

**One-pot synthesis of grafted brush copolymers via a chain-growth radical/oxidative dual polymerization system**

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Complete List of Authors:	Patakamuri, Govindaiah; Yonsei University, Chemical and Biomolecular Engineering Kim, Yong Seok; Yonsei University, Chemical and Biomolecular Engineering Hong, Jae Keun; Yonsei University, Chemical and Biomolecular Engineering Cheong, In Woo; Kyungpook National University, Department of Applied Chemistry Kim, Jung Hyun; Yonsei University, Chemical and Biomolecular Engineering
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1 **One-pot synthesis of grafted brush copolymers via a chain-growth**
2 **radical/oxidative dual polymerization system**

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4 Patakamuri Govindaiah,^{a‡} Yong Seok Kim,^{a,c‡} Jae Keun Hong,^a Jung Hyun Kim,^{a*} and In Woo
5 Cheong^{b*}

6 *^aDepartment of Chemical and Biomolecular Engineering, Yonsei University, Yonsei University, 50*
7 *Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea*

8 *^bDepartment of Applied Chemistry, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu*
9 *702-701, Republic of Korea*

10 *^cDepartment of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-*
11 *2136, USA*

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13
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19 *Corresponding authors:

20 Professor Jung Hyun Kim, Tel.: +82-2-2123-7633. Fax: +82-2-312-0305.

21 E-mail: jayhkim@yonsei.ac.kr

22 Associate Professor In Woo Cheong, Tel.: +82-53-950-7590. Fax: +82-53-950-6594.

23 E-mail: inwoo@knu.ac.kr

24 ‡These authors contributed equally to this work.

25

26 **ABSTRACT**

27 This article describes the facile synthesis of grafted brush copolymers via
28 combination of metal-catalyzed chain-growth radical polymerization and oxidative
29 polymerization, using a dual functional monomer. The most significant finding was the
30 possibility to perform free-radical polymerization and oxidative polymerization in a single
31 step, using copper bromide as a recyclable catalyst. Cu^+ initiated the radical polymerization
32 via a chain growth mechanism, and Cu^{2+} initiated the oxidative polymerization, leading to
33 grafted brush copolymers in which π -conjugated polymers formed the main chains and
34 poly(styrene sulfonate) (PSS) formed the high-density brushes. Nuclear-magnetic-resonance
35 and Fourier-transform-infrared spectroscopic analyses revealed the formations of
36 poly(thiophene)-*co*-poly(styrene sulfonate) (PTh-*co*-PSS) and poly(3,4-
37 ethylenedioxythiophene)-*co*-polystyrene sulfonate (PEDOT-*co*-PSS). Ultraviolet and
38 photoluminescence analyses confirmed the formation of the π -conjugated polymers during
39 the dual polymerization process. These grafted brush copolymers had exceptionally good
40 solubilities in *N,N*-dimethylformamide.

41

42 Keywords: Dual initiation, block copolymer, polythiophene, chain-growth, oxidative
43 polymerization

44

45 INTRODUCTION

46 π -Conjugated polymer materials have potential applications in electrically
47 conducting,¹ field-effect transistors,² light-emitting diodes,³ and polymer solar cells^{4,5} due to
48 their excellent optical and electrical properties. However, the poor solubilities of
49 unsubstituted π -conjugated polymers in common solvents often limit both their
50 processabilities and potential uses in practical applications. A variety of alkyl-substituted and
51 dendritic-type π -conjugated polymers have been synthesized for better solubility and
52 processability.^{6,7} Several attempts have also been focused on synthesizing copolymers with
53 conjugated moieties.⁸⁻¹⁰ In most of these attempts, a vinyl-polymer backbone with a
54 thiophene side chain was prepared via a free-radical polymerization, and then the thiophene
55 from the backbone was polymerized via oxidative polymerization. However, this type of
56 copolymer shows poor fluorescent ability due to the stacking of the brushed polythiophene
57 side chains. To overcome conjugated stacking, we focused on synthesizing block copolymer
58 with polythiophene forming the main backbone and polar vinyl polymer forming the side
59 chains.

60 Block copolymers are a fascinating class of materials that combine two or more
61 chemically different polymer chains via covalent bonding.¹¹ The mechanical, thermal, optical,
62 and solubility behaviors of block copolymers can be controlled by the careful selection of
63 each segment and their compositions.¹²⁻¹⁶ Graft copolymers are composed of a main polymer
64 chain chemically (through covalent bonds) connected to one or more side chains. Various
65 graft copolymers were developed for diverse of applications like blending of immiscible
66 materials and dispersion of nano- and micro-fillers for enhanced mechanical strength and
67 thermal stability.¹⁷⁻²² Well-defined graft copolymers can be prepared by controlled
68 polymerization.^{17, 18, 23-25} Controlled radical polymerization is a widely used technique for the
69 synthesis of block copolymers that utilizes the sequential addition of one monomer, followed

70 by chain extension with a different monomer.²⁶ It is now possible to extend the range of
71 monomers incorporated into a block copolymer by combining dual initiation polymerization
72 systems. In recent years, various dual initiation polymerization systems have been developed
73 for the preparation of block copolymers.²⁷ The combination of two or more different
74 polymerizations from anionic, cationic, radical, condensation, and/or ring-opening reactions
75 has been discussed to synthesize block copolymers by using dual or heterofunctional
76 initiators.²⁷ However, to our knowledge, there have been few reports on the synthesis of
77 diblock conjugated copolymers²⁸⁻³¹ via sequential addition in multiple steps, and the
78 preparation of diblock conjugated copolymers via a dual polymerization process in a single
79 step has not been reported. Moreover one-pot synthesis can be a facile process saving time
80 and resources by avoiding a lengthy separation process and purification of the intermediates.

