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Synthesis of Homopolymer Containing Diphenyl End-Capped Oligothiophene Co-oligomer Unit in the Side Chain

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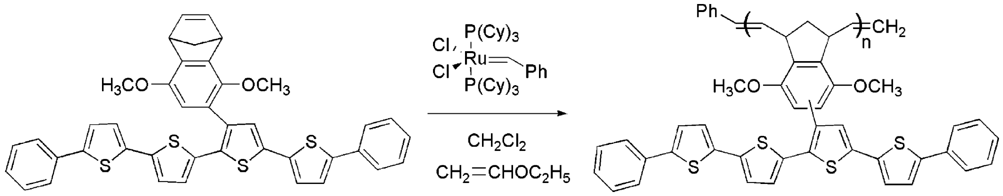
ABSTRACT



A new polymer with the diphenyl end-capped oligothiophene co-oligomer unit in the side chain was obtained by the ROMP method. The polymer showed good photophysical characteristics, thermal stability, and film-forming properties. A photovoltaic cell fabricated from this polymer showed relatively large open-circuit voltage (V_{OC} = 0.7 V), moderate short-circuit current (I_{SC} = 0.7 μA/cm^2), and excellent device stability under ambient conditions.

Thiophene-based π-conjugated oligomers and polymers[1] have been well investigated in the past decades due to their chemical and environmental stability and their potential applications in many fields such as field-effect transistors,[1c,h,*l*] photoswitches,[1e] photovoltaic cells,[1f] or light modulators.[1g] Extensive studies have been carried out on polymers obtained by oxidative or electropolymerization of thiophenes,[2] bithiophenes,[3] and terthiophenes.[4] However, this research on conjugated polythiophenes was plagued by difficulties in processing the intractable materials and imperfections in the conjugated polymer microstructures. Conjugated oligothiophene derivatives that have well-defined structures and interesting physical, electronic, and optical properties have emerged as model compounds to rationalize and predict the properties of the corresponding polymeric analogues.[5]

The incorporation of conjugated oligomers into polymer structures combines the properties of the specific oligomer with the desirable properties of polymer such as mechanical strength and film-forming properties. A few reports[2,6] showed that oligothiophenes can be attached to nonpolar vinyl-type monomers as well as methacrylate polymers as side chains. These polymers showed an electrical conductivity in the

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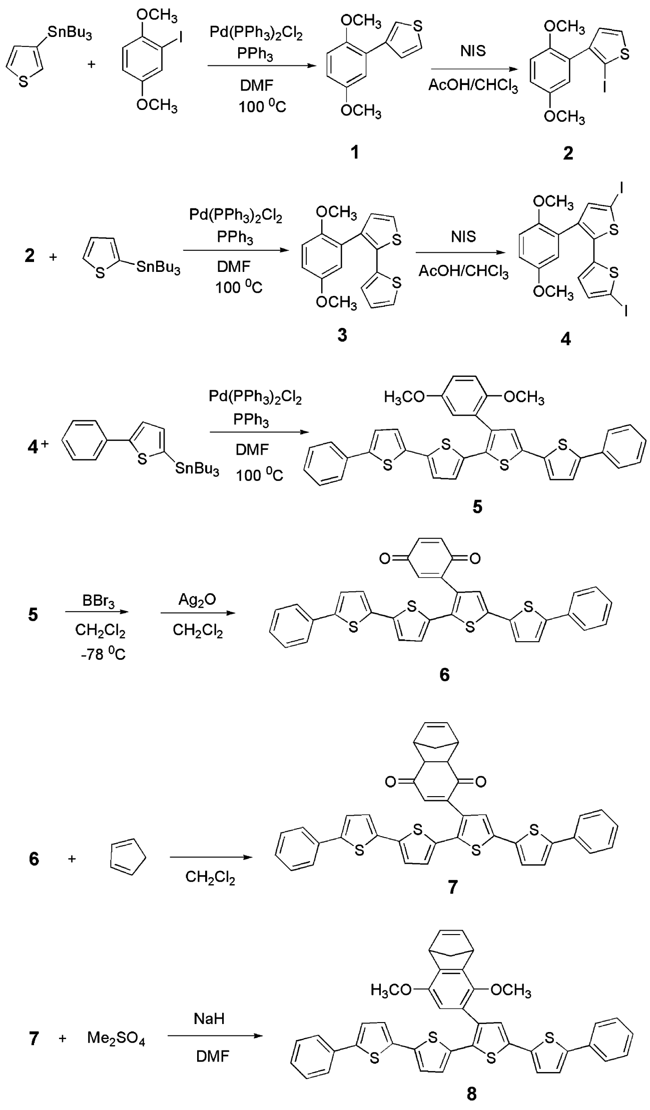
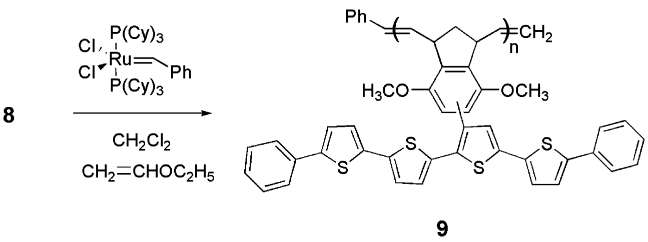
Scheme 1. Synthesis of Oligothiophene-Functionalized Norbornene Monomer **8**



