THE PENNSYLVANIA STATE UNIVERSITY SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

EFFECT OF MOLECULAR WEIGHT ON THE GLASS TRANSITION TEMPERATURE OF CONJUGATED POLYMERS

NICHOLAS CAGGIANO SPRING 2017

A thesis submitted in partial fulfillment of the requirements for a baccalaureate degree in Chemical Engineering with honors in Chemical Engineering

Reviewed and approved* by the following:

Enrique Gomez Associate Professor of Chemical Engineering Thesis Supervisor/Honors Adviser

Michael Janik Associate Professor of Chemical Engineering Faculty Reader

*Signatures are on file in the Schreyer Honors College.

ABSTRACT

Fully conjugated polymers, with their delocalized π networks, can serve as charge carriers in organic photovoltaic (OPV) devices. It is important to characterize the material properties of such polymers for future device fabrication. In this work the conjugated polymers PFTBT and PCDTBT were synthesized by a two-phase Suzuki polycondensation reaction. Molecular weight was varied by adjusting the monomer ratio during synthesis.

Four batches of PFTBT and two batches of PCDTBT of varying weights were synthesized and characterized by GPC to obtain molecular weight. The glass transition temperature (T_g) was measured by a rheological temperature ramp study. Analysis shows that the glass transition temperature of the polymers increases with increasing molecular weight.

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Chapter 1

Introduction

Although fossil fuels still supply the vast majority of the world's electricity needs, interest in—and adoption of—renewable energy technology has grown. In 2015 renewable sources were responsible for 23.7% of global electricity production. Solar photovoltaic technology accounted for an estimated 1.2% of global electricity production, with 227 gigawatts of power generation capacity worldwide [1].

Current solar technology is dominated by crystalline silicon cells [2], which can achieve efficiencies approaching 25% [3]. Organic photovoltaics (OPVs) made of semiconducting organic polymers represent an exciting new development in the solar energy field. Polymers offer versatile and chemically modifiable properties, including the ability to form thin, flexible sheets. With further development, OPVs offer the potential of lower-cost, easier to manufacture solar cells to compete with current silicon technology [4, 5].

1.1 Conjugated Polymers

Specifically, this work investigates the controlled synthesis and resulting properties of conjugated polymers for applications in OPVs. The delocalized π orbitals of conjugated polymers enable charge conduction within the polymer network of an OPV. The polymers may be chemically functionalized in order to influence electronic and mechanical properties, as well as characteristics important for downstream processing, such as solubility [5]. The Gomez Group

has been investigating OPVs with donor/acceptor conjugated block copolymers, reporting near 3% efficiency in 2013, shown in Figure 1 [6]. In such a device, the absorption of a photon from sunlight results in the formation of an exciton, or electron-hole pair. This exciton is localized but can move from molecule to molecule down a polymer chain. Eventually the negative and positive (hole) charges are separated, and charge transport occurs between the anode and cathode of the cell, creating a circuit that can power an electronic device [4, 7].



Figure 1. Depiction of charge separation and migration in a P3HT-b-PFTBT OPV cell [6, reproduced with permission]

1.2 Polymer Synthesis

Two conjugated polymers were synthesized in this work: poly-((9,9-dioctylfluorene)-2,7diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2"-diyl) (PFTBT, also called AFPO3), and poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT).

Both PFTBT and PCDTBT were synthesized here by a Suzuki polycondensation reaction between a fluorene (or carbazole) boronic ester (F or CD) and a dibromo functionalized benzothiadiazole (TBT). This reaction is performed in the presence of a base, which activates the boronic ester group. The reaction is facilitated by a palladium catalyst and occurs at the toluene/water phase interface. Thus, Starks' catalyst (Aliquat® 336) was used as a phase transfer catalyst, along with rapid physical mixing, to increase interfacial area. Figures 2 and 3 show the reaction schemes for PFTBT and PCDTBT.



