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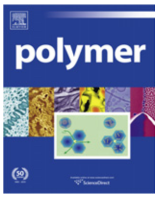

A facile and rapid synthesis of unsubstituted polythiophene with high electrical conductivity using binary organic solvents

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ABSTRACT

Dichloromethane and acetonitrile containing thiophene and oxidant, respectively, were adopted as a binary organic solvent for oxidative synthesis of unsubstituted polythiophene (UPTh) under various conditions, i.e., oxidant/monomer molar ratio, polymerization temperature, and reaction time. We also investigated the effects of polymerization medium on the chemical and physical properties of the UPTh. The electrical conductivities of the UPThs polymerized in only acetonitrile or aqueous medium were 1.0×10^{-4} $\mathrm{Scm^{-1}}$ and zero, respectively. However, the UPTh obtained in binary organic solvent system exhibited the highest electrical conductivity of 20.1 $\mathrm{Scm^{-1}}$ without post-doping process under an oxidant/monomer molar ratio of 5:1 and a reaction time of 0.2 h at 0 °C. Furthermore, it showed an enhanced crystalline structure, thermal stability, and longer π-conjugation length than those in acetonitrile or aqueous medium. We also found that the presence of water as a polymerization medium inevitably gave rise to the incorporation of hydroxyl and carbonyl groups into the UPTh main chains by nucleophilic attack of water molecules. Therefore, these undesired structures broke the conjugated structures, resulting in UPTh with an electrically non-conducting property. The morphology of UPTh prepared in binary organic solvent appeared to be an aggregate of nanoparticles (50–200 nm). The combination of organic solvents should provide another systematic approach to the facile and rapid synthesis of UPThs with high conductivity.

1. Introduction

Among electrically conducting polymers, polythiophene (PTh) and its derivatives are some of the most important materials because of their distinctive electrochemical, magnetic, and optical properties, as well as their wide range of applications [1–3]. Current important application areas include solar cells [4], supercapacitors [5], catalyst support materials [6], sensors [7], and other electronic devices [8–10]. However, a great deal of the present research has focused on thiophene derivatives including oligothiophenes, 3,4-ethylenedioxythiophene, and other beta-substituted thiophenes owing to their good electrical properties, excellent processabilities, and easy syntheses.

Although extensive studies have been performed for the synthesis and application of substituted PThs, relatively few investigations have targeted the synthesis of unsubstituted polythiophene (UPTh) because of their lack of monomer reactivity and very low conversion [2]. Nonetheless, there have been two main routes for synthesizing UPTh, chemical oxidative and electrochemical polymerizations. It was reported that UPTh films were prepared by electrochemical synthesis in an acetonitrile (CH_3CN) solution with boron fluoride-ethyl ether as an electrolyte [11]. The electrical conductivity of the UPTh film obtained under the optimal conditions was as high as 153 $\mathrm{Scm^{-1}}$. However, unfortunately, since the UPTh of the electrochemical method was only polymerized within a limited area of the electrode, productivity is very low and production cost is high. Although the chemical synthesis method can surmount the drawbacks of electropolymerization, chemical syntheses of UPTh have been mainly performed in anhydrous organic solvents such as chloroform ($CHCl_3$) and CH_3CN. It was reported that UPTh with wall-type plates was chemically synthesized by slow dropping of thiophene solution dissolved in chloroform to a $FeCl_3$ solution of chloroform [12]. Although UPTh exhibited the high electrical conductivity of ~20 $\mathrm{Scm^{-1}}$, it was only achieved by the post-doping process in $FeCl_3$ solution of 0.3 M. More recently, Li et al. reported the chemical synthesis of UPTh nanoparticles in CH_3CN with a minute amount of cetyltrimethylammonium bromide [13]. The UPTh nanoparticles

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obtained by this method had a very high electrical conductivity up to 50 $\mathrm{Scm^{-1}}$ via a post-doping process in iodine vapor. However, as-prepared UPThs generally had low and variable electrical conductivities from 10^{-9} through 10^{-4} $\mathrm{Scm^{-1}}$ without a post-doping process. Moreover, although it was reported that UPTh nanoparticles were successfully synthesized via a Fe^{3+}-catalyzed oxidative polymerization method in aqueous medium [14,15], not only the electrical properties of the obtained UPThs were not investigated, but also the effect of water molecules on the structure of the obtained UPTh was not considered. Generally, it is known that hydroxyl and carbonyl groups in the UPTh chains are inevitably introduced by the nucleophilic attack of water molecules in the aqueous polymerization process of UPTh [16,17]. Therefore, it would be of great interest to develop a new facile route to obtain UPTh with high electrical conductivity as well as enhanced optical, structural, and thermal properties.

We present here a facile and rapid chemical oxidative synthesis of UPTh nanoparticles with high electrical conductivity using binary organic solvent. To the best of our knowledge, this is the first report describing the high electrical conductivity of 20.1 $\mathrm{Scm^{-1}}$ for the UPTh prepared without post-doping process by chemical oxidative polymerization. In this study, because the solubility of $FeCl_3$ in dichloromethane ($ClCH_2Cl$) is somewhat low, UPTh polymerized in a single organic solvent of $ClCH_2Cl$ showed a very low yield and poor electrical conductivity ($\sim 10^{-7}$ $\mathrm{Scm^{-1}}$). Therefore, CH_3CN, being soluble with $FeCl_3$ as well as miscible with $ClCH_2Cl$, was adopted as a solvent for the dissolution of the oxidant. The combination of $ClCH_2Cl$ and CH_3CN containing thiophene monomer and $FeCl_3$ as oxidants was firstly introduced for synthesis of UPTh. The electrical property, yield, structure, and morphology of the UPTh prepared in this new combination of organic solvents were thoroughly investigated using WAXD, FT-IR, and UV–vis spectroscopy, as well as SEM, TEM, elemental analysis, and TGA methods. To compare the properties of the UPTh prepared using this system to those of the UPThs prepared in single medium, UPThs were also synthesized in CH_3CN and aqueous mediums.