Scheme 2. Ring-Opening Metathesis Polymerization of **8**



range of semiconductors and have potential applications in electrochromic devices.Polymers containing π-conjugated oligomers in the side chain are of particular interest because of the variety of possible oligomers, processability, supramolecular self-assembly properties attainable by the appropriate choice of the side group, and potential applications in electronic devices.[2] On the basis of these grounds, we became interested in attaching π-conjugated oligothiophene−phenylene co-oligomer in the side chain because of the rigid rodlike structures and useful optoelectronic properties of these oligomers.[7] For this purpose, we report here a new polynorbornene system with π-conjugated oligomers fused to the backbone as shown in Scheme 2. The polynorbornene was prepared by a ring-opening metathesis polymerization (ROMP) of laterally attached rodlike norbornene monomer, using the first-generation Grubbs' catalyst as the initiator.

The reactions used for the preparation of monomer **8** and polymer **9** are outlined in Scheme 1 and Scheme 2. The compound 4′-(2,5-dimethoxyphenyl)-5,5‴-diphenyl-2,2′;5′,2″;5″,2‴-quaterthiophene **5** was prepared in five steps commencing from 2-iodo-1,4-dimethoxybenzene by known chemistries including a palladium-catalyzed Stille cross-coupling[8] with 3-(tributylstannyl)thiophene and regioselective iodination on one of the α-positions of the resulting thiophene unit.[9]

It is worth mentioning that in the course of the purification of 3-(2,5-dimethoxyphenyl)thiophene **1**, we observed that this intermediate was somewhat difficult to purify because of its similar polarity to 1,4-dimethoxybenzene, a contaminant resulting from the selective monoiodination of 1,4-dimethoxybenzene. Gratifyingly, the presence of this side product has no detrimental effect on the two following steps, and it can be completely removed from the less polar dithienyl-substituted dimethoxybenzene **3**. A regioselective diiodination of **3** gave diiodo bithiophene **4** in 99% yield. This intermediate was subject to another Stille coupling with 5-phenyl-2-(tributylstannyl)thiophene to afford hexamer **5** in 75% yield. This compound can be purified by column chromatography on silica gel or by recrystallization and is partially soluble in CH_2Cl_2 and $CHCl_3$. Conversion of the dimethoxybenzene moiety in **5** to the corresponding quinone **6** was carried out following a standard deprotection−oxidation protocol involving removal of the dimethoxy protecting groups (BBr_3, CH_2Cl_2) followed by oxidation of the intermediate hydroquinone (Ag_2O, CH_2Cl_2).[10] A Diels−Alder reaction of quinone **6** with excess cyclopentadiene provided a norbornene derivative **7** in nearly quantitative

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yield. This intermediate was then deprotonated to give bis-enolates followed by methylation with dimethyl sulfate in a one-pot procedure to furnish monomer **8**.[11]

