End-capping of conductive poly(3.4-ethylene)dioxy-thiophene chain using 2-thienylmethyl methacrylate monomer

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Abstract. Structure of poly(3.4-ethylene)dioxythiophene (PEDOT) has been modified by end-capping the chain using a thiophene base monomer. End-capping was carried out to study the effect of PEDOT structures on the conductivity of the PEDOT/PSS films. The monomer used for the end-capping was 2-thienylmethyl methacrylate (2TMM). End-capping of PEDOT with 2TMM was achieved by oxidative polymerisation of 3.4-ethylenedioxythiophene (EDOT) monomer in the presence of PSS as a dopant in aqueous solvent, and Na2S2O8 and Fe2(SO4)3 as oxidation agents. The reactions performed using ratio EDOT:PSS of 1:2.5, with the addition of varying concentrations of end-capping agent: 10%, 20%, 30%, 40% and 50% by weight with respect to the EDOT monomer. Chemical characterisations of the structures were analysed using NMR and FTIR. PEDOT/PSS dispersions were also analysed using dynamic light scattering (DLS), capillary electrophoresis (CE), scanning electron microscopy (SEM), and conductivity measurements using the four point probe method. The results showed that the end-capping PEDOT was successfully employed using 2TMM monomer. The higher ratio of end-capping agent resulted in smaller PEDOT as indicated by CE and DLS results. Films surface were smoother with an increase in the ratio of end-capping monomer. While the conductivities of the films decreased with an increase in the ratio of 2TMM monomer.

1. Introduction
End-capping of conducting polymers is a possible method for the direct control of the molecular weight, and possibly conductivity of these polymers. This method involves the copolymerisation of the conductive monomer units with small amounts of end-capping monomer. By end-capping, the site for further growth of polymerisation is blocked by pendant functionality. The size of polymer can be controlled directly by varying the ratio of monomer and capping unit [1]. The polymerisation is a function of controlling time of reaction [2], or controlling the feed ratio of the initiator to monomers [3, 4]. Our previous report has described the effect of time reaction and PSS ratio to the particle size, processability of dispersion, and the conductivity of the PEDOT/PSS films [5-8].

So far, only a few research has been done in modification of poly(3,4-ethylenedioxythiophene) or PEDOT structure by end-capping with other monomers. For example TDA Research, Inc. has synthesised block copolymers with alternating conducting and non-conducting blocks [9]. The end-capped PEDOT oligomers were synthesised by oxidative copolymerisation of end-capping monomers and EDOT monomers (US patent application No. US2003/0088032 A1) using Fe(III) p-TSA as the
oxidation agent and in acetonitrile solvent. The statistical average oligomer length was set theoretically by the stoichiometry of EDOT and end-capping monomers. The conducting segments provide the electronic properties, while the non-conducting segments are designed to promote dispersion. These blocks consist of PEDOT in the center and two end-capped units. The products of end-capped PEDOT oligomers are called Aedotron™ and Oligotron™. These PEDOT oligomers can theoretically be printed using a lithographic technique by crosslinking the oligomers at the methacrylate groups, or formulated them as organic solution into inks form for inkjet printing.

The effort to investigate PEDOT/PSS by modification the structure in order to enhance the properties, such as conductivity and solubility attracts many researchers. Various modifications of PEDOT/PSS for more applications has been done to enhance conductivities and their potential use as electrodes [10]. This study reports the modification of PEDOT by end-capping with 2-thiophene-based monomers via oxidative polymerisation in the presence of PSS using modified method described in our previous studies [5-8]. The general route of end-capping PEDOT with thiophene-based monomers via oxidative polymerisation in the presence of PSS can be seen in figure 1. The end-capping thiophene-based monomer used in this project is 2-thienylmethyl methacrylate (2TMM).

![Figure 1. General route of end-capping PEDOT with 2TMM in the presence of PSS via oxidative polymerisation.](image)

2. Research Method

2.1 Materials
Poly(styrene sulfonate) (PSS, MW = 70 kDa), 3,4-Ethylenedioxythiophene (EDOT), oxidizing agents Na2S2O8 and Fe2(SO4)3 were purchased from Sigma-Aldrich Australia and used as received. PEDOT/PSS Clevios P was purchased from H.C. Starck (Munich, Germany), and referred as to PP-C. 2-thienylmethyl methacrylate (2TMM) was synthesised in house and purified prior to use. All solvents and chemicals were used as of analytical grade.

