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Single-Step Preparation of Polythiophene Bearing Branched Chains by Dual Initiation Polymerization

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Abstract: A facile approach for the single-step preparation of branched polythiophenes using a copper(II) catalyst *via* a dual initiation polymerization process is reported. The synthetic route of dual initiation polymerization involves both oxidative polymerization and metal-catalyzed radical polymerization. In this process, two kinds of polymerization can be performed concurrently as a one-pot reaction using a Cu^{2+}/Cu^{+} switchable catalytic system. Differential scanning calorimetry and photoluminescence studies confirmed the formation of the π-conjugated polymer structure. Our results provide new insights on the various grafting of copolymers with polythiophene copolymers and functional branched chains using a single-step process. This process could lead the way for enhanced processability towards novel functionalized π-conjugated polymers

Keywords: dual initiation, graft copolymer, polythiophene.

Introduction

Conjugated polymers have received a great amount of attention during recent decades due to their unique properties such as charge transport and electroluminescence, which originate from their π-conjugated carbon backbones. Such properties of π-conjugated polymer chains are particularly important for applications such as polymer photovoltaic cells,[1-3] chemical biosensors,[4-6] light-emitting cells,[7] field effect transistors,[8] and charge storage devices.[9] Among the conjugated polymers, polythiophene is of particular importance as it displays both thermal and environmental stability, along with high electrical conductivity.[10] However, polythiophene has very poor solubility due to the strong π-stacking interactions between the aromatic rings which compose the main polymer backbone.[11] Thus, polythiophene derivatives bearing side chain functionalization have been widely studied, not only to enhance their processability by improving solubility in water or organic solvents, but also to alter their material characteristics, such as electrical and optical properties. The introduction of various substituents along the conjugated backbone has been reported to affect both the planar and nonplanar structure transitions, and the twisting mechanism of the conjugated backbone.[10]

A number of synthetic routes have been reported for the preparation of polythiophene, including a metal-catalyzed coupling *via* the Grignard reaction of 2,5-dihalogenated thiophene monomers,[12-14] cathodic/anodic electrochemical polymerization,[15,16] and chemical oxidation polymerization.[17-21] However, polythiophenes bearing branched functional side chains tend to be prepared *via* multi-step processes because of differences between the polymerization mechanism for π-conjugated polymer chains and that of branched polymeric structures with functional side chains.

In addition, the preparation of diverse π-conjugated polymers with varied functional substituents has been reported, with these compounds displaying improved solubility and processability.[22,23] There has also been a number of studies focusing on improving the solubility of π-conjugated polymers, and imparting temperature/pH sensitivity to the final polymer products *via* sequential oxidative polymerization and atom transfer radical polymerization (ATRP) processes.[24-29] In this ordered process of oxidative polymerization and ATRP, ATRP provides a relatively straightforward route to controlling the molecular weight of the branched polymer and also allows the incorporation of different monomers to yield a conjugated polymer backbone containing functionalized side chains. However, the majority of the studies into branched π-conjugated polymers involve multi-step procedures because of the different reaction mechanisms involved in each transformation.

In recent years, a number of multi-initiating processes have been developed to combine two or more distinct polymerization steps, including anionic/cationic, radical, condensation, and ring opening polymerizations.[30] However, the preparation of branched conjugated polymers *via* a single step dual polymerization process has not yet been reported.

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We herein report a facile approach for the preparation of branched polythiophene copolymers in a single-step process by dual initiation polymerization. The proposed synthetic route for this process involves both oxidative polymerization and metal-catalyzed radical polymerization. We report the use of Cu^{2+} ions as a dual initiating catalyst for the oxidative polymerization of polythiophene and for radical polymerization of branched polymer chains. This process is expected to allow simultaneous one-pot polymerization steps to be carried out using the same metal catalyst system for all stages. Finally, we demonstrate the thermal and optical properties of π-conjugated polymers bearing different branched chains.

Experimental

Materials. 3-Thiophene ethanol (3-TPEtOH), α-bromoisobutyryl bromide, styrene, methylmethacrylate (MMA), di(ethylene glycol) methyl ether methacrylate (DEGMEMA), *N*-isopropylacrylamide (NIPAM), Cu(II) bromide ($CuBr_2$), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylene-triamine (PMDETA), anhydrous dichloromethane, diethyl ether, and methyl alcohol were purchased from Sigma Aldrich (St. Louis, MO, USA). Triethylamine (TEA), dimethylformamide (DMF), and anhydrous chloroform ($CHCl_3$) were purchased from Junsei Chemicals (Tokyo, Japan). All reagents were used as received without further purification. Distilled deionized (DDI) water was used throughout the experiment.