81 Typically, incompatible chain and step-growth radical polymerizations are
82 simultaneously performed using a metal-catalyzed dual polymerization process.³² In our
83 previous work, we developed a dual polymerization system to simultaneously initiate both
84 the radical and oxidative polymerizations by using FeCl₃/H₂O₂ as a recyclable catalyst.³³⁻³⁶ In
85 this recyclable catalyst system, Fe³⁺ ions initiated the thiophene polymerization, and
86 generated •OH radicals simultaneously initiated the vinyl polymerization to prepare
87 polythiophene/polystyrene core/shell particles in a one-step process. This recyclable dual
88 polymerization process not only reduced the consumption of catalyst/initiator but also
89 minimized the reaction steps. Previous researchers have determined that Cu²⁺ and Fe³⁺ ions
90 are effective oxidants for the chemical polymerization of thiophene derivatives.³⁷⁻³⁹ Further,
91 our current study focused on the combination of an oxidative/chain-growth radical
92 polymerization system using Cu⁺/Cu²⁺ as a recyclable catalyst.

93 In this paper, we describe a facile preparation of grafted brush copolymers with main
94 backbones composed of π -conjugated polymer and brushes composed of vinyl polymers,

95 employing a one-pot reaction that combined chain-growth radical and oxidative
96 polymerization protocols. Herein, we report a facile route to synthesize grafted copolymers
97 with a combination of π -conjugated and vinyl moieties. We also demonstrate the solubility,
98 thermal, optical, and morphological behaviors of the synthesized grafted brush copolymers.

99

100 **MATERIALS AND METHODS**

101 *Materials*

102 Triethylamine (TEA), 3-thiophene ethanol (ThOH), α -bromoisobutyryl bromide
103 (BIBB), hydroxymethyl-3,4-ethylenedioxythiophene (EDOTOH), N,N,N',N'',N'' -
104 pentamethyldiethylenetriamine (PMDETA), copper (I) bromide (CuBr), sodium 4-
105 vinylbenzenesulfonate (NaSS), and dichloromethane were purchased from Sigma-Aldrich
106 (St. Louis, MO). N,N -dimethylformamide (DMF) was purchased from Junsei Chemicals
107 (Tokyo, Japan). All reagents were used as received without further purification. Double-
108 distilled and deionized (DDI) water was used throughout the experiments.

109

110 *Synthesis of 3-thiophene and 3-ethylenedioxythiophene ATRP initiators*

111 ThOH (2.0 g, 0.0156 mol) and TEA (1.74 g, 0.0172 mol) were dissolved in 30 mL
112 dichloromethane. The solution was stirred and cooled in an ice bath. BIBB (3.98 g, 0.0173
113 mol) in 5 mL dichloromethane solution was then added dropwise to the cooled solution to
114 prepare the 3-thiophene ATRP initiator. The reaction mixture was stirred for 24 h at room
115 temperature under an N_2 atmosphere. The product solution was washed with saturated NaCl
116 water 3 times and then with DDI water 2 times. Finally, the solution was dried with $MgSO_4$,
117 and the product was concentrated using a rotary evaporator.

118 For the preparation of the 3-ethylenedioxythiophene (EDOT) ATRP initiator,
119 EDOTOH (0.5 g, 0.0029 mol) and TEA (0.345 g, 0.0034 mol) were dissolved in 15 mL

120 dichloromethane, and BIBB (0.804 g, 0.0034 mol) was dissolved in 3 mL dichloromethane.

121 The synthetic procedure was the same as described above.

122 *Synthesis of PTh/PSS and PEDOT/PSS grafted brush copolymers*

123 To a jacketed vessel containing 3-thiophene ATRP initiator (1.5 g, 0.0045 mol), CuBr
124 (0.210 g, 0.00146 mol); PMDETA (0.258 g, 0.00148 mol); and the appropriate amount of
125 NaSS (1.0, 1.5, or 2.0 g), dissolved in 30 mL DMF, were added to initiate the
126 radical/oxidative polymerization. The reaction mixture for PTh/PSS grafted brush copolymer
127 was stirred at 100 °C for 48 h under nitrogen. The mixture changed from a blue to a brown
128 color upon completion of the reaction. Afterwards, the reaction was filtered through a neutral
129 alumina column to remove the copper. Finally, the filtered polymer solution was dialyzed
130 against DDI water for 24 h to remove the common solvent. The same procedure was also
131 applied to synthesize PEDOT/PSS grafted brush copolymer.

132 *Self-assembly of PTh/PSS grafted brush copolymer*

133 PTh/PSS grafted brush copolymers in DMF was transferred into DDI water by
134 dialysis against DDI water for 24h. During dialysis the grafted brush copolymer get self-
135 assembled to form micelles in DDI water. PTh/PSS grafted brush copolymers in DDI water
136 with different concentrations were sonicated for 15 min and the dispersion was then dropped
137 on a carbon coated copper grid. The copper grid was dried overnight at room temperature for
138 TEM analysis.