2.2 End-capping PEDOT with 2TMM via oxidative polymerisation
Synthesis of PEDOT end-capped 2TMM were run using Louwet, et al method [11] as discribed previously [5-8] by additional of various concentrations of end capping agent 2TMM, i.e. 10%, 20%, 30%, 40% and 50% by weight to EDOT monomer. Detailed description of procedure synthesis of 2-thienylmethyl methacrylate monomer will be reported elsewhere. The products of PEDOT/PSS end-capped 2TMM aqueous dispersions are referred to as according their concentrations. For example, the product of PEDOT/PSS using end-capping unit 2TMM 10% is referred to as PP-TMM10.
2.3 Characterisations
PEDOT/PSS end-capped thiophene-based monomer 2TMM aqueous dispersions were characterized using dynamic light scattering (DLS), zeta potential, capillary electrophoresis, UV spectrometer analysis, scanning electron microscopy (SEM), and conductivity measurements using the four point probe method as previously discribed [5-8]. Structures were analysed using NMR and FTIR. $^1$H NMR and $^{13}$C NMR were measured in deuterated water (D$_2$O) for PEDOT/PSS dispersions on a Bruker Biospin Ascend TM 400 Spectrometer. FTIR spectra were recorded as neat samples on a Perkin Elmer Spectra Two ATR FTIR.

3. Results and Discussion

3.1 Characterisation of end-capped PEDOT/PSS aqueous dispersions
Product of PP-TMM aqueous dispersions are dark blue dispersions. The presence of excess PSS in the PP-TMM dispersions made it difficult to use IR and NMR spectroscopic techniques to characterise the endcapped PEDOT. In order to confirm successful endcapping with 2TMM by spectroscopic techniques, it was necessary to eliminate interfering PSS, thus, 2TMM-endcapped PEDOT without PSS (from hereon referred to as PnoP-TMM) was synthesised by conducting the reaction in dichloromethane.

The evidence of successfully synthesised end-capped PEDOT-TMM was characterised using FTIR spectra of the pure product in absence of PSS (PnoP-TMM). Figure 2 shows the FTIR spectra of PnoP-TMM, EDOT and 2TMM. The FTIR spectrum of PP-TMM (with PSS) is not presented here as only the peaks attributable to PSS were observed and it did not give information on the presence of PEDOT and 2TMM in the system. Despite the difficulty encountered to get a clear FTIR spectrum of PnoP-TMM, some peaks are able to be identified as representation of the functional groups of PEDOT end-capped 2TMM. The IR band at 895 cm$^{-1}$ due to the C=O bending of EDOT dissappeared in PnoP-TMM demonstrating successful formation PEDOT chains with C$_2$-C$_2$-coupling.[12, 13] The band at 1475 and 1359 cm$^{-1}$ are attributed to the stretching modes of C=C and C-C in the thiophene ring, whereas bands at 1205 and 1058 cm$^{-1}$ are due to the stretching mode of ethylenedioxy group or C-O-C bond stretching, respectively.[12, 13] The vibration at 1438 cm$^{-1}$ is attributed to –CH$_3$ from the end-capping unit, while broad band at 1155 cm$^{-1}$ is attributed to –C-O-C- ester group stretching vibrations from 2TMM, respectively.[14] Peaks at 857 cm$^{-1}$ is assigned to -C-S bond stretching in the thiophene ring.[15-17] Functional groups from the end-capping agent 2TMM especially C=O and C=C stretching are represented as small broad peaks at 1700-1650 cm$^{-1}$.

The $^1$H, $^{13}$C DEPTQ, and HSQC NMR spectra of PP-TMM in D$_2$O can be seen in figure 3 with peak assignments corresponding to the given labelled structures. These peak assignments have also been compared and deduced from the peaks observed for the monomers. The $^1$H NMR spectrum of PP-TMM (figure 3 A) shows clearly the peaks due to the aromatic hydrogens of PSS at 7.4 - 7.7 ppm (peak 5) and 6.5 - 6.7 ppm (peak 4). The peaks at 1.3 – 1.7 ppm (peaks 1 and 2) correspond to the –CH$_3$- and –CH-backbone peaks of PSS, respectively. While the PSS peaks have been very prominent, other peaks that can be attributed to the thiophene moieties have also been observed. The peak at 3.6 ppm (peak 7) has been assigned to –CH$_2$O- of PEDOT while the peaks at 1.3 ppm (peak g), and 4.3 ppm (peak e) have been attributed to the –CH$_3$, and –CH$_2$- of the endcapping unit 2TMM, respectively.
Figure 2. FTIR spectra of PnOP-TMM, EDOT and TMM monomers.

Figure 3 NMR spectra of PP-TMM50 in D$_2$O solution: (A) $^1$H NMR; (B) and $^{13}$C DEPTQ.