Synthesis of Dual Functional Initiator 3-[1-ethyl-2-(2-bromoisobutyrate)]thiophene (DFI). 3-TPEtOH (2.6 g, 0.02 mol) and TEA (2.2 g, 0.022 mol), were dissolved in anhydrous dichloromethane (20 mL) under an inert atmosphere at 0 °C with stirring. A solution of α-bromoisobutyryl bromide (5.1 g, 0.022 mol) in dichloromethane (5 mL) was added dropwise to the cooled solution, and the resulting mixture was stirred for a further 24 h at room temperature to give the dual functional initiator (DFI) 3-[1-ethyl-2-(2-bromoisobutyrate)] thiophene for the dual initiation process. The resulting solution was then washed with saturated NaCl aq. solution (3 × mL), and the organic phase dried over anhydrous $MgSO_4$ with vigorous stirring for 24 h. Finally, the organic phase was separated by filtration and concentrated using a rotary evaporator as clear yellow-brown colored liquid. (4.9 g, 64% yield)

Polymerization of Polythiophenes Bearing Branched Chains. $CuBr_2$ (0.2010 g, 0.0009 mol) and PMDETA (1.5597 g, 0.009 mol) were dissolved in anhydrous chloroform ($CHCl_3$) (40 mL) under an inert atmosphere in schlenk flask with a screw valve at 25 °C for 24 h. The desired degassed monomers (styrene, MMA, DEGMEMA, and NIPAM) were then added (see Table I) and the resulting mixture was stirred for 15 min. Finally, the dual functional initiator (DFI) (4.154 g, 0.015 mol) in chloroform (10 mL) was added to the reaction mixture, the flask was tightly sealed, and the mixture heated by means of a thermostatic oil bath at 80 °C for 36 h. When the reaction had reached completion, the polymer mixture solution was precipitated using diethyl ether. The resulting precipitate was filtered, dissolved in dimethylformamide (DMF), and passed through a short neutral alumina column to remove the copper salt. The precipitation procedure was repeated two times and the polymer was dried in a vacuum oven for 24 h. Monomer conversions were calculated by measuring the solid weight in polymerization mixture at each reaction time. The solid weight in polymerization mixture was evaluated by drying the acquired polymerization mixture at each reaction time in vacuum oven at 25 °C for 24 h.

Characterization. ^1H NMR spectra were recorded in $CDCl_3$ using a Bruker 400 MHz spectrometer using standard parameters. Molecular weight and molecular weight distribution (M_w/M_n) were measured in tetrahydrofuran (THF) by using a ACME 9000 gel permeation chromatography (GPC) equipped with a series of Waters columns (HR4, HR3, HR2, HR1), HPLC pump, RI detector and column oven (Younglin instrument, South Korea). FTIR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR Spectrometer. UV-visible absorption spectra were measured using a UV-1601PC UV-Vis spectrophotometer (Shimadzu, Japan). Photoluminescence (PL) spectra were recorded using a fluorospectrophotometer (RF-5301PC, Shimadzu, Japan). The excitation was vertically incident onto the front face of the sample and the reflected emission was recorded at an angle of 90° with respect to the surface normal. The glass transition temperature (T_g) was recorded using a differential scanning calorimeter (DSC, Q10, TA Instrument, USA). The samples were heated under an atmosphere of N_2 from 20-250 °C at a rate of 10 °C/min, and annealed for 2 min at the end of the cycle to eliminate the prior thermal and

Table I. Experimental Conditions for the Preparation of PTh-*g*-PS, PTh-*g*-PMMA, PTh-*g*-(PMMA-*co*-PDEGMEMA), and PTh-*g*-(PMMA-*co*-PNIPAM) Copolymers *via* the Dual Initiation Polymerization Process[a]

Entry	Monomer Ratio					Time (h)	Conversion (%)	M_n	M_w/M_n
	DFI	Styrene	MMA	DEGMEMA	NIPAM				
1	0.015	0.15				24	42	6,900	1.67
2	0.015		0.15			24	56	15,100	2.06
3	0.015		0.075	0.075		24	58	18,600	2.11
4	0.015		0.075		0.075	24	50	14,200	2.09

[a] Temp. =80 °C, carried out in anhydrous chloroform.

