Synthesis and Characterization of Graft Polymethacrylates Containing Conducting Diphenyldithiophene for Organic Thin-Film Transistors

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ABSTRACT: A class of [5,5']-diphenyl-[5,5']-dithiophene (PTTP)modified methacrylates has been synthesized and free radically polymerized to form graft polymethacrylates with the conducting PTTP segments as pendant side chains. Both the terminal alkyl side chain and spacer between the PTTP segments and polymer backbone could be varied to study fundamental structure–property relationships for this class of materials. Specifically, a group of three different PTTP graft polymethacrylates has been successfully synthesized with the alkyl side chain varying from hexyl to dodecyl. For the dodecyl-terminated poly(4-(5'-(4-dodecylphenyl)-[2,2'-bithiophen]-5-yl)phenethyl methacrylate), p(DPTTPEM), a counterpart, poly(4-(5'-(4-dodecylphenyl)-[2,2'-bithiophen]-5-yl)phenbutyl methacrylate), p(DPTTPBM), where the ethyl spacer was replaced by a butyl

INTRODUCTION Organic semiconductors used as the active layer in electronic devices have attracted considerable attention for a wide range of applications including organic lightemitting diodes, organic field-effect transistors, and photovoltaic devices.¹⁻⁵ Realization of desirable molecular architectures for organic semiconductors with well-defined dimensions and functions is one of the current challenges for research in the field of organic semiconducting materials.⁶ It is critically important to precisely build molecular architectures to afford necessary performance attributes such as good solubility, long-term thermal and oxidative stability, and enhanced π -stacking for superior electrical conductivity.^{7,8} Through the techniques of advanced organic synthesis which uses approaches such as the Suzuki reaction,⁹ the Stille coupling,¹⁰ the Wittig reaction,¹¹ and others,¹² a variety of complex new building blocks including fluorene,¹³⁻¹⁵ carbazole,^{16,17} isothianaphthene,^{18,19} cyclopentadithiophene,^{20–22} benzothiadiazole,²³ along with many others^{24–29} have been successfully developed and introduced into polymer backbones.

Among these new structures, the [5,5']-diphenyl-[2,2']-bithiophene (PTTP) co-oligomer family has emerged as an attractive candidate for thin-film transistors (TFTs) affording a good group, was synthesized. The experimental results indicated that both the alkyl side chain and spacer significantly affected the reactivity of the PTTP-modified methacrylates during free radical polymerization as well as the physical properties of the resultant graft polymers including solubility, morphology, and electrochemical and electrical properties. Typical field-effect mobilities on the order of 10^{-5} cm² V⁻¹ s⁻¹ were observed for all the PTTP monomers in air, which was attributed to their crystalline phase as revealed by differential scanning calorimetry and X-ray diffraction studies. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 199–206, 2012

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combination of mobilities and $I_{\rm on}/I_{\rm off}$ ratios owing both to its molecular geometry and energy levels.^{30–32} For example, both p-channel and n-channel mobilities higher than $0.1 \text{ cm}^2 \text{ V}^{-1}$ s⁻¹ have been recently reported for disubstituted PTTPs.^{33,34} However, all of these studies have exclusively focused on PTTP small molecules. Good reproducibility of device performance remains a challenge for these solution-processed materials.³² Nonuniform films were common when organic solvents such as benzene, toluene, chloroform, and 1,2,4-trichlorobenzne (TCB) were used for semiconductor processing. The occasional smooth films obtained from casting with these solvents were not easily reproducible.³² Given the advantages of polymers versus small molecules, particularly in terms of uniform film formation, mechanical flexibility, and excellent rheology properties,^{35,36} it is of practical significance to incorporate PTTP conducting blocks into polymeric systems to facilitate creation of uniform thin films with variations in device performance. To the best of our knowledge, PTTP-based semiconducting polymers for TFT applications are yet to be reported. It is anticipated that such materials would exhibit improved film formation upon solution processing in comparison to their small molecule PTTP counterparts.