2. Experimental

2.1. Materials

Thiophene monomer (Sigma–Aldrich) was purified by distillation under reduced pressure and stored in refrigerator prior to use. Ammonium persulfate (APS, Sigma–Aldrich, 98%), iron (III) chloride ($FeCl_3$, Sigma–Aldrich, 97%), dodecylbenzenesulfonic acid (DBSA, Kanto), dichloromethane ($ClCH_2Cl$, Sigma–Aldrich, $\geq$ 99%), and acetonitrile (CH_3CN, Sigma–Aldrich, $\geq$ 99%) were used as received.

2.2. Synthesis

In a typical polymerization using binary organic solvent, thiophene (0.02 mol) was mixed with $ClCH_2Cl$ (100 mL) in a double-jacketed reaction vessel at 0 °C. A fresh solution of anhydrous $FeCl_3$ (0.1 mol) in 50 mL CH_3CN was added to the monomeric solution. The polymerization was allowed to proceed for 24 h with stirring. The precipitated UPThs were filtered and washed with acetone and CH_3CN several times and then dried in a vacuum oven at 60 °C for 24 h.

For the synthesis of UPTh in CH_3CN, thiophene (0.02 mol) was mixed with CH_3CN (100 mL) in a double-jacketed reaction vessel at 0 °C. A fresh solution of anhydrous $FeCl_3$ (0.1 mol) in 50 mL CH_3CN was added to the monomeric solution. The polymerization was allowed to proceed for 24 h with stirring. The purification and drying processes were the same as in the above UPTh preparation method.

The synthesis of UPTh in aqueous medium was performed using an adapted Fe^{3+}-catalyzed oxidative polymerization process described by Lee et al. [14,15]. DBSA (0.02 mol) was dissolved in deionized water (100 mL). Thiophene (0.02 mol) was dropped into the aqueous DBSA solution, and then APS (0.01 mol) in 10 mL deionized water was added to the above mixture. After 1 h, $FeCl_3$ (0.002 mol) in 20 mL deionized water was added dropwise to the reaction mixture with vigorous stirring for 24 h at 0 °C. The precipitated UPThs were filtered and washed with water and acetone several times, and then dried in a vacuum oven at 60 °C for 24 h.

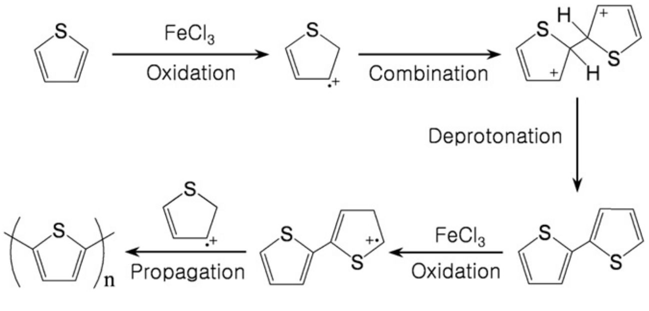
2.3. Characterization

Apparently, all samples investigated were prepared and studied in the oxidized/doped state. The electrical conductivity (298 K) of a compressed pellet of the thoroughly washed and dried UPThs was measured by the four-point microprobe method using a Jandel contact probe connected to a Keithley 238 high-current source measure unit. The electrical conductivity data were measured from three independent samples of a single synthesis. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Wide-angle X-ray diffraction measurements were carried out on a Rigaku Denki X-ray generator (Rigaku, D/MAX-2500), using Cu Kα (λ = 1.5418 Å) radiation operated at 40 kV and 100 mA. The scan angle covered $5^\circ < 2\theta < 50^\circ$ at a speed of 5°/min. The UPTh morphology was observed using scanning electron microscopy (SEM, JEOL, JSM6340) and transmission electron microscopy (TEM, JEOL 2010). Particle size distributions of UPThs were determined by laser diffraction/scattering particle size analysis (Cilas 1090 Particle size analyzer). UV–vis spectra of the UPThs in $ClCH_2Cl$ were recorded using a UV–Visible spectroscopy system (Unicam 8700 series). The chemical compositions of UPThs were determined using elemental analysis (EA). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Sigma Probe (Thermo VG, UK) system equipped with a monochromatic Al Kα X-ray source (1486.6 eV). Thermogravimetric analysis (TGA) was carried out with a Perkin Elmer TGA at a heating rate of 10 °C/min from 30 to 800 °C in a nitrogen atmosphere. The change in surface resistivity for the UPThs was measured with a Keithley 2000 multimeter equipped with a hot stage (Mettler Toledo FP82HT). The samples were heated to 200 °C at a rate of 10 °C/min in a nitrogen atmosphere.

3. Results and discussion

3.1. Synthesis of the UPTh

Scheme 1 describes a typical mechanism for chemical oxidative polymerization of thiophene. First, radical cations are produced by the oxidation of thiophene monomer. And then, two radical cations



Scheme 1. Chemical oxidative polymerization of thiophene.

are coupled to a dimer with deprotonation. After that, the thiophene dimers are re-oxidized and coupled with other radical cations. The oxidation and coupling process continues to produce UPTh during propagation step. For the chemical oxidative synthesis of UPTh, polymerization medium seems to be crucial, because the electrical conductivities and polymerization yield of UPTh significantly vary according to the type of polymerization medium. However, few studies have been performed to clarify the effect of polymerization medium. We have found that the combination of $ClCH_2Cl$ and CH_3CN as a solvent for dissolving thiophene and oxidant, respectively, is very suitable for the polymerization of UPTh. Moreover, we discovered that the 2:1 volume ratio of $ClCH_2Cl$ and CH_3CN is the most optimal composition to obtain UPTh with the high electrical conductivity. In the lower concentration range of CH_3CN than optimal composition, the electrical conductivity and yield of the resulting UPTh decrease due to the very low solubility of $FeCl_3$ as an oxidant in $ClCH_2Cl$. On the contrary, too high concentration of CH_3CN induces side reaction of thiophene in CH_3CN. The side reaction of thiophene in CH_3CN will be discussed later in detail. And, we also investigated the effects of oxidant/monomer molar ratio, polymerization temperature, and reaction time on electrical conductivity and polymerization yields to find optimal synthetic conditions.