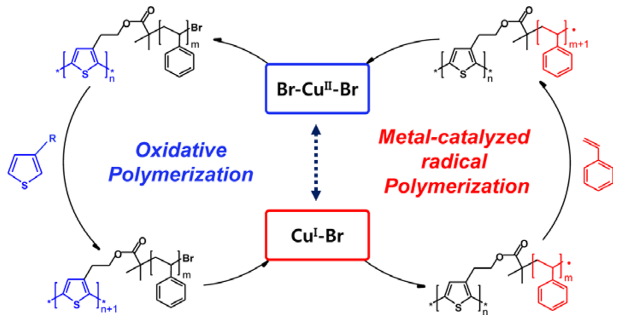
solvent history. The T_g was recorded during the second heating cycle.

Results and Discussion

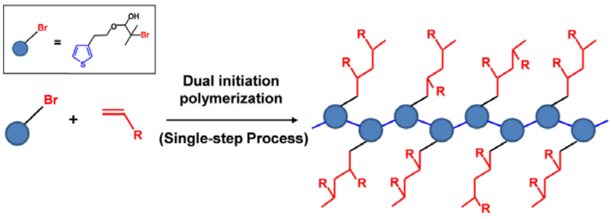
In this study, we adopted the dual initiation polymerization process for the preparation of branched π-conjugated polymers *via* a single-step process. In this process, oxidative polymerization and metal-catalyzed radical polymerization were performed simultaneously using the metal catalyst system shown in Scheme I. Firstly, oxidative polymerization is initiated by the reduction of copper Cu^{2+} ions to Cu^+ ions as described in 'Oxidative polymerization' cycle in Scheme I. It has previously been reported that a range of Cu^{2+} salts can be used as a catalyst for the chemical oxidative polymerization of polythiophene polymers.[31] The initial reductive reaction of copper ions in the dual initiation polymerization is crucial in initiating the metal-catalyzed radical polymerization cycle by generation of monovalent copper ions (Cu^+) which can make active radical sites at the end of the dual functional initiator as described in 'Metal-catalyzed radical polymerization' cycle in Scheme I.

In this dual initiation polymerization, the prepared polymer structure *via* oxidative polymerization could be certainly distinguished from the other polymer structure prepared by chain growth radical polymerization because of differences in monomer selectivity between the two polymerization processes. Oxidative polymerization mainly involves the detachment of two hydrogen atoms from cyclic compounds that have resonance structures with delocalized π-orbitals such as aromatics, thiofurans, and their derivatives. The monomers suitable for use in the oxidative polymerization process are therefore limited to only a few species. In contrast, the unsaturated monomer structures are attached only at the end of the radical chains, and so alkyl-based branched chains can be prepared by metal-catalyzed radical polymerization. Consequently, our one-step dual initiation polymerization process can be utilized in a facile preparation of comb-like graft copolymers as described in Scheme II.

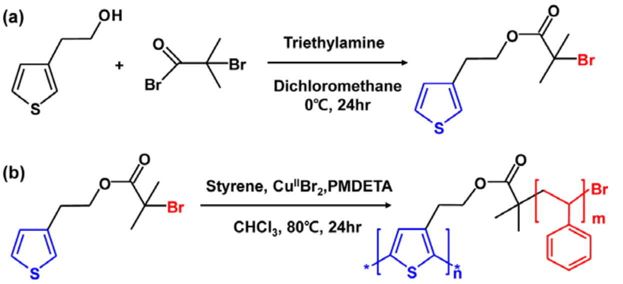
For the one-step synthesis of polythiophene bearing branched chains, the dual-functional initiator was used. This dual-functional initiator possesses two different initiating sites, namely the thiophene moiety for oxidative polymerization, which could be initiated by the reduction of transition metals, and the 2-bromoisobutylate moiety, which could be activated *via* the metal-catalyzed radical polymerization mechanism. Dual functional initiator for dual initiation was synthesized by nucleophilic acyl substitution of 3-thiophene ethanol and α-bromoisobutyryl bromide in dichloromethane as described in Scheme III(a).



