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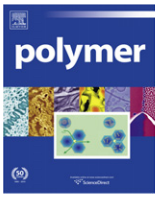

Macro-counterions in a precursor to poly(phenylene vinylene): Toward defect-free luminescent films

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Thermal elimination of a water soluble poly(xylylidene) precursor to poly(phenylene vinylene) (PPV) was accomplished in air at 80 °C using the macro-counterion poly(ethylene glycol)-4-nonylphenyl-3-sulfopropyl ether (PEGNOPS). The high relative photoluminescence efficiency was ascribed to the low carbonyl content, with a possible contribution from PPV chain separation, which minimizes radiationless interchain exciton formation. In addition, the PEGNOPS precursor showed no carbonyl formation on long term storage, in contrast to the precursors with dodecylbenzene sulfonate and chloride counterions.

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1. Introduction

Conjugated polymers have been researched extensively for use in optoelectronic applications [1,2] including organic light emitting diodes (OLEDs) [1,3–6], field effect transistors [1,7,8], polymer solar cells [6,9] and flexible electronic devices [8]. OLEDs built from poly(phenylene vinylene), PPV, and its derivatives have demonstrated promising efficiency [10]. The insolubility of PPV, which complicates processing [2,11,12], has been addressed by using lower molecular weight material [11], or by introducing non-conjugated spacers, or by adding soluble side chains [13]. Another method to overcome the processing challenge is *via* a precursor route. Scheme 1 shows a common approach, where a water soluble poly(xylylidene) with tetrahydrothiophene (THT) as a good leaving group permits relatively low temperature thermal elimination to yield PPV.

While the ability to convert PPV precursor to PPV at low temperature has advantages, especially in LED applications in which other, thermally sensitive, materials are involved, the thermal elimination route introduces various defects into the polymer backbone. For example PPV suffers from side reactions which lead to carbonyl groups in the backbone [14]. These carbonyl defects, reported by Murase et al. [15], who prepared PPV in air according to Scheme 1, caused a drop in the electrical conductivity of PPV. Hydroxyl defects on the PPV backbone prepared *via* the same route were reported by Hsieh et al. [16]. When research in conjugated polymers turned to potential OLED applications, it was quickly found that defects, especially carbonyls, severely compromised photoluminescence (PL) [17,18]. For example, Yan et al. [19] reported that PL is reduced by factor of two for every one carbonyl per 400 PPV repeat units. Such a carbonyl quenching mechanism, which occurs for all derivatives of PPV, and its dramatic effect on PL intensity of PPV, is now well documented [3,17,19–24]. OLEDs rely on electroluminescence (EL) to generate light. Since the conversion of excited state energy to light is similar in EL and PL, the latter is usually employed to gauge the potential maximum efficiency of OLEDs [17,25–27].

The counterion, A^- in Scheme 1, was shown to have a significant impact on elimination temperature [14]. PXT with halide as a counterion is fully eliminated at 200 °C while that with acetate must be heated to 350 °C. At this high temperature, carbonyl formation increases, even under high vacuum or under ultrapure argon [17]. Thermal elimination at lower temperatures leaves a significant amount of unconverted precursor, which also yields low PL efficiency. It was reported that PXT with dodecylbenzene-sulfonate (DBS) (Fig. 1) as a counterion can be converted to highly conjugated PPV within 3 min at 115 °C [28]. A significant feature of this work was that conversion occurred under atmospheric conditions (i.e., in the presence of air) without the use of a dynamic vacuum or inert gas. As DBS is a hydrophobic counterion it caused precipitation of PXT on exchange with chloride [28]. To prevent the precipitation, NaCl aliquots were added to PXT-DBS exchange

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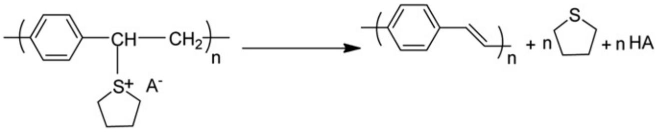


Scheme 1. A precursor route to PPV.

solutions [28]. Treger et al. reported that using sodium dodecyl sulfate (SDS) as counterion for PPV derivatives enhances its optical properties and inhibits the photo-oxidation of the film [29]. Using SDS as a counterion increased the half life of degradation of PPV derivative by 3 fold.