139 *Characterization*

140 Proton-nuclear-magnetic-resonance (^1H NMR) spectra were recorded on a Bruker
141 400 MHz spectrometer using standard parameters and DMSO- d_6 as the NMR solvent.
142 Fourier-transform-infrared (FTIR) spectra were taken on a Bruker Tensor 27 using KBr
143 pellets. The morphology was analyzed on a transmission electron microscope (TEM, JEM-
144 2010, JEOL, Tokyo, Japan). Ultraviolet–visible (UV-vis) absorption spectra were measured

145 on a UV-vis spectrophotometer (UV-1601PC, Shimadzu, Kyoto, Japan). Photoluminescence
146 (PL) spectra were recorded on a fluorospectrophotometer (RF-5301PC, Shimadzu).
147 Excitation was vertically incident on the front face of the sample, and the reflected emission
148 was recorded at an angle of 90° with respect to the surface normal. The thermal
149 decomposition of copolymers was analyzed by thermogravimetric analysis (TGA, Q50, TA
150 Instruments, New Castle, DE). The samples were heated under an N_2 atmosphere from $30^\circ C$
151 to $800^\circ C$ at a heating rate of $10^\circ C/min$, and the weight loss was recorded. The glass-
152 transition temperature (T_g) was recorded with differential scanning calorimetry (DSC, Q10,
153 TA Instruments). The samples were heated under an N_2 atmosphere from $-20^\circ C$ to $250^\circ C$ at
154 a rate of $10^\circ C/min$ and annealed for 2 min at the end of the cycle to eliminate the prior
155 thermal and solvent history. T_g values were recorded during the second heating cycle.

156

157 RESULTS AND DISCUSSION

158 In this study, a dual polymerization system was adopted to synthesize block
159 copolymers due to its incorporation of both chain-growth radical and oxidative
160 polymerizations in a one-step process. Fig. 1 describes the radical/oxidative dual
161 polymerization process using copper bromide as a recyclable catalyst. The key here involved
162 using a recyclable catalyst that could readily switch between two oxidation states, *i.e.*, Cu^+
163 and Cu^{2+} . As shown in Fig. 1(a), a Cu^+ ion first interacted with an ATRP initiator molecule to
164 activate the organic free radicals and then Cu^+ switched to Cu^{2+} . The free radicals then
165 quickly polymerized vinyl monomers via a chain-growth mechanism,³² while the Cu^{2+} ions
166 initiated oxidative polymerization. The salts of Cu^{2+} ions have been reported as capable
167 oxidants for the chemical polymerization of thiophene derivatives.^{39,40} As described in Fig.
168 1(a), during the oxidative polymerization, Cu^{2+} ions were recycled to Cu^+ ions. This
169 recyclable catalytic system helped to maximize the conversion and minimize the

170 consumption of the catalyst. Fig. 1(b) describes the general mechanism for the preparation of
171 comb-type block copolymers using copper bromide as a catalyst in a chain-growth
172 radical/oxidative dual polymerization system.

173 As shown in Fig. 2, we first synthesized the thiophene derivatives bearing bromide
174 moieties to initiate free-radical polymerization. The 3-thiophene ATRP initiator was capable
175 of initiating two different kinds of polymerizations simultaneously under suitable catalytic
176 conditions. Chain-growth polymerization could be initiated with a bromide moiety;
177 simultaneously, oxidative polymerization could also be initiated at the 1 and 4 positions with
178 a thiophene moiety. NaSS was used as a vinyl monomer for radical polymerization.⁴¹ Dual
179 polymerization was verified at thiophene/NaSS molar feed ratios (1.5/1, 1/1, and 1/1.5) in
180 DMF using CuBr as the recyclable catalyst. The maximum conversion of 60% was achieved
181 at the equimolar feed ratio. The color of the solution changed from blue to brown as the
182 polymerization proceeded. The grafted brush copolymers were all soluble in polar solvents,
183 including DMSO, DMF, and water. In general, π -conjugated polymers have poor solubilities
184 in common solvents due to the π - π interactions between planar polymer backbones. However,
185 the PSS brushes on the PTh backbone effectively improved the copolymer solubilities in
186 polar solvents.

187 **Figure 1**

188 **Figure 2**

189 The chemical structure of 3-thiophene ATRP initiator and that of the resulting block
190 copolymers were confirmed by ¹H NMR analysis. As shown in Fig. 3, the methyl protons
191 adjacent to the bromide were shifted from 1.86 ppm to 1.23 ppm after polymerization, and
192 the aromatic protons adjacent to -SO₃H appeared at 8.00 ppm, confirming the formation of
193 the PSS brushes through the chain-growth mechanism. The intensity of the signal at 7.2 ppm
194 of the PTh moiety decreased, and the signal intensity of the 3-substituted PTh protons at 6.5

195 ppm increased after oxidative polymerization, also confirming the formation of the PTh
196 backbone in the dual polymerization process. This result was further confirmed by FTIR
197 analysis. Fig. 4 shows the FTIR spectrum of the PTh-*co*-PSS copolymer. The stretching
198 bands at around 2920 cm^{-1} and 2850 cm^{-1} were attributed to aliphatic $-\text{C}-\text{H}$ bonds, and the
199 peaks at around 3096 cm^{-1} and 3072 cm^{-1} indicated the vibrations of the aromatic $-\text{C}-\text{H}$
200 protons of the PTh and PSS segments. The characteristic peaks at 1725 cm^{-1} correlated with
201 the $-\text{C}=\text{O}$ stretching bands of the copolymer. The peak at 1076 cm^{-1} was due to the $-\text{C}-\text{O}-\text{C}-$
202 stretching band. The stretching bands from 1650 cm^{-1} to 1435 cm^{-1} originated from $-\text{C}=\text{C}-$.
203 The broad peaks around 3430 cm^{-1} were due to the $-\text{OH}$ group, and the characteristic peaks
204 for the $-\text{SO}_3$ stretching vibrations at 1076 cm^{-1} indicated the formation of the PSS brushes.