Fig. 1 shows the effect of the $FeCl_3$/thiophene molar ratio on the electrical conductivity and yield of UPTh prepared at 0 °C for 24 h. By increasing the $FeCl_3$/thiophene molar ratio from 1:1 to 6:1, the polymerization yield increases up to 67%. It is known that in the case of the chemical synthesis of UPTh or polypyrrole, the $FeCl_3$/monomer molar ratio for optimal doping and polymerization yield is theoretically 2.33:1 [18]. However, since the reactivity of thiophene monomer is very low, more oxidant should be used to reach the maximum yield. The electrical conductivity reached a maximum of 1.2 Scm^{-1} at $FeCl_3$/thiophene molar ratio of 5:1, after which it then slightly decreased due to over-oxidation.

The influence of polymerization temperature on the electrical conductivity and UPTh yield prepared at a $FeCl_3$/thiophene molar ratio of 5:1 and a polymerization time of 24 h is shown in Fig. 2. It can be seen that yield gradually increased from 42 to 69% with increasing temperature, however, electrical conductivity reached a maximum at 0 °C and gradually decreased at higher temperatures. These results can be explained by the increase in monomer reactivity at elevated temperatures [19–21]. As the temperature of the polymerization medium increases, the probability of radical coupling among oxidized thiophenes also increases due to the enhancement of the thermal mobilities of the monomers and oxidants in the low viscosity polymerization medium [19]. However, the increased thermal mobilities of reactants at higher temperatures induce the rapid production of many reaction sites. Ultimately this yields the formation of an UPTh with low electrical conductivity, resulting from structural irregularities such as $\alpha-\beta$ couplings or $\alpha-\alpha$ couplings not rotated of thiophene rings in the same manner of polypyrrole [2]. On the other hand, the slight decline of conductivity at −10 °C is likely due to the decreased polymerizability by the decrease in monomer reactivity at lowered temperature [20,21].

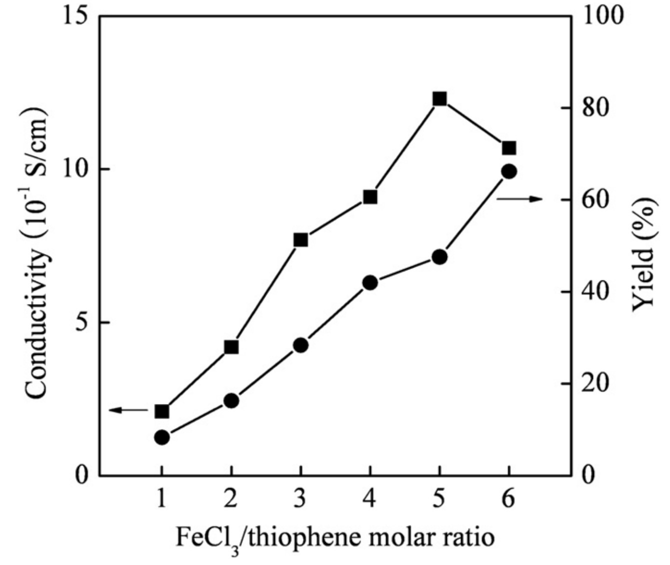


Fig. 1. The electrical conductivities and yields of UPTh prepared at various $FeCl_3$/monomer molar ratios. Polymerization time was 24 h and polymerization temperature was 0 °C.

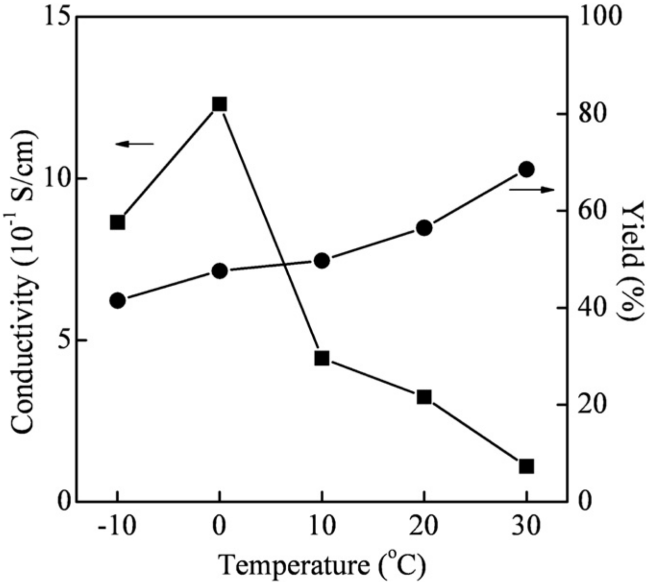


Fig. 2. The electrical conductivities and yields of UPTh prepared at various temperatures. The $FeCl_3$/monomer molar ratio was 5:1 and polymerization time was 24 h.

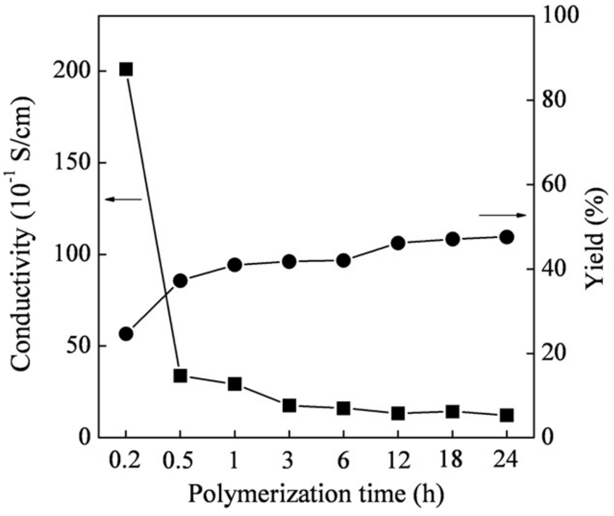


Fig. 3. The changes in electrical conductivity and yields with polymerization time of UPTh prepared with a $FeCl_3$/monomer molar ratio of 5:1 at 0 °C.