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(i) (1) n-BuLi, THF, -78 °C, (2) BUSNCI3. (ii) Pd(PPH3)4, DMF, 85 °C. (iii) NBS, DMF, r.t. (iv) Pyridine/NEt3, r.t. (v) Bis(tributyltin), Pd(PPH3)4, Refulx in Toluene. (vi) AIBN, Toluene, 70 °C

SCHEME 1 Synthetic route of PTTP graft polymers.

Recently, we have successfully developed a strategy to synthesize electroactive graft polymers via incorporation of conjugated oligothiophenes onto conventional polystyrene backbones as pendant side chains.³⁷ In contrast to main-chain conjugated polymers, graft polymers are regarded as attractive because of the ease in tuning mechanical and rheological properties, by varying the polymer main-chain structures while retaining electrical properties that are inherited primarily from pendant semiconductor cores. Previously, graft poly(methyl methacrylate)s with alkyl sexithiophene as pendant side chains have been synthesized via anodic polymerization by Shirota and coworkers.^{38,39} However, no FET performance has been reported in those studies. Inspired by the concept of graft polymer-based materials, a class of polymethacrylate derivatives containing conjugated PTTP cores as pendant side chains has been synthesized via direct free radical polymerization of PTTP-modified methacrylic monomers. The effect of fundamental changes in chemical structure of the PTTP graft polymers (e.g., alkyl side chain and aliphatic spacer) on the physical properties of the resultant polymers has been systematically studied by synthesizing the PTTP graft polymers having the alkyl chain length varying from hexyl to dodecyl (C_6 , C_8 , and C_{12}). Pertinent properties that were evaluated included morphology, solubility and electrical characteristics. Particularly for the dodecyl-terminated PTTP graft polymer systems, the effect of the spacer on the polymer's flexibility and solubility has also been studied by substitution of the ethyl group between the methacrylate backbone and the PTTP segments with a butyl unit.

TFTs were fabricated from both the PTTP monomers and graft polymers by spin-coating solutions of each material in chloroform onto the device substrate to characterize their field-effect performance.

RESULTS AND DISCUSSION

Synthesis of PTTP Monomers and Graft Polymers

Unlike the symmetric disubstituted PTTP and derivatives previously synthesized and tested for their field-effect transistor performance, it is more challenging to synthesize asymmetric small molecule analogs via multiple step reactions. As outlined in Scheme 1, a long alkyl chain was attached to one end of the PTTP segment to enhance overall solubility of the desired product, using a 4-bromo-alkylbenzene as the starting material. The final PTTP methacrylic monomers were synthesized via the Stille coupling reaction between bromo-alkylphenyl bithiophene (3a, 3b, or 3c) and 4-tributyltin-phenalkyl methacrylate (5a or 5b). By varying the sizes of the alkyl side chain and spacer, a total of four different PTTP monomers were successfully synthesized including 4-(5'-(4-hexylphenyl)-[2,2'-bithiophen]-5-yl)phenethyl methacrylate (HPTTPEM), 4-(5'-(4-octylphenyl)-[2,2'bithiophen]-5-yl)phenethyl methacrylate (OPTTPEM), 4-(5'-(4-dodecylphenyl)-[2,2'-bithiophen]-5-yl)phenethyl methacrylate (DPTTPEM), and 4-(5'-(4-dodecylphenyl)-[2,2'-bithiophen]-5-yl)phenbutyl methacrylate (DPTTPBM), as shown in Scheme 1. These reactive monomers were further free radically polymerized to form four different PTTP graft



FIGURE 1 ¹H NMR spectra of (a) DPTTPBM and (b) p(DPTTPBM).

polymethacrylates accordingly. The ¹H spectra of DPTTPBM and poly(4-(5'-(4-dodecylphenyl)-[2,2'-bithiophen]-5-yl)phenbutyl methacrylate), p(DPTTPBM), shown in Figure 1, are representative of the series of materials prepared here. Detailed NMR information for all other PTTP compounds can be found in Supporting Information.