In addition to the caveats on carbonyls, Yan et al. [30] pointed out the virtues of separating PPV chains, which encourages the formation of (emissive) intrachain excitons as opposed to (non-emissive) interchain excitons. Diluting PPV derivatives in blends or in solution enhanced intrachain excitons. Larger counterions would be more efficient at keeping PPV chains separated. The exchange of PXT counterions is rather straightforward. To maintain water solubility of this precursor, A^- should be hydrophilic. We were interested in the use of a hydrophilic macroscopic counterion. In particular we were intrigued by a counterion that could enhance solid state ionic conductivity, which might be useful in the light emitting electrochemical cells described by Cao et al. [31,32] The counterion used in this study was poly(ethylene glycol)-4-nonylphenyl-3-sulfopropyl ether (PEGNOPS) which is a long chain surfactant (Fig. 1). PEGNOPS has a hydrophilic moiety, twenty ($-O-CH_2-CH_2$) units, that prevents PXT precipitation. We found that a PXT-PEGNOPS precursor required exceptionally low conversion temperatures, yielded low carbonyl formation and PPV with high relative PL.

2. Experimental

Dodecylbenzenesulfonate sodium salt (DBS), poly(ethylene glycol)-4-nonylphenyl-3-sulfopropyl ether potassium (PEGNOPS) and α,ά-dichloro-*p*-xylene (98%) were used as received from Aldrich. Monomer synthesis: p-xylylenebis(tetrahydrothiophenium chloride) was prepared by refluxing α, ά-dichloro-p-xylene with tetrahydrothiophene at 80 °C for 20 h in methanol under Ar. The dried product was purified by washing with cold acetone [33]. Poly(xylylidenetetrahydrothiophenium chloride) (PXT-Cl) was prepared following a literature procedure [33]. PXT-Cl was purified by dialyzing against distilled water using 12,000–14,000 molecular weight cutoff dialysis tubing (Spectra/Pro).

2.1. Ion exchange

The chloride ion was exchanged by mixing 10 mM PXT-Cl with 1.42 mM PEGNOPS dissolved in ethanol and dialyzing against a large excess of 200 mM PEGNOPS solution for 24 h, then for 48 h against distilled water. Chloride was exchanged by DBS using the method of Marletta et al. [28]. Films were cast under atmospheric conditions at room temperature on the relevant substrate. Elemental analysis on the ion exchanged PXT-PEGNOPS (Atlantic Microlab): C 57.05%, H7.87%, S 7.71%, Cl 0.65%; showing that 78% of the chloride was exchanged by PEGNOPS.

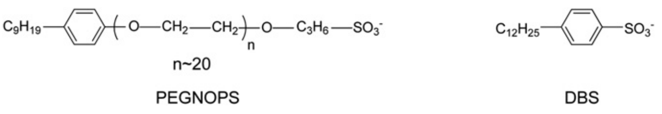


Fig. 1. Structures of PEGNOPS and DBS.

2.2. Optical measurements

Infrared (IR) spectroscopy was performed using a nitrogen purged FT-IR (Nicolet Nexus 470 with a DTGS detector) spectrometer. Resolution was 4 cm^{-1} with 36 averaged scans on samples, which were prepared on double-side polished silicon (Si⟨100⟩) wafers. The sample holder was held at 15° off-perpendicular to avoid interference fringes on the spectra. UV–vis spectra were recorded on a Varian Cary 100 UV–vis double beam spectrophotometer. Samples were prepared on fused quartz disks (GM Associates, 2 mm thick, 1 inch diameter). Photoluminescence was recorded on a Cary Eclipse fluorescence spectrophotometer. Samples were excited at different wavelengths and emission was recorded to 800 nm.