Polymerization time was also found to be a critical factor affecting electrical conductivity and yield, as shown in Fig. 3. The UPTh prepared at a $FeCl_3$/thiophene molar ratio of 5:1 and 0 °C, surprisingly, exhibited the maximum electrical conductivity of 20.1 Scm^{-1} at a polymerization time of only 0.2 h. At longer polymerization times the electrical conductivity sharply decreased to 1.8 Scm^{-1} at 3 h and then leveled off from 3 to 24 h. After 0.2 h, the electrical conductivity appears to decrease due to over-oxidation. On the contrary, the yield gradually rises from 25 to 47% with increasing polymerization time. Although the results were not shown in Fig. 3, the conductivity and yield at 0.1 h were as low as 0.4 Scm^{-1} and 7.4%, respectively. Too short polymerization time would cause very low degree of polymerization of thiophene and insufficient doping. From the above results, $FeCl_3$/thiophene molar ratio of 5:1, a polymerization temperature of 0 °C, and a polymerization time of 0.2 h would be the optimal conditions for the synthesis of UPTh with the highest electrical conductivity. However, the electrical conductivities of the UPThs polymerized in only CH_3CN or aqueous medium were 1.0×10^{-4} Scm^{-1} and zero, respectively, similar to the results of Li's work [13]. Hereafter, UPTh prepared under these optimal conditions in binary organic solvent was used in all analyses to compare with UPTh samples synthesized in CH_3CN and aqueous mediums.

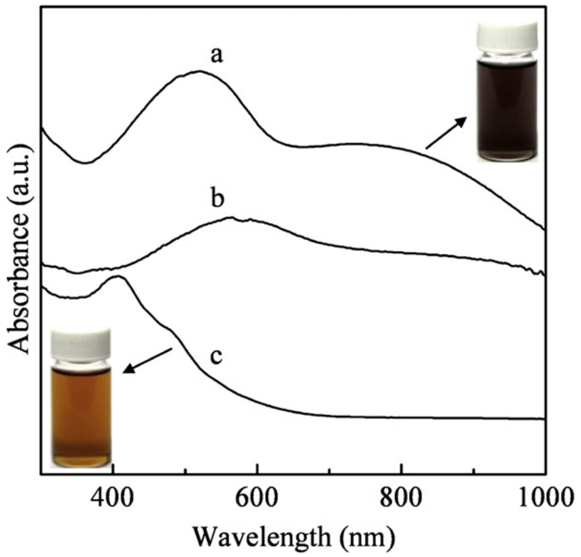


Fig. 5. UV–vis spectra of UPTh samples prepared in (a) binary organic solvent, (b) CH_3CN, and (c) aqueous medium. The inset pictures show UPThs dispersed in $ClCH_2Cl$.

3.2. Morphology and size of the UPTh

The UPTh synthesized in our binary organic solvent system exhibits quite different morphological, structural, electrical, and thermal properties from those of the other UPThs synthesized in CH_3CN or aqueous mediums. The morphological observations using SEM and TEM show that the type of polymerization medium strongly affects the final UPTh morphology (Fig. 4). Aggregated ellipsoidal UPTh nanoparticles of 50–200 nm are observed in our binary organic solvent system (Fig. 4a and inset), while bulky shapeless UPTh microstructures are obtained in CH_3CN (Fig. 4b). SEM and TEM images (Fig. 4c and inset) of the UPTh prepared in aqueous medium exhibited a somewhat globular morphology with a primary particle size range of 30–70 nm. However, the particle size distributions (Fig. 4d, e, f) determined by the particle size analyzer for each sample provide larger mean particle size than that observed from SEM and TEM images. This discrepancy might be due to the aggregations of primary UPTh particles.

3.3. UV–vis and FT-IR spectra

The UV–vis spectra of the UPTh synthesized in different mediums are shown in Fig. 5. The very different UV–vis spectra of the UPThs appear to depend on the polymerization medium, suggesting different π-conjugated structures. The UPTh with black color (Fig. 5, inset top) prepared in binary organic solvent shows a strong absorption band at approximately 520 nm and a broad band at 780 nm corresponding to the polarons and bipolarons

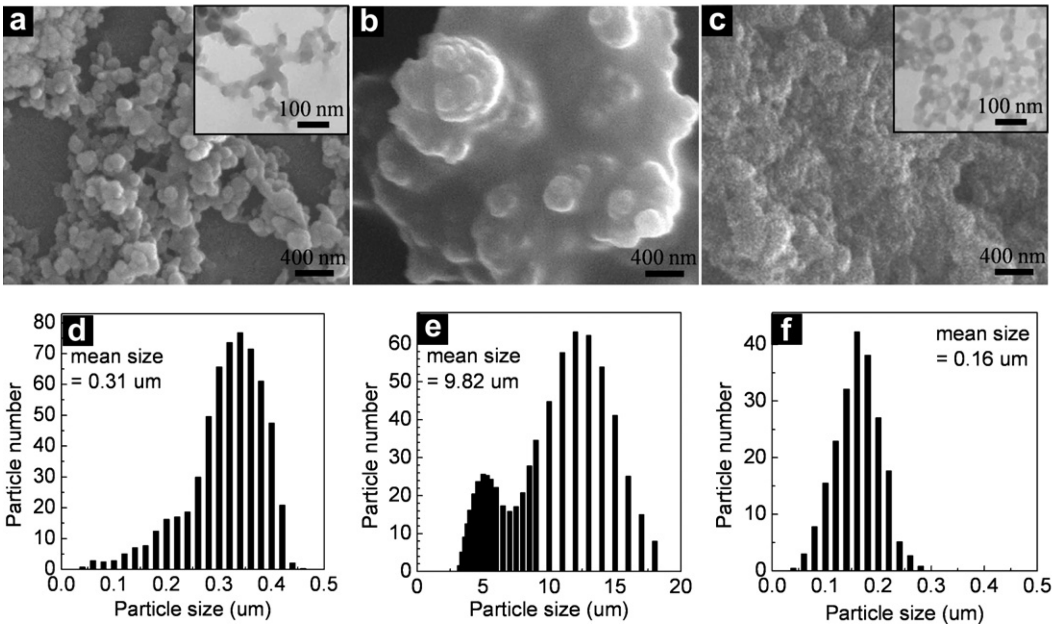


Fig. 4. SEM images and particle size distributions for UPTh synthesized in (a,d) binary organic solvent, (b,e) CH_3CN, and (c,f) aqueous medium. The insets in (a) and (c) show magnified TEM images.