All the aforementioned PTTP monomers had good solubility in common organic solvents such as dichloromethane, chloroform, and tetrahydrofuran. After free radical polymerization, the solubility of the resultant PTTP graft polymers was significantly affected by the length of both the alkyl side chain and spacer. Specifically, the yellow p(HPTTPEM) powder displayed very limited solubility in many common organic solvents at room temperature. However, poly(4-(5'-(4dodecylphenyl)-[2,2'-bithiophen]-5-yl)phenethyl methacrylate), p(DPTTPEM), could dissolve in hot TCB and chlorobenzene and was partially soluble in chloroform. The solubility was further enhanced for p(DPTTPBM) where the ethyl spacer was replaced with a butyl unit. As deduced from GPC evaluation as seen Table 1, the length of the alkyl side chain had no significant effect on the reactivity of the PTTP methacrylic monomers. Both poly(4-(5'-(4-octylphenyl)-[2,2'-bithiophen]-5-yl) phenethyl methacrylate), p(OPTTPEM), and

TABLE 1 Molecular Weight, Polydispersity Index (PDI), Degreeof Polymerization (DP), and Thermal Stability of PTTP GraftPolymers

	<i>M</i> n (kg mol ⁻¹)	<i>M</i> _w (kg mol ^{−1})	PDI	DP	<i>T</i> d (°C)
p(HPTTPEM)	-	-	-	-	359
p(OPTTPEM)	12,500	36,200	2.9	23	355
p(DPTTPEM)	13,500	34,500	2.5	23	378
p(DPTTPBM)	7,600	26,500	3.4	12	405

Materials

p(DPTTPEM) shared the same degree of polymerization (*n*, 23). Alternatively, introduction of the butyl spacer was seen to decrease the reactivity of DPTTPBM, whose degree of polymerization was found to be only 12. Compared to DPTTPEM, the analog that possessed the same dodecyl side chain, the butyl spacer in DPTTPBM was believed to increase steric hindrance which in turn lowered the reactivity of the monomer. The significantly lower molecular weight of p(DPTTPBM) could also explain its much improved solubility compared to the other PTTP graft polymers examined here.

All PTTP graft polymers demonstrated good thermal stability with decomposition temperatures (5 wt % loss) higher than 350 °C, as determined by thermogravimetric analysis (Fig. 1S in Supporting Information). Crystallization and melting features of the PTTP monomers and graft polymers were elucidated through differential scanning calorimetry (DSC). A typical DSC curve of a monomer displayed two distinct transitions in either the heating or cooling process (DPTTPEM was an exception, where the endothermic transition at low temperature during cooling was undetectable). As shown in Figure 2(a), transitions for HPTTPEM were clearly observed at 120, 225 °C during heating and 62, 220 °C during the cooling cycle. The DSC curves of these PTTP small molecules appeared to be very similar to that of a dihexyl PTTP semiconductor previously reported by Marks and coworkers,³² where the exothermic transition at 120 °C was attributed to an S_A/nematic liquid crystalline phase transition. In this study, the liquid crystalline phase was not visually observed by temperature-dependent polarized optical microscopy (POM). Rather, crystallites with a domain size in the micrometer range were consistently observed for a sublimed HPTTPEM film by both POM and atomic force microscopy (Fig. 2S in Supporting Information), indicative of the strong dependence of the formation of a liquid crystalline phase on parameters such as chemical structure, temperature, and



FIGURE 2 DSC curves of (a) PTTP monomers and (b) graft polymers. The figure displays the results for the first heating cycle and the *y*-axis was shifted accordingly.

substrate surface. The second thermal peak observed at ~225 °C during heating was related to the crystallization-melting of HPTTPEM. In the cooling cycle for this compound, a shoulder on the high temperature side could be discerned, suggesting that melting and crystallization occurred in two steps, possibly via an intermediate-layered mesophase of smectic symmetry.⁴⁰ As the alkyl chain length increased, both thermal transitions gradually moved to lower temperatures. The transitions for DPTTPEM were observed at 114 and 214 °C, compared to 120 and 225 °C for HPTTPEM upon heating. Meanwhile, the spacer was also found to have impact on the thermal transition temperatures. Replacing the ethyl linker in DPTTPEM with a butyl unit, as in DPTTBM, afforded a decrease in the thermal transition temperatures by ~20 °C.