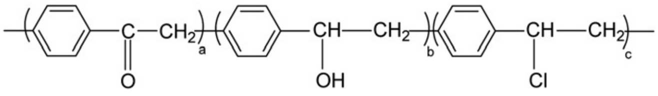
2.3. Thermal annealing

PXT films were converted either under vacuum on a vacuum line equipped with an oil diffusion pump, or under atmospheric conditions. In both cases, samples were monitored by a thermocouple in direct contact with the substrate on which the film was cast. PXT with different counterions was converted at 80 °C for different times under atmospheric conditions, then cooled and subjected to spectroscopic analysis. For comparison, PXT-Cl was converted under vacuum for 10 min at 210 °C [19,28].

3. Results and discussion

While the aqueous precursor route to PPV (Scheme 1) enhances processibility, especially film formation, potential defects affect optical and electrical properties. Scheme 2 shows some of the possible chemical defects that can be formed prior to, during, or after thermal annealing of PXT. For example, since THT is a good leaving group it can be substituted during synthesis or storage by Cl^- and OH^- ions which are nucleophiles (unit c and b Scheme 2, respectively). Hydroxide is usually added to initiate polymerization where Cl^- is from residual HCl that is added to quench polymerization. The defects break conjugation along the backbone, but can be partially removed by elimination at higher temperature. A counterion such as PEGNOPS has a sulfonate, which is a weak nucleophile, and its long chain possibly decreases nucleophilicity further due to steric hindrance. A critical chemical defect that may occur in the backbone of PXT or/and PPV is carbonyl (unit a, Scheme 2) formed *via* oxidation. The carbonyl defect is problematic because it is hard to remove at high temperature. In fact, higher annealing temperatures promotes carbonyl formation, as does photo-oxidation during storage. Considerable research has focused on the effect of these chemical defects on PPV. All have emphasized the strong (negative) impact that carbonyl has on PPV optical properties [3,17,19,21,24].

Fig. 2 shows the PL intensity of PPV prepared from PXT-Cl at 80 °C in air in comparison to the amount of carbonyl and extent of elimination in the film. The relative extent of elimination is estimated by the ratio of a PPV band at 3024 cm^{-1} (vinylene mode) to the area of 1515 cm^{-1} (in plane bending of H on benzene ring) [14,22]. The latter was found to be approximately constant during



Scheme 2. Possible chemical defects on PPV formed prior to, during or after thermal annealing of the PXT precursor. a) backbone oxidation to yield carbonyls b) hydroxide substitution during synthesis c) chloride substitution during storage.

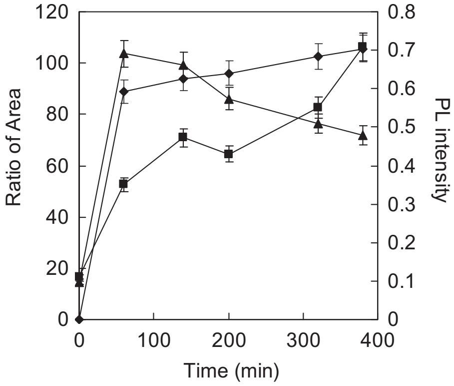


Fig. 2. PL intensity of PXT-Cl thermally annealed at 80 °C under atmospheric conditions. (▲) PL intensity, in arbitrary units, at $\lambda = 525$ nm vs. time of thermal annealing at 80 °C in air. (◆) Area of IR peak at 3024 cm^{-1} (trans vinylene C–H stretch in PPV) normalized to the 1512 cm^{-1} peak area (in plane C–H stretch of benzene ring). (■) Normalized IR area of 1690 cm^{-1} band (carbonyl stretch) relative to 1512 cm^{-1} peak.

elimination. The carbonyl intensity is also normalized to the 1515 cm^{-1}. While the extent of elimination increases with time of thermal annealing, the PL intensity, after an initial increase, falls off with further heating. At the same time, the carbonyl content increases, consistent with the decrease in PL efficiency. For efficient PL quenching of the fluorophore (conjugated backbone) and the quencher (carbonyl) should be in proximity. The fact that carbonyl is embedded in the backbone unfortunately maximizes quenching, decreasing the quantum efficiency of devices based on PPV.

