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Improved TTF functionalization of polymers for two-dimensional charge-transfer networks

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Covalent conjugation of tetrathiafulvalene (TTF) moieties to macromolecular backbones combines unique properties of polymers, such as processability and high functional group density, with the outstanding redox properties of TTF to expand applications in organic electronics, chemical sensors, molecular switches, and nonlinear optical materials among others. Herein, we report the synthesis of a polymethacrylate backbone with 4-(hydroxymethyl)TTF (hmTTF) as the pendant group using post-polymerization modification of poly(*N*-hydroxysuccinimide methacrylate) to obtain the product polymer with a wide range of molecular weights (18 ≤ M_n ≤ 126 kDa) and up to *ca.* 70 mol% (76 wt%) TTF. The electrochemical and electronic properties of phmTTFMA are analogous to that of monomeric TTF. Film-forming phmTTFMA-based charge-transfer complexes (CTCs) with various electron acceptors including iodine, TCNQ, and chloranil showed an isotropic electrical conductivity. The magnitude of the conductivities of phmTTFMA-based CTCs is primarily affected by the electron affinity of the electron acceptors. The morphology of the amorphous phmTTFMA is strongly dependent on its electronic interactions with small-molecule electron acceptors. For example, a lamellar-like structure is observed when phmTTFMA is mixed with chloranil.

Introduction

As a prototypical electron donor, tetrathiafulvalene (TTF) exhibits outstanding redox properties that are applicable for organic electronics, chemical sensors, molecular switches, and nonlinear optical materials.[1] When combined with various π-electron acceptors, TTF stacks in the solid state to form highly electrically conducting charge-transfer complexes (CTCs).[2-5] The discovery of metallic behavior of CTCs composed of TTF and 7,7,8,8-tetracyanoquinodimethane (TCNQ)[4] has generated numerous reports on the syntheses, properties and applications of TTF-based CTCs.[5] Despite the inherent electronic advantages, most of the TTF-based CTCs exhibit quasi-one-dimensional electrical conductivity due to their highly ordered stacking. Higher dimensions in conductivity are achieved by increasing sulfur content or replacing sulfur with a different chalcogen (Se, Te) in TTF.[6] However, CTCs with bis(ethylenedithio)tetrathiafulvalene, tetraselenafulvalenes, or tetratellurafulvalenes as the donor tend to be brittle and unprocessable.[7] An alternative approach to achieve higher dimensionality in conducting compounds involves the incorporation of molecular CTCs into a polymeric scaffold.[8-10] Integrating TTF into polymeric materials enhances processability and significantly influences solid-state organization.

Many attempts have been made to prepare polymeric materials with TTF pendant groups. Direct polymerization of monomers with TTF motif remains a great challenge.[11] Several reports have demonstrated that TTF is an inhibitor in anionic polymerization and free radical polymerization.[9, 10] The TTF moiety also interferes with cationic polymerization.[12] Bulk polymerizations of monomers containing TTF motif have been reported, yet the products are poorly characterized due to limited solubility.[6] Shimizu and Yamamoto successfully synthesized soluble poly(acetylene)s bearing TTF side chains using a rhodium catalyst through coordination polymerization.[13, 14] However, their products exhibited low molecular weight with wide molecular weight distributions.

Compared to direct polymerization, post-polymerization modification (PPM) is a preferable approach for synthesizing polymers bearing pendant TTF units. The PPM approach begins with facile and highly controllable polymerizations to afford various polymer precursors bearing reactive pendant groups capable of undergoing highly efficient coupling chemistries with functionally-active units.[15, 16] Chujo and colleagues reported PPM of a polymethacrylate backbone by attaching TTF via azide-alkyne cycloaddition chemistry. This strategy was limited to a maximum of 59 mol% of TTF functionalization.[17] The incomplete degree of functionalization is proposed to result from steric hindrance between the neighboring triazole and/or TTF moieties.[17]

To explore the electronic properties of polymers with higher TTF content, we herein report a facile PPM procedure