As shown in Figure 2(b), the thermal behavior of the associated PTTP graft polymers was also investigated by DSC. Similar to those of the monomers, the lengths of both the alkyl side chain and spacer clearly influenced the melting temperatures of the polymers. Polymerization of the PTTP monomers was thought to immobilize both the aliphatic moieties and aromatic PTTP cores by reducing the degree of segment relaxation, which was supported by the increase of about 20 °C in the melting temperature for each PTTP graft polymer compared to its allied monomer. Crystalline phase transitions at low temperature, similar to those found for the monomers, were not found for the PTTP graft polymers; a result which is consistent with a previous report and thought to result from the lack of ordered alignment of the PTTP segments along a given direction.⁴¹ Additionally, with the enhanced flexibility of the PTTP pendant side chains attributed to the longer aliphatic segments, a glass transition temperature became detectable for p(DPTTPEM) at 181 °C and further decreased to 169 °C for p(DPTTPBM).

The morphology of the PTTP compounds was further studied by micro-X-ray diffraction. All monomers showed strong reflection signals up to multiple orders, consistent with the crystalline nature of these compounds revealed by both DSC and POM (Fig. 2S in Supporting Information). As shown in Table 2, the first order *d*-spacing varied from about 28 Å in HPTTPEM to about 35 Å as the alkyl side chain length increased. These values are consistent with those previously reported for other, analogous PTTP derivatives.^{32,34} Upon replacing the ethyl spacer with a butyl unit, the *d*-spacing decreased slightly from about 35 Å in DPTTPEM to about 31 Å in DPTTPBM. As revealed by DSC, it is speculated that the enhanced flexibility of DPTTPBM induced by the longer butyl spacer allowed for folding of the alkyl moieties as well as possible interdigitated alkyl chain packing, which eventually resulted in the decreased interlayer *d*-spacing. It is noteworthy that the alkyl side chain also played a significant role in the formation of the crystalline phase. As shown in Figure 3, besides the first-order reflection, two sets of the high-order reflection peaks were observed specifically for DPTTEM, suggesting the formation of a mixture of at least two different crystalline phases; the NMR spectra demonstrated the high

TABLE 2 X-Ray Diffraction θ -2 θ Data for Sublimed PTTP Films

	Sublimed Film at 25 °C			
	o	Other Observable		
Compound	d (A)	Reflections (Order)		
HPTTPEM	27.8	3, 4		
OPTTPEM	31.8	3, 4		
DPTTPEM	35.0	3, 4, 5, 6 (3', 4', 5', 6')		
DPTTPBM	31.3	3, 4		



FIGURE 3 Micro-X-ray diffraction θ -2 θ scans of sublimed DPTTPEM film and p(DPTTPEM) powder at room temperature.

purity of this compound (>99%) after column chromatography. No second set of crystalline structures was observed for the other PTTP compounds explored (Fig. 3S in Supporting Information). The three major reflection peaks at $\sim 19^{\circ}$, 22° , and 27° , observed for all four PTTP monomers, were very similar to those previously observed for an oligothiophene, indicative of the presence of a layered morphology.⁴² Pertaining to the related graft polymers, major reflection features diminished in the small-angle regions, indicating the formation of amorphous state for these materials. These outcomes were well correlated with the DSC results, in which the crystalline phase transition observed at lower temperatures for relevant monomers disappeared for the related polymers. However, the three major peaks in the wideangle regions $(19^{\circ}-27^{\circ})$, as shown in Figure 3, remained essentially unchanged. According to the folded chain structure for a PTTP block copolymer proposed by Okamoto and coworkers,⁴³ this result may be indicative of a face-to-face alignment of the PTTP pendant side chains along the polymer backbone.