Figure 2. PFTBT synthesis scheme

For PFTBT, monomers 1 (9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester) (F) and 2 (4,7-Bis(2-bromo-5-thienyl)-2,1,3-benzothiadiazole) (TBT) are combined in the presence of the palladium(0) catalyst and base. The reaction mixture is allowed to reflux at 80 °C overnight (12-24 hours), affording the product 3 (PFTBT).



Figure 3. PCDTBT synthesis scheme

For PCDTBT, monomers 1 (9-(9-Heptadecanyl)-9H-carbazole-2,7-diboronic acid bis(pinacol) ester) (CD) and 2 (4,7-Bis(2-bromo-5-thienyl)-2,1,3-benzothiadiazole) (TBT) are combined in the presence of the palladium(0) catalyst and base. The reaction mixture is allowed to reflux at 80 °C overnight (12-24 hours), affording the product 3 (PCDTBT).

The reaction mechanism begins with the catalytic palladium(0) complex, which undergoes an oxidative addition with the bis-brominated monomer (TBT). One bromine is removed from the monomer and forms a Pd-Br bond with the catalyst. A Pd-carbon bond is also formed between the catalyst and the monomer (with the carbon to which the bromine was previously bonded). The palladium is now in its +2 oxidation state. The base present in the mixture then replaces the bromine on the catalyst complex with a hydroxyl group. The base also activates the boronic acid ester of the F or CD monomer prior transmetallation, in which a Pdcarbon bond is formed with the F or CD monomer, displacing the boronic ester. Both monomers (TBT and F or CD) are now bound to the catalyst. A reductive elimination joins the two monomers, creating a carbon-carbon bond, and regenerates the original palladium(0) complex. Since each monomer has two reactive groups—one at each end—this mechanism can continue, forming successively longer chains. The reaction is terminated with bromobenzene, capping each end of the polymer with a phenyl group [8-11].

The goal was to synthesize a low, medium, and high molecular weight batch for each polymer, in order to study the effect of molecular weight on the properties of the polymer. This was done by altering the ratio of the two monomers. For a particular target molecular weight, the target degree of polymerization \bar{X}_n was calculated by

$$\bar{X}_n = \frac{M_n}{M_0}$$
,

where M_n is the target number average molecular weight, and M_0 is the weight of one repeat unit. The monomer ratio *r* (TBT/F or TBT/CD) was then calculated according to Carothers equation for step-growth polymerization [12],

$$\bar{X}_n = \frac{1+r}{1-r}$$

In the case of step-growth polymerization, polymer growth is exponential, not linear. Thus, the molecular weight cannot be controlled accurately by reaction time alone. That is why the monomer ratio was instead altered, creating a stoichiometrically limiting reagent to limit chain length. As will be seen, this method is not without limitations.

Chapter 2

Materials and Methods

2.1 Materials and Equipment

All materials were obtained from the suppliers listed below and used without further

purification.

Material	Full Chemical Name	Supplier
F	9,9-Dioctylfluorene-2,7-diboronic acid	Sigma-Aldrich
	bis(1,3-propanediol) ester	
TBT	4,7-Bis(2-bromo-5-thienyl)-2,1,3-	Sigma-Aldrich
	benzothiadiazole	
CD	9-(9-Heptadecanyl)-9H-carbazole-2,7-	Sigma-Aldrich
	diboronic acid bis(pinacol) ester	
Pd(PPh ₃) ₄	Tetrakis(triphenylphosphine)palladium(0)	Merck Millipore
TEA-OH	Tetraethylammonium hydroxide	Sigma-Aldrich
(20% in water)		
Aliquat® 336	Stark's catalyst	Sigma-Aldrich
	Bromobenzene	Sigma-Aldrich

Table 1. List of Materials

Figure 4 shows the reactor used for the synthesis. The screw valve controls the flow to a Schlenk line system, which can either pull vacuum or feed argon gas. The reactor was placed in an oven overnight prior to synthesis.



