



# Solution aging and degradation of a transparent conducting polymer dispersion



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## ABSTRACT

As organic electronics improve, there is increased research interest on the longevity and stability of both the device and individual material components. Most of these studies focus on post deposition degradation and aging of the film. In this article, we examine the stability of polyelectrolyte dispersions before film coating. We observe substantial differences in the solution properties of the transparent conducting polymer, S-P3MEET, when comparing fresh versus aged dispersions and relate these solution differences to film properties. The aged dispersion contains large agglomerates and exhibits a typical shear-thinning rheological behavior, which results in non-uniformity of the spin-coated films. Near edge X-ray absorption fine structure measurements were used to differentiate the changes in bonding and oxidation states and show that aged S-P3MEET is more highly self-doped than fresh S-P3MEET. We also show that addition of acid, salt or heat to fresh S-P3MEET can accelerate the degradation/aging process but are subjected to different mechanisms. Conductivity measurements of S-P3MEET films illustrate that there is a tradeoff between increased work function and decreased conductivity upon perfluorinated ionomer (PFI) loading. The formation of nanostructure in solution is also correlated to film morphology variations obtained from atomic force microscopy. We expect that dispersion aging is a process that commonly exists in most solution-dispersed polyelectrolyte materials and that the methodologies presented in this paper might be beneficial to future degradation/stability studies.

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## 1. Introduction

There has been considerable interest in the development of solution processed organic electronic devices, such as organic photovoltaics (OPV) and organic light emitting diodes (OLED), as they show potential as low-cost alternatives compared to their inorganic counterparts [1,2]. Although device efficiency continues to improve [3–5], relatively little attention has been paid to the stability and longevity of these devices and related materials. An extensive study on the degradation/aging process is a prerequisite to develop a useful commercial technology [6,7].

Organic electronic devices are commonly fabricated by solution processing, as shown in Fig. 1. Dissolved materials are either coated or printed onto substrates to form continuous films and device structures [8]. Various factors have been reported that lead to

device degradation. Based on the origin, two types of degradation mechanism are possible. First, extrinsic degradation is the chemical and/or physical changes induced by external triggers. For example, OPV devices with active layers composed of poly(phenylene vinylene) (PPV) or poly(3-hexylthiophene-2,5-diyl) (P3HT) have been shown to be susceptible to degradation by water and oxygen [9–11]. In addition, extrinsic degradation can also occur when exposing devices to UV light [12,13], elevated temperatures [14,15], high drive current [16], etc. Intrinsic degradation, on the other hand, results from factors that are built into the device, such as interfacial instability, molecular diffusion, phase separation, or reaction between components. Interfacial reactions, for instance, have been observed at the metal electrodes (e.g. Al)/active layer interface [17–19] as well as the PEDOT:PSS/active layer interface [20–22]. Recent research reveals that phase separation and/or diffusion of small organic molecules, such as fullerenes [23,24] and molecular dopants [25–27], may also affect device stability [28]. Furthermore, it is widely accepted that intrinsic degradation can be accelerated by external environmental factors [29].

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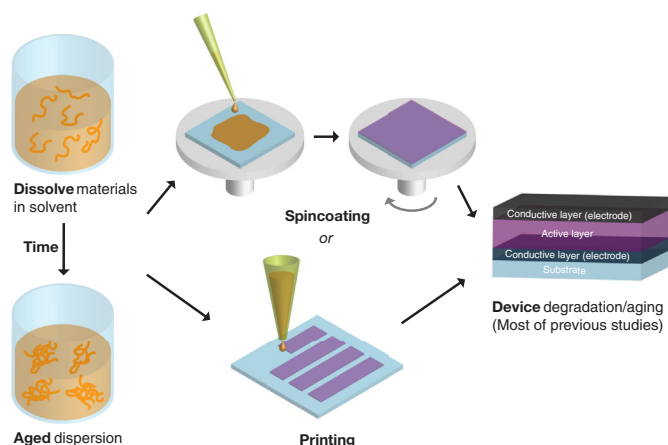


Fig. 1. Schematic of solution process and dispersion degradation/aging.

Most of these degradation/aging studies focus on the post deposition films and devices. However, contributions to degradation/aging processes which occur upstream of the end product should also be considered. Researchers frequently purchase ill-defined solutions (e.g. PEDOT:PSS or photoactive inks) and assume that they will maintain desired properties until replacement with a new batch. We will show here that this is not a good assumption. Some solutions are intrinsically unstable or can be triggered extrinsically to aggregate [30,31]. We posit that the aging of solutions can contribute to inconsistent results published in different groups [32] and even within the same group and even when the same sample preparation procedures and experimental conditions are precisely controlled. The solution stability is crucial in most of solution-processed systems and will considerably affect the film morphology and thus the device performance [33]. Therefore, degradation/aging studies on polymer dispersions are necessary. Although degradation and stabilization problems related to polymer dispersions are known for years [34,35], in the field of transparent conducting polymers or polyelectrolytes, relatively few solution stability studies have been published to the best of our knowledge [36].