Interchain interactions of polymer chains were further studied using UV-vis spectroscopy. As shown in Table 3, the changes in chemical structure, that is, alkyl side chain and spacer, had little effect on the absorbance spectra of the monomers, which repeatedly showed an absorbance maximum at 380 nm. This result is not unexpected because the alkyl side chains have only limited contribution to the PTTPconjugated system and therefore are not expected to affect the energy levels of the units in solution. A blue shift was previously observed for an oligofluorene graft polystyrene compared to its monomer due to the twisted confirmation of polymer backbone upon polymerization.⁴⁴ Twisting of polymer backbone was thought to be negligible for these PTTP graft polymer systems because no significant blue shift was observed between each monomer/polymer pair in solution, with both maxima at \sim 380 nm, whereas a significant blue shift was observed upon comparison of the absorbance spectra of either monomer or polymer in solution to those in the solid state. As seen in Figure 4, the absorbance maximum shifted from 385 nm in solution to 350 nm in thin-film state for p(DPTTPBM), a result which is significantly different from the normally observed red shift for most conjugated polymer solid films.⁴⁵ A similar 50-nm blue shift was observed for DPTTPBM. According to Okamoto and coworkers, two distinct modes of aggregation of molecules could occur: J- and H-aggregation.⁴³ These different forms result in distinct photoelectronic properties. Specifically, Jaggregation, which occurs by an end-to-end arrangement of π -molecules, displays red-shifted J-bands, whereas a face-toface assembly affords blue-shifted H-bands. The blue shift observed for the PTTP materials is thought to be related with H-aggregation, that is, the formation of face-to-face stacking between the pendant PTTP segments.34,46 This explanation is realistic, specifically for the graft polymers under investigation, because the end-to-end aggregation of the PTTP pendant side chains is expected to be severely impaired by the shielding of the alkyl terminal groups attached to the PTTP cores, whereas face-to-face aggregation between neighboring PTTP segments is highly possible.³⁷

TABLE 3 Electrochemical and Electrical Properties of PTTP Monomers and Graft Polymers

	UV Absorption			CV		FET Device		
	Solution (nm)	Film (nm)ª	Band Gap (eV) ^b	HOMO (eV)	LUMO (eV)	Hole Mobility (cm ² V ⁻¹ s ⁻¹)	I _{on} /I _{off}	Threshold Voltage (<i>V</i> _T , V)
HPTTPEM	379	330*, 359	2.82	5.38	2.56	$5.4 imes 10^{-5}$	8.2×10^2	-12.8
OPTTPEM	379	331*, 359	2.80	5.36	2.56	$\textbf{2.2}\times\textbf{10}^{-5}$	8.4×10^2	0.7
DPTTPEM	380	330*, 355	2.81	5.38	2.57	$1.3 imes 10^{-5}$	1.2×10^3	-14.9
DPTTPBM	380	340*, 358, 429	2.80	5.34	2.54	$9.2 imes 10^{-6}$	3.2×10^2	-10.9
p(HPTTPEM)	384	_	2.77	5.42	2.65	_	-	_
p(OPTTPEM)	384	364*, 431	2.76	5.47	2.71	-	_	-
p(DPTTPEM)	384	349*, 393, 423	2.75	5.48	2.73	5.6×10^{-7}	13	-1.52
p(DPTTPBM)	380	350*, 394, 425	2.74	5.47	2.73	$1.7 imes 10^{-7}$	5	-32.8

 $^{\rm a}$ Absolute maximum indicated by asterisk. Uniform and reproducible films could not obtain for p(HPTTPEM) due to its poor solubility in p-xylene.

^b Optical band gaps of p(OPTTPEM), p(DPTTPEM), and p(DPTTPBM) were identified from the film absorption, and they were identified from the solution absorbance spectra for all the other listed materials.





FIGURE 4 UV-vis absorption spectra of DPTTPBM and p(DPTTPBM).