Scheme I. Schematic illustration of the dual initiation polymerization process.



Scheme II. Schematic illustration of the synthesis of π-conjugated polymers bearing branched chains *via* the dual initiation polymerization process.



Scheme III. Synthetic route to (a) dual functional initiator by nucleophilic acyl substitution and (b) polystyrene-branched polythiophenes *via* the dual initiation polymerization process.

Branched polythiophene copolymers were prepared in chloroform at 80 °C over 36 h *via* the dual initiation polymerization process. Copper(II) bromide and PMDETA were used for the preparation of redox-active transition metal complexes for the metal-catalyzed radical polymerization process. In addition, the Cu^{2+} ion present in the transition metal complex took part in the oxidative polymerization of thiophene molecules in dual functional initiators in Scheme III(b).

Figure 1 shows the conversion-time profiles of the dual initiation polymerization process to give polythiophene-*grafted*-polystyrene (PTh-*g*-PS) and polythiophene-*grafted*-polymethylmethacrylate (PTh-*g*-PMMA) in $CHCl_3$ at 80 °C using the $CuBr_2$/PMDETA complex as catalyst and M_w/M_n values of PTh-*g*-PS copolymers versus total monomer conversion.

From Figure 1(a), the polymer conversion steadily increased after initiation of polymerization. Therefore, it was confirmed that oxidative polymerization successfully regenerated the Cu^+ ions for the metal-catalyzed radical polymerization step and that metal-catalyzed radical polymerization using the generated Cu^+ ions had indeed taken place. Copper Cu^{2+}, an initial ingredient of reaction mixture, cannot initiate metal-catalyzed radical polymerization by itself. Figure 1(b) shows that the average molecular weight and M_w/M_n value increased as

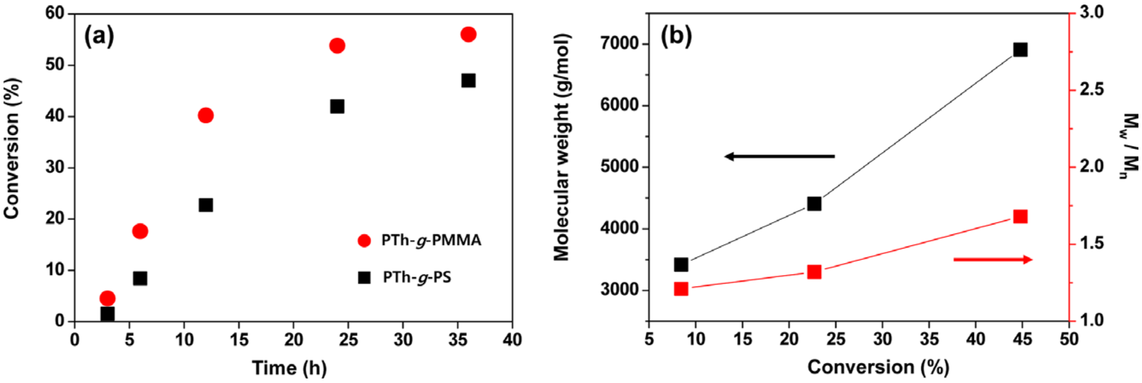


Figure 1. (a) Conversion-time profiles of dual initiation polymerization for the synthesis of PTh-*g*-PS and PTh-*g*-PMMA in $CHCl_3$ at 80 °C using the $CuBr_2$/PMDETA complex as catalyst. (b) Molecular weight (M_w) and M_w/M_n values of PTh-*g*-PS copolymers versus total monomer conversion.

the polymer conversion increased. This is because every grafted polymer chain had grown onto different lengths of polythiophene backbone chain during the dual initiation polymerization process.