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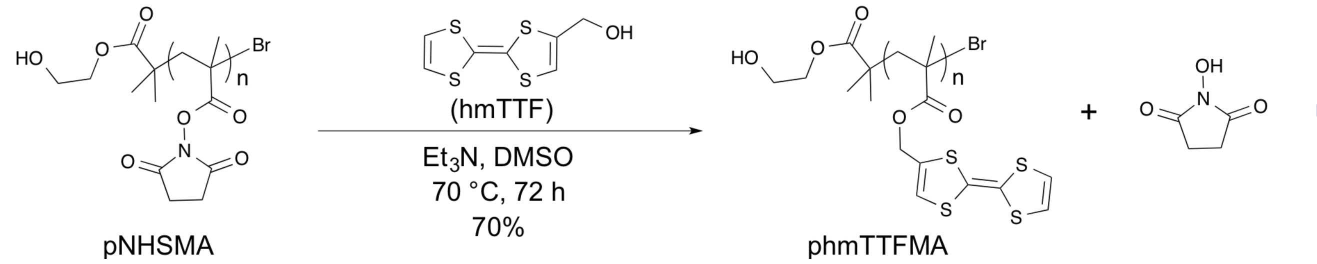
Scheme 1. Synthesis of poly(hmTTF methacrylate) through PPM using an acyl substitution reaction with an active ester.



using a substitution reaction between 4-(hydroxylmethyl)TTF (hmTTF) and poly(*N*-hydroxylsuccinimide methacrylate) (pNHSMA), where NHS groups are replaced with TTF groups via nucleophilic acyl substitution (Scheme 1). With this method, we improved the TTF incorporation to *ca.* 70 mol% (76 wt%). The electrochemical and electric properties of the polymer have been studied and are shown to be analogous to that of molecular TTF. The conductivity and morphology of the obtained polymer are easily tuned by its electronic interactions with various electron acceptors.

Experimental Section

Materials

Unless otherwise stated, all reagents and solvents were purchased from commercial sources and were used as received. *N*-hydroxysuccinimide methacrylate was recrystallized from a mixture of ethyl acetate and hexanes (v:v = 1:1) and dried under vacuum overnight before usage. Anhydrous dimethyl sulfoxide (DMSO), triethylamine, and methanol were obtained from an anhydrous solvent delivery system (SDS) equipped with activated alumina columns. Flash column chromatography was conducted with silica gel 60 (230-400 mesh) from Silicycle. All reactions were performed under an inert atmosphere (dry nitrogen gas) using standard Schlenk and vacuum line techniques. Poly(*N*-hydroxysuccinimide methacrylate) (pNHSMA), p(NHSMA$_{60}$-co-MMA$_{40}$), poly[*N*-(acryloyloxy)succinimide] (pNAS), and 4-(hydroxymethyl)TTF (hmTTF) were synthesized according to reported literature procedures.[18-20]

Instrumentation and measurements

^1H and ^{13}C NMR spectra were obtained using either a Varian 400 MHz or 500 MHz spectrometer in the VOICE NMR laboratory at the University of Illinois. All chemical shifts (ppm) were calibrated to the residual proton peak of the deuterated solvent. Coupling constants (*J*) are expressed in Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), dd (doublet of doublets), and m (multiplet).

Mass spectra were obtained through the Mass Spectrometry Facility, School of Chemical Sciences (SCS), at the University of Illinois – Urbana-Champaign. Elemental analysis data were obtained through the SCS Microanalysis Laboratory, University of Illinois at Urbana-Champaign. UV-Vis spectra were recorded in DMSO using a Shimadzu UV-2401PC. Standard quartz cells with a path length of 2 mm from Starna Cells, Inc. were used. Infrared spectra were collected on a NEXUS 670 serial FTIR spectrophotometer. Thermal gravimetric analysis (TGA) was conducted using TA instrument Q50 at a ramping rate of 10°C min^{-1} under a dry nitrogen atmosphere.

Analytical Gel Permeation Chromatography (GPC) was performed on a system equipped with a Model 1200 isocratic pump (Agilent Technology, Santa Clara, CA, U.S.A.) in series with a Waters 717 autosampler, a DAWN HELEOS multiangle laser light scattering detector (MALLS) (Wyatt Technology, Santa Barbara, CA, U.S.A.), and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA, U.S.A.). Separations were performed using serially connected size exclusion columns (10^2 Å, 10^3 Å, 10^4 Å, 10^5 Å, 10^6 Å Phenogel columns, 5 µm, 300 × 7.8 mm, Phenomenex, Torrance, CA, USA) at 60°C using *N,N*-dimethylformamide containing 0.1 mol/L LiBr as the mobile phase at a flow rate of 1 mL min^{-1}. Samples were filtered through a 0.45 µm PTFE filter before analysis. Absolute molecular weights of polymers were determined using ASTRA 6.1.1.17 software (Wyatt Technology, Santa Barbara, CA, U.S.A.) and calculated from *dn/dc* values assuming 100% mass recovery.