Consistent with the observation in the UV-vis spectra, a structural change in the alkyl side chain or spacer did not significantly affect the HOMO energy levels of the monomers, which lay in the narrow range of 5.34–5.38 eV as shown in Figure 5. The relatively deeper HOMO levels of these compounds compared to oligothiophenes, normally in 4.8–5.1 eV, demonstrated improved oxidative stability. It was thought to be a result of the delocalization of electron density on the conjugated PTTP system through the incorporation of phenylene units.^{30,32} All the PTTP compounds studied here (monomers and polymers) could not be reduced using the experimental conditions described; thus, the LUMO energy levels were extracted from the difference between the HOMO level and the optical band gap determined from the onset of the UV-vis absorbance spectrum. As summarized in Table 3, a negligible difference in the HOMO levels was observed for all the PTTP monomers and graft polymers. Because of the shorter band gap, the PTTP graft polymers possessed slightly higher LUMO levels than those of the monomers.

A bottom-gate, bottom-contact TFT device configuration was utilized in the characterization of FET properties of PTTP monomers and graft polymers. The thermal silicon oxide layer (SiO₂, \sim 300 nm in thickness) on the silicon wafer surface functioned as the gate dielectric. The p-channel semiconductors were deposited by spin coating from chloroform solution. TFTs were characterized in air without taking



FIGURE 5 Cyclic voltammograms of (a) PTTP monomers and (b) graft polymers.



FIGURE 6 LV characteristics of a representative TFT device fabricated from HPTTPEM in chloroform solution (3 mg mL⁻¹): (a) Output curves at different gate voltages and (b) transfer curve in the saturated regime at a constant source-drain voltage of -50 V and square root of the absolute value of the drain current as a function of gate voltage.

precautionary measures to isolate the devices from exposure to atmospheric oxygen, moisture, or ambient light. Except for the two graft polymers, p(HPTTPEM) and p(OPTTPEM), having shorter alkyl side chains, which could not be solution processed due to their relatively poor solubility in chloroform, all other materials exhibited characteristic p-channel FET behavior. As the example shown in Figure 6, the output curves of HPTTPEM displayed good saturation behavior with no obvious contact resistance. The extracted mobilities in the saturated regime were on the order of 10^{-5} cm² V⁻¹ s⁻¹, which were similar to values previously reported for PTTP derivatives without device optimization.⁴⁷ It should be noted here that the chemical structure of the PTTP small molecules did affect their FET performance. The mobility gradually decreased as the size of the PTTP molecule increased. This result is consistent with previous results showing that rather than aligning in a geometry perpendicular to the substrate, PTTP cores having aliphatic appendages that occupy a large volume tend to tilt toward the substrate.⁴⁷ Similar to a previous report related to a dimethacrylate-functionalized PTTP monomer,48 polymerization enhanced the thermal and oxidative stability of the resultant polymers, while accordingly, the rigid polymer backbone distorted the lamellar structures observed in the monomer state. Also, the increase in grain boundaries associated with polymer domains could be a source of charge trapping. Both facts were thought to deleteriously affect the mobility of the resultant polymers.

CONCLUSIONS

Here, we have synthesized a class of PTTP-modified methacrylic monomers with variable alkyl side chains and spacer units. The monomers were further free radically polymerized to form PTTP graft polymers. A relatively low-molecularweight polymer, p(DPTTPBM), was obtained from the dodecyl-PTTP butyl methacrylate due to increased steric hindrance induced by the bulky spacer even though this polymer possessed the best solubility in common organic



solvents among all the PTTP graft polymers examined. A crystalline nature was observed for all the PTTP monomers with the transition temperatures being significantly affected by both the alkyl side chains and spacers. Longer aliphatic chains enhanced the overall flexibility of the PTTP molecules and therefore lowered their crystallization-melting temperatures. The face-to-face alignment of the pendant PTTP side chains along the polymer chains resulted in a distinct blue shift in their UV-vis spectra. Although the aliphatic moieties negligibly affected the HOMO/LUMO energy levels, longer side chain did result in decreased p-channel mobilities for TFT devices prepared from the materials. Compared to alternative well-developed organic semiconductor materials, there is still substantial space to improve on the FET performance characteristics through optimization of the structure of the PTTP materials investigated here. The introduction of the concept of a graft polymer approach could also contribute to the development of new chemical architectures and/or building blocks for applications related to organic electronics.

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