In the literature, the problem of carbonyl formation has been tackled by changing thermal annealing and/or storage conditions. (We typically store PXT in the dark at low temperatures to minimize photo-oxidation.) For example, thermal annealing has been carried out under Ar (99.999%), under high vacuum, or under a blanket of reducing gas (85% nitrogen, 15% hydrogen) [17]. But in all these, a significant amount of carbonyl was formed, and in the best case only 40% $-C{=}O$ reduction was reported [17]. The second approach involves performing the elimination at low temperature which results in a partly eliminated PXT with low PL intensity [3]. The reactivity of the PPV backbone can be decreased by adding electron withdrawing side groups, such as phenyl or trifluoromethyl [34], which reduces the oxidation of PPV backbone [35]. Shielding the PPV backbone by attaching bulky groups as a side chain also aids in reducing backbone oxidation. Finally, the PPV precursor has been blended with PEG which improves atmospheric stability and optical properties of PPV [36,37].

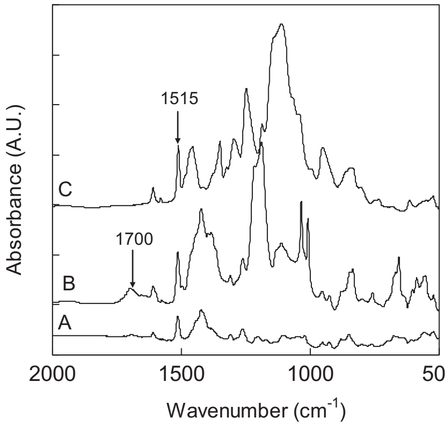


Fig. 3. IR absorption spectra of cast films of (A) PXT-Cl (B) PXT-DBS (C) PXT-PEGNOPS stored at room temperature in the presence of ambient light for 30 days. The peak at 1700 cm^{-1} corresponds to the carbonyl stretch. The spectra have been normalized to the 1512 cm^{-1} aromatic band. In spectra B and C this band is presented at twice the height of spectrum A to account for the contribution to the band from the counterion.

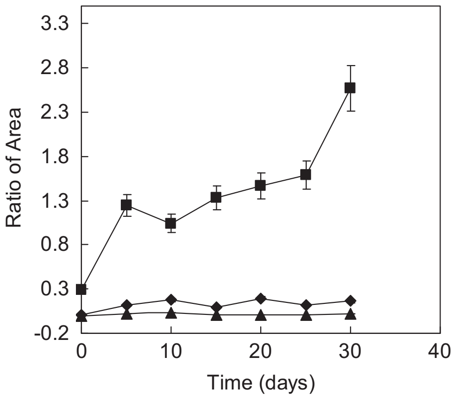


Fig. 4. Ratio of area under FT-IR peak at 1700 cm^{-1} carbonyl stretch to area of 1512 cm^{-1} peak in plane stretch of benzene ring C–H for (■) PXT-DBS, (◆) PXT-Cl; and (▲) PXT-PEGNOPS which are stored at room temperature under ambient light.

