

Anionic Oxidative Polymerization: The Synthesis of Poly(phenylenedicyanovinylene) (PPCN2V)

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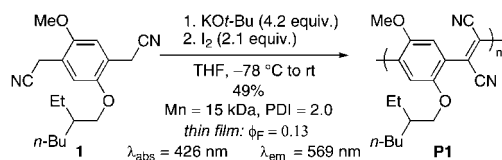
Received August 8, 2008; E-mail: tswager@mit.edu

The application of polymeric semiconductors to organic light emitting diodes,¹ field-effect transistors,² and photovoltaic cells³ requires both p- and n-type materials. Although p-type polymers are readily available,⁴ stable n-type polymers remain largely elusive.⁵ Access to conjugated high electron affinity polymers remains a critical challenge within the field of polymer synthesis. One of the most successful strategies has been the construction of poly(phenylene vinylenes) (PPVs) containing cyano-substituted olefins via a polymeric Knoevenagel condensation.^{1,6} The cyano substituents greatly increase the electron affinity, while allowing for the tuning of the polymer properties via variation of the aryl rings.

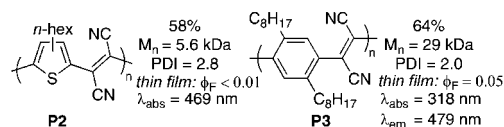
Despite the utility of the Knoevenagel polymerization, the technique cannot be adapted to form dicyano-PPVs (PPCN2Vs). Such polymers would have even greater electron affinities than the monocyno variants, but no syntheses of such systems have been described. Here we report a new polymerization technique, which provides access to PPCN2V polymers. The procedure affords higher molecular weights than the Knoevenagel polymerization and requires only a single starting material. The resulting polymers are highly photostable, easily reduced, and soluble in organic solvents.

The oxidative dimerization of phenyl acetonitrile using an alkoxide base and iodine was first communicated in 1892⁷ and has found recent use in materials chemistry.⁸ It had not, however, been explored in the synthesis of polymeric systems. Monomer **1**⁹ was chosen to test the polymerization technique based on the prevalence of MEH-PPV. We found that the addition of 4 equiv of potassium *tert*-butoxide to **1** at reduced temperature, followed by the gradual addition of iodine, with concurrent warming, resulted in efficient formation of **P1** (Scheme 1). As expected cyclic voltammetry of **P1** demonstrated that it possessed a smaller reduction potential than that of the CN-MEH-PPV polymer derived from condensation polymerization.¹⁰

Scheme 1



other PPCN2Vs synthesized:

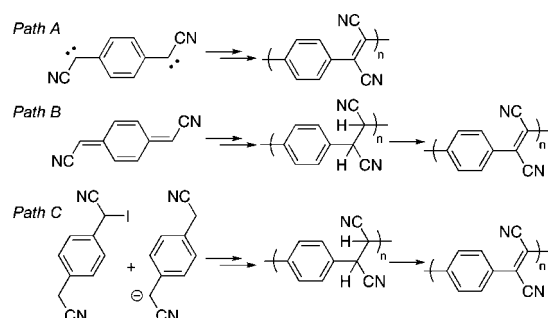


Additional monomers were also found to be compatible with this polymerization technique (Scheme 1).¹¹ Based on the interest

in poly-3-hexylthiophene (P3HT) in materials science,¹² the corresponding PPCN2V **P2** was generated, which also demonstrated that heterocycles are well tolerated by this polymerization technique. The low quantum yield of **P2** is consistent with the weak fluorescence of a related monocyno variant.¹³ **P2** showed negative solvatochromism and displayed modestly higher quantum yields in nonpolar solvents,¹⁴ which possibly supports the existence of a charge transfer deactivation of the excited state. Less electron-rich systems, relative to **P1**, also appear viable as shown by the synthesis of **P3**. In all cases the polymers were free of side products as determined by NMR and elemental analysis.¹⁵

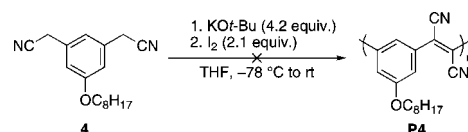
There are many potential pathways that this polymerization could be proceeding through (Scheme 2). *Path A* is distinguished from other pathways by the absence of a saturated intermediate during polymerization. By using fewer equivalents of base/oxidant, we were able to test for the existence of a saturated intermediate and in fact a copolymer featuring both saturated and unsaturated repeat units was observed. This polymer can be converted to its fully oxidized form (**P3**) by re-exposure to the polymerization conditions.