Electrochemical experiments were performed in an inert environment using a CHI1242b portable bipotentiostat (CH Instruments, Austin, TX). Solutions were prepared in an argon atmosphere glovebox. Cyclic voltammograms (CVs) were obtained using a silver wire as a quasi-reference electrode (QRE) and a platinum wire as a counter electrode. All potentials are reported versus the QRE. A Signatone Pro4-440N four-point-probe and a KLA-Tencor P-6 stylus surface profilometer were used to determine the electrical conductivity of casting films composed of phmTTFMA and phmTTFMA-based CTCs. The phmTTFMA-TCNQ and phmTTFMA-chloranil CTCs were prepared by mixing equimolar of phmTTFMA with TCNQ and chloranil, respectively, in DMSO. The solution was stirred at room temperature for 2 h before casting on a glass slide. A steady stream of dry nitrogen was used to evaporate DMSO overnight. The sample was further dried under vacuum at 40 °C for 24 h. Similar techniques were employed to produce phmTTFMA film for conductivity measurement. The phmTTFMA-iodine sample was prepared by exposing phmTTFMA film with iodine vapor for 2 h. For the conductivity measurement, three samples were used and each sample was measured at least five times. Powder XRD patterns were recorded on a Rigaku MiniFlex at a scanning rate of 0.02 ° s^{-1} in two-theta ranging from 5 to 50 °. Samples for the XRD measurements were prepared by casting films on a zero diffraction plate purchased from MTI Corporation.

The degree of TTF functionalization for a PPM polymer was calculated from 1) absorbance spectra of the crude polymer in DMSO by using the Beer-Lambert law (see SI-I); 2) ^{1}H NMR spectra of the as-obtained polymer in deuterated DMSO by using the integral ratio of (TTF peak area)/[(TTF peak area)+(NHS peak area)] (see SI-II); and 3) weight percent of sulfur and nitrogen from elemental analysis data (see SI-III).

Synthetic procedures

Synthesis of [2,2'-bi(1,3-dithiolylidene)]-4-ylmethyl methacrylate (1)

To a Schlenk flask were added 4-(hydroxymethyl)TTF (0.65 g, 2.8 mmol) and *N*-succinimidyl methacrylate (0.48 g, 2.6 mmol). The solids were dissolved in anhydrous DMSO (6.5 mL) and triethylamine (3.3 mL) under nitrogen. The reaction mixture was left stirring at 70 °C for 12 h. Water (50 mL) was added and the aqueous layer was extracted with dichloromethane (4 × 50 mL). The combined organic phase was dried over $MgSO_4$. After filtration, the mixture was concentrated *in vacuo*. Purification of the residue by flash column (SiO_2, hexanes: ethyl acetate = 1:1 v/v) afforded the pure product as an orange solid. Yield: 0.73 g (92 %). ^{1}H NMR (500 MHz, $CDCl_3$): d 6.34 (s, 1H), 6.31 (s, 2H), 6.20-6.18 (m, 1H), 5.68-5.64 (m, 1H), 4.93-4.91 (d, *J* = 1.0 Hz, 2H), 1.96 (dd, *J* = 1.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): d 166.8, 135.7, 131.3, 126.8, 119.2, 119.1, 199.1, 111.7, 109.4, 61.2, 18.4; HRMS (ESI) calcd for $C_{11}H_{10}O_2S_4$ 301.9564, found 301.9557.

Typical procedure for PPM of pNHSMA

In a typical experiment, the polymer precursor pNHSMA (200 mg) and the desired amount of 4-(hydroxymethyl)TTF (Tables 1 and 2) were weighed into a Schlenk flask and dissolved in anhydrous DMSO (2.0 mL) and triethylamine (1.0 mL) under nitrogen. The reaction mixture was left stirring at 70 °C for 72 h and then brought to room temperature. The polymer precipitated by pouring the reaction solution into acetone/ether (200 mL, 1:1 v/v) and was collected by filtration. The isolated polymer was further purified by re-dissolving into DMSO and re-precipitating the DMSO solution into an acetone/ether mixture. The collected re-precipitate was washed several times with acetone/ether and immediately dried under vacuum at 40 °C for 24 h. The yield of PPM ranged from 85 % to 92%, whereas the TTF functionalization varied depending on reaction conditions (Tables 1 and 2).