Figure 4. Reactor used for synthesis

2.2 General Procedure for Polymer Synthesis

The general procedure described below was used to synthesize both PFTBT and PCDTBT. A few ratios were kept approximately constant across all batches. The solid (mg) to organic solvent (mL) ratio was kept in the range of 120-130. The ratio of volumes of aqueous to organic solvent was maintained at approximately 0.3. Overall reaction volume was approximately 15 mL. The monomer F or CD was kept at 0.3 mmol for most syntheses, and the amount of TBT was varied in order to achieve the proper monomer ratio. Catalyst loading was

usually kept between 5 and 7.5 mol% relative to either F or CD (26 mg catalyst for a typical PFTBT batch).

Reagent Charging and Purging

The reactor was first charged with monomers (TBT and F or CD). Toluene was then added, along with a magnetic stir bar. This mixture was stirred vigorously for a few minutes in order to begin solubilizing the monomers (often they did not completely dissolve in this stage). TEA-OH and DI H₂O were then charged to the reactor, followed by Stark's catalyst.

The screw valve was closed tightly, and a septum was used to seal the top of the reactor. The reactor was purged with argon gas for approximately 5 minutes using a needle through the septum. Another needle was inserted through the septum to allow a flow of gas. After purging, the septum was removed and the catalyst added. Care was taken to minimize exposure of the catalyst to oxygen. (The catalyst was stored in an inert nitrogen glovebox until just prior to synthesis.) The septum was replaced and the reactor purged with argon for another 5 minutes. Upon addition of the catalyst, the mixture began to darken in color.

Freeze-Pump-Thaw

The mixture then underwent three freeze-pump-thaw cycles in order to remove any oxygen dissolved in the liquids. First the reactor was transitioned to a vacuum by removing the argon purge line and connecting the Schlenk line to the arm of the reactor, leaving the screw valve closed. The reactor was then submerged in a liquid nitrogen bath (Figure 5) until the entire mixture was visibly solid. While still submerged, the screw valve was opened to pull vacuum on

the reactor for about one minute. The valve was then closed, the reactor was removed from the nitrogen bath, and the entire reaction mixture was allowed to thaw. This was sometimes expedited by placing the reactor in a cool water bath over a magnetic stir plate. This process was repeated three times. After the freeze-pump-thaw cycles, the reactor was carefully transitioned back to an inert argon atmosphere using the Schlenk line.



Figure 5. Reactor submersed in liquid nitrogen during Freeze-Pump-Thaw

Reaction

The reactor was then transferred to a hot oil bath (80-90 °C, but not exceeding 90 °C), shown in Figure 6. (In this setup the hot plate was typically set to ~140 °C.) The reaction mixture was stirred vigorously for the duration of the reaction in order to promote transfer between the aqueous and organic phases by increasing the interfacial area. The reaction was allowed to proceed for 12-24 hours. The reaction mixture typically darkened noticeably as it heated and began to reflux.



Figure 6. Reactor in oil bath

Termination

After the reaction period, the mixture was typically deep purple in color. Bromobenzene (4 mL) was injected into the reactor through the septum to terminate the reaction. The mixture was allowed to reflux for a minimum of one hour in the oil bath to ensure termination, thus adding terminal phenyl groups to the polymer.

Separation and Precipitation

The entire reaction mixture was then transferred to a separatory funnel, rinsing the reactor with a minimal volumes of toluene and DI H_2O . The organic phase contained the polymer, while the aqueous phase was discarded. The organic phase was then discharged into ~500 mL of

methanol at room temperature. This mixture was kept at room temperature for roughly 24 hours, allowing the polymer fibers to precipitate and settle.

Filtration, Soxhlet Washing, and Drying

As much methanol as possible was decanted before filtration. The polymer was then filtered from the liquid using a funnel lined with a paper filter. The filter (containing the polymer) was then transferred to a cellulose Soxhlet filter. The cellulose filter was placed in a Soxhlet extractor, where it was washed sequentially with methanol, acetone, and sometimes hexane, each for roughly 24 hours (Figure 7).