205 **Figure 3**

206 **Figure 4**

207 We measured the thermal properties of our synthesized conjugated block copolymers
208 using DSC and TGA, as shown in Figs. 5 and 6. PTh-*co*-PSS and PEDOT-*co*-PSS
209 copolymers showed two endothermic glass transitions, while the PSS homo polymer showed
210 a single broad T_g around 120 $^{\circ}\text{C}$. In the case of block copolymers, the T_g around 50 $^{\circ}\text{C}$
211 corresponded to the PTh/PEDOT segment and the broad T_g around 120 $^{\circ}\text{C}$ corresponded to
212 the brushed PSS segment. These two glass transitions indicated the formation of the block
213 copolymers. The T_g of the PSS block was very broad due to the formation of the brushes. Fig.
214 6 presents a comparison of the weight losses of the pristine PSS, PTh-*co*-PSS, and PEDOT-
215 *co*-PSS copolymers upon heating under an N_2 atmosphere. The TGA analysis of pristine PSS
216 showed a two-step thermal decomposition between 400 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$. However, TGA
217 analysis of the PTh-*co*-PSS and PEDOT-*co*-PSS copolymers showed three-step thermal
218 decompositions between 250 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ (see Table 1). The maximum decomposition at 300
219 $^{\circ}\text{C}$ corresponded to the PTh/PEDOT segment, and the remaining two maximum

220 decompositions around 440 °C and 500 °C could be assigned to the PSS segment of the block
221 copolymer.

222 **Table 1**

223 **Figure 5**

224 **Figure 6**

225 Fig. 7 shows the TEM images of the PTh-*co*-PSS copolymer. Self-assembled
226 morphologies were formed by π - π intermolecular interactions of the hydrophobic π -
227 conjugated polymer backbone and hydrophilic brushes in aqueous solution. Previous
228 researchers have examined the conformational changes of grafted brush copolymers in
229 solvents.^{31,42} In the case of high-density grafted brush copolymers, spherical globule
230 morphology can occur when the polymer backbone is insoluble but the grafted brushes are
231 soluble.³¹ The polymer backbone can then collapse, forming a spherical globule morphology
232 in extremely unfavorable solvents. Water is a poor solvent for polythiophene backbones but a
233 good solvent for PSS brushes. Aqueous solutions apparently promoted aggregation of the
234 strong π - π intermolecular interactions between insoluble polythiophene backbones, but
235 hydrophilic PSS brushes remained in a solution state, ultimately forming aggregated
236 polythiophene cores and soluble PSS brushes shells. As shown in Fig. 7(a), the TEM image
237 indicated the formation of a spherical core-shell morphology at lower polymer concentrations
238 (1 mg/10 mL water) in aqueous solutions. More interestingly, a fiber-like morphology was
239 observed at higher polymer concentrations (10 mg/10 mL Water) in aqueous solutions [Figs.
240 7(b) and 7(c)]. However, the self-assembled morphology of the π -conjugated block
241 copolymers in solution could be controlled by carefully selecting both the solvent type and
242 the concentration.⁴³

243 **Figure 7**

244 The UV-vis absorption spectra of the PTh-*co*-PSS and PEDOT-*co*-PSS copolymers in

245 DMF solution is shown in Fig. 8. As shown in Fig. 8, the absorption bands of the PTh-*co*-PSS
246 and PEDOT-*co*-PSS copolymers occurred around 425 and 510 nm, respectively, and each
247 copolymer demonstrated a single broad absorption band. The absorption bands in visible
248 regions corresponded to the absorption of the PTh main chains. These results confirmed the
249 polymerization of thiophene, which formed the backbones. The fluorescence emission spectra
250 of the PTh-*co*-PSS and PEDOT-*co*-PSS copolymers in DMF solution with excitation
251 wavelength at 425 and 510 nm, respectively, are overlaid in Fig. 9. PTh-*co*-PSS showed an
252 emission peak at around 500 nm, while PEDOT-*co*-PSS showed one at 550 nm.
253 Luminescence quantum yields (ϕ) of the PTh-*co*-PSS and PEDOT-*co*-PSS copolymers in
254 DMF solution were estimated by comparing them with the known quantum yield of quinine
255 sulfate.⁴⁴ The quantum yields of PTh-*co*-PSS and PEDOT-*co*-PSS were estimated to be 12
256 and 6, respectively. Fig. 10 shows photographs of PTh-*co*-PSS in DMF before and after UV
257 irradiation. After UV irradiation, the solution emitted yellow light at 365 nm. UV-vis
258 absorption and PL spectroscopic results indicated that the water-soluble PSS brushes
259 enhanced the luminescence behavior of the polythiophene backbones.

260 **Figure 8**

261 **Figure 9**

262 **Figure 10**

263 **CONCLUSION**

264 We have demonstrated the possibility of combining chain-growth radical and
265 oxidative polymerizations for the synthesis of grafted brush copolymers using a recyclable
266 dual catalyst. PTh-*co*-PSS and PEDOT-*co*-PSS copolymers were synthesized via a dual
267 polymerization process using copper bromide as a recyclable catalyst. The comb type block
268 copolymer formation was confirmed by FTIR, NMR, DSC, and TGA studies. PSS brushes on
269 the polythiophene backbones greatly improved the copolymers' solubilities in polar solvents.

270 TEM results revealed the formation of spherical globules and fiber-like micelles at different
271 polymer concentrations in aqueous solution. UV-vis and PL spectroscopic results indicated
272 that PSS brushes improved the luminescence capability of the polythiophene backbones.
273 Further studies are in progress in order to better correlate the relationships between the
274 structures, morphologies, and optical properties.

275

276

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283

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359

360 **Figure captions:**

361

362 Figure 1. (a) General mechanism of the chain-growth and oxidative polymerization and (b) a
363 schematic representation of the dual polymerization system.

364 Figure 2. A schematic representation of the synthesis of PSS brushed polythiophene via a
365 dual polymerization system.