We were somewhat surprised to find a significant counterion dependence of defect formation on storage of the PXT precursor. Fig. 3 shows the IR spectra of PXT-Cl, PXT-DBS and PXT-PEGNOPS solutions after 30 days of storage under ambient conditions. Both Cl and DBS precursors formed carbonyls (see stretch at ~1700 cm^{-1}). In comparison, the amount of carbonyl formed for PXT-PEGNOPS under the same conditions was minimal. The normalized area of the carbonyl stretch versus storage time under ambient conditions for the three different counterions is plotted in Fig. 4. PXT-DBS had a higher tendency to form carbonyls than PXT-Cl over 5 days, which is a relatively short storage time. For PXT-Cl, carbonyl formation was constant after 5 days of storage, whereas carbonyl formation increased continually for DBS. The highest carbonyl ratio PXT-PEGNOPS reached is 0.017 ± 0.002 which is 76 times less than PXT-DBS. Even after 14 months of storage, PXT-PEGNOPS has a carbonyl peak ratio 24 times smaller than that of PXT-DBS after 30 days of storage. These results show the unexpected effectiveness of PEGNOPS as a counterion to prevent premature carbonyl formation on storage of PXT, even under ambient temperature and light exposure conditions.

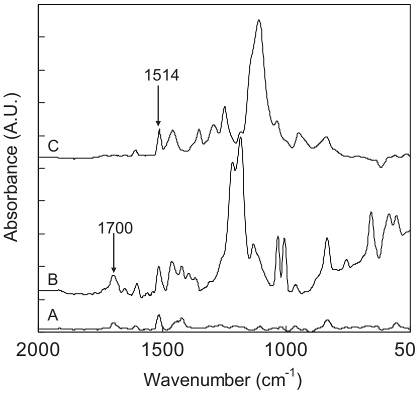


Fig. 5. IR absorption spectra of (A) PXT-Cl (B) PXT-DBS (C) PXT-PEGNOPS films annealed at 80 °C for 20 min under atmospheric conditions. The peak at 1700 cm^{-1} corresponds to the carbonyl stretch. The spectra have been normalized to the 1512 cm^{-1} aromatic band as in Fig. 3.

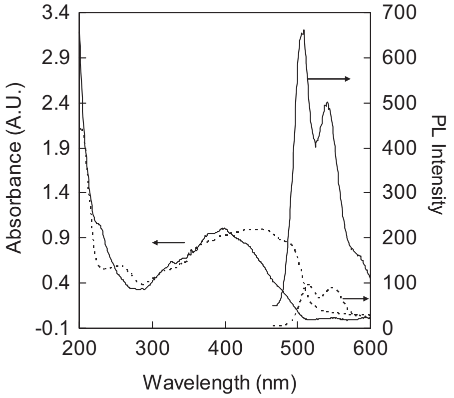
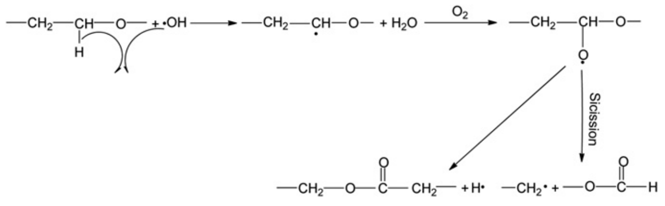


Fig. 6. UV–vis and normalized (to the 400–450 nm absorption band) PL spectra of (a) PXT-Cl film thermally annealed at 210 °C under vacuum for 10 min (dotted lines) (b) PXT-PEGNOPS film thermally annealed at 80 °C under atmospheric conditions for 20 min (solid lines).

The maximum conversion of PXT-Cl to PPV films is done at high temperatures, typically 210 °C–300 °C, under vacuum or a blanket of high purity inert gas. These conditions yield PPV with nominally the most extended conjugation (indicated by red shifted UV–vis absorption) but also lead to low PL intensity due to carbonyl defects. High temperatures are unfavorable for most PPV applications, since other materials used in conjunction with PPV to make devices can suffer from changes in properties. In addition, PPV is often deposited on a transparent conductive electrode, such as glass coated with indium tin oxide (ITO) to make OLED devices. This type of anode is known to be unsuitable for PPV prepared by aqueous route where Cl is a counterion. During conversion of PXT-Cl to PPV, hydrogen chloride, formed as a by-product, reacts with ITO to form $InCl_3$ which quenches luminescence and causes non-uniformity in the current distribution in OLEDs [38–41]. In the case of PXT-PEGNOPS, the by-product is not mobile and thus may not react with the electrode.