[22–24], respectively, with a long tail to near infrared regions. It was suggested that the UPTh prepared in binary organic solvent was not only more oxidized and doped state, but also had a longer conjugation length than those of the other samples. The UPTh synthesized in CH_3CN exhibited a weak absorbance at approximately 570 nm, corresponding to the polaronic band. On the other hand, the UPTh polymerized in aqueous medium displayed a weak absorption band at 406 nm along with a shoulder peak at 480 nm, ascribable to a $\pi-\pi^*$ transition in the neutral state of UPTh and blue-shifted polaron band, respectively [22,23]. The blue shift may be representative of the decrease in UPTh conjugation length resulting from structural irregularity. In addition, UPTh in the neutral state exhibited a brown color (Fig. 5, inset bottom) and a non-conducting property, as mentioned above.

The widely variable π-conjugated structures and electrical properties among UPThs can be explained by the structural differences in UPThs prepared in different polymerization media. Fig. 6 presents the FT-IR spectra of various UPThs. The FT-IR spectra of the UPThs synthesized in binary organic solvent and CH_3CN exhibited similar characteristic UPTh peaks around 1482 and 1437 cm^{-1}, indicative of the C═C asymmetric and symmetric ring stretching modes, respectively [13,17]. The peak around 1310 cm^{-1} was attributed to the C—C stretching vibration mode of the thiophene ring [13,17]. Peaks at 1197, 1090, and 786 cm^{-1} were attributed to C—H deformation vibration modes, whereas the peak at 728 cm^{-1} was assigned to a C—S stretching vibration [13,17]. However, unlike the UPThs synthesized in binary organic solvent and CH_3CN, the strong C═O band at about 1680 cm^{-1} was observed in UPTh prepared in aqueous medium, accompanied with other shifted absorption peaks. In particular, it is very interesting that the absorption band of the C═O group was also observed in the UPTh sample prepared using the same procedure as that of a previous work [15]. (data not shown) This undesired structure presented in the UPTh may arise from water molecules in the polymerization medium. Nucleophilic attack of water molecules on positively charged UPTh chain centers can cause incorporation of carbonyl groups. The water molecules have been shown by others to lead to undesirable carbonyl formation [16,17].

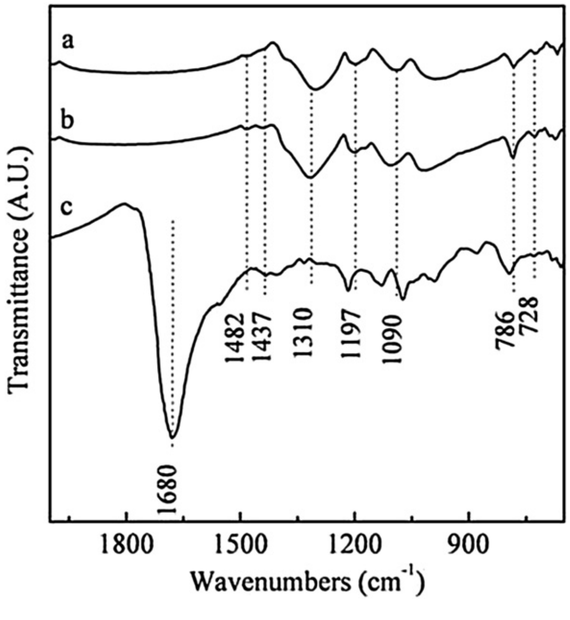
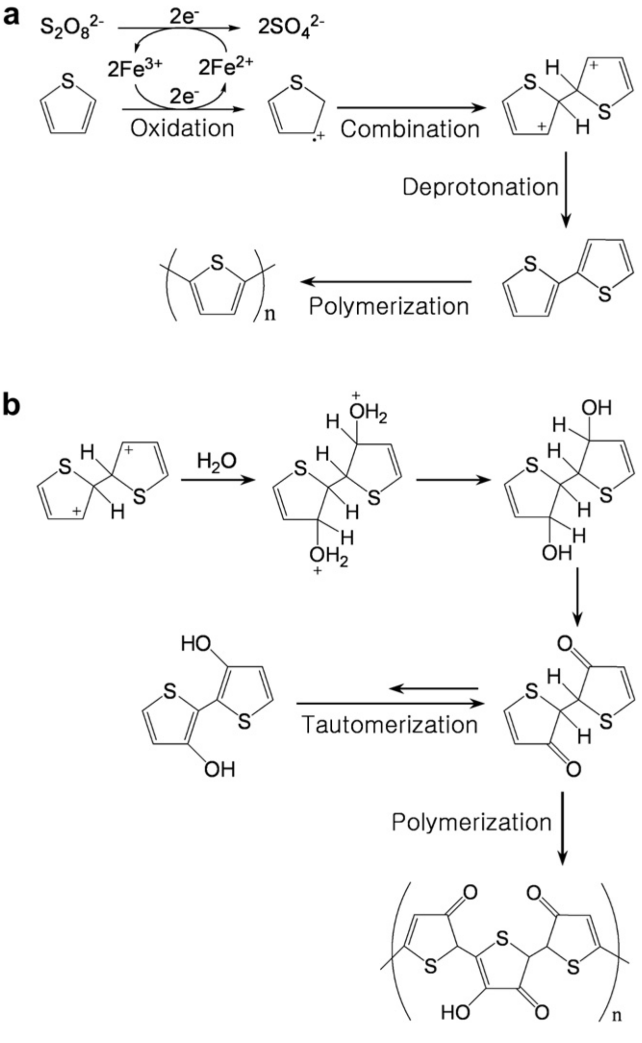


Fig. 6. FT-IR spectra of UPTh samples prepared in (a) binary organic solvent, (b) CH_3CN, and (c) aqueous medium.