366 Figure 3. ^1H NMR spectra of PTh-*co*-PSS in DMSO- d_6 .

367 Figure 4. FTIR spectra of the PTh-*co*-PSS grafted brush copolymer.

368 Figure 5. DSC thermograms of the PTh-*co*-PSS and PEDOT-*co*-PSS grafted brush
369 copolymers.

370 Figure 6. TGA thermograms of the PTh-*co*-PSS and PEDOT-*co*-PSS grafted brush
371 copolymers.

372 Figure 7. TEM micrographs of PTh-*co*-PSS in (a) 1 mg/10 mL water and (b and c) 10 mg/10
373 mL water.

374 Figure 8. UV-vis spectra of the PTh-*co*-PSS and PEDOT-*co*-PSS grafted brush copolymers in
375 DMF.

376 Figure 9. Photoluminescence spectra of the PTh-*co*-PSS and PEDOT-*co*-PSS grafted brush
377 copolymers in DMF solution, excited at 420 and 510 nm, respectively.

378 Figure 10. Photographic images of the PTh-*co*-PSS copolymer in DMF solution. (a) Under
379 visible light and (b) under UV irradiation at 365 nm.

380

381

382 Table 1: Thermal analysis data of graft copolymers

Sample	Glass transition temperature (°C)		Thermal decomposition temperature (°C)		
	T _g (1)	T _g (2)	T ₁	T ₂	T ₃
PSS	-	120	-	445	695
PTh- <i>co</i> -PSS	50	120	320	428	695
PEDOT- <i>co</i> -PSS	53	120	300	428	-