A distortionless enhancement by polarization transfer including the detection of the quaternary nuclei (DEPTQ-135) $^{13}$C NMR spectrum of PP-TMM is also given in figure 3 (B). One of the advantages of a $^{13}$C DEPTQ-135 is that the spectrum can show quaternary carbons present in 180 degrees out of phase, as with -CH$_2$-, with respect to -CH- and -CH$_3$ carbons.[18, 19] Thus, the peaks at 40 ppm, 125 ppm and 127 ppm have been assigned to –CH- peaks 2, 5 and 4, respectively, whilst 42 ppm has been assigned to –CH$_2$ peak 1. The peaks at 140 ppm and 149 ppm can only be quaternary and have been assigned as peaks 6 and 3, respectively. Most peaks corresponding to PEDOT and 2TMM end groups have not been visible as they overlap and are lost within the more prominent PSS peaks. However, peaks...
observed at 20 ppm and two peaks at 63 and 58 ppm could very well correspond to –CH₃ of 2TMM (g), –CH₂- of 2TMM (e) and –OCH₂- of PEDOT (7), respectively.

The effect of the concentration of end-capping monomer to the length of PEDOT and their doping to PSS in PP-TMM aqueous dispersions can be seen from the CE electropherograms (see figure 4), were studied by CE. The representative PP-TMM complexes (A and B) have longer migration time or higher electrophoretic mobility than the PEDOT/PSS complex in PP-C (C). The higher concentration of end-capping agent (A) could be resulted in smaller PEDOT-TMM segment doped to PSS, and the complex is manifested as a broad peak in the electropherogram. Decreasing the concentration of 2TMM to 20% (B) resulted in bigger PEDOT-TMM segment doped to PSS, and the complex is shown as spikes in the electropherogram.

![Electropherograms](image)

**Figure 4.** CE analysis of PP-TMM aqueous dispersions: (A) PP-TMM50; (B) PP-TMM20; and (C) PP-C, (BGE: sodium borate buffer 20 mM, pH 9.2); SEM images of surface morphology e taken at magnification 12000x; and conductivity of the corresponding films.

The representative surface morphology images of PP-TMM films show that they are not uniform, wavy, and rougher at 12000 times magnification than that obtained from PP-C film (C). The surface of the PP-TMM20 films is rougher than that obtained from the PP-TMM50 film, and seem to be similar to the film without end-capping, as can be seen in previous report.[5] The morphology images also exhibit some white patches on the surface as can be seen in the commercial and other films presumably due to aggregation of PSS,[20] which occurred during drying of PP-TMM films. The average conductivity of PP-TMM films has been found to decrease with increasing concentration of 2TMM. Conductivity of PP-TMM20 film (1.5 ± 0.5 $10^{-1}$ cm$^{-1}$) was obtained higher and suggests that longer PEDOT chains than that obtained from PP-TMM50 film (0.8 ± 0.1 $10^{-1}$ cm$^{-1}$) as those comparable to the size PEDOT and PEDOT/PSS complexes.

### 3.2 Particles size distributions and zeta potential of PP-TMM dispersions

PP-TMM aqueous dispersions were analysed using DLS to study the particle size and aggregation of particles. Table 1 shows data of particle size distribution from triplicate measurements of representative dispersions. The results indicate that the particles predominantly exist in aggregate form which tends to become larger with increasing analysis time. Aggregation of the particles may occur as part of the doping state of PEDOT in excess of PSS. In general, the size of cluster aggregates decrease with increasing concentration of 2TMM. Zeta potential distributions of PP-TMM dispersions do not
differ significantly, all zeta potential values are >-40 mV indicating the dispersions are stable.[21-23] These zeta potential values are lower than that of PP-C dispersion (-57 mV) showing that the commercial PEDOT/PSS is a more stable dispersion.

Table 1. Average* particle size distributions and zeta-potential of PP-TMM aqueous dispersions synthesised at various concentrations of end-capping monomer compare PP-C dispersion.

| Sample   | Peak 1, nm | Peak 2, nm | Peak 3, nm | Zeta potential** (mV) |
|----------|------------|------------|------------|-----------------------|
| PP-TMM20 | 187 ± 52   | 31 ± 2     | -          | -45                   |
| PP-TMM50 | 184 ± 42   | 73         | 41         | -47                   |
| PP-C     | 223 ± 4    | 22 ± 1     | -          | -57                   |

*From 3 measurements
**Values taken from 3rd measurement after dispersion has settled and equilibrated.

3.3 UV spectra of PP-TMM films
UV analysis of PP-TMM films (80-100 nm thick) have been recorded on quartz substrates compare to PSS and PP-C films by UV spectrometer and are shown in figure 5. All spectra exhibit peak of absorbance at ~230 nm due to the phenyl groups of PSS, which decreased in the presence of PEDOT.[24-28] This spectra show as consistent as our previous resport.[6] Spectra of those films show an increase of absorbance at 240-280 nm from PSS to PP-C and to PP-TMM films. These increasing peaks absorbance could be attributed to an increase the amount of PEDOT particles doped to PSS as also shown in the previous chapters. These spectra can be attributed as higher doping PEDOT to PSS in PP-TMM films than PP-C film. Previous study reported that presence of oligomer PEDOT in the films increased appearance of peak at 260 nm which corresponds to =C-H of EDOT.[28]

