Continuous flow methods are employed for the controlled polymerization of the roll-to-roll (R2R) compatible polymer PBDTTTz-4 including optimization and upscaling experiments. The polymerization rate and materials’ quality can be increased significantly with the continuous flow method where reaction times down to 10 min afforded PBDTTTz-4 with high molecular weight and a constant quality. The flow method enables full control of the molecular weight via tuning of the flow speed, catalyst loading, and temperature and avoids variation in materials’ quality associated with conventional batch synthesis. Upscaling from 300 mg batch synthesis to 10 g flow synthesis affords PBDTTTz-4 with a production rate of up to 120 g day−1 for a very simple in-house build flow reactor. An average power conversion efficiency (PCE) of 3.5% is achieved on a small scale (1 cm2) and an average PCE of 3.3% is achieved on a large scale (29 cm2). This shows that small device efficiencies can be scaled when using full R2R processing of flexible and encapsulated carbon-based modules without the use of vacuum, indium-tin-oxide, or silver, with the best achieving a PCE of 3.8% PCE.