383

Figure 1

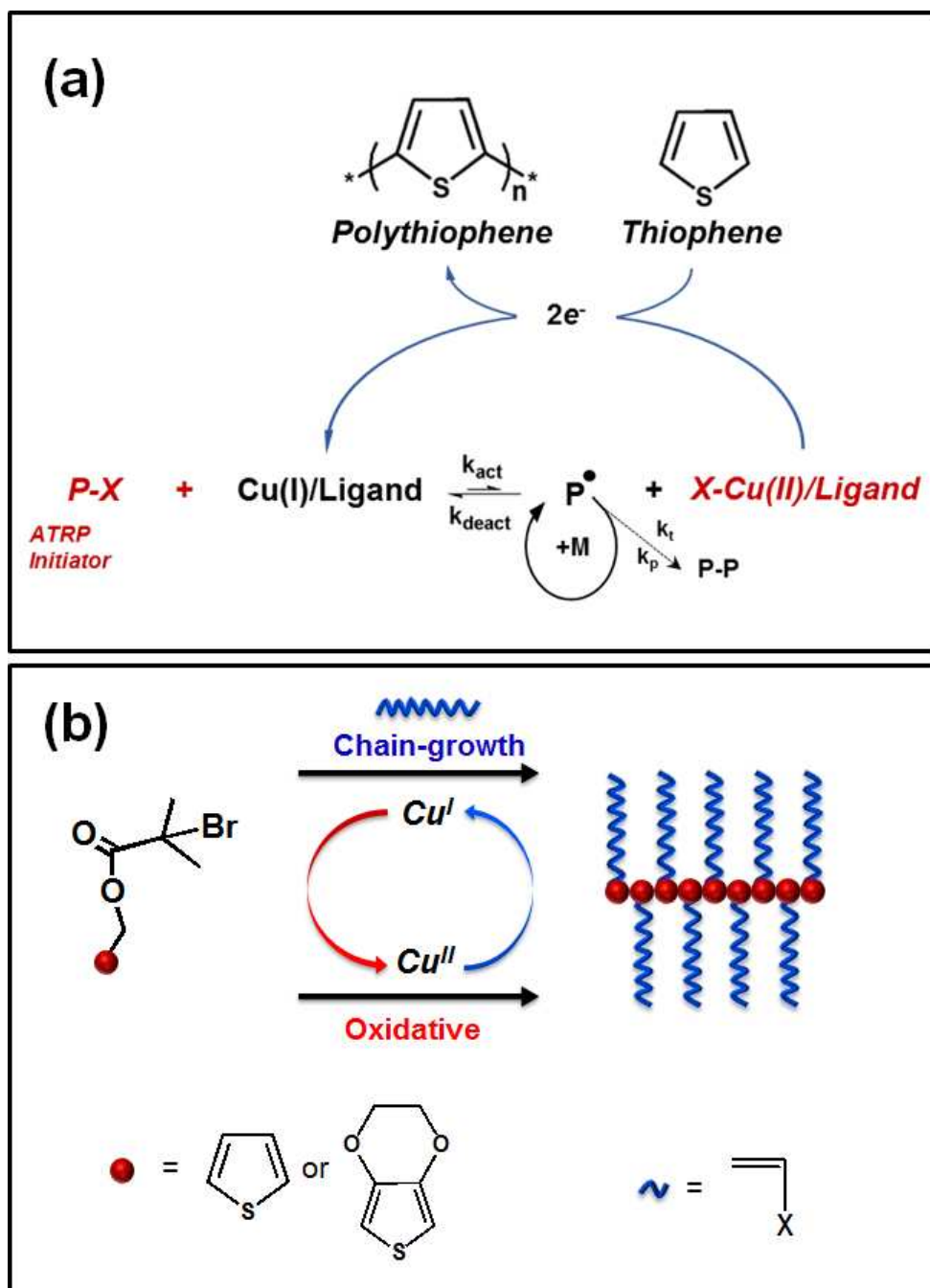


Figure 2

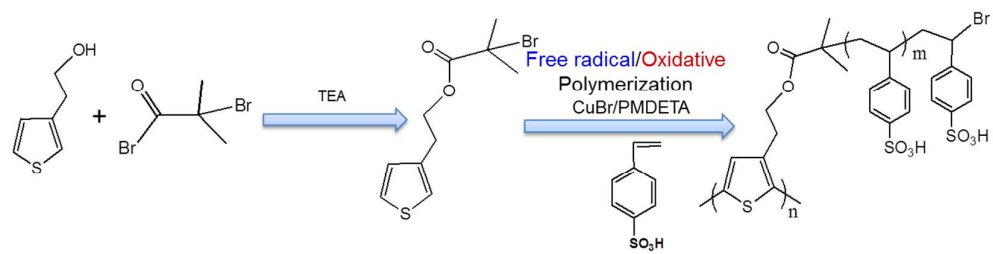


Figure 3

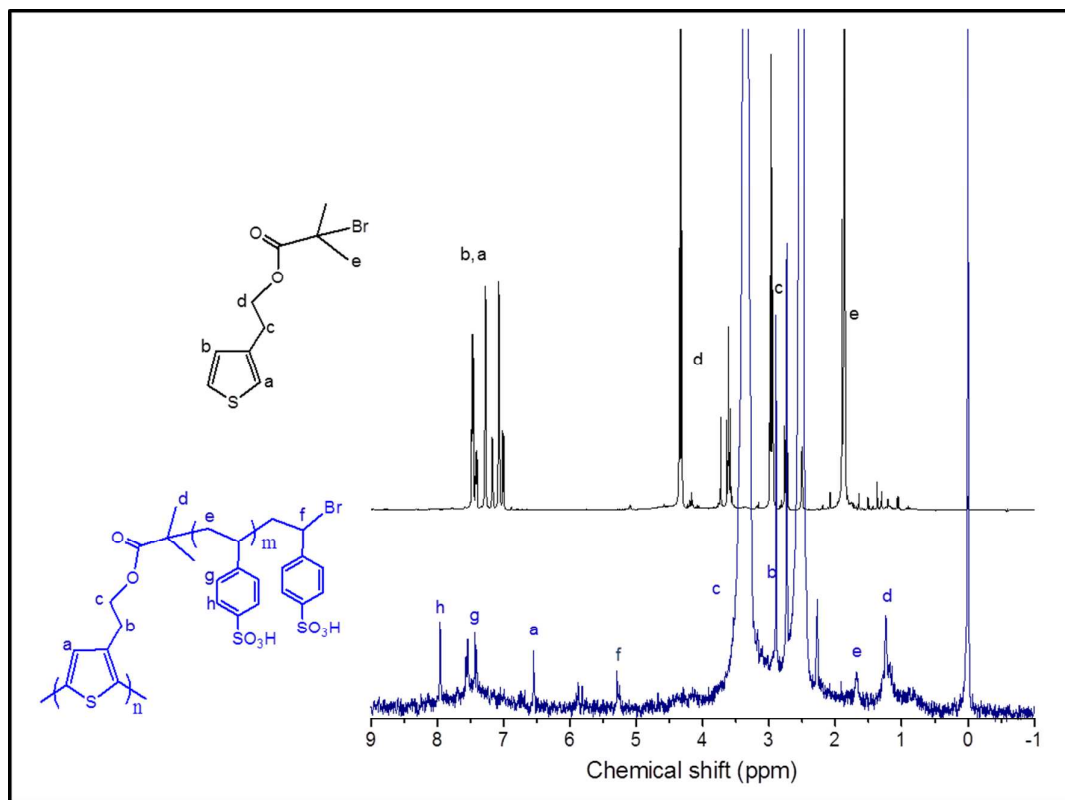


Figure 4

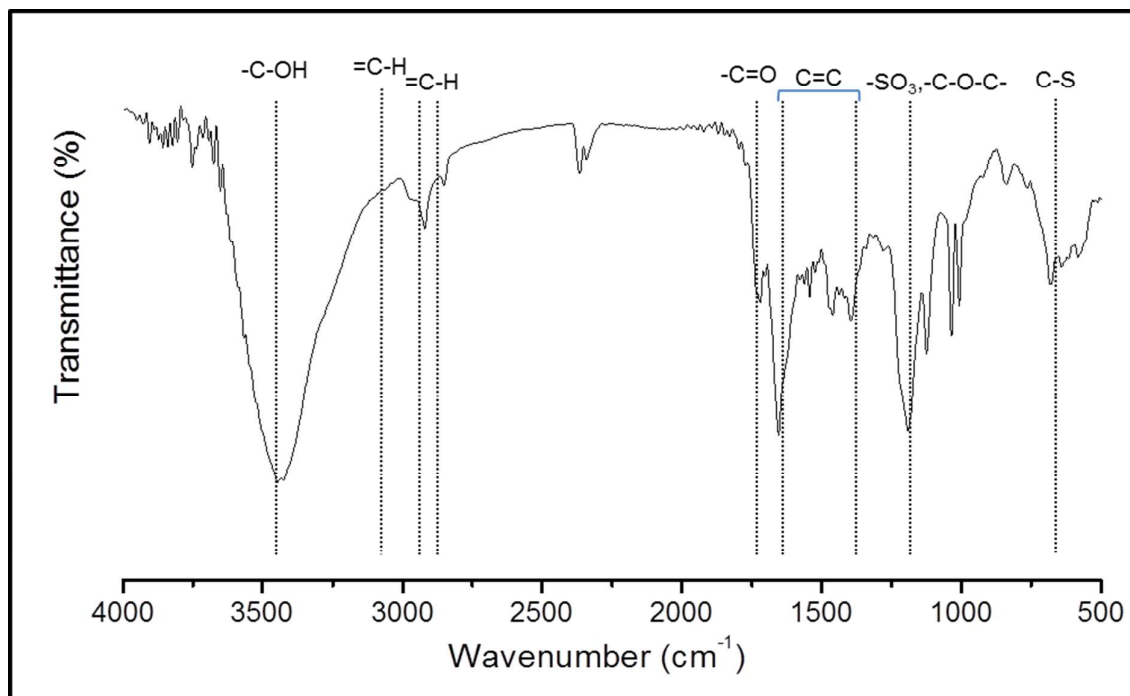


Figure 5

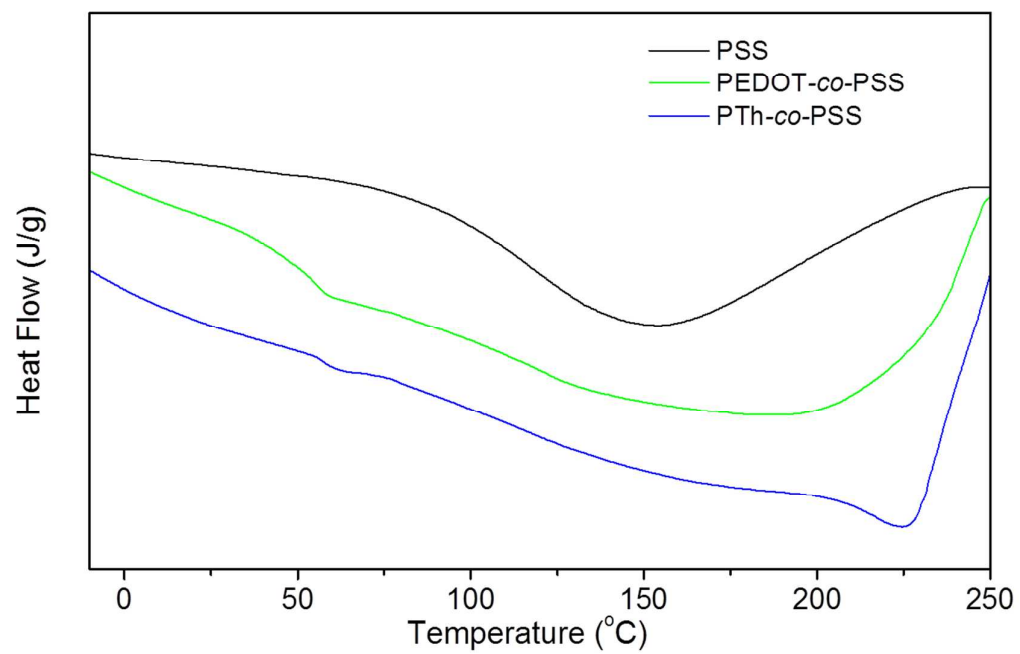


Figure 6

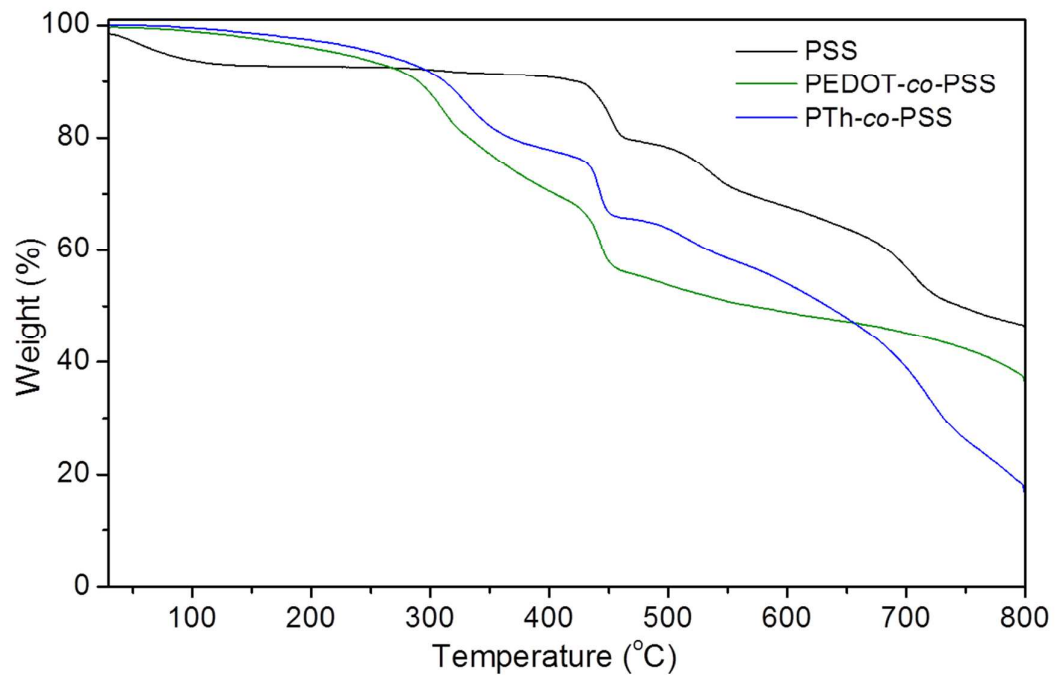


Figure 7

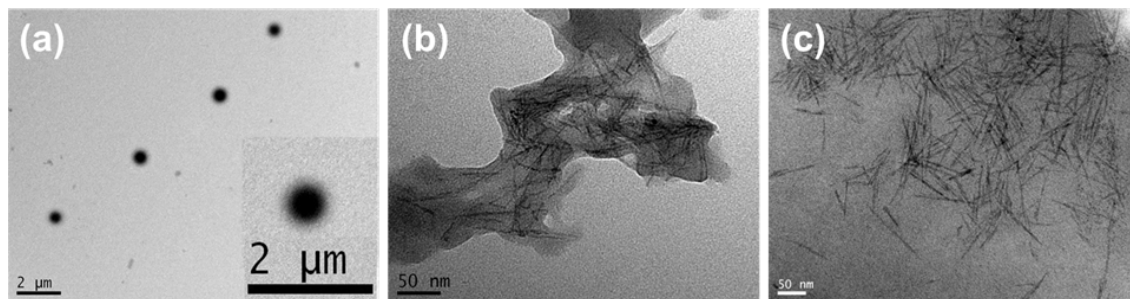


Figure 8

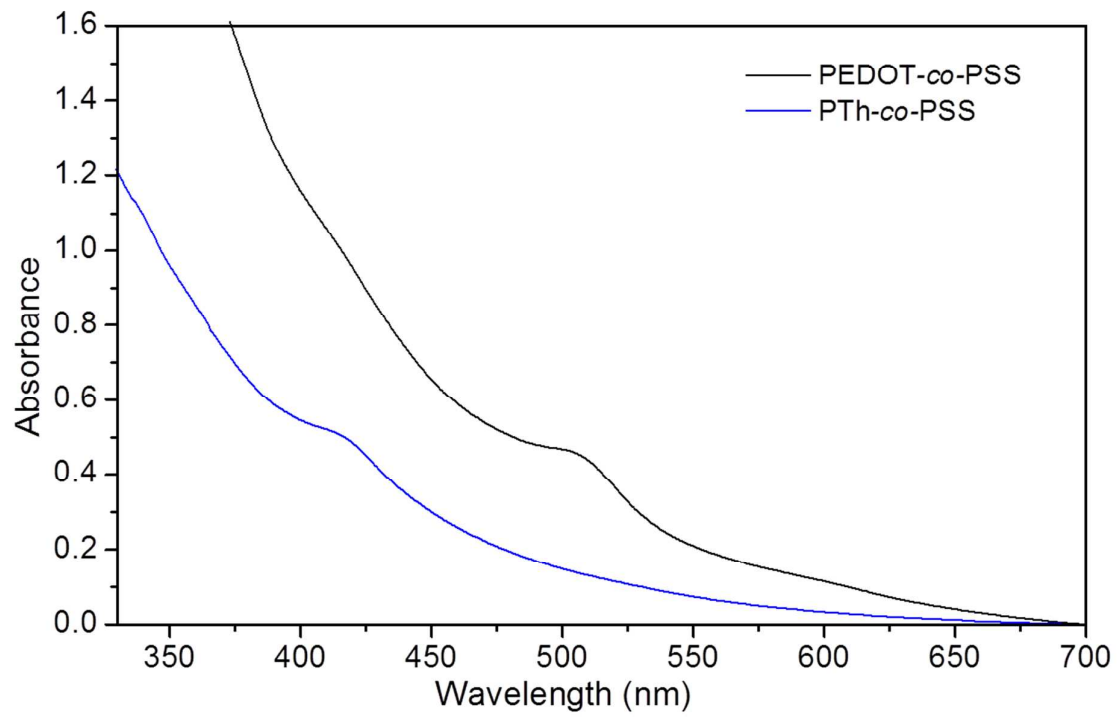


Figure 9

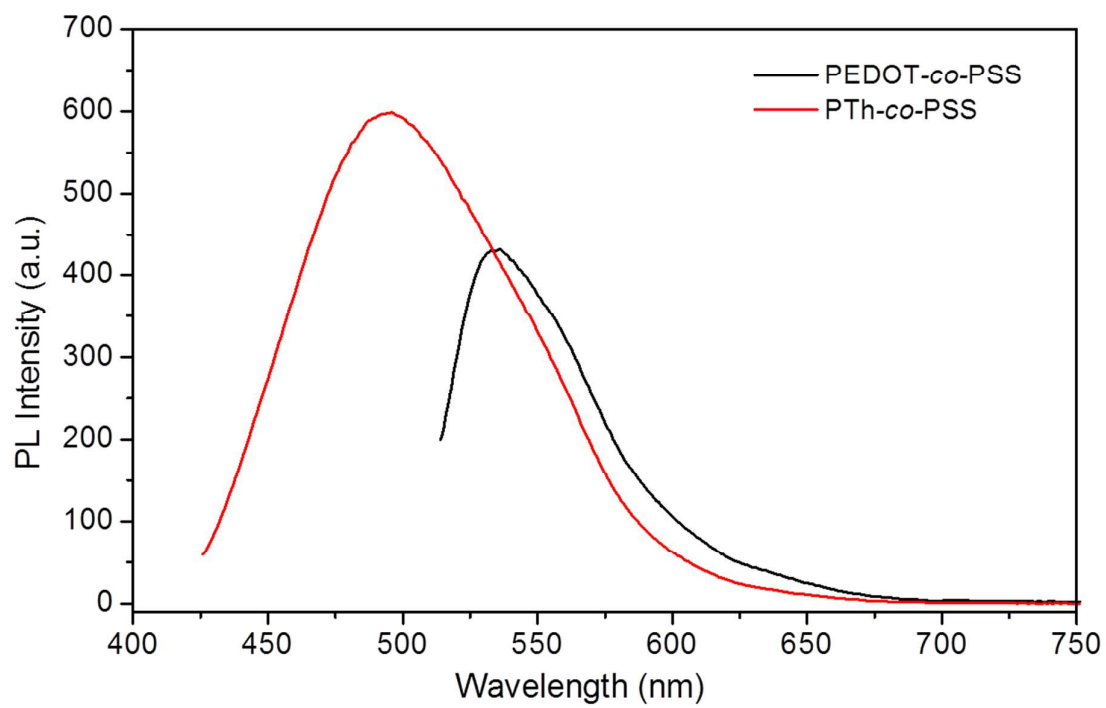


Figure 10