Scheme 2



Thus, it seems reasonable to conclude that *Path A* is not operating in this polymerization.¹⁶ If *Path B* is the predominant mechanism then *meta*-substituted aromatic systems are unlikely to polymerize efficiently. In comparison, in an S_N2 pathway (*Path C*) as well as a carbene pathway (*Path A*) the geometric relationship between the acetonitrile substituents is irrelevant and *meta*-systems should behave similarly to the *para*-systems; this was not observed to be the case (Scheme 3). Thus, it would appear that the reaction likely proceeds most favorably through a quinoidal intermediate as with the Gilch polymerization.¹⁷

Scheme 3



The PPCN2Vs have unusual photophysical characteristics in thin films. Prolonged irradiation¹⁸ of thin films of **P1** and **P3** resulted in increased photoluminescence (Figure 1).¹⁹ Placing the thin film in the dark for 48 h does not result in the quantum yield reverting to its original value; rather it matched that observed when irradiation was halted. The excellent photostability of the PPCN2Vs is exemplified by contrasting their behavior with that of MEH-PPV, which bleaches almost instantly under the same conditions, as well as BEHP-PPV, which is marketed as a photostable PPV but showed a steady decline in fluorescence after 60 min of irradiation (Figure 1). In comparison, **P3** possessed a greater quantum yield than its initial value, even after continuous excitation for 3 h. Bleaching of the even harder **P1** was not observed.

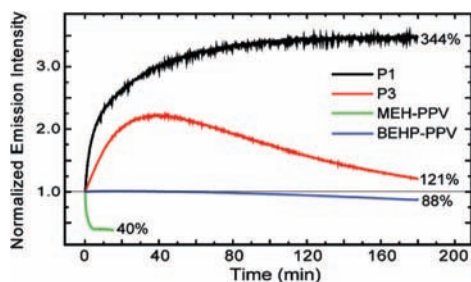


Figure 1. Evolution of emission intensity of thin films with continuous irradiation at maximum absorption: 426 (**P1**), 318 (**P2**), 485 (MEH-PPV), and 402 nm (BEHP-PPV).

We initially thought the observed increase in quantum yield was the result of photodegradation of a quenching impurity. However, neither extensive purification of the polymer¹⁵ nor performing the irradiation under inert atmosphere altered the observed increase in quantum yield. We now favor that this unique behavior results from a *cis/trans* isomerization in some of the subunits of the polymer, as is known to occur with stilbene systems.²⁰ This is illustrated conceptually in Figure 2. In the initial, spun-cast, film (A) the polymers are closely packed and a majority of excitons are deactivated by self-quenching.²¹ Irradiation of the thin film results in *cis/trans* isomerization of the olefins in the PPV that disrupts the tight packing due to the significant geometrical change associated with such isomerizations (B). The accompanying diminished interpolymer associations reduce quenching. Removal of the polymer from light could result in the polymers returning to their original conformer distribution (C). However, the reduced mobility of polymer chains in the film makes thermal reformation unlikely; thus the increased quantum yield persists.

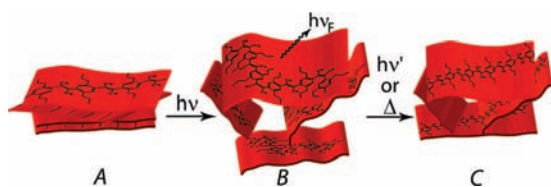


Figure 2. *Cis/trans* isomerization as a rationale for the observed increase in quantum yield in the thin film.

Proof of the topological change proposed in Figure 2 was obtained by irradiating a thin film of **P1** at 400 nm with a laser using a parallel-line interference pattern and examining the film by atomic force microscopy (AFM) (Figure 3). The images show a pronounced increase in film thickness, ~12 nm on average,²² at

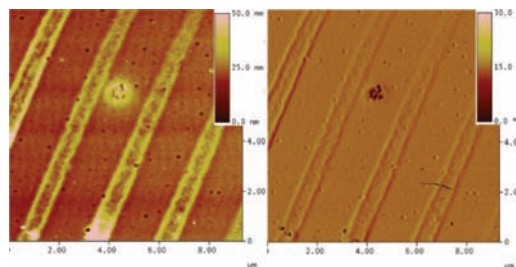


Figure 3. AFM height (left) and phase (right) images of a 196 nm thick film of **P1** after exposure to a parallel line interference pattern (400 nm, 2 mW, 150 fs pulses, at 60 Hz for 10 s). The circular mark near the center corresponds to a film defect.

the sites of irradiation. No such effect is observed using BEHP-PPV, suggesting that the swelling is not a result of localized heating but rather is a consequence of the disruption of the packing in the thin film caused by the *cis/trans* isomerizations.

In summary, anionic oxidative polymerization represents a new means to access conducting polymers, and it has allowed for the first ever synthesis of PPCN2V systems. The polymers presented herein are extremely photostable and represent easily accessible, high electron affinity conductive polymers.

Acknowledgment. We were supported by the U.S. Army Medical Research (W81XWH-07-1-0649) and the Army Research Office's IED Stand-Off Detection Research Program (W911NF-07-1-0654).

Supporting Information Available: Spectroscopic information and representative experimental procedures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA808256N