The elimination of PXT with the PEGNOPS counterion provides for the lowest conversion temperature reported and may be performed under atmospheric conditions. Furthermore, the formation of carbonyl groups is significantly suppressed, leading to enhanced PL. Fig. 5 shows IR spectra of PPV annealed at 80 °C under atmospheric conditions for 20 min. Both Cl and DBS have formed carbonyls during annealing while PEGNOPS shows relatively few carbonyls. In fact, the normalized area of the carbonyl peak (in curve 5C) was found to be lower than the area formed after 30 days room temperature storage of PXT-Cl.

Fig. 6 depicts PL and UV–vis absorption spectra of PPV prepared from PXT-Cl at 210 °C for 10 min under vacuum compared to PXT-PEGNOPS heated at 80 °C for 20 min under atmospheric conditions. These conditions, reached following extensive experiments varying time and temperature, were found to yield PPV films with the highest PL intensities. The spectra are scaled such that the absorbance at 400–450 nm is the same height, which allows comparison of the relative PL efficiency. Although PPV prepared from PXT-Cl is more conjugated, judging from the red shifting of the absorbance band, it has a lower luminescence intensity compared to PPV prepared from PXT-PEGNOPS under atmospheric conditions. This finding is interpreted to result from the lower concentration of carbonyls on the backbone for the latter. The lesser conjugation is believed to be a result of the residual chloride counterions. The PXT appeared to behave as a copolymer, where PEGNOPS-compensated units eliminate at a lower temperature than Cl^- units. This intriguing possibility for controlling conjugation length is being explored further.



Scheme 3. PEG oxidation reaction.

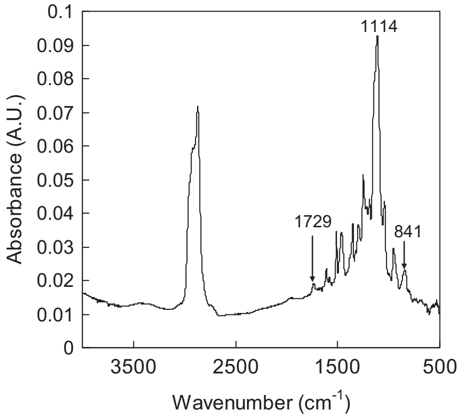


Fig. 7. FT-IR spectra of PEGNOPS extracted from a PXT-PEGNOPS film thermally annealed at 80 °C in air.

The ability of PEGNOPS to retard PPV oxidation at both room temperature in solution and at slightly elevated temperatures was surprising. The lower carbonyl content on elimination, even in air, is a clear consequence of the significantly reduced elimination temperature. Molecular dynamics simulations, to be reported in detail later, suggest that the bulky polymeric anion actually sets up the PXT backbone for anti-elimination to give trans-PPV. An additional role for PEGNOPS could be to slow oxygen diffusion to the PPV backbone. Additionally, PEGNOPS may undergo sacrificial oxidation to form peroxide or/and carbonyl. Scheme 3 shows a known mechanism of polyether oxidation. Fig. 7 depicts an IR spectrum of PEGNOPS extracted with ethanol from thermally annealed PXT-PEGNOPS film. A small band at 1729 cm^{-1} reveals PEGNOPS oxidation. The bands at 1114 and 841 cm^{-1} are from the C–O stretches of the PEG units in PEGNOPS.

4. Conclusions

The polyether counterion to a PPV precursor provides for several benefits. First, the elimination to PPV occurs at a significantly lower temperature when compared to the traditional chloride counterion precursor. Second, the number of carbonyl groups is lower, and the photoluminescence yield is higher, even though elimination is carried out in air. Third, precursor solutions stored at room temperature remained carbonyl-free. The final composite, being rich in polyether units, should be capable of transporting lithium ions well for devices that rely on electrochemical excitation for light emission.

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Appendix. Supporting information

The supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.polymer.2010.05.016.

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