3.4. Side reactions

Due to the undesirable introduction of the C═O defects into UPTh rings, conjugation structures are broken and eventually, UPTh exhibits a non-conducting and neutral state, as shown in the UV–vis and electrical conductivity results presented above. A detailed polymerization mechanism and side reactions by water molecules in aqueous media are shown in Scheme 2. Scheme 2a demonstrates the ideal reaction mechanisms of thiophenes in aqueous medium via Fe^{3+}-catalyzed oxidative polymerization [14,15]. In the initiation step, thiophene radical cations are created by oxidation via reproducible oxidant/catalyst (APS/$FeCl_3$) systems. Thiophene dimers are formed by radical–radical coupling and deprotonation. Finally UPThs are formed by successive reoxidation during the propagation step. However, Scheme 2b actually represents the possible chemical structure of UPTh during polymerization in aqueous medium. When cationic thiophene dimers are formed by radical coupling, nucleophilic attacks of water molecules on cationic thiophene dimers lead to the production of β-hydroxylated thiophene structures. As a consequence of tautomerization, carbonyl groups are predominantly generated into the UPTh main chains [25].



Scheme 2. (a) Synthesis of thiophene via Fe^{3+}-catalyzed oxidative polymerization in aqueous medium and (b) a possible mechanism of carbonyl and hydroxyl groups generation within the UPTh main chains through the nucleophilic attack of water molecules on thiophene rings in aqueous medium.

Table 1
Chemical compositions and electrical conductivities of the UPTh samples synthesized in various polymerization media.

Polymerization medium	C	H	S	O[b]		Cl	DBSA	Conductivity (Scm^{-1})
				C–O	C=O			
Theoritical value[a]	4.00	2.00	1.00	–	–	–	–	–
Binary organic solvent	3.97	1.82	1.00	0.1	0.08	0.32	–	20.1
CH_3CN	4.08	2.06	1.00	0.23	0.15	0.26	–	1.0×10^{-4}
Aqueous medium	4.00	2.29	1.00	0.34	1.11	0.12	0.09	–

[a] Theoritical chemical composition of neutral UPTh.
[b] Values estimated from the O 1s core level spectra analysis using XPS.

To examine the introduction of the carbonyl groups, elemental analysis for chemical species was performed on UPThs prepared in each polymerization medium. The results of elemental composition analyses of the UPTh samples by EA and XPS are shown in Table 1. The carbon and sulfur stoichiometries in all UPThs coincide well with theoretical values. The doping levels, expressed by chlorine content (in case of aqueous medium, chlorine% + DBSA%) in the UPTh samples, increased with increasing electrical conductivity. An excess of covalently-bonded oxygens composed of C–O of 0.34 and C=O of 1.11 per thiophene ring are observed in UPTh prepared in aqueous media, which is attributable to the generation of the hydroxyl and carbonyl groups by nucleophilic attacks of water molecules, in good accordance with FT-IR data and our proposed polymerization scheme 2b. In addition, 0.18 (C–O of 0.1 and C=O of 0.08) and 0.38 (C–O of 0.23 and C=O of 0.15) oxygen molecules per thiophene unit were observed even in samples prepared in binary organic solvent and CH_3CN, respectively. This may also be due to the generation of carbonyl and hydroxyl groups into UPTh chains, in the same manner as in aqueous media, by the unavoidable introduction of moisture during the polymerization and workup processes, even when synthesis is performed in an anhydrous system. However, carbonyl groups of 0.08 and 0.15 per thiophene of UPThs synthesized in binary organic solvent and CH_3CN, respectively, were not detected in FT-IR analysis because of their small portion.

For additional experimental evidence, carbon 1s (C 1s) XPS core level spectra for the UPThs were analyzed as shown in Fig. 7. Four-component peaks were fitted to each spectrum. The peak components at about ~284.4 and ~285.2 eV is attributable to β and α carbon in the thiophene ring, respectively [26,27]. Broad shoulder on the high binding energy side of the C 1s spectra, which is deconvoluted into two peaks at about ~286.5 and ~287.7 eV, is assigned to the C–O and C=O species, respectively [28,29]. The composition ratio of α carbon in all samples was about ~0.5 (0.51, 0.50, and 0.52 in (a), (b), (c), respectively), whereas the composition of β carbon decreased with developing C–O and C=O groups as shown in Fig. 7. This indicates that C–O and C=O groups were mainly introduced in the β position of thiophene ring. Based on the XPS C 1s spectra of UPThs, we verified that C–O and C=O groups were introduced in UPTh rings. In addition, the composition of C–O and C=O groups corresponded well with the chemical composition data of oxygen in Table 1.

