparation of monomer **5**. All new compounds were characterized by NMR spectroscopy, UV−vis spectroscopy, and mass spectrometry.

ROMP reactions of monomer **5** were performed under rigorously inert conditions in a Schlenk tube. The polymerization process was initiated with commercially available bis(tricyclohexylphosphine)benzylidine ruthenium(IV)dichloride (Grubbs' catalyst).[9] The polymerizations were then terminated by quenching the reaction mixtures with excess ethyl vinyl ether. The homopolymers were conveniently isolated in pure forms by precipitating them from cold ether and then washing with the same solvent to remove the catalyst and any unreacted monomer. Homopolymers with varying molecular weights were synthesized in a systematic fashion by changing the molar amount (1−4 mol %) of Grubbs's catalyst used to initiate the reaction. In all cases, the ROMP reactions were reproducible, affording polymers **1a**−**c** as off-white powders in good yields (~75%).

The ^1H NMR spectra of the precipitates from the ROMP reactions lack the signals corresponding to the double bond (6.56 ppm) and bridgehead protons (5.38 ppm) of the strained bicyclic olefin **5**, showing that any unreacted monomer was washed away in the isolation process. These signals are replaced by characteristically broadened peaks at 6.1 and 4.6 ppm for the polymers.

The polymeric products were all readily soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and benzene. They are air-stable solids of reasonable number-average molecular weights (M_n) and relatively narrow polydispersities (M_w/M_n) as determined by gel permeation chromatographic analyses calibrated by polystyrene (Table 1).

Table 1 also summarizes the UV−vis properties of THF solutions of the novel polymers along with those for monomer **5**. All polymers show typical absorbances for the colorless-open forms of the 1,2-bis(3-thienyl)cyclopentene photochrome at 248 nm. Photoinduced isomerization studies were carried out by irradiating the THF solutions of **1a**−**c**

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(5) (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (b) Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4975. (c) Robson, D. A.; Gibson, V. C.; Davies, R. G.; North, M. *Macromolecules* **1999**, *32*, 6371 and references therein.

(6) For other examples of polymers using dithienyl and diarylalkenes, see: (a) Wakashima, H.; Irie, M. *Polym. J.* **1998**, *30*, 985. (b) Kawai, T.; Kunitake, T.; Irie, M. *Chem. Lett.* **1999**, 905. (c) Stellacci, F.; Bertarelli, C.; Toscano, F.; Gallazzi, M. C.; Zotti, G.; Zerbi, G. *Adv. Mater.* **1999**, *64*, 292. (d) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Furuichi, K. *J. Am. Chem. Soc.* **1996**, *118*, 3305.

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(8) Lucas, L. N.; van Esch, J.; Kellog, R. M.; Feringa, B. L. *Chem. Commun.* **1998**, 2313.

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Table 1. Polymer Yields and Characterization

photochrome	equivalents of monomer	yield, %	M_n	M_w	M_w/M_n	λ_{max} (nm) open form	λ_{max} (nm) closed form[a]
1a	25	76	7920	11917	1.50	248	512
1b	50	78	16771	24577	1.47	248	512
1c	100	75	28007	43820	1.56	248	512
5						248	512

[a] After a 40 s irradiation period (λ = 254 nm).

at 254 nm with a short-wavelength hand-held lamp. Spectral changes were monitored in the UV−vis region (Figure 2).

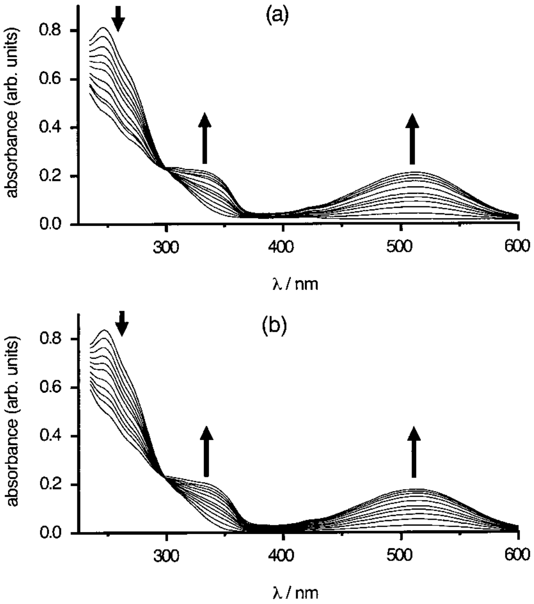

Figure 2. Changes in the UV−vis absorption spectra of THF solutions of (a) monomer **5** (3×10^{-5} M) and (b) polymer **1a** (approximately 1.2×10^{-6} M, corresponding to an equivalent concentration of the photochromic unit as for solutions of monomer **5**) upon irradiation with 254 nm light. Irradiation periods are 2, 4, 6, 8, 10, 15, 20, 25, 30, and 40 s.

In all cases, irradiation produced an immediate decrease in the absorbances corresponding to the open form of the dithienylethene photochrome at 248 nm. The decrease in these absorbances was accompanied by the appearance of broad absorbances for the pink closed form of the photochrome centered at 512 nm. The similarity of the absorption spectrum for monomer **5** and those of the polymers in both open and closed forms illustrates that the intimacy of the photochromes covalently linked to the polymer backbone affects neither the ground-state nor the excited-state properties of the photochrome.

The polymers can be easily decolorized by subsequent irradiation for 1 min with light of wavelength greater than 434 nm using a high power lamp with an appropriate cutoff filter. The photoisomerization process is thermally irreversible, and solutions of the closed forms kept in the dark showed no changes in their absorption spectra.

The polymers were very robust, and their thin films were easily cast by layering toluene solutions of **1a**−**c** onto water. After slow evaporation of the toluene, the resulting transparent films were transferred to slides. Transmission electron microscopy of the films revealed a smooth surface possessing no topological features. These films immediately turned from colorless to pink when exposed for brief periods (60 s) at 254 nm. As with the polymers in solution, the films could be decolorized with light at a wavelength greater than 434 nm.

The polymers described in this study lend support to the mildness of the ROMP process. The selective ring-opening of the strained olefin in the monomer should be emphasized.

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Supporting Information Available: Experimental procedures for preparation of compounds **2**, **4**, and **5** and polymers **1a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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