The structure of the synthesized dual functional initiator and the resulting polythiophene copolymers bearing branched chains were analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of the synthesized products critically shows the combination of π-conjugated polythiophene units and branched polymers. From Figure 2(a) and (b), the signals at 6.9-7.2 ppm corresponding to the proton peaks from the thiophene ring became broader following polymerization. However, the signals at 7.0, 7.1, 7.3 ppm correspond to the proton peaks from the thiophene ring and the characteristic peaks at 4.4 ppm correspond to the alkyl protons adjacent to the oxygen atom of the dual functional initiator (DFI) as shown in Figure 2(c). The characteristic peaks at 4.4 ppm, corresponding to the alkyl protons adjacent to the thiophene ring, were also found to be broader following polymerization, thus confirming the formation of the desired PTh conjugated polymers. In addition, the presence of signals at 6.2-7.8 ppm corresponding to the aromatic protons of PS, or alternatively, the presence of a signal at 3.6 ppm corresponding to PMMA, indicated the formation of PS or PMMA branched chains, respectively. The peak b at 6.9-7.2 ppm in Figure 2(b) (and Figure S4) was assigned to the proton on the thiophene ring and the peak k at 3.6 ppm represented the three protons on the methyl group of PMMA. The integration area of peaks b and k of each component was 1:55. The values obtained by calculating the molar ratio based on the peak area ratio of each component were 5.3 mol% (13.3 wt%) of polythiophene and 94.7 mol% (86.7 wt%) of PMMA in the PTh-PMMA copolymer. The degree of oxidative polymerization of polythiophene was 7.25, calculated using the molecular weight of the PTh-PMMA copolymer. However, the polythiophene mol% in the PTh-PMMA copolymer was lower than the initially charged 10 mol% thiophene. This implied that the oxidative polymerization was prevented by steric hindrance posed by the growing branched PMMA chain during the dual initiation polymerization process.

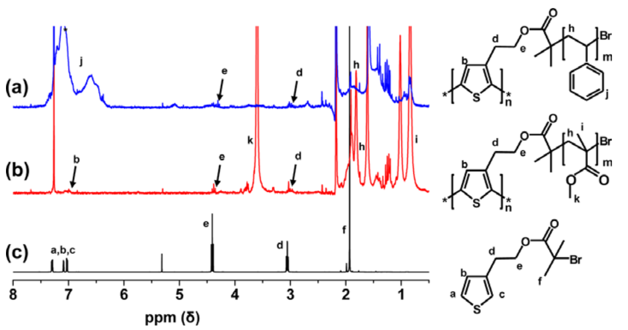


Figure 2. ^{1}H NMR spectra ($CDCl_3$) of (a) PTh-*g*-PS, (b) PTh-*g*-PMMA, and (c) dual functional initiator (DFI) for dual initiation polymerization.

Figure 3 shows the FTIR spectra of (a) PTh-*g*-PS, (b) PTh-*g*-PMMA, (c) polythiophene grafted with (polymethylmethacrylate-*copolymer*-poly di(ethylene glycol) methyl ether methacrylate) (PTh-*g*-(PMMA-*co*-PDEGMEMA)), and (d) polythiophene grafted with (polymethylmethacrylate-*co*-isopropylacrylamide) (PTh-*g*-(PMMA-*co*-PNIPAM)). The characteristic peak at approximately 1702 cm^{-1} correlates with the C=O vibration bands of the thiophene macro- initiator and the copolymers which are branched onto the polythiophene structure. The peak at 690 cm^{-1} corresponds to the C-S vibration mode of the thiophene polymer. In addition, the peaks at approximately 1240 cm^{-1} and 1150 cm^{-1} correspond to the strong stretching vibrations of the -C-O and -C-O-C- protons of the PDEGMEMA segments. The observation of all peaks corresponding to the -C=O, -C-O, and -C-O-C- vibrations therefore confirms the formation of PTh-*g*-(PMMA-*co*-PDEGMEMA) in Figure 3(c). Finally, the broad peaks observed at approximately 3300-3500 cm^{-1} can be attributed to the -NH group in Figure 3(d), thus further confirming the synthesis of the PMMA-*co*-PNIPAM copolymer within the polythiophene chains.

We measured the thermal properties of our synthesized polythiophene copolymers bearing a range of different branched chains using DSC. The DSC thermograms of (a) PTh-*g*-PS, (b)