The monomer was polymerized by using the ROMP method in accordance with Scheme 2. The polymerization was performed with commercially available bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride (first-generation Grubbs' catalyst)[12] as initiator in dry CH_2Cl_2 under an inert atmosphere. The ratio of monomer to initiator was close to 100:1. The polymerization was allowed to run at 25 °C for 22 h and then terminated by quenching the reaction mixture with excess ethyl vinyl ether. The homopolymer were conveniently obtained in pure form by filtration of the precipitate formed from the reaction mixture followed by washing with ether for the removal of catalyst and unreacted monomer. Our attempts to directly polymerize monomer **7** have been unsuccessful so far, which was in agreement with other *endo*-monomers of norbornene derivatives.[12a,13] On the contrary, the polymerization of monomer **8** went smoothly under the same conditions within 22 h, providing oligothiophene−phenylene co-oligomer functionalized polynorbornene in 83% yield.

The ^1H NMR spectrum of the polymer shows broadened peaks compared to those of the monomer and the signal of vinylic protons appeared at 5.59 ppm, which is shifted upfield. The molecular weight of the polymer was determined by gel permeation chromatography (GPC), using THF as the eluent and polystyrene as the standard. The number average molecular weight (M_n) was determined to be 65 217, and the polydispersity was narrow (PDI = 1.08). The thermal properties were evaluated by means of thermogravimetric analysis (TGA) under a nitrogen atmosphere. The TGA plot (Supporting Information S1) of the polymer measured at a heating rate of 10 °C min^{-1} revealed that this polymer exhibited good thermal stability up to 411 °C.

The photophysical properties of both the monomer and polymer were investigated in solutions and also as a solid thin film for the polymer, prepared by spin-coating from a $CHCl_3$ solution. Owing to the comparatively large size and higher rigidity of the laterally attached co-oligomer relative to the more fexible polymeric backbone, the thiophene−phenylene co-oligomer moieties on the side chains are expected to have slightly weaker interactions with one another when compared to the individual monomers. This is supported by the observation that the λ_{max} value observed for optical absorption of the polymer (422 nm) in $CHCl_3$ was slightly blue-shifted when compared to that of the monomer (430 nm). On the other hand, the λ_{max} for the emission of the polymer (551 nm) was red-shifted and the band was essentially structureless when compared to that of the monomer (510, 538 nm) (Supporting Information S2). The UV−vis absorption and emission spectra of polymer **9** in $CHCl_3$ solution and as thin film are depicted in Figure 1.

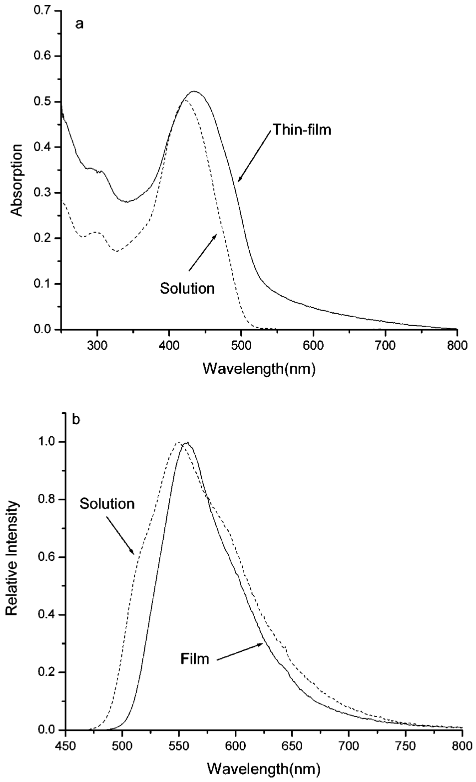

Figure 1. (a) UV−vis absorption spectra of polymer **9** in $CHCl_3$ solution and as a thin film. (b) Normalized photoluminescence spectra of polymer **9** in $CHCl_3$ solution and as a thin film.