Furthermore, the higher oxygen content in CH_3CN medium than in binary organic solvent may be due to not only the higher moisture absorption of CH_3CN miscible with H_2O but CH_3CN hydrolysis reaction. We proposed the possible CH_3CN hydrolysis reaction, as shown in Scheme 3. First, CH_3CN can form coordination complex **1** with $FeCl_3$ [30], and then the intermediate complex **1** can be attacked by electrophilic aromatic substitution of thiophene followed by deprotonation **2**. The addition of acid that occurs due to oxidative polymerization of UPTh produces 1-(thiophen-2-yl) ethanimine **3**. Finally, the imine form is hydrolyzed to a ketone form and produces 2-acetylthiophene **4** [31]. Both CH_3CN and $ClCH_2Cl$ are polar aprotic solvents, however, the dipole moment of CH_3CN (3.92 D) is much higher than that of $ClCH_2Cl$ (1.60 D). CH_3CN with high dipole moment can act as an electrophile through coordination with $FeCl_3$ and can induce side reaction as described in Scheme 3. Therefore, relatively inert $ClCH_2Cl$ seems to be much more stable than CH_3CN under chemical oxidative polymerization condition. We also had similar results of high electrical conductivity (15.3 Scm^{-1}) when dichlroroehtane ($ClCH_2CH_2Cl$) with dipole moment of 1.80 D instead of $ClCH_2Cl$ was adopted as polymerization medium. However, in case of binary organic solvent system of thiophene monomers in chloroform ($CHCl_3$) and $FeCl_3$ in CH_3CN, the resulting UPThs exhibited low electrical conductivity of $\sim 10^{-4}$ Scm^{-1}. It is thought that this is due to the low solubility of $FeCl_3$ in $CHCl_3$ arising from much low dipole moment (1.04D) of non-polar $CHCl_3$. Although CH_3CN containing $FeCl_3$ adds to the thiophene solution of $CHCl_3$ and thiophene monomers are polymerized, non-polar UPThs in non-polar $CHCl_3$ cannot be effectively oxidized and doped with polar anions produced by $FeCl_3$ reduction. In addition, we discovered that when adopting tetrahydrofuran (THF) as a solvent for polymerization of thiophene, UPThs were absolutely not synthesized. While, it is true that the dipole moment of THF is 1.75 D similar to those of $ClCH_2Cl$ and $ClCH_2CH_2Cl$, the oxygen center of THF can coordinate to Fe^{3+}, Lewis acid, forming adducts [32]. Therefore, $FeCl_3$ does no more function as oxidizing agent of thiopnene. When considering both the possibility of side reactions in synthesis of UPTh and the activity of $FeCl_3$ as oxidant in a selected solvent, dipole moments of organic solvents brought by the molecular structures as well as moisture control of polymerization medium seem to be crucial factors in chemical oxidative synthesis of UPThs. And now we are further investigating the other reasons about the solvent (polymerization medium) dependence for properties of UPThs synthesized by chemical oxidative polymerization.

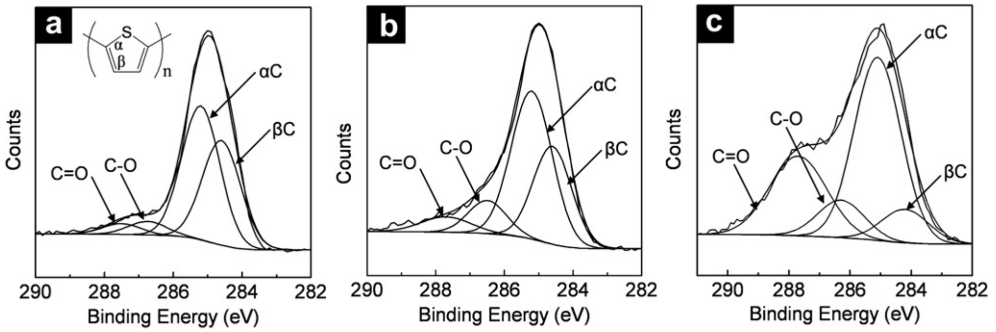
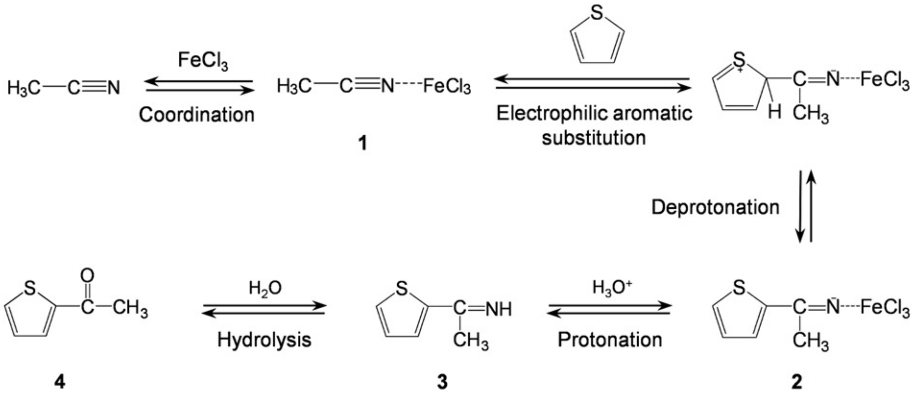


Fig. 7. Carbon 1s (C 1s) XPS core level spectra of UPTh samples prepared in (a) binary organic solvent, (b) CH_3CN, and (c) aqueous medium. The top line through the data exhibits the best fit obtained from the superposition of the peaks of the lower lines.



Scheme 3. A proposed hydrolysis reaction in CH_3CN medium containing water molecules.

3.5. WAXD patterns

The structural differences among the UPTh samples prepared in different polymerization media are observed via the different XRD patterns (Fig. 8). The XRD pattern of UPTh prepared in aqueous medium had a broad scattering amorphous structure, while the XRD pattern of sample prepared in CH_3CN had a broad scattering along with a small peak at $2\theta \approx 26.4^\circ$. The fully amorphous structure of UPTh prepared in aqueous medium could be attributed to the destruction of the ordered structures by the random introduction of carbonyl groups into the UPTh main chains. However, more interestingly, two distinct new peaks at $2\theta \approx 17.7^\circ$ and 26.3° were only observed in UPTh prepared in binary organic solvent, a novel observation [7,13,33]. Although clear interpretation of this structural change was not possible because of the lack of structural characterization for UPTh, similar results were observed in the works of Li and Yamamoto [19,34]. According to these papers, new XRD peaks at approximately $2\theta \approx 18^\circ$ and 26° were developed in UPThs with high electrical conductivity and extensive doping, but were not observed in other amorphous UPThs. Therefore, it is worth noting that highly doped and/or highly electrically conductive UPThs seem to arise from improved structural order, as was illustrated by our results.