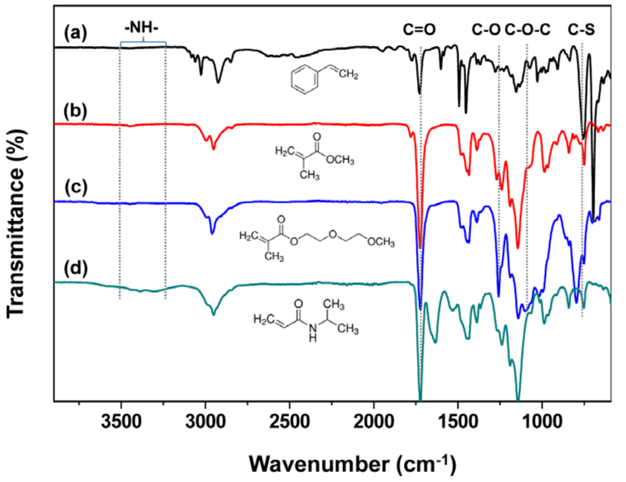


Figure 3. FTIR spectra of (a) PTh-*g*-PS, (b) PTh-*g*-PMMA, (c) PTh-*g*-(PMMA-*co*-PDEGMEMA), and (d) PTh-*g*-(PMMA-*co*-PNIPAM) copolymers.

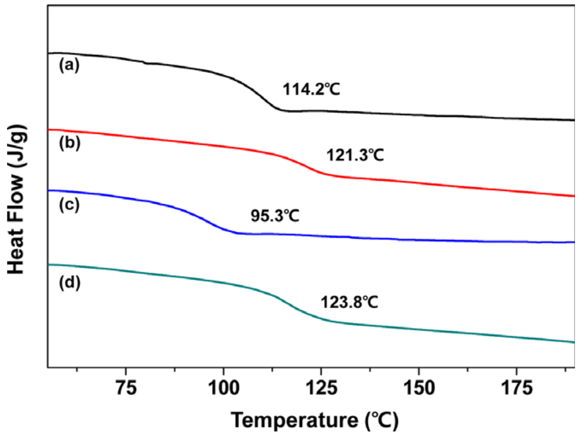


Figure 4. DSC thermograms of (a) PTh-*g*-PS, (b) PTh-*g*-PMMA, (c) PTh-*g*-(PMMA-*co*-PDEGMEMA), and (d) PTh-*g*-(PMMA-*co*-PNIPAM) copolymers.

PTh-*g*-PMMA, (c) PTh-*g*-(PMMA-*co*-PDEGMEMA), and (d) PTh-*g*-(PMMA-*co*-PNIPAM) were measured in Figure 4. All prepared copolymers displayed endothermic grass transitions, where the T_gs at approximately 95-124 ºC corresponds to the branched chains. The different glass transitions in each product are therefore indicative of the successful formation of branched structures comprising the polythiophene copolymer and branched polymers. Furthermore, the T_gs of the branched chains in π-conjugated products are higher than those observed in the homopolymers, due to the adhered chain end of the comb-like or multi-linked structures in the π-conjugated polymers.

The UV-Vis absorption spectra of the PTh-*g*-PS, PTh-*g*-PMMA, PTh-*g*-(PMMA-*co*-MAA), and PTh-*g*-(PMMA-*co*-PDEGMEMA) copolymers in DMSO are shown in Figure 5(A). It can be seen from the spectra that all samples displayed an absorption band at approximately 420 nm, corresponding to the π-π* transition of the π-conjugated structure, thus also confirming the successful polymerization of thiophene. The fluorescence emission (photoluminescence) spectra of the (a)