In this work, we will investigate the solution stability of a transparent conductive polymer, poly(thiophene-3-[2-(2-methoxy-ethoxy)ethoxy]-2,5-diyl) (S-P3MEET) (Fig. 2). S-P3MEET was chosen (1) because S-P3MEET is a self-doped (meaning, oxidatively doped) polymer and its immobile sulfonate moieties will not cause unintended phase separation compared with PEDOT:PSS [37] and (2) because self-doped at reduced pH

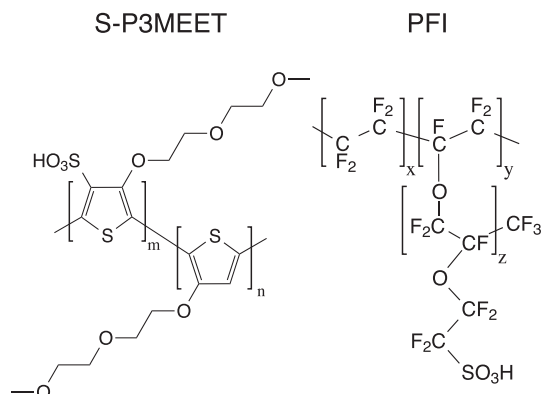


Fig. 2. Chemical structures of S-P3MEET (left) and perfluorinated ionomer PFI (right).

alternatives to PEDOT:PSS are increasingly sought for the specific purpose of increased device performance as well as lifetime [38,39]. Recently, we showed that similar to PEDOT:PSS where the work function can be altered using secondary dopants [40,41], the work function of S-P3MEET can also be tuned via the addition of a perfluorinated ionomer (PFI) (Fig. 2) [42]. In this study, we define doping as any and all redox processes that occur between the conjugated polymer backbone and other media, which can be internal groups (e.g. sulfonate moieties in the S-P3MEET) and external reactants (e.g. acidic additive). In addition, we also name the S-P3MEET that has been stored in the solution state (in the dark in a sealed container at 5 °C) for one year as aged S-P3MEET in order to differentiate it from its fresh counterpart. We will use particle size, zeta potential and rheological measurements to characterize the solution properties and aggregation of the polymer dispersions. A systematic comparison of these properties with their oxidation states is used to define the mechanism of aging. Comparative additive and heating experiments are also conducted to reveal the origin of this degradation/aging process. Finally, we return to externally blend S-P3MEET with acidic PFI and address the concern that mixed S-P3MEET films might be rendered unstable by the presence of the PFI. Therefore, PFI concentration-dependent conductivity and morphology of S-P3MEET films are also thoroughly investigated.

## 2. Materials and methods

### 2.1. Materials and sample preparation

The S-P3MEET (Plexcore OC RG-1100) was provided by Plextronics, Inc. The aged S-P3MEET used has been stored in the refrigerator in the dark for 12 months without external stimulations. A single batch of S-P3MEET was used for all work in this study. PFI (Liquion LG-1115) was purchased from Nafion Store. PEDOT:PSS (Clevios P VP Al 4083) was purchased from Heraeus. All chemicals were used as-received unless otherwise indicated.

For sample preparation, all substrates were rinsed using ultrasonic baths of acetone, 5% mucasol solution, and deionized water, successively, followed by nitrogen drying. The substrates were then exposed to UV/ozone for 30 min before use. Solutions of S-P3MEET and PFI were mixed in appropriate ratios to reach the desired loading levels. The blend solutions were then diluted using a solvent mixture that consisted of 50% isopropyl alcohol, 40% 1,3-propanediol, and 10% deionized water by volume (IPW solvent mixture). The films were spin-coated on clean substrates from blend solutions, and placed on a hot plate set to 110 °C for 3 min to remove residual solvent.

### 2.2. Characterization

Particle size and zeta potential were measured using a Zetasizer Nano ZS (Malvern Instruments). For the additive experiments, 0.05 mL of 1.0 M HCl, NaOH or NaCl was added into a 1 mL fresh S-P3MEET solution. For the heating experiment, the fresh S-P3MEET solution was heated at 110 °C for 10 h in a sealed container. All samples were diluted using the IPW solvent mixture described above and measurements were performed at 25 °C. A minimum of three measurements were performed for each sample.

Rheological measurements were performed at 25 °C using an AR 1000-N rheometer (TA Instruments) with a cone and plate geometry. A minimum of three measurements were also performed for each sample.

Near edge X-ray absorption fine structure (NEXAFS) measurements were performed on beamline 6.3.1 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). S-

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