Figure 7. Soxhlet washing setup

After washing was complete, the filter was wrapped loosely in foil and placed in a vacuum oven at room temperature and 30 bar of vacuum for 24 hours to remove residual solvent. At this point the polymer was ready for further analysis (GPC, rheology).

Rheology Sample Preparation

A sample of polymer was formed into a 1 mm thick and 3 mm or 8 mm diameter puck in a nitrogen-filled glovebox (H₂O < 1 ppm, O₂ < 10 ppm). Air bubbles were removed by heating above the melting temperature of the polymers (~260 °C) under a vacuum, and the pucks were formed by compression with approximately 1 MPa of pressure. An ARES-LS rheometer was used to characterize the sample under nitrogen. After loading the puck into the rheometer, the sample was heated to approximately 250 °C to create good contact with between the sample and rheometer plates [13]. The glass transition temperature was measured by performing a temperature ramp test at 5 °C/min with a constant oscillatory frequency of 10 rad/s. The storage modulus G' and loss modulus G'' were measured and plotted against temperature. The T_g was measured as the temperature corresponding to the maximum G'' value during the heating cycle.

Chapter 3

Results and Discussion

3.1 PFTBT

Table 2 shows a list of the PFTBTs synthesized, along with selected synthesis

parameters. More detailed batch records may be found in Appendix A.

	NC101	NC102	NC103	NC104
	(MA3125)	(MA3177)		
r = TBT/F (planned)	1	0.75	0.88	0.92
$r = TBT/F$ (actual, by M_n)	0.92	0.89	0.86	0.87
Theoretical M _n [kg mol ⁻¹]	∞	4.8	11.0	15.5
M _n [kg mol ⁻¹]	16.0	11.7	9.3	9.7
M _w [kg mol ⁻¹]	67.8	52.6	36.5	53.1
Ð	4.23	4.50	3.93	5.49
$T_{g} [^{\circ}C] \pm 1$	140	132	128	_
Yield [mg]	143, 69%	150, 81%	170, 87%	191, 96%
Reaction Time [hr]	16	16	15	23

Table 2. PFTBT Batch Summary

Four batches of PFTBT were synthesized: a high molecular weight target (NC101), a low molecular weight target (NC102), and two medium molecular weight target (NC103, NC104). In general, PFTBT is a deep purple polymer. Lower molecular weight samples often appeared as short, loose fibers, while higher molecular weight samples often formed an entangled mass or ball. PFTBT is difficult to solubilize and could not be characterized reliably by standard gel permeation chromatography (GPC) at 40 °C. Samples were instead characterized by high-temperature (GPC) (Agilent PL-GPC 220) in 1,2,4-trichlorobenzene at 150 °C. A sample

preparation system was used (Agilent PL-SP 260VS), and samples were completely dissolved overnight. The GPC used universal calibration and concentration and viscosity detectors in order to characterize the molecular weight distribution. Number average molecular weight (M_n), mass average molecular weight (M_w), and polydispersity ($\tilde{D} = M_w/M_n$) are reported.

GPC is a form of size-exclusion chromatography; longer polymer chains will move more slowly through the stationary phase and therefore be retained in column for a longer period of time. A detector measures the refractive index of the eluting sample relative to that of the mobile phase. Since the refractive index of a polymer-containing solution will differ from that of a clean solution, polymer-containing fractions are able to be detected as they exit the column. The refractive index is then plotted against the retention time. Figure 8 shows GPC traces for the four batches of PFTBT.



Figure 8. GPC Traces for PFTBTs in 1,2,4-trichlorobenzene at 150 °C

Molecular weight was obtained by integration of the GPC trace. The GPC results show that the PFTBT samples were polydisperse, with NC104 having the most disperse distribution. All samples had varying degrees of bimodality, indicating the presence of at least two significant chain lengths.