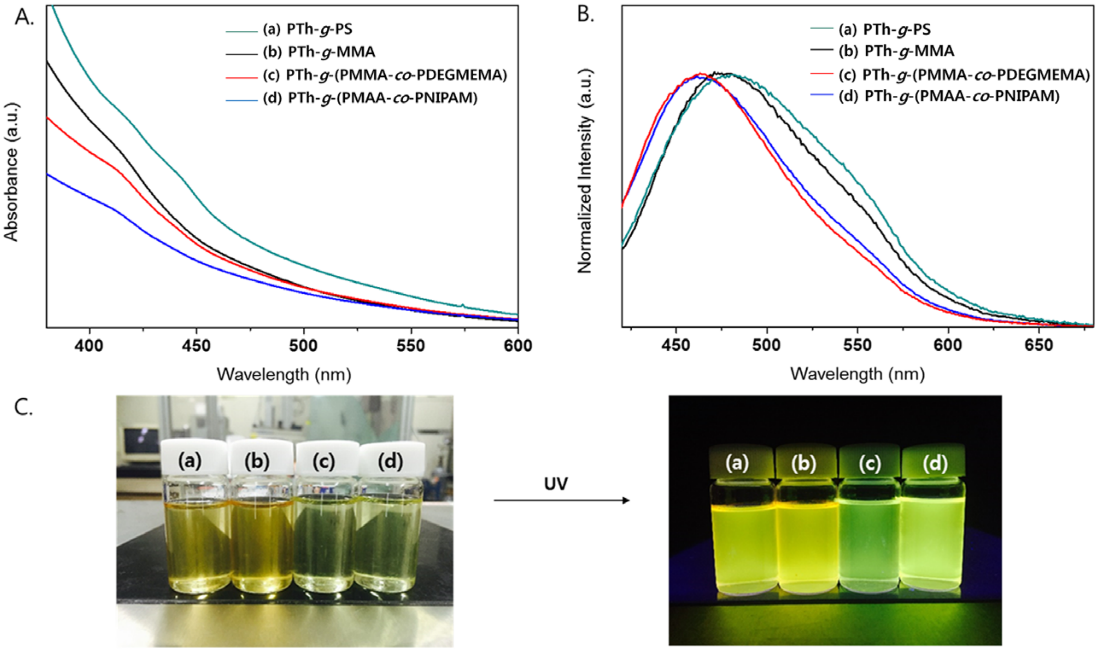


Figure 5. A) UV-Vis spectra of (a) PTh-*g*-PS, (b) PTh-*g*-PMMA, (c) PTh-*g*-(PMMA-*co*-PDEGMEMA), and (d) PTh-*g*-(PMMA-*co*-PNIPAM) copolymers dissolved in DMSO. B) Photoluminescence spectra of DMSO solutions of (a) PTh-*g*-PS, (b) PTh-*g*-PMMA, (c) PTh-*g*-(PMMA-*co*-PDEGMEMA), and (d) PTh-*g*-(PMMA-*co*-PNIPAM) copolymers. C) Photographic images of (a) PTh-*g*-PS, (b) PTh-*g*-PMMA, (c) PTh-*g*-(PMMA-*co*-PDEGMEMA), and (d) PTh-*g*-(PMMA-*co*-PNIPAM) copolymers dissolved in DMSO under visible light and under UV irradiation at 365 nm.

PTh-*g*-PS, (b) PTh-*g*-PMMA, (c) PTh-*g*-(PMMA-*co*-PDEGMEMA), and (d) PTh-*g*-(PMMA-*co*-PNIPAM) copolymers were recorded in DMSO, with an excitation wavelength of 420 nm in Figure 5(B). Emission peaks were observed for (a) PTh-*g*-PS and (b) PTh-*g*-PMMA at approximately 478 nm, while those of PTh-*g*-(PMMA-*co*-MAA) and PTh-*g*-(PMMA-*co*-PDEGMEMA) were measured at approximately 460 nm. This phenomenon was attributed to the alteration of polarity in the branched polymer chains due to an increase in hydrophilicity of the polymers through polymer-solvent interactions.[32] Figure 5(C) shows photographs of PTh-*g*-PS, PTh-*g*-PMMA, PTh-*g*-(PMMA-*co*-MAA), and PTh-*g*-(PMMA-*co*-PDEGMEMA) in DMSO before and after UV irradiation. After UV irradiation, the emitted solution colour at 365 nm slightly changed yellow light to yellow green as increasing hydrophilicity of the branched polymers.

Conclusions

We have demonstrated a facile route for the preparation of polythiophene copolymers bearing branched chains, consisting of a single-step copper-catalyzed process through the combination of oxidative polymerization and metal-catalyzed radical polymerization. In this dual initiation polymerization process, oxidative polymerization and chain growth radical polymerization were carried out simultaneously using alternate reduction and oxidation states of the copper catalyst. The structures of the polythiophene-*b*-PS/PMMA and polythiophene-*b*-copolymers were confirmed by ^{1}H NMR spectroscopy, FTIR, DSC, and photoelectric analysis. It was found that a range of monomers could be utilized for synthesis of the branched chain in the dual initiation process in order to control of the properties of the polythiophene copolymers. Studies are currently underway to investigate the preparation of alternative conjugated polymers *via* dual initiation process.

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Supporting Information: Information is available regarding the ^{13}C NMR spectra of DFI and the gel permeation chromatography traces of synthesized polythiophene bearing branched chains. The materials are available *via* the Internet at http://www.springer.com/13233.

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