Typical procedure for PPM of phmTTFMA with methanol

In a typical experiment, phmTTFMA (100 mg) and an excess amount of anhydrous methanol (0.4 mL) were added into a Schlenk flask and dissolved in anhydrous DMSO (1.0 mL) and triethylamine (1.0 mL) under nitrogen. The reaction mixture was left stirring at 70 °C for 24 h and then brought to room temperature. The polymer precipitated by pouring the reaction solution into acetone/ether (100 mL, 1:1 v/v) and was collected by filtration. The isolated polymer was further purified by re-dissolving into DMSO and re-precipitating the DMSO solution into an acetone/ether mixture. The collected re-precipitate was washed several times with acetone/ether and immediately dried under vacuum at 40 °C for 24 h. The yield of the reaction is approximately 80%.

Results and discussion

To synthesize polymers bearing pendant TTF motifs by PPM, we first synthesized the macromolecular precursor pNHSMA by atom-transfer radical polymerization (ATRP),[12] followed by nucleophilic acyl substitution. Unlike Chujo's work employing azide-alkyne cycloaddition that yielded bulky pendant trizaoles, we chose to use activated esters. We hypothesized that replacing sterically hindered NHS esters with TTF during PPM is a favorable process and allows for the improved extent of side-chain functionalization. Strong nucleophiles, such as primary amines, are frequently used in PPM due to their quantitative substitution with NHS esters. However, 4-(aminomethyl)TTF has very low stability and decomposes within a few hours at room temperature.[21] We also attempted the synthesis of amine-functionalized TTF analogs with an alkyl spacer to improve stability, but neither the substitution of protected amines nor reduction of an azide was successful (Scheme S1).[22]

In order to avoid the use of amine-functionalized TTF, we successfully synthesized hmTTF, a TTF derivative that is stable up to 150 °C and investigated its potential as the PPM nucleophile (Fig. S5). Synthesis of model compound **1** via a nucleophilic acyl substitution reaction between hmTTF[19] and NHSMA monomer was facile and proceeded in near-quantitative yield (Scheme 2). Subsequently, hmTTF was reacted with pNHSMA resulting in the polymer phmTTFMA (Scheme 1). Optimized PPM conditions to maximize TTF loading required reactions in DMSO at 70 °C for 3 d with an excess amount of triethylamine. The triethylamine was needed to suppress side reactions, such as succinimide ring opening.[15] TTF incorporation to the polymer backbone reached a plateau after 72 h of reaction time.

Direct polymerization of TTF-functionalized monomer was compared to PPM by subjecting **1** to both radical and anionic polymerization conditions. We attempted various polymerization methods, including free radical polymerization and reversible addition-fragmentation chain transfer using azobisisobutyronitrile, ATRP and single-electron transfer living radical polymerization using ethyl α-bromoisobutyrate, and anionic polymerization using *n*-BuLi; however, no polymerization was observed and near-quantitative amount of starting material **1** was recovered. Agreeing with previously published reports,[9, 10] these results support the claim that PPM is the preferred approach for incorporating the TTF motifs into polymers.

Scheme 2. Synthesis of hmTTF methacrylate, **1**, through substitution reaction between 4-(hydroxymethyl)TTF and NHSMA.

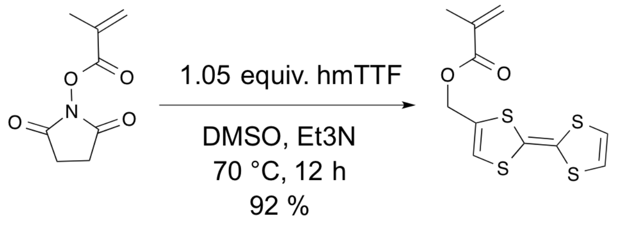


Table 1. PPM results of pNHSMA (M_n = 55.3 kDa, PDI = 1.64) with varying amount of hmTTF used in the substitution reaction.