Three substantially different molecular weights were observed, and the two medium molecular weight targets achieved similar M_n values (9.3 and 9.7 kg mol⁻¹). Thus, it is seen that variation of the monomer ratio was able to provide relative control over the molecular weight but not exact control, as the measured M_n values were not similar to the theoretical M_n values. Additionally, NC102, the low molecular weight target batch, was measured to have a larger M_n than the medium molecular weight target NC103 (11.7 vs 9.3 kg mol⁻¹). Although the monomer ratios were set to 0.88 and 0.75, respectively, back-calculating the monomer ratio from the measured M_n values results in similar values of 0.89 and 0.86. This could be evidence of monomer precipitation during the synthesis. Reagents were on the order of 97% purity, and no further purification was conducted before synthesis. This could also influence the actual monomer ratio.

This example highlights that just a 3% change in the monomer ratio can result in a >25% change in the resulting M_n . This indicates that although variation of the monomer ratio can give relative control over the resulting molecular weight, it is quite difficult to produce a desired molecular weight with accuracy.

PFTBT Glass Transition

PFTBT batches NC101, NC102, and NC103 were analyzed using an ARES-LS rheometer to characterize the glass transition temperatures. NC104 was not measured because it was deemed too polydisperse. This work was performed by Renxuan Xie and is reported in detail in a recently submitted paper [13].

First a sample of polymer was melted and compressed into a 1 mm thick and 3 mm or 8 mm diameter puck in a nitrogen-filled glovebox. All air bubbles were removed by heating above the melting temperature under a vacuum. The glass transition temperature was obtained by performing a temperature ramp test at 5 °C/min with a constant oscillatory frequency of 10 rad/s. The storage modulus G' and loss modulus G'' were measured and plotted against temperature. The glass transition temperature reported corresponds to the maximum G'' value during the heating cycle. Plots of G'' and G' are shown in Figure 9 and Figure 10 for all batches tested.



Figure 9. Plot of G'' vs Temperature. Temperature ramp at 5 °C/min with oscillatory frequency 10 rad/s.



Figure 10. Plot of G' vs Temperature. Temperature ramp at 5°C/min with oscillatory frequency 10 rad/s.

The glass transition temperature of the PFTBT samples increased with molecular weight. The T_g of NC101, the highest molecular weight batch, was measured to be 140 °C, while medium and low molecular weight samples NC102 and NC103 reported T_g values of 132 °C and 128 °C, respectively. This trend in T_g matches what might be expected; with longer polymer chain length, a higher temperature would be required for the chains to begin to "slide" past one another. Figure 11 shows this increasing trend of T_g with M_n.



Figure 11. Plot of T_g vs 1/M_n

3.2 PCDTBT

Table 3 shows a list of the PCDTBTs synthesized, along with selected synthesis parameters. More detailed batch records may be found in Appendix A.

	NC105	NC106
$\mathbf{r} = \mathbf{C}\mathbf{D}/\mathbf{F}$	1	0.75
r = CD/F (actual, by M _n)	_	0.71
Theoretical Mn (kg/mol)	∞	5.0
Mn (kg/mol)	_	4.2
M _w (kg/mol)	-	4.7
Ð	_	1.10
$T_{g}(^{\circ}C) \pm 1$	115	107
Yield (mg)	122, 87%	159, 84%
Reaction Time [hr]	22	22

Table 3. PCDTBT Batch Summary

Two batches of PCDTBT were synthesized: a high molecular weight target (NC105) and a low molecular weight target (NC106). Unfortunately, PCDTBT is even less soluble than PFTBT, and NC105 was unable to be solubilized for standard GPC testing. The lower molecular weight NC106 did dissolve in chlorobenzene and could be tested in our standard GPC (Agilent 1260 Infinity) with a polystyrene reference. However, with standard GPC some polymer may remain undissolved and be filtered out prior to testing, affecting the molecular weight distribution. Thus for the sake of comparison across PCDTBT batches and with PFTBTs, all samples should ideally be sent for high temperature GPC analysis. A plot of the standard GPC result for NC106 is displayed in Figure 12.



