

# Stepwise heating in Stille polycondensation toward no batch-to-batch variations in polymer solar cell performance

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## Abstract

For a given  $\pi$ -conjugated polymer, the batch-to-batch variations in molecular weight (Mw) and polydispersity index ( $\mathcal{D}$ ) can lead to inconsistent process-dependent material properties and consequent performance variations in the device application. Using a stepwise heating protocol in the Stille polycondensation in conjunction with optimized processing, we obtained an ultrahigh-quality PTB7 polymer having high Mw and very narrow  $\mathcal{D}$ . The resulting ultrahigh-quality polymer-based solar cells demonstrate up to 9.97% power conversion efficiencies (PCEs), which is over 24% enhancement from the control devices fabricated with commercially available PTB7. Moreover, we observe almost negligible batch-to-batch variations in the overall PCE values from ultrahigh-quality polymer-based devices. The proposed stepwise polymerization demonstrates a facile and effective strategy for synthesizing high-quality semiconducting polymers that can significantly improve device yield in polymer-based solar cells, an important factor for the commercialization of organic solar cells, by mitigating device-to-device variations.

## Introduction

We report an efficient and facile stepwise Stille polycondensation with an additionally embedded low-temperature step for the preferential step growth of low-Mw fractions to formulate high-quality polymers. We choose a well-known high-performance polymer, poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophene-4,6-diyl] (PTB7), as a test-bed polymeric material for our study. After extensive screenings of the key aspects of the polymerization in context, we employ stepwise Stille polycondensation upon the optimized synthesis condition, affording ultrahigh-quality PTB7 having high Mw (223 kDa) and very narrow  $\mathcal{D}$  (1.21). Despite the similar optical, electrochemical, and morphological properties between the stepwise protocol-derived and commercially available PTB7 polymers, the resulting ultrahigh-quality polymer-based solar cells exhibit superior PCEs of up to 9.97% with impressively negligible device-to-device performance variations, constituting a substantial improvement from control devices based on the commercial polymer. The stepwise Stille polycondensation process is readily applicable to a wide variety of other

polymer systems requiring ultrahigh quality and can be immediately incorporated into synthetic organic chemists' repertoire as a principal reaction protocol.

## Reagents

All the chemicals and reagents were bought from Sigma-Aldrich, Alfa Aesar chemical company, Tokyo Chemical Industry Co., Ltd., Derthon Optoelectronic Materials Science Technology Co., Ltd. and unless otherwise specified used without any further purification. (Caution: Trimethyltin chloride and other organotin-related compounds are highly toxic to cause irritation and burns of the skin and eyes with fatal damage on the central nervous system. High and repeated exposure can cause loss of hearing, weakness, confusion and seizures.) 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene was synthesized according to the literature and 2-ethylhexyl-4,6-dibromothiopheno[3,4-b]thiophene-2-carboxylate was purchased from Derthon, both of which were purified with recrystallization and chromatography using a reverse-phase column, JAIGEL-ODS-AP, SP-120-10 (2.0 cm $\phi$   $\times$  25 cm, i.d., Japan Analytical Industry Co., Ltd.) in a mixture of acetonitrile and THF as the mobile phase. The elution was monitored at 256 nm with a UV detector.

## Equipment

To react with monomers for Stille polymerization, a long Schlenk tube with argon purging systems and a hot-plate with a stirring system are needed. As for purification of polymers, a Soxhlet tube with a reflux condenser and a heating mantle are needed.

## Procedure

1. Dissolve two monomers in a binary mixture of toluene and DMF as a 4:1 ratio in a long Schlenk tube.
2. After intensive bubbling with argon for 20 min, inject the solution of Pd catalyst in toluene with subsequent purging for 10 min.
3. We reacted the mixture in a preheated oil bath at 120 °C for 1 h for the initial stage, after which allowed the temperature to reduce and kept the tube cooled for 11 h.
4. Reset the temperature to 120 °C and continuously maintain this temperature for 1 day.

5. After cooling to room temperature, purify the precipitates in methanol by Soxhlet extraction with methanol, acetone, hexane, and chloroform.

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