Mol. equiv. of hmTTF[a]	Degree of TTF substitution (% of repeat units TTF)[b]
0.3	31 (**P1**)
0.4	40 (**P2**)
0.6	59 (**P3**)
0.8	65 (**P4**)
1	70 (**P5**)
1.2	71 (**P6**)
4	70 (**P7**)

[a] Calculated relative to the NHS repeating unit
[b] Determined from UV-Vis data where the standard

We determined the maximum TTF functionalization of polymer by using various amount of hmTTF in the substitution reaction. As shown in Table 1, the molar equivalent of hmTTF used in the substitution reaction corresponded to the percent TTF functionalization of the yielded polymer until 0.6 equivalent of hmTTF was reached. Based on the absorbance spectra, the maximum TTF functionalization into the pNHSMA was ca. 70 mol% (ca. 76 wt%) (Fig. S1-S3). Similar compositions were measured by ^{1}H NMR (Table S1-S2) and sulfur or nitrogen elemental analysis (Table S3-S4).

We attributed the observed incomplete conversion to the steric hindrance of neighboring TTF/NHS moieties and supported this hypothesis by synthesizing less compact precursor polymers.[23] We synthesized a random copolymer of p(NHS$_{40}$-co-MMA$_{60}$) where MMA is used as the comonomer. When p(NHS$_{40}$-co-MMA$_{60}$) was subjected to PPM with hmTTF, the conversion of NHS repeat units to TTF pendants was improved to over 80 mol% completion. We also synthesized pNAS where the less sterically congested acrylate monomer was used as the polymer backbone. When pNAS was subjected to the PPM conditions, the TTF incorporation was improved to 78 mol%. These results support our hypothesis that bulky groups hinder the completion of PPM. In addition, we subjected phmTTFMA to a reaction with methanol. The IR spectrum of the obtained polymer is similar to that of p(hmTTFMA$_{40}$-co-MMA$_{60}$) and the NHS peaks are significantly decreased, nearly to the limit of detection (Fig. S4). The integral ratio (TTF peak area)/[(TTF peak area) + (NHS peak area)] from the ^{1}H NMR spectrum of the isolated polymer increased from 64% to 71% after reacting phmTTFMA with methanol. An additional resonance from the methoxy group appeared in the ^{1}H NMR spectrum as well. These results indicated that the remaining NHS group in the phmTTFMA remains active and is substituted by less sterically congested nucleophiles such as methoxy.

Table 2. PPM results of pNHSMA with varying molecular weight. The molar equivalent of hmTTF is 1.2 with respect to the NHS repeating unit.

Molecular weight of pNHSMA (PDI)	Degree of TTF substitution (% of repeat units TTF)
18.2 kDa (1.32)	68 (**P8**)
30.2 kDa (1.57)	68 (**P9**)
55.3 kDa (1.64)	71(**P6**)
81.8 kDa (1.42)	68 (**P10**)
125.7 kDa (1.52)	69 (**P11**)

A series of pNHSMA polymers of different molecular weight were subjected to PPM conditions to probe whether the molecular weight of polymer precursor affect the extent of TTF functionalization. As shown in Table 2, when reacted with hmTTF using the conditions listed in Scheme 1, pNHSMAs with molecular weight varying from 18 to 126 kDa showed a consistent ca. 70 mol % of TTF functionalization. The obtained phmTTFMAs were soluble in DMSO and DMF, but insoluble in other common organic solvents. This result is an improvement from previous methacrylate based polymers containing TTF pendants having a relatively short linker (the solubility of the reported polymer being limited to strong acids).[10]

To determine if TTF retains its electrochemical properties when incorporated into a polymer, we characterized the polymer's redox activity by cyclic voltammetry measurements. Although the anodic peaks of the polymer are broadened, they are detectable. Both TTF and phmTTFMA in DMF give rise to $E_{pa}(1)/E_{pa}(2)$ at similar positions, -0.04/0.25 and -0.03/0.23 V, respectively (Fig. 1). A silver wire was used as a quasi-reference electrode (QRE) and all potentials are reported versus the QRE. These results revealed that the TTF unit in the polymer exhibits analogous redox reactivity as the molecular counterpart.