Figure 12. GPC Trace for PCDTBT NC106 in chlorobenzene at 40 °C

The M_n of the NC106 sample was measured to be 4.2 kg mol⁻¹, close to the theoretical M_n of 5.0 kg mol⁻¹, and exhibits low polydispersity. The trimodal distribution indicates the presence of three main chain lengths. It is not known why the measured and theoretical M_n values are much more similar for this particular batch of PCDTBT than was observed for the PFTBT batches, but full judgment should be reserved until additional PCDTBT batches are synthesized and characterized by high temperature GPC.

As with PFTBT, the PCDTBT samples were characterized using an ARES-LS rheometer. The glass transition temperature was measured as the maximum G'' value using a temperature ramp of 5 °C/min with oscillatory frequency 10 rad/s (the same conditions as PFTBT). Figures 13 and 14 show plots of of the loss modulus G'' and storage modulus G' with temperature.



Figure 13. Plot of G'' vs Temperature. Temperature ramp at 5°C/min with oscillatory frequency 10 rad/s.



Figure 14. Plot of G' vs Temperature. Temperature ramp at 5°C/min with oscillatory frequency 10 rad/s.

The high molecular weight NC105 batch was measured to have a T_g of 117 °C, while the low molecular weight NC106 had a T_g of 107 °C. Although the molecular weight NC105 was unable to be characterized in our standard GPC due to its poor solubility, the batch was visually observed to have longer, more entangled fibers as compared to NC106, a sign of higher molecular weight. Its poor solubility and higher T_g also support the qualitative observation that the molecular weight of NC105 is larger than that of NC106; however, the difference between the two cannot be quantified until both are characterized by high temperature GPC.

3.3 Conclusions

Four batches of PFTBT and two batches of PCDTBT were synthesized by a two-phase Suzuki polycondensation reaction. GPC analysis showed that variation of the monomer ratio allowed relative control over resulting molecular weight, but achieving accuracy with respect to a target weight was difficult.

The glass transition temperatures of three PFTBT samples (the fourth batch was deemed too polydisperse to characterize) were found to increase with molecular weight, which is what would be expected; more thermal energy is required for the longer chains to begin to flow past one another. The two PCDTBT samples showed the same trend; however, both batches should be characterized by high temperature GPC to enable more accurate comparison of M_n between the PCDTBTs and with the PFTBTs.

3.4 Future Work

Additional batches of PCDTBT should be synthesized in order to probe trends in the glass transition temperature. However, this work was material limited. One additional batch of very low molecular weight PFTBT ($r \sim 0.5$) will be synthesized in order to probe the nematic to isotropic phase transition as a function of molecular weight. This will be included in a future paper by Renxuan Xie.

A one-phase Suzuki reaction could also be studied in the future, as compared to the twophase reaction used here. A one-phase reaction would eliminate the need for Stark's catalyst but would likely require the use of surfactants to solubilize the monomers. However, a one-phase reaction could potentially improve the polymerization kinetics and avoid issues related to monomers crashing out of solution during synthesis. This could lead to more accurate control of molecular weight.

Appendix A

Batch Records

NC101 (PFTBT)

repeat uni	t molecular weight (g/mol)	
	F	388.6
	TBT	298.4
	FTBT	687

target molecular weight	1000000	= 1 + r TBT
target Xn	1455.60	$X_n = \frac{1-r}{1-r}$; $r = \frac{1}{F}$
solve for r	1.00	

	molecular			amt	
monomer	weight	equiv.	mmol	(mg)	Actual
F	558.41	1	0.3	167.5	167.5
diboronic acid bis(1,3-propanediol) ester					
ТВТ	458.21	1	0.3	137.5	137.5
Sigma					
other components					
toluene	12				
mg solid: mL organic solvent ratio	121.7				
TEA-OH 20% in H₂O	3.6				
mL aqueous: mL organic solvent ratio	0.30				
aliquat336	2 drops				
Pd(PPh3)4	1155.56	0.075	0.0225	26.0	26.0
bromobenzene	4 mL				