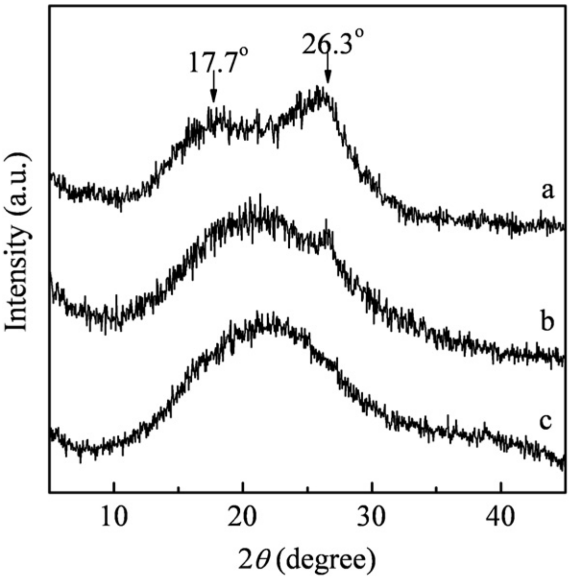


Fig. 8. XRD patterns of UPTh samples prepared in (a) binary organic solvent, (b) CH_3CN, and (c) aqueous medium.

3.6. Thermal stability

The differences in structural order among the UPTh samples prepared in various polymerization media also appeared to have a significant effect on the thermal stability. Fig. 9 shows the TGA thermograms of the UPTh samples in a nitrogen atmosphere. Surprisingly, UPTh prepared in binary organic solvent exhibited the highest thermal stability in all temperature ranges compared to the other UPThs. The 10 wt% loss temperatures were 225 and 245 °C in the UPThs prepared in CH_3CN and aqueous media, respectively, while the UPTh prepared in binary organic solvent exhibited a 10 wt% loss temperature of 525 °C, nearly 280 °C higher than that in CH_3CN. The final weight residue of the UPTh prepared in binary organic solvent at 800 °C (~70 wt%) was also much higher than those in CH_3CN (~62 wt%) or aqueous media (~45 wt%). That the lowest thermal stability was for the UPTh prepared in aqueous medium can be attributed to a rapid oxidative decomposition due to the presence of a large amount of carbonyl groups in the thiophene ring.

The differences in UPTh thermal stability were confirmed through the real-time surface resistivity changes ranging from 30 to 200 °C in a nitrogen atmosphere (Fig. 9, inset). Surface resistivity

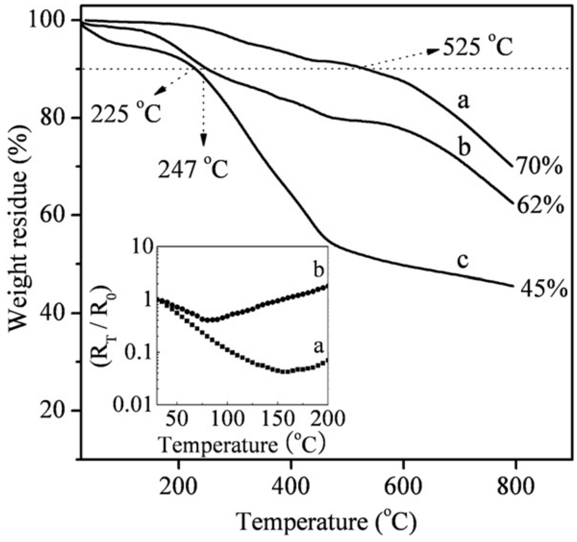


Fig. 9. TGA curves of UPTh samples prepared in (a) binary organic solvent, (b) CH_3CN, and (c) aqueous medium. The inset shows normalized surface resistivity changes of UPThs synthesized in (a) binary organic solvent, and (b) CH_3CN. R_T/R_0 is the resistance (R_T) normalized to the initial resistance (R_0).

decreased at temperatures up to 82 °C ($R_T/R_0 = 0.4$) and then gradually increased over the range of 82–200 °C ($R_T/R_0 = 1.4$) in the UPTh prepared in CH_3CN, while in binary organic solvent surface resistivity decreased in temperatures up to 160 °C ($R_T/R_0 = 0.04$) and then increased from 160 to 200 °C ($R_T/R_0 = 0.07$). The initial decrease in R_T/R_0 is simply caused by enhanced electron mobility and electron transfer through molecular rearrangement [35]. The increase in R_T/R_0 can be attributed to the degradation of main chains and the volatilization of dopants [36]. In the case of UPThs prepared in CH_3CN, because of the relatively high oxygen concentration and the low structural order due to the hydrolysis reaction of CH_3CN or nucleophilic attack on UPTh chains, the thermal stability is likely to be lower than those in binary organic solvent. Taken together, it was possible to conclude that thermal stability as well as electrical properties is likely governed by the structural differences brought on by the different polymerization media.

4. Conclusion

In this study, UPTh with high electrical conductivity and improved thermal stability was successfully synthesized via a facile and rapid chemical oxidative polymerization method in the binary organic solvent of $ClCH_2Cl$ and CH_3CN. The black UPTh with a relatively highly ordered structure exhibited the highest electrical conductivity of 20.1 Scm^{-1} without a post-doping process under the optimal conditions of an $FeCl_3$/thiophene molar ratio of 5:1 and a reaction time of 0.2 h at 0 °C. However, the UPTh prepared in CH_3CN had a very low electrical conductivity of 1.0×10^{-4} Scm^{-1}, and the brown UPTh with a fully amorphous structure prepared in aqueous medium exhibited a neutral non-conducting property. This was due to the destruction of the conjugation structures by the generation of carbonyl groups within the UPTh main chains through the nucleophilic attack of water molecules on thiophene rings. We have shown that the differences in structural order brought on by the polymerization medium type can have a profound effect on the electrical properties and the thermal stability of the resulting UPTh. The synthetic method of UPThs discussed here has advantages of easy synthesis, fast reaction time, a several hundred nanometer size, low cost, high electrical quality, and excellent thermal stability. In addition, now we are further investigating the function of polymerization mediums (solvents) on the physical and chemical properties of chemically synthesized UPThs.

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