Consistent with TTF small molecule, phmTTFMA readily formed CTCs with TCNQ, and the CTCs were characterized by UV-Vis and IR spectroscopy. Dissolving phmTTFMA in DMSO containing 1.0 equiv of TCNQ with respect to TTF afforded a dark green solution. The absorption bands that appear at 420 nm and between 650-900 nm are assigned to the radical anion of TCNQ (Fig. 2a).[24] The IR spectrum of phmTTFMA-TCNQ exhibits a broad absorption band (2500-3500 cm^{-1}) suggesting the formation of CTC (Fig. 2b).[25] The degree of CT for phmTTFMA-TCNQ sample is determined by the frequency of the nitrile-stretching band of TCNQ.[26] The IR spectrum of phmTTFMA-TCNQ (1:1 molar ratio) shows a major band in the nitrile-stretching region at 2180 cm^{-1} and a minor band at 2149 cm^{-1}. With the addition of excess amount of TCNQ to the phmTTFMA, an uncomplexed nitrile-stretching band around

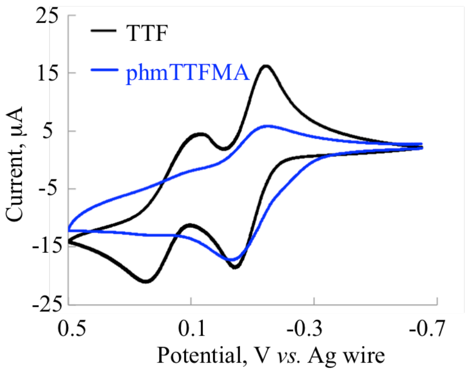


Figure 1. Cyclic voltammograms of phmTTFMA (10 mM) and TTF (5 mM) in DMF containing 0.1 M [NBu$_4$]PF$_6$ at 50 mV s^{-1}. A silver wire was used as a quasi-reference electrode.

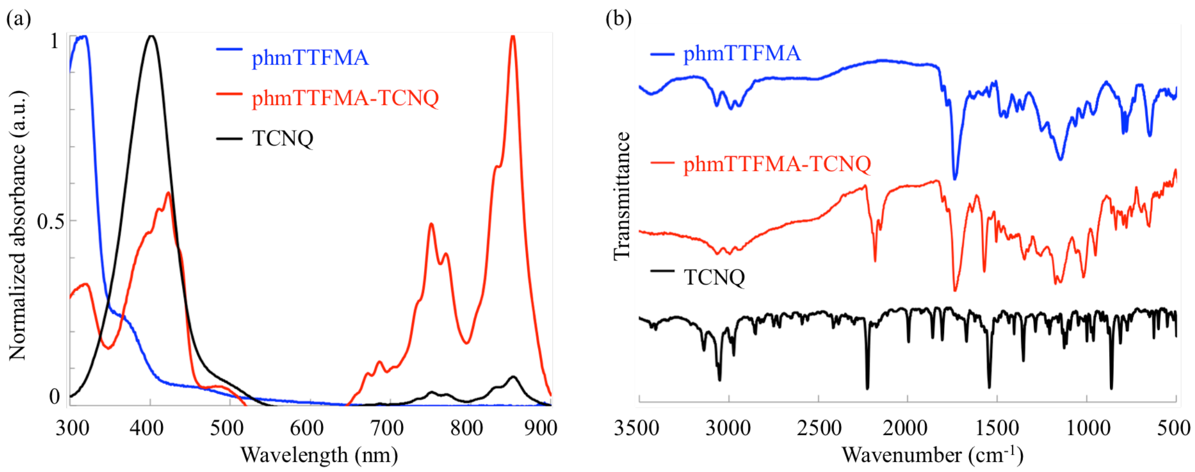


Figure 2. (a) UV-Vis spectra (b) IR spectra of phmTTFMA, TCNQ, and phmTTFMA-TCNQ.

2222 cm^{-1} appeared in the IR spectrum while the bands at 2149 cm^{-1} and 2180 cm^{-1} persisted and were assigned to the anion radical of TCNQ, which is consistent with the UV-Vis absorption analysis. The UV-Vis and IR spectra suggest that the TTF unit in phmTTFMA and TTF possess analogous chemical reactivity toward TCNQ.