Figure 5. UV spectrum of PSS, PP-C and PP-TMM films (80-100 nm thick)

4. Conclusion
Overall, 2TMM has been successful to end-capped PEDOT via oxidative polymerisation as evident from spectroscopic analyses (UV, FTIR and NMR). PP-TMM aqueous dispersions can generate conductive films one to two order magnitudes higher than the commercial dispersion PP-C. Different ratios of 2TMM affected to the size of PEDOT particles. The higher ratio of 2TMM resulted in smaller size aggregation of PP-TMM and higher the stability as demonstrated by DLS and zeta potential, and decrease their film conductivities.
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References
[1] Osaka I and McCullough R D 2008 Accounts of Chemical Research 41 1202-1214
[2] Kline R J, McGehee M D, Kadnikova E N, Liu J and Fréchet J M J 2003 Advanced Materials 15 1519-1522
[3] Miyakoshi R, Yokoyama A and Yokozawa T 2008 Journal of Polymer Science Part A: Polymer Chemistry 46 753-765
[4] Vallat P, Lamps J P, Schosseler F, Rawiso M and Catala J M 2007 Macromolecules 40 2600-2602
[5] Diah A W M, Quirino J P, Belcher W, and Holdsworth C I 2014 Electrophoresis, 35 1976-1983
[6] Diah A W M, Holdsworth C I, Holdsworth J L, Belcher W, and Quirino J P 2012 Journal of Chromatography A, 1267 246-251
[7] Diah A W M, Holdsworth C I, Nur D and Beh E 2016 Current Analytical Chemistry 12 124-140
[8] Diah A W M, Quirino J P, Belcher W and Holdsworth C I 2016 Macromolecular Chemistry and Physics 217 1907-1916
[9] Elliott B, and Ellis W W 2004 IChE Fall Meeting, November, 7-11
[10] Na S I, Wang G, Kim S S, Kim T, Oh S H and Yu B K 2009 Journal of Materials Chemistry 19 9045-9053
[11] Louwet F, Groenendaal L, Dhaen J, Manca J, Van Luppen J and Verdonck E 2003 Synthetic Metals 135-136 115-117
[12] Zhan L, Song Z, Zhang J, Tang J, Zhan H and Zhou Y 2008 Electrochimica Acta 53 8319-8323
[13] Selvaganesh S V, Mathiyarasu J, Phani KLN and Yegnaraman V 2007 Nanoscale Research Letters 2 546-549
[14] Çirpan A, Alkan S, Toppare L, Hepuzer Y, and Yaşıcı Y 2002 Journal of Polymer Science Part A: Polymer Chemistry 40 4131-4140
[15] Nagarajan S, Kumar J, Bruno F F, Samuelson L A, and Nagarajan R 2008 Macromolecules, 41 3049-3052
[16] Yang Y, Jiang Y, Xu J, and Yu J 2007 Polymer 48 4459-4465
[17] Tintula K K P, Sridhar S, and Shukla P A K 2010 Bulletin of Materials Science 33 157-163
[18] Wang B, Shen F, Lu P, Tang S, Zhang W and Pan S 2008 Journal of Polymer Science Part A: Polymer Chemistry 46 3120-3127
[19] Fei T, Cheng G, Hu D, Lu P and Ma Y 2009 Journal of Polymer Science Part A: Polymer Chemistry 47 4784-4792
[20] Xia Y and Ouyang J 2011 Journal of Materials Chemistry 21 4927-4936
[21] Mohanraj V J and Chen Y 2006 Tropical Journal of Pharmaceutical Research 5 561 - 573
[22] Chang C R L, Tsing-Tshih Tsung, Hong-Ming Lin, Chung-Kwei Lin, Chih-Hung Lo and Hung-Ting Su 2004 Materials Transactions 45 1375 - 1378
[23] Saraiva A M, Cardoso I, Saraiva M J, Tauer K, Pereira M C, Coelho M A N 2010 Macromolecular Bioscience 10 1152-1163
[24] Smith R R, Smith A P, Stricker J T, Taylor B E and Durstock M F 2006 Macromolecules 39 6071-6074
[25] Wakizaka D, Fushimi T, Ohkita H, and Ito S 2004 Polymer, 45 8561-8565
[26] Vaccia P, Petrocino M, Miscioscia R, Nenna G, Minarini C and Della Sala D 2008 Thin Solid Films, 516 4232-4237
[27] Memarzadeh R, Javadpour S, Panahi F, Yoon-Bho Shim 2012 IMCS 2012 - The 14th International Meeting on Chemical Sensors 1105 - 1108
[28] Wang J, Cai G, Zhu X and Zhou X 2012 Journal of Applied Polymer Science 124 109-115