	yield
206.11	theoretical yield
143	actual yield
0.6938107	percent yield

NC102 (PFTBT)

repeat unit molecular weight (g/mol)		
F	388.6	
TBT	298.4	
FTBT	687	
target molecular weight	4800	$\overline{1+r}$ TBT
target Xn	6.99	$X_n = \frac{1-r}{1-r}; r = \frac{1}{F}$
solve for r	0.75	

	molecular			amt	
monomer	weight	equiv.	mmol	(mg)	Actual
F	558.41	1	0.3	167.5	167.8
diboronic acid bis(1,3-propanediol) ester					
ТВТ	458.21	0.75	0.225	103.1	103.1
Sigma					
other components					
toluene	12				
mg solid: mL organic solvent ratio	118.8				
TEA-OH 20% in H₂O	3.6				2
mL aqueous: mL organic solvent ratio	0.30			2	
aliquat336	2 drops				
Pd(PPh3)4	1155.56	0.075	0.0225	26.0	26.2
bromobenzene	4 mL				
1				~ J	

	yield	
theore	tical yield	183.91
ac	tual yield	149.6
per	cent yield	0.8134212

NC103 (PFTBT)

repeat unit molecular weight (g/mol)		
F	388.6	
TBT	298.4	
FTBT	687	
target molecular weight	11000	\overline{T} 1 + r TBT
target Xn	16.01	$X_n = \frac{1-r}{1-r}$; $r = \frac{1}{F}$
solve for r	0.88	

	molecular			amt	
monomer	weight	equiv.	mmol	(mg)	Actual
F	558.41	1	0.3	167.5	167.6
diboronic acid bis(1,3-propanediol) ester					
ТВТ	458.21	0.88	0.264	121.0	120.9
Sigma					
other components					
toluene	12				
mg solid: mL organic solvent ratio	120.3				
TEA-OH 20% in H₂O	3.6				
mL aqueous: mL organic solvent ratio	0.30				
· · · ·					
aliquat336	2 drops				
Pd(PPh3)4	1155.56	0.075	0.0225	26.0	26.2
· · · · ·					
bromobenzene	4 mL				· · · · · · · · · · · · · · · · · · ·
	C	8 S	9	1	

yield	
theoretical yield	195.37
actual yield	170
percent yield	0.870156

NC104 (PFTBT)

repeat unit molecular weight (g/mol)		
F	388.6	
TBT	298.4	
FTBT	687	
target molecular weight	15500	\overline{T} 1 + r TBT
target Xn	22.56	$X_n = \frac{1-r}{1-r}; r = \frac{1-r}{F}$
solve for r	0.92	

	molecular			amt	
monomer	weight	equiv.	mmol	(mg)	Actual
F	558.41	1	0.3	167.5	167.2
diboronic acid bis(1,3-propanediol) ester					
TBT	458.21	0.92	0.276	126.5	126.6
Sigma					
other components					
toluene	12				
mg solid: mL organic solvent ratio	120.8				
TEA-OH 20% in H₂O	3.6				
mL aqueous: mL organic solvent ratio	0.30				
aliquat336	2 drops				
Pd(PPh3)4	1155.56	0.075	0.0225	26.0	26.4
bromobenzene	4 mL				· · · · · · · · · · · · · · · · · · ·
		8 S	2 2		

	yield	
theo	retical yield	198.80
	actual yield	191
р	ercent yield	0.9607602

NC105 (PCDTBT)

repeat unit molecular weight (g/mol)		
CD	402.6	
ТВТ	298.4	
CDTBT	701	
target molecular weight	1000000	\overline{T} 1 + r TBT
target Xn	1426.53	$X_n = \frac{1-r}{1-r}; r = \frac{1-r}{F}$
solve for r	1.00	