The λ_{max} of the polymer in solution was around 422 nm, while the thin film was bathochromically shifted to 435 nm, and the λ_{max} for the emission of polymer thin film (558 nm) also undergoes a red-shifting in comparison with that in solution (551 nm). The red-shifting effect was presumably due to increased $\pi-\pi$ stacking in the solid state. Accordingly, the optical band gap values of the polymer in solution and as a film were found to be 2.48 and 2.10 eV. Cyclic voltammetric measurement of polymer **9** (Supporting Information S4) showed two reversible one-electron oxidations at +0.96 and +1.13 V (versus SCE).

This polymer has been incorporated into a simple organic photovoltaic cell by spin-coating a $CHCl_3$ solution of the polymer **9** on an indium−tin oxide (ITO) covered glass substrate and depositing an aluminum film (50 nm) on top of the polymer materials. Figure 2 shows the current−voltage characteristics of the Al/polymer/ITO device in the dark and under illumination at an intensity of 50 mW/cm^2. The device

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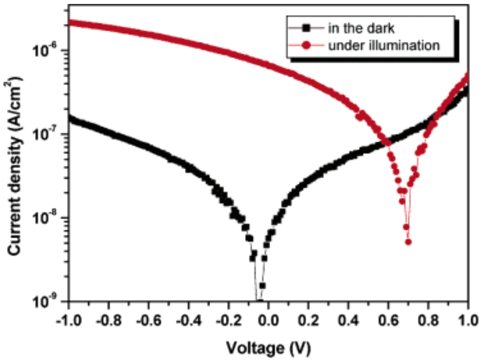

Figure 2. Current−voltage ($I-V$) characteristics of a Al/polymer/ITO device test structure when measured in the dark and under white light illumination (50 mW/cm^2).

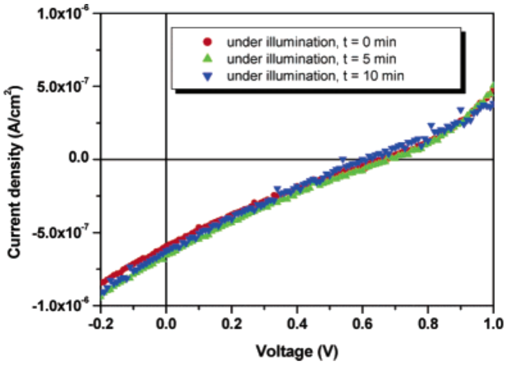

Figure 3. Current−voltage ($I-V$) curves of a Al/polymer/ITO structure under illumination with white light at an intensity of 50 mW/cm^2 obtained by repeated measurements at 5-min intervals.

clearly shows a rectifying behavior in the dark and exhibits significant photovoltaic effects under illumination. These preliminary results showed that our photovoltaic cell has a large open-circuit voltage ($V_{\mathrm{OC}} = 0.7$ V) and moderate short-circuit current ($I_{\mathrm{SC}} = 0.7\ \mu$A/cm^2). Interestingly, we observed that this photovoltaic cell showed excellent device stability under ambient conditions as depicted in Figure 3. By repeatedly measuring the device performance at 5-min intervals, one finds that their $I-V$ characteristics remain essentially unchanged and this sort of device stability is in sharp contrast to other solar cells fabricated from polythiophenes where their device performance showed a much faster decay upon repeated measurements.

In summary, a novel polynorbornene functionalized with thiophene−phenylene co-oligomer in the side chain was synthesized by the ROMP method. Overall, the polymer showed good photophysical properties for the side-chain appended co-oligomer, as well as excellent thermal stability and film-forming properties due to the polynorbornene backbone. More importantly, it is observed that a photovoltaic cell fabricated from this polymer showed relatively large open-circuit voltage, moderate short-circuit current, and excellent device stability under ambient conditions. In light of the good film-forming and promising photovoltaic properties of this polymer system, further study toward the optimization of polymer structure by changing the spacers between the polymer backbone and co-oligomer unit and construction of corresponding solar cell devices is currently underway.

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Supporting Information Available: Experimental procedures, absorption and photoluminescence spectra of the monomer **8**, and cyclic voltammogram of polymer **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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