We further compared the electrical conductivity and processability between phmTTFMA and TTF. Polymeric samples (phmTTFMA) form free-standing films with an electrical conductivity of 1.4×10^{-6} S/cm (Fig. S7). We doped phmTTFMA with three different electron acceptors that possess varying electron affinity. When the film was oxidized by iodine and TCNQ, the electrical conductivity increased to 2.3×10^{-3} S/cm and 2.3×10^{-5} S/cm, respectively. The electrical conductivity of the phmTTFMA-TCNQ complex showed about one order of magnitude improvement, compared to that of phmTTFMA. This result was attributed to the inhomogenous degree of CT in phmTTFMA-TCNQ samples as shown by its IR spectrum. Nevertheless, unlike TTF-TCNQ co-crystal whose electrical conductivity along the stacking direction is about three orders of magnitude higher than that in the perpendicular direction,[6] phmTTFMA-TCNQ exhibits similar electrical conductivity in all directions. The conductivity of the film increased slightly to 1.5×10^{-6} S/cm when chloranil, a weaker electron acceptor, was used. This is expected since the small molecule analog is mostly neutral.[27] The conductivity studies revealed that phmTTFMA-based CTCs exhibit higher electrical conductivities when electron acceptors with higher electron affinities are employed.

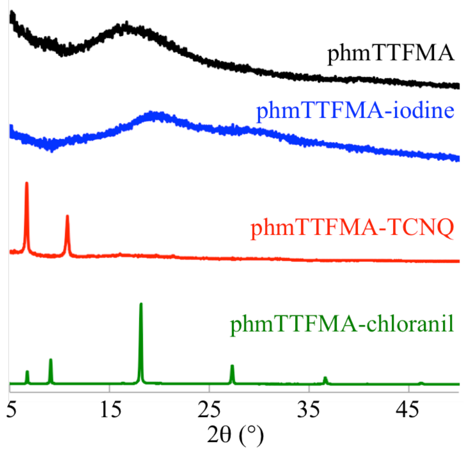


Figure 3. X-ray patterns of the cast films of phmTTFMA and its CTCs with iodine, TCNQ, and chloranil from DMSO.

We further investigated how the morphology of phmTTFMA-based CTCs impacts conductivity. X-ray patterns of phmTTFMA showed only one broad peak around 16.6 degrees two-theta, suggesting that the inter-planar spacing of the TTF planes in the polymer is around 5.3 Å (Fig. 3). The polymer remained amorphous after doping with iodine vapor. No crystalline peaks were observed when less than 0.3 equivalent of TCNQ/chloranil were added to the polymer system. However, when doping with 1 equivalent of TCNQ, sharp peaks at 6.7 and 10.7° appeared indicating an increase in crystallinity. Upon addition of chloranil to phmTTFMA, a sharp reflection appeared at 9.1° with higher-order reflections at 18.2, 27.3, 36.4, and 45.5° indicating high crystallinity and lamella-like structures for phmTTFMA-chloranil complex. Phase separation occurred when phmTTFMA with less TTF functionalization (**P1**) was used (Fig. S6). The X-ray patterns of phmTTFMA and its CTCs indicated the materials morphologies depend on the specific electron acceptor.

Conclusions

In summary, we developed an efficient method to graft TTF side chains to a polymethacrylate backbone using PPM by a nucleophilic acyl substitution reaction. With this method, we achieved a degree of TTF functionalization to *ca.* 70 mol% (76 wt%) on polymers over a wide range of molecular weights (18 ≤ M_n ≤ 126 kDa). The incomplete conversion is attributed to the steric hindrance of neighboring TTF/NHS moieties, especially when a congested polymer backbone was employed. The electrochemical and conductivity properties of the obtained polymer were measured and are analogous to that of molecular TTF. Unlike its brittle small-molecule analogs whose applications have been limited due to their one-dimensional conductivity, film-forming phmTTFMA-based CTCs with various electron acceptors including iodine, TCNQ, and chloranil showed an isotropic electrical conductivity. Compared to the uncomplexed phmTTFMA with a conductivity of 2.3×10^{-5} S/cm, all of the polymeric CTCs showed enhanced electrical conductivity, which is primarily influenced by the electron affinity of the electron acceptors used in the CTCs. Lastly, the morphology of the phmTTFMA depends on its electronic interactions with different electron acceptors.

Acknowledgements

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