molecular			amt	
r weight	equiv.	mmol	(mg)	Actual
657.58	1	0.2	131.5	131.5
r				
Г 458.21	1	0.2	91.6	91.8
a				
s				
e 12				
b 114.9				
3.6				
0.30				
6 2 drops				
1155.56	0.05	0.01	11.6	26.9
e 4 mL				
	molecular weight D 657.58 T 458.21 a T 458.21 a c 114.9 D 3.6 o 0.30 C 3.6 o 0.30 C 3.6 o 0.30 C 4 1155.56 c 4 mL	molecular equiv. molecular equiv. D 657.58 1 T 458.21 1 a	molecular weight equiv. mmol D 657.58 1 0.2 T 458.21 1 0.2 T 458.21 1 0.2 a	molecular weight equiv. mmol amt (mg) D 657.58 1 0.2 131.5 D 657.58 1 0.2 131.5 T 458.21 1 0.2 91.6 a

	yield	
the	eoretical yield	140.29
	actual yield	122.3
	percent yield	0.8717464

NC106 (PCDTBT)

repeat unit molecular weight (g/mol)		
CD	402.6	
ТВТ	298.4	
CDTBT	701	
target molecular weight	5000	\overline{T} 1 + r TBT
target Xn	7.13	$X_n = \frac{1}{1-r}; r = \frac{1}{CD}$
solve for r	0.75	

	molecular			amt	
monomer	weight	equiv.	mmol	(mg)	Actual
CD	657.58	1	0.3	197.3	197.4
diboronic acid bis(pinacol) ester					
TBT	458.21	0.75	0.225	103.1	103.6
Sigma					
other components					
toluene	12				
mg solid: mL organic solvent ratio	121.3				
TEA-OH 20% in H ₂ O	3.6				
mL aqueous: mL organic solvent ratio	0.30				
aliquat336	2 drops				
Pd(PPh3)4	1155.56	0.05	0.015	17.3	17.7
bromobenzene	4 mL				-
	n an an air an				
	3 C			5	

yield	
theoretical yield	188.32
actual yield	158.9
percent yield	0.8437562

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Nicholas Caggiano njcaggiano@gmail.com

EDUCATION	Bachelor of Science in Chemical Engineering Minor in Economics	May 2017	
	Schreyer Honors College, The Pennsylvania State University, University Park, PA		
	Study Abroad , Florence, Italy (Summer Semester) International Studies Institute at Palazzo Rucellai	May-June 2014	
EXPERIENCE	CSD Engineering Intern, Bristol-Myers Squibb, NewStudied impact of agitated drying on API particle attrition at pilot plant scale	Brunswick, NJ May-August 2016 size to predict levels of particle	
	 Research Intern, Axalta Coating Systems, Wilmington, DE June-August 2015 Investigated the interactions of an additive compound with components of refinish and liquid industrial epoxy primer formulations as part of a four phase project 		
	 Undergraduate Researcher, Gomez Group, Universit. Performed research on the synthesis and rheologic polymers for use in organic photovoltaic cells 	y Park, PA January 2016-May 2017 cal properties of conjugated	
LEADERSHIP	Engineering Ambassador , Penn State College of Eng Librarian , Penn State Marching Blue Band Secretary , Penn State Marching Blue Band	ineering April 2015-May 2017 December 2015-March 2016 March 2016-March 2017	
SKILLS	 Organic synthesis and laboratory techniques Purification Techniques: Distillation, Column Chromatography, Crystallization, Extraction Instruments: NMR, FT-IR, XRF, GPC, UV-Vis, DSC, BET, SEM, light microscopy Mathematica, Excel, Electronic Laboratory Notebook entry 		
LANGUAGES	English Italian (Moderate Proficiency)		
ACTIVITIES	National AIChE Penn State Marching Blue Band	Blue Band THON Concert Band	
AWARDS	The President Sparks Award Schreyer Ambassador Travel Grant The President's Freshman Award Schreyer Honors College Academic Excellence Scholars College of Engineering Scholarship Penn State Provost Award Scholarship	March 2015 May-June 2014 March 2014 2013-